PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16547728
Filing Date	2019-08-22
First Named Inventor	Stephen Richard COULSON
Art Unit	1767
Examiner Name	NICOLE M. BUIE-HATCHER
Attorney Docket Number	GBL0007/US/2

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	2716638	A	1955-08-30	Cohen et al.	
	2	3816564	A	1974-06-11	Holliday et al.	
	3	4562091	A	1985-12-31	Sachdev et al.	
	4	5804669	A	1998-09-08	Tropsch et al.	
	5	6207238	B1	2001-03-27	Affinito	
	6	6214423	B1	2001-04-10	Lee et al.	
	7	6551950	B1	2003-04-22	Badyal et al.	
	8	7439315	B2	2008-10-21	Kunimi, et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16547728
	Filing Date	2019-08-22
	First Named Inventor	Stephen Richard COULSON
	Art Unit	1767
	Examiner Name	NICOLE M. BUIE-HATCHER
	Attorney Docket Number	GBL0007/US/2

	9	10421876	B2	2019-09-24	Coulson et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20050034667	A1	2005-02-17	Tsuji et al.	
	2	20050141738	A1	2005-06-30	Karamuk	
	3	20060122301	A1	2006-06-08	Nair et al.	
	4	20110148979	A1	2011-06-23	Breton et al.	
	5	20130136936	A1	2013-05-30	Morozumi et al.	
	6	20130176700	A1	2013-07-11	Stevens et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16547728
	Filing Date	2019-08-22
	First Named Inventor	Stephen Richard COULSON
	Art Unit	1767
	Examiner Name	NICOLE M. BUIE-HATCHER
	Attorney Docket Number	GBL0007/US/2

	1	9964662	WO	A1	1999-12-16	Badyal et al.		
	2	2012168440	WO	A1	2012-12-13	Taesler		
	3	2014026967	WO	A1	2014-02-20	Legein et al.		

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	Petition for Inter Partes Review for US Patent Application No. 10,421,876, mailed July 17, 2020, (90 pages).	
	2	Yao et al., "Fluorinated poly(meth)acrylate: Synthesis and properties," Vol. 55, Isse. 24, Pages 6197-6211, 2014, (15 pages).	
	3	Sartomer Company Material Safety Data Sheet, Product CD406, dated June 9, 2005, (7 pages).	
	4	Declaration of Dr. Karen Gleason, Exhibit 1002, Case IPR2020-01198, filed July 17, 2020, (117 pages).	
	5	Curriculum Vitae for Karen K. Gleason, Exhibit 1003, Case IPR2020-01198, filed July 17, 2020, (34 pages).	
	6	Francesch et al., "Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived Monomer", Plasma Processes and Polymers, Vol. 2, Isse. 8, pages 605-611, 2005, (7 pages).	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16547728
	Filing Date	2019-08-22
	First Named Inventor	Stephen Richard COULSON
	Art Unit	1767
	Examiner Name	NICOLE M. BUIE-HATCHER
	Attorney Docket Number	GBL0007/US/2

	7	Declaration of Dr. Salvador Borrós Gómez, Exhibit 1010, Case IPR2020-01198, filed July 17, 2020, (3 pages).
	8	Coulson et al., "Ultralow Surface Energy Plasma Polymer Films", Chemistry of Materials, Vol. 12, No. 7, pages 2031-2038, 2000, (8 pages).
	9	Tarducci et al., "Synthesis of Cross-Linked Ethylene Glycol Dimethacrylate and Cyclic Methacrylic Anhydride Polymer Structures by Pulsed Plasma Deposition", Macromolecules, Vol. 35, No. 23, pages 8724-8727, 2002, (4 pages).
	10	Yagüe et al., "Enhanced Cross-Linked Density by Annealing on Fluorinated Polymers Synthesized via Initiated Chemical Vapor Deposition To Prevent Surface Reconstruction", Macromolecules, Vol. 46, Isse. 16, pages 6379-6670, 2013, (7 pages).
	11	Yasuda, "Plasma Polymerization", Academic Press, London, 1985, (58 pages).
	12	Kurosawa et al., "Detection of deposition rate of plasma-polymerized acrylate and methacrylate derivatives using quartz crystal microbalance," Thin Solid Films, Vol. 457, Isse. 1, pages 26-33, 2004, (8 pages).
	13	Kurosawa et al., "Detection of deposition rate of plasma-polymerized silicon-containing films by quartz crystal microbalance," Thin Solid Films, Vol. 407, Isses. 1-2, pages 1-6, 2002, (6 pages).
	14	Joback et al., "Estimation of Pure-Component Properties from Group-Contributions," CHEMICAL ENGINEERING COMMUNICATIONS, Vol. 57, Isses. 1-6, pages 233-243, 1987, (12 pages).
	15	"Experimental Physico-chemical Properties" retrieved from 'www.chemspider.com/Chemical-Structure.68328.html?rid=8eaa4787-5d2d-42d7-a4bb-7b352bcd4806', on July 9, 2020, (14 pages).
	16	Declaration of S. Rampersad, Exhibit 1020, Case IPR2020-01198, filed July 17, 2020, (7 pages).

If you wish to add additional non-patent literature document citation information please click the Add button Add

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16547728
	Filing Date	2019-08-22
	First Named Inventor	Stephen Richard COULSON
	Art Unit	1767
	Examiner Name	NICOLE M. BUIE-HATCHER
	Attorney Docket Number	GBL0007/US/2

EXAMINER SIGNATURE			
Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16547728
Filing Date	2019-08-22
First Named Inventor	Stephen Richard COULSON
Art Unit	1767
Examiner Name	NICOLE M. BUIE-HATCHER
Attorney Docket Number	GBL0007/US/2

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Paul J. Parins/	Date (YYYY-MM-DD)	2019-10-08
Name/Print	Paul J. Parins	Registration Number	54,358

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

FAVORED TECH CORPORATION,

Petitioner,

v.

P2I LTD.,

Patent Owner.

CASE: IPR2020-01198

Patent No. 10,421,876

PETITION FOR *INTER PARTES* REVIEW OF U.S. PATENT NO. 10,421,876

Mail Stop PATENT BOARD
Patent Trial and Appeal Board
P.O. Box 1450
Alexandria, VA 22313-1450

July 17, 2020

TABLE OF CONTENTS

Page

I. Introduction 1

II. Mandatory notices 2

A. Real party in interest 2

B. Related matters 2

C. Counsel and service information 2

III. Requirements for *inter partes* review 3

A. Grounds for standing 4

B. Identification of challenge 4

IV. The '876 patent and protective coatings for electronic devices 5

A. The earliest priority date is June 9, 2015 6

B. The state of the art by June 2015 6

1. Ubiquitous portable electronics were being coated to protect against environmental contaminants 6

2. Plasma polymerization was routine and had been used to apply protective coatings to electronics 7

3. Fluorinated acrylate and methacrylate monomers had long been used for coating many substrates, including electronics 8

4. Crosslinkers were commonplace in polymer production 10

C. Overview of prior-art references 12

1. Coulson-122 described protective plasma-polymer coatings for electronics made using PFAC8 and PFMAC8 12

2. Badyal described plasma-polymer coatings combining PFAC8 or PFMAC8 with a generic crosslinker 12

3. Cohen, Holliday, Padiyath, Francesch, and Tropsch described crosslinkers with the claimed bridging groups 13

D. Overview of the '876 patent 14

1. Specification and claims 14

TABLE OF CONTENTS
(continued)

Page

2. Prosecution history 17

E. Level of ordinary skill in the art 18

V. Claim construction 18

A. "Halogen" includes at least fluorine, chlorine, and bromine 19

VI. The cited references are prior art 19

A. Coulson-122 20

B. Badyal 20

C. Cohen 20

D. Holliday 20

E. Padiyath 20

F. Francesch 20

G. Tropsch 21

VII. Detailed discussion of the grounds for unpatentability 21

A. All Grounds: Coulson-122 and Badyal described coatings applied using the same polymerization techniques, the same monomeric compounds, and the same group of crosslinkers as the '876 patent 22

B. Ground 1: Claims 1-3, 9, and 11-15 were obvious over Coulson-122, Badyal, and Cohen 25

1. Claim 1 26

a. Claim limitations 26

b. Motivation to combine Coulson-122, Badyal, and Cohen's crosslinking reagent 34

c. Reasonable expectation of success 38

2. Claims 2, 3 39

3. Claim 9 40

4. Claim 11 40

5. Claims 12, 13 41

6. Claims 14, 15 41

TABLE OF CONTENTS
(continued)

Page

C. Ground 2: Claims 1-8 and 10-15 were obvious over Coulson-122, Badyal, and Holliday 42

1. Claim 1 42

a. Claim limitations 42

b. Motivation to combine and reasonable expectation of success 44

2. Claims 2, 3 46

3. Claim 4 47

4. Claims 5, 6 48

5. Claim 7 49

6. Claim 8 50

7. Claim 10 51

8. Claim 11 51

9. Claims 12, 13 51

10. Claims 14, 15 52

D. Ground 3: Claims 1-4, 10, and 12-15 were obvious over Coulson-122, Badyal, and Padiyath 52

1. Claim 1 52

a. Claim limitations 52

b. Motivation to combine and reasonable expectation of success 54

2. Claims 2, 3 56

3. Claim 4 56

4. Claim 10 56

5. Claims 12, 13 56

6. Claims 14, 15 57

E. Ground 4: Claims 1-3, 5-8, and 11-15 were obvious over Coulson-122, Badyal, and Francesch 57

1. Claim 1 57

TABLE OF CONTENTS
(continued)

Page

a. Claim limitations....57

b. Motivation to combine and reasonable expectation of success....59

2. Claims 2, 3....61

3. Claims 5, 6....61

4. Claim 7....61

5. Claim 8....62

6. Claim 11....63

7. Claims 12, 13....63

8. Claims 14, 15....63

F. Ground 5: Claims 1-3, 5-8, and 12-15 were obvious over Coulson-122, Badyal, and Tropsch....64

1. Claim 1....64

a. Claim limitations....64

b. Motivation to combine and reasonable expectation of success....65

2. Claims 2, 3....67

3. Claims 5, 6, 8....67

4. Claim 7....68

5. Claims 12, 13....69

6. Claims 14, 15....69

G. All Grounds: Claims 2 and 3 would have been obvious over the cited prior-art combinations....69

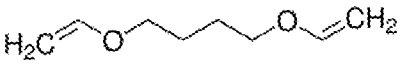
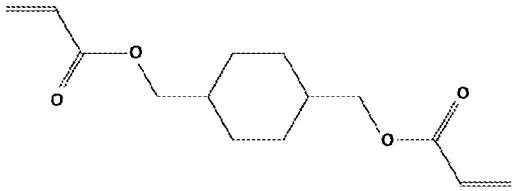
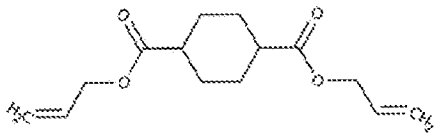
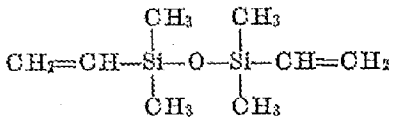
1. Claim 2....69

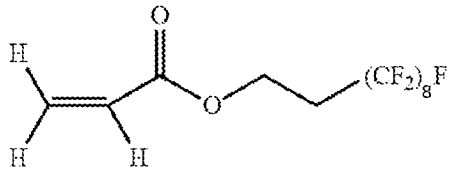
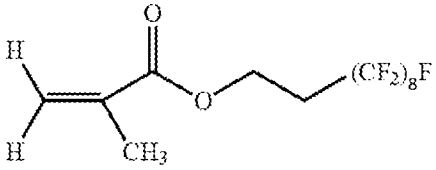
2. Claim 3....72

VIII. Statement regarding § 325(d)....74

IX. Conclusion....76

TABLE OF ABBREVIATIONS AND CONVENTIONS

AIA	America Invents Act
Badyal	International Publication No. WO 99/64662, "Surface Coatings," to Jas Pal Singh Badyal, et al. (Ex. 1005)
BDVE	1,4-butanediol divinyl ether 
Board	Patent Trial and Appeal Board
CDMDA	cyclohexane-1,4-dimethanol diacrylate 
Coulson-122	International Publication No. WO 2007/083122, "Novel Products," to Stephen Coulson (Ex. 1004)
Cohen	U.S. Patent 2,716,638, "Divinyltetramethyldisiloxane and Polymers Therefrom," to Merrill Cohen and John R. Ladd (Ex. 1006)
DCHD	diallyl 1,4-cyclohexanedicarboxylate 
DVTMDS	divinyl tetramethyl disiloxane 
Favored or Petitioner	petitioner Favored Tech Corporation

Francesch	, L. et al, "Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived Monomer," *Plasma Processes and Polymers*, 2:605–611 (2005) (Ex. 1009)
HDVE	1,6-hexanediol divinyl ether 
Holliday	U.S. Patent 3,816,564, "Insulation Coating Compositions," to Harvey Ray Holliday and Gary Lee Schurter (Ex. 1007)
IPR	*inter partes* review
Padiyath	U.S. Patent Application Publication US 2007/0020451, "Moisture Barrier Coatings," to Raghunath Padiyath and Moses M. David (Ex. 1008)
PFAC8	1H, 1H, 2H, 2H-perfluorodecyl acrylate 
PFMAC8	1H, 1H, 2H, 2H-perfluorodecyl methacrylate 
POSA	person of ordinary skill in the art
P2i	patent owner P2i Ltd.
Tropsch	U.S. Patent 5,804,669, "Preparation of Polymers Comprising Peroxycarboxyl Groups," to Jürgen Tropsch and Jörg Breitenbach (Ex. 1011)
WCA	static water contact angle

the '876 patent	U.S. Patent 10,421,876 (Ex. 1001)
xx:*yy*-*zz*	column *xx*, lines *yy* to *zz*

EXHIBIT LIST[1]

Ex. 1001	U.S. Patent 10,421,876, "Coatings," to Stephen Richard Coulson, et al. ("the '876 patent")
Ex. 1002	Declaration of Dr. Karen Gleason
Ex. 1003	Curriculum vitae for Dr. Karen Gleason
Ex. 1004	International Publication WO 2007/083122, "Novel Products," to Stephen Coulson ("Coulson-122")
Ex. 1005	International Publication No. WO 99/64662, "Surface Coatings," to Jas Pal Singh Badyal, et al. ("Badyal")
Ex. 1006	U.S. Patent 2,716,638, "Divinyltetramethyldisiloxane and Polymers Therefrom," to Merrill Cohen and John R. Ladd ("Cohen")
Ex. 1007	U.S. Patent 3,816,564, "Insulation Coating Compositions," to Harvey Ray Holliday and Gary Lee Schurter ("Holliday")
Ex. 1008	U.S. Patent Application Publication US 2007/0020451, "Moisture Barrier Coatings," to Raghunath Padiyath and Moses M. David ("Padiyath")

[1] Citation convention: Where an exhibit contains original page numbering that uniquely identifies each page in the exhibit, this petition uses those page numbers to refer to the pages in the exhibit. Where an exhibit contains original page numbering that does not clearly and uniquely identify each page in the exhibit (such as in the '876 patent's file history, Ex. 1028), or does not contain page numbering at all, unique page numbering added in the lower right corner of the exhibit will be used.

Ex. 1009	Francesch, L. et al, "Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived Monomer," *Plasma Processes and Polymers*, 2:605–11 (2005) ("Francesch")
Ex. 1010	Declaration of Dr. Salvador Borrós Gómez
Ex. 1011	U.S. Patent 5,804,669, "Preparation of Polymers Comprising Peroxycarboxyl Groups," to Jürgen Tropsch and Jörg Breitenbach ("Tropsch")
Ex. 1012	International Publication WO 2012/158953, "Coated Electronic Devices and Associated Methods," to Filip Legein, et al.
Ex. 1013	U.S. Patent Application Publication US 2013/0176700, "Electronic Devices with Internal Moisture Resistant Coatings," to Blake Stevens, et al.
Ex. 1014	International Publication WO 2014/026967, "Surface Coatings," to Filip Legein, et al.
Ex. 1015	U.S. Patent Application Publication US 2005/0141738, "Hydrophobic Coating of Individual Components of Hearing Aid Devices," to Erdal Karamuk
Ex. 1016	U.S. Patent 6,551,950, "Surface Coatings," to Jas P S Badyal, et al.
Ex. 1017	U.S. Patent 4,562,091, "Use of Plasma Polymerized Organosilicon Films in Fabrication of Lift-Off Masks," to Harbans S. Sachdev and Krishna G. Sachdev
Ex. 1018	U.S. Patent 7,439,315, "Polymer Film and Method for Producing the Same," to Nobutaka Kunimi, et al.
Ex. 1019	Coulson, S.R., et al., "Ultralow Surface Energy Plasma Polymer Films," *Chemistry of Materials* 12(7):2031–2038 (2000)
Ex. 1020	Declaration of S. Rampersad

Ex. 1021	U.S. Patent Application Publication US 2010/0203347, "Method for Liquid Proofing an Item by Plasma Graft Polymerisation," to Stephen Coulson (Coulson-347)
Ex. 1022	International Publication WO 98/58117, "Surface Coatings," to Jas Pal Singh Badyal, et al.
Ex. 1023	Tarducci, C., et al., "Synthesis of Cross-Linked Ethylene Glycol Dimethacrylate and Cyclic Methacrylic Anhydride Polymer Structures by Pulsed Plasma Deposition," *Macromolecules* 35(23):8724–8727 (2002)
Ex. 1024	U.S. Patent 6,214,423, "Method of Forming a Polymer on a Surface," to Wei William Lee, et al.
Ex. 1025	International Publication WO 2012/168440, "A Coated Substrate Having Hydrophobic Moiety-Repelling Surface Characteristics and Process for Preparing the Same," to Christian Taesler
Ex. 1026	Yagüe, J.L. and Gleason, K.K., "Enhanced Cross-Linked Density by Annealing on Fluorinated Polymers Synthesized via Initiated Chemical Vapor Deposition to Prevent Surface Reconstruction," *Macromolecules* 46(16):6548-6554 (2013)
Ex. 1027	U.S. Patent 6,207,238, "Plasma Enhanced Chemical Deposition for High and/or Low Index of Refraction Polymers," to John D. Affinito
Ex. 1028	Prosecution history of the '876 patent
Ex. 1029	Yao, W., et al., "Fluorinated poly(meth)acrylate: Synthesis and properties," *Polymer* 55(24):6197-6211 (2014)
Ex. 1030	U.S. Patent Application Publication US 2013/0135936, "Gas Barrier Base Material and Gas Barrier Laminate," to Takeshi Morozumi, et al.
Ex. 1031	U.S. Patent Application Publication US 2011/0148979, "Curable Phase Change Inks," to Marcel P. Breton, et al.

Ex. 1032	Sartomer Company Material Safety Data Sheet, Product CD406, dated June 9, 2005
Ex. 1033	U.S. Patent Application Publication US2005/0034667, "Method and Apparatus for Forming Silicon-Containing Insulation Film Having Low Dielectric Constant," to Naoto Tsuji, et al.
Ex. 1034	Yasuda, H., *Plasma Polymerization*, 1985 Academic Press, London (Excerpts)
Ex. 1035	Kurosawa, S., et al., "Detection of deposition rate of plasma-polymerized acrylate and methacrylate derivatives using quartz crystal microbalance," *Thin Solid Films* 457:26-33 (2004)
Ex. 1036	Kurosawa, S., et al., "Detection of deposition rate of plasma-polymerized silicon-containing films by quartz crystal microbalance," *Thin Solid Films* 407:1–6 (2002)
Ex. 1037	Joback, K.G. and Reid, R.C., "Estimation of Pure-Component Properties from Group-Contributions," *Chem. Eng. Comm.* 57:233-243 (1987)
Ex. 1038	U.S. Patent Application Publication US 2006/0122301, "Fluorinated divinyl ethers," to Haridasan K. Nair and David Nalewajek
Ex. 1039	Chemical information obtained from chemspider.com

I. Introduction

Petitioner Favored Tech Corporation ("Favored" or "Petitioner") requests IPR and cancelation of claims 1-15 of U.S. Patent 10,421,876 ('876 patent) (Ex. 1001).

Patent owner P2i first applied for the '876 patent in 2015. The '876 patent claims electronics having a protective coating applied by co-polymerizing prior-art fluorinated monomers with prior-art crosslinking reagents under known plasma conditions. But P2i and others had already long-since described (and repeatedly patented) using the same monomers and the same plasma-coating approach to protect various articles, including electronics, against water and other contaminants. P2i had also described combining those same fluorinated monomers with a crosslinking reagent to obtain protective coatings with enhanced durability. By 2007, every aspect of the '876 claims was well known: protecting electronics with polymer coatings, combining a fluorinated monomer with a crosslinker to make such coatings, and using plasma polymerization to apply them.

P2i's effort to obtain still more claims on fluorinated plasma-polymer coatings through the '876 patent eventually turned on identifying a hodgepodge of specific crosslinkers that the examiner failed to uncover in the prior art during prosecution. As a result, the claims recite various crosslinkers having two double bonds and a mix of different bridging groups from several different structural categories. All of those claimed crosslinkers, however, fell within a prior-art genus that had been

described for use with the claimed monomers more than 15 years earlier. Furthermore, the claimed crosslinkers—like the prior-art genus to which they all belonged—were well known and long used in the polymer art. For example, the claims cover divinyl tetramethyl disiloxane (DVTMDS), which had been used since the 1950s as a crosslinker in water-repellent polymer coatings for electrical devices.

In short, the '876 claims represent the combination of familiar elements according to known methods with predictable results. They present a textbook case of obviousness and should be canceled on the grounds presented here. Favored asks that the Board institute IPR and hold the challenged claims unpatentable under 35 U.S.C. § 103.

II. Mandatory notices

In compliance with 37 C.F.R. § 42.8(b), Petitioner submits the following mandatory notices.

A. Real party in interest

The real-parties-in-interest are Favored Tech Corporation; Shenzhen Favored Nanotechnology Co., Ltd.; and Jiangsu Favored Nanotechnology Co., Ltd.

B. Related matters

Petitioner and counsel for Petitioner are not aware of any judicial or administrative matter that would affect, or be affected by, a decision in this proceeding.

C. Counsel and service information

Pursuant to 37 C.F.R. §§ 42.8(b) and 42.10(a), Petitioner appoints the

following lead and back-up counsel:

Lead Counsel	**Back-Up Counsel**
Andrew T. Dufresne Reg. No. 66,636 PERKINS COIE LLP 33 East Main Street, Suite 201 Madison, WI 53703 tel: 608.663.7460 fax: 608.663.7499 dufresne-ptab@perkinscoie.com	Han-Wei Chen Reg. No. 75,350 PERKINS COIE LLP 3150 Porter Drive Palo Alto, CA 94304 tel: 650.838.4300 fax: 650.838.4350 chen-ptab@perkinscoie.com
Back-Up Counsel	**Back-Up Counsel**
Nathan K. Kelley Reg. No. 45,295 PERKINS COIE LLP 700 13th Street N.W., Suite 800 Washington, DC 20005 tel: 202.654.6200 fax: 202.654.6211 kelley_nathan-ptab@perkinscoie.com	Mengke Xing Reg. No. 76,534 PERKINS COIE LLP 11452 El Camino Real, Suite 300 San Diego, CA 92130 tel: 858.720.5700 fax: 858.720 5799 xing-ptab@perkinscoie.com

Counsel can be reached using the contact information provided above, and Petitioner consents to electronic service at the indicated e-mail addresses. Petitioner has executed and is filing a corresponding power of attorney.

III. Requirements for *inter partes* review

This petition complies with all requirements, including 37 C.F.R. §§ 42.104, 42.105, and 42.15, and should be accorded a filing date under 37 C.F.R. § 42.106. Petitioner authorizes the Director to charge any required fees to Deposit Account

50-0665, charge number 127908.0001.

A. Grounds for standing

Petitioner certifies under § 42.104(a) that the '876 patent is available for IPR and that Favored is not barred or estopped from requesting IPR on the grounds identified. Favored meets all requirements under 35 U.S.C. §§ 315(a)(1), 315(b), and 315(e)(1), and 37 C.F.R. §§ 42.73(d)(1), 42.101, and 42.102.

B. Identification of challenge

Under 37 C.F.R. §§ 42.104(b) and 42.22, Petitioner requests IPR and cancelation of claims 1-15 on the following grounds under § 103:

Ground	Claims	Basis for Unpatentability
Ground 1	1-3, 9, 11-15	Obvious over Coulson-122, Badyal, and Cohen
Ground 2	1-8, 10-15	Obvious over Coulson-122, Badyal, and Holliday
Ground 3	1-4, 10, 12-15	Obvious over Coulson-122, Badyal, and Padiyath
Ground 4	1-3, 5-8, 11-15	Obvious over Coulson-122, Badyal, and Francesch
Ground 5	1-3, 5-8, 12-15	Obvious over Coulson-122, Badyal, and Tropsch

Each ground includes Coulson-122 (Ex. 1004) and Badyal (Ex. 1005). Coulson-122 and Badyal described protective plasma-polymer coatings prepared using the same fluorinated monomers claimed in the '876 patent, and Badyal described combining those monomers with the same family of crosslinkers as the '876 patent. The third reference differs in each ground: Cohen (Ex. 1006), Holliday (Ex. 1007),

Padiyath (Ex. 1008), Francesch (Ex. 1009), and Tropsch (Ex. 1011). Those references described specific, prior-art crosslinkers that fell within Badyal's prior-art genus and had bridging groups matching the various structures specified in each subset of the '876 claims.

Coulson-122 was considered during prosecution, but the remaining references (Badyal, Cohen, Holliday, Padiyath, Francesch, and Tropsch) were not before the examiner. Petitioner further relies on the declaration of Dr. Karen Gleason (Ex. 1002) and other references in the exhibit list. Section VII details how the claims are unpatentable and identifies where each limitation appeared in the prior art.

IV. The '876 patent and protective coatings for electronic devices

The '876 patent claims electronics with a protective coating applied under plasma conditions using two components: (1) an acrylate-based monomer, and (2) a crosslinking reagent having two double bonds and a bridging group with one of several structural formulas.

Those features were well known by the patent's asserted priority date in June 2015. Portable electronics were everywhere, and the recognized risk of damage from spills and environmental exposure provided ample motivation to apply protective, water-repellent coatings. Plasma polymerization was by then widely used to apply such coatings to various substrates, including electronics. Moreover, the types of monomers and crosslinkers in the '876 claims were known, and the prior art had

already suggested using them together. The '876 patent simply claimed the use of known compounds according to their known functions to produce an expected result. Those claims were obvious over the prior art.

A. The earliest priority date is June 9, 2015

The '876 patent claims priority to European Patent Application No. 15386017, filed on June 9, 2015. For purposes of this proceeding, Petitioner assumes but does not concede that priority date. The AIA versions of 35 U.S.C. §§ 102 and 103 apply.

B. The state of the art by June 2015

1. Ubiquitous portable electronics were being coated to protect against environmental contaminants

By June 2015, portable electronics like mobile phones and laptop computers were commonplace. It was well known that such devices could be damaged by environmental contaminants, including corrosive gases like water vapor or oxygen and liquids from rain, spills, etc. *E.g.*, Ex. 1004 1:9-34; Ex. 1012 1:9-2:12; Ex. 1013 ¶¶ 1-2; Ex. 1008 ¶ 2. Accordingly, skilled artisans had described various polymer coatings to protect electronic devices against such damage. Ex. 1004 Abstract; Ex. 1008 ¶¶ 5, 21-24; Ex. 1012 2:8-3:14, 7:3-21; Ex. 1013 ¶¶ 2-6, 44-46; Ex. 1014 4:14-6:11; Ex. 1015 ¶¶ 11, 30-34. Such coatings were designed to serve known functions like repelling water (Ex. 1012 11:4-11; Ex. 1013 ¶¶ 3-4, 41-46; Ex. 1014 11:17-12:25; Ex. 1015 ¶ 11), creating a barrier against passage of water or other molecules between the device and the environment (Ex. 1008 ¶ 24; Ex. 1012 7:3-10; Ex. 1013 ¶¶ 39-40;

Ex. 1014 16:7-9), and providing electrical insulation (Ex. 1012 7:3-10; Ex. 1014 5:13). *See* Ex. 1002 ¶¶56-58, 128.

2. Plasma polymerization was routine and had been used to apply protective coatings to electronics

One common method for applying prior-art coatings was plasma polymerization. Ex. 1004 2:33-4:3; Ex. 1012 7:22-8:7; Ex. 1014 6:10-11; Ex. 1008 ¶11; 1013 ¶¶45-46; Ex. 1015 ¶29.

Plasma polymerization referred to forming polymeric materials under plasma conditions. Ex. 1002 ¶32; Ex. 1004 2:33-3:12; Ex. 1012 3:5-14. Typically, plasma polymerization involved vaporizing one or more organic compounds and passing the resulting gas through an enclosed plasma chamber, where an electrical field was applied to induce a plasma state. Ex. 1002 ¶¶33-38; Ex. 1004 3:20-4:3, 7:6-17; Ex. 1012 11:17-13:20; Ex. 1014 21:20-25. The term *plasma* described gas in an ionized state, which POSAs sometimes referred to as a "glow discharge" because plasmas often give off visible light. Ex. 1002 ¶¶32, 34; Ex. 1004 7:14-17; Ex. 1017 3:26-33. When a substrate is present, reactive species in the plasma impinge on the substrate where they form a plasma-polymer film on its surface. Ex. 1002 ¶36; Ex. 1005 2:14-24; Ex. 1012 13:5-20; Ex. 1014 21:20-22:2; Ex. 1018 8:17-48.

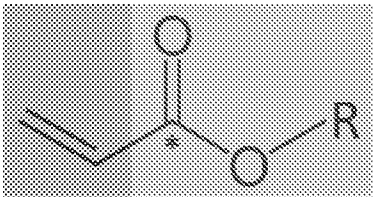
Plasma polymerization was widely used by 2015. Ex. 1002 ¶¶32, 64, 134. The '876 patent acknowledges that conditions for applying plasma-polymer coatings could be determined "using routine methods." Ex. 1001 14:59-67. Plasma

polymerization had by then been "quite widely used for the deposition of polymeric coatings onto a range of surfaces," and equipment for applying plasma coatings was "conventional" and "known in the art." Ex. 1005 2:10-12, 11:26-27; *see also* Ex. 1004 6:25-7:12; Ex. 1005 10:8-12, 11:26-27; Ex. 1012 8:22-10:12; Ex. 1016 1:40-50; Ex. 1017 3:26-40; Ex. 1027 1:20-41; Ex. 1002 ¶¶27, 54, 64.

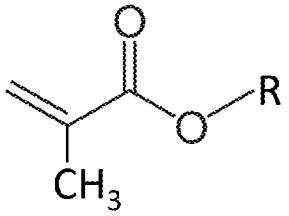
3. Fluorinated acrylate and methacrylate monomers had long been used for coating many substrates, including electronics

Polymers created via plasma polymerization (or other conventional activation techniques) generally comprise repeating monomers linked together to form larger chains or networks. Ex. 1002 ¶¶32, 40-41. Monomers for polymer production typically included at least one reactive group, such as a double bond, capable of facilitating intermolecular bond formation. Ex. 1002 ¶¶39-41.

Acrylate-based molecules were among the most well-known and widely used monomers for polymer production. Ex. 1002 ¶¶39, 42-44. Most acrylates used for polymerization were acrylate esters, as illustrated below:

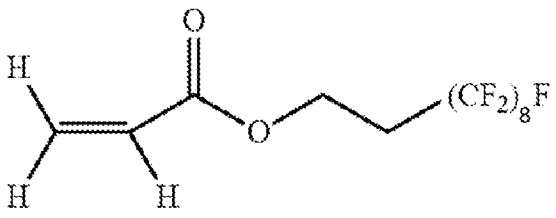


Ex. 1002 ¶43. Acrylate esters characteristically contained a vinyl group (blue) directly linked to the carbonyl carbon (starred) of an ester group (green). *Id.* Methacrylates, a common type of modified acrylate, contained a methylated vinyl group:

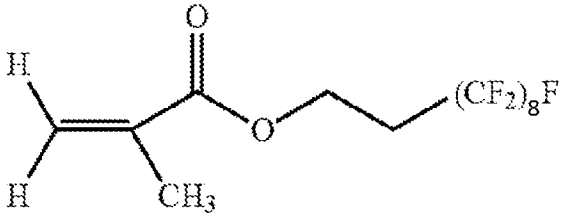


Id.

Acrylate-based monomers were known as bifunctional and versatile: the vinyl group's double bond facilitated polymerization, and the ester group could introduce various functional substituents at the variable R position. Ex. 1002 ¶¶43-44. By 2015, acrylate and methacrylate monomers with fluoroalkyl groups had long been used for their beneficial properties in plasma-polymer coatings, including water repellency and electrical insulation. Ex. 1002 ¶¶43-44, 47. Two such monomers were 1H,1H,2H,2H-perfluorodecyl acrylate (PFAC8) and 1H,1H,2H,2H-perfluorodecyl methacrylate (PFMAC8):



PFAC8



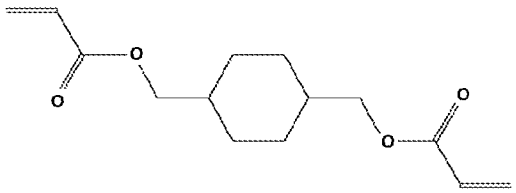
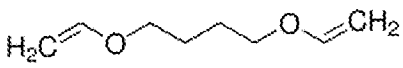
PFMAC8

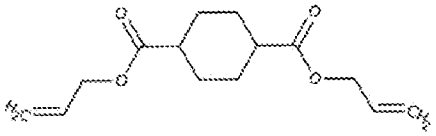
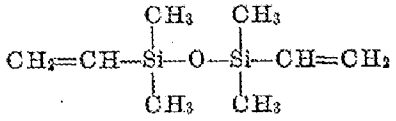
Ex. 1002 ¶45; Ex. 1004 12:7-22, 14:7-23; Ex. 1005 8:15-9:27, Ex. 1014 16:16-27; Ex. 1019 at 2032; Ex. 1016 7:49-67; Ex. 2021 ¶28; Ex. 1022 6:1-7:31, 16:19-17:3. Those and other structurally similar fluorinated monomers had been used for protective coatings on various substrates, including electronics. Ex. 1002 ¶¶45, 48; *e.g.*,

Ex. 1004 12:7-14:23; Ex. 1014 16:11-27; Ex. 1029 at 6197-98.

4. Crosslinkers were commonplace in polymer production

In addition to monomers like PFAC8 and PFMAC8, POSAs regularly incorporated crosslinkers into prior-art polymer coatings. In general, crosslinkers have at least two reactive sites, usually two double bonds. Ex. 1002 ¶51. Numerous crosslinking reagents containing two double bonds had been used with acrylate-based monomers to produce crosslinked coatings. Ex. 1002 ¶¶50-53, 117; *e.g.*, Ex. 1006 1:15-30, 3:50-65; Ex. 1007 3:20-60; Ex. 1008 ¶¶11, 52-54; Ex. 1009 at 607; Ex. 1011 3:1-4:39; Ex. 1025 ¶¶11, 20. Crosslinkers were often grouped into families characterized by their structural configurations around the reactive double bonds. Familiar categories included diacrylate, divinyl ether, diallyl, and divinyl crosslinkers:

Diacrylate	
configuration	CH_2=CH-(C=O)-O-Z-O-(C=O)-CH=CH_2
example	 cyclohexane-1,4-dimethanol diacrylate (CDMDA)
Divinyl ether	
configuration	CH_2=CH-O-Z-O-CH=CH_2
example	 1,4-butanediol divinyl ether (BDVE)

Diallyl	
configuration	CH_2=CH-CH_2-Z-CH_2-CH=CH_2
example	 diallyl 1,4-cyclohexanedicarboxylate (DCHD)
Divinyl	
configuration	CH_2=CH-X-Z-X-CH=CH_2 ***X is not O, O-(C=O), or CH_2*
example	 divinyl tetramethyl disiloxane (DVTMDS)

Ex. 1002 ¶51.

Crosslinking was known to impart "good chemical and mechanical stability characteristics." Ex. 1023 at 8724. For example, the prior art taught that water-repellent coatings could be improved by co-polymerizing fluorinated acrylate-based monomers with a crosslinking reagent. Ex. 1005 4:1-9. The resulting crosslinked coating that demonstrated improved durability while retaining protective properties obtained with the monomer alone. Ex. 1005 4:1-9, 4:17-5:5; Ex. 1002 ¶¶49-50.

POSAs also knew that crosslinking led to improved barrier properties against passage of liquids or gases and resulted in greater solvent and chemical resistance. Ex. 1002 ¶50; Ex. 1006 3:50-65; Ex. 1008 ¶¶2, 11, 25, 52; Ex. 1025 ¶¶20-21, 34, 36; Ex. 1009 at 610. When used with monomers like PFAC8, crosslinkers were also

known to reduce the tendency of hydrophobic fluorinated groups to migrate away from the coating surface when exposed to water (known as hysteresis), thus improving water repellency under wet conditions. Ex. 1002 ¶ 50; Ex. 1026 at 6552.

C. Overview of prior-art references

The prior art taught the use of plasma polymerization to provide protective coatings for electronics, the beneficial use of crosslinking reagents in protective polymeric coatings, and specific examples of such reagents.

1. Coulson-122 described protective plasma-polymer coatings for electronics made using PFAC8 and PFMAC8

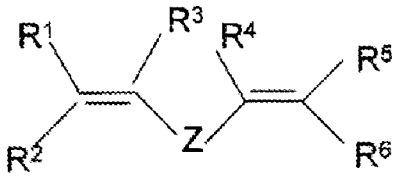
Coulson-122 (Ex. 1004) described electronics with liquid-repellent polymer coatings. Ex. 1004 Abstract. The coatings were applied by plasma polymerizing fluorinated monomers including PFAC8 or PFMAC8. Ex. 1004 3:14-25, 11:1-12:22; Ex. 1002 ¶¶ 66-68, 114. Coulson-122 taught that such monomers produced "highly liquid-repellent nano-coatings," such that treated devices like mobile phones could be "fully immersed in water … without any lasting harm." Ex. 1004 3:14-18, 4:29-5:10.

2. Badyal described plasma-polymer coatings combining PFAC8 or PFMAC8 with a generic crosslinker

Badyal (Ex. 1005) described liquid-repellent plasma-polymer coatings that could be applied to "any solid substrate" using the same PFAC8 and PFMAC8 monomers in Coulson-122. Ex. 1005 7:17-9:19, 9:28-30, 11:19-24; Ex. 1002 ¶¶ 69, 115.

To improve the durability of such coatings, Badyal taught combining the

monomer with a crosslinker, preferably of the following generic formula:

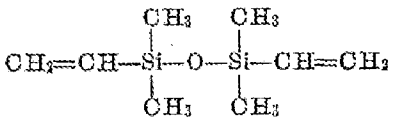
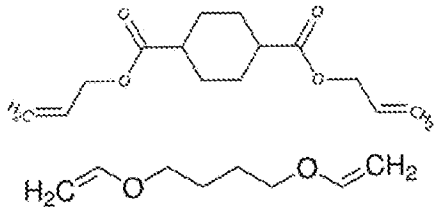
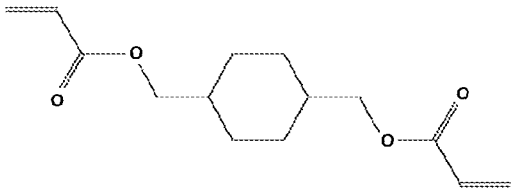
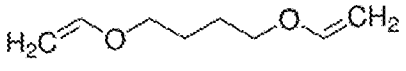


Ex. 1005 4:1-5:5. The R_1-R_6 positions could include hydrogen or alkyl groups, and bridging group Z could include substituents "known in the polymer art," including alkyl groups interposed with oxygen atoms. Ex. 1005 5:1-5, 5:18-23. Badyal thus described suitable crosslinkers in expansive terms but provided few examples of specific bridging groups. Ex. 1005 6:15-20; Ex. 1002 ¶¶69-70, 116.

Plasma polymerizing monomers like PFAC8 with a crosslinker produced crosslinked, well-adhered coatings with excellent water-repellency and durability. Ex. 1005 4:4-29, 10:32-11:17.

3. Cohen, Holliday, Padiyath, Francesch, and Tropsch described crosslinkers with the claimed bridging groups

While Badyal taught the value of crosslinkers and described them in broad terms, other references described specific crosslinking reagents. Cohen, Holliday, Padiyath, Francesch, and Tropsch described specific crosslinkers having the same generic structure described by Badyal, each with two double bonds separated by a bridging group:

Cohen (Ex. 1006 1:25-30)	DVTMDS	
Holliday (Ex. 1007 3:34-35, 3:52-53)	DCHD BDVE	
Padiyath (Ex. 1008 ¶54)	CDMDA	
Francesch (Ex. 1009 at 606-07)	BDVE	
Tropsch (Ex. 1011 4:34-39)	HDVE	

D. Overview of the '876 patent

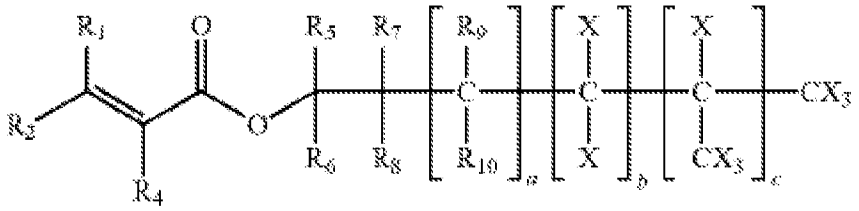
The '876 patent claims electronic devices with a plasma-polymer coating prepared using an acrylate or methacrylate monomer and a crosslinker. Ex. 1001 2:10-21, 18:26-19:57 (claim 1). Every feature of the '876 claims was known, and they recite the predictable use of known compounds for known purposes. The claims are therefore unpatentable over the prior art.

1. Specification and claims

In the '876 patent, coated devices include "a wide variety of substrates" like smartphones, microphones, or circuit boards. Ex. 1001 14:30-58. Conditions for applying the plasma polymers are flexible and "can be determined using routine methods." Ex. 1001 14:59-67. Most of the specification focuses on the structures of the

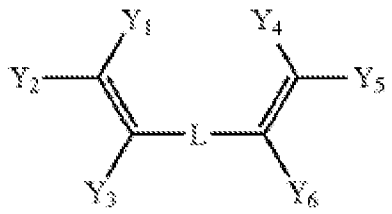
monomer and crosslinker in the claimed coatings. Ex. 1001 4:36-13:8; Ex. 1002 ¶ 59.

Claim 1, the sole independent claim, recites a monomer with the following generic structure:



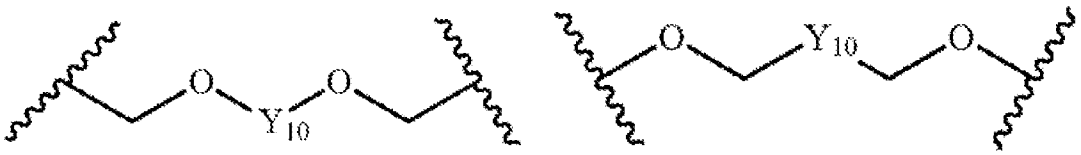
Ex. 1001 18:30-53. The monomer is an acrylate, with a vinyl group, an ester group and an optionally halogen-substituted alkyl tail. Ex. 1002 ¶ 60; Ex. 1001 18:49-53. PFAC8 and PFMAC8 both satisfy the generic formula recited in claim 1, and both are described as particularly preferred embodiments. Ex. 1001 10:22-11:56, 21:7-22:21 (claims 12-15); Ex. 1002 ¶¶ 60, 122. The '876 patent admits that such monomers were known and used to make hydrophobic plasma-polymer coatings. Ex. 1001 1:16-46 (citing Ex. 1022).

For the crosslinker, claim 1 recites the following generic structure:

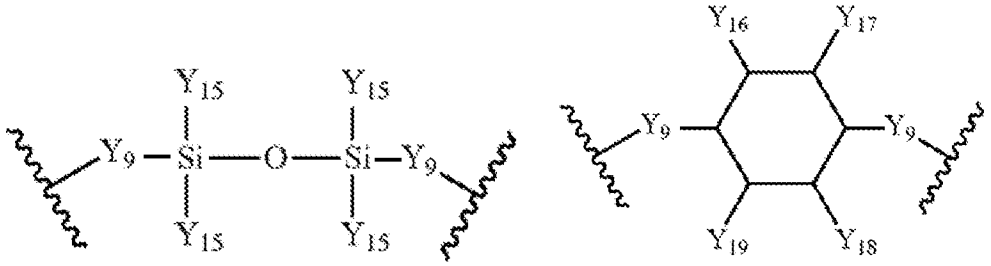


Ex. 1001 18:54-19:8.[1] That structure includes two double bonds flanking a generic bridging group ("linker moiety L"). Ex. 1001 4:51-67; Ex. 1002 ¶61. The '876 patent explains that the "basic requirement" for a crosslinker is two or more unsaturated bonds. Ex. 1001 4:36-40; Ex. 1002 ¶61. In contrast, the bridging group "is not especially limited" and need only bridge the two double bonds. Ex. 1001 4:40-42.

Claim 1 covers four alternative generic structures for the bridging group. The claims group the first two as "formula A":



Ex. 1001 19:9-19. The next two represent "formula B":



Ex. 1002 ¶62; *see* Ex. 1001 19:20-57. Those four generic structures encompass a wide variety of diacrylate, divinyl ether, diallyl, and divinyl crosslinkers. Ex. 1002 ¶¶63, 51; *see* Ex. 1001 5:1-9:20. Dependent claims 4-10 add further structural

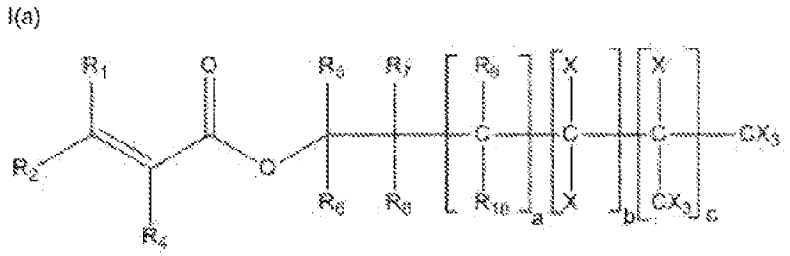
[1] Alternatively, claim 1 recites crosslinkers having two triple bonds. Ex. 1001 19:1-4. Those compounds are not relevant to the asserted grounds.

limitations within one or more of the claimed bridging-group configurations. Ex. 1001 19:65-20:64. Several specific examples appear in Table 1 and dependent claim 11. Ex. 1001 8:19-9:20, 20:65-21:6 (claim 11).

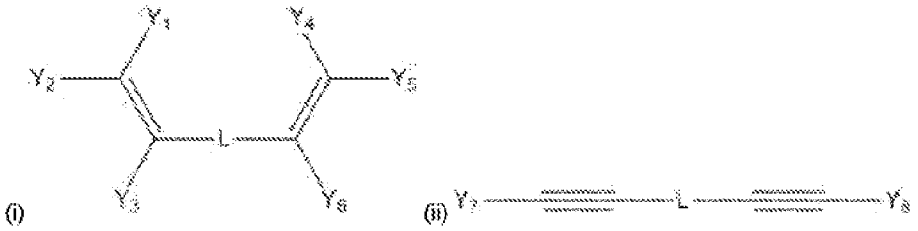
Other dependent claims recite that the coating provides liquid repellency or a physical barrier (claims 2-3), or recite specific monomer species, including PFAC8 and PFMAC8 (claims 12-15). Ex. 1001 19:58-64, 21:7-22:21.

2. Prosecution history

The initial claims during prosecution recited a coating made using any acrylate-based monomer of formula 1(a)



and any crosslinker of structure (i) or (ii)



Ex. 1028 at 177-84 (preliminary amendment). Numerous dependent claims specified options for the bridging group. Ex. 1028 at 180-82.

The examiner's first action indicated allowable subject matter in dependent claims 7 and 12-15 because the examiner had not identified art showing the bridging

groups in those claims. Ex. 1028 at 251. The remaining 14 claims were rejected for obviousness over U.S. 2010/0203347 (Coulson-347, Ex. 1021) and Coulson-122 (Ex. 1004). Ex. 1028 at 243, 247-51.

The applicant responded by amending claim 1 to incorporate the various bridging groups from original claims 5, 7, 12, and 14 as "Formula A" or "Formula B." Ex. 1028 at 295, 391-93. Less than two months later, the examiner allowed the claims. Ex. 1028 at 400. According to the examiner, the claims were allowed because Coulson-347 and Coulson-122 did not teach those specific crosslinking reagents. Ex. 1028 at 406-07.

The examiner did not consider Badyal's teachings about the benefits of cross-linking or the specific prior-art crosslinkers described by Cohen, Holliday, Padiyath, Francesch, and Tropsch. Those references were not before the examiner.

E. Level of ordinary skill in the art

A person of ordinary skill in the art ("POSA") in June 2015 would have had at least a bachelor's degree in a field such as chemistry, physics, or chemical engineering, as well as at least two years of experience with plasma-polymerization techniques. Ex. 1002 ¶¶ 22-29.

V. Claim construction

The Board construes claims "using the same claim construction standard that would be used in a civil action." 37 C.F.R. § 42.100(b). Accordingly, "a claim

receives the meaning it would have to persons in the field of the invention, when read and understood in light of the entire specification and prosecution history." *Fenner Invs., Ltd. v. Cellco P'ship*, 778 F.3d 1320, 1323 (Fed. Cir. 2015).

A. "Halogen" includes at least fluorine, chlorine, and bromine

As understood by a POSA in light of the intrinsic record, the term "halogen" in claim 1 includes at least fluorine, chlorine, and bromine.

The '876 patent refers to a halogen as an optional substituent at selected sites in some monomers. Ex. 1001 Abstract, 2:35-43, 9:45, 9:64, 10:36-37, 10:55. Several preferred monomers include fluorine at those same sites. Ex. 1001 11:16-17, 11:30-56. Furthermore, the specification expressly states that "[t]he halogen may be chlorine or bromine, but is preferably fluorine." Ex. 1001 10:57-58. The specification therefore demonstrates that "halogen" includes at least fluorine, chlorine, and bromine. That is also consistent with the ordinary understanding in the art. Ex. 1002 ¶¶ 109-111. POSAs understood "halogen" as a generic term for the elements within Group 17 of the periodic table, which was known to include fluorine, chlorine, and bromine, among others. *Id.*

Accordingly, a POSA would have understood "halogen" as used in the claims to include at least fluorine, chlorine, and bromine.

VI. The cited references are prior art

Each of the cited patents and printed publications was patented or published

before June 9, 2015.

A. Coulson-122

Coulson-122 (Ex. 1004) was published as International Publication WO 2007/083122 on 7-26-2007 and is therefore prior art under § 102(a)(1). Coulson-122 was before the examiner during prosecution of the '876 patent.

B. Badyal

Badyal (Ex. 1005) published as International Publication WO 99/64662 on 12-16-1999 and is prior art under § 102(a)(1). Badyal was not before the examiner.

C. Cohen

Cohen (Ex. 1006) issued as U.S. Patent 2,716,638 on 8-30-1955 and qualifies as prior art under § 102(a)(1). Cohen was not before the examiner.

D. Holliday

Holliday (Ex. 1007) issued as U.S. Patent 3,816,564 on 6-11-1974 and qualifies as prior art under § 102(a)(1). Holliday was not before the examiner.

E. Padiyath

Padiyath (Ex. 1008) published on 1-25-2007, as U.S. Patent Application Publication US 2007/0020451 and is prior art under § 102(a)(1). Padiyath was not before the examiner.

F. Francesch

Francesch (Ex. 1009) is a scientific article entitled "Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived

Monomer," published in the journal *Plasma Processes and Polymers*. Francesch bears a year-2005 copyright notice as a publication of Wiley-VCH Verlag GmbH & Co., as well an abbreviated citation bearing the year 2005 ("*Plasma Process. Polym.* 2005, 2, 605–611"). Ex. 1009 at 605. A POSA would have recognized Wiley as an established publisher of scientific and technical articles and would have been familiar with *Plasma Processes and Polymers* as a well-known scientific journal in the polymer field. Ex. 1002 ¶77. The copyright and citation dates thus demonstrate that Francesch became publicly available as a printed publication during the year 2005. *See Hulu, LLC v. Sound View Innovations, LLC*, IPR2018-01039, Paper 29 at 19-20 (PTAB Dec. 20, 2019) (precedential). In addition, the accompanying declaration provided by an author of the article demonstrates that Francesch was made publicly available in September 2005. Ex. 1010. Accordingly, Francesch is a prior-art printed publication under § 102(a)(1). Francesch was not before the examiner during prosecution.

G. Tropsch

Tropsch (Ex. 1011) issued as U.S. Patent 5,804,669 on 9-8-1998 and is prior art under § 102(a)(1). Tropsch was not before the examiner.

VII. Detailed discussion of the grounds for unpatentability

Every claim in the '876 patent would have been obvious over the prior art. The claims cover protective coatings applied to an electronic device by plasma

polymerizing PFAC8 or PFMAC8 with a crosslinker having two double bonds and one of several different bridging groups. Applying protective plasma-polymer coatings to electronics was well known, and the prior art described using the claimed monomers and using crosslinkers with those monomers.

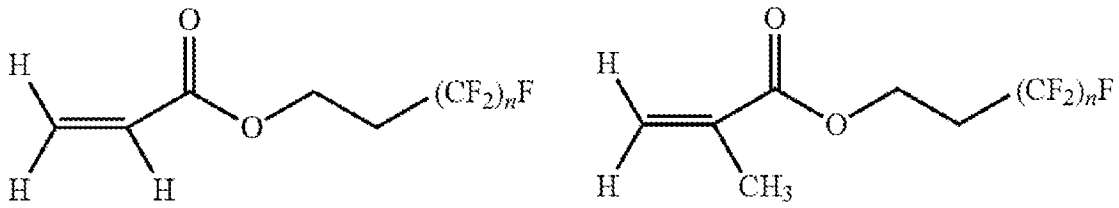
The '876 patent was nevertheless allowed to issue by claiming a jumble of crosslinkers because the examiner concluded that crosslinkers with several claimed bridging-group structures were absent from the prior art. That conclusion was wrong. As detailed below, the prior art taught *every* aspect the claims—including the collection of bridging groups in claim 1 and those recited separately in various dependent claims. Crosslinking reagents with each of those bridging groups were known and would have been obvious for use in prior-art coatings. The asserted grounds have not previously been considered by the Office, and they demonstrate that the '876 patent never should have issued.

A. <u>All Grounds</u>: Coulson-122 and Badyal described coatings applied using the same polymerization techniques, the same monomeric compounds, and the same group of crosslinkers as the '876 patent

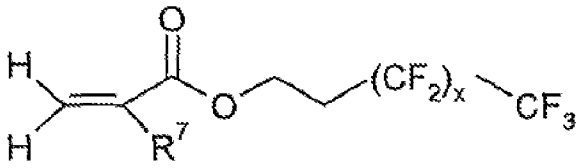
Coulson-122 and Badyal both were published well before June 2015, and those references together described nearly every aspect of the '876 claims.

Coulson-122 emphasized the "well-known" and "acute" need to protect electronic devices from liquids. *E.g.*, Ex. 1004 1:3-34. It then described coating electronics with protective, liquid-repellent polymer coatings formed by plasma

deposition using the same acrylate and methacrylate monomers as the '876 patent, including monomers *identical* to those specified in claims 12-15. *E.g.*, Ex. 1004 3:20-4:3, 12:7-23; Ex. 1001 21:7-22:21. For example, claims 1-15 all cover one or both of the following acrylate and methacrylate fluorinated monomer structures:



where *n* is 2-10, such as eight (PFAC8/PFMAC8). Ex. 1001 21:7-22:21 (dependent claims 12-15), 11:27-56; Ex. 1002 ¶60. Coulson-122 had long before described using the same monomers, as shown below:

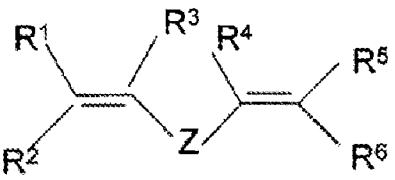


Ex. 1004 12:13-22. In particular, R^7 was described as hydrogen or methyl, and *x* was 1-9, such as seven (*i.e.*, PFAC8/PFMAC8).[2] Ex. 1004 12:13-22; Ex. 1002 ¶¶67, 114, 120. Badyal taught coatings applied to "any solid substrate," and described using the

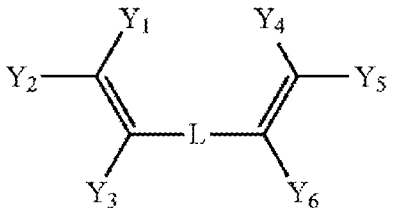
[2] Specifying *x* as seven in Coulson-122 and *n* as eight in the '876 patent identifies the same compounds (PFAC8 and PFMAC8) because Coulson-122 depicted the terminal CF_3 group separately from the repeating CF_2 chain, while the '876 patent presented the terminal carbon as part of the chain. Ex. 1002 ¶¶44, 114.

same monomers as Coulson-122 to apply liquid-repellent coatings by plasma polymerization. Ex. 1005 4:11-23, 7:20-9:34, 10:32-11:27; Ex. 1002 ¶¶69, 115, 118, 121.

Badyal further taught combining those monomers with a crosslinker to form crosslinked plasma-polymer coatings with improved durability. Ex. 1005 4:1-5:23. And Badyal described crosslinking reagents of the *same basic structure* as those claimed in the '876 patent:



Badyal



'876 patent

Ex. 1005 5:1-5 (Badyal Formula (I)); Ex. 1001 4:51-67, 18:60-67 ('876 patent formula (i), claim 1). The generic crosslinker structures reproduced above are identical. Ex. 1002 ¶116. Each has two double bonds, six substituent positions (R^1-R^6 and Y_1-Y_6), and a generic "bridging" or "linking" group (Z and L, respectively). Badyal taught that R^1-R^6 are hydrogen, halo, or optionally substituted alkyl or aryl, and preferably all hydrogen. Ex. 1005 5:3-5, 6:5-7. In the '876 patent, Y_1-Y_6 are likewise hydrogen or optionally substituted alkyl or aryl, with every preferred crosslinker

defining Y_1-Y_6 as hydrogen. Ex. 1001 4:64-67, Table 1.

Those references differed from the '876 claims in only *one* part of *one* component of the claimed coatings—specifically, the bridging group of the crosslinking reagent. Badyal described some exemplary bridging groups, especially those containing oxygen atoms, but more broadly taught that "suitable bridging groups … are those known in the polymer art." Ex. 1005 5:18-6:20. A POSA would have taken that advice and plugged in bridging groups from well-known crosslinkers to arrive at the '876 claims. In particular, each claim of the '876 patent recites crosslinkers that had long been known and used in the polymer art. Selecting known crosslinkers from Badyal's known crosslinker genus for use in a known plasma-coating procedure amounted to no more than altering "a structure already known in the prior art … by the mere substitution of one element for another known in the field." *KSR*, 550 U.S. at 416. Accordingly, the claims of the '876 patent would have been obvious over the prior art.

B. Ground 1: Claims 1-3, 9, and 11-15 were obvious over Coulson-122, Badyal, and Cohen

Coulson-122 and Badyal together expressly disclosed every limitation of the '876 claims except for the specific bridging-group structures. Cohen taught one claimed crosslinker that had been known and used for decades to create crosslinked co-polymer coatings used for electrical insulation. Coulson-122, Badyal, and Cohen together would have rendered claims 1-3, 9, and 11-15 of the '876 patent obvious.

1. Claim 1

a. Claim limitations

[*Preamble*] "An electronic or electrical device or electronic or electrical component thereof comprising"

To the extent this preamble is limiting, Coulson-122 described electronic devices and components with protective coatings applied via plasma polymerization. Ex. 1004 Abstract, 3:20-4:3, 4:17-5:26. Cohen similarly described polymer compositions used for insulating electrical devices, Ex. 1006 5:8-25, and Badyal taught that plasma deposition could be used to coat "any solid substrate," which a POSA would have known to include electronic devices, Ex. 1005 9:28-30, 2:10-20, 11:19-24; Ex. 1002 ¶118.

[*1a*] "a protective cross-linked polymeric coating on a surface of said device or component; wherein the protective cross-linked polymeric coating is obtained by exposing said device or component to a plasma comprising a monomer compound and a crosslinking reagent for a period of time sufficient to allow formation of the protective cross-linked polymeric coating on a surface thereof,"

The '876 patent explains that a coating can be protective by repelling water or by forming a barrier to provide electrical insulation. Ex. 1001 1:8-13; Ex. 1002 ¶119. Both Coulson-122 and Badyal described water-repellent coatings applied by plasma polymerization using a hydrophobic monomer, and Badyal expressly described co-polymerizing the monomer with a crosslinking reagent to create crosslinked polymers as claimed.

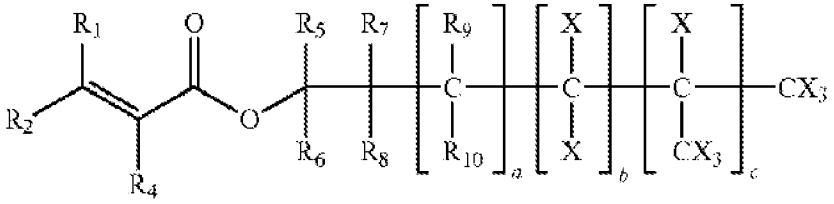
Coulson-122 described electronic devices having a polymeric, liquid-

repellent coating "formed by exposing said device to pulsed plasma." Ex. 1004 3:14-22. The substrates were exposed to a plasma comprising a monomer compound until a protective, water-repellent coating formed on the substrate surface. Ex. 1004 12:24-13:17, 7:14-30, 9:25-28, 10:11-16, 14:7-23.

Badyal also described producing water-repellent coatings on a substrate surface. Ex. 1005 1:3-5, 9:28-32, 11:19-24. The coatings were formed by exposing the substrate to a plasma comprising multiple organic compounds, including a monomer and at least one crosslinking reagent comprising two double bonds, "so as to form a layer of cross-linked polymer" on the substrate's surface. Ex. 1005 4:4-9; *see also id.* 4:17-27. Suitable monomers included the same water-repellent perhalogenated monomers described by Coulson-122. Ex. 1005 6:24-7:15, 8:15-9:19, 11:15-17; Ex. 1002 ¶¶69, 115, 121. Badyal described exposing the substrate to the plasma for a sufficient time to form a protective, water-repellent coating on the substrate surface. Ex. 1005 10:27-11:9; 12:5-9, 4:17-27. Badyal taught that its crosslinked coatings provided improved durability. Ex. 1005 4:1-9, 4:17-29.

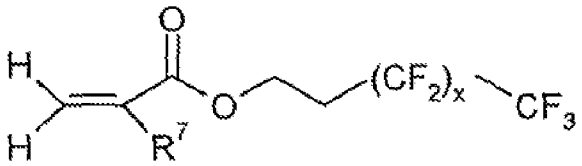
[*1b*] "wherein the monomer compound is a compound of formula I(a):

I(a)



wherein each of R_1, R_2, R_4 and R_5 to R_{10} is independently selected from hydrogen or an optionally substituted C_1-C_6 branched or straight chain alkyl group; each X is independently hydrogen or halogen; a is from 0-10; b is from 3 to 7; and c is 0 or 1;"

Coulson-122 and Badyal both disclosed using monomer compounds matching the acrylate-based structure in claim 1. Coulson-122 described using acrylate-based monomers having the following structure:

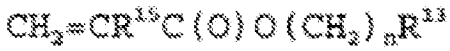


Ex. 1004 12:14-22; Ex. 1002 ¶¶67, 114, 120. Preferred substituents at the R^7 position were hydrogen or methyl, and the number of CF_2 groups (x) was preferably 7. Ex. 1004 12:13-21. A POSA would have recognized the resulting preferred monomers as PFAC8 and PFMAC8.[3] Ex. 1002 ¶120.

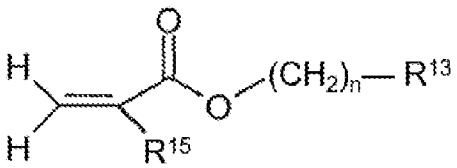
Badyal described the same fluorinated, acrylate-based monomers—PFAC8 and PFMAC8—as Coulson-122. Badyal provided the following preferred monomer

[3] In Example 1, Coulson-122 identified PFAC8 by its unique Chemical Abstracts Service (CAS) number 27905-45-9 and as "1H, 1H, 2H, 2H-heptadecaf luorodecylacylate," which a POSA would have understood as a misspelling of a common synonym for PFAC8: 1H,1H,2H,2H-heptadecafluorodecyl acrylate. Ex. 1004 14:7-10; Ex. 1002 ¶67.

formula:



Ex. 1005 9:10-16. A POSA would have understood that formula as corresponding to the following chemical structure:



Ex. 1002 ¶121. Badyal taught that R^{15} was hydrogen or an "alkyl, such as methyl." Ex. 1005 9:16. The number of CH_2 groups could be from 1-10, preferably two.[4] Ex. 1005 9:15-16, 7:20-28, 8:26-28. And R^{13} was preferably a perfluoroalkyl chain of the formula C_sF_{2s+1}, such as C_8F_{17}. Ex. 1005 8:15-18, 9:15-16. From that description, a POSA would have recognized PFAC8 and PFMAC8 as preferred monomer species. Ex. 1002 ¶121.

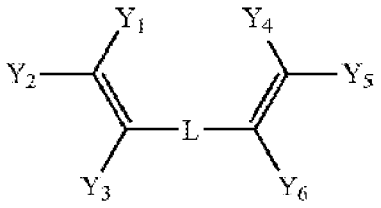
PFAC8 and PFMAC8 both satisfied the claimed monomer formula: (1) R_1, R_2, and R_5-R_8 of claim 1 can be hydrogen; (2) R_4 of claim 1 includes hydrogen (like

[4] Badyal's monomer formula enumerated the CH_2 group using ***n***, but the supporting text referred to ***m***, and a POSA would have understood the formula should read $(CH_2)_m$ to align with the supporting discussion. Ex. 1005 9:15-16, 7:20-28, 8:26-28; Ex. 1002 ¶121.

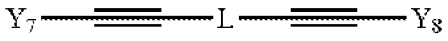
PFAC8) or C_1 alkyl (*i.e.*, methyl, like PFMAC8); (3) each X in claim 1 can be halogen, which includes fluorine; (4) claim 1 includes defining *a* and *c* as zero; and (5) claim 1 includes defining *b* as 7. Ex. 1002 ¶122. Furthermore, PFAC8 and PFMAC8 necessarily fell within the scope of claim 1 because claims 13 and 15 depend from claim 1 and specifically recite PFAC8 and PFMAC8, respectively, as covered monomers. Ex. 1001 21:20-22:21; *Alcon Research, Ltd. v. Apotex Inc.*, 687 F.3d 1362, 1367 (Fed. Cir. 2012).

[*1c*] "and wherein the crosslinking reagent comprises two or more unsaturated bonds attached by means of one or more linker moieties and has a boiling point of less than 500° C. at standard pressure, the crosslinking reagent having one of the following structures:

(i)

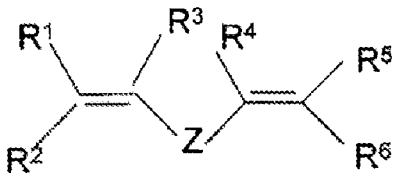


(ii)



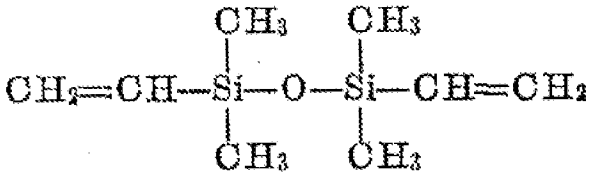
where Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7 and Y_8 are each independently selected from hydrogen, optionally substituted cyclic, branched or straight chain C_1-C_6 alkyl or aryl; and L is a linker moiety;"

Badyal described a crosslinking reagent that matched structure (i) in '876 claim 1. Badyal's crosslinking reagent comprised two double bonds attached through a linker moiety identified as "bridging group Z":



Ex. 1005 4:31-5:5. POSAs knew that a double bond is one type of unsaturated bond. Ex. 1002 ¶124. Badyal disclosed that R^1-R^6 in the prior-art crosslinking reagents could be hydrogen or alkyl, among others, and were preferably hydrogen. Ex. 1005 5:3-5, 6:5-8. Within the disclosed generic crosslinking structure above, Badyal taught that "suitable bridging groups Z" included "those known in the polymer art." Ex. 1005 5:18-19.

Cohen described one specific crosslinking reagent that matched the same generic structure in both Badyal and claim 1 and was "known in the polymer art" since at least 1955: divinyl tetramethyl disiloxane (DVTMDS). The structure of DVTMDS is shown below:



Ex. 1006 1:25-30. DVTMDS contained two double bonds, hydrogen at each of Badyal's R^1-R^6 positions (positions $Y_{1\text{-}6}$ in claim 1), and a tetramethyl disiloxane bridging group. Ex. 1002 ¶125. As a POSA would have known, the boiling point of DVTMDS at standard pressure is approximately 137°C (well below 500°C). Ex. 1006 3:44-45. Cohen taught that DVTMDS could be "copolymerized with other

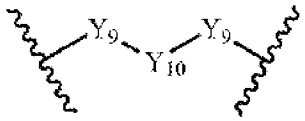
copolymerizable materials," especially molecules such as acrylates and methacrylates that contain a double bond. Ex. 1006 1:31-34, 2:14-30, 4:18-31. In addition, Cohen taught that DVTMDS copolymers could be made into films and that copolymerizing DVTMDS with a methacrylate produced a crosslinked polymer product. Ex. 1006 2:60-63, 3:52-65.

[*1d*] [*Formula A*] "wherein for compound (i) L is of formula A having one of the following structures:



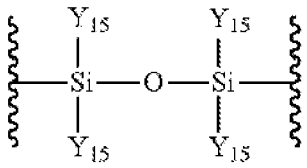
and Y_{10} is selected from optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene and a siloxane group; or

[*Formula B*] wherein for compound (i) L is of formula B having the following formula:



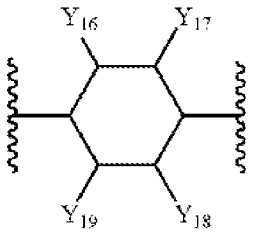
where each Y_9 is independently selected from, a bond, —O—, —O—C(O)—, —C(O)—O—, —Y_{11}—O—C(O)—, —C(O)—O—Y_{11}—, —OY_{11}—, and —Y_{11}O—, where Y_{11} is an optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene; and

[*Formula B1*] wherein Y_{10} has the following formula:



and each Y_{15} is independently selected from optionally substituted branched or straight chain C_1-C_6 alkyl; or

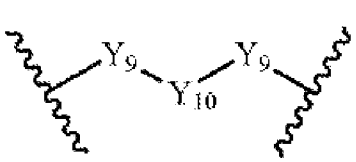
[*Formula B2*] wherein Y_{10} has the following formula:

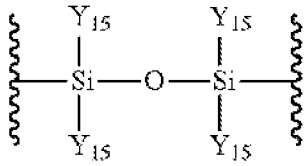


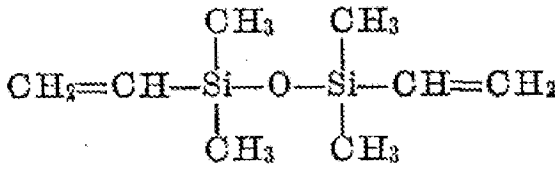
and Y_{16} to Y_{19} are each independently selected from H and optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl."

Claim 1 concludes by reciting several alternative structures, any one of which can make up the crosslinking reagent's bridging group. Claim 1 divides the covered structures into Formulas A and B, and the claim further presents two alternative sub-structures for Y_{10} of Formula B—denoted above as Formulas B1 and B2.

Cohen disclosed DVTMDS, which fell within the scope of Formula B1. For comparison, Formulas B and B1 are compared with DVTMDS below:







As shown, the bridging group in DVTMDS satisfied Formula B1 because it contained: (1) a bond at each Y_9 position of Formula B; (2) the disiloxane structure of

Formula B1 at the Y_{10} position of Formula B; and (3) C_1-C_6 alkyl, specifically methyl, at each Y_{15} position of Formula B1. Ex. 1002 ¶127. Furthermore, DVTMDS necessarily fell within the scope of claim 1 because claim 11, which depends from claim 1, specifically recites DVTMDS as a covered crosslinker. Ex. 1001 21:2-3; *Alcon*, 687 F.3d at 1367.

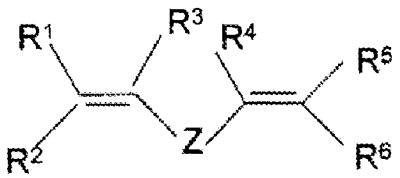
b. Motivation to combine Coulson-122, Badyal, and Cohen's crosslinking reagent

As documented by Coulson-122 and numerous other references, there was by 2015 a clear market incentive to protect sensitive electronic devices from damage due to environmental exposure—driven especially by the ongoing proliferation of portable electronics. Ex. 1004 1:9-34; Ex. 1002 ¶¶58, 128. That design incentive would have motivated a POSA to improve upon preexisting technology, like Coulson-122, to seek new and more robust protective coatings for electronic devices. Ex. 1002 ¶¶128-131; *KSR*, 550 U.S. at 417-18.

Coulson-122 identified plasma polymerization as a clean, dry, and efficient technique for coating various surfaces, Ex. 1001 2:33-3:12, and described PFAC8 and PFMAC8 as specific fluorinated, acrylate-based monomers that safely provided effective liquid-repellent coatings on electronic devices through plasma polymerization, Ex. 1001 3:14-18, 4:29-5:13, 12:7-22. Badyal would have motivated the POSA to improve the Coulson-122 coatings by adding a crosslinking reagent during plasma polymerization because Badyal taught—and a POSA would have known—that

crosslinked polymer coatings typically exhibited improved durability, barrier properties, smoothness, and solvent resistance. Ex. 1005 1:31-2:1, 4:1-29; Ex. 1006 3:51-65; Ex. 1002 ¶¶129-131. A POSA would have viewed protective coatings with enhanced durability as highly desirable, particularly for devices like mobile phones that typically receive daily use under various conditions for years on end. Ex. 1002 ¶129. Furthermore, Badyal described successfully producing crosslinked coatings containing the same monomers used in Coulson-122, so a POSA would naturally have looked to Badyal for guidance on which crosslinking reagents to add into Coulson-122's plasma-polymer coatings.[5] Ex. 1002 ¶131.

Badyal taught that suitable crosslinkers should comprise two double bonds and conform to the following basic structure:



[5] Badyal's preferred embodiments drawn to coated fabrics rather than electronics "do not negate the motivation to combine the references." *In re Hyon*, 679 F.3d 1363, 1366 (Fed. Cir. 2012). Badyal's teachings were not limited to preferred fabric embodiments—the crosslinked coatings could be applied to "any solid substrate." Ex. 1005 9:28-34, 11:19-24; Ex. 1002 ¶131.

Ex. 1005 4:31-5:5. Regarding the bridging group Z, Badyal broadly taught that suitable structures "are those known in the polymer art." Ex. 1005 5:18-19. Badyal further taught that the linker group could be interposed with oxygen atoms and need not include haloalkyl substitutions, particularly when using a monomer—like the perfluorinated acrylate derivatives of Coulson-122—that contains a halogenated group. Ex. 1005 6:24-7:2. Based on Coulson-122 and Badyal, a POSA would have been motivated to coat electronic devices via plasma polymerization using the prior-art Coulson-122 monomers combined with a crosslinker that was known in the polymer art, consistent with Badyal's established crosslinker formula, and preferably associated with protective properties for electronics. Ex. 1002 ¶132. A POSA also would have preferred crosslinking reagents like DVTMDS with a normal boiling point close to or less than those of PFAC8 and PFMAC8 (approximately 267°C and 300°C, respectively) to facilitate supplying a plasma chamber with monomer and crosslinker vapors. Ex. 1002 ¶¶47, 126, 133.

With the knowledge and incentives from Coulson-122 and Badyal described above, a POSA would have identified and been motivated to use DVTMDS as a suitable crosslinker in view of Cohen. As indicated by Cohen's issue date in 1955, DVTMDS was familiar and had been widely used in the polymer art by June 2015. Ex.1006 2:10-14, 3:51-65; Ex. 1002 ¶¶125, 132-133. DVTMDS matched Badyal's generic structural formula for suitable crosslinking reagents. Ex. 1002 ¶¶125, 132.

DVTMDS also had known properties that would have commended its use to a POSA as a crosslinker with the teachings of Coulson-122 and Badyal. A POSA would have known that DVTMDS was widely compatible for co-polymerization with other compounds, including acrylate derivatives. Ex. 1006 2:14-27, 3:51-65, 4:18-56; Ex. 1002 ¶¶73, 125, 132. A POSA also would have known that DVTMDS was compatible with various polymerization methods, including plasma polymerization Ex. 1002 ¶132; *see e.g.*, Ex. 1006 1:31-34; Ex. 1017 Abstract, 4:1-30; Ex. 1033 at [0040-43]. In addition, a POSA would have known that DVTMDS had been used in polymers applied to electronics, Ex. 1002 ¶132; *see* Ex. 1006 5:1-25, and that coatings containing DVTMDS or other organosilicon compounds were associated with water-repellent, barrier, and electrically insulating properties, Ex. 1002 ¶132; *see also* Ex. 1006 5:1-12 (insulating); Ex. 1018 1:6-11 (insulating); Ex. 1033 ¶¶37, 40-45, (insulating) Ex. 1017 3:27-41, 6:31-36 (moisture-resistant, barrier); Ex. 1014 4:5-5:13 (insulating, water-repellent). In addition, a POSA would have recognized that the relatively low boiling point of DVTMDS (137°C) would have been compatible for combined use with vaporized PFAC8 or PFMAC8 in plasma polymerization. Ex. 1002 ¶¶54-55, 126, 133.

Accordingly, the combined teachings of Coulson-122, Badyal, and Cohen would have motivated a POSA to prepare an electronic device bearing a protective plasma-polymer coating as recited in claim 1.

c. Reasonable expectation of success

A POSA reasonably would have expected to succeed in combining Coulson-122, Badyal, and Cohen as in claim 1 because the claimed combination represented no more than known elements with each performing its known and expected function.

Plasma polymerization was routine and well within the skill of a POSA by June 2015. Ex. 1002 ¶¶32, 64, 134; Ex. 1001 14:59-67; Ex. 1005 2:10-13, 10:8-12. A POSA would have expected a known compound like DVTMDS that fit Badyal's generic crosslinker structure to yield protective coatings when co-polymerized under plasma with Coulson-122's PFAC8 and PFMAC8 monomers because Badyal taught that crosslinkers sharing the same basic structure would be suitable for that purpose. Ex. 1002 ¶135; Ex. 1005 4:17-5:19. In addition, Cohen taught that DVTMDS was broadly compatible for co-polymerization with various compounds including modified acrylates using various polymerization techniques. Ex. 1006 1:31-34, 2:14-27. A POSA thus would have expected DVTMDS to serve as an effective crosslinker in the Coulson-122/Badyal combination because PFAC8 and PFMAC8 are also acrylate-based monomers and because a POSA would have known that DVTMDS had been used for plasma polymerization and at any rate a polymerization reaction successfully carried out using one activation method (like free-radical polymerization) generally can be carried out using another (like plasma polymerization). Ex. 1002

¶¶ 53, 135. Badyal reinforced that understanding by teaching that suitable crosslinking structures included those known "in the *polymer art*," without subdividing by activation technique. Ex. 1005 4:18-19 (emphasis added); Ex. 1002 ¶ 53.

Given the known properties associated with DVTMDS as described above, a POSA would have expected coatings to exhibit protective water-repellent and barrier properties. Ex. 1002 ¶¶ 132, 135. And a POSA would have expected the combined coating to be successful as applied to electronic devices because Coulson-122 and Cohen described electronics applications for the relevant polymer substituents and Badyal taught that the crosslinked combination could be applied to any solid surface. Ex. 1002 ¶ 135.

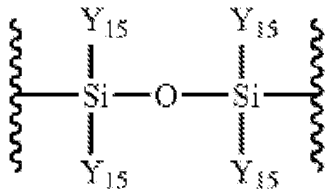
In view of the foregoing, claim 1 would have been obvious over Coulson-122, Badyal, and Cohen.

2. Claims 2, 3

These claims are discussed in light of all grounds in Subsection G, below.

3. Claim 9

"The device or component according to claim 1, wherein when for compound (i) L is of formula B and Y_{10} has the following formula:



each Y_{15} is methyl, and each Y_9 is a bond."

As explained above, DVTMDS has the methylated Formula B1 bridging-group structure recited in claim 9. Ex. 1002 ¶¶ 127, 137. Accordingly, claim 9 would have been obvious over the combination of Coulson-122, Badyal, and Cohen for the same reasons as claim 1.

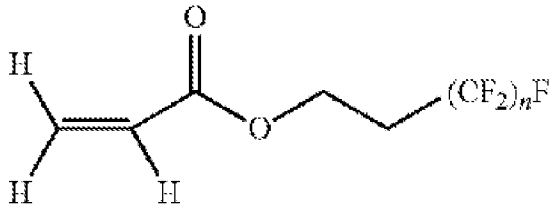
4. Claim 11

"The device or component according to claim 1, wherein the crosslinking reagent is selected from divinyl adipate (DVA), 1,4-butanediol divinyl ether (BDVE), 1,4-cyclohexanedimethanol divinyl ether (CDDE), 1,7-octadiene (17OD), 1,2,4-trivinylcyclohexane (TVCH), 1,3-divinyltetramethyldisiloxane (DVTMDS), diallyl 1,4-cyclohexanedicarboxylate (DCHD), 1,6-divinylperfluorohexane (DVPFH), 1H,1H,6H,6H-perfluorohexanediol diacrylate (PFHDA) and glyoxal bis (diallyl acetal) (GBDA)."

As explained above, DVTMDS is the crosslinker in the asserted combination of Coulson-122, Badyal, and Cohen. Accordingly, claim 11 would have been obvious for the same reasons as claim 1.

5. Claims 12, 13

"12. The device or component according to claim 1, wherein the compound of formula I(a) has the following formula:



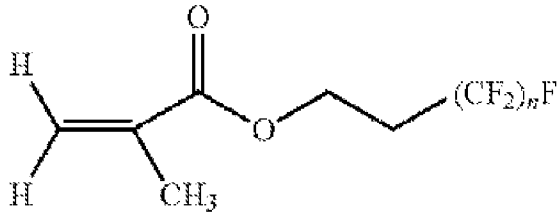
where n is from 2 to 10."

"13. The device or component according to claim 12, wherein the compound of formula I(a) is selected from 1H,1H,2H,2H-perfluorohexyl acrylate (PFAC4), 1H,1H,2H,2H-perfluorooctyl acrylate (PFAC6), 1H,1H,2H,2H-perfluorodecyl acrylate (PFAC8) and 1H, 1H,2H,2H-perfluorododecyl acrylate (PFAC10)."

As explained above for claim 1, both Coulson-122 and Badyal described PFAC8 as a preferred monomer. Claims 12 and 13 therefore would have been obvious for the same reasons as claim 1.

6. Claims 14, 15

"14. The device or component according to claim 1, wherein the compound of formula I(a) has the following formula:



where n is from 2 to 10."

"15. The device or component according to claim 14, wherein the compound of formula I(a) is selected from 1H,1H,2H,2H-pefluorohexyl methacrylate (PFMAC4), 1H,1H,2H,2H-perfluorooctyl methacrylate (PFMAC6) and 1H,1H,2H,2H-perfluorodecyl methacrylate (PFMAC8)."

As explained above for claim 1, both Coulson-122 and Badyal described PFMAC8 as a preferred monomer. Claims 14 and 15 therefore would have been obvious for the same reasons as claim 1.

C. Ground 2: Claims 1-8 and 10-15 were obvious over Coulson-122, Badyal, and Holliday

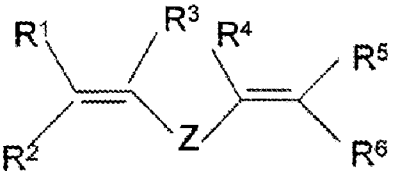
1. Claim 1

a. Claim limitations

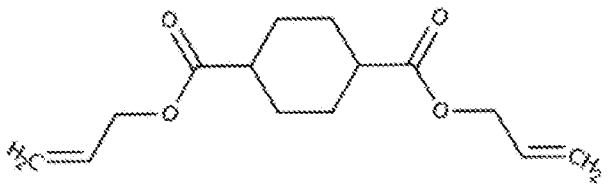
As explained above in Sections VII.A and VII.B.1, Coulson-122 and Badyal described every limitation of claim 1 except the specific bridging groups identified for the crosslinking reagent, and those references would have motivated a POSA to use structurally compatible crosslinkers that had favorable properties and were known in the polymer art.

Holliday taught polymer compositions "for use in providing electrical insulation." Ex. 1007 1:11-12; Ex. 1002 ¶¶ 74, 143. Holliday described applying a mixture of a polyolefin, polyvinyl chloride, and at least one crosslinking compound to an electrical device or component and then initiating polymerization, which "cured" the composition "to form a crosslinked insulation layer." Ex. 1007 2:39-70; Ex. 1002 ¶ 143. Holliday identified several crosslinking reagents for use in those coatings,

including two that matched Badyal's specified structural criteria: diallyl-1,4-cyclohexanedicarboxylate (DCHD) and 1,4-divinyl-oxybutane (also known as 1,4-butanediol divinyl ether (BDVE)):



Badyal



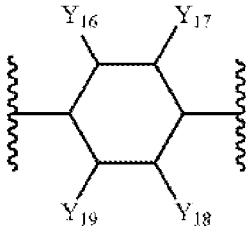
DCHD



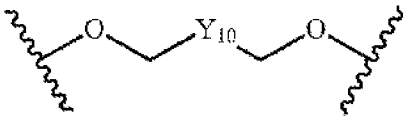
BDVE

Ex. 1002 ¶ 144; Ex. 1005 5:1-5; Ex. 1007 3:34-35, 3:52-53.

As shown, DCHD and BDVE both contained two double bonds. DCHD satisfied Formula B2 of claim 1, where Y_{1-6} are hydrogen, Y_9 is —Y_{11}—O—C(O)—, Y_{11} is C_1 alkylene, Y_{10} is



and Y_{16-19} are hydrogen. Ex. 1002 ¶ 148. BDVE satisfied Formula A, where Y_{1-6} are hydrogen, the linker group is



and Y_{10} is straight-chain C_2 alkylene. Ex. 1002 ¶149. The calculated boiling points of DCHD and BDVE are approximately 331°C and 201°C, respectively. Ex. 1002 ¶¶145-147. Furthermore, DCHD and BDVE necessarily fell within the scope of claim 1 because claim 11, which depends from claim 1, specifically recites both as covered crosslinkers. Ex. 1001 20:67, 21:3-4.

b. Motivation to combine and reasonable expectation of success

A POSA would have been motivated to use Holliday's DCHD and BDVE crosslinkers in the Coulson-122/Badyal combination because those compounds were known in the polymer art, aligned with Badyal's suitable crosslinking reagents, and had useful properties for applying protective coatings to electronics. DCHD and BDVE were known crosslinkers in the polymer art at least since Holliday's issue date in 1974. Ex. 1007; Ex. 1002 ¶150. Both fit well within Badyal's class of preferred crosslinking structures, including linker moieties comprising "alkyl groups … interposed with oxygen atoms." Ex. 1005 5:18-21; Ex. 1002 ¶150. Furthermore, both had boiling points near to or less than the boiling points of PFAC8 and PFMAC8, which a POSA would have known would provide good compatibility for supplying those reagents together to a plasma chamber. Ex. 1002 ¶¶145-147, 152. Holliday directed POSAs to include acrylate or methacrylate compounds in the

disclosed polymerizable mixture, Ex. 1007 3:55-60, which would have suggested to a POSA that DCHD and BDVE would be compatible for polymerizing with the preferred acrylate/methacrylate monomers (PFAC8/PFMAC8) of Coulson-122 and Badyal. Ex. 1002 ¶151. Holliday taught that its crosslinkers could be cured using multiple polymerization techniques. Ex. 1007 2:50-52, 2:68-70 (peroxide and irradiation curing). And Holliday taught that polymer coatings produced with the disclosed crosslinkers provided excellent durability, chemical resistance, and electrical insulation. Ex. 1007 5:34-54. Accordingly, a POSA reading Holliday would have been motivated to use DCHD and BDVE as crosslinking reagents in combination with Coulson-122/Badyal to produce protective polymer coatings as in claim 1. Ex. 1002 ¶¶151-152.

In addition, a POSA reasonably would have expected to succeed with those prior-art combinations. As noted above in Sections IV.B.2 and VII.B.1.c, POSAs considered plasma polymerization routine by June 2015. In addition, a POSA would have expected compounds like DCHD and BDVE that fit Badyal's generic crosslinker structure to successfully co-polymerize with the Coulson-122 monomers because Badyal taught that such crosslinkers would work. Ex. 1002 ¶153; Ex. 1005 4:17-5:19. In addition, Holliday taught that its crosslinkers were compatible with acrylates and methacrylates and with various polymerization activators. Ex. 1007 2:50-70, 3:55-60. A POSA thus would have expected DCHD and BDVE to serve as

effective crosslinkers in the Coulson-122/Badyal combination because those references used acrylate-based PFAC8 and PFMAC8 monomers and because a POSA would have known that a polymerization reaction successfully carried out using one activation method (like irradiation) generally can be carried out using another (like plasma polymerization). Ex. 1002 ¶¶53, 153. Furthermore, a POSA would have been aware the BDVE had already been used as a crosslinker for plasma polymerization. Ex. 1002 ¶153; Ex. 1009 at 606-07. And a POSA would have expected the combined coating to be successful as applied to electronic devices because Coulson-122 and Holliday described electronics applications for the relevant polymer substituents and Badyal taught that the crosslinked combination could be applied to any solid surface. Ex. 1002 ¶153.

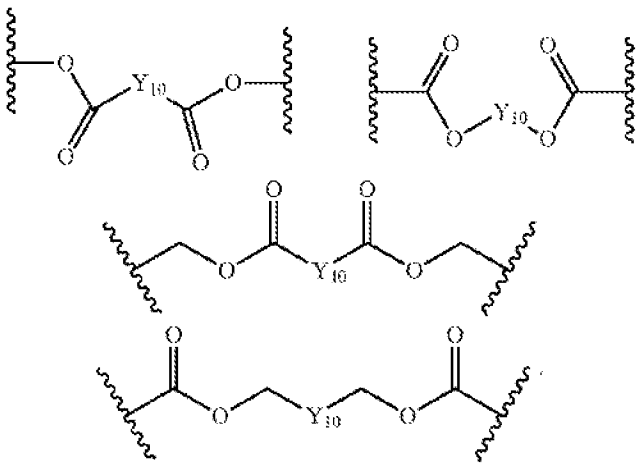
Accordingly, claim 1 would have been obvious over Coulson-122, Badyal, and Holliday.

2. Claims 2, 3

See Subsection G below.

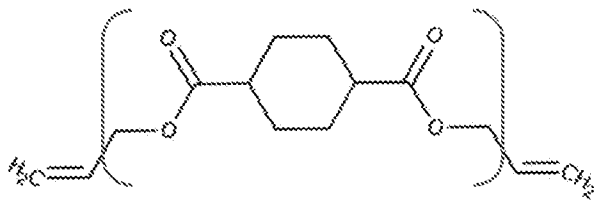
3. Claim 4

"The device or component according to claim 1, wherein when for compound (i) L is of the formula B, L has one of the following structures:



"

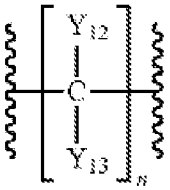
As described, the combination of Coulson-122, Badyal, and Holliday includes devices coated using DCHD as the crosslinking reagent. As described, DCHD matches formula B2 of claim 1, and the third of the four linker structures shown in claim 4 matches the linker moiety of DCHD (bracketed in red below):



Ex. 1002 ¶155. Accordingly, claim 4 would have been obvious over the combination of Coulson-122, Badyal, and Holliday's disclosure of DCHD as a known, suitable crosslinking reagent for the same reasons as claim 1.

4. Claims 5, 6

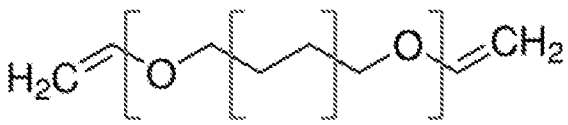
"5. The device or component according to claim 1, wherein when for compound (i) L is of formula A, Y_{10} has the following formula:



wherein each Y_{12} and Y_{13} is independently selected from H, halo, optionally substituted cyclic, branched or straight chain alkyl, or —OY_{14}, where Y_{14} is selected from optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl, and n is an integer from 1 to 10."

"6. The device or component according to claim 5, wherein each Y_{12} is H and each Y_{13} is H."

As described, the combination of Coulson-122, Badyal, and Holliday includes devices coated using BDVE as the crosslinking reagent. The linker moiety of BDVE (bracketed in blue below) matches Formula A and includes a two-carbon chain (bracketed in red below) corresponding to Y_{10} in claim 1, where Y_{12} and Y_{13} are both hydrogen and *n* is 2:



Ex. 1002 ¶¶156-157. Accordingly, claims 5 and 6 would have been obvious over the combination of Coulson-122, Badyal, and Holliday's disclosure of BDVE as a known, suitable crosslinking reagent for the same reasons as claim 1.

5. Claim 7

"The device or component according to claim 5, wherein each Y_{12} is fluoro and each Y_{13} is fluoro."

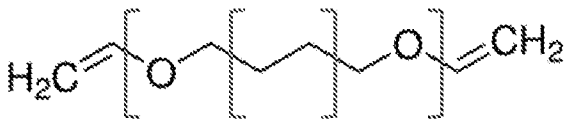
As noted for claims 5 and 6, BDVE contains a CH_2-CH_2 chain corresponding to Y_{10} of Formula A. Badyal taught that alkyl chains in bridging group Z could be perfluoroalkyl chains and that highly fluorinated coatings exhibit "super-hydrophobicity." Ex. 1005 5:18-23, 10:32-11:1. Consistent with Badyal's teachings, it was well known that perfluorinated alkyl groups were strongly hydrophobic when incorporated into polymer coatings, Ex. 1005 1:19-23, and a POSA would have wanted to maximize hydrophobicity in protective coatings intended for electronic devices. Ex. 1002 ¶¶58, 158. A POSA therefore would have been motivated to substitute fluorine at every Y_{12} and Y_{13} hydrogen position in BDVE for enhanced hydrophobicity while maintaining the flanking alkylene spacers to preserve reagent stability and a POSA would have reasonably expected to succeed because methods for preparing fluorinated divinyl ethers were known and because Badyal taught that the bridging group could include fluorine substitutions. Ex. 1002 ¶¶158, 46; Ex. 1005 at 5:18-6:13.

Accordingly, claim 7 would have been obvious over the combination of Coulson-122, Badyal, and Holliday.

6. Claim 8

"The device or component claim 5, wherein n is from 4 to 6."

As noted for claims 5 and 6, BDVE contains a CH_2-CH_2 chain corresponding to Y_{10} of Formula A. A POSA would have known that the longer an alkyl chain is, the more hydrophobic and flexible the resulting molecule will be. Ex. 1002 ¶159. Accordingly, a POSA seeking to make a protective, resilient, water-repellent coating for an electronic device in view of Coulson-122, Badyal, and Holliday would have been motivated to lengthen the two-carbon alkyl chain of the disclosed BDVE crosslinker (bracketed red below) to produce more hydrophobic coatings, such as by doubling its length. *Id.*

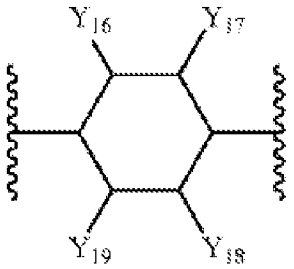


Doing so would have resulted in a crosslinker with four CH_2 groups, just as recited in claim 8. A POSA reasonably would have expected to succeed in making and using the resulting crosslinker (HDVE) because the change required only straightforward chemical modification, which would have been well within the skill of a POSA and because HDVE was a known crosslinker that had been used with acrylate-based monomers. *Id.*

Accordingly, claim 8 would have been obvious over the combination of Coulson-122, Badyal, and Holliday.

7. Claim 10

"The device or component according to claim 1, wherein when for compound (i) L is of formula B and Y_{10} has the following formula:



Y_{18} is H or vinylene, and Y_{16}, Y_{17} and Y_{19} are each H."

As explained for claim 1, the combination of Coulson-122, Badyal, and Holliday includes devices coated using DCHD as the crosslinking reagent, and the linker moiety of DCHD has the same formula recited in claim 10, where Y_{16}-Y_{19} are each hydrogen. Ex. 1002 ¶¶148, 160. Accordingly, claim 10 would have been obvious for the same reasons as claim 1.

8. Claim 11

The asserted combination of Coulson-122, Badyal, and Holliday included DCHD and BDVE as crosslinking reagents. Accordingly, claim 11 would have been obvious for the same reasons as claim 1.

9. Claims 12, 13

As explained above in Sections VII.B.1 and VII.B.5, both Coulson-122 and Badyal described PFAC8 as a preferred monomer. Claims 12 and 13 therefore would have been obvious for the same reasons as claim 1.

10. Claims 14, 15

As explained above in Sections VII.B.1 and VII.B.6, both Coulson-122 and Badyal described PFMAC8 as a preferred monomer. Claims 14 and 15 therefore would have been obvious for the same reasons as claim 1.

D. Ground 3: Claims 1-4, 10, and 12-15 were obvious over Coulson-122, Badyal, and Padiyath

1. Claim 1

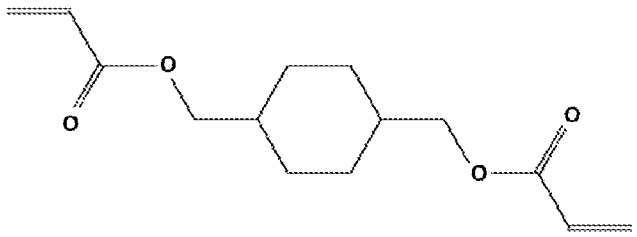
a. Claim limitations

As explained above in Sections VII.A and VII.B.1, Coulson-122 and Badyal described every limitation of claim 1 except the specific linker moieties identified for the crosslinking reagent, and those references would have motivated a POSA to use structurally compatible crosslinkers that had favorable properties and were known in the polymer art.

Padiyath disclosed such a prior-art crosslinker. That reference described "barrier films for protection of moisture or oxygen sensitive articles." Ex. 1008 ¶0001. The barrier coatings reduced or prevented "transfer of moisture and oxygen, or other contaminants, to an underlying substrate," Ex. 1008 ¶0024, particularly electronics such as LCD or OLED display devices, Ex. 1008 ¶¶0023-24, 0027, 0063-64. Padiyath's barrier coatings comprised one or more polymers, which could be homopolymers or copolymers and could be applied using plasma polymerization. Ex. 1008 ¶¶0005-07, 0011, 0025, Fig. 3. Padiyath taught that the polymers were preferably

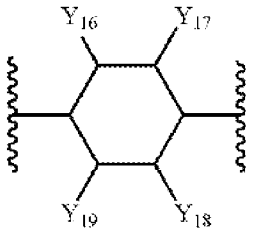
crosslinked. Ex. 1008 ¶¶0002, 0025, 0052.

Particularly preferred compounds for preparing the disclosed polymer layers included acrylates and methacrylates used alone or in combination with other acrylates or methacrylates. Ex. 1008 ¶0052. As one especially preferred compound, Padiyath described "cyclohexane dimethanol diacrylate esters (e.g., CD-406, commercially available from Sartomer Co.)." *Id.* ¶0054. A POSA would have understood Padiyath as identifying the following reagent, more commonly known as cyclohexane-1,4-dimethanol diacrylate (CDMDA):



Ex. 1002 ¶¶76, 166; Ex. 1030 ¶¶144-46 (identifying Sartomer CD406 as CDMDA); Ex. 1031 ¶27 (same); Ex. 1032 (Sartomer data sheet for CD406). The boiling point of CDMDA at standard pressure is approximately 333°C. Ex. 1002 ¶168. A POSA would have recognized that CDMDA was a crosslinking reagent because it was a multifunctional diacrylate containing two double bonds, each capable of bonding with other molecules. Ex. 1002 ¶167; Ex. 1008 ¶¶52, 54.

CDMDA satisfied crosslinker Formula B2 of claim 1, where Y_1-Y_6 are hydrogen, Y_9 is —C(O)—O—Y_{11}—, Y_{11} is C_1 alkylene, Y_{10} is



and Y_{16}-Y_{19} are hydrogen. Ex. 1002 ¶¶166, 169.

b. Motivation to combine and reasonable expectation of success

A POSA would have been motivated to use Padiyath's CDMDA crosslinker in the Coulson-122/Badyal combination because CDMDA was known in the polymer art, had a structure consistent with Badyal's suitable crosslinking reagents, and had been used in protective barrier coatings for electronics. Ex. 1002 ¶¶164, 170-72. CDMDA fit within Badyal's class of preferred crosslinking reagents, including those with linker moieties comprising "alkyl groups … interposed with oxygen atoms." Ex. 1005 5:1-21; Ex. 1002 ¶171. Padiyath taught that CDMDA is volatile, and CDMDA's boiling point fell near those of PFAC8 and PFMAC8, which would have suggested good compatibility for plasma polymerization. Ex. 1008 ¶54; Ex. 1002 ¶¶168, 172, 174. Furthermore, Padiyath taught that its barrier coatings could be formed using plasma polymerization and that CDMDA could be copolymerized with other acrylates or methacrylates, which would have further encouraged a POSA to select CDMDA as a crosslinker with Coulson-122 and Badyal. Ex. 1008 ¶¶11, 52; Ex. 1002 ¶¶167, 172. A POSA also would have been motivated to select CDMDA because Padiyath had demonstrated its utility for preparing protective, moisture-

resistant barrier coatings on electronic devices. Ex. 1002 ¶¶ 164-165, 171-72.

In addition, a POSA reasonably would have expected to succeed using the combination of Coulson-122, Badyal, and Padiyath. As noted in Sections IV.B.2 and VII.B.1.c above, POSAs considered plasma polymerization routine by June 2015. In addition, a POSA would have expected CDMDA to co-polymerize successfully with PFAC8 and PFMAC8 because Badyal taught that compounds matching its generic crosslinker structure would work. Ex. 1002 ¶ 173; Ex. 1005 4:17-5:19. Moreover, Padiyath taught its preferred compounds like CDMDA could be used in combination with other acrylates or methacrylates, Ex. 1008 ¶¶ 0011, 0052, which would have indicated to a POSA that CDMDA could successfully be combined PFAC8 and PFMAC8. Ex. 1002 ¶¶ 167, 173. Padiyath described protective barrier properties for CDMDA-derived polymer coatings, so a POSA would have expected coatings produced by the combination of Coulson-122, Badyal, and Padiyath to exhibit protective water-repellent and barrier properties. Ex. 1002 ¶ 173. And a POSA would have expected the combined coating to be successful as applied to electronic devices because Coulson-122 and Padiyath described polymer-coated electronic devices and Badyal taught that the crosslinked combination could be applied to any solid surface. Ex. 1002 ¶¶ 165, 171, 173.

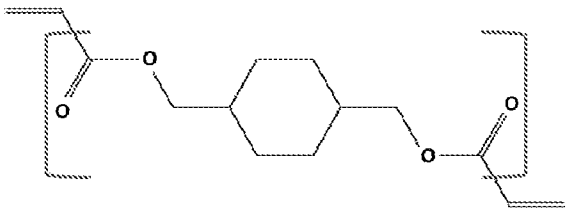
Accordingly, claim 1 would have been obvious over Coulson-122, Badyal, and Padiyath.

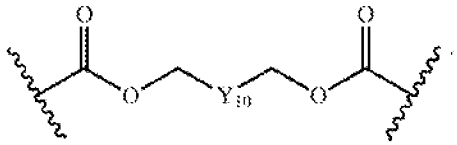
2. Claims 2, 3

See subsection G, below.

3. Claim 4

CDMDA fits Formula B2 of claim 1, as described above. Furthermore, the linker moiety of CDMDA (bracketed in red below) also matches the fourth of the four generic linker structures specified in claim 4:





Ex. 1002 ¶176. Accordingly, claim 4 would have been obvious over the combination of Coulson-122, Badyal, and Padiyath for the same reasons as claim 1.

4. Claim 10

The linker moiety of CDMDA includes the same cyclic substructure recited in claim 10, where Y_{16}-Y_{19} are each hydrogen. Ex. 1002 ¶177. Accordingly, claim 10 would have been obvious for the same reasons as claim 1.

5. Claims 12, 13

As explained above in Sections VII.B.1 and VII.B.5, both Coulson-122 and Badyal described PFAC8 as a preferred monomer. Claims 12 and 13 therefore would

have been obvious for the same reasons as claim 1.

6. Claims 14, 15

As explained above in Sections VII.B.1 and VII.B.6, both Coulson-122 and Badyal described PFMAC8 as a preferred monomer. Claims 14 and 15 therefore would have been obvious for the same reasons as claim 1.

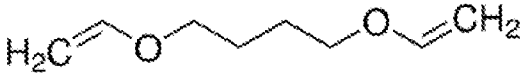
E. Ground 4: Claims 1-3, 5-8, and 11-15 were obvious over Coulson-122, Badyal, and Francesch

1. Claim 1

a. Claim limitations

As explained above in Sections VII.A and VII.B.1, Coulson-122 and Badyal described every limitation of claim 1 except the specific linker moieties identified for the crosslinking reagent, and those references would have motivated a POSA to use structurally compatible crosslinkers that had favorable properties and were known in the polymer art.

Francesch described polymer coatings containing a labile pentafluorophenyl surface group that could subsequently be used to attach a biotin ligand for versatile surface functionalization. Ex. 1009 at 606. The disclosed copolymer coatings were produced by plasma polymerization using a fluorinated methacrylate (pentafluorophenyl methacrylate) with BDVE as a crosslinker. Ex. 1009 at 606-07.



BDVE

Ex. 1002 ¶181. As noted in Section VII.C.1 above, BDVE fit within Badyal's structurally defined group of suitable crosslinkers and has a normal boiling point less than 500°C. Ex. 1005 4:31-5:5; Ex. 1002 ¶¶144-147, 149.

The copolymer coatings were applied to silicon-wafer substrates. Ex. 1009 at 607. Francesch taught performing plasma deposition for 2-8 hours and disclosed that the BDVE-crosslinked copolymer was deposited at a rate of 8 nm per hour, so a POSA would have understood that Francesch taught applying such polymer coatings at thicknesses of 16-64 nm. Ex. 1009 607-08; Ex. 1002 ¶184. The resulting coatings showed flat, homogenous, pinhole-free surfaces. Ex. 1009 at 609-610; Ex. 1002 ¶184. Francesch taught BDVE was included as a crosslinker "to improve the solvent resistance of the resulting deposited thin films." Ex. 1009 at 610.

As explained in Section VII.C.1 above, BDVE was a crosslinking reagent under Formula A of claim 1.[6] In addition, BDVE necessarily fell within the scope of claim 1 because claim 11, which depends from claim 1, specifically recites BDVE

[6] The other crosslinker Francesch described, 1,7-octadiene (Ex. 1009 at 607), was also identified as a most-preferred choice in the '876 patent, Ex. 1001 8:6. A POSA seeking a crosslinker for use in coatings like those described by Coulson-122 and Badyal would have selected BDVE over 1,7-octadiene because of the oxygen atoms in the bridging group of BDVE. Ex. 1002 ¶182; Ex. 1005 5:18-6:20.

as a covered crosslinker. Ex. 1001 20:67, 21:3-4.

b. Motivation to combine and reasonable expectation of success

A POSA would have been motivated to use BDVE as a crosslinker in view of Coulson-122/Badyal and Francesch because BDVE was a known crosslinker for plasma deposition applications in the polymer art, aligned with Badyal's suitable crosslinking reagents, had a boiling point compatible for plasma polymerization with PFAC8 or PFMAC8, and had useful properties for applying protective coatings to electronics. Ex. 1002 ¶¶145-147, 151-152, 180, 182, 184-186. As Francesch expressly taught, BDVE was a crosslinker used in plasma polymerization well before the '876 patent's priority date. Ex. 1009 at 606-07; Ex. 1002 ¶¶183-184. BDVE fit well within Badyal's class of preferred crosslinking structures, including linker moieties comprising "alkyl groups … interposed with oxygen atoms." Ex. 1005 5:18-21; Ex. 1002 ¶¶182-183. In addition, Francesch showed that a "methacrylate was successfully used as a monomer for plasma polymerization … copolymerized with" BDVE, Ex. 1009 at 610, which further would have motivated a POSA to use BDVE as a crosslinking reagent in the Coulson-122/Badyal combination because those references described using similar fluorinated acrylate and methacrylate monomers, Ex. 1002 ¶183.

Francesch also taught that the coatings made with BDVE showed solvent resistance and a uniform structure without pinholes, Ex. 1009 at 609-10, both

properties that would have been valued by a POSA seeking to produce protective barrier coatings. Ex. 1002 ¶184. The coatings could be applied at a thickness of at least 64 nm, which a POSA would have recognized as a coating thickness well suited to protective barrier applications. *Id.*; *see* Ex. 1001 3:5-8. Accordingly, a POSA would have been motivated to use BDVE as a crosslinking reagent, as described by Francesch, in combination with Coulson-122/Badyal to produce protective polymer coatings as in claim 1.

In addition, a POSA reasonably would have expected to succeed with the asserted combination based on teachings from Coulson-122, Badyal, and Francesch. As noted in Sections IV.B.2 and VII.B.1.c, POSAs considered plasma polymerization routine by June 2015. In addition, a POSA would have expected BDVE, which fit Badyal's generic structural criteria for suitable crosslinkers, to successfully copolymerize with the fluorinated monomers like PFAC8 and PFMAC8 taught by Coulson-122 and Badyal because Badyal taught that such crosslinkers would work. Ex. 1002 ¶¶153, 183; Ex. 1005 4:17-5:19. In addition, Francesch taught that BDVE was compatible for plasma coating applications with another fluorinated methacrylate (pentafluorophenyl methacrylate). Ex. 1009 606-07. A POSA thus would have expected BDVE to serve as an effective crosslinker in the Coulson-122/Badyal combination because those references used acrylate-based PFAC8 and PFMAC8 monomers similar to the monomer successfully used by Francesch. Ex. 1002 ¶¶183, 185.

Given the known properties associated with BDVE and the BDVE-based coatings disclosed by Francesch, a POSA would have expected coatings based on BDVE co-polymerized with PFAC8 or PFMAC8 based on the combination of Coulson-122, Badyal, and Francesch to exhibit protective water-repellent and barrier properties. Ex. 1002 ¶185. And a POSA would have expected the combined coating to be successful as applied to electronic devices because Coulson-122 described electronics applications for the relevant polymer substituents, Francesch taught applying BDVE-based coatings to solid silicon substrates, and Badyal taught that the cross-linked combination could be applied to any solid surface. Ex. 1002 ¶186.

Accordingly, claim 1 would have been obvious over Coulson-122, Badyal, and Francesch.

2. Claims 2, 3

See Subsection G below.

3. Claims 5, 6

The asserted combination of Coulson-122, Badyal, and Francesch includes devices coated using BDVE as the crosslinking reagent. As described in Section VII.C.4 above, the linker moiety of BDVE meets every limitation of claims 5 and 6. Accordingly, claims 5 and 6 would have been obvious over the combination of Coulson-122, Badyal, and Francesch for the same reasons as claim 1.

4. Claim 7

BDVE contains a CH_2-CH_2 chain corresponding to Y_{10} of Formula A. Badyal

taught that alkyl chains in bridging group Z could be perfluoroalkyl chains and that highly fluorinated coatings exhibit "super-hydrophobicity." Ex. 1005 5:18-23, 10:32-11:1. Consistent with Badyal's teachings, it was well known that perfluorinated alkyl groups were strongly hydrophobic when incorporated into polymer coatings, Ex. 1005 1:19-23, and a POSA would have wanted to maximize hydrophobicity in protective coatings intended for electronic devices. Ex. 1002 ¶158. A POSA therefore would have been motivated to substitute fluorine at every Y_{12} and Y_{13} hydrogen position in BDVE for enhanced hydrophobicity while maintaining the flanking alkylene spacers to preserve reagent stability, and a POSA would have reasonably expected to succeed because methods for preparing fluorinated divinyl ethers were known and because Badyal taught that the bridging group could include fluorine substitutions. Ex. 1002 ¶¶158, 189, 46; Ex. 1005 at 5:18-6:13.

Accordingly, claim 7 would have been obvious over Coulson-122, Badyal, and Francesch combined using the ordinary skill and creativity of a POSA.

5. Claim 8

BDVE contains a CH_2-CH_2 chain corresponding to Y_{10} of Formula A. A POSA would have known that the longer an alkyl chain is, the more hydrophobic the resulting molecule will be. Ex. 1002 ¶159. Accordingly, a POSA seeking to make a protective, water-repellent coating for an electronic device in view of Coulson-122, Badyal, and Francesch would have been motivated to lengthen the two-

carbon alkyl chain of the disclosed BDVE crosslinker to produce more hydrophobic coatings, such as by doubling or tripling its length. Ex. 1002 ¶¶ 159, 190. Doing so would have resulted in a crosslinker with 4-6 CH_2 groups, just as recited in claim 8. A POSA reasonably would have expected to succeed in making that straightforward chemical modification, which would have been well within the skill of a POSA. *Id.*

Accordingly, claim 8 would have been obvious over the combination of Coulson-122, Badyal, and Francesch.

6. Claim 11

The asserted combination of Coulson-122, Badyal, and Francesch included BDVE as the crosslinking reagent. Accordingly, claim 11 would have been obvious for the same reasons as claim 1.

7. Claims 12, 13

As explained above in Sections VII.B.1 and VII.B.5, both Coulson-122 and Badyal described PFAC8 as a preferred monomer. Claims 12 and 13 therefore would have been obvious for the same reasons as claim 1.

8. Claims 14, 15

As explained above in Sections VII.B.1 and VII.B.6, both Coulson-122 and Badyal described PFMAC8 as a preferred monomer. Claims 14 and 15 therefore would have been obvious for the same reasons as claim 1.

F. Ground 5: Claims 1-3, 5-8, and 12-15 were obvious over Coulson-122, Badyal, and Tropsch

1. Claim 1

a. Claim limitations

As explained above in Sections VII.A and VII.B.1, Coulson-122 and Badyal described every limitation of claim 1 except the specific linker moieties identified for the crosslinking reagent, and those references would have motivated a POSA to use structurally compatible crosslinkers that had favorable properties and were known in the polymer art.

Tropsch described a two-step process for preparing polymers containing peroxycarboxyl groups. Ex. 1011. Tropsch's methods required first preparing or obtaining a polymer, and then reacting that polymer with hydrogen peroxide. Ex. 1011 1:49-2:2. The input polymer contained at least an unsaturated dicarboxylic anhydride monomer. Ex. 1011 1:51-53, 2:13-39. The input polymer could further contain a comonomer, such as an acrylate or methacrylate, as well as a crosslinker. Ex. 1011 1:65-2:2, 3:1-8, 3:47-54. Preferred crosslinkers included 1,6-hexanediol divinyl ether (HDVE):

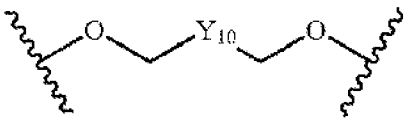


HDVE

Ex. 1011 4:34-39; Ex. 1002 ¶195. HDVE fit within Badyal's structurally defined group of suitable crosslinkers—it had two double bonds where R^1-R^6 were hydrogen

and contained an alkyl bridging group interposed with oxygen atoms. Ex. 1005 4:41-5:21; Ex. 1002 ¶¶ 194-195, 197.

HDVE was a crosslinker within the scope of claim 1. It satisfied Formula A, where Y_{1-6} are hydrogen, the linker group is



and Y_{10} is straight-chain C_4 (HDVE) alkylene. Ex. 1002 ¶195-196. The boiling point of HDVE at standard pressure is approximately 233°C. Ex. 1002 ¶ 195

b. Motivation to combine and reasonable expectation of success

A POSA would have been motivated to use Tropsch's HDVE crosslinker in the Coulson-122/Badyal combination because HDVE was known in the polymer art, aligned with Badyal's suitable crosslinking reagents, and would have been expected to have beneficial properties for applying protective coatings to electronics. HDVE was a known crosslinker in the polymer art, as demonstrated by Tropsch's 1998 disclosure. Ex. 1002 ¶ 197. HDVE fit well within Badyal's class of preferred cross-linking structures, including linker moieties comprising "alkyl groups … interposed with oxygen atoms." Ex. 1005 5:18-21; Ex. 1002 ¶¶ 195, 197. Tropsch disclosed that HDVE could be used to crosslink polymers containing acrylate and methacrylate monomers, Ex. 1011 3:1-10, which would have suggested to a POSA that HDVE would be compatible for polymerizing with the acrylate/methacrylate monomers

(PFAC8/PFMAC8) of Coulson-122 and Badyal. Ex. 1002 ¶197. In addition, a POSA would have been motivated to use HDVE as a crosslinker for protective barrier coatings on electronics because a POSA would have believed that the relatively long alkyl chains in the HDVE linker group would promote hydrophobicity in polymers containing that compound. *Id.*

Tropsch taught that its input polymers containing HDVE could be prepared using multiple polymerization methods, including suspension or precipitation polymerization. Ex. 1011 5:26-30. A POSA reading Tropsch would have expected that HDVE could also be polymerized using plasma activation because one activation technique can usually be substituted for another when using compatible reagents. Ex. 1002 ¶¶53, 198. In addition, the boiling point of HDVE would have indicated compatibility with PFAC8 and PFMAC8 for plasma applications. Ex. 1002 ¶197. Accordingly, a POSA reading Tropsch would have been motivated to use HDVE as a crosslinking reagent in combination with Coulson-122/Badyal to produce protective polymer coatings as in claim 1. Ex. 1002 ¶¶197-199.

In addition, a POSA reasonably would have expected to succeed with that prior-art combination. As noted in Sections IV.B.2 and VII.B.1.c, POSAs considered plasma polymerization routine by June 2015. In addition, a POSA "would have expected compounds like HDVE that fit Badyal's generic crosslinker structure to successfully co-polymerize with the PFAC8/PFMAC8 monomers of Coulson-122 and

Badyal because Badyal taught that such crosslinkers would work." Ex. 1002 ¶199; Ex. 1005 4:17-5:19. Furthermore, Tropsch taught that its crosslinkers were compatible with acrylates and methacrylates and with various polymerization activators. Ex. 1011 3:55-60. HDVE was also structurally similar to BDVE, which was known to be used successfully in plasma polymerization as a crosslinker with another fluorinated acrylate monomer, Ex. 1009 at 606-07, so a POSA would have expected similar performance from HDVE. Ex. 1002 ¶198. A POSA thus would have expected HDVE to serve as an effective crosslinker in the Coulson-122/Badyal combination because those references used acrylate-based PFAC8 and PFMAC8 monomers and because a POSA would have known that a polymerization reaction successfully carried out using one activation method (like irradiation) generally can be carried out using another (like plasma polymerization). Ex. 1002 ¶¶198-199.

Accordingly, claim 1 would have been obvious over Coulson-122, Badyal, and Tropsch.

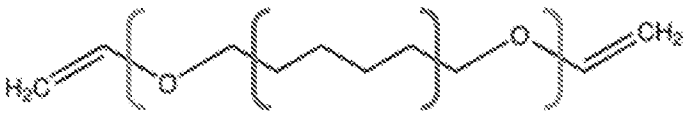
2. Claims 2, 3

See Subsection G below.

3. Claims 5, 6, 8

The asserted combination of Coulson-122, Badyal, and Tropsch includes polymer coatings containing HDVE as the crosslinking reagent. The linker moiety of HDVE (bracketed blue below) met every limitation of claims 5, 6, and 8.

Specifically, Y_{10} (bracketed red below) is $(CH_2)_4$ in HDVE.



HDVE

Ex. 1002 ¶201. For claims 5 and 6, Y_{10} in HDVE is a 4-carbon chain (thus n is 4, between 1 and 10) and where each Y_{12} and Y_{13} is hydrogen. Ex. 1002 ¶202. For claim 8, the 4-carbon chain for Y_{10} means that n=4. Ex. 1002 ¶¶202-203. Accordingly, claims 5, 6, and 8 would have been obvious over the combination of Coulson-122, Badyal, and Tropsch for the same reasons as claim 1.

4. Claim 7

HDVE contained a CH_2-CH_2 chain corresponding to Y_{10} of Formula A. Badyal taught that alkyl chains in bridging group Z could be perfluoroalkyl chains and that highly fluorinated coatings exhibit "super-hydrophobicity." Ex. 1005 5:18-23, 10:32-11:1. Consistent with Badyal's teachings, it was well known that perfluorinated alkyl groups were strongly hydrophobic when incorporated into polymer coatings, Ex. 1005 1:19-23, and a POSA would have wanted to maximize hydrophobicity in protective coatings intended for electronic devices. Ex. 1002 ¶¶158, 204. A POSA therefore would have been motivated to substitute fluorine at every Y_{12} and Y_{13} hydrogen position in HDVE for enhanced hydrophobicity while maintaining the flanking alkylene spacers to preserve reagent stability, and a POSA would have reasonably expected to succeed because methods for preparing fluorinated divinyl

ethers were known and because Badyal taught that the bridging group could include fluorine substitutions. Ex. 1002 ¶204, 46; Ex. 1005 at 5:18-6:13.

Accordingly, claim 7 would have been obvious over Coulson-122, Badyal, and Tropsch combined using the ordinary skill and creativity of a POSA.

5. Claims 12, 13

As explained above in Sections VII.B.1 and VII.B.5, both Coulson-122 and Badyal described PFAC8 as a preferred monomer. Claims 12 and 13 therefore would have been obvious for the same reasons as claim 1.

6. Claims 14, 15

As explained above in Sections VII.B.1 and VII.B.6, both Coulson-122 and Badyal described PFMAC8 as a preferred monomer. Claims 14 and 15 therefore would have been obvious for the same reasons as claim 1.

G. All Grounds: Claims 2 and 3 would have been obvious over the cited prior-art combinations

1. Claim 2

"The device or component according to claim 1, wherein the protective cross-linked polymeric coating is a physical barrier to mass and electron transport."

As explained for each ground above, it would have been obvious to prepare the coated device of claim 1 in view of Coulson-122, Badyal, and each of the asserted references describing a compatible prior-art crosslinker. Claim 2 specifies barrier properties of the coating in claim 1. That would have been an expected and routine

result of each of those obvious combinations or inherent in those asserted combinations. Under either analysis, claim 2 would have been obvious over the references cited in each ground.

A POSA would have understood that a barrier to mass transport includes restricting passage of molecules, like water or oxygen, and that a barrier to electron transport restricts passage of electrons—in other words, an electrical insulator. Ex. 1002 ¶207; *see also* Ex. 1001 3:1-6, 3:41. A POSA would have viewed those as desirable properties when preparing a protective coating for electronics. Ex. 1002 ¶207. A POSA also would have known that polymer coatings made using PFAC8 and PFMAC8 monomers had insulating and molecular barrier properties. Ex. 1002 ¶208. Furthermore, a POSA would have expected crosslinking to improve barrier properties of such coatings by reducing crystallinity and the associated likelihood of channels for molecules or electrical conductance through the coatings, and prior-art crosslinkers in the asserted grounds had been used in coatings to prevent the passage of molecules and/or provide electrical insulation. *Id.*

A POSA therefore would have sought and expected coatings based on the asserted combinations to exhibit the claimed barrier properties. Ex. 1002 ¶¶208-211. The '876 patent admits that producing those properties using the prior-art monomers and crosslinkers of claim 1 would have been within the skill of a POSA. Ex. 1001 14:22-28. Similarly, the '876 patent indicates that a coating thickness of at least 50

nm typically suffices to provide a barrier coating, Ex. 1001 3:5-7, and a POSA would have known that greater coating thickness facilitates barrier properties and would have known how to increase coating thickness simply by increasing plasma polymerization time. Ex. 1002 ¶210; Ex. 1014 9:15-17, 28:23-25; Ex. 1009 at 608. The barrier properties recited in claim 2 thus would have been expected and easy for a POSA to achieve using the monomer/crosslinker combinations and plasma polymerization techniques of the asserted prior-art combinations. Ex. 1002 ¶¶208-210.

Alternatively, the barrier properties in claim 2 would have been inherent in the prior-art combinations asserted in each ground against claim 1. Inherency applies in an obviousness analysis "where the limitation at issue is 'the natural result of the *combination of prior art elements*.'" *Persion Pharm. LLC v. Alvogen Malta Operations Ltd.*, 945 F.3d 1184, 1191 (Fed. Cir. 2019) (quoting *PAR Pharm., Inc. v. TWI Pharm., Inc.*, 773 F.3d 1186, 1194-95 (Fed. Cir. 2014)). A polymer's properties depend on its components. Ex. 1002 ¶211. It has long been established that coatings based on highly fluorinated organic compounds like the perfluorinated monomers described by Coulson-122 and Badyal are electrically insulating and restrict the passage of molecules. Ex. 1002 ¶208. Similarly, crosslinkers in the asserted grounds were also known to produce coatings with those properties. Ex. 1002 ¶¶132, 151, 153, 165, 171-172, 184, 197, 209. Combining two compounds having the claimed

barrier properties to form a copolymer coating would naturally and necessarily yield a copolymer exhibiting the same barrier properties. Ex. 1002 ¶211. Because the properties recited in claim 2 are the inherent result of combining components in the asserted grounds, claim 2 would have been obvious over the same combinations.

2. Claim 3

"The device or component according to claim 1, wherein the protective cross-linked polymeric coating forms a liquid repellent surface defined by a static water contact angle (WCA) of at least 90°."

As explained for each Ground above, it would have been obvious to prepare the coated device of claim 1 in view of each of the cited combinations of prior-art references. Claim 3 specifies a surface WCA of at least 90° for the same coated device of claim 1. That recited property would have been an expected and routine result of those obvious combinations or would have been inherent in those combinations. Either way, claim 3 would have been obvious over the prior art cited in each Ground.

By June 2015, WCA was a well-known measure of surface hydrophobicity, and POSAs understood that water-repellent surfaces exhibit WCA greater than 90°. Ex. 1002 ¶212; Ex. 1001 4:27-29. As described in Sections IV.B.3, VII.A, and VII.B.1, the fluorinated PFAC8/PFMAC8 monomers that would have been used under every asserted Ground were known to be hydrophobic and form water-repellent coatings. Ex. 1002 ¶¶66-69, 213-214. Furthermore, a POSA would have known or

expected that each prior-art crosslinker raised in the cited Grounds would have hydrophobic properties based on prior-art teachings regarding those compounds as well as well-established structure/function relationships for organic compounds known in the art. Ex. 1002 ¶213; Ex. 1005 4:21-23; Ex. 1014 16:7-14.

For each Ground, a POSA therefore would have expected coatings prepared by combining a hydrophobic monomer with a hydrophobic crosslinker to exhibit water repellency and, as a result, a WCA greater than 90°. Ex. 1002 ¶213. The '876 patent does not describe any specific requirements needed for a coating to achieve the claimed WCA. Rather, the patent admits that producing the claimed WCA using the prior-art monomers and crosslinkers of claim 1 would have been within the knowledge and skill of a POSA. Ex. 1001 14:22-28. The WCA recited in claim 3 thus would have been an obvious and expected property for a POSA to achieve with co-polymer coatings prepared according to the combined teachings of the asserted prior art. Ex. 1002 ¶¶213-214 (cite Ex. 1029); *see Southwire Co. v. Cerro Wire LLC*, 870 F.3d 1306, 1312 (Fed. Cir. 2017) (claims reciting "mere quantification of the results of a known process" held obvious); *Ritchie v. Vast Res., Inc.*, 563 F.3d 1334, 1337 (Fed. Cir. 2009) (known properties of known components did not suffice to render combination nonobvious).

Alternatively, the WCA recited in claim 3 would have been an inherent result of the combination of claim 1. The molecular composition of a polymer determines

hydrophobicity. Ex. 1002 ¶214. It had long been established that highly fluorinated organic compounds like the perfluorinated monomers described by Coulson-122 and Badyal are exceedingly hydrophobic and yield hydrophobic coatings when applied as a surface coating. Ex. 1002 ¶¶66-69, 213-214. Similarly, organosilicons like DVTMDS and hydrocarbon-based compounds like DCHD, BDVE, CDMDA, and HDVE were known to exhibit hydrophobic properties. Ex. 1002 ¶¶132, 165, 171, 184, 197, 213. As a POSA would have known, combining a hydrophobic crosslinker with the highly hydrophobic PFAC8 or PFMAC8 monomer to form a copolymer coating would naturally and necessarily yield hydrophobicity, manifesting with a WCA of at least 90°, in the resulting products. Ex. 1002 ¶214. Because the property recited in claim 3 is the natural, inherent result of combining hydrophobic components in the polymer composition recited in claim 1, claim 3 would have been obvious over the same asserted combination of prior art. *Santarus, Inc. v. Par Pharm., Inc.*, 694 F.3d 1344, 1354 (Fed. Cir. 2012) ("merely testing and claiming an inherent property" cannot render an otherwise obvious formulation patentable).

VIII. Statement regarding § 325(d)

The Board should not deny institution under § 325(d). The same or substantially the same art or arguments were not previously presented, and the examiner erred in allowing the challenged claims during prosecution.

Regarding the prior art, the examiner cited Coulson-122, but the other

references in the grounds asserted here (Badyal, Cohen, Holliday, Padiyath, Francesch, and Tropsch) were not before the examiner during prosecution, much less used in a rejection. Cohen, Holliday, Padiyath, Francesch, and Tropsch are asserted here to supply teachings and to support arguments that were wholly absent during prosecution—namely, that the prior art *expressly described* the structures and properties of various claimed crosslinkers that would have made it obvious to use them for crosslinking the Coulson-122 and Badyal coatings. *Oticon Med. AB v. Cochlear Ltd.*, IPR2019-00975, Paper 15 at 15-16 (PTAB Oct. 16, 2019) (precedential in pertinent part). The examiner failed to identify a single prior-art crosslinker that satisfied Formulas A or B from claim 1 and did not consider any combination including such a compound. Ex. 1028 at 247-252, 406-07. Similarly, Badyal's cited teachings, including those about the durability benefits of crosslinking, were absent from prosecution. Ex. 1005 4:1-29. The prior art asserted here is thus materially different and not cumulative with that considered during prosecution.

Furthermore, there was error during prosecution. The issued claims received limited substantive evaluation: even as to the little prior art that *was* considered, the examiner effectively issued a first-action allowance regarding the subject matter of the issued claims. Ex. 1028 at 251. Furthermore, the examiner made no apparent effort to identify references describing the claimed crosslinker structures. Ex. 1028 at 251, 406-07. As demonstrated in this petition, the prior art contained numerous

references describing those very crosslinkers and their use in polymer-coating applications, and the examiner "was simply not aware" of those teachings. *Oticon*, IPR2019-00975, Paper 15 at 19-20. That was substantial error.

In view of the substantially different art and arguments presented here, and the errors during prosecution of the '876 patent, § 325(d) does not apply.

IX. Conclusion

Petitioner respectfully requests institution and cancelation of the challenged claims.

Dated: July 17, 2020

Respectfully submitted,

/Andrew T. Dufresne/

Lead Counsel
Andrew T. Dufresne, Reg. No. 66,636

Back-Up Counsel
Han-Wei Chen, Reg. No. 75,350

Back-Up Counsel
Nathan K. Kelley, Reg. No. 45,295

Back-Up Counsel
Mengke Xing, Reg. No. 76,534

Counsel for Petitioner
Favored Tech Corporation

PERKINS COIE LLP
33 East Main Street, Suite 201
Madison, Wisconsin 53703
(608) 663-7492 (phone)
(608) 663-7499 (fax)

CERTIFICATE OF WORD COUNT UNDER 37 CFR § 42.24(d)

Under 37 C.F.R. § 42.24(d), the undersigned certifies that this petition for *inter partes* review totals 13,988 words, excluding the parts exempted by 37 C.F.R. § 42.24(a). The word count was made using the built-in word count function in the Microsoft® Word software used to prepare this document.

Dated: July 17, 2020

Respectfully submitted,

/Andrew T. Dufresne/

Lead Counsel
Andrew T. Dufresne, Reg. No. 66,636

Back-Up Counsel
Han-Wei Chen, Reg. No. 75,350

Back-Up Counsel
Nathan K. Kelley, Reg. No. 45,295

Back-Up Counsel
Mengke Xing, Reg. No. 76,534

Counsel for Petitioner
Favored Tech Corporation

PERKINS COIE LLP
33 East Main Street, Suite 201
Madison, Wisconsin 53703
(608) 663-7492 (phone)
(608) 663-7499 (fax)

CERTIFICATE OF SERVICE

The undersigned hereby certifies that true copies of this petition for *inter partes* review of U.S. Patent 10,421,876 and supporting materials (power of attorney and Exhibits 1001-1039) have been served in their entireties on the patent owner by Federal Express at the correspondence address for the attorney of record for the '876 patent shown in the Office's Public PAIR system:

Kagan Binder, PLLC
Suite 200, Maple Island Building
221 Main Street North
Stillwater, Minnesota 55082

Service was also made on counsel for patent owner via e-mail:

PHenkelmann@fitcheven.com
Tpmalo@fitcheven.com

Dated: July 17, 2020

Respectfully submitted,

/Andrew T. Dufresne/

Lead Counsel
Andrew T. Dufresne, Reg. No. 66,636

Back-Up Counsel
Han-Wei Chen, Reg. No. 75,350

Back-Up Counsel
Nathan K. Kelley, Reg. No. 45,295

Back-Up Counsel
Mengke Xing, Reg. No. 76,534

Counsel for Petitioner
Favored Tech Corporation

PERKINS COIE LLP
33 East Main Street, Suite 201
Madison, Wisconsin 53703
(608) 663-7492 (phone)
(608) 663-7499 (fax)

Polymer 55 (2014) 6197–6210

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Feature article

Fluorinated poly(meth)acrylate: Synthesis and properties

Wenqiang Yao, Yongjun Li**, Xiaoyu Huang*

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form
15 September 2014
Accepted 17 September 2014
Available online 30 September 2014

Keywords:
Fluorinated (meth)acrylate
Poly(meth)acrylate
Radical polymerization

ABSTRACT

Due to good reactivity of fluorinated (meth)acrylates with other monomers or polymer segments, fluorinated poly(meth)acrylates possess more economical and convenient synthesis routes than other fluoropolymers. This feature article initially summarizes different types of fluorinated (meth)acrylates, which can be divided into fluorinated alkyl (meth)acrylates and fluorinated aryl (meth)acrylates. Subsequently, various approaches for synthesizing fluorinated poly(meth)acrylates including random, block, graft or star copolymers are described. Conventional free radical polymerization can be used in synthesizing random copolymers, while controlled/"living" radical polymerization can provide well-defined copolymers with accurate control over molecular weight and special structures as expected. In particular, introduction of fluorinated components into as-prepared copolymers offers an alternative route to synthesize fluorinated poly(meth)acrylates which are difficult to be obtained directly via polymerization. The incorporation of fluorine can confer unique and highly desirable properties to poly(meth)acrylates such as low surface energy, thermal stability, chemical and weather resistance, low refractive index, and self-organization characteristics. Such properties are described in great details based on many recent articles.

© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

1. Introduction

Fluorinated polymers present a number of interesting and peculiar properties provided mainly by the unique features of fluorine atom. Fluorine atom is a better atom substituting hydrogen than other heteroatoms and allows for the replacement of C–H bond with C–F bond with only minor changes in conformational mobility and steric hindrance of the resulting molecule due to its non-bulkiness. Fluoropolymers have many unique properties including high thermal, chemical, aging, and weather resistance; low dielectric constant, refractive index, surface energy, and flammability; excellent inertness to solvents, hydrocarbons, acids, alkalies, and moisture adsorption as well as interesting oil and water repellency [1–5]. Hence, these niche polymers have been involved in many applications in spite of their high price, such as chemical resistant coatings, noncorrosive materials, antifouling coatings, and interlayer dielectrics.

However, their utility is very limited because of the incompatibility of fluorocarbons with conventional hydrocarbon polymers. In order to further utilize many unique advantages conferred by fluorinated group, synthesis of copolymers, in which more fluorinated groups are incorporated, is essential. Recently, fluorinated poly(meth)acrylates have been the focus of numerous studies because they suit this purpose typically. On one hand, good reactivity of fluorinated (meth)acrylates with other monomers or polymer segments makes the products more economical; on the other hand, the low crystallinity and good solubility of these copolymers can improve their processability.

Copolymerization of fluorinated monomers with common hydrocarbon monomers usually results in copolymers that exhibit properties intermediate between those of parent homopolymers or enhance the range of attainable properties. For the wide specialty range and properties of transparency and resistance to deterioration by environmental effects, poly(meth)acrylates such as poly(methyl methacrylate) (PMMA) are used in a wide variety of applications [6–10]. Poly(meth)acrylate copolymers containing fluorinated groups possess more unique and interesting characteristics, such as remarkably low surface energies, low friction coefficients, and strong incompatibility with conventional solvents [11–13].

Fluorinated poly(meth)acrylates are usually derived from monomer mixtures containing fluorinated (meth)acrylates, common hydrocarbon monomers containing one vinyl linkage or a

* Corresponding author. Tel.: +86 21 54925310; fax: +86 21 64166128.
** Corresponding author. Tel.: +86 21 54925309; fax: +86 21 664166128.
E-mail addresses: liyongjun78@mail.sioc.ac.cn (Y. Li), xyhuang@mail.sioc.ac.cn (X. Huang).

http://dx.doi.org/10.1016/j.polymer.2014.09.036
0032-3861/© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

further group to induce cross-linking reactions, and occasionally ionic monomers with water solubilizing anions. With the rapid development of controlled radical polymerization, a large number of well-defined copolymers such as block copolymers based on fluorinated (meth)acrylates have emerged. Several reviews have summarized the synthesis of fluorinated copolymers [14–18], but the synthesis and properties of fluorinated poly(meth)acrylates have not been described systematically.

Extensive researches have furnished various acrylic-based materials and architectures to show their special characteristics. In order to summarize the achievements on the synthesis and properties of well-defined fluorinated copolymers, we found the time opportune to make this review on the basis of recent corresponding reports which were mostly published since 2000. In this feature article, we first describe two types of fluorinated (meth)acrylates, and then the synthesis of fluorinated poly(meth)acrylates; finally, we discuss the properties of these copolymers in detail.

2. Different fluorinated (meth)acrylate monomers

Fluorinated poly(meth)acrylates are usually obtained from copolymerization of fluorinated (meth)acrylates with common hydrocarbon monomers. Fluorinated (meth)acrylates can be divided into following two types: fluorinated alkyl (meth)acrylates and fluorinated aryl (meth)acrylates.

2.1. Fluorinated alkyl (meth)acrylates

Among fluorinated (meth)acrylates, (meth)acrylates substituted with fluorinated alkyl groups represented as $CF_3(CF_2)_m(CH_2)_n$ or $(CF_3)_2CF(CF_2)_{m-1}(CH_2)_n$ moiety (Fig. 1) are now commercially available [16]. Monomers with trifluoromethyl at α-position of vinyl represented as methyl 2-trifluoromethylacrylate ($CH_2{=}C(CF_3)COOCH_3$) are also available. Most of their homopolymers are sparsely soluble in organic solvents and, in particular, polymers with a fluorinated carbon ($CF_3(CF_2)_m$) number of eight or more are generally insoluble in organic solvents, except for highly fluorinated compounds.

Researches on anionic polymerization reactivity of (meth)acrylates possessing fluoroalkyl groups in ester moieties have demonstrated that fluorine substituents have an extremely large effect on the reactivity of vinyl. For example, anionic polymerization of hexafluoroisopropyl methacrylate ($CH_2{=}C(CH_3)COOCH(CF_3)_2$) initiated by triethylaluminum produced the polymer in high yields, although methyl methacrylate had a low polymerization reactivity under similar polymerization conditions because the initiation reactivity of organo-aluminums was lowered than that of organo-lithiums and organo-magnesiums [19].

Adding a spacer between acrylic group and fluorinated group could improve the properties of acrylic monomers and their polymers. To develop new liquid crystal materials, Hartman et al. synthesized a series of fluorinated acrylic monomers with a biphenyl core and hydrocarbon spacer $(CH_2)_m$ of various length ($m = 0, 6, 11$) [20]. It was illustrated that the monomer containing intermediate length of spacer $(-CH_2)_6$ could favor the organization of rigid perfluoroalkylated biphenyl side groups in bulk in comparison with the corresponding fluorinated monomer ($m = 0$), for the self-organization of fluorinated chains could be reinforced by the lower compatibility between perfluorinated and hydrocarbon groups.

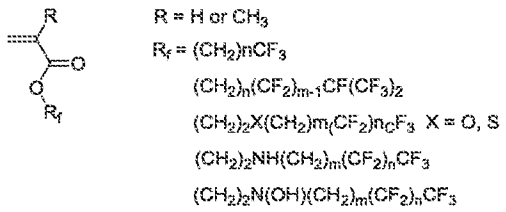


Fig. 1. Commercially available fluorinated alkyl (meth)acrylates.

2.2. Fluorinated aryl (meth)acrylates

As an acrylic species, fluorinated aryl (meth)acrylates have been investigated for their special characters [21]. These monomers often contain an activated ester group with one or more fluorine substituents in aromatic ring, represented as pentafluorophenyl acrylate and methacrylate [22]. Pentafluorophenyl group can be substituted by aliphatic primary and secondary amines easily, so it may bring an unforeseen richness to the use of these compounds. Fluorinated aryl (meth)acrylates (Fig. 2) could be prepared by acylation of corresponding phenols with acryloyl chloride [23]. A hindered pyridine (2,6-lutidine) was used as proton acceptor in place of pyridine itself in order to prevent *in situ* polymerization of monomers. However, the obtained polymeric material after polymerizing them in bulk was insoluble and consequently no size exclusion chromatography or any other detailed characterization could be presented.

Eberhardt et al. realized the successful polymerization of pentafluorophenyl-acrylate and methacrylate yielding soluble polymeric active esters [22]. Canak et al. developed a novel fluorinated monomer of 3,5-bis(perfluorobenzyloxy)benzyl acrylate, which bore more than one fluorinated phenyl ring that contributed a more stiff structure to the polymer [24]. The fluorinated monomer and its homopolymer or copolymers could dissolve in most common solvents easily, in contrast to most fluorinated polymers.

A recent advance in the incorporation of fluorine into polymers with high performance involved a step-growth cycloaddition polymerization of trifluorovinyl aryl ether monomers to provide a kind of fluoropolymer containing perfluoro-cyclobutyl (PFCB) linkage. PFCB aryl ether-based polymer not only provides the conventional properties of fluoropolymer, but possesses many other advantages including optical transparency and improved processability. However, copolymerization of trifluorovinyl ether monomers with common vinyl monomers is very difficult due to different mechanism ($[2\pi + 2\pi]$ step-growth cyclopolymerization) and relatively high polymerization temperature (>150 °C). Tong et al. used commercially available 4-methylphenol as starting material to synthesize a novel methacrylate monomer with the incorporation of PFCB linkage as a side group [25]. Li et al. improved this method and developed a new class of PFCB- containing methacrylate monomers (Fig. 3) whose synthesis included crossing-dimerization, demethylation, and esterification using commercially available *p*-substituted phenol, tetrafluoroethylene, and methacryloyl chloride as starting materials [26,27].

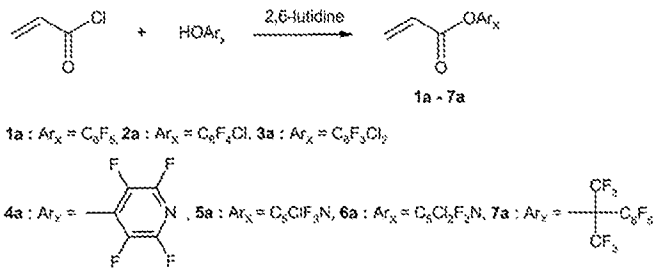


Fig. 2. Synthesis of fluorinated aryl acrylates. Reprinted with permission from Ref. [23].

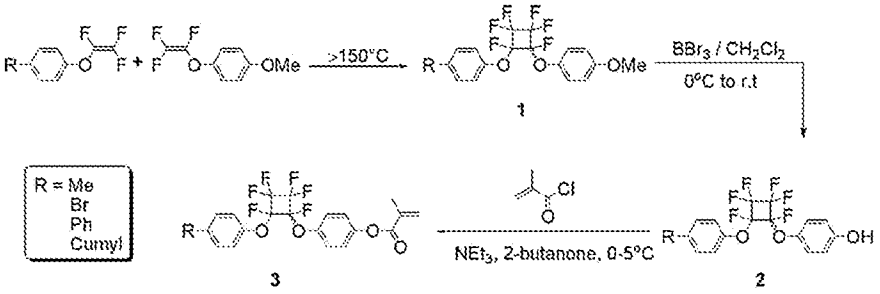


Fig. 3. Synthesis of PFCB-containing methacrylates. Reprinted with permission from Ref. [26].

Compared with traditional trifluorovinyl ether monomers, this kind of monomers can be polymerized via conventional free radical polymerization as well as living radical polymerization such as atom transfer radical polymerization (ATRP) and therefore, it enables direct chain copolymerization of this type of PFCB-containing monomers with usual vinyl monomers to afford tailor-made polymers or copolymers with well-defined architecture and function, which has certainly widened the application of PFCB-based fluoropolymers [26].

3. Synthesis of fluorinated poly(meth)acrylates

Fluorinated poly(meth)acrylates involve random copolymers, block copolymers, and graft/star copolymers. They can be synthesized via many approaches, for example, copolymerization of several monomers or obtaining from as-prepared copolymers. It is worth summarizing the preparation of these copolymers.

3.1. Synthesis of random copolymers

The reported fluorinated poly(meth)acrylates are mainly divided into random copolymers and block copolymers. Random copolymerization is the most general method to perform effective systematic changes in polymer properties, and many studies have been reported on the random copolymerization of fluorinated (meth)acrylates with other monomers mainly for those containing fluorinated groups suitable for a variety of applications. In this section, synthesis of fluorinated poly(meth)acrylates-based random copolymers will be described, and in later sections, useful examples will be presented on the synthesis of fluorinated poly(meth)acrylates-based block copolymers.

3.1.1. Synthesis via radical polymerization

In general, fluorinated poly(meth)acrylates are prepared by conventional free radical polymerization. The early exploration on this copolymerization technique using AIBN as initiator was achieved by DeSimone et al. in 1992 [28]. They synthesized random copolymers of 1,1-dihydroperfluorooctyl acrylate with methyl methacrylate (MMA), styrene, butyl acrylate (BA), and ethylene severally in supercritical CO_2. It could resolve the impediment to the synthesis of variants of commercially available amorphous fluoropolymers for their general insolubility in most solvents.

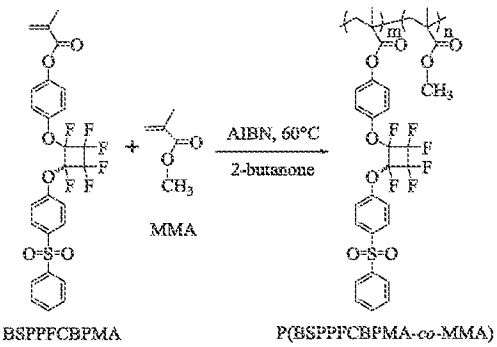


Fig. 4. Synthesis of P(BSPPFCBPMA-*co*-MMA) random copolymer. Reprinted with permission from Ref. [27].

And then, this method was applied in synthesis of fluorinated copolymers with good solubility in conventional solvents [27,29–35]. For example, Li et al. [27] synthesized a novel PFCB-containing random copolymer, which was obtained by the copolymerization of BSPPFCBPMA and MMA initiated by AIBN in 2-butanone (Fig. 4). Subsequent investigation showed that mole ratios of PBSPPFCBPMA moiety in P(BSPPFCBPMA-*co*-MMA) copolymers rose with the increasing of the fraction of BSPPFCBPMA monomer in the feeding ratio. Moreover, the compositions of PBSPPFCBPMA in copolymers were all higher than the fractions in the feeding ratios, indicating the higher copolymerization reactivity of BSPPFCBPMA compared to that of MMA in the current copolymerization system. This is the first example of direct copolymerization of PFCB units with usual vinyl monomers. He et al. [30] reported a fluorinated polyacrylate copolymer obtained by radical polymerization using the monomers of dodecafluoroheptyl methacrylate (DFHM), BA, and MMA. The solution of P(BA-*co*-MMA-*co*-DFHM) had a low molar mass, narrow molecular weight distribution, and low glass transition temperatures as proposed beforehand.

Peroxide and persulfide such as *tert*-butyl 2,2-dimethylperoxypropanoate (TBPPi) and potassium persulfate are also used in random copolymerization of fluorinated (meth)acrylates with other acrylates [36–39]. As showed in Fig. 5A, fluorinated copolymers based on 2,2,2-trifluoroethyl α-fluoroacrylate (FATRIFE) and *tert*-butyl α-trifluoromethylacrylate (MAF-TBE) were synthesized by radical process initiated by TBPPi to provide P(FATRIFE-*co*-MAF-TBE) random copolymers [36]. Moreover, fluorinated terpolymers were prepared by copolymerizing fluorinated monomers, BA, and MMA (Fig. 5B), which were initiated by potassium persulfate in water [39]. The good solubility of persulfide in water enabled them adequately suit for emulsion polymerization.

3.1.2. Synthesis via controlled/"living" radical polymerization

Because the active polymer chains can react with one another either by radical combination or by disproportionation in radical polymerization, the productions often have broad molecular weight distributions. Sometimes, the highly different reactivities of disparate vinyl monomers (e.g. acrylates and α-alkenes) made copolymers containing various monomer units in moderate amounts generally difficult to be formed. In order to get narrow-dispersed random copolymers with accurate control over molecular weight and moderate amounts of various monomer units, controlled/"living" radical polymerization (CLRP) such as reversible addition-

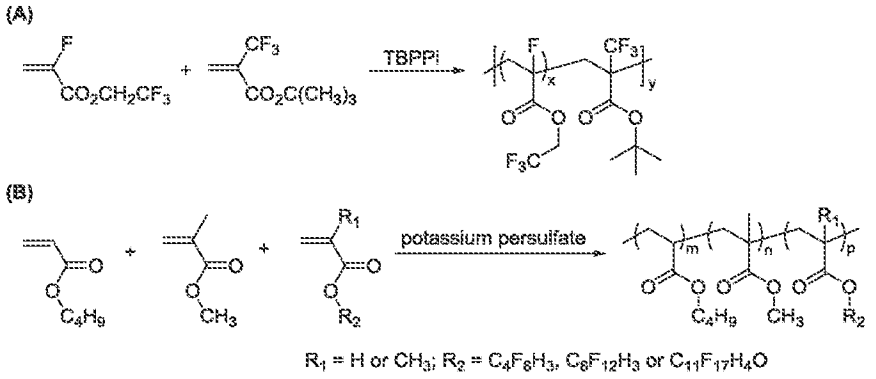


Fig. 5. Random copolymerization initiated by peroxide and persulfide initiators. Reprinted with permission from Refs. [36,39].

fragmentation chain transfer (RAFT) polymerization [40,41], atom transfer radical polymerization (ATRP) [42–44], nitroxide-mediated radical polymerization (NMP) [45,46], and iodine transfer polymerization (ITP) [47] can be used in random copolymerization of acrylates with other monomers.

Such methods could be similarly applied in synthesis of fluorinated poly(meth)acrylate-based copolymers with low polydispersity. For example, perfluoroalkyl ethyl methacrylate could be copolymerized with MMA under ATRP conditions [48]. The final products of polymerization showed molecular weights close to the expected values and their polydispersity indices (PDIs) were below 1.20. Boyer and Ameduri [49] successfully synthesized poly(VDF-*co*-TFMA) copolymers (where VDF and TFMA stand for vinylidene fluoride and α-trifluoromethacrylic acid, respectively) by ITP and PDIs of copolymers were analyzed by size exclusion chromatogram (SEC) as shown in Fig. 6. It showed that ITP could lead to a low PDI compared with radical polymerization in the absence of chain transfer agent (CTA). Therefore, the use of CLRP as opposed to conventional radical polymerization resulted in polymers with narrow molecular weight distributions and controlled molecular weights.

However, in the random copolymerization of acrylate and α-olefins, structurally well-controlled copolymers with low PDIs were obtained only when low degree of polymerization and low α-alkenes insertion ratios (molar fraction of α-alkene below 0.26) were both attained. This was due to the accumulation of dormant species terminated by α-alkene monomers, the reactivity of which in regenerating the polymer-end radicals was much less than those terminated by acrylate monomer [50]. One of the most effective methods is to add strong Lewis acids to increase molar fraction of α-alkene (0.27–0.50) and PDI control [47]. Besides, the development of polymerization technique could also solve these problems.

Very recently, Mishima et al. reported the random copolymerization of 1-octene and (meth)acrylates [51], such as methyl acrylate (MA), trifluoroethyl acrylate (TFEA), MMA, and trifluoroethyl methacrylate (TFEMA), under organotellurium-mediated living radical polymerization conditions (Fig. 7). Polymerization under photoirradiation gave copolymers with narrow molecular weight distributions (PDI = 1.22–1.45) and the molar fraction of 1-octene reached ~0.5 in the copolymerization.

3.1.3. Synthesis via polymers bearing activated groups

Another approach for synthesizing random copolymers was to utilize functional polymers bearing activated groups. One of the best choices was active ester polymers which could react with nucleophilic reagents easily. Poly(pentafluorophenyl (meth)acrylate) was a kind of good active ester polymer for the high reactivity

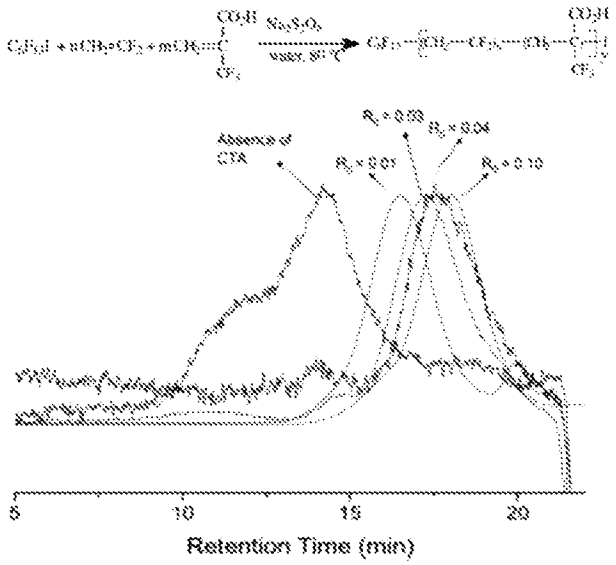


Fig. 6. SEC chromatograms of poly(TFMA-*co*-VDF) random copolymers obtained by ITP with different feeding ratios (R_0 = $[CTA]_0$/($[VDF]_0$+$[TFMA]_0$). Reprinted with permission from Ref. [49].

of pentafluorophenyl esters as shown in Fig. 8 [22]. These polymers reacted satisfactorily with aliphatic primary and secondary amines to provide fluorinated random copolymers, which could react with other nucleophilic reagents sequentially to give new copolymers.

Another choice was to graft the fluorinated groups on the copolymers with functional groups. Casazza et al. [52] synthesized an acrylic terpolymer with pendent perfluoroether segments via grafting fluorinated groups into a poly(butyl methacrylate-*co*-hydroxyehtyl acrylate-*co*-ethyl acrylate) random copolymer through hexamethylene diisocyanate functionality. Malshe et al. [53,54] studied the coating properties of fluorinated acrylic

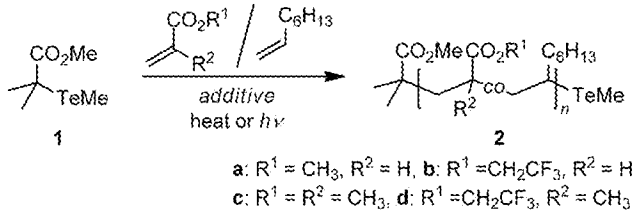


Fig. 7. Random copolymerization of (meth)acrylates and 1-octene. Reprinted with permission from Ref. [51].

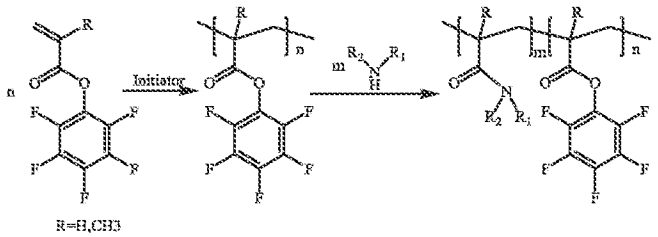


Fig. 8. Synthesis of fluorinated random copolymers from active ester polymers. Reprinted with permission from Ref. [72].

copolymers based on MMA, BA, and 2-hydroxyethyl methacrylate (HEMA). They partially esterified hydroxyl functionality of HEMA with tetrafluoro propanoic acid and cured the polymer with butylated melamine formaldehyde resin. Such methods were suited for the synthesis of copolymers containing complicated fluorinated groups or difficult to be provided directly by living polymerization.

3.2. Synthesis of block copolymers

Compared with random copolymers, block copolymers can exhibit dramatically different properties in that fluorinated groups are concentrated to a block. They are interesting mainly because they can "microphase separate" to form periodic nanoscale assemblies, which are difficult to be formed in random copolymers for fluorinated groups are randomly distributed and isolated from each other in the polymeric chain.

Block copolymers are typically synthesized by the methodology based on CLRP. Recent progress of CLRP allows the synthesis of fluorinated poly(meth)acrylate-based block copolymers with well-defined architectures and compositions, precisely controlled chain lengths, and narrow molecular weight distributions. They can be synthesized directly from commercially available polymers or through sequential addition of two or several monomers. Furthermore, introduction of fluorinated components into as-prepared block copolymers bearing activated groups is also an alternative approach for the synthesis of well-defined block copolymers.

3.2.1. Synthesis from commercially available polymers

It is widely accepted that blending of commercially available polymers is the most convenient and economical route to create novel structural or functional materials with more advanced properties than those synthesized from virgin monomers. In general, commercially available polymers can be easily processed from dilute solutions such as water and methoxyethanol so that they can form block copolymers with fluorinated (meth)acrylates conveniently via living/controlled polymerization.

He et al. [58] reported the synthesis of pentablock copolymer consisting of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer (PEO-*b*-PPO-*b*-PEO) and poly(2,2,3,3,4,4,5,5-octafluoropentyl methacrylate) segment (Fig. 9). Commercially available Pluronics, PEO-*b*-PPO-*b*- PEO triblock copolymer was a group of nonionic macromolecular surfactant with different PPO/PEO ratios that can self-assemble into micelles in aqueous media. Using bifunctional potassium alcoholate of K^+O^--PEO-*b*-PPO-*b*-PEO-O^-K^+ as macroinitiator, POFPMA-*b*-PEO-*b*-PPO-*b*-PEO-*b*-POFPMA pentablock copolymer could be synthesized via oxyanion-initiated polymerization.

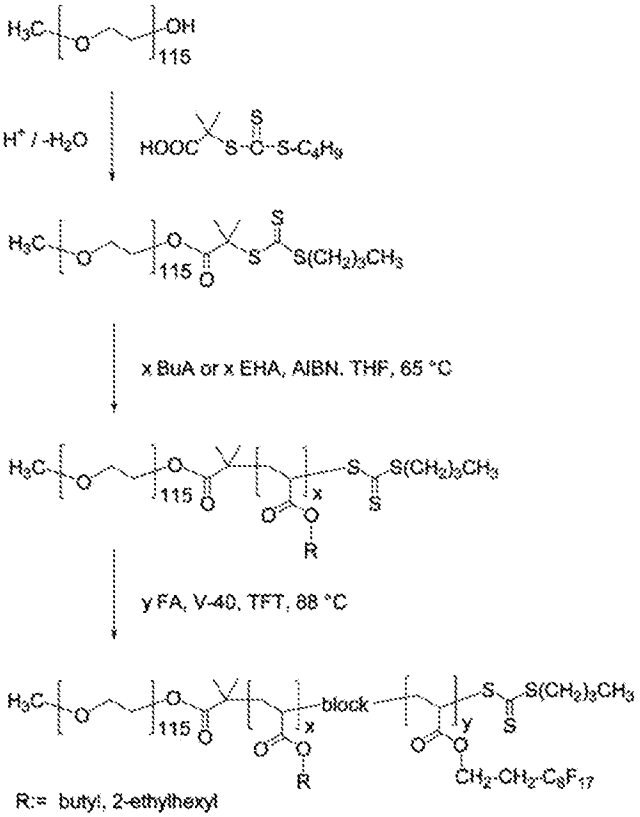


Fig. 10. Synthesis route of PEO-*b*-PBA-*b*-PFA and PEO-*b*-PEHA-*b*-PFA. Reprinted with permission from Ref. [56].

However, not all the commercially available polymer can be used in synthesis of block copolymers directly as macroinitiator, especially in the synthetic procedure through two or more successive polymerization steps. Generally, this problem can be solved by terminal functionalization of commercially available polymer to form macro-RAFT agent or ATRP macroinitiator.

Skrabania et al. [56] synthesized linear amphiphilic triblock copolymers by RAFT approach in two successive steps using a PEO macro-CTA, which was prepared by the esterification of 2-

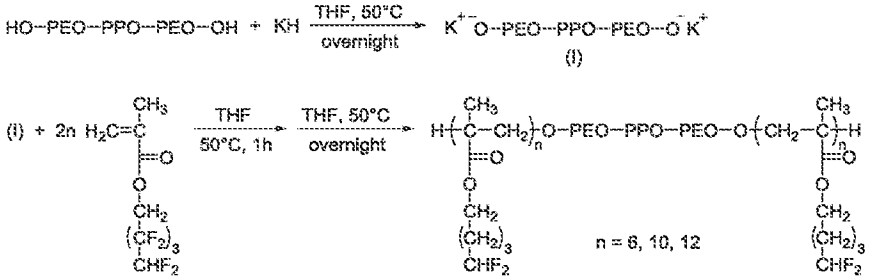


Fig. 9. Synthesis of fluorine-containing pentablock copolymer via oxyanion-initiated polymerization. Reprinted with permission from Ref. [58].

(butylsulfanylthiocarbonylsulfanyl)-2-methyl propionic acid with PEO monomethyl ether (MPEO, M_n~5000 g/mol) as shown in Fig. 10. Amphiphilic diblock copolymers of PEO-*b*-PBA and PEO-*b*-PEHA were synthesized by RAFT polymerization of hydrophobic monomers of BA and 2-ethylhexyl acrylate (EHA) with PEO macro-RAFT agent to be efficient macro-RAFT agent for the successful construction of the third fluorophilic block. Finally, PEO-*b*-PBA-*b*-PFA and PEO-*b*-PEHA-*b*-PFA triblock copolymers were obtained by dialyzing against ethanol to remove unreacted fluorinated monomer. Li et al. [57] used similar PEG5000-CTA to synthesize amphiphilic triblock azide copolymers containing PEG and poly(2,2,3,4,4,4-hexafluorobutyl acrylate) (PHFA) blocks. Firstly, 4-azidophenyl methacrylate (APM) was copolymerized with MA at room temperature using PEG5000-CTA as a macro-CTA with BPO/DMA as redox initiator, forming PEG5000-*b*-P(MA-*co*-APM) block copolymer. And then, PEG5000-*b*-P(MA-*co*- APM)-*b*-PHFA triblock copolymer was provided by polymerization of HFA under the same condition using PEG5000-*b*-P(MA-*co*-APM) as macro-CTA. Yi et al. [58] reported the synthesis of poly(2,2,2-trifluoroethyl acrylate)-*b*-PEO amphiphilic diblock copolymer via RAFT polymerization using dithiobenzoyl-terminated PEO as a CTA. This PEO macroCTA capped with dithiobenzoate groups could be easily prepared without specific purification because of high capping efficiency of maleic anhydride (MAh) group on PEO and high addition reaction efficiency of MAh group with dithiobenzoic acid.

PEO with end functionality could also be used as ATRP macroinitiator [25,59,60]. Tong et al. [25] synthesized PFCB aryl ether-based amphiphilic diblock copolymers by ATRP with PEO-based macroinitiators, which were prepared by reacting MPEO with 2-bromopropionyl chloride. ATRP of 4-(4′-p-tolyloxyperfluorocyclobutoxy)- benzyl methacrylate was initiated by PEO macroinitiators with different molecular weights to obtain well-defined amphiphilic diblock copolymers and the number of PFCB linkage can be tuned by the feeding ratio and the conversion of fluorine-containing methacrylate monomer.

In brief, it is a general convenient approach for the synthesis of block copolymers by CLRP starting from commercially available polymers to reduce the number of chain extension steps.

3.2.2. Synthesis via sequential polymerization

The outstanding contribution of CLRP techniques in the past decade allowed for development of advanced block copolymers having predictable molecular weights and narrow molecular weight distributions via sequential polymerization. These techniques also permitted advanced fluorinated materials to be synthesized. Many block copolymers consisting of fluorinated blocks had been synthesized by CLRP methods, such as ATRP [61–68], NMP [4,69], or RAFT [70–72] polymerization. In most cases, fluorinated (meth)acrylate monomers were used as the second monomer in a sequential polymerization so that fluorinated monomers could be radically polymerized in a controlled manner. Acrylate copolymers consisting of both a fluorocarbon and a hydrocarbon segment were synthesized earlier by Guan and DeSimone in 1994 [73].

Among CLRP methods, ATRP was a general convenient approach to synthesize fluorinated block copolymers. Recently, Li et al. [66] demonstrated that methacrylate monomers with PFCB-containing ester group underwent ATRP to afford diblock copolymers containing hydrophilic poly(acrylic acid) (PAA) segment (Fig. 11). The amphiphilic block copolymers were synthesized via successive ATRP using Br-end-functionalized poly(*tert*-butyl acrylate) (P*t*BA) as macroinitiator followed by the acidolysis of P*t*BA block into PAA

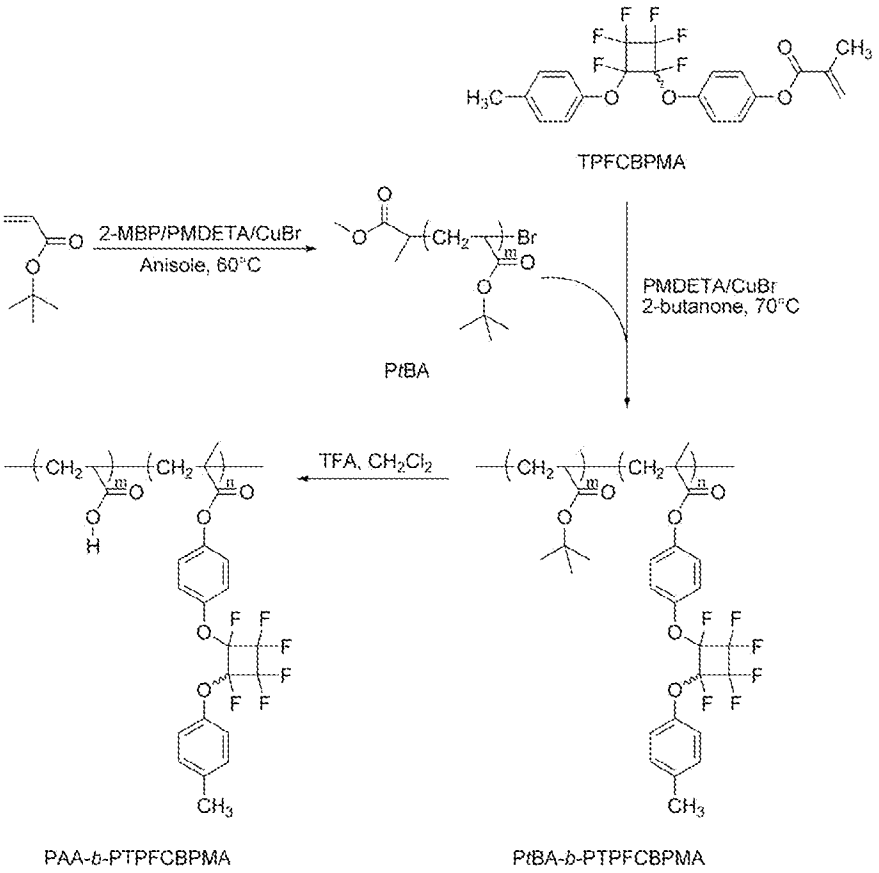


Fig. 11. Synthesis of PAA-*b*-PTPFCBPMA amphiphilic diblock copolymer by successive ATRP. Reprinted with permission from Ref. [66].

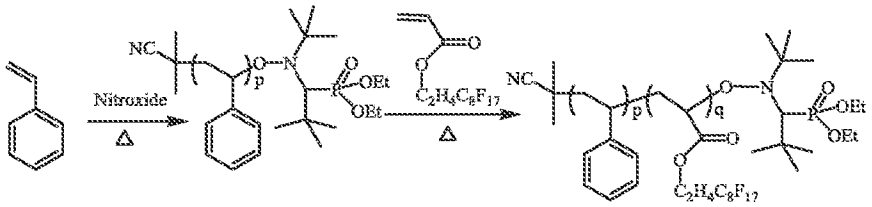


Fig. 12. Synthesis of PS-*b*-PFDA diblock copolymer by NMP. Reprinted with permission from Ref. [68].

segment. Sun et al. [61] synthesized a fluorinated macroinitiator of poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) via ATRP and a series of fluorinated block copolymers with different fluorine contents were prepared by the second step ATRP initiated by the macroinitiator.

One advantage of NMP over ATRP is the absence of organometallic complexes as catalysts, which are sensitive to solvent effects. In NMP, large substituents normally have a positive effect on the performance of nitroxide although only to a certain extent for their polarity as well as steric factors. Lacroix-Desmazes et al. [63] reported sequential polymerization of styrene and 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA) by NMP using *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*- oxyl (DEPN) as nitroxide. Polymerizations were run in cyclohexanone at 123 °C using AIBN as initiator to increase polymerization rates. Polystyrene-DEPN (PS-DEPN) macroinitiators (4000–10,000 g/mol) with narrow molecular weight distributions (M_w/M_n < 1.14) were obtained by utilizing AIBN/DEPN initiation system and block copolymers with various lengths were synthesized from FDA using these PS-DEPN macroinitiators (Fig. 12). Low polydispersities (PDI<1.15) were found in all cases for the relatively large polymers (43,000–50,000 g/mol) by SEC analysis.

RAFT polymerization can also take place over a wide range of temperatures (ambient to 140 °C) and in most conventional solvents even in alcohols and water. Especially, RAFT agents are tolerated with most monomers. For instance, Yi et al. [70] reported a reactive amphiphilic diblock copolymer which was incorporated with epoxy groups (Fig. 13). This block copolymer was synthesized by sequential RAFT polymerizations with 2-phenylpropyldithiobenzoate as a starting CTA. Yao et al. [71] synthesized a series of fluorine-containing amphiphilic diblock copolymers comprising hydrophobic poly(*p*-(2-(*p*-tolyloxy) perfluorocyclobutoxy)phenyl methacrylate) and hydrophilic poly(2-(diethylamino)ethyl methacrylate) segments via successive

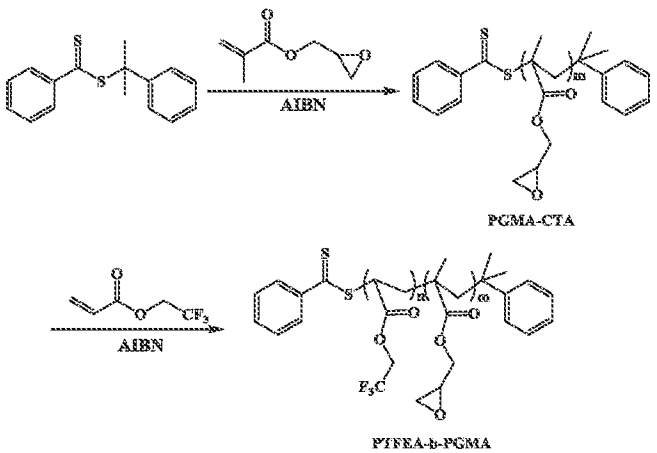


Fig. 13. Synthesis of PTFEA-*b*-PGMA diblock copolymer by successive RAFT polymerization. Reprinted with permission from Ref. [70].

RAFT polymerizations. Grignard et al. [72] also prepared a diblock copolymer of (PFDA-*co*-AA)-*b*-PAN using sequential RAFT method. This block copolymer was made of poly(heptadecafluorodecyl acrylate-*co*-acrylic acid) (PFDA-*co*-AA) random copolymer as the first block and polyacrylonitrile (PAN) as the second one.

Furthermore, anionic polymerization could be applied in polymerization of fluorinated methacrylates. Several diblock copolymers of MMA and methacrylates substituted with $CHF_2(CF_2)_3CH_2$, $CF_3(CF_2)_6CH_2$, and $CF_3(CF_2)_5(CH_2)_2$ groups were synthesized by anionic block copolymerization with the initiation system of *tert*-BuLi and 2,6-di-*tert*-butyl-4-methylphenoxy diisopropylaluminum [74]. Living anionic polymerization system had provided an excellent procedure for the synthesis of a variety of well-defined block copolymers composed of PS, polyisoprene, poly(1,3- butadiene), PMMA, and P*t*BMA with fluorinated polymethacrylates severally [75–77]. Recently, a new diblock copolymer, poly[3-(triisopropyloxysilyl)propyl methacrylate]-*b*-poly[2-(perfluorooctyl)ethyl methacrylate] (PIPSMA-*b*-PFOEMA) [78], that bore a fluorinated PFOEMA block and a sol–gel forming PIPSMA block was synthesized by sequential anionic polymerization. Films made of polymer-coated silica particles were shown to be more resistant to NaOH etching than ordinary films.

Sometimes, site transformation strategy could be adopted when it was difficult to synthesize block copolymers via sequential polymerization using one method. Usually, the first block was polymerized by one polymerization method, and then another polymerization method was used to prepare next block. For example, ring-opening polymerization (ROP) could be used in polymerization of ε-caprolactone [79] but not suit for the polymerization of fluorinated methacrylates so that block copolymers consisting of poly(1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate) and poly(ε-caprolactone) [80] were provided by the combination of ROP and ATRP (Fig. 14).

3.2.3. Synthesis via functionalization of as-prepared block copolymer

By combining polymers with complicated fluorinated groups, block copolymers are difficult to be prepared by the direct polymerization of the respective acryl monomers for their large structure and low solubility. As mentioned before, one approach of synthesis of such copolymers is to utilize functional polymers bearing activated groups. Wang et al. [81] have prepared block copolymers with semifluorinated side chains by introducing hydroxyls into polyisoprene block of polystyrene-*b*-polyisoprene diblock copolymer followed by esterification with semifluorinated carboxylic acids.

First, polymer analogous reactions have been used to prepare polymers with functional side chains. Thus, the next step in the progression of polymer chemistry is combining the known functionalization of polymers via the reaction of polymeric activated groups with fluorinated components as "click" reactions, thereby generating possibilities to realize highly functionalized polymer architectures.

Krishnan et al. [82] synthesized surface-active block copolymer of poly(ethoxylated fluoroalkyl acrylate)-*block*-polystyrene by

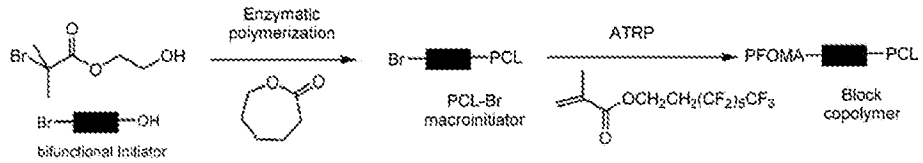


Fig. 14. Synthesis of fluorine-containing PFOMA-*b*-PCL diblock copolymer by sequential ROP and ATRP. Reprinted with permission from Ref. [80].

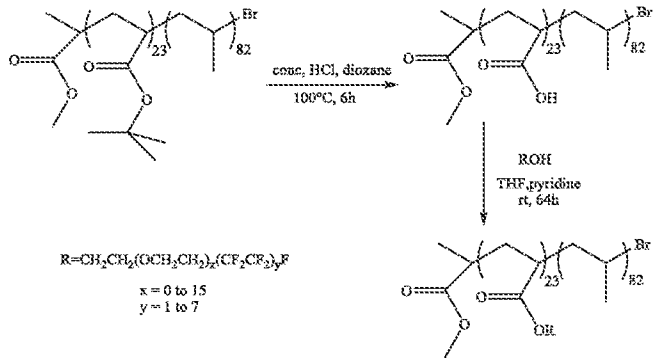


Fig. 15. Synthesis of poly(ethoxylated fluoroalkyl acrylate)-*block*-polystyrene. Reprinted with permission from Ref. [82].

grafting fluorinated molecules with hydrophobic and hydrophilic segments to a block copolymer precursor (Fig. 15). P*t*BA block was quantitatively hydrolyzed to poly(acrylic acid) using concentrated HCl and the following esterification at room temperature using DCC and DMAP resulted in a high degree of attachment (at least 95%) of fluorinated PEG (R groups) to poly(acrylic acid) backbone.

Such a route makes it possible to synthesize fluorinated block copolymers that are difficult to be produced directly by CLRP. The advantage of this route is that a precursor block copolymer with a well-defined structure can be reliably synthesized and, via the reaction of polymeric activated groups with fluorinated components, a new fluorinated block copolymer can be obtained. Accordingly, functionalization of polymers via introduction of fluorinated components into as-prepared block copolymers provides an alternative route for the synthesis of well-defined fluorinated poly(meth) acrylate-based block copolymers.

3.3. Synthesis of graft and star fluorinated copolymers

In contrast to numerous studies on the surface structures of fluorinated poly(meth)acrylate-based block copolymers, little has been reported on fluorinated poly(meth)acrylate-based graft and star copolymers, although the influence of branched architecture on surface and bulk structures may be of particular interest. The synthesis of graft and star fluorinated poly(meth)acrylate-based copolymer will be discussed in this section.

In the design of graft and star copolymers having predictable molecular weights and narrow molecular weight distributions, consecutive CLRP methods are often employed. Generally, a well-defined structure with several initiation groups or more is reliably prepared as macroinitiator, by which other monomers can be polymerized in the next step. For instance, 4-arm star-branched block copolymers comprised of poly(oligo(ethylene glycol) methacrylate) and poly(F_8H_2-MA) [83] were provided by sequential ATRP as shown in Fig. 16.

Recently, Durmaz et al. [84] developed a novel approach to synthesize a graft copolymer carrying perfectly alternating, well-defined poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] and PS side chain grafts (Fig. 17). This graft copolymer was prepared by Suzuki polycondensation of the respective aryl diboronic acid diester and aryl dihalide macromonomers. Such a synthetic.method seemed more effective than the method via grafting of other polymers onto a poly(*p*-phenylene) backbone for the disappearance of PS precursor trace analyzed by SEC, indicating its quantitative reaction.

In this section, we have discussed the synthesis of random copolymers, block copolymers, graft and star fluorinated copolymers. Recent progress of living/controlled polymerizations via different mechanisms allows for the synthesis of various fluorinated poly(meth)acrylate-based copolymers. Moreover, new fluorinated star-branched and dendritic hyperbranched poly(meth)acrylate-based polymers are presented. Possible synthesis of a variety of these copolymers will lead to a myriad of novel fluorinated poly(meth)acrylate-based copolymers with very interesting properties and many potential applications.

4. Properties of fluorinated poly(meth)acrylate-based copolymers

For their unique combination of remarkable properties of fluorine atom and strong C–F bond (131 kcal/mol) in comparison with C–H bond (99 kcal/mol), fluorinated poly(meth)acrylate-based copolymers exhibit many outstanding properties. In particular, the incorporation of fluorinated segments into amphiphilic block copolymers can result in interesting self-assembly characteristics due to the combination of hydrophobicity and lipophobicity in fluorinated polymers [85,86]. These properties make fluorinated poly(meth)acrylate-based copolymers good candidates for hydrophobic optical, electrical, and coating materials.

4.1. Low surface energy

It is well-known that incorporation of fluorine atoms to a polymer renders its surface energy substantially lower. Such leads to low wettability with conventional liquids and thus low adhesion

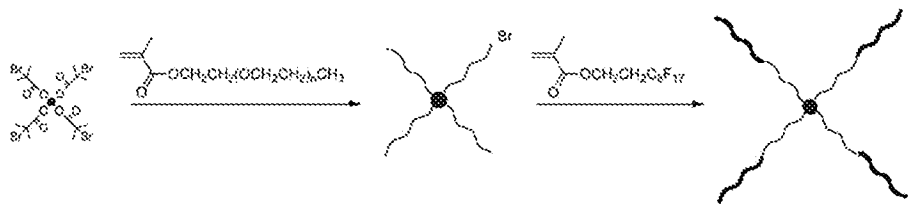


Fig. 16. Synthesis of 4-arm star-branched block copolymer by successive ATRP. Reprinted with permission from Ref. [83].

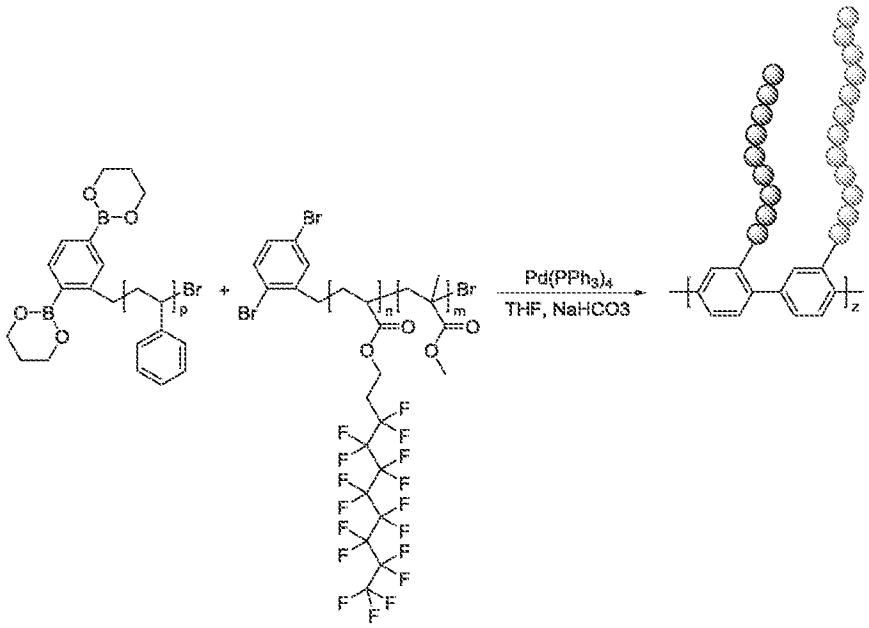


Fig. 17. Synthesis of graft copolymer by Suzuki polycondensation. Reprinted with permission from Ref. [84].

properties. Many properties of a material are dependent on the surface structure and on the chemical composition of outermost surface layer as wetting and coating characteristics are examples of such properties. For low surface energy, fluorinated poly(meth) acrylate-based copolymers own oil and water repellent surface, and they are expected to find applications in various specialty coatings of substrates such as textiles, papers, leather, wood, etc.

Low surface energy of fluorinated poly(meth)acrylate-based copolymers can be showed by the increasing of contact angle (θ). It quantifies the wettability of a solid surface by a liquid. The surface component, orientation packing, and end groups will affect the surface behavior of polymer films. A functional group that has lower surface energy than its polymeric backbone will segregate to the surface in order to reduce the overall surface energy of the system. When the surface is uniformly covered with fluorinated array, a very low energy surface can be achieved. The contact angle of these polymers will be higher than that of their fluorine free analogs.

To seek a good high-solids coatings, Alyamac et al. [31] synthesized a series of low, medium, and high molecular weight random copolymers containing MMA, BA, HEMA, and 2,2,2-trifluoroethyl methacrylate (TFEMA) by solution polymerization under monomer-starved conditions. An enrichment of fluorinated units at the acrylic surface was directly verified by measuring dynamic contact angles. Contact angle measurements indicated that the surface of fluorinated poly(meth)acrylate-based copolymers had more hydrophobic character as compared to fluorine-free acrylates, and contact angle elevated when the amount of fluorine was increased in the copolymer composition. The surface energies of P(MMA-*r*-BA-*r*-HEMA-*r*-TFEMA) were consistently lower than their P(MMA-*r*-BA-*r*-HEMA) fluorine free analogs. The lowest surface energies (around 27 mJ/m^2) were reported for the series containing high concentration of TFEMA (about 10 vol.%), which might be explained on the basis of the difference in the electronegativity between fluorine and hydrogen, the higher carbon–fluorine bond strength, and the smaller bond polarization of C–F bond. Compared to copolymers of non-fluorinated and fluorinated polymers, the core–shell latex with the fluorinated moieties in the shell exhibits a very low surface tension for their enrichment on the surface during film-formation while the non-fluorinated chains in the core coalesce and remain in the bulk. Chen et al. [87] reported a two-step emulsion polymerization to prepare core–shell latex with low surface tension (14 mJ/m^2) with 12.83 wt% fluorine content.

Fluorinated poly(meth)acrylate-based block copolymers are also excellent because such a lower surface energy block can be efficiently partitioned to the surface to form a surface phase-separated domain. Kassis et al. [88] have synthesized poly(-styrene-*block*-1,1-dihydroperfluorooctyl acrylate) by an iniferter process and examined surface aggregation states by angular-dependent X-ray photoelectron spectroscopy to demonstrate that fluorinated segments were enriched in the surface region of approximately 8 nm from the outermost surface.

In order to investigate the surface activity affected by the distribution of fluorinated segments, Hikita et al. [67] synthesized well-defined poly(styrene-*block*- 2-perfluorooctyl ethyl acrylate) [P(St-*b*-PFA)] copolymers with various chemical compositions by sequential ATRP. For a comparison, P(St-*r*-PFA) random copolymers were also synthesized by conventional radical polymerization. All of them were characterized by contact angle measurements. The difference between the advancing (θ_A) and receding (θ_R) angles was referred to contact angle hysteresis, an important diagnostic tool of surface studies. Fig. 18 showed the relationship between dynamic contact angle and PPFA content in P(St-*b*-PFA) and P(St-ran-PFA) films for (a) water and (b) dodecane. The θ_A for water monotonically increased with increasing PFA content, and the values for block copolymers were larger than those for the random ones at a given PFA content. The θ_R for P(St-*b*-PFA) films abruptly increased at around 18.7 mol%. This indicated that the surface wettability for P(St-*b*-PFA) films became more stable and excellent once PFA content went beyond 18.7 mol%. In the case of P(St-*b*-PFA) with PFA content higher than 18.7 mol%, both θ_A and θ_R for water were 120° and even larger with almost no hysteresis. In addition, extremely excellent oil-repellent surface properties such as advancing and receding contact angles for dodecane of 76° and 75° were also observed. However, these intriguing liquid-repellent properties were not observed in P(St-*r*-PFA) films. Thus, it could be concluded that internal structure beneath the surface as well as the surface itself should be deeply considered to design excellent and stable liquid-repellent materials.

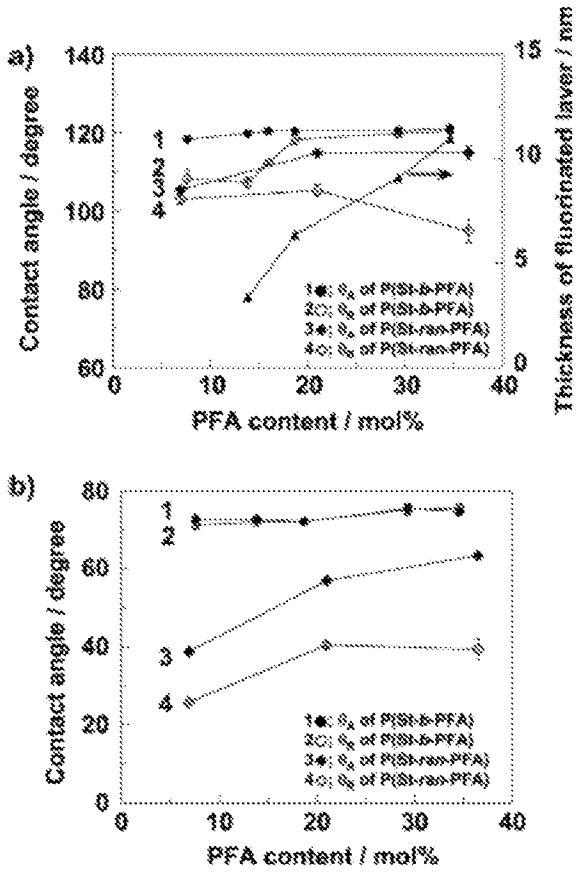


Fig. 18. Relation of dynamic contact angle to PFA content: (a) water and (b) dodecane. Reprinted with permission from Ref. [67].

Recently, Xiong et al. [78] developed a super-amphiphobic diblock copolymer, PIPSMA-*b*-PFOEMA (P1). As mentioned before, this copolymer was synthesized by sequential anionic polymerization. At sufficiently high P1-to-silica mass feed ratios, P1 was chemically grafted onto Si surfaces by sol–gel reactions of PIPSMA block to yield a monolayer. These films were super-amphiphobic, and both water and oil droplets (cooking oil, diodomethane, and hexadecane) possessed large contact angles. The contact angles could be readily changed by using Si particles that were coated using different P1-to-Si mass ratios m_p/m_s. Fig. 19 showed photographs of water droplets that were dispensed onto films of an uncoated Si particle and films of Si particles that were prepared using m_p/m_s values of 0.015, 0.045, and 0.08, respectively. These m_p/m_s values corresponded to Q values [$Q = m_p/(m_s + m_p)$] of 1.2, 4.2, and 5.8%, respectively. Evidently, the water contact angles increased as Q increased.

The surface tensions (γ_S) of acrylic films would decrease with the increasing concentration of fluorine. Eroglu [80] demonstrated this tendency by varying the amount of fluorinated monomer inclusion of copolymers. Copolymer networks of HEMA and 2-(*N*-ethyl perfluorooctane sulfonamido) ethyl acrylate (FOSEA) were prepared by radical polymerization. Ethylene glycol dimethacrylate was used as crosslinker and AIBN was used as initiator. HEMA/FOSEA ratio of copolymer networks changed from 50/1 to 10/1 (mol/mol). The contact angles of water, ethylene glycol, glycerin, diiodomethane, paraffin, and formamide were measured on copolymer surfaces and results were used to evaluate the surface free energy. As showed in Fig. 20, surface tensions of networks decreased drastically with the rising of FOSEA content.

Because fluorinated polymers own water repellent property, incorporation of fluorinated alkyl acrylate monomer units into non-fluorinated acrylic chain can modify the wetting behavior. For instance, PMMA had a tendency to absorb water; however, when fluorinated monomer was incorporated into MMA, the absorption was greatly decreased. As mentioned above, Canak et al. [24] developed a new fluorinated monomer of 3,5-bis(perfluorobenzyloxy)benzyl acrylate (FM). Copolymers of FM with MMA were prepared via radical polymerization at 80 °C in toluene with AIBN as initiator. A typical water absorption tendency of P(FM-*co*- MMA)-10/90 copolymer was shown in Fig. 21. Even for a 9 mol% of FM content in copolymer, the water absorption was found to decrease one-third compared with that of pure PMMA. The decreasing water absorption could have resulted from the hydrophobic surface and bulkiness of copolymer containing fluorinated aromatic rings.

4.2. Thermal stability

The presence of fluorinated moiety in the polymer offers good thermal stability mainly due to strong C–F bond. It will greatly increase the heat resistance performance of polymer materials by adding fluorinated components. The improvement of thermal stability in random copolymers is obvious for the fluorinated groups are randomly distributed and isolated from each other in the polymer chain. However, this change is not so evident in block copolymers [65] containing fluorinated blocks and fluorine-free blocks because fluorinated groups are concentrated in one block and have little impact on other blocks.

Thermal stability of copolymers can be evaluated by thermogravimetry (TG), to verify if fluorinated repeated units could improve stability. PMMA is a transparent thermoplastic, often used as a lightweight or shatter-resistant alternative to glass. The modified PMMA by copolymerization of fluorinated monomers with MMA achieved high thermal resistance, which could be quantitatively shown by TG. To observe this improvement, Liang et al. [38] synthesized three core–shell fluorinated polymethacrylate-based copolymer latices with different fluorinated side chain structure by semicontinuous seed emulsion polymerization, using MMA and BA as acrylate monomers and trifluoroethyl methacrylate (TFEM), hexafluorobutyl methacrylate (HFBM), and dodecafluoroheptyl methacrylate (DFHM) as fluorine-containing acrylate monomers. TG analysis revealed that the introduction of fluorine atoms into

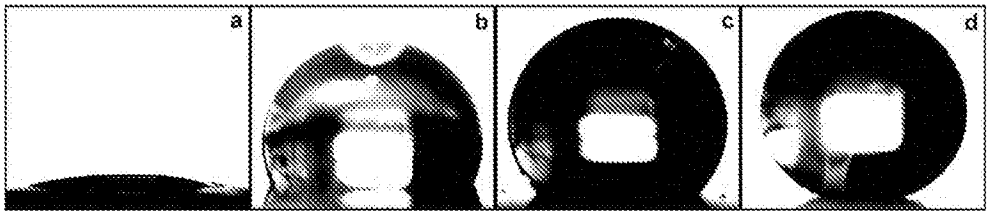
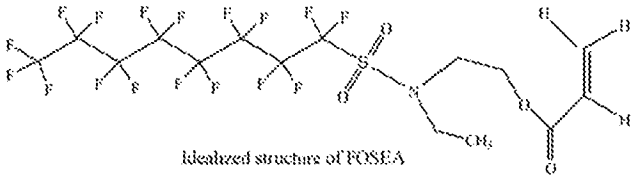


Fig. 19. Photographs of water droplets sitting on films prepared from Si (a) and Si bearing 1.2% (b), 4.8% (c), and 5.8% (d) of P1. Reprinted with permission from Ref. [78].



Run no	HEMA/FOSA (mol/mol)	γ_S (mJ/m^2)
	PHEMA[a]	55.9
1	50/1	25.2
2	35/1	20.6
3	20/1	12.1
4	10/1	9.1

Fig. 20. Structure of FOSEA and surface tensions (γ_S) of copolymer networks. Reprinted with permission from Ref.[89].

PPM really led to a great increase in thermal stability. In particular, DFHM could effectively contribute to improve thermal stability of acrylate copolymer through yielding core–shell structure copolymer with long fluorinated side chains.

Li et al. [27] also demonstrated the raising in thermal stability of PMMA by copolymerization of MMA with fluorinated monomers. Investigation on thermal stability of copolymers by TG (Fig. 22A) showed that incorporation of BSPPFCBPMA units into PMMA domain (Fig. 4) had a significant effect on the elevation of decomposition temperature (T_d) of copolymers and their thermostabilities increased with the rising of BSPPFCBPMA contents. While raising the mole ratio of BSPPFCBPMA from 3.8% to 14.3%, T_d was increased from 298 °C to 317 °C. The thermolysis (Fig. 22B) of P(BSPPFCBPMA-*co*-MMA) copolymers showed a two-step degradation process around about 305 °C–392 °C similar to PBSPPFCBPMA homopolymer (5e in Fig. 22), which corresponding respectively to end-initiated degradation and random scission [90].

Cracowski et al. [37] demonstrated that α-fluoroacrylates had an effective influence in increasing thermal stability of fluorinated polymers. Copolymers based on 2,2,2-trifluoroethyl methacrylate (MATRIFE) and 2,2,2-trichlororoethyl α-fluoroacrylate (FATRICE) were synthesized by radical process and their thermal properties were examined by TG, which showed that 5% weight loss of copolymer degradation occurred from 220 °C to 295 °C as the molar ratio of FATRICE increased from 0.09 to 0.92 in copolymers. And then, Raihane et al. [91] found the presence of highly electrophilic vinylidene cyanide (VCN) homodyads could improve the thermal stability of fluorinated polymers. TG analysis of poly(VCN-*co*-MATRIFE) copolymer showed good thermal stability, and its main pyrolytic degradation took place only above 368 °C as the pyrolytic decomposition of MATRIFE homopolymer started at 246 °C [92].

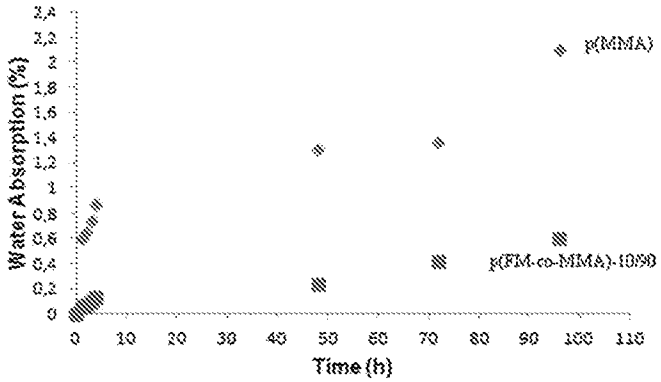


Fig. 21. Water absorption of pure PMMA and P(FM-*co*-MMA)-10/90. Reprinted with permission from Ref. [24].

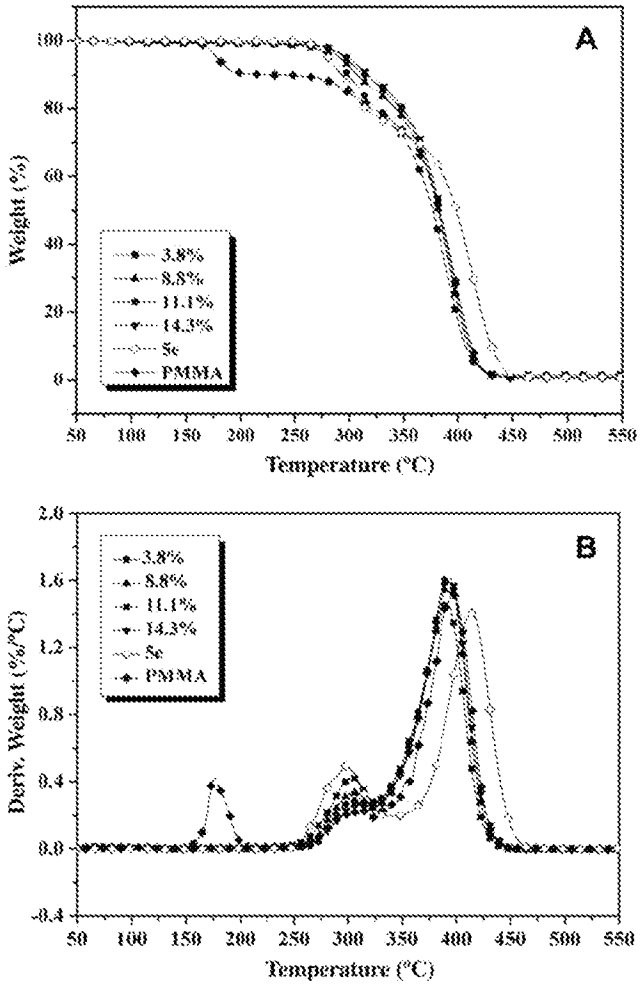


Fig. 22. TG (A) and DTG (B) curves of P(BSPPFCBPMA-*co*-MMA) with different compositions and PMMA (M_n = 35,000, M_w/M_n = 1.64). Reprinted with permission from Ref. [27].

Sanfelice et al. [29] recently exploited the properties of fluorinated methacrylates to improve the thermal stability of azopolymers, which was suitable for optical applications owing to the *trans-cis* photoisomerization process [93]. As expected, copolymers of 2,2,2-trifluorethyl methacrylate (TFEMA) or 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) and 4′-[*N*-ethyl-*N*-(2-methacryloxyethyl)]- amine-4-nitro-azobenzene (DR13MA) exhibited much higher thermal stability than conventional azopolymers. As showed in Fig. 23, the stability of azobenzene homopolymer (HPDR13MA) was poor with a two-step weight loss, with decomposition starting at T_d = 50 °C and 10% weight loss at 180 °C. The fluorinated homopolymer and P(TFEMA-*co*-DR13MA) copolymers had higher thermal stability, with T_d around 220 °C and 10% weight loss at 270–280 °C. Further investigation showed that P(OFPMA-*co*-DR13MA) copolymer was slightly more stable than P(TFEMA-*co*-DR13MA) copolymer.

4.3. Chemical and weather resistance

When metallic materials are put into corrosive environments, they tend to have chemical reactions with air and/or water, leading

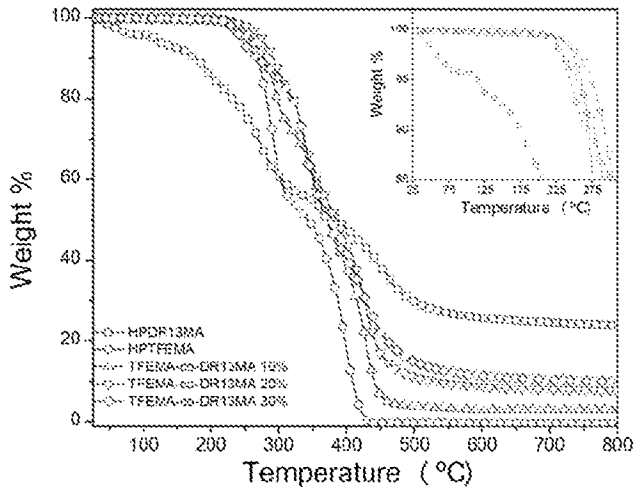


Fig. 23. TG curves of P(TFEMA-*co*-DR13MA) copolymers along with HPTFEMA and HPDR13MA homopolymers. Reprinted with permission from Ref. [29].

to a gradual destruction. Therefore, new processes for corrosion protection are constantly in progress to stop this destruction. At present, the protection by organic coatings and more exactly by systems of paintings is attracting the interest of scientists.

Because C–F bond is the most stable one among all possible carbon-element bonds, introduction of fluorine atoms into polymer structures improves their chemical stability, in addition to give weather resistance as a consequence of photochemical stability, solvent resistance, and oxidation resistance brought by fluorinated groups. In the long term, fluorinated poly(meth)acrylate-based copolymers are adequate to satisfactorily improve the durability and performance of acrylic polymers, with good adhesion and film forming properties.

Malshe et al. [93] studied the coating properties of fluorinated acrylic copolymers based on MMA, BA, HEMA, and tetrafluoropropanoic acid. Incorporation of fluorine was found to extend the protective ability of coatings against atmospheric corrosion compared with their non-fluorinated analogs. It was worthwhile to note that low levels of fluorine used in the copolymer did not change the coating properties of film drastically, but acrylic films with higher solvent and oxidation resistance were obtained. Chen et al. [39] demonstrated that chemical resistance of fluorinated acrylate latex (Fig. 5B) increased with the rising of the number of fluorine atom in the fluorinated monomer. The contact angles of polymer films were examined after immersed into a solution of 5% H_2SO_4 at room temperature for 24 h and the results indicated that the reducing degree of contact angles decreased with the increasing of the number of fluorine atom in the fluorinated monomer, implying the increased chemical resistance of polymer film. Xiong et al. [78] showed that films composed of P1-coated silica particles (P1 represented PIPSMA-*b*-PFOEMA) had substantial resistance to etching by aqueous NaOH solution. They found no physical changes for P1-coated silica films after they were immersed in 1.0 M NaOH aqueous solution between 3 h and 5 h and the water contact angles on these films did not change after these films were dried, confirming the film intactness.

Chianotore et al. [94] first reported the systematic investigation on the photochemical stability and photo degradation pathways of main-chain and side-chain fluorinated poly(meth)acrylate-based copolymers. The photochemical stability and photo-degradation pathways of copolymers of 1*H*,1*H*,2*H*,2*H*-perfuorodecyl methacrylate (XFDMA) with 2-ethylhexyl methacrylate were investigated under artificial solar light irradiation for 2000 h, showing good stability with only minor molecular changes. And then, they studied the photochemical stability of a series of copolymers of XFDMA with acrylic or methacrylic unfluorinated esters [34,35] under artificial solar light irradiation. In XFDMA/MA, the degradation mainly occurred on the tertiary position of acrylic units, followed by extensive chain scissions. In the copolymers with BA, butyl methacrylate, and lauryl methacrylate, XFDMA units were not affected by oxidative degradation reaction.

Such excellent properties enabled fluorinated poly(meth) acrylate-based copolymers to be applied in the long-term preservation of materials, apparatus or antiques. For instance, P(BA-*co*-MMA-*co*-DFHM) copolymers could be applied to protect stone from corrosion [30]. The protective treatment on stone samples was performed by capillary absorption from a filter paper pad saturated with copolymer solution, and their preliminary protecting efficiency was evaluated by testing water resistance, freeze/thaw stability, and UV resistance of treated stone samples, showing the films exhibited a good protective performance. PEG5000-*b*-P(MA-*co*-APM)-*b*- PHFA block copolymers could be covalently attached to the surface of cotton fabric by the reaction of azide groups with cotton fabric based on nitrene chemistry via UV irradiation [57]. Due to the introduction of fluorinated polymer chains, cotton fabric was transformed from hydrophilicity to super-hydrophobicity with a water contact angle of 155°. After fluorinated polymer chains were covalently attached on the surface of cotton fabric, the super-hydrophobic cotton fabric displayed high resistance to acid, basic, and organic solvents. Grignard et al. [72] utilized (PFDA-*co*-AA)-*b*-PAN diblock copolymer film onto Al substrate and demonstrated that the so-formed super-hydrophobic coating showed good adhesion to Al surfaces, resulting in excellent corrosion resistance.

4.4. Low refractive index and high transmittance

Refractive index (n_D) is the ratio of the speed of light in vacuum and the phase speed of light in a material. If a material intends to find applications in optical and electro-optical devices, it has to own appropriate refractive index to match the requirement of devices. As optical materials [95,96], polymethacrylate materials have the disadvantage of high refractive index to limit their application, such as PMMA ($n_D = 1.490$). Highly fluorinated polymers are known to have extremely low refractive indices. For example, polytetrafluorethylene has a refractive index of 1.35 and poly(1*H*,1*H*-heptafluorobutyl methacrylate) has a lower refractive index of 1.3860 [97]. It is well-known that refractive index of a polymer can be tuned by copolymerization of two appropriate monomers; therefore, the preparation of new fluorinated poly(meth)acrylate-based copolymers can reduce the refractive index of primary materials according to the composition of copolymer. Besides, the high transmittance of fluorinated poly(meth)acrylate-based copolymers enlarges their use.

In pursuit of photo-curable adhesive for optical communication, Jang et al. [33] synthesized dual-curable acrylic oligomers (AOs) having alkoxy silane group, fluorine atoms, and vinyl as a pendent group. They obtained an optimum adhesive formulation, based on AO, epoxy acrylate, isobonyl methacrylate, and photo initiator. As the content of AO was increased in the optical adhesive formulation, refractive index decreased but transmittance increased due to the increasing in fluorine content. The optical transmittance at the range of 1.30–1.55 mm was higher than 90%.

Cracowski et al. [36] reported that the modification of the composition of P(FATRIFE-*co*-MAF-TBE) copolymers (Fig. 5A) allowed a precise control over refractive index measured at 633, 1320, and 1550 nm. As shown in Fig. 24, refractive index of P(FATRIFE-*co*-MAF-TBE) copolymer was found to decrease with increasing weight content of fluorine atoms and refractive indices of the resulting films were in the range of 1.387–1.394 at 1550 nm.

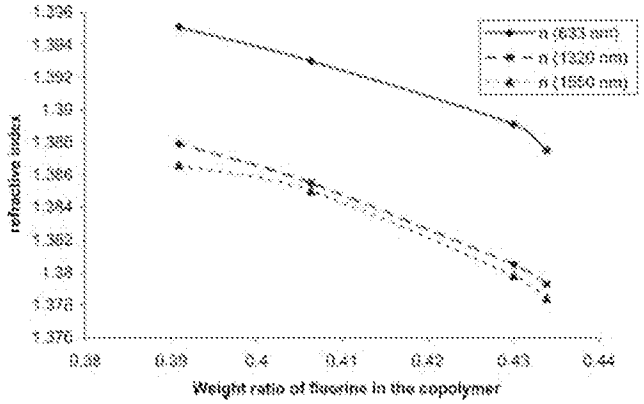


Fig. 24. Refractive index (20 °C) *vs.* weight content of fluorine in poly(FATRIFE-*co*-MAF-TBE) copolymers, measured at three different wavelengths: 633, 1320, and 1550 nm. Reprinted with permission from Ref. [56].

Zhou et al. [98] demonstrated that refractive index of fluorinated acrylate was generally much lower than that of corresponding non-fluorinated acrylate using poly(hexafluoroisopropyl methacrylate-*co*-MMA) as sample. They found that refractive indices of copolymer, measured at 532, 633, and 839 nm, were lower than that of PMMA and showed a linear relationship with monomer composition in the copolymers.

4.5. Self-organization

In film formation, fluorinated poly(meth)acrylate-based random copolymers often exhibit improved physical and chemical properties such as self-organization. Because of the differences in hydrophobic properties and surface tension, fluorinated groups might preferentially migrate to the surface during film formation [99]. In contrast, fluorine-free acrylic core assembled in the bulk and provided the materials with good adhesion towards substrate. Wang et al. [97,100] investigated a series of fluorine-containing polyacrylate latex with core–shell structure by X-ray photoelectron spectroscopy and demonstrated that fluorine content in the air-film interface was almost twice higher than the average in the bulk, and decreased rapidly in the film–glass interface, which was in good agreement with the water contact angle measurements. Water contact angle (116°) of emulsifier-free core–shell fluorine-containing polyacrylate film was higher than that of emulsifier-free core–shell fluorine-free polyacrylate film (71°), which was attributed to the hydrophobic fluorinated groups preferentially located at the surface of film.

Similarly, in almost all fluorinated poly(meth)acrylate-based copolymers, their film surfaces are observed to consist predominately of fluorinated segments that cover all surface areas. For example, the film of a triblock terpolymer composed of PHEMA, P*t*BMA, and poly(2-(perfluorobutyl)ethyl methacrylate) (F4H2-MA) segments showed a high F atom percent (43%) in surface analyzed by angle-dependent X-ray photoelectron spectroscopy [101]. *N*-ethyl-pentadecafluorooctanamide capped polybutylene isophtalates (PBI) with fluorine content from 0 to 5 mol% also show an obvious drop of fluorine concentration from the film surface down to the inner bulk, and enriched perfluoroalkyl segments covered the rough disordered crystalline topography of PBI, which resulted in a dramatic decrease of surface tension from 33.2 to 16.0 mJ/m^2 [102]. This was exactly the same value as for the homopolymer of F4H2-MA, indicating that the top surface was predominantly covered with terminal P(F4H2-MA) sequence in the block copolymer.

In selective solvents, the incorporation of fluorinated segments into amphiphilic block copolymers can result in interesting self-assembly characteristics to form nanoparticles with various morphologies [55,103]. The replacement of hydrocarbon block with fluorinated block in amphiphilic copolymers can imbue favorable properties to nanomaterials such as thermal stability, chemical resistance, low surface energy, low refractive index, and high insulating ability [104–106].

POFPMA-PEO-PPO-PEO-POFPMA pentablock copolymer (Fig. 9) could self-assemble in aqueous solution to form various micellar morphologies including spherical micelles, large compound micelles, and vesicles when the length of fluorinated blocks varied [55]. Surface tension and cloud point measurements showed that the pentablock copolymers had lower surface tension and clouding point compared with the original PEO-PPO-PEO triblock copolymer and they decreased with the increasing of fluorinated blocks and the aqueous solution concentrations. PEO-*b*-PBA-*b*-PFA and PEO-*b*-PEHA-*b*-PFA triblock copolymers (Fig. 10) could self-assemble in water into spherical micellar aggregates [56]. Imaging by cryogenic transmission electron microscopy revealed that micellar cores of aggregates could undergo local phase separation to form a unique ultra-structure, appearing that extended non-spherical domains. This novel internal structure of a micellar core was attributed to the mutual incompatibility of fluorocarbon and hydrocarbon side chains in combination with the tendency of used fluorocarbon acrylate monomer to undergo side-chain crystallization. PAA-*b*-PTPFCBPMA amphiphilic diblock copolymers (Fig. 11) could aggregate in aqueous solution to form micelles with PAA-corona and PTPFCBPMA-core, and the micellar size of copolymer was found to be related with the length of hydrophobic PTPFCBPMA segment [66].

Recently, Qin et al. [63] demonstrated the interesting hierarchical assembly of a fluorine-containing block polymer of P*t*BA-*b*-P(2-[(perfluorononenyl)oxy]ethyl methacrylate) into nanospheres through water induced aggregation. The sizes of nanospheres could be tuned by water addition rates through a gradually growing process. And the inside onion-like structures consisting of several polygon stripes (Fig. 25) illustrated that super-strong segregation of fluorinated segments and preferential lamellar packing of

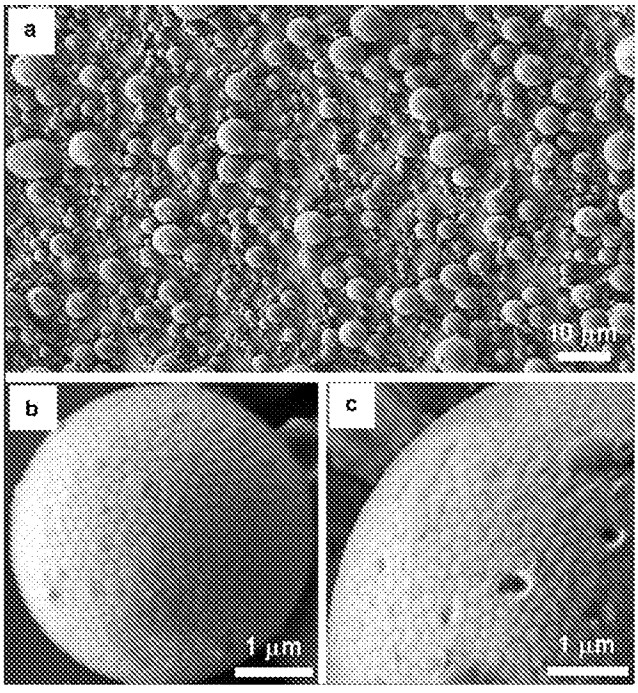


Fig. 25. SEM images of microspheres of P*t*BA-*b*-P(2-[(perfluorononenyl)oxy]ethyl methacrylate) copolymer. Reprinted with permission from Ref. [63].

crystallized fluorocarbon side chains might play significant roles in determining the morphology. Peng et al. [103] studied the effects of co-solvent, acetone or DMF, on the assembly properties of PAA-*b*-P(BA-*co*-TFEA) copolymers and found that large, diffuse aggregates were obtained in pure DMF, while in acetone cylindrical structures were formed. On addition of water to the solutions, both systems formed cylindrical micelles.

With the special self-assembly property, fluorinated poly(meth) acrylate-based block copolymers are likely to be useful in applications such as magnetic resonance imaging (MRI) agents [107] and liquid crystal [108,109]. Fluoroalkyl groups with liquid crystalline mesogenic properties can assemble into lamellar layers of a smectic mesophase, and in addition to this level of organization, individual side chains are structured within each smectic lamella. Fluorinated liquid crystals showed to have highly hydrophobic and stable surfaces [109].

Furthermore, fluorinated poly(meth)acrylate-based copolymers have many other excellent properties, such as high fracture toughness and elasticity [70,110], low dielectric constant [111], and low crystallinity [59]. With such excellent properties, fluorinated poly(meth)acrylate-based copolymers are capable of continuously attracting the interest of scientists and more materials based on these copolymers will emerge ceaselessly.

5. Conclusion

Good reactivity of acrylic monomers during polymerization makes fluorinated poly(meth)acrylate-based copolymers more economical and low crystallinity improves their processability. The incorporation of fluorine provides many unique and highly desirable properties to polymers so that fluorinated poly(meth)acrylate-based copolymers can be applied in many fields such as hydrophobic optical, electrical, and coating materials. Over the last decade, researches and applications pertaining to fluorinated poly(meth)acrylate-based copolymers have grown significantly. Researchers have shown that fluorinated poly(meth)acrylate-based copolymers can be using in corrosion protection with a satisfactory result. It has also been demonstrated that fluorinated poly(meth) acrylate-based block copolymers with liquid crystalline side chains have the potential to be high-performance liquid crystalline materials.

The application of various fluorinated (meth)acrylate monomers have produced a large number of novel materials including random, block, graft, and star copolymers, with unsurpassed and unique properties. The challenge of synthesizing these novel materials has still existed for new monomer, and new polymer structures need to be designed to be suitable for the requirement of new materials. The synthesis and properties of fluorinated poly(meth)acrylate-based copolymers reviewed herein serve as a platform for further research on potential applications of these materials. Understanding the production process and application of fluorinated poly(meth)acrylate-based copolymers will produce more novel structures.

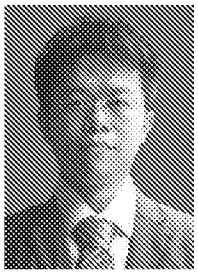
Acknowledgments

The authors thank the financial supports from National Natural Science Foundation of China (20674094, 21074145, 21204098, and 21274162) and Shanghai Scientific and Technological Innovation Project (11ZR1445900, 12JC1410500, 13ZR1464800, 14QA1404500, and 14JC1493400).

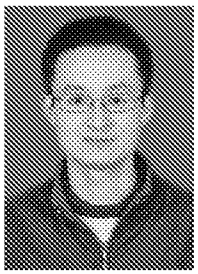
References

[1] Park JJ, Lee SB, Choi DK. J Appl Polym Sci 1994;54:1449–54.
[2] McCain SJ, Sauer BB, Firment LE. Macromolecules 1996;29:8211–6.
[3] Fu GD, Kang ET, Neoh KG, Lin CC, Liaw DJ. Macromolecules 2005;38:7593–600.
[4] Roche V, Vercandio F, Bertin D, Marsiani Y. J Electrocerom 2006;16:41–7.
[5] Liu MF, Chen YL, Zhang C, He ZS. Chin J Polym Sci 2012;30:308–15.
[6] Beck S, Boger A. Acta Biomater 2009;5:2503–7.
[7] Stefanescu EA, Tan XL, Liu ZQ, Bowler N, Kessler MR. Polym 2011;52:2016–24.
[8] Xu GF, Zhu WP. Chin J Polym Sci 2011;29:288–95.
[9] Kishi SK, Swain SK. Chin J Polym Sci 2012;30:397–404.
[10] Liu WD, Zhang YH, Fang LF, Zhu SK, Zhu LP. Chin J Polym Sci 2012;30:568–77.
[11] Thomas RR, Anton DR, Graham WF, Darmon MJ, Sauer BB, Stika KM, et al. Macromolecules 1997;30:2883–90.
[12] Domercq B, Hreha RD, Zhang YD, Larribeau N, Haddock JN, Schultz C, et al. Chem Mater 2003;15:1491–6.
[13] Erol I, Sen O, Dedeloglu A, Cilci C. J Appl Polym Sci 2009;114:3351–9.
[14] Reitinger JJ, Hillmyer MA. Prog Polym Sci 2002;27:971–1008.
[15] Hansen NML, Jankova K, Hvilsted S. Eur Polym J 2007;43:255–93.
[16] Hirao A, Sugiyama K, Yokoyama H. Prog Polym Sci 2007;32:1393–438.
[17] Ameduri B. Chem Rev 2009;109:6632–86.
[18] Ameduri B. Macromolecules 2010;43:10163–84.
[19] Narita T. Polym J 2011;43:497–515.
[20] Hartmann PC, Collet A, Viguier M, Blanc C. J Fluor Chem 2004;125:1909–18.
[21] Theato P. J Polym Sci Polym Chem 2008;46:6677–87.
[22] Eberhardt M, Mruk R, Zentel R, Theato P. Eur Polym J 2005;41:1569–75.
[23] Blazejewski JC, Hofsuraat JW, Lequeux C, Wakselman C, Wiersum UE. J Fluor Chem 1999;97:191–6.
[24] Canak TC, Hamuryudan E, Serhatli IE. J Appl Polym Sci 2013;128:1456–61.
[25] Tong L, Shen Z, Zhang S, Li YJ, Lu GL, Huang XY. Polymer 2008;49:4534–40.
[26] Li YJ, Shen Z, Tong L, Lu QH, Li WX, Lu GL, et al. J Fluor Chem 2008;130:254–60.
[27] Li YJ, Chen S, Shen Z, Li QH, Lu GL, Li WX, et al. Polymer 2009;50:5192–8.
[28] DeSimone JM, Guan ZB, Elsbernd CS. Science 1992;257:945–7.
[29] Sanfelice RC, Pavinatto FJ, Cardoso MR, Mendonca CR, Balogh DT, Oliveira ON. Polymer 2011;52:4703–8.
[30] He L, Liang JY, Zhao X, Li WD, Luo HJ. Prog Org Coat 2010;68:352–8.
[31] Alyamac E, Soucek MD. Prog Org Coat 2011;71:213–24.
[32] Souzy R, Ameduri B, Boutevin B. Macromol Chem Phys 2004;205:476–85.
[33] Jang SC, Yi SC, Kim YB, Hong JW. Polym Adv Technol 2005;16:484–8.
[34] Lazzari M, Aglietto M, Castelvetro V, Chiantore O. Chem Mater 2001;13:2843–9.
[35] Lazzari M, Chiantore O, Castelvetro V. Polym Int 2001;50:863–8.
[36] Cracowski JM, Montembault V, Hardy I, Bosc D, Ameduri B, Fontaine L. J Polym Sci Polym Chem 2008;46:4283–91.
[37] Cracowski J-M, Montembault V, Ameduri B. J Polym Sci Polym Chem 2010;48:2154–61.
[38] Liang JJ, He L, Zheng YS. J Appl Polym Sci 2009;112:1615–21.
[39] Chen JJ, Wu FQ. J Appl Polym Sci 2012;125:376–81.
[40] Park EJ, Nichez AP, Birkin NA, Lee H, Arrowsmith N, Thurecht KJ, et al. Polymer 2011;52:5403–9.
[41] Liu S, Gu B, Rowlands HA, Sen A. Macromolecules 2004;37:7924–9.
[42] Peng BL, Grishkewich N, Yao ZL, Han X, Liu HL, Tam KC. ACS Macro Lett 2012;1:632–5.
[43] Tanaka K, Matyjaszewski K. Macromolecules 2007;40:5255–60.
[44] Tanaka K, Matyjaszewski K. Macromol Symp 2008;261:1–9.
[45] Eggenhuisen TM, Beer CR, Fijten MWM, Eckardt R, Hoogenboom R, Schubert US. Macromolecules 2008;41:5132–40.
[46] Gu B, Liu S, Leber JD, Sen A. Macromolecules 2004;37:5142–4.
[47] Koumura K, Satoh K, Kamigaito M. Macromolecules 2009;42:2497–504.
[48] Perrier S, Jackson SG, Haddleton DM, Ameduri B, Boutevin B. Tetrahedron 2002;58:4053–9.
[49] Boyer C, Ameduri BV. J Polym Sci Polym Chem 2009;47:4710–22.
[50] Venkatesh R, Vergouwen F, Klumperman B. Macromol Chem Phys 2005;206:547–52.
[51] Mishima E, Tamura T, Yamago S. Macromolecules 2012;45:2993–9003.
[52] Canzarra E, Marian A, Ricco L, Russo S. Polymer 2002;43:1207–14.
[53] Malshe VC, Sangaj NS. Prog Org Coat 2005;53:207–11.
[54] Malshe VC, Elango S, Bhagwat SS, Magisabi SS. Prog Org Coat 2005;53:212–6.
[55] He JL, Ni PH, Liu CC. J Polym Sci Polym Chem 2008;46:3029–41.
[56] Ekrabania K, Laschewsky A, Berlepsch HV, Bottcher C. Langmuir 2009;25:7594–601.
[57] Li C, Zheng HT, Wang H, Dong QB, Bai RY. Polymer 2010;51:1940–6.
[58] Yi PP, Zheng SX, Liu TX. J Phys Chem B 2009;113:1857–68.
[59] Hussain H, Budde H, Boring S, Busse K, Kressler J. Macromol Chem Phys 2002;203:2103–12.
[60] Guo WJ, Tang ND, Xu J, Wang X, Chen Y, Yu FQ, et al. J Polym Sci Polym Chem 2011;49:1523–34.
[61] Sun Y, Liu WQ. J Fluor Chem 2011;132:9–14.
[62] Li K, Wu PP, Han ZW. Polymer 2002;43:4079–86.
[63] Qin S, Li H, Yuan WZ, Zhang YG. Polymer 2011;52:1191–6.
[64] Martinelli E, Famoni C, Galloi B, Glisenti A, Galli G. Macromol Symp 2010;296:294–302.
[65] Hansen NML, Gerstenberg M, Haddleton DM, Hvilsted S. J Polym Sci Polym Chem 2008;46:8097–111.

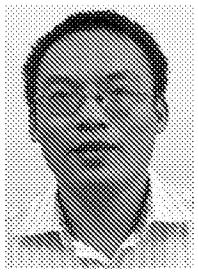
[66] Li YJ, Zhang S, Liu H, Li QX, Li WX, Huang XY. J Polym Sci Polym Chem 2010;48:5419–29.
[67] Hikita M, Tanaka K, Nakamura T, Kajiyama T, Takahara A. Langmuir 2004;20:5304–10.
[68] Zhu Y, Ford WT. Macromolecules 2008;41:6089–93.
[69] Lacroix-Desmazes P, Andre P, DeSimone JM, Ruzette AV, Boutevin B. J Polym Sci Polym Chem 2004;42:3537–52.
[70] Yi FP, Yu RT, Zheng SY, Li XH. Polymer 2011;52:5669–80.
[71] Yao WQ, Li YJ, Zhang S, Liu H, Huang XY. J Polym Sci Polym Chem 2011;49:4433–40.
[72] Grignard B, Vaillant A, Coninck J, Pirms M, Jonas AM, Detrembleur C, et al. Langmuir 2011;27:335–42.
[73] Guan ZB, DeSimone JM. Macromolecules 1994;27:5527–32.
[74] Yong TM, Hems WP, van Nunen JLM, Holmes AB, Steinke JHG, Taylor PL, et al. Chem Commun 1997:1811–2.
[75] Li L, Yokoyama H, Nemoto T, Sugiyama K. Adv Mater 2004;16:1226–9.
[76] Yokoyama H, Sugiyama K. Macromolecules 2005;38:10516–22.
[77] Li L, Nemoto T, Sugiyama K, Yokoyama H. Macromolecules 2006;39:4746–55.
[78] Xiong DA, Liu GJ, Hong LZ. Chem Mater 2011;23:4357–66.
[79] Benkenfoud K, Harrane A, Belbachir M. Chin J Polym Sci 2012;30:56–62.
[80] Villarroya S, Zhou JK, Duxbury CJ, Heise A, Howdle SM. Macromolecules 2006;39:633–40.
[81] Wang J, Mao G, Ober CK, Kramer EJ. Macromolecules 1997;30:1906–14.
[82] Krishnan S, Ayothi R, Hexemer A, Finlay JA, Sohn KE, Perry R, et al. Langmuir 2006;22:5075–86.
[83] Shemper BS, Mathias LJ. Eur Polym J 2004;40:651–55.
[84] Durmaz YY, Sahkulubey EE, Yagci Y, Martinelli E, Galli G. J Polym Sci Polym Chem 2012;50:4911–9.
[85] Zhou Z, Li Z, Ren Y, Hillmyer MA, Lodge TP. J Am Chem Soc 2003;125:10182–3.
[86] Li Z, Kesselman E, Talmon Y, Hillmyer MA, Lodge TP. Science 2004;306:98–101.
[87] Chen YB, Wang ZG. Polymer 2013;54:3047–54.
[88] Kassis CM, Steehler JK, Betts DE, Guan Z, Romack TJ, DeSimone JM, et al. Macromolecules 1996;29:3247–54.
[89] Eroglu MS. J Appl Polym Sci 2006;101:3543–7.
[90] Granel C, Dubois P, Jerome R, Teyssie P. Macromolecules 1996;29:8576–82.
[91] Raihane M, Castelvetro V, Bianchi S, Atlas S, Ameduri B. J Polym Sci Polym Chem 2010;48:4900–8.
[92] Merkini A, Raihane M, Ameduri B, Hakme C, Sage D, Stevenson I, et al. Eur Polym J 2009;45:804–12.
[93] Oliveira ON, Santos DE, Balogh DT, Zucolotto V, Mendonca CR. Adv Colloid Interf Sci 2005;116:179–92.
[94] Chiantore O, Lazzari M, Aglietto M, Castelvetro V, Ciardelli F. Polym Degrad Stabil 2000;67:461–7.
[95] Ebdon L, Xu C, Stengel RMI, Shacklett LW, Yardley JT. J Light Technol 1996;14:1704–13.
[96] Hida Y, Onodo H, Imamura S. Jpn J Appl Phys 1995;34:6415–22.
[97] Cheng XL, Chen ZX, Shi TS, Wang HY. Colloids Surf A 2007;292:119–24.
[98] Zhou DY, Teng HK, Koike Y, Koike Y, Okamoto Y. J Polym Sci Polym Chem 2008;46:4748–55.
[99] Ito F, Ma G, Nagai M, Omi S. Colloids Surf A 2003;216:109–22.
[100] Cui XJ, Zhong SL, Wang HY. Colloids Surf A 2007;303:173–8.
[101] Ishizone T, Sugiyama K, Sakano Y, Mori H, Hirao A, Nakahama S. Polym J 1999;31:983–8.
[102] Wang ZC, Li WJ, Zhao XL, Zhu DJ, You J. J Phys Chem B 2009;113:15205–11.
[103] Peng H, Thurecht KJ, Blakey I, Taran E, Andrew R, Whittaker AK. Macromolecules 2012;45:8681–90.
[104] Soucy R, Ameduri B, Boutevin B. Prog Polym Sci 2004;29:75–106.
[105] Li H, Zhang YM, Zhang H, Xue MZ, Liu YG. J Polym Sci Polym Chem 2006;44:3853–8.
[106] Krafft MP, Riess JG. J Polym Sci Polym Chem 2007;45:1185–98.
[107] Peng H, Blakey I, Dargaville B, Rasoul F, Rose S, Whittaker AK. Biomacromolecules 2009;10:374–81.
[108] Gopalan P, Andruzzi L, Li XF, Ober CK. Macromol Chem Phys 2002;203:1573–83.
[109] Busch P, Krishnan S, Paik M, Toombes GES, Smilgies DM, Gruner SM, et al. Macromolecules 2007;40:81–9.
[110] Cengiz U, Gengec NA, Kaya NU, Erbil HY, Sara AS. J Fluor Chem 2011;132:348–55.
[111] Soucy R, Boutevin B, Ameduri B. Macromolecules 2012;45:3145–60.



Dr. Wenqiang Yao was born in Fujian, China in 1982. After received his B.S in chemistry from Nanjing University in 2005, he worked in Jiangsu Heng Rui Medicine Co. Ltd. for four years. He was enrolled into Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences as a graduate student in 2009. In 2014, he earned Ph.D. degree in polymer chemistry & physics under the supervision of Prof. Xiaoyu Huang from SIOC. His graduate research was mainly focused on the synthesis and self-assembly behavior of perfluorocyclobutyl aryl ether-based amphiphilic copolymer.



Dr. Yongjun Li was born in Shannxi, China in 1978. After received his Ph.D. degree in inorganic chemistry from Shanghai Institute of Applied Physics, Chinese Academy of Sciences (CAS) in 2010, he joined Prof. Xiaoyu Huang's group in Shanghai Institute of Organic Chemistry, CAS as a research assistant and has been promoted as a research associate in 2013. His work is mainly focused on the synthesis and application of fluorine-containing polymer materials.



Prof. Xiaoyu Huang was born in Shanghai, China in 1973. He received his BS degree in polymer chemistry from the Special Class for Young Gift, Nanjing University in 1993 and Ph.D. degree in polymer science (supervised by Prof. Junlian Huang) from Fudan University in 1998. After three years of postdoctoral research in University of Toronto and University of Akron, he was enrolled by the Hundreds of Talents Project co-sponsored by the Ministry of Finance and Chinese Academy of Sciences (CAS) and joined the faulty at Shanghai Institute of Organic Chemistry (SIOC), CAS as a full professor in 2001. His main research interests include the synthesis and self-assembly of well-defined graft polymers and the high-performance fluoropolymers.

Sartomer Company
Material Safety Data Sheet

Product: CD406 Revised Date: 06-09-2005
MSDS ID: S-000440 Replaces Date: 01-17-2005

01. GENERAL INFORMATION

Sartomer Company, Inc.
Oaklands Corporate Center
502 Thomas Jones Way
Exton, Pennsylvania 19341

Emergency phone numbers:
800/424-9300 (CHEMTREC)
610/692-8401 (Sartomer Co., Inc.)
Product information:
610/363-4100

GENERIC NAME
Cyclohexane Dimethanol Diacrylate

DOT PROPER SHIPPING NAME
N/AP

UN/NA NUMBER
N/AP

DOT HAZARD CLASS
Not regulated

02. SUMMARY OF HAZARDS

WARNING

PHYSICAL HAZARDS:	Unstable (reactive) upon depletion of inhibitor
ACUTE HEALTH EFFECTS: (SHORT-TERM)	Suspect eye irritation hazard Suspect skin irritation/sensitization hazard Suspect respiratory tract irritation hazard Suspect skin absorption hazard Suspect slight ingestion hazard
CHRONIC HEALTH EFFECTS: (LONG-TERM)	No chronic health effects data are available for this material.

03. COMPONENTS

COMPONENT NAME	CAS NUMBER	% COMPOSITION (BY WT.)
Cyclohexane Dimethanol Diacrylate Esters	67905-41-3	AP 100

04. PHYSICAL AND CHEMICAL DATA

BOILING POINT
N/DA

pH
AP 6.8 to 7.2

MELTING POINT
82C/180F

DRY POINT
N/DA

SPECIFIC GRAVITY (H20=1 at 39.2F)
N/AP

VOLATILE CHARACTERISTICS
Negligible

VISCOSITY UNITS, TEMP. (Brookfield)
N/AP

SOLUBILITY IN WATER
Negligible

VAPOR PRESSURE

STABILITY

N/DA
VAPOR SP GR (AIR=1 at 60 - 90F)
N/DA

Stable
HAZARDOUS POLYMERIZATION
May occur

APPEARANCE AND ODOR
Waxy white solid at room temperature

CONDITIONS AND MATERIALS TO AVOID
High temperatures, localized heat sources (ie, drum or band heaters), oxidizing conditions, direct sunlight, ultraviolet radiation, inert gas blanketing;
Strong oxidizers, strong reducers, free radical initiators, inert gases, oxygen scavengers

HAZARDOUS DECOMPOSITION PRODUCTS
Acrid smoke-fumes/carbon monoxide/carbon dioxide and perhaps other toxic vapors may be released during a fire involving this product.

05. OCCUPATIONAL EXPOSURE LIMITS

SUBSTANCE	SOURCE	DATE	TYPE	VALUE	TIME

A PEL or TLV has not been established

06. FIRE AND EXPLOSION

FLASH POINT METHOD=(Estimated)
GT 93C/200F

AUTOIGNITION TEMP. METHOD=
N/DA

FLAMMABLE LIMITS (% VOLUME IN AIR)
LOWER: N/DA UPPER: N/DA

FIRE AND EXPLOSION HAZARDS
High temperatures, inhibitor depletion, accidental impurities, or exposure to radiation or oxidizers may cause spontaneous polymerizing reaction generating heat/pressure. Closed containers may rupture or explode during runaway polymerization.

EXTINGUISHING MEDIA
Dry chemical
CO2
Water spray
Foam
Water fog

SPECIAL FIREFIGHTING PROCEDURES
Do not enter fire area without proper protection. See Section 4 - decomposition products possible. Fight fire from safe distance/protected location. Heat/impurities may increase temperature/build pressure/rupture closed containers, spreading fire, increasing risk of burns/injuries. Water may be ineffective in firefighting due to low solubility. Use water spray/fog for cooling. Pressure relief system may plug with solids,

increasing risk of overpressure. Notify authorities if liquid enters sewer/public waters.

07. HEALTH HAZARDS

ROUTES OF EXPOSURE

INHALATION
No significant signs or symptoms indicative of any adverse health effects are expected to occur at standard conditions. However, aerosols or vapors which may be generated during processing may cause respiratory tract irritation. Symptoms of irritation may include sore throat, coughing, mucous production, and shortness of breath.

EYE CONTACT -- PRIMARY ROUTE
Although no appropriate human or animal health effects data are known to exist, this material is expected to cause eye irritation.
Symptoms may include pain or burning sensation, redness, tearing, excessive blinking and swelling.

SKIN ABSORPTION -- PRIMARY ROUTE
Although no appropriate human or animal health effects data are known to exist, this material is expected to be a health hazard by skin absorption.

SKIN IRRITATION -- PRIMARY ROUTE
Although no appropriate human or animal health effects data are known to exist, this material is expected to be a skin irritant.
Symptoms of irritation may include localized redness or rash and swelling of the affected area. Symptoms may be delayed.
Although no appropriate human or animal health effects data is known to exist, this material may cause an allergic skin reaction (sensitization) in susceptible individuals upon repeated exposure.

INGESTION
Although no appropriate human or animal health effects data are known to exist, this material is expected to be a slight ingestion hazard.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE
No additional medical information found.

08. PROTECTIVE EQUIPMENT / CONTROL MEASURES

RESPIRATORY PROTECTION
If this material is handled at elevated temperature or under mist forming conditions, NIOSH/MSHA approved respiratory protection equipment should be used.

EYE PROTECTION
Eye protection such as chemical splash goggles and/or face shield must be worn when possibility exists for eye contact due to splashing or spraying liquid, airborne particles, or vapor. Contact lenses should not be worn.

SKIN PROTECTION
When skin contact is possible, protective clothing including gloves, apron, sleeves, boots, head and face protection should be worn. This equipment must be cleaned thoroughly after each use.

ENGINEERING CONTROLS
If handling results in aerosol or vapor generation, local exhaust ventilation is recommended.

OTHER HYGIENIC PRACTICES
Emergency eye wash fountains and safety showers should be available in the immediate vicinity of any potential exposure.

OTHER WORK PRACTICES
Use good personal hygiene practices. Wash hands before eating, drinking, smoking, or using toilet facilities. Promptly remove soiled clothing/wash thoroughly before reuse. Shower after work using plenty of soap and water.

09. EMERGENCY AND FIRST AID

INHALATION
If overcome by exposure, remove victim to fresh air immediately. Give oxygen or artificial respiration as needed. Obtain emergency medical attention. Prompt action is essential.

EYE CONTACT
In case of eye contact, immediately rinse with clean water for 20-30 minutes. Retract eyelids often. Obtain emergency medical attention.

SKIN CONTACT
Immediately remove contaminated clothing. Wash skin thoroughly with mild soap/water. Flush w/lukewarm water for 15 minutes. If sticky, use waterless cleaner first. Seek medical attention if ill effect or irritation develops.

INGESTION
If large quantity swallowed, give lukewarm water (pint) if victim completely conscious/alert. Do not induce vomiting/risk of damage to lungs exceeds poisoning risk. Obtain emergency medical attention.

EMERGENCY MEDICAL TREATMENT PROCEDURES
Treat symptomatically.

10. SPILL AND DISPOSAL

PRECAUTIONS IF MATERIAL IS SPILLED OR RELEASED
Spilled or released material may polymerize and release heat/gases. Extinguish all ignition sources and ventilate area. Wear protective equipment during clean-up. Dike and recover large spill. Soak up small spill with inert solids (such as vermiculite, clay) and sweep/shovel into vented disposal container. Wash spill area with a strong detergent and water solution; rinse with water but minimize water use during clean-up. For

spills on water, contain, minimize dispersion and collect. Dispose/report per regulatory requirements.

WASTE DISPOSAL METHODS
Non-contaminated, properly inhibited product is not a RCRA hazardous waste. However, contaminated product/soil/water may be RCRA/OSHA hazardous waste due to potential for internal heat generation (see 40 CFR 261 and 29 CFR 1910). It is the responsibility of the generator to determine at the time of disposal whether the product meets the criteria of a hazardous waste. Comply with all applicable federal, state and local regulations. Use registered transporters. Disposal options include landfilling solids at permitted sites; fuel blending or incinerating liquids. Assure emissions comply with applicable regulations. Dilute aqueous waste may biodegrade; avoid overloading/poisoning plant biomass. Assure effluent complies with applicable regulations.

11. ADDITIONAL PRECAUTIONS

HANDLING AND STORAGE PROCEDURES
This material is supplied as a solid. To facilitate product transfer from original container, container may be heated to 90C/194F for not more than 24 hours. Do NOT use localized heat sources such as band heaters to heat/melt product. Do NOT use steam. Hot boxes or hot rooms are recommended for heating/melting material. The hot box or hot room should be set at a maximum temperature of 90C/194F. Do not overheat--this may compromise product quality and/or result in an uncontrolled hazardous polymerization. Check product before use/processing to ensure it is thoroughly and completely melted. Gently mixing may be required. Product must be completely melted and in a homogeneous state prior to use. Product should be consumed in its entirety after heating/melting--avoid multiple "re-heats" which may affect product quality or result in product degradation. Product is packaged with inhibitor(s). Unless inhibited, product can polymerize, raising temperature and pressure possibly rupturing container. Check inhibitor content periodically, adding to bulk material if needed. In addition, the product's inhibitor(s) require the presence of dissolved oxygen. Maintain, at a minimum, the original headspace in the product container and do not blanket or mix with oxygen-free gas as it renders inhibitor ineffective. Store product indoors at temperatures greater than 10C/50F and below 38C/100F. Avoid prolonged (longer than shelf-life) storage temperatures above 38C/100F. Store in tightly closed containers in a properly vented storage area away from: heat, sparks, open flame, strong oxidizers, radiation, and other initiators. Prevent contamination by foreign materials. Prevent moisture contact. Use only non-sparking tools and limit storage time. Shelf-life is 6 months from receipt of product.

DECONTAMINATION PROCEDURES
Follow standard plant procedures or supervisor's instructions for decontamination operations.

12. LABEL INFORMATION

USE STATEMENT

FOR INDUSTRIAL USE ONLY
SIGNAL WORD
WARNING
PHYSICAL HAZARDS
UNSTABLE (REACTIVE) UPON LOSS OF INHIBITOR
HEALTH HAZARDS
MAY CAUSE EYE AND SKIN IRRITATION
MAY CAUSE ALLERGIC SKIN REACTION
PRECAUTIONARY MEASURES
HAZARDOUS POLYMERIZATION MAY OCCUR UPON DEPLETION OF INHIBITOR.
DO NOT HANDLE NEAR HEAT, SPARKS, OR OPEN FLAME.
AVOID CONTACT WITH EYES, SKIN AND CLOTHING.
AVOID BREATHING VAPORS/AEROSOLS.
USE ONLY WITH ADEQUATE VENTILATION/PERSONAL PROTECTION.
WASH THOROUGHLY AFTER HANDLING.
KEEP CONTAINER CLOSED WHEN NOT IN USE.
BEFORE USING PRODUCT, READ MATERIAL SAFETY DATA SHEET (MSDS).

13. SUPPLEMENT

NPCA HMIS RATING

Health	2
Flammability	1
Reactivity	2
Personal Protection**	D

**Respiratory protection may be necessary depending on conditions of use.

REGULATORY INFORMATION

TSCA STATUS

TSCA status: All components of this product are listed, or excluded from listing, on the United States Environmental Protection Agency Toxic Substances Control Act (TSCA) inventory.

CALIFORNIA PROPOSITION 65

California Proposition 65 Information: This product contains, or may contain, trace quantities of a substance(s) known to the state of California to cause cancer and/or reproductive toxicity.

INTERNATIONAL STATUS

Australia (AICS):	not included on inventory
Canada (DSL):	included on NDSL
China (CECS):	not included on inventory
Europe (EINECS):	included on inventory
Japan (ENCS):	not included on inventory
Korea (ECL):	not included on inventory
Philippines (PICCS):	not included on inventory

This material contains an inhibitor (HQ, MEHQ, etc.) at <1%. The type and amount meet product specifications. Contact a company representative for exact concentrations and details on inhibitor level maintenance.

*Note - qualifiers and codes used in this MSDS
EQ = Equal; AP = Approximately; LT = Less Than; GT = Greater Than;
TR = Trace; UK = Unknown; N/AP = Not Applicable; N/P = No Applicable Information Found; N/DA = No Data Available

14. DISCLAIMERS

Some of the information presented and conclusions drawn herein are from sources other than direct test data on the product itself. The information in this MSDS was obtained from sources which we believe are reliable. However, the information is provided without any warranty, express or implied, regarding its correctness. The conditions or methods of handling, storage, use and disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal of the product. This MSDS was prepared and is to be used only for this product. If the product is used as a component in another product, this MSDS information may not be applicable. This MSDS has been prepared in accordance with the requirements of the OSHA Hazard Communication Standard (29 CFR 1910.1200).

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

FAVORED TECH CORPORATION,

Petitioner,

v.

P2I LTD.,

Patent Owner.

CASE: IPR2020-01198

Patent No. 10,421,876

DECLARATION OF DR. KAREN GLEASON IN SUPPORT OF PETITION FOR INTER PARTES REVIEW

TABLE OF CONTENTS

I. INTRODUCTION 1
II. QUALIFICATIONS AND EXPERIENCE 1
A. Education and Professional Experience 1
Education 2
Professional Career 2
Scientific Publications 4
B. Compensation 5
C. Documents and other materials relied upon 5
III. STATEMENT OF LEGAL PRINCIPLES 5
A. Legal standards for obviousness 5
B. Claim construction 8
IV. LEVEL OF ORDINARY SKILL IN THE ART 8
V. SUMMARY OF OPINIONS 11
VI. TECHNICAL BACKGROUND 11
A. Plasma polymerization 12
B. Monomer reagents for plasma polymerization 14
C. Crosslinking and crosslinking reagents 21
D. Applications for plasma polymerization 27
VII. SUMMARY OF THE '876 PATENT 29
VIII. THE PRIOR ART 33
A. Exhibit 1004 – "Coulson-122" 33
B. Exhibit 1005 – "Badyal" 35
C. Exhibit 1006 – "Cohen" 37
D. Exhibit 1007 – "Holliday" 37
E. Exhibit 1008 – "Padiyath" 38
F. Exhibit 1009 – "Francesch" 40
G. Exhibit 1011 – "Tropsch" 41
H. Other References 42

IX. CLAIM CONSTRUCTION 49

A. "Halogen" 50

B. Other claim terms 50

X. ANALYSIS OF THE CLAIMS OF THE '876 PATENT 51

A. All Grounds: Coulson-122 and Badyal described preparing plasma-polymer films by copolymerizing monomers including PFAC8 or PFMAC8 with a crosslinker 51

B. Ground 1: Coulson-122, Badyal, and Cohen 57

1. Claim 1 57

2. Claims 2, 3 65

3. Claims 9 and 11-15 65

C. Ground 2: Coulson-122, Badyal, and Holliday 67

1. Claim 1 69

2. Claims 2, 3 76

3. Claim 4 77

4. Claims 5 and 6 78

5. Claim 7 79

6. Claim 8 80

7. Claim 10 81

8. Claims 11-15 81

D. Ground 3: Coulson-122, Badyal, and Padiyath 82

1. Claim 1 83

2. Claims 2, 3 90

3. Claim 4 91

4. Claim 10 92

5. Claims 12-15 92

E. Ground 4: Coulson-122, Badyal, and Francesch 92

1. Claim 1 93

2. Claims 2, 3 97

3. Claims 5 and 6 97

4. Claim 7 97
5. Claim 8 98
6. Claims 11-15 98
F. Ground 5: Coulson-122, Badyal, and Tropsch 98
1. Claim 1 99
2. Claims 2, 3 104
3. Claims 5, 6, and 8 104
4. Claim 7 105
5. Claims 12-15 106
G. All Grounds: Claims 2 and 3 106
1. Claim 2 107
2. Claim 3 110

I. INTRODUCTION

1. My name is Dr. Karen K. Gleason.

2. I have been engaged by Petitioner Favored Tech Corporation to investigate and opine on certain issues relating to U.S. Patent 10,421,876 (Ex. 1001), which I will refer to here as the '876 patent, in connection with Favored Tech's petition for *inter partes* review of the '876 patent.

3. In this declaration, I will first discuss the technical background relating to the '876 patent, and then I will provide my analyses and opinions relating to claims 1-15 of the '876 patent.

4. This declaration is based on the information currently available to me. To the extent that additional information becomes available, I reserve the right to continue my investigation and study, which may include reviewing documents and information that may be produced, as well as testimony from depositions that may be taken.

II. QUALIFICATIONS AND EXPERIENCE

A. Education and Professional Experience

5. Ex. 1003 is a copy of my curriculum vitae (CV), which provides listings of my educational background, professional experience, and scientific publications that are relevant to the subject matter of this proceeding. I possess the knowledge, skills, experience, training, and education to form an expert opinion and provide expert testimony in this matter.

6. I have 33 years of experience in the field of chemical engineering, with the last 24 years having a specific focus on polymer chemistry and production of polymer coatings.

Education

7. I received bachelor of science (S.B.) and master of science (S.M.) degrees in Chemical Engineering from the Massachusetts Institute of Technology (M.I.T.) in 1982. I also received All-American honors in swimming while a student at M.I.T. I received a Ph.D. in Chemical Engineering from the University of California, Berkeley, in 1987. My doctoral thesis identified the molecular structure of defects in thin films used in the fabrication of solar cells. These thin films were produced by Chemical Vapor Deposition (CVD).

Professional Career

8. I have been employed as a professor of chemical engineering at M.I.T. since 1987. I was an assistant professor from 1987-1993 and an associate professor from 1993-2000, and I have been a full professor from 2000 to the present. I held the Herman P. Meissner Career Development Professorship in Chemical Engineering from 1987-1990 and the Esther and Harold E. Edgerton Career Development Professorship from 1991-1995. From 2006 to January 2020, I was the Alexander and I. Michael Kasser Professor of Chemical Engineering. Since January 2020, I have assumed the title of Alexander and I. Michael Kasser Professor of Chemical

Engineering, Emerita.

9. I have served in additional roles at M.I.T. during my time as a professor. I was the Executive Officer (vice chair) of the Department of Chemical Engineering from 2001-2004, the Associate Director of the Institute for Soldier Nanotechnology from 2005-2008, the Associate Dean of Engineering for Research from 2008-2011, and the Associate Provost for Space Planning and Industrial Relationships from 2014-2018.

10. I am a member of the National Academy of Engineering and a fellow of the American Institute of Chemical Engineering.

11. I am also the co-founder and Chief Scientific Advisor for GVD Corporation, which was founded in 2001. GVD manufactures CVD polymer release coatings used in the molding of rubber tires for vehicles and for seal and gasket applications.

12. The focus of my work in the most recent 24 years of my professional career has been on elucidating the mechanisms of CVD polymer growth and inventing new methods of CVD polymerization. For this research, my laboratory has built more than a dozen custom CVD reactors. My group has published on both continuous wave and pulsed plasma polymerization, also known as plasma enhanced CVD (PECVD). The applications explored ranged from low dielectric constant layers for microelectric circuits to biopassive coatings for implantable medi-

cal devices. By adding an initiator species to the reactive gas inlet, the power required for plasma polymerization is greatly reduced, a method we named iPECVD. Recently, we demonstrated that thin iPECVD layers can serve as membranes for separating individual gases from a mixture of gases. By understanding the mechanisms of plasma polymerization, two new polymer CVD methods were developed: initiated CVD (iCVD) and oxidative CVD (oCVD). Neither method requires a plasma and thus allows complete fidelity in chemical structure between the inlet monomer and the resulting polymer thin film. Using iCVD and oCVD, over 100 different monomers have been polymerized. In 2018, oCVD achieved the record for the highest electrical conductivity (>6000 S/cm) of the polymer polyethylene dioxythiophene (PEDOT), a material of great interest for fabricating flexible electronic devices.

Scientific Publications

13. I have authored more than 300 scientific publications in the fields of chemical engineering and polymer chemistry. I am the sole editor of the book *CVD Polymers Fabrication of Organic Surfaces and Devices*, first published by Wiley in 2015. I am a named inventor of more than 35 issued U.S. patents. I have also spoken about my work at numerous scientific conferences and symposia. My accompanying CV includes listings of my publications, professional speaking engagements, and patents. Ex. 1003.

B. Compensation

14. I am being compensated for the services I am providing under my engagement with Favored Tech Corporation, including the preparation of this declaration. That compensation is not contingent upon my performance, the outcome of this *inter partes* review or any other proceeding, or any issues involved in or related to this *inter partes* review or any other proceeding.

C. Documents and other materials relied upon

15. In forming my opinions, I have relied on information and evidence identified in this declaration, including the '876 patent, its prosecution history, and other references listed as exhibits in Favored Tech's *inter partes* review petition.

III. STATEMENT OF LEGAL PRINCIPLES

A. Legal standards for obviousness

16. I understand that where a prior art reference does not disclose all of the elements of a given patent claim, that patent claim is invalid if the differences between the claimed subject matter and the prior art reference are such that the claimed subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the relevant art. Obviousness can be based on a single prior art reference or a combination of references that either expressly or inherently disclose all elements of the claimed invention.

17. I further understand that, in determining whether a patent claim was obvious, one can consider whether there would have been any teaching, suggestion

or motivation ("the TSM test") to combine the teachings of two or more prior art references that, together, contain all of the elements of the patent claim. In other words, one can consider whether the combined prior art, taken as a whole, would have rendered the claimed invention obvious to one of ordinary skill in the art at the time of the invention. I further understand that to determine whether an invention would have been obvious at the time it was made, the Board will look to four factors: (1) the scope and content of the prior art; (2) the differences between the prior art and the claimed invention; (3) the level of skill in the pertinent art; and (4) any secondary considerations of non-obviousness.

18. I understand that secondary considerations that may indicate non-obviousness can include: (1) whether there was a long-felt need for the claimed invention; (2) whether the claimed invention has achieved commercial success; (3) whether there was copying of the claimed invention by others; (4) whether there were failed attempts by others to make the claimed invention; (5) whether there was praise of the claimed invention in the field; and (6) whether there was skepticism in the field whether the claimed invention could be achieved. For secondary considerations to be accorded substantial weight, I understand that there must be a nexus between the secondary considerations and the claimed invention. For example, if a secondary consideration results from something other than what is claimed and novel, then there is no nexus. In addition, I understand that another potential

factor of that can suggest that a claimed invention *was* obviousness is the independent simultaneous invention by others.

19. To determine whether there was motivation to modify or combine prior art references to obtain the claimed invention, I am informed that such motivation may come from the nature of the problem to be solved, which would lead inventors to look to certain references for possible solutions to that problem. In other words, the test may be said to be whether a person of ordinary skill in the art would have reasonably expected to use the solution that is claimed in the patent, if the person were seeking to solve the problem addressed by the patent and that person had the prior art before them at the time. Motivation to modify references may be found in the references themselves, as well as in the general knowledge of persons skilled in the art.

20. I also understand that the TSM test is not necessarily required, and a claim can be determined obvious if the claimed combination would have resulted from common sense, would have been obvious to try (such as being one of a relatively small number of possible approaches to the problem that would have been reasonably expected to succeed), or would have been the predictable result of using prior art elements according to their known functions. I also understand that obviousness can take into account the inferences and creative steps that a person of ordinary skill in the art would employ.

B. Claim construction

21. I understand from counsel that a claim term in an unexpired patent must be given its ordinary meaning as understood by a person of ordinary skill in the art in the same field as the patent when considered in context of the patent's claims, specification, and prosecution history. I also understand that when interpreting a term's meaning, one should consider what the inventor actually invented and intended to be covered by the claim in which the term appears. When determining a claim term's meaning, one should also consider the patent's specification and the prosecution history. In some cases, the inventor may use terms in a manner other than in their ordinary meaning by clearly, deliberately, and precisely stating that special definition in the patent specification or in the file history. I further understand that, under the legal principle of claim differentiation, two different claims in the same patent (and in particular, an independent claim and one of its dependent claims) should not be interpreted in a way that would render them identical in scope, if that result can be avoided

IV. LEVEL OF ORDINARY SKILL IN THE ART

22. I understand from counsel that the claims and specification of a patent must be read and construed through the eyes of a person of ordinary skill in the art (POSA) at the time of the patent's priority date. To determine the appropriate qualifications of a POSA, I understand that the following factors may be considered:

(a) the types of problems encountered by those working in the field and prior art solutions to such problems; (b) the sophistication of the technology in question; and (c) the typical level of training for active workers in the field.

23. I understand from counsel that I should assume for purposes of my analysis that the priority date for the '876 patent was June 9, 2015.

24. The '876 patent describes protective coatings applied to a variety of electronic devices and electronic components. Ex. 1001 at 1:5-13, 14:30-58. The patent indicates that the coatings can repel liquids such as water or can provide an electrically insulating barrier layer. Ex. 1001 at 1:8-13, 2:56-3:11.

25. The coatings are applied using plasma polymerization with a plasma containing two main components: a monomer and a crosslinker. Ex. 1001 at Abstract, 2:10-20, 2:49-55, 4:36-13:8. For the monomer, the '876 patent identifies perfluoroalkyl acrylates or perfluoroalkyl methacrylates as preferred substances. Ex. 1001 at 11:27-56, 21:7-22:21. By 2015, those monomers had been used to create hydrophobic coatings through plasma polymerization for many years, as the '876 patent acknowledges. Ex. 1001 at 1:17-19 (citing Ex. 1022, published in 1998).

26. According to the specification, combining the monomer with a crosslinker produces crosslinked co-polymer coatings that retain the monomer structure for good hydrophobicity while providing stability due to the crosslinked structure

of the coatings. Ex. 1001 at 2:49-60, 14:18-29. At the time of the '876 patent's priority date in June 2015, POSAs were familiar with the use of crosslinking reagents in polymer coatings, including coatings applied through plasma polymerization and including many of the same preferred crosslinkers in the '876 patent. Ex. 1005 4:1-9, 4:26-29, Ex. 1006 at 3:51-62, Ex. 1009 at 610, Ex. 1023 at 8724, Ex. 1026 at 6553; Ex. 1001 at 8:3-11 (most preferred crosslinkers).

27. As the '876 patent indicates, plasma polymerization was well known to POSAs by June 2015, and POSAs could perform plasma deposition using existing equipment and routine methods and would have known how to adjust plasma composition and reaction conditions to achieve desired properties in the polymer coating. Ex. 1001 at 13:61-67, 14:18-28, 14:59-67, 15:6-8. None of the coating techniques described in the '876 patent would have required advanced technical knowledge or expertise to implement.

28. A worker in the relevant field with an ordinary level of skill at the '876 patent's priority date would have required familiarity with technical principles relating to polymer chemistry and plasma generation and would have needed at least some experience operating and adjusting the operating conditions for a plasma polymerization chamber. In my experience, such workers in the field with an ordinary level of skill at the time typically had at least a bachelor's degree in a relevant discipline and some experience with plasma polymerization.

29. Based on the considerations discussed above, it is my opinion that a POSA at the time of the priority date for the '876 patent would have had at least a bachelor's degree in a field such as chemistry, physics, or chemical engineering, as well as at least two years of experience with plasma-polymerization techniques.

V. SUMMARY OF OPINIONS

30. For the reasons explained below, it is my opinion that the claims of the '876 patent would have been obvious to a POSA by June 2015. Plasma polymerization was well known by that time, as was its use for applying protective coatings to electronics. The monomers recited in the claims were known by that priority date, as the specification of the '876 patent acknowledges, the claimed crosslinking reagents were also known in the polymer field, and the prior art had already specifically suggested combining those known monomers with the same broad class of known crosslinkers to devise protective coatings with improved durability. There was nothing innovative about implementing that suggestion and combining known compounds by a known method to apply protective coatings to electronic devices that had long been targets of such treatments. I therefore conclude that the claims would have been obvious to a POSA over the prior art discussed here.

VI. TECHNICAL BACKGROUND

31. I understand that I should assume the '876 patent has a priority date of

June 9, 2015. The discussion in this section summarizes the relevant technology and the state of the art by June 2015.

A. Plasma polymerization

32. In general, a polymer is a collection of repeating structural units and is produced from small-molecule reactants, referred to as monomers, which are linked together to form extended chains or networks. By 2015, plasma polymerization was a common technique for generating polymers that had been widely used to deposit thin-film coatings on various substrates for many years. Ex. 1004 at 2:33-3:18; Ex. 1005 at 2:10-20; Ex. 1034 at 1-2. Plasma polymerization involves forming polymeric materials under plasma, which is a gas in an at least partially ionized state that contains charged molecules or atoms and free electrons. Ex. 1034 at 19.

33. In general, plasma polymerization involves vaporizing at least one monomer compound that supplies the input material to be polymerized. Ex. 1004 at 2:33-3:18. A wide variety of organic compounds have been utilized as monomers used for plasma polymerization. Ex. 1034 at 2-3.

34. The plasma state can be induced in a gas containing monomer vapor through various means, but applying an electromagnetic field was the simplest and most commonly used approach. Ex. 1004 at 3:2-5; Ex. 1005 at 2:14-20; Ex. 1019 at 2032; Ex. 1014 at 21:20-22:2; Ex. 1034 at 19. The optical excited species in the

plasma often gives off visible light emanating from at least a portion of the resulting plasma—often referred to in the field as a "glow discharge." Ex. 1004 at 7:14-17; Ex. 1005 at 10:17-18; Ex. 1019 at 2032; Ex. 1034 at 19-20. One example of a glow discharge occurs upon illuminating a common neon sign, which applies an electromagnetic field to a gas-filled chamber within such signs to create their familiar luminous appearance.

35. When applying an electromagnetic field to a gas to generate plasma, the electrical power was commonly applied in one of two ways: continuously (known as "continuous wave" plasma generation) or in rapid on/off cycles (known as "pulsed" plasma generation). Ex. 1019 at 2032-33 (Table 2). Pulsed plasma had recognized advantages for many coating applications because it permits application of sufficient electrical power to generate and maintain plasma but subjects the gas-phase monomer to that power for only part of the total polymerization time, thus resulting in less applied power and better preserving functional groups (such as hydrophobic perfluorocarbon pendant chains) from the original monomer structure against fragmentation or other structure rearrangement in the resulting plasma polymer coating. Ex. 1019 at 2035-36; Ex. 1023 at 8724. Better preservation of the monomer's functional groups generally leads to better preserved functional properties in the resulting plasma polymer coatings.

36. When a plasma generated from a gas-phase monomer comes in con-

tact with a substrate, the species in the plasma impinge on the substrate surface and react to form a polymer film that is deposited as a coating on the substrate. The plasma polymerization process creates complex branched and crosslinked molecular chains due to partial fragmentation of the original monomer molecule. That resulting structural complexity distinguishes plasma polymerization from molecular polymerization techniques in which monomer molecules combine through chemical reactions to form relatively uniform chains or networks of repeating monomer units.

37. During plasma polymerization, it was very common to supply the gas-phase monomer for plasma polymerization in a mixture with an additional carrier gas, often an inert gas like helium or argon. Ex. 1004 at 7:19-23; Ex. 1021 ¶ 63; Ex. 1022 5:20-22.

38. Plasma polymerization is traditionally carried out in enclosed chambers to contain the gaseous reagents and the associated plasma during operation. Plasma chambers vary widely in size and configuration. Most were designed to be evacuated and maintained at low pressure during operation. At low pressures, the plasma can be made uniform over large substrate areas.

B. Monomer reagents for plasma polymerization

39. Monomers for plasma polymerization often contained unsaturated reactive groups, such as a vinyl group or an acrylic group, useful for forming bonds

with other molecules. Ex. 1004 at 3:20-4:3; Ex. 1005 at 7:4-32; Ex. 1014 at 16:7-19; Ex. 1022 3:14-25, 7:21-27; Ex. 1034 at 81. The monomer for a given application was typically selected based on desired polymer properties. For example, it was well known that perfluorinated carbon chains confer strong hydrophobicity, so plasma polymerization processes intended to form water-repellent polymers commonly used monomer compounds containing a perfluorinated pendant functional chain. Ex. 1004 at 12:5-22; Ex. 1005 at 9:1-16, 8:4-10; Ex. 1019 at 2032; Ex. 1022 5:3-6, 16:19-19:2.

40. Subjecting a monomer vapor to a plasma produces a mixture of reactive species that can result in polymer film formation on a surface. The plasma polymer film tends to have a more complex chemical structure than the repeating monomeric units resulting from conventional polymer synthesis. Ex. 1005 at 2:14-24; Ex. 1023 at 8724. However, some plasma conditions, such as pulsed excitation, favor the identical reaction pathways present in conventional polymerization. Ex. 1019 at 2032.

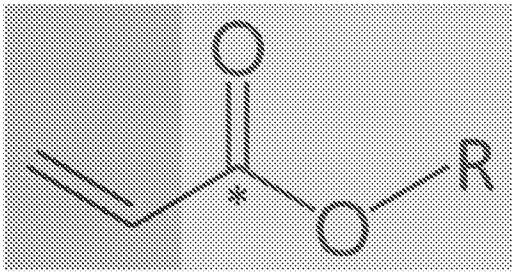
41. Plasma conditions are desired which allow a fraction of the monomers to remain intact, while the remaining fraction of the monomers decompose to form other species, including free radicals. Free radical species can combine with intact monomers to promote the conventional free radical polymerization pathway, provided the monomers contain a carbon-carbon double bond. The free radical forms a

bond to the monomer through one of the carbons of the double bond. The product is a single species where 1) the double bond is replaced by a single bond and 2) the other carbon of the former double bond becomes a free radical site, where this carbon participates in three covalent chemical bonds and retains one unpaired electron. The free radical product can react with another monomer to increase the chain length of the polymer and produce another free radical, a process known as free-radical propagation. The propagation can repeat tens or hundreds of times before another type of reaction terminates the chain growth. By 2015, monomers used for plasma polymerization frequently contained at least one double bond to take advantage of that propagation mechanism. Free radical polymerization is desirable because the resulting polymers retain the chemical functional groups present in the monomer. Ex. 1023 at 8724. The functional groups incorporated in the polymers determine the film properties.

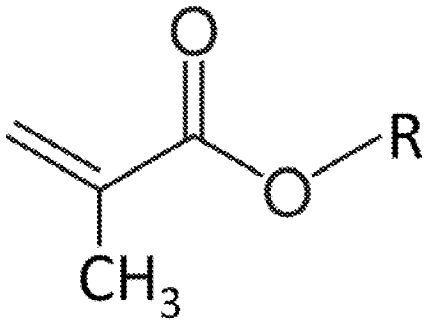
42. The plasma polymerization of acrylate monomers having different functional groups has been systematically explored and the highest average deposition rates were reported for acrylate monomers with fluorine-containing functional groups. Ex. 1035 at 26-32 and Tables 1, 2.

43. Fluorinated acrylate and methacrylate were very well-known monomers for polymer production and commonly used in plasma polymerization by 2015. Ex. 1029; Ex. 1004 12:7-22; Ex. 1005 9:10-16; Ex. 1014 11:14-12:3; Ex.

1035 at 26-33. Most acrylate monomers were esters with a vinyl group (containing a carbon-carbon double bond) linked to an ester group:



The blue shading above indicates the vinyl group, and the green shading indicates the ester group. The vinyl group is connected by a bond to the carbonyl carbon (indicated above by a star) of the ester group, and the ester group can include a variety of functional groups, indicated by an R. The structure above shows a generic acrylate monomer. In a methacrylate, the carbon-carbon double bond has an added methyl (CH_3) substituent, as shown below.



44. Fluorinated acrylates and methacrylates have been commonly used as monomers for polymer production because their reactivity allows for convenient and cost-effective polymer synthesis and because the presence of fluorinated groups provide many desirable properties. Ex. 1005 at 1:16-23; Ex. 1019 at 2032;

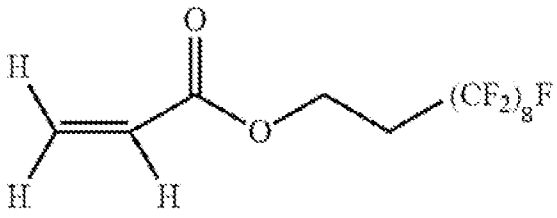
Ex. 1022 at 9:13-20; Ex. 1029 at Abstract. The acrylate and methacrylate bonding configurations of these monomers allow for rapid polymerization. Ex. 1035 at 26-33. The designation "alpha carbon" is given to the carbon atom in the double bond directly attached to the ester group. The electron density on the alpha carbon is pulled away by electronegative ester group. The reactivity of the double bond increases as the alpha carbon becomes electron poor. Electronegative functional groups, R, on the ester, can further deplete the electron density on the alpha carbon and thus enhance the reactivity of the carbon-carbon double bond. An example of an electronegative functional group is a perfluorocarbon carbon chain, such as C_8. The chemical structure of a C_8 pendent group which contains eight perfluorinated carbon atoms is shown below:

$$-(CF_2)_8-F \text{ or equivalently } -(CF_2)_7-CF_3.$$

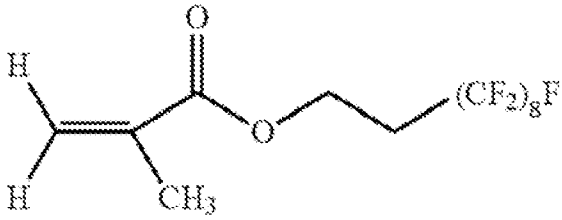
The C_8 perfluorinated chain was known to be advantageous for use in liquid-repellent coatings. Ex. 1004 at 12; Ex. 1026 at 6548-6654. Fluoropolymers like those made using fluorinated acrylates and methacrylates have many desirable properties. Ex. 1029 at 6197. For example, the low surface energy of fluoropolymers makes them difficult to wet with water and other liquids. Ex. 1029 at 6204. Fluorinated polymers, including those incorporating a fluoroalkyl chain, are known to be water repellant. Ex. 1029 at 6206. Fluorinated acrylates and methacrylates were known to have low surface energy, good thermal stability, and good chemical

resistance. Ex. 1029 at Abstract. Also, C-F bonds are strong (131 kcal/mol) relative to C-H bonds (99 kcal/mol), making fluoropolymers more thermal stable than hydrocarbon polymers. Ex. 1029 at 6204, 6209. Fluoropolymers were also known to form electrically insulating layers with low dielectric constants. Ex. 1026 at 6548.

45. Two fluorinated monomers that were routinely used for producing plasma-polymer coatings by 2015 were 1H,1H,2H,2H-perfluorodecyl acrylate (PFAC8) (CAS No. 27905-45-9; also known as 1H,1H,2H,2H heptadecafluorodecyl acrylate) and 1H,1H,2H,2H-perfluorodecyl methacrylate (PFMAC8) (CAS No. 1996-88-9). Those monomers had been used to apply protective coatings to various surfaces, including electronics. Ex. 1004 at 12:7-22, 14:7-23; Ex. 1005 at 8:15-9:27, Ex. 1014 at 16:16-27; Ex. 1019 at 2032; Ex. 1016 7:49-67; Ex. 2021 at ¶ 28; Ex. 1022 at 6:1-7:31, 16:19-17:3. The structures of PFAC8 and PFMAC8 are shown below.



PFAC8



PFMAC8

Both monomers contain the same C_8 perfluorocarbon pendant functional group. In PFAC8 and PFMAC8, the perfluorinated C_8 group is attached to the carbonyl carbon of the ester group by a methylene bridge ($-CH_2-CH_2-$). The resulting pendant

group is formally designated as 1H,1H,2H,2H-perfluorodecyl as shown below:

$$-CH_2-CH_2-(CF_2)_8-F$$

46. As I noted above, PFAC8 and PFMAC8 both contain methylene bridge separating the fluorinated group from the oxygen atoms within those molecules. In the cases of PFAC8 and PFMAC8, the methylene bridge is a C2 alkylene (CH_2-CH_2). Fluorinated compounds containing such alkylene spacers of approximately C1-C10 in length were prevalent in the field by 2015. Ex. 1005 at 8:26-28; Ex. 1004 at 11:26-28; Ex. 1012 at 2:13-3:14; Ex. 1014 at 16:16-17:4; Ex. 1038 at Abstract. Such alkylene spacers were used to avoid positioning fluorocarbon chains and oxygen-bearing groups adjacent to one another because, as a POSA would have known, fluorocarbon chains and oxygen-bearing groups tend to be reactive, and as a result placing such groups adjacent to one another tends to compromise the stability of the reagent. Ex. 1038 at Abstract, [0005-06].

47. The normal boiling point (boiling point at standard atmospheric pressure of 1 atm) for PFAC8 is approximately 267°C, and for PFMAC8 is approximately 300°C (verified on chemspider.com using the CAS numbers noted above) (Ex. 1039 at 11-14). A POSA would have known or been able to determine those standard boiling points by consulting common reference materials or using basic experimental methods such as measuring the temperature of a boiling sample of the reagent at standard pressure.

48. Their properties motivate the use of fluoropolymers as protective coatings in a variety of applications. Fluoropolymer coatings are widely utilized in the manufacture of liquid-repellent textiles. Ex. 1022 at 26-27. For the protection of clothing and footwear, fluoropolymer coatings the preferred monomers include both the fluoroacrylate PFAC8 and the fluoromethacrylate PFMAC8. Ex. 1021 at [0028]. Fluorinated polymers are known as moisture-resistant coatings for electronic components assembled on a circuit board. Ex. 1013 at [0045]. Fluorine-containing plasma polymers are also valued for the protection of electrical components and devices, including for biomedical applications such as hearing aids. Ex. 1015 at [0030], claim 6. Plasma-polymerization from fluorine-containing acrylate and methacrylate monomers is also preferred for protecting electronic components from corrosion and exposure to liquids. Ex. 1004 at 12:7-14:23; Ex. 1014 at 11:20-12:25; Ex. 1012 at 10:13-11:16. Such protection is of particular value for the printed circuit board and SIM-cards of mobile electronic devices, including smartphones. Ex. 1014 at 1:2-12, 4:22-5:9, 10:14-12:25.

C. Crosslinking and crosslinking reagents

49. Crosslinking refers to connecting linear polymer chains by chemical bonds to form a network. Ex. 1008 at [0011]. Crosslinking is a long-standing and widely-adopted means to optimize polymer properties for a specific application. For example, crosslinking provides improved mechanical, electrical, and chemical

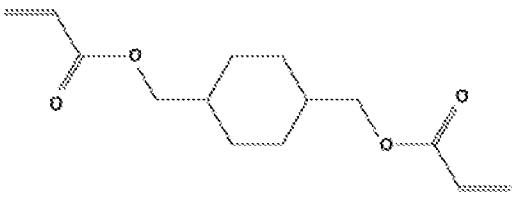
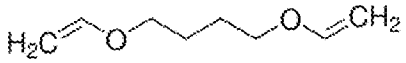
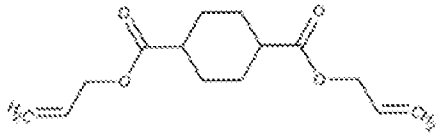
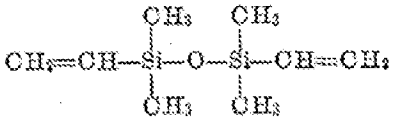
properties in polymer coatings used in the protection of electrical conductors and connectors. Ex. 1007 at 2:42-46; Ex. 1008 at [0002]. In plasma polymerization, it was well known that the amount of crosslinking could be controlled by co-polymerizing the monomer with varying amounts of a crosslinking reagent. Ex. 1024 at 10:2-7.

50. Plasma methods using crosslinkers have been reported for the synthesis of crosslinked polymer networks in the form of a thin film coating. Ex. 1005 at 4:4-9; Ex. 1008 at [0011], [0052-54]; Ex. 1009 at 607; Ex. 1023 at 8726. Crosslinking reduces the solubility of polymers in water and other liquids, thus enhances the stability of crosslinked polymer films. Ex. 1008 at [0011]; Ex. 1025 at [0034]. Many linear polymers form semi-crystalline films in which the grain boundaries between crystallites are pathways for the diffusion of small molecules such as water. Crosslinking tends to make polymer films amorphous. Ex. 1008 at [0039]; Ex. 1026 at 6551. Amorphous films lack grain boundary defects, thus improving the ability of amorphous films to act a protective barrier against moisture, oxygen, and other types of vapors and liquids. The lack of defects also makes amorphous crosslinked coatings resistant against aging and more reproducible to manufacture because when random defects appear, manufacturing yield decreases. Crosslinking can dramatically reduce the surface roughness of fluoropolymer films vapor-deposited from the PFAC8 monomer. Ex. 1026 at 6550-51. The degree of cross-

linking also controls the mechanical properties and wetting behavior of polymer films vapor deposited from PFAC8. Ex. 1026 at 6552-53. For example, crosslinking of PFAC8-based coatings was known to improve surface wetting properties by reducing contact angle hysteresis. Ex. 1026 at 6552-53. Films comprised of linear fluoroacrylate homopolymers thus were known to display excellent water repellency but could lack other characteristics desired for protective applications, such as durability and barrier performance. In contrast, crosslinked fluoroacrylate plasma polymers were known to simultaneously provide durability with water repellency. Ex. 1005 4:1-9, 4:17-5:5.

51. The formation of a crosslinked network is usually achieved using crosslinking molecules or groups. Ex. 1008 at [0011]. Cross-linked plasma polymer coatings form by using at least one organic monomer which containing two double bonds. Ex. 1005 at 4:4-5:5. The general formula for chemical structure of a cross-linking monomer as described in the prior art contains independent selection of the bridging group between the two carbon-carbon double bonds and the six substituent groups attached to the double bonded carbon groups. Ex. 1005 at 4:31-5:5. Examples included a multitude of diallyic, divinyl, divinyl either, and polyacrylate compounds. Ex. 1007 at 3:22-4:2. I have illustrated those classes of cross-linkers below, showing the generic configuration of the two double bonds characterizing each class as well as a specific example showing an exemplary bridging

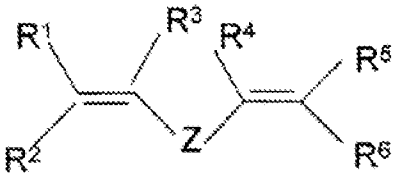
group Z for each type.

Diacrylate	
configuration	CH_2=CH-(C=O)-O-Z-O-(C=O)-CH=CH_2
example	 cyclohexane-1,4-dimethanol diacrylate (CDMDA)
Divinyl ether	
configuration	CH_2=CH-O-Z-O-CH=CH_2
example	 1,4-butanediol divinyl ether (BDVE)
Diallyl	
configuration	CH_2=CH-CH_2-Z-CH_2-CH=CH_2
example	 diallyl 1,4-cyclohexanedicarboxylate (DCHD)
Divinyl	
configuration	CH_2=CH-X-Z-X-CH=CH_2 ***X is not O, O-(C=O), or CH_2*
example	 divinyl tetramethyl disiloxane (DVTMDS)

52. Many examples from those various classes of crosslinkers had been used in combination with acrylate monomers to produce crosslinked polymer coat-

ings. Ex. 1006 at 1:15-30, 3:50-65; Ex. 1007 at 3:20-60, Ex. 1008 at ¶¶ 11, 52-54, Ex. 1009 at 607; Ex. 1011 at 3:1-4:39; Ex. 1025 at ¶¶ 11, 20; Ex. 1029 at 6197-98.

53. Plasma polymerization is characterized by its use of plasma ignition to initiate its polymerization reactions. Once activated, plasma polymerization was known to proceed at least in part according to reaction pathways similar to those that occur following conventional activation techniques (like free-radical, solution-phase, or heat-based polymerization). Ex. 1034 at 81. POSAs therefore understood and expected that the same types of crosslinking reagents used for conventional polymerization would also work in plasma polymerization reactions. For example, Badyal taught that crosslinkers for its plasma-based techniques could be any known in the entire "polymer art," without limiting consideration to reagents specific for plasma or any other type of polymerization. Ex. 1005 at 4:18-19. As another example, the use of ethylene glycol dimethacrylate (EGDMA) in plasma polymerization was motivated by the use of EGDMA as a crosslinking agent in conventional solution polymer synthesis. Ex. 1023 at 8725; Ex. 1029 at 6206; see also Ex. 1005 at 6:25-20 (Formula A) (describing the analogous non-methylated diacrylate ethylene glycol diacrylate (EGDA) as an exemplary crosslinking reagent for plasma polymerization). Thus, as with conventional polymerization, crosslinking agents used for plasma polymerization often were also molecules containing two or more carbon-carbon double bonds, generally depicted as



Ex. 1005 4:1-5:5. That known generic crosslinker structure encompassed diacrylate, divinyl ether, diallyl, and divinyl crosslinkers.

54. For plasma co-polymerization, both the monomer and the crosslinker must enter the vacuum reaction chamber as vapors. Ex. 1012 at 9:17-10:12. At laboratory conditions, both reactants are typically liquids. By applying heat to the vessels containing each pure liquid, two inlet vapor flows are produced. Liquids with a high boiling point will require more heating to reach a given vapor pressure than low boiling point liquids. Before entering the chamber, each type of vapor goes through a conventional delivery system that was well known in the prior art and made up of control valves and tubing. Ex. 1001 at 13:61-67; Ex. 1009 at 606 (Scheme 2); Ex. 1004 at 7:6-12, 9:4-9; Ex. 1012 at 11:17-12:11; Ex. 1014 at 25:14-22; Ex. 1025 at [0053-55], [0060-70].

55. For both reactants to flow into the chamber, the pressure developed in each delivery system must exceed the pressure in the chamber. Thus, both the monomer and the crosslinker must be heated sufficiently to achieve a vapor pressure greater than that of the pressure in the growth chamber. Reactants with higher normal boiling points are less volatile and require more heating to achieve a vapor

pressure sufficient to introduce into a vacuum chamber, so POSAs knew that reactants with lower boiling points were generally easier to vaporize and deliver to a plasma chamber. In general, molecules of higher molecular weight tend to have higher normal boiling points.

D. Applications for plasma polymerization

56. Plasma polymerization had been quite widely employed for coating a range of surfaces by 2015. Ex. 1005 at 2:10-12, 10:8-12, 11:26-27; Ex. 1004 at 6:25-7:12; Ex. 1012 at 8:22-10:12; Ex. 1016 at 1:40-50; Ex. 1017 at 3:26-40; Ex. 1027 at 1:20-41. Plasma polymerization has been used to apply thin-film coatings utilized in the fabrication of semiconductor devices such as integrated circuits. Ex. 1017 at Abstract; Ex. 1024 at Abstract. Lipid-repellent and protein-repellant plasma coatings, including crosslinked plasma coatings, have a wide range of applications including cosmetics packaging, modification of laboratory vessels, and biopassivation of implantable medical devices, such as stents, catheter, and pacemakers. Ex. 1025 [0002], [0006], [0015], [0036], [0038]; Ex. 1009 at Abstract. Plasma polymer coatings were also preferred for the protection of electronic and electrical components and devices from damage by the environment. Plasma polymers were utilized in applications that require a barrier against attack from moisture and oxygen, thus avoiding detrimental effects such as corrosion. Ex. 1008. At [0011], [0021-24]; Ex. 1013 [0046], Ex. 1014 at Abstract, 16:7-27, 32:14-33:3. For

example, water resistant plasma polymer coatings were used for preventing corrosion in electronic medical devices such as hearing aids. Ex. 1015 [0002], [0011], [0029-35]

57. POSAs in 2015 also knew that functionalizing solid surfaces with plasma fluoropolymers provided excellent repellency against liquids. Ex. 1019 at 2038. Plasma fluoropolymer coatings which resist wetting by water and oils were pursued for preserving solid surfaces including metals, ceramics, glass, paper, and plastics and for the surface modification of cloth. Ex. 1005 at 1:8-12. Plasma-modified fabrics can be waterproof and soil-resistant, making them desirable in the production of clothing such as outerwear, sports jerseys, and military uniforms. Ex. 1005 at 1:14-19. Plasma fluoropolymers with durable water repellency and soil-resistance are also desirable other outdoor products and components manufactured from fabrics and leather, such as footwear, umbrellas, tents, sleeping bags, and awnings. Ex. 1021 at [0001-12]. The plasma coating method is capable of coating the substrate surface without infilling the spaces the between surface features. Thus, the coated substrates can still retain openings for the passage of air. Crosslinking of the plasma fluoropolymers was known to be desired for durability of the coating against wear. Ex. 1005 at 4:25-29.

58. Liquid-resistant plasma coatings based on fluorinated monomers like PFAC8, PFMAC8, and other structurally similar compounds were by 2015 well

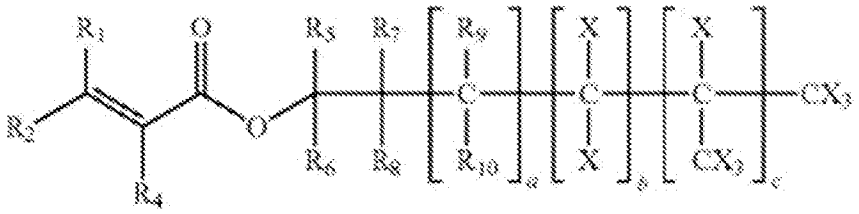
known and commonly used to protect against irreversible damage that can result from the exposure of electrical circuits to liquids, such as water. Ex. 1004 at 1:1-34, 12:7-14:23; Ex. 1014 at 16:11-27; Ex. 1029 at 6197-98. Rain has the potential to damage electronics which are located outdoors, such as lighting, antennas, and communication equipment. Accidental spillage and plumbing leaks can threaten indoor electronics, such as computers and instrumentation. Portable electronics are used both indoor and out and their small size makes them prone to accidental immersion. Mobile devices such as laptops, mobile phones, radios, cameras, and hearing aids have many different electronic components including printed circuit boards (PCBs), batteries, microphones, SIM-cards, wires, connectors, lenses, touchscreens, and external buttons that can be protected using plasma fluoropolymer coatings. Ex. 1004 at 4:17-5:6, 6:19-23; Ex. 1014 at 1:9-12, 10:14-12:25.

VII. SUMMARY OF THE '876 PATENT

59. The '876 patent (Ex. 1001) is titled "Coatings." The patent discusses crosslinked plasma polymer coatings applied to electronic devices. According to the '876 patent, the coatings can be water repellent or can form a barrier to protect the underlying electronics from damage. Ex. 1001 at 1:5-13. Most of the information provided in the patent pertains to the compounds used as monomers and crosslinkers to prepare the coatings.

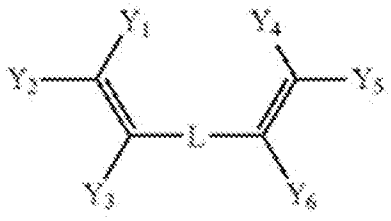
60. The patent describes monomers having a double bond. Ex. 1009 at

9:23-35. For producing "particularly preferred" types of coatings, the monomer has the following generic structure (identified as Formula I(a)):

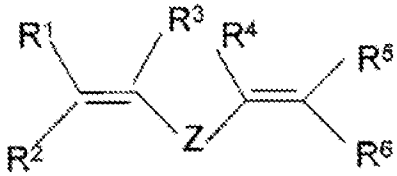


Ex. 1001 at 10:22-40 and claim 1. As a POSA would have recognized from the structure provided in the patent, that preferred monomer is an acrylate, with a vinyl group, and ester group, and an optionally halogenated functional group. A POSA also would have recognized that PFAC8 and PFMAC8 were known monomers, used for plasma deposition of protective coatings onto substrates including electronics, that fell within Formula I(a). Ex. 1004 at 12:5-22; Ex. 1005 at 7:17-9:19; Ex. 1014 at 16:11-25; see also Ex. 1001 at 1:15-20, 11:27-56, claims 12-15 (recognizing that the monomers used in the '876 patent were previously known for use in plasma polymers and describing PFAC8 and PFMAC8 as preferred).

61. For a crosslinking reagent used in the coatings, the patent states that a basic requirement the presence of two or more unsaturated bonds. Ex. 1001 at 4:36-40. The following generic crosslinker structure for a crosslinker with two double bonds joined by a bridging group ("linker moiety L") is pointed out as a preferable form for the crosslinker:

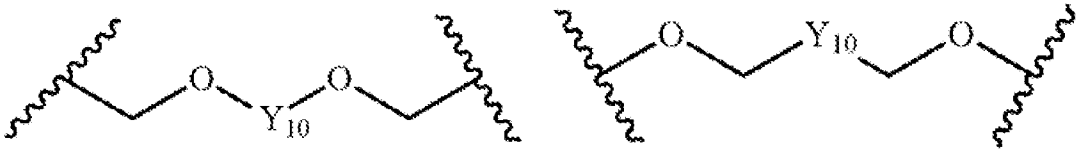


Ex. 1001 at 4:51-67, claim 1. The patent states that the identity of the bridging group is "not especially limited," which would have indicated to a POSA that a variety of crosslinkers having different bridging-group structures between the double bonds could be used. Ex. 1001 at 4:40-45. As a POSA would have known, the same crosslinker structure had previously been described as suitable for use with acrylate monomers including PFAC8 and PFMAC8:

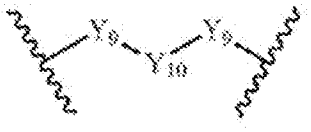


Ex. 1005 at 4:1-5:5.

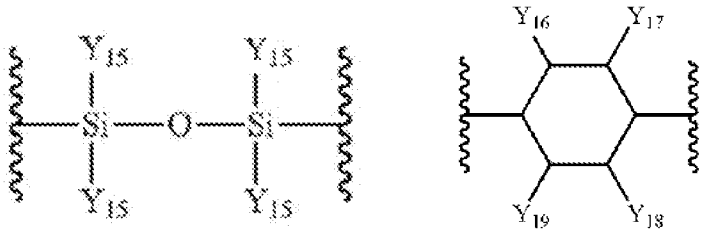
62. The '876 patent describes a large genus of crosslinkers with numerous options for the bridging group. Ex. 1001 at 5:1-8:18. Claim 1 specifies four different generic structures that can be used for the bridging group, divided into Formula A and Formula B. Claim 1 refers to the first two generic structures as Formula A:



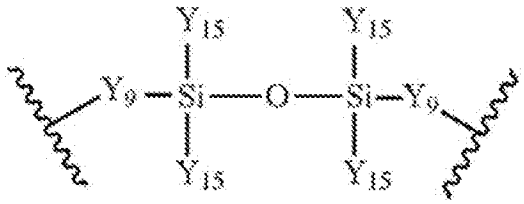
Ex. 1001 at 19:9-19. Formula B has the following generic structure:



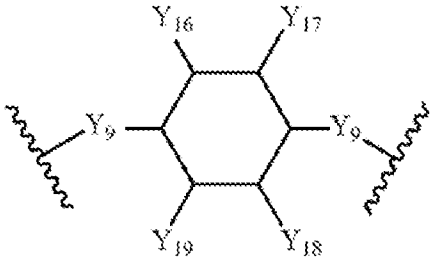
Ex. 1001 at 19:20-33. Under Formula B, claim 1 further specifies two alternative structures for substituent Y_{10} in Formula B



Ex. 1001 at 19:33-57. I have prepared figures showing what those Y_{10} structures would look like when incorporated into Formula B, yielding the two alternative Formula B structures under claim 1 that I will refer to as Formula B1



and Formula B2



See Ex. 1001 at 19:20-57.

63. A POSA would have recognized that crosslinkers with one of the two Formula A or two Formula B bridging group structures from claim 1 could include many different diacrylate, divinyl ether, diallyl, or divinyl crosslinkers. For example, Table 1 in the specification includes several examples such as DVTMDS (divinyl), BDVE (divinyl ether), DCHD (diallyl). Ex. 1001 at 8:20-67 (Table 1). In addition, the specification also highlights acrylate crosslinker structures as preferable. Ex. 1001 at 6:4-29 (structures (viii) and (x)), claim 4.

64. The specification describes using a monomer and crosslinker to apply plasma polymer coatings to an electronic device with standard equipment and conditions for plasma coating applications that would have been familiar to a POSA in June 2015. Ex. 1001 at 13:9-14:30, 14:59-67; *e.g.*, Ex. 1004 at 6:29-10:34, Ex. 1005 at 10:8-11:13, Ex. 1009 at 606-07; Ex. 1014 at 20:1-26:3.

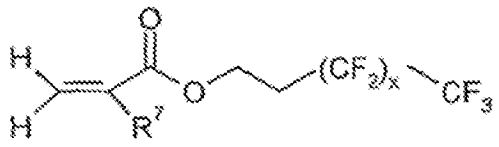
VIII. THE PRIOR ART

65. I understand from counsel that the following documents are prior art relative to the '876 patent, except for Exhibit 1028, which I understand is a copy of the '876 patent's prosecution records before the patent office, and Exhibit 1039, which is a collection of chemical information obtained from chemspider.com.

A. Exhibit 1004 – "Coulson-122"

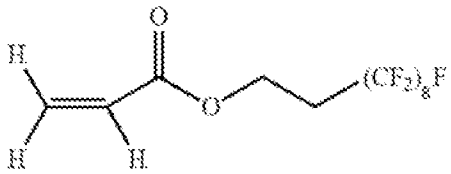
66. Coulson-122 (Ex. 1004) is International Patent Application Publication No. WO 2007/083122. The first page of the document states a publication date

of July 26, 2007. Coulson-122 described electronic or electrical devices with liquid-repellent polymer coatings to protect the devices from liquid damage. Ex. 1004 at Abstract, 1:3-2:17. To achieve liquid-repellent coating, Coulson-122 taught exposing the devices to pulsed plasma containing unsaturated monomers including those of the following formula:



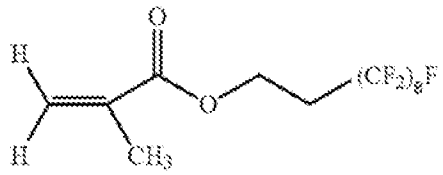
Ex. 1004 at 3:14-4:3, 11:1-12:22. The R7 position could be a hydrogen or a C1-6 alkyl group such as a methyl group, and x is an integer from 1 to 9. Ex. 1004 at 12:19-22.

67. A POSA would have understood Coulson-122's monomers of the above formula to be fluorinated acrylate or methacrylate monomers. In particular, Coulson-122 identified 1H, 1H, 2H, 2H-heptadecafluorodecylacrylate (also known as 1H, 1H, 2H, 2H-perfluorodecyl acrylate (PFAC8)), having the following structure:



Ex. 1004 at 12:21-22, 14:7-10, Claim 28. In some instances, Coulson-122 referred to that compound as "1H, 1H, 2H, 2H-heptadecafluorodecylacylate." Ex. 1004 at

12:21-22, 14:7-10. But a POSA would have understood that to be a typographical error, and that the correct form is 1H, 1H, 2H, 2H-heptadecafluorodecylacrylate, especially because Coulson-122 also uses the correct CAS Number for PFAC8 (27905-45-9). Ex. 1004 at 14:7-10; Ex. 1039 at 11. Alternatively, if the hydrogen at the R7 position is substituted for a methyl group, as also taught by Coulson-122 (Ex. 1004 at 12:10-21), the monomer would become 1H, 1H, 2H, 2H-perfluorodecyl methacrylate (PFMAC8) with the following structure:



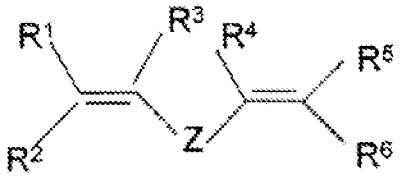
68. Coulson-122 also taught that plasma polymerization of such monomers produced "highly liquid-repellent nano-coatings," such that treated devices like mobile phones could be "fully immersed in water … without any lasting harm." Ex. 1004 at 3:14-18, 4:29-5:10.

B. Exhibit 1005 – "Badyal"

69. Badyal (Ex. 1005) is International Patent Application Publication No. WO 99/64662. The first page states a publication date of December 16, 1999. Badyal concerned "the production of oil- and water-repellent surfaces" and taught that "[p]lasma deposition techniques have been quite widely used for the deposition of polymeric coatings onto a range of surfaces." Ex. 1005 at 1:3-5, 2:10-12. Badyal's polymeric coatings having oil- or water-repellent properties were pro-

duced by exposing "any solid substrate" to a plasma containing the same monomers as disclosed in Coulson-122, including PFAC8 and PFMAC8. Ex. 1005 4:4-15, 7:17-9:19, 9:28-30, 11:19-24. In particular, Badyal states that substrates can include fabrics and "solid materials such as biomedical devices." Ex. 1005 at 11:22-24.

70. Furthermore, to improve the durability of such coatings, Badyal taught combining the monomer with a crosslinker, preferably of the following generic formula:

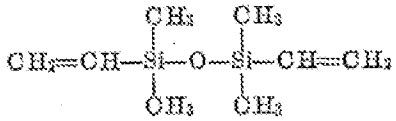


Ex. 1005 at 4:1-5:5. The R1-R6 positions could be hydrogen or alkyl groups, and bridging group Z could include substituents "known in the polymer art," including "alkyl groups . . . interposed with oxygen atoms." Ex. 1005 at 5:1-5, 5:18-23. Badyal provided two particular examples of specific bridging groups that fit the described general formula. Ex. 1005 6:15-20.

71. According to Badyal, the described plasma polymerization using monomers like PFAC8 and a crosslinker produced cross-linked, well-adhered coatings with excellent liquid-repellency and durability. Ex. 1005 at 4:4-29, 10:32-11:17.

C. Exhibit 1006 – "Cohen"

72. Cohen (Ex. 1007) is U.S. Patent No. 2,716,638 and says, "Patented Aug. 30, 1955," which I understand means the patent issued on that date. Cohen is titled "Divinyltetramethyldisiloxane and polymers therefrom" and described processes of polymerizing divinyltetramethyldisiloxane (DVTMDS) to form insulating materials for electrical devices. Ex. 1007 at 1:15-20, 5:1-12. As shown in Cohen, DVTMDS has the following chemical structure:



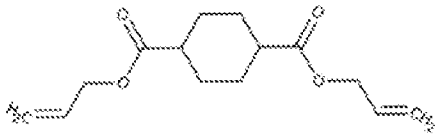
Ex. 1006 at 1:30.

73. Cohen also taught that DVTMDS can be copolymerized with other compounds, particularly esters of acrylic and methacrylic acids such as methyl acrylate, ethyl acrylate, and methyl methacrylate. Ex. 1006 at 2:25-27.

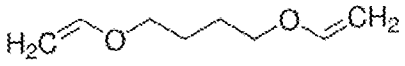
D. Exhibit 1007 – "Holliday"

74. Holliday (Ex. 1007) is U.S. Patent No. 3,816,564 and says, "Patented June 11, 1974," which I understand means that the patent issued on that date. Holliday is entitled "Insulation coating compositions" and described polymer compositions "for use in providing electrical insulation." Ex. 1007 at 1:11-12. Holliday's composition comprised "a mixture of a polyolefin, polyvinyl chloride and a reactive allylic or vinylic monomer which can be crosslinked." Ex. 1007 at 2:39-46.

Holliday taught applying the mixture to an electrical device or component and then initiating polymerization, which "cured" the composition "to form a crosslinked insulation layer" having excellent insulation properties. Ex. 1007 at 2:47-70. Holliday identified several crosslinking reagents for use in those coatings, including diallyl-1,4-cyclohexanedicarboxylate (DCHD) and 1,4-divinyl-oxybutane (also known as 1,4-butanediol divinyl ether (BDVE)), Ex. 1007 at 3:34-35, 3:52-53, which a POSA would have understood to correspond to the following chemical structures:



DCHD;



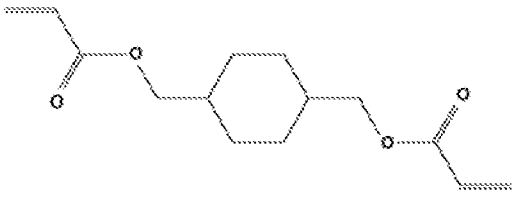
BDVE.

E. Exhibit 1008 – "Padiyath"

75. Padiyath (Ex. 1008) is U.S. Patent Application Publication No. 2007/0020451. The first page states a publication date of January 25, 2007. Padiyath concerned barrier assemblies having multilayer coatings and described "barrier films for protection of moisture or oxygen sensitive articles." Ex. 1008 at Abstract, [0001]. The barrier coatings reduced or prevented "transfer of moisture and oxygen, or other contaminants, to an underlying substrate," particularly electronic devices such as LCD or OLED display devices. Ex. 1008 at [0023-24], [0027], [0063-64]. Padiyath's barrier coatings comprised one or more polymers, which

could be homopolymers or copolymers and could be derived from plasma polymerization. Ex. 1008 at [0005-07], [0011]. Padiyath taught that the polymers were preferably cross-linked, which was known to enhance barrier performance. Ex. 1008 at [0002], [0025], [0052].

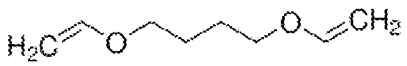
76. Particularly preferred polymers were formed by crosslinking acrylate monomers, methacrylate monomers, or their multifunctional derivatives. Ex. 1008 at [0052]. Suitable monofunctional (meth)acrylates included fluorinated (meth)acrylates in a molecular weight range between 400 and 3,000. Ex. 1008 at [0052]. As one especially preferred compound for the disclosed polymers, Padiyath described "cyclohexane dimethanol diacrylate esters (e.g., CD-406, commercially available from Sartomer Co., T_g = about 110 ºC)." Ex. 1008 at [0054]. As evidenced in the Material Safety Data Sheet by Sartomer Company for product CD406 (Ex. 1032) and disclosures in other patent office publications available by 2015 (Ex. 1030 at [0144], and Ex. 1031 at [0027], [0060], [0090]), a POSA would have understood Padiyath's reference to CD-406 as identifying the following reagent, more commonly known as cyclohexane-1,4-dimethanol diacrylate (CDMDA):



F. Exhibit 1009 – "Francesch"

77. Francesch (Ex. 1009) is a scientific journal article that was published in the journal *Plasma Processes and Polymers*. Ex. 1009. *Plasma Processes and Polymers* is a prominent journal published by Wiley-VCH Verlag GmbH & Co. in the polymer field that would have been well-known to a POSA by 2015. The copyright notice printed on the first page of the Francesch reference indicates that the article was published in the year 2005, consistent with the citation printed on each page of the article. A POSA reading Francesch would thus have understood from those notations that the article had been published and made available to the public in 2005. Additionally, a declaration signed by Dr. Salvador Borrós Gómez, whom I know to be a co-author of the Francesch article, further demonstrates that the article was made publicly available when it was published online in September 2005. Ex. 1010.

78. Francesch concerned the development of biomaterials and described methods of plasma polymerizing a new acrylate-type monomer, pentafluorophenyl methacrylate (PFM), for subsequent biotin binding to achieve versatile surface functionalization. Ex. 1009 at 605-06. For polymerization of PFM, Francesch described copolymerizing PFM with crosslinkers, including 1,4-butanediol divinyl ether (BDVE). Ex. 1009 at 606-07. As would have been known to a POSA, BDVE has the following chemical structure:



79. In particular, Francesch taught performing plasma deposition for 2-8 hours and depositing the BDVE-crosslinked copolymer at a rate of 8 nm per hour, which a POSA would have understood to translate into polymer coatings at thicknesses of 16-64 nm. Ex. 1009 at 607-08. The resulting coatings showed flat, homogenous, pinhole-free surfaces. Ex. 1009 at 609-10. Francesch taught that the BDVE crosslinker was included "to improve the solvent resistance of the resulting deposited thin films." Ex. 1009 at 610.

G. Exhibit 1011 – "Tropsch"

80. Tropsch (Ex. 1011) is U.S. Patent No. 5,804,669. The first page states the date of the patent as September 8, 1998, which I understand to be when the patent was issued. Tropsch described a two-phase process for preparing polymers comprising peroxycarboxyl groups. Ex. 1011 at Abstract, 1:4-7, 1:49-2:2. Tropsch's methods required first preparing or obtaining a polymer, and then reacting that polymer with hydrogen peroxide. Ex. 1011 at 1:49-2:2. The input polymer contained at least an unsaturated dicarboxylic anhydride monomer. Ex. 1011 at 2:3-7, 2:13-39. The input polymer further contains a comonomer, such as an acrylate or methacrylate. Ex. 1011 at 2:3-7, 3:1-8. Tropsch also disclosed the use of crosslinkers in preparing the polymer. Ex. 1011 at 3:48-51. Specifically, Tropsch taught that the "preferably employed" crosslinkers are "divinylbenzene, divi-

nylethyleneurea, alkadienes or divinyl alkyl ethers. The latter are preferably selected from α,ω-alkadienes, preferably 1,9-decadiene, or 1,4-butanediol divinyl ether, 1,6-hexanediol divinyl ether or 1,8-octanediol divinyl ether." Ex. 1011 at 4:34-39. A POSA wound have understood that 1,6-hexanediol divinyl ether (HDVE) has the chemical structure of



and 1,8-octanediol divinyl ether has the chemical structure of



H. Other References

81. Exhibit 1012 is International Patent Application Publication No. WO 2012/158953 to Legein, et al. The first page states a publication date of November 22, 2012.

82. Exhibit 1013 is U.S. Patent Application Publication No. 2013/0176700 to Stevens, et al. The first page states a publication date of July 11, 2013.

83. Exhibit 1014 is International Patent Application Publication No. WO 2014/026967 to Legein, et al. The first page states a publication date of February 20, 2014.

84. Exhibit 1015 is U.S. Patent Application Publication No.

2005/0141738 to Karamuk. The first page states a publication date of June 30, 2005.

85. Exhibit 1016 is U.S. Patent No. 6,551,950 to Badyal, et al. The first page states the date of the patent as April 22, 2003, which I understand to be when the patent was issued.

86. Exhibit 1017 is U.S. Patent No. 4,562,091 to Sachdev, et al. The first page states the date of the patent as December 31, 1985, which I understand to be when the patent was issued.

87. Exhibit 1018 is U.S. Patent No. 7,439,315 to Kunimi, et al. The first page states the date of the patent as October 21, 2008, which I understand to be when the patent was issued.

88. Exhibit 1019 is a publication by S.R. Coulson, the first named inventor of the '876 patent, and colleagues in the journal *Chemistry of Materials*, which is a well-recognized publication of the American Chemical Society (ACS). By June 2015, POSAs knew the ACS as a well-established publisher of scientific and technical literature in the field, and *Chemistry of Materials* was one such prominent journal publication that would have been well known to a POSA. The copyright notice and the journal citation printed on each page of Exhibit 1019 indicate that the article was published in 2000, consistent with the additional notation printed near the bottom of the article's first page indicating that it was "Published on

Web 06/28/2000." By 2000, ACS and other academic journals in the field were commonly publishing their articles in online and print form, and based on that common and by then widespread practice, a POSA reading Exhibit 1019 would have understood from those notations and believed that the article had been published and made available to the public in 2000, and specifically made publicly available on the internet by June 28, 2000.

89. I understand that Exhibit 1020 is a declaration provided by the British Library regarding the date that a print copy of the Coulson article published in *Chemistry of Materials* (Exhibit 1019) was received and made available for public use by that institution.

90. Exhibit 1021 is U.S. Patent Application Publication No. 2010/0203347 to Coulson. The first page states a publication date of August 12, 2010.

91. Exhibit 1022 is International Patent Application Publication No. WO 98/58117 to Badyal, et al. The document lists a publication date of December 23, 1998, on its first page. Exhibit 1022 is referenced in the '876 patent as prior art that previously described "[t]he perfluoroalkyl chain monomers . . . used for generating hydrophobic surfaces from pulsed plasma deposition processes." Ex. 1001 at 1:17-19.

92. Exhibit 1023 is a publication by C. Tarducci and colleagues in the

journal *Macromolecules*, which was a recognized journal in the field published by the ACS that would have been well known to a POSA in June 2015. The copyright notice and the journal citation printed on each page of Exhibit 1023 indicate that the article was published in 2002, consistent with the additional notation printed near the bottom of the first page indicating that it was "Published on Web 10/12/2002." A POSA reading Exhibit 1023 would have understood from those notations and believed that the article had been published and made available to the public in 2002, and specifically made publicly available on the internet by October 12, 2002.

93. Exhibit 1024 is U.S. Patent No. 6,214,423 to Lee, et al. The first page states the date of the patent as April 10, 2001, which I understand to be when the patent was issued.

94. Exhibit 1025 is International Patent Application Publication No. WO 2012/168440 to Taesler. The document lists a publication date of December 13, 2012.

95. Exhibit 1026 is a publication authored by me and my colleague, Jose Luis Yagüe, in the journal of *Macromolecules*. Near the bottom of the first page, the article states that it was published on August 13, 2013. That date is consistent with my own recollection. Based on my personal knowledge as an author of the article, I know that Exhibit 1026 was published in 2013.

96. Exhibit 1027 is U.S. Patent No. 6,207,238 to Affinito. The first page states the date of the patent as March 27, 2001, which I understand to be when the patent was issued.

97. I understand that Exhibit 1028 is a copy of the prosecution history of the '876 patent.

98. Ex. 1029 is a publication by W. Yao, et al., in the journal *Polymer*, which was a recognized journal in the field published by Elsevier that would have been well known to a POSA by June 2015. Elsevier was known to POSAs as a well-established publisher of scientific journals. The copyright notice and the journal citation printed on each page of Exhibit 1029 indicate that the article was published in 2014. In addition, the "Article Info" section on the first page near the abstract states that the article was made available online as of September 30, 2014. A POSA reading Exhibit 1029 would have understood from those notations and believed that the article had been published and made available to the public in 2014, and specifically made publicly available on the internet by September 30, 2014.

99. Exhibit 1030 is U.S. Patent Application Publication No. 2013/0136936 to Morozumi, et al. The document lists a publication date of May 30, 2013.

100. Exhibit 1031 is U.S. Patent Application Publication No. 2011/0148979 to Breton, et al. The document lists a publication date of June 23,

2011.

101. Exhibit 1032 is Sartomer Company Material Safety Data Sheet for Product CD406, revised on June 9, 2005. The document identifies the CD406 product as cyclohexane dimethanol diacrylate, CAS Number 67905-41-3. Ex. 1032 at 1. The CAS Chemical Registry is a global standard for uniquely identifying chemical substances and has been used since the 1960s. A POSA in 2015 would have been very familiar with CAS registry numbers and would have known that CAS Number 67905-41-3 identified cyclohexane dimethanol diacrylate, also known as cyclohexane 1,4-dimethanol diacrylate (CDMDA). Ex. 1039 at 7. Material Safety Data Sheets would have been familiar to POSAs as product information that companies provide to their customers when offering and when supplying chemical reagents. A POSA reading Exhibit 1032 would have understood from the revision notations and believed that Exhibit 1032 was published and made available to the public in 2005.

102. Exhibit 1033 is U.S. Patent Application Publication No. 2005/0034667 to Tsuji, et al. The document lists a publication date of February 17, 2005.

103. Exhibit 1034 is an excerpted copy of a book by H. Yasuda entitled *Plasma Polymerization*. Exhibit 1034 would have been familiar to a POSA, and I have used that book as a reference for years, going back well before 2015. The

copyright notations on Exhibit 1034 indicate that it was published in 1985 by Academic Press. Academic Press was known to POSAs as a well-established publisher in the field. A POSA reading Exhibit 1034 would have understood from those copyright notations and believed that Exhibit 1034 was published and made available to the public in 1985.

104. Ex. 1035 is a publication by S. Kurosawa, et al., in the journal *Thin Solid Films*, which was a recognized journal in the field published by Elsevier that would have been known to a POSA. The copyright notice near the bottom of the first page lists a 2003 copyright date, and the journal citation printed on each page indicate that the article was published as part of the 2004 volume of *Thin Solid Films*. A POSA reading Exhibit 1035 would have understood from those notations and believed that the article had been published and made available to the public by 2004.

105. Ex. 1036 is a publication by S. Kurosawa, et al., in the journal *Thin Solid Films*, which was a recognized journal in the field published by Elsevier that would have been known to a POSA. The copyright notice near the bottom of the first page lists a 2002 copyright date, and the journal citation printed on each page indicate that the article was published as part of the 2002 volume of *Thin Solid Films*. A POSA reading Exhibit 1036 would have understood from those notations and believed that the article had been published and made available to the public

by 2002.

106. Ex. 1037 is a publication by K.G. Joback and R.C. Reid in the journal *Chemical Engineering Communications*, which was a recognized journal in the field published by Taylor & Francis that would have been well known to a POSA by June 2015. Taylor & Francis was known to POSAs as a well-established publisher of scientific journals. The copyright notice and the journal citation printed on page 233 of Exhibit 1037 indicate that the article was published in 1987. In addition, the cover page to the article near states that the article was published online as of May 21, 2007. A POSA reading Exhibit 1037 would have understood from those notations and believed that the article had been published and made available to the public before 2015, and specifically made publicly available in print in 1987 and on the internet in 2007.

107. Ex. 1038 is U.S. Patent Application Publication US 2006/0122301 to Nair and Nalewajek. The document lists a publication date of June 8, 2006. Ex. 1039 is a collection chemical information obtained from chemspider.com, which is an online resource maintained by the Royal Society of Chemistry that I and others in the field consider reliable and use regularly to look up properties of chemical reagents, such as molecular structure, boiling point, molecular weight, density, etc.

IX. CLAIM CONSTRUCTION

108. In conducting my analyses of the claims of the '876 patent, I have ap-

plied the understandings I set out below regarding the meanings of terms used in the claims. I reserve the right to update or modify my analyses if necessary to account for different meanings assigned to any of the claims.

A. "Halogen"

109. In my opinion, a POSA would have understood the term "halogen" in claim 1 of the '876 patent to include at least at least fluorine, chlorine, and bromine. That meaning is consistent with how that term was used by those in the field in 2015 and is consistent with how that term is used in the '876 patent's specification.

110. Halogens are a group of non-metallic elements that appear in Group 17 (Group VIIa) of the periodic table. Each halogen is electronegative and typically participates in only a single chemical bond. The halogen elements in the first four periods of the periodic table were in common use in chemical synthesis well before 2015. These are fluorine, chlorine, bromine, and iodine. Ex. 1005 at 5.

111. In the '876 patent, the term "halogen" is used in a manner consistent with that ordinary understanding. The specification says that a halogen may be chlorine or bromine but is preferably fluorine. Ex. 1001 at 10:57-59, 7:11-14.

112. For these reasons, I conclude that "halogen" in the '876 patent's claims includes at least fluorine, chlorine, and bromine.

B. Other claim terms

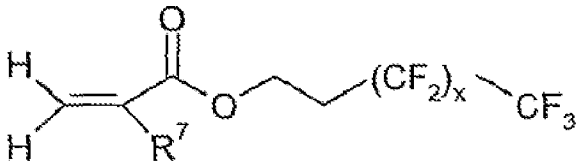
113. For purposes of this petition and comparison to the prior art, I under-

stand that all other terms in Claims 1-15 of the '876 patent should be construed according to their ordinary meaning to a POSA in the context of the '876 patent.

X. ANALYSIS OF THE CLAIMS OF THE '876 PATENT

A. All Grounds: Coulson-122 and Badyal described preparing plasma-polymer films by copolymerizing monomers including PFAC8 or PFMAC8 with a crosslinker

114. Coulson-122 taught that plasma polymer coatings provide protection for a diverse array of electronic or electrical devices against damage by liquids such as water and oil. Ex. 1004 at 1-6. Coulson-122 also taught that both PFAC8 and PFMAC8 were preferred monomers for forming liquid-repellent coatings by plasma polymerization, displaying the chemical structure as



where x is an integer and preferably 7. Ex. 1004 at 11-12. When x=7 in the structure above, the pendant perhaloalkyl functional group is known as the C8 perfluorocarbon moiety because it includes eight fluorinated carbon atoms (seven CF_2 repeats plus the terminal CF_3). Coulson-122 further specified that R^7 can be hydrogen or methyl. Ex. 1004 at 12. When x=7 and R^7 is hydrogen, the monomer is the acrylate PFAC8. When x=7 and R^7 is methyl, the monomer is the methacrylate PFMAC8. Those structures are the same as setting n=8 in the monomers shown at column 11, lines 30-47 of the '876 patent; the only difference is that the molecules

were drawn in the '876 patent with the terminal carbon group folded into the repeating chain.

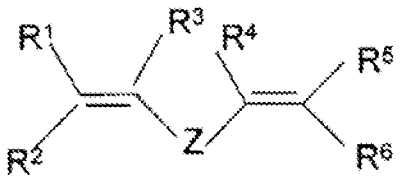
115. Badyal described the using the same monomers as Coulson-122 to prepare liquid-repelling halogen-containing plasma polymer coatings. Ex. 1005 at 7-9. Badyal taught that cross-linked plasma polymers on surfaces can form by the plasma copolymerization of a mixture of a cross-linking monomer with a further monomer. Ex. 1005 at 12 -14. For this further monomer, Badyal described the use of haloalkyl substituents and the preference for have one double bond, with acrylate monomers as a specific embodiment. Ex. 1005 at 12-14. For oil and water repellant properties, Badyal teaches that the presence of perhaloalkyl chains is preferred, along with cross-linking to provide good durability. Ex. 1005 at 4. A preferred monomer formula provided by Badyal is

$$CH_2=CR^{15}C(O)O(CH_2)_nR^{13}$$

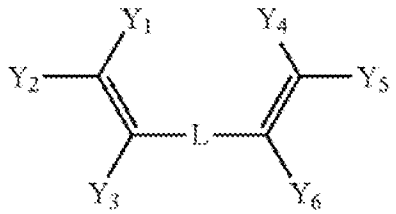
where the integer 2 was the preferred value of n, and the C8 perfluoroalkyl chain, C_8F_{18}, was preferred for R^{13}. Ex. 1005 at 6-9, 14. Using hydrogen and methyl from listed as possibilities for R^{15} gives PFAC8, and PFMAC8, respectively.

116. Badyal also stated the desire to improve the durability of these coatings. Ex. 1005 at 3-4. Badyal taught that increased durability can be accomplished by including at least one compound possessing two double bonds can form a cross-linked plasma polymer on a surface. Ex. 1005 at 4:1-5:23. Badyal taught the cross-

linking compound according to the generic structure below, with two double bonds has a bridging or linking group between its two double bonds and does not place any limitation on the chemical structure of the bridging unit (identified as Z):



Ex. 1005 at 5:1-23. That structure is identical to the generic crosslinker with two double bonds described in the '876 patent and shown in claim 1:



Ex. 1001 at 4:51-60, 18:60-67.

117. The oil and water repellency of fluoropolymers, including fluorinated acrylate and methacrylate polymers and use of pendent C8 perfluoro functional groups, as well as copolymerization with cross-linkers containing two double bonds were all well known in the polymer art. Ex. 1004 at 13:30-14:23; Ex. 1005 at 3-5; Ex. 1019 at 2031-32, 2037-38; Ex. 1029 at 6197 and 6204-6206; Ex. 1026 at 6548-6553.

[*Preamble*] "An electronic or electrical device or electronic or electrical component thereof comprising"

118. Coulson-122 described coating electronics (Ex. 1004 at 1:3-7), and

Badyal stated that its crosslinked coatings could be used for coating any solid substrate, including those of materials such as fabric, metal, glass, ceramics, paper, or polymers. Ex. 1005 at 9:28-34. By the priority date of '876 patent, it had been widely established that that the dielectric properties of plasma polymer coatings enabled them to form as electrical insulating and protective coatings on electronic and electrical devices. Ex. 1004 at 1:3-4:3, Ex. 1012 at 1:9-4:4, Ex. 1013 at [0038], Ex. 1014 at 1:3-5:5. A POSA therefore would have recognized electronics as important solid substrates among those that could be coated with Badyal's versatile crosslinked coatings. As a further indication, Badyal taught as a specific example that the plasma polymer coatings could be applied to biomedical devices. Ex. 1005 at 11:19-24. A POSA would have known that a variety of biomedical devices, including wearable sensors for physiological monitoring and hearing aids, contain a variety of electronic components, Ex. 1015 at [0006], and thus can also be called electrical or electronic devices.

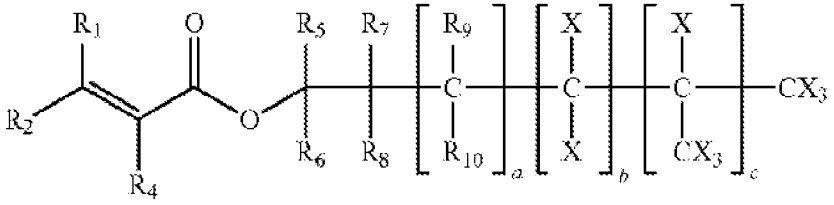
> **[*Element 1a*] "a protective cross-linked polymeric coating on a surface of said device or component; wherein the protective cross-linked polymeric coating is obtained by exposing said device or component to a plasma comprising a monomer compound and a crosslinking reagent for a period of time sufficient to allow formation of the protective cross-linked polymeric coating on a surface thereof,"**

119. A POSA would have known that coatings used on electronics can protect the underlying electronics in a number of ways, including repelling water or other liquids, providing electrical insulation, and/or by providing a barrier to the

passage of liquids or gases. Ex. 1004 at 1:1-34, 4:9-15; Ex. 1008 at [0023-24]; Ex. 1014:4:5-5:13; Ex. 1017 at 3:27-41, 6:31-36; Ex. 1018 at 1:5-11. The description of protective coatings in the '876 patent is consistent with that understanding. Ex. 1001 at 1:8-13.

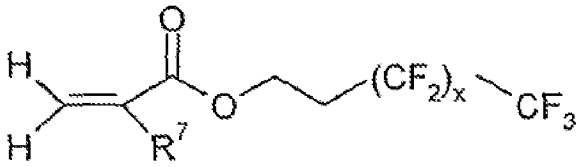
[*Element 1b*] "wherein the monomer compound is a compound of formula I(a):

I(a)



wherein each of R1, R2, R4 and R5 to R10 is independently selected from hydrogen or an optionally substituted C1-C6 branched or straight chain alkyl group; each X is independently hydrogen or halogen; a is from 0-10; b is from 3 to 7; and c is 0 or 1,"

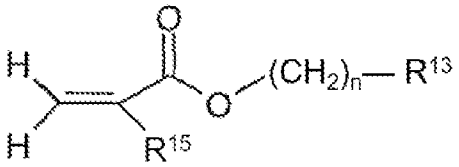
120. As noted above, Coulson-122 described preferred monomers with a structure



where and x preferably was 7 repeating CF_2 groups and R^7 was preferably hydrogen or methyl, Ex. 1003 at 12:13-21, which a POSA would have recognized as describing PFAC8 and PFMAC8, respectively.

121. Badyal also described monomers including PFAC8 and PFMAC8.

Badyal showed a preferred monomer formula of $CH_2=CR^{15}C(O)O(CH_2)_nR^{13}$. Ex. 1005 at 9:10-16 (Formula V). I have provided below the corresponding structure that any POSA would have understood from that formula:



Badyal described R^{15} as including hydrogen or methyl, which a POSA would have recognized as yielding an acrylate or methacrylate, respectively. Ex. 1005 at 9:16. I note that the formula provided by Badyal and shown above designated the number of CH_2 groups using the variable *n* (Ex. 1005 at 9:13), but the text used the variable *m* when describing the number of CH_2 groups (Ex. 1005 at 7:27-28, 8:26-28, 9:15). Based on those disclosures, a POSA would in my opinion have understood that Badyal's Formula V was intended to include m rather n as the variable designating the number of CH_2 groups. To a POSA, Badyal therefore described the number of CH_2 groups as being from 1-10, preferably 2. Ex. 1005 at 9:15-16, 7:20-28, 8:26-28. As to R^{13}, Badyal described perfluorinated alkyl chains of the formula C_sF_{2s+1} as preferred, especially where s is 10 or 8 (i.e., C_8F_{17}). Ex. 1005 at 9:15-16, 8:15-18. In view of those collective disclosures, a POSA would have recognized Badyal's preferred monomers included PFAC8 (with n/m as 2, R^{13} as C_8F_{17}, and R^{15} as hydrogen) and PFMAC8 (with n/m as 2, R^{13} as C_8F_{17}, and R^{15} as methyl).

122. Formula I(a) in claim 1 of the '876 patent encompasses the specific

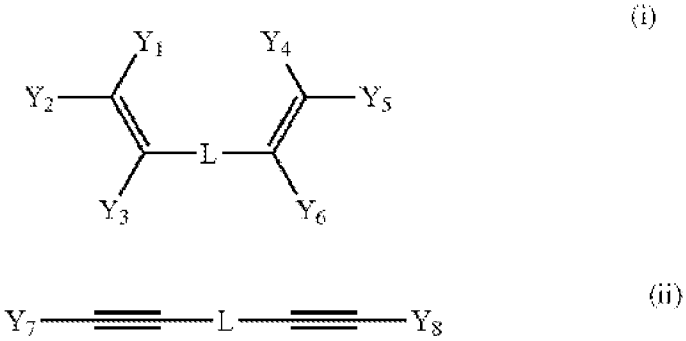
structures of PFAC8 and PFMAC8. The structures PFAC8 and PFMAC8 correspond to selecting the substituents R_1, R_2, R_5, R_6, R_7, and R_8 in Formula I(a) as hydrogen; choosing a=0, b=7, and c=0; and selecting X as the halogen element fluorine. Selecting R_4 as hydrogen or the methyl alkyl group, results in the precise chemical formulas for PFAC8 and PFMAC8, respectively.

B. Ground 1: Coulson-122, Badyal, and Cohen

123. In my opinion, as explained in more detail below, claims 1-3, 9, and 11-15 of the '876 patent would have been obvious over Coulson-122 and Badyal combined with Cohen.

1. Claim 1

[*Element 1c*] "and wherein the crosslinking reagent comprises two or more unsaturated bonds attached by means of one or more linker moieties and has a boiling point of less than 500° C. at standard pressure, the crosslinking reagent having one of the following structures:

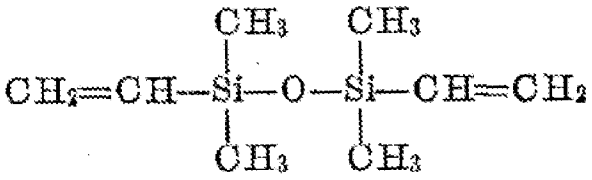


where Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7 and Y_8 are each independently selected from hydrogen, optionally substituted cyclic, branched or straight chain C_1-C_6 alkyl or aryl; and L is a linker moiety;"

124. Badyal taught that crosslinked polymers form when at least one of the

monomeric reagents contains two double bonds. Ex. 1005 at 4:1-29. As a matter of basic chemistry, a POSA would have known that double bonds (and triple bonds) are types of unsaturated bonds, as compared to saturated organic compounds that have only single bonds between carbon atoms and therefore tend to be less reactive. As I've noted Badyal described the same generic crosslinking reagent structure as formula (i) shown in claim 1 of the '876 patent, containing two carbon-carbon double bonds and a bridging structure which links between the two double bonds. Ex. 1005 at 5:1-5. In Badyal the bridging structure was denoted by the letter Z, and it is denoted instead by the letter L in claim 1 of the '876 patent. This change in nomenclature does not represent any change in chemical formulas encompassed between the two crosslinker structures.

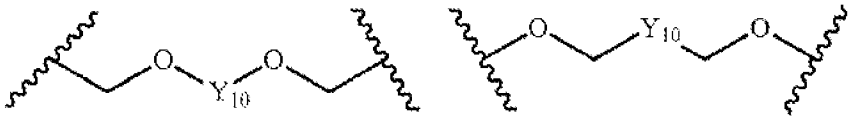
125. Badyal taught that such crosslinkers containing any bridging group known in the polymer art would be suitable for use in making the described cross-linked polymers. Ex. 1005 at 5:18-23. A POSA therefore would have considered known crosslinkers that fit Badyal's generic structure. By 2015, one well-known example in the polymer art of a crosslinking reagent with two double bonds separated by a bridging group was divinyl tetramethyl disiloxane (DVTMDS). Ex. 1006 at 1:15-34. Selecting hydrogen for each of the R^1-R^6 positions in Badyal's generic crosslinker formula and utilizing tetramethyl disiloxane to bridge between the double bonds results in the chemical structure of DVTMDS;



DVTMDS was known as a versatile crosslinker that can be copolymerized with many different monomers including members of the acrylate and methacrylate families. Ex. 1006 at 2:14-30, 4:18-65.

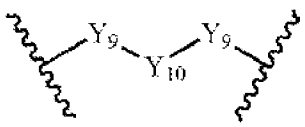
126. The boiling point of a reagent at standard pressure (also known as the normal boiling point) is a fixed physical property of that reagent. The normal boiling point of DVTMDS is approximately 137°C. Ex. 1006 at 3:44-45. Additionally, a POSA would have known that DVTMDS has sufficient volatility and reactivity for use in plasma polymerization. Ex. 1036 at 4-6.

[*Element 1d*] [*Formula A*] "wherein for compound (i) L is of formula A having one of the following structures:



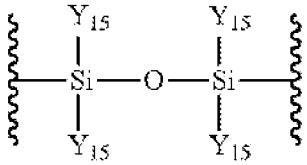
and Y_{10} is selected from optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene and a siloxane group; or

[*Formula B*] wherein for compound (i) L is of formula B having the following formula:



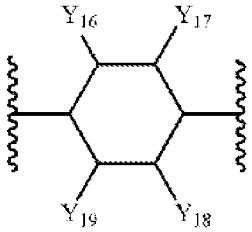
where each Y_9 is independently selected from, a bond, —O—, —O—C(O)—, —C(O)—O—, —Y_{11}—O—C(O)—, —C(O)—O—Y_{11}—, —OY_{11}—, and —Y_{11}O—, where Y_{11} is an optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene; and

[*Formula B1*] wherein Y_{10} has the following formula:



and each Y_{15} is independently selected from optionally substituted branched or straight chain C_1-C_6 alkyl; or

[*Formula B2*] wherein Y_{10} has the following formula:



and Y_{16} to Y_{19} are each independently selected from H and optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl."

127. Formula B1 of '876 claim 1 encompasses the specific chemical structure of DVTMDS, where Y_9 is a single bond between carbon and silicon atoms and Y_{10} is a disiloxane structure having its four Y_{15} substituents each selected as a methyl alkyl group. The specific use of DVTMDS is also described as a preferred example of a crosslinker in the '876 patent. Ex. 1001 at 8:7-8.

A POSA would have used Cohen's DVTMDS crosslinker in the coatings described by Coulson-122 and Badyal

128. As a POSA would have known in 2015, the expanding market of mo-

bile electronic devices and the well-known sensitivity of those devices to damage from exposure to environmental contaminants created incentives to protect those devices, and one common approach was to apply protective polymer coatings. Ex. 1004 at 1:1-34, 4:29-5:34. Such protective polymer coatings were often applied through plasma polymerization and provided liquid-repellency, electrical insulation, and/or barrier properties. Ex. 1004 at 4:29-5:6, 14:7-23; Ex. 1008 at Abstract, [0011], [0021]; Ex. 1012 at 2:6-20, 7:3-21; Ex. 1013 at [0003-04], [0046]; Ex. 1015 at [0001-02], [0011], [0029]. In my opinion, the recognized and growing market for such coatings in 2015 would have motivated POSAs to look for ways to improve on existing protective coatings, such as those described by Coulson-122.

129. Coulson-122 taught the value of liquid-repellent coatings for electronic protection and described forming such coatings from the plasma polymerization of fluorinated monomers including PFAC8 or PFMAC8. Ex. 1004 at 1:1-34, 12:7-22. A POSA also would have known that Badyal taught that the durability of plasma polymer coatings produced from PFAC8 or PFMAC8 could be increased by copolymerization with a crosslinking agent possessing two double bonds. Ex. 1005 at 4:1-29. A POSA would have recognized that durability is important for protective coatings applied to electronics like mobile phones or medical devices, which are used continuously for years while often being exposed to challenging conditions like liquid exposure.

130. Badyal's copolymerization method could produce crosslinked plasma polymer coatings on any solid substrate, including biomedical devices, which POSAs would have known to frequently contain electronics. Ex. 1005 at 9:28-30, 11:19-24. Furthermore, a POSA would have known that crosslinking of polymer coatings typically resulted in improved barrier properties, smoothness, and solvent resistance. Ex, 1006 at 3:50-65 (showing improved solvent resistance after cross-linking); Ex. 1026 at 6551-53 (showing that crosslinking improved smoothness, reduced hysteresis, and reduced crystallinity which reduces channels through the polymer layer thus providing a more effective barrier).

131. Thus, to improve the durability of protective coatings for electronic devices—which are solid substrates, and some of which are used as biomedical devices—a POSA would have been motivated to apply the method for crosslinked plasma polymer coatings described in Badyal with application taught by Coulson-122, particularly since both patents taught a preference for plasma polymerization of the same fluorine-containing monomers, PFAC8 or PFMAC8. A POSA reading those disclosures and noting those similarities would not have been discouraged from applying Badyal's crosslinking technique in the Coulson-122 coatings by Badyal's use of fabrics as an exemplary substrate because of the similarities between Badyal and Coulson-122 and because Badyal described the applications for its techniques much more broadly. Ex. 1005 at 9:28-34, 11:22-24. Badyal specifi-

cally emphasized that such crosslinked coatings were not limited to fabrics and could be used to protect "any solid substrate," and a POSA would have known that electronics and electronic components are solid substrates. In addition, Badyal pointed out biomedical devices as one specific example of a solid substrate, and a POSA would have known that many biomedical devices, such as hearing aids and pacemakers, are electronic devices.

132. Badyal taught the selection of the cross-linking agent from those structures known in the polymer art. Ex. 1005 at 5:1-5, 5:18-23. An example of a known crosslinker in the polymer art with the required structure and desirable known properties was DVTMDS, which a POSA would have known had been widely used in polymer production for years before 2015. Ex. 1006 at 1:20-35; Ex. 1018 at 3:60-4:25; Ex. 1017 at 3:41-4:10. Cohen had described DVTMDS as a crosslinker useful for producing electrically insulating, solvent-resistant polymers used as dielectric layers in electronic devices. Ex. 1006 at 5:1-25; Ex. 1018 at 1:6-11; Ex. 1033 at [0037], [0045]. DVTMDS was known to be compatible with various polymerization techniques, including plasma polymerization. Ex. 1006 at 1:32-62; Ex. 1017 at Abstract, 3:40-4:24; Ex. 1027 at 1:5-11, 8:30-35; Ex. 1033 at [0037-45]; Ex. 1036 at 3-6. Coatings containing DVTMDS had been associated with water repellency, barrier, and insulating properties. Ex. 1006 at 5:1-12; Ex. 1017 at 3:27-41, 6:31-36; Ex. 1033 at [0037]. Cohen also taught that DVTMDS

may be copolymerized with a great number of copolymerizable compounds containing a double bond, including fluorine-containing monomers as well as acrylate and methacrylate monomers. Ex. 1006 at 2:14-30, 4:18-57. Those are all properties that a POSA would have been looking for in a crosslinker in view of Coulson-122 and Badyal.

133. Thus, a POSA's knowledge of DVTMDS, its structure, reactivity, and properties would have provided motivation to use DVTMDS as the crosslinker for the acrylate and methacrylate monomers of Badyal and Coulson-122 to obtain durable electrically insulating plasma polymer coatings. Additionally, a POSA would have known that the low normal boiling point of approximately 137°C for the DVTMDS enables the easy introduction of vapors of this crosslinking reagent into the vacuum chamber used for plasma deposition, including in combination with a monomer like PFAC8 or PFMAC8.

134. Plasma polymerization was a commonplace and straightforward procedure that would have been familiar and simple for a POSA to carry out in 2015. Ex. 1017 at 3:27-40; Ex. 1021 at ¶¶ 58-60; Ex. 1012 at 8:1-10:12; Ex. 1025 at ¶¶ 38-48; Ex. 1001 at 14:59-67; Ex. 1005 at 2:10-13, 10:8-12.

135. The POSA would have expected DVTMDS to work as a crosslinker for plasma polymerization with PFAC8 or PFMAC8 because Badyal taught that known crosslinkers fitting the same general structure with two double bonds and a

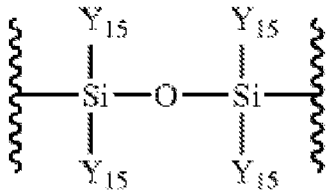
known bridging group would work for preparing the disclosed durable coatings. Ex. 1005 at 4:17-5:23. Given the known and favorable properties and applications of polymers containing DVTMDS that I described above, a POSA would have expected to be able to achieve those same properties when incorporating DVTMDS into coatings with similar properties based on monomers like PFAC8 and PFMAC8 as described by Coulson-122 and Badyal. In addition, a POSA would have known DVTMDS was compatible for co-polymerization with acrylate monomers (Ex. 1006 at 1:31-34, 2:14-29) and had been used in plasma polymerization (Ex. 1017 at 3:42-4:11; Ex. 1033 at [0040-43], Ex. 1027 at 7:64-8:34). Finally, the POSA would have expected plasma coatings prepared using PFAC8 or PFMAC8 and DVTMDS to be successful as applied to electronics because Coulson-122 and Cohen described electronics applications for those reagents, and Badyal taught that such a crosslinked combination could be applied to *any* solid surface, including that of a biomedical device.

2. Claims 2, 3

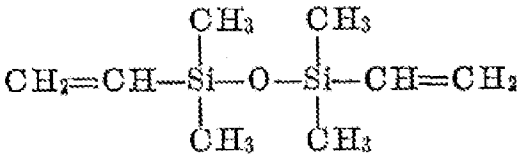
136. Claims 2 and 3 identify physical properties of the polymer coatings in claim 1. I discuss claims 2 and 3 in Section G below.

3. Claims 9 and 11-15

137. Regarding claim 9, the DVTMDS crosslinker taught by Cohen has the Formula B1 bridging group specified in claim 9, which is:



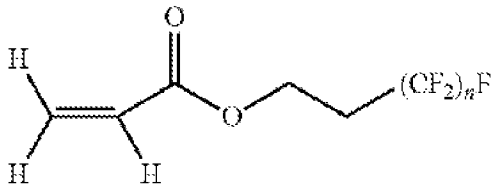
where each Y_{15} is methyl (CH_3). Ex. 1001 at 20:39-50. DVTMDS matches that same bridging-group structure



with each Y_9 in Formula B being a bond connecting silicon atoms of the bridging group to the double-bonded carbon atoms.

138. In claim 11, DVTMDS is stated as one of the specified crosslinking reagents. Ex. 1001 at 21:2-3.

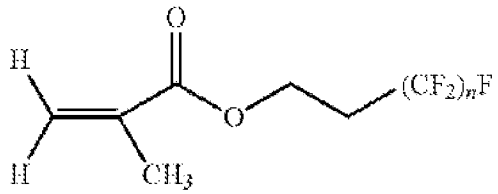
139. Claims 12 and 13 specify a subset of monomers under the generic Formula I(a) in claim 1, and the PFAC8 monomer taught by Coulson-122 and Badyal is included in both of those claims. Claim 13 states PFAC8 specifically. Claim 12 calls for a monomer with the structure



where n is from 2 to 10. Ex. 1001 at 21:7-19. PFAC8 matches that structure exactly with an 8-carbon perfluorinated tail. In other words, PFAC8 is included in the

structure above when n = 8.

140. Claims 14 and 15 specify a subset of monomers under the generic Formula I(a) in claim 1, and the PFMAC8 monomer taught by Coulson-122 and Badyal is included in both of those claims. Claim 15 states PFMAC8 specifically. Claim 14 calls for a monomer with the structure



where n is from 2 to 10. Ex. 1001 at 22:4-15. PFMAC8 matches that structure exactly with an 8-carbon perfluorinated tail. In other words, PFMAC8 is included in the structure above when n = 8.

C. Ground 2: Coulson-122, Badyal, and Holliday

141. In my opinion, as explained in more detail below, claims 1-8 and 10-15 of the '876 patent would have been obvious over Coulson-122 and Badyal combined with Holliday.

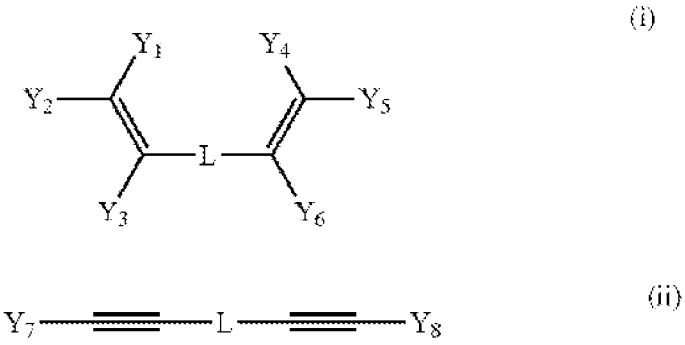
142. As I've explained above, a POSA would have been aware of Coulson-122 and Badyal and would have been seeking known crosslinkers that fit Badyal's generic crosslinker structure with two double bonds and a bridging group and preferably were suitable for use in plasma polymerization and had been associated with properties beneficial for preparing protective coatings for electronics. In my opin-

ion, Holliday described known crosslinking reagents that a POSA would have considered suitable for preparing crosslinked coatings in view of Coulson-122 and Badyal.

143. Holliday described crosslinked polymers useful for providing electrical insulation that could be applied to protect electrical conductors and connectors with electrical and chemical resistance properties. Ex. 1007 at 1:10-26, 2:17-46. Holliday refers to "curable" polymer compositions made using reagents "which can be crosslinked." Ex. 1007 at 1:10-20, 2:17-21, 2:39-46. A POSA would have known that curing is used in the field as a synonym for crosslinking, and Holliday's references to improved electrical, chemical, and mechanical properties of "cured" polymers refers to properties achieved after crosslinking with a crosslinking reagent. Ex. 1007 at 2:39-46, 2:50-52, 2:68-70, 4:72-5:57. Below I discuss crosslinkers described by Holliday that a POSA would have recognized as suitable and consistent with the desired crosslinker structure and properties for use in the Coulson-122/Badyal combination.

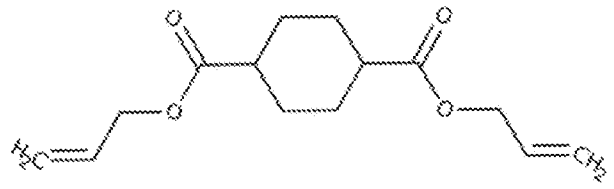
1. Claim 1

[*Element 1c*] "and wherein the crosslinking reagent comprises two or more unsaturated bonds attached by means of one or more linker moieties and has a boiling point of less than 500° C. at standard pressure, the crosslinking reagent having one of the following structures:



where Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7 and Y_8 are each independently selected from hydrogen, optionally substituted cyclic, branched or straight chain C_1-C_6 alkyl or aryl; and L is a linker moiety;"

144. Holliday described several crosslinking reagents, including two that a POSA would have recognized as familiar and consistent with Badyal's generic crosslinker structure: diallyl-1,4-cyclohexanedicarboxylate (DCHD) and 1,4-divinyl-oxybutane (which to a POSA is also known as 1,4-butanediol divinyl ether (BDVE)). Ex. 1007 at 3:34-35, 3:52-53; Ex. 1005 at 5:1-5. The structures of those reagents would have been known to a POSA and are shown below:



DCHD



BDVE

Both DCHD and BDVE match the structural formula (i) in claim 1 where Y_1 thru Y_6 are all hydrogen. Both DCHD and BDVE contain two carbon-carbon double bonds bridged with a linker moiety.

145. The normal boiling point of a reagent is measured at standard pressure and is a fixed physical property of that reagent. The normal boiling point of DCHD is approximately 331°C (verified using chemspider.com, CAS No. 20306-22-3) (Ex. 1039 at 3). The normal boiling point of BDVE is approximately 201°C (verified using chemspider.com, CAS No. 3891-33-6) (Ex. 1039 at 5). A POSA in 2015 using standard references would have known or been able to look up the normal boiling points of DCHD and BDVE. A POSA also would have known how to determine the normal boiling points of DCHD and BDVE using well known laboratory techniques, such as measuring the temperature of a boiling sample of each reagent at standard pressure.

146. A POSA also would have been able to accurately estimate the boiling point of an organic compound like DCHD and BDVE. For example, I calculated the normal boiling points of DCHD and BDVE using a longstanding and widely cited calculation method described by Joback and Reid in 1987. Ex. 1037. In short, knowledge of an organic compound's structure allows accurate estimation of the

compound's boiling point based on the component groups that make up its structure: the normal boiling point (in Kelvin) is estimated to equal 198.2 plus the sum of the values assigned to each constituent group in the molecule, as identified in Table 3. Ex. 1037 at 234-38, example calculation at 239. The result in Kelvin can be converted to °C by subtracting 273.15.

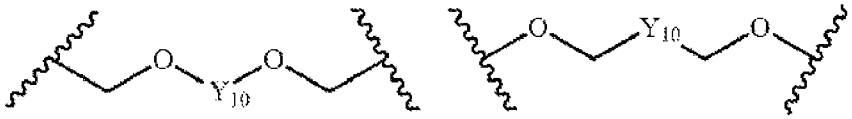
DCHD			
Group	*Contribution*	*No.*	*Total*
$=CH_2$	18.18	2	36.36
=CH-	24.96	2	49.92
$-CH_2-$	22.88	2	45.76
COO	81.1	2	162.2
CH ring	21.78	2	43.56
CH_2 ring	27.15	4	108.6
Total			446.4
Boiling Point (K)			644.6
Boiling Point (°C)			371.45

BDVE			
Group	*Contribution*	*No.*	*Total*
$=CH_2$	18.18	2	36.36
=CH-	24.96	2	49.92
$-CH_2-$	22.88	4	91.52
O nonring	22.42	2	44.84
Total			222.64
Boiling Point (K)			420.84
Boiling Point (°C)			147.69

147. Using the Joback and Reid method, a POSA would have calculated the normal boiling points of DCHD and BDVE to be approximately 371°C and 148°C, respectively, and both well below 500°C. The normal boiling points of

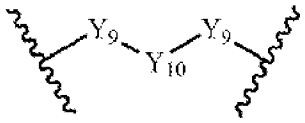
DCHD and BDVE indicate sufficient volatility to allow vapors of these crosslinking agents to enter a vacuum reaction chamber used for plasma polymerization because they were near or below the normal boiling points of other reagents that were known to be volatilizable and suitable for use in plasma polymerization. Ex. 1004 at 12:8-22 (PFAC8 and PFMAC8); Ex. 1008 at [0054], [0011] (CDMDA).

[*Element 1d*] [*Formula A*] "wherein for compound (i) L is of formula A having one of the following structures:



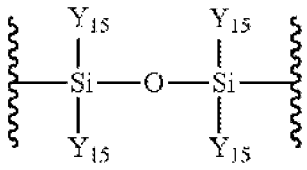
and Y_{10} is selected from optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene and a siloxane group; or

[*Formula B*] wherein for compound (i) L is of formula B having the following formula:



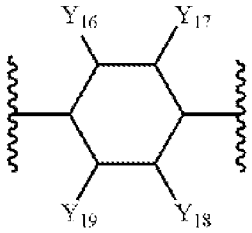
where each Y_9 is independently selected from, a bond, —O—, —O—C(O)—, —C(O)—O—, —Y_{11}—O—C(O)—, —C(O)—O—Y_{11}—, —OY_{11}—, and —Y_{11}O—, where Y_{11} is an optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene; and

[*Formula B1*] wherein Y_{10} has the following formula:



and each Y_{15} is independently selected from optionally substituted branched or straight chain C_1-C_6 alkyl; or

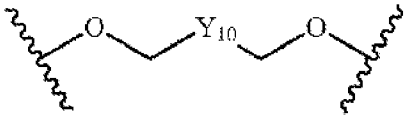
[*Formula B2*] wherein Y_{10} has the following formula:



and Y_{16} to Y_{19} are each independently selected from H and optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl."

148. The bridging group of DCHD follows Formula B and B2 of claim 1. Ex. 1001 at 19:20-34, 19:44-57. For Y_{10}, DCHD contains the same 6-carbon ring as in Formula B2, and the ring substituents Y_{16} to Y_{19} are all selected to be hydrogen. For Y_9, DCHD contains —C(O)—O—Y_{11}— and —Y_{11}—O—C(O)— to the sides of Y_{10}. For both Y_9 selections, the Y_{11} substituent is the C1 alkylene group, methylene (–CH_2–). This makes the Y_9 the selections —C(O)—O—CH_2— and —CH_2—O—C(O)—, respectively.

149. The bridging group of BDVE follows Formula A of claim 1 with the structure



where Y_{10} is a C2 alkylene chain (–CH_2–)$_2$.

A POSA would have used Holliday's DCHD and BDVE crosslinkers in the coatings described by Coulson-122 and Badyal

150. As Holliday shows, DCHD and BDVE both were crosslinkers that were known to those in the field well before 2015. Both have the same generic structure as the preferred crosslinker structure from Badyal: two double bonds separated by a bridging group, with hydrogen in the R1-R6 positions, and with alkyl groups interposed with oxygen atoms in the bridging group Z. Ex. 1005 at 5:1-5, 5:18-20.

151. In my opinion, a POSA would have been motivated to use the DCHD and BDVE crosslinkers described by Holliday in protective polymer films with PFAC8 or PFMAC8 based on the Coulson-122/Badyal combination. Based on Badyal's disclosures, a POSA would have viewed the structures of DCHD and BDVE consistent with those described as suitable for creating protecting plasma polymer coatings with monomers like PFAC8 and PFMAC8. Ex. 1005 at 5:1-5, 5:18-20. A POSA would have been aware that Holliday taught that both DCHD and BDVE as useful crosslinkers for protecting electrical components because the crosslinked polymers formed using DCHD or BDVE have improved mechanical, chemical, and electrical resistance properties. Ex. 1007 at 1:10-26. Holliday also taught that acrylate and methacrylate monomers could be added to the polymerizable mixture which contained the crosslinking agent. Ex. 1007 at 3:54-4:2. This would have suggested to the POSA that the DCHD and BDVE crosslinkers are re-

active with the family of acrylate and methacrylate monomers, which includes PFAC8 and PFMAC8. Since both Holliday and Coulson taught methods for producing films for electronic protection applications, a POSA would be motivated to combine one of the crosslinkers specified by Holliday, such as DCHD or BDVE, with one of the fluorine-containing monomers specified by Coulson-122 so as to achieve durable crosslinked protective coatings on the surfaces of electronic devices and components.

152. In addition, a POSA would be aware that vapors of the monomers PFAC8 and PFMAC8 could be introduced into the vacuum chamber. Since the normal boiling points of PFAC8 and PFMAC8, approximately 267°C and 300°C, respectively, are near or higher than the normal boiling points of DCHD and BDVE, a POSA would conclude that DCHD and BDVE vapors likely could be effectively introduced in the plasma reactor with PFAC8 or PFMAC8 vapors. Based on the known structures, properties, and established uses of DCHD and BDVE, a POSA would have been motivated to use DCHD and BDVE as crosslinkers in combination with PFAC8 or PFMAC8.

153. In my opinion, a POSA would have reasonably expected to succeed using Holliday's DCHD and BDVE crosslinkers to prepare plasma polymer films like those described by Coulson-122 and Badyal for a number of reasons. As I've noted, plasma polymerization was well-known and routine in the polymer field by

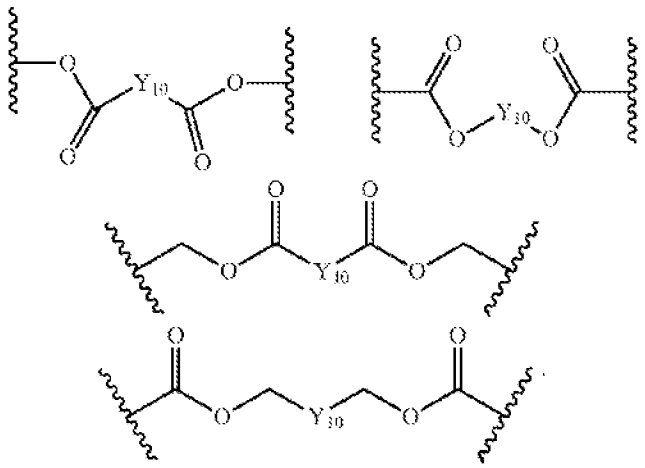
2015, and Badyal taught that crosslinkers of a generic structure that included DCHD and BDVE would be suitable for plasma co-polymerization with PFAC8 and PFMAC8. Likewise, a POSA would have known that PFAC8 and PFMAC8 are acrylate-based monomers, and Holliday taught that DCHD and BDVE could be used to make polymer coatings in conjunction with acrylates or methacrylates. Ex. 1007 at 3:55-60. A POSA would have known that BDVE could be used in plasma polymerization. Ex. 1009 at 606-07. In addition, Holliday taught that its coating reagents could be used flexibly with multiple polymerization techniques, including free-radical polymerization which is a mechanism POSAs would have known occurs during plasma deposition. Ex. 1007 at 2:47-70, 3:27-31. A POSA therefore would have expected both BDVE and DCHD to also be suitable crosslinkers for plasma polymerization. Finally, Holliday taught that DCHD and BDVE had been used successfully as crosslinkers in coatings for electronics that provided electrical insulation and chemical resistance (Ex. 1007 at 1:10-26, 2:39-46), so a POSA would have expected to attain at least those similar beneficial properties when using BDVE or DCHD in combination with PFAC8 or PFMAC8 in view of Coulson-122, Badyal, and Holliday.

2. Claims 2, 3

154. Claims 2 and 3 identify physical properties of the polymer coatings in claim 1. I discuss claims 2 and 3 in Section G below.

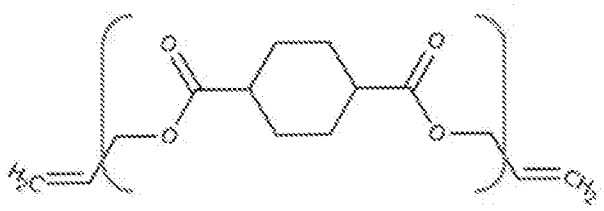
3. Claim 4

"The device or component according to claim 1, wherein when for compound (i) L is of the formula B, L has one of the following structures:

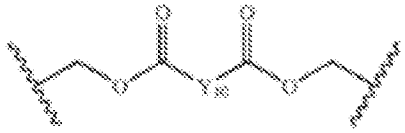


"

155. As I noted when discussing claim 1, the DCHD crosslinker in Holliday satisfies bridging group Formula B from '876 claim 1. Claim 4 further specifies the bridging group structure has one of four structures, as shown above. Below I've shown the structure of DCHD with the bridging group bracketed in red.



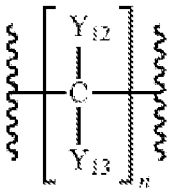
The bridging group of DCHD, emphasized above, is consistent with the third of four bridging group structures shown in claim 4



with Y_{10} in DCHD taking the form of a para-substituted 6-carbon cyclohexane ring, consistent with Formula B2 of claim 1.

4. Claims 5 and 6

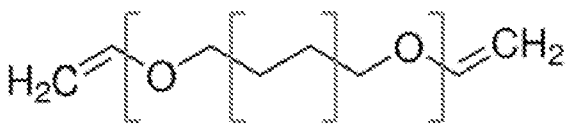
"5. The device or component according to claim 1, wherein when for compound (i) L is of formula A, Y_{10} has the following formula:



wherein each Y_{12} and Y_{13} is independently selected from H, halo, optionally substituted cyclic, branched or straight chain alkyl, or —OY_{14}, where Y_{14} is selected from optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl, and n is an integer from 1 to 10."

"6. The device or component according to claim 5, wherein each Y_{12} is H and each Y_{13} is H"

156. As I noted above with reference to claim 1, the BDVE crosslinker in Holliday fits Formula A of claim 1. Claims 5 and 6 specify that Y_{10} in Formula A has the structural formula above with n being an integer between 1 and 10, and claim 6 further specifies that each Y_{12} and Y_{13} is hydrogen. Ex. 1001 at 20:17-35. Below I have shown the structure of BDVE with the bridging group bracketed in blue and the Y_{10} moiety bracketed in red.



157. For purposes of claims 5 and 6, the use of BDVE as the crosslinker

fits the specified structure because it contains a C2 alkylene $(–CH_2–)_2$ group in the Y_{10} position and therefore matches the claimed structure with Y_{12} and Y_{13} as hydrogen and n = 2.

5. Claim 7

"The device or component according to claim 5, wherein each Y_{12} is fluoro and each Y_{13} is fluoro."

158. A POSA would have known that perfluorinated alkyl chains confer strong hydrophobicity. Ex. 1005 5:18-23, 10:32-11:1; Ex. 1019 at 2031. In addition, Badyal taught that the bridging group in a suitable crosslinker could be perfluorinated. Ex. 1005 at 5:18-23. And a POSA would have known that water-repellency was desirable when making protective coatings for electronics. Ex. 1004 at 4:9-15. In my opinion, a POSA considering BDVE for use with Coulson-122, and Badyal therefore would have been motivated to substitute fluorine at every Y_{12} and Y_{13} position in BDVE to improve hydrophobicity in the resulting protective coatings. A POSA would have retained BDVE's alkylene (CH_2) groups separating the Y_{12} and Y_{13} groups from the oxygen of the ether groups to maintain a spacer between the oxygen and fluorocarbon moieties to promote stability of the resulting fluorine-substituted crosslinking reagent. Ex. 1038 at [0005-06]. In addition, a POSA in 2015 would have reasonably expected to succeed in obtaining and using the fluorine-substituted version of BDVE because methods to prepare fluorine-substituted divinyl ethers were known (Ex. 1038), and because Badyal taught

that the crosslinker's bridging group could include perfluoroalkyl groups, Ex. 1005 at 5:18-6:13.

6. Claim 8

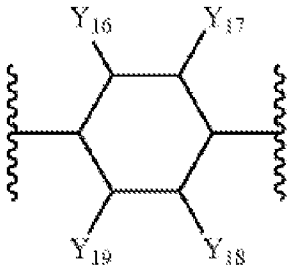
"The device or component claim 5, wherein n is from 4 to 6."

159. A POSA also would have known as a basic matter of chemistry that longer alkyl chains, which contain a series of saturated hydrophobic $–CH_2–$ groups, tend to confer greater hydrophobicity and steric flexibility with greater length (and therefore a greater number of hydrophobic $–CH_2–$ groups). And a POSA would have known that water-repellency was desirable when making protective coatings for electronics. Ex. 1004 at 4:9-15. In my opinion, a POSA considering BDVE for use with Coulson-122 and Badyal therefore would have been motivated to extend the $(CH_2)_2\ Y_{10}$ group in BDVE, for example by doubling its length, to improve the hydrophobicity of the resulting protective coatings. That would have yielded a crosslinker with four $–CH_2–$ groups as recited in claim 8, and a POSA would have recognized the resulting crosslinker as 1,6-hexanediol divinyl ether (HDVE). A POSA reasonably would have expected to succeed in obtaining and using such a modified version of BDVE because HDVE was already a known reagent in the polymer field and had been used previously as a crosslinker in combination with acrylate-based monomers. Ex. 1011 at 3:46-54, 3:1-14. In addition, a POSA in 2015 would have reasonably expected to succeed in making a variant of BDVE

with an extended alkylene chain because such modifications to the alkyl structure would have required only simple and straightforward techniques of organic synthesis that would have been known and conventional to a POSA.

7. Claim 10

"The device or component according to claim 1, wherein when for compound (i) L is of formula B and Y_{10} has the following formula:



Y_{18} is H or vinylene, and Y_{16}, Y_{17} and Y_{19} are each H."

160. As I have described above, DCHD has a bridging group containing the same formula specified in claim 10, including a para-substituted 6-carbon cyclohexane ring like the one shown above and that includes hydrogen atoms at each of the positions labeled Y_{16}-Y_{19} above.

8. Claims 11-15

161. In claim 11, both DCHD and BDVE are stated as specified crosslinking reagents. Ex. 1001 at 20:67, 21:3-4.

162. As I've already described, Coulson-122 and Badyal taught PFAC8 and PFMAC8 as monomers that would be used in the proposed combination of Holliday, Coulson-122, and Badyal, and those monomers meet the requirements set forth in claims 12-15.

D. Ground 3: Coulson-122, Badyal, and Padiyath

163. In my opinion, as explained in more detail below, claims 1-4, 10, and 12-15 of the '876 patent would have been obvious over Coulson-122 and Badyal combined with Padiyath.

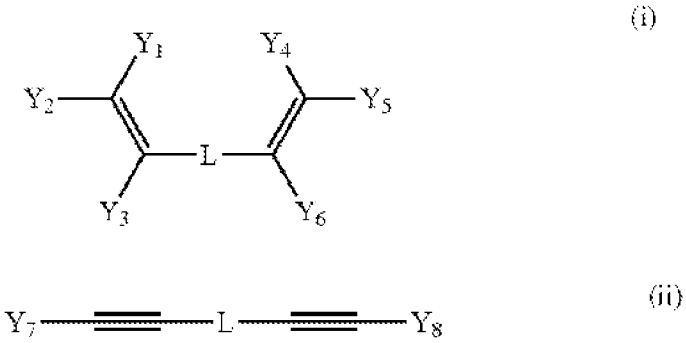
164. As previously explained, a POSA would have been aware of Coulson-122 and Badyal and would have been seeking known crosslinkers that fit Badyal's generic crosslinker structure with two double bonds and a bridging group and properties beneficial for preparing protective coatings for electronics. In my opinion, Padiyath described a known crosslinking reagent that would have met those criteria and that a POSA would have considered suitable for preparing crosslinked coatings in view of Coulson-122 and Badyal.

165. Padiyath described polymers useful for preparing barrier coatings to protect moisture or oxygen sensitive electronic devices such as organic light-emitting diodes (OLEDs), which are often used in screens for devices like televisions and mobile phones. Ex. 1008 at [0001], [0023-24], [0027], [0063-64]. Padiyath's barrier coatings could contain one or more polymer layers that could be prepared using plasma polymerization. Ex. 1008 at [0005-07], [0011], [0025], Fig. 3. The polymer layers were prepared using organic reagents, especially acrylates and methacrylates. Ex. 1008 at [0052], [0054]. Padiyath described the polymer layers as being preferably crosslinked, usually using crosslinking molecules. Ex. 1008 at

[0011], [0025], [0052]. Below I discuss Padiyath's description of a crosslinking reagent with two double bonds that a POSA would have recognized as suitable and consistent with the crosslinker structure and properties desired for use in the Coulson-122/Badyal combination.

1. Claim 1

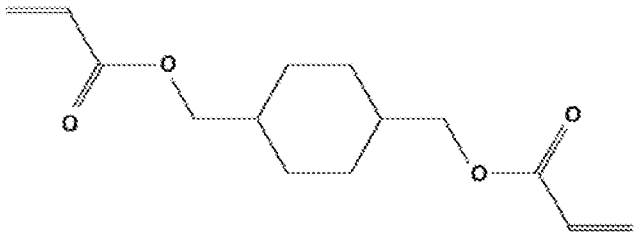
[*Element 1c*] "and wherein the crosslinking reagent comprises two or more unsaturated bonds attached by means of one or more linker moieties and has a boiling point of less than 500° C. at standard pressure, the crosslinking reagent having one of the following structures:



where Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7 and Y_8 are each independently selected from hydrogen, optionally substituted cyclic, branched or straight chain C_1-C_6 alkyl or aryl; and L is a linker moiety;"

166. Padiyath teaches crosslinking agents possessing two double bonds which are diacrylate and dimethacrylate monomers. Ex. 1008 at [0052]. A preferred crosslinker taught by Padiyath was commercially available from the Sartomer Co. under the name CD-406, which a POSA would have known was a formulation using 100% of a component with the CAS number 67905-41-3, cyclohexane 1,4-dimethanol diacrylate (CDMDA) (also known as cyclohexane dimethanol di-

acrylate or cyclohexane dimethanol diacrylate esters). Ex. 1008 [0054]; Ex. 1030 at [0144]; Ex. 1031 at [0027]; Ex. 1032 at 1. A POSA would have known that the structure of CDMDA is as shown below:



Ex. 1030 at [0144] (and showing the structural formula of CDMDA in the provided below paragraph [0146]). Formula (i) of Claim 1 shown above matches CDMDA when the six substituents on the two double bonds, Y_1 to Y_6, are selected as hydrogen and, as will be discussed below, the appropriate bridging group bridges between the two double bonds.

167. The two unsaturated bonds of CDMDA are both part of acrylate bonding configurations, and a POSA would have expected those bonds to readily react with other acrylate and methacrylate monomers, such as PFAC8 and PFMAC8, because acrylate and methacrylate groups were known to be highly reactive in polymer applications. Padiyath, for example, indicated that it was particularly preferred to polymerize multifunctional acrylates (i.e., those like CDMDA having two or more reactive acrylate groups capable of forming bonds with other molecules) alone or in combination with other multifunctional acrylates or methacrylates or monofunctional acrylates or methacrylates (i.e., those with only one reactive acry-

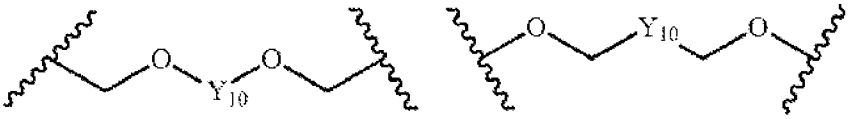
late group, like PFAC8 and PFMAC8). Ex. 1008 at [0052].

168. Padiyath taught that CDMDA is a volatilizable monomer. Ex. 1008 at [0054]. The boiling point of a reagent is a fixed physical property of the reagent. A POSA would have known that the normal boiling point of CDMDA is approximately 333°C (verified on chemspider.com using CAS No. 67905-41-3) (Ex. 1039 at 7). A POSA would have known that boiling point of CDMDA, or would have been able to look it up using standard chemistry reference materials and determine it experimentally using basic laboratory techniques like measuring the temperature of a boiling sample of CDMDA at standard pressure. A POSA also would have been able to accurately estimate the normal boiling point of CDMDA using the Joback method (Ex. 1037) as I've shown below:

CDMDA			
Group	*Contribution*	*No.*	*Total*
$=CH_2$	18.18	2	36.36
=CH-	24.96	2	49.92
$-CH_2-$	22.88	2	45.76
COO	81.1	2	162.2
CH ring	21.78	2	43.56
CH_2 ring	27.15	4	108.6
Total			446.4
Boiling Point (K)			644.6
Boiling Point (°C)			371.45

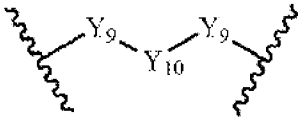
A POSA thus would have estimated the normal boiling point of CDMDA to be approximately 371°C—close to the actual normal boiling point and similarly well below 500°C and near the normal boiling points of PFAC8 and PFMAC8.

[*Element 1d*] [*Formula A*] "wherein for compound (i) L is of formula A having one of the following structures:



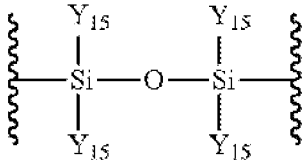
and Y_{10} is selected from optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene and a siloxane group; or

[*Formula B*] wherein for compound (i) L is of formula B having the following formula:



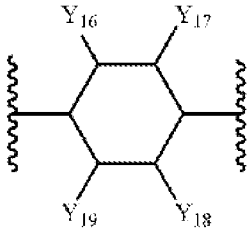
where each Y_9 is independently selected from, a bond, —O—, —O—C(O)—, —C(O)—O—, —Y_{11}—O—C(O)—, —C(O)—O—Y_{11}—, —OY_{11}—, and —Y_{11}O—, where Y_{11} is an optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene; and

[*Formula B1*] wherein Y_{10} has the following formula:



and each Y_{15} is independently selected from optionally substituted branched or straight chain C_1-C_6 alkyl; or

[*Formula B2*] wherein Y_{10} has the following formula:



and Y_{16} to Y_{19} are each independently selected from H and optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl."

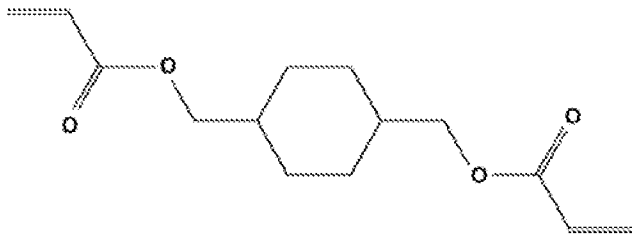
169. The bridging group of CDMDA follows Formula B and B2 of claim 1. For Y_{10}, the substituents Y_{16} to Y_{19} shown in Formula B2 are all hydrogen. For Y_9, the two independent selections for the left and right sides of Y_{10} are —C(O) —O— Y_{11}— and —Y_{11}—O—C(O)—, respectively. For both Y_9 selections, the Y_{11} substituent is the C1 alkylene group, methylene –CH_2-. Thus, the left and right selections for Y_9 are —C(O)—O—CH_2— and —CH_2—O—C(O)— , respectively.

A POSA would have used Padiyath's CDMDA crosslinker in the coatings described by Coulson-122 and Badyal

170. Based on the teachings of Badyal, a POSA would have been aware that crosslinking improves the durability of plasma polymers utilized as protective barriers against liquids and grown using PFAC8 and PFMAC8. Ex. 1005 at 4:1-27, 8:15-18, 9:10-26. A POSA would also have known from the teachings of Coulson-122 that the plasma polymerization of PFAC8 and PFMAC8 is useful for protecting electronic devices and components. Ex. 1004 at 1:3-23, 12:7-22, 13:30-14:23.

171. A POSA motivated to select a specific crosslinking agent which followed the formula prescribed by Badyal would have considered Padiyath and its disclosure of CDMDA as a known crosslinking reagent for use in preparing protective polymer coatings. A POSA would have been aware that Padiyath taught crosslinked, multilayer polymer barriers for protecting electronic devices against water

and oxygen [0001], [0011], [0023-24], [0027], [0063-64]. And as I explained above, one reagent that Padiyath described using to make such polymers was CDMDA (Ex. 1008 at [0054]), which a POSA would have recognized as a multi-functional acrylate with two double bonds



that was consistent with the generic structure for suitable crosslinkers set forth by Badyal, including having an alkyl bridging group interposed with oxygen atoms (Ex. 1005 at 5:1-23).

172. Because CDMDA was a multifunctional diacrylate and was volatile (Ex. 1008 at [0054]) and could therefore be easily vaporized, a POSA would have recognized CDMDA as a desirable crosslinker for plasma polymerization. Padiyath reinforced that understanding because it taught that the protective barrier stack could be made entirely of polymer layers (Ex. 1008 at [0018], [0025], Fig. 3), that those polymers could be made using CDMDA (Ex. 1008 at [0054]), and that those polymers could be formed by plasma polymerization. Ex. 1008 at [0011], [0054], [0061]. Based on Padiyath's disclosures indicating the volatility of CDMDA, its suitability in preparing barrier coatings, and its suitability for plasma polymerization, along with the fact that CDMDA fit with Badyal's stated structural require-

ments for a suitable crosslinker, a POSA reading Padiyath would have been motivated to use CDMDA as a crosslinker when preparing protective coatings for electronics in view of Coulson-122 and Badyal.

173. A POSA also would reasonably have expected that the diacrylate structure of CDMDA would successfully copolymerize with other compounds in the family of acrylate and methacrylate monomers, which includes PFAC8 and PFMAC8 to create protective coatings. For one thing, Badyal taught that crosslinkers like CDMDA that have its generic crosslinker formula with two double bonds and a bridging group would be suitable for copolymerization with fluorinated monomers including PFAC8 and PFMAC8—particularly where the crosslinker (like CDMDA) does not include a fluorinated group. Ex. 1005 at 5:1-23, 6:24-7:2, 9:10-26, 8:15-19. For another, Padiyath taught that the barrier polymer layers could include monofunctional (meth)acrylates used in combination with multifunctional (meth)acrylates. Ex. 1008 at [0052]. According to Padiyath, suitable monofunctional (meth)acrylates included fluorinated (meth)acrylates in a molecular weight range between 400 and 3,000 (Ex. 1008 at [0052]), and a POSA already aware of Coulson-122 and Badyal would have known that PFAC8 (MW = 518.17) and PFMAC8 (MW = 532.19) fit within that range, so a POSA would have expected to succeed copolymerizing monofunctional fluorinated (meth)acrylates like PFAC8 and PFMAC8 with a disclosed, especially preferred multifunctional acry-

late like CDMDA (Ex. 1008 at [0052], [0054]). In addition, since both Padiyath and Coulson taught methods for producing films for electronic protection applications, a POSA would have reasonably expected to succeed to combine the crosslinker specified by Padiyath, CDMDA, with one of the fluorine-containing monomers specified by Coulson-122 to achieve durable crosslinked protective coatings on the surface of electronic devices and components.

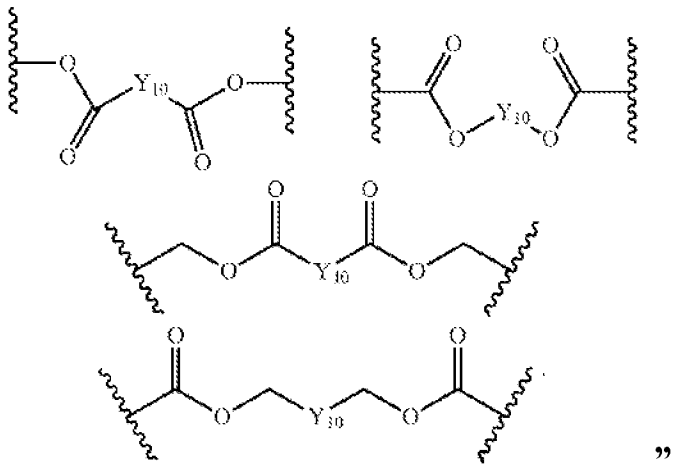
174. A POSA also would have been aware that the normal boiling points of PFAC8 and PFMAC8 are near the normal boiling point of CDMDA and therefore would have expected vapors of the monomers PFAC8 and PFMAC8 could be readily introduced into the vacuum chamber of a plasma reactor together with CDMDA crosslinking vapors.

2. Claims 2, 3

175. Claims 2 and 3 identify physical properties of the polymer coatings in claim 1. I discuss claims 2 and 3 in Section G below.

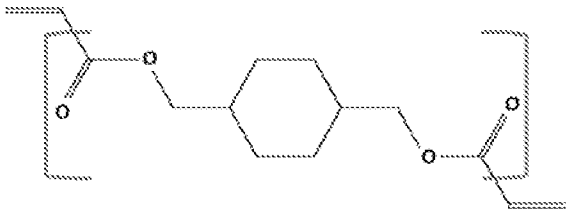
3. Claim 4

"The device or component according to claim 1, wherein when for compound (i) L is of the formula B, L has one of the following structures:

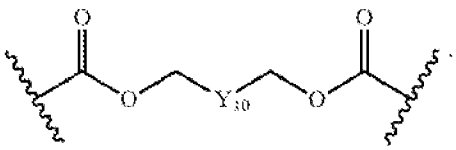


"

176. As noted above, the structure of CDMDA fits Formula B of claim 1. It further matches the fourth of the four bridging group structures specified in claim 4. I have provided the structure of CDMDA below, with the bridging group bracketed in red



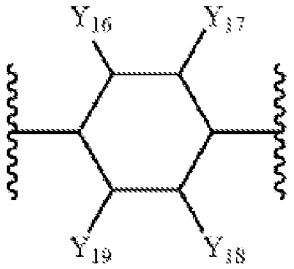
That bridging group of CDMDA matches the following claimed bridging group structure from claim 4



where for Y_{10} CDMDA has a 6-carbon cyclohexane ring consistent with Formula B2 of claim 1.

4. Claim 10

"The device or component according to claim 1, wherein when for compound (i) L is of formula B and Y_{10} has the following formula:



Y_{18} is H or vinylene, and Y_{16}, Y_{17} and Y_{19} are each H."

177. The bridging group of CDMDA has a 6-carbon ring identical to the one shown in claim 10, and the corresponding Y_{16}-Y_{19} positions in the ring of CDMDA are all occupied by hydrogen, just as specified in claim 10.

5. Claims 12-15

178. As I've already described, Coulson-122 and Badyal taught PFAC8 and PFMAC8 as monomers that would be used in the proposed combination of Padiyath, Coulson-122, and Badyal, and those monomers meet the requirements set forth in claims 12-15.

E. Ground 4: Coulson-122, Badyal, and Francesch

179. In my opinion, as explained in more detail below, claims 1-3, 5-8, and 11-15 of the '876 patent would have been obvious over Coulson-122 and Badyal combined with Francesch.

180. As previously explained, a POSA would have been aware of Coulson-122 and Badyal and would have been seeking known crosslinkers that fit Badyal's generic crosslinker structure with two double bonds and a bridging group and properties beneficial for preparing protective coatings for electronics. In my opinion, Francesch described applying plasma polymer coatings to silicon surfaces using a fluorinated methacrylate monomer and a known crosslinking reagent—BDVE—that a POSA would have considered suitable for preparing crosslinked coatings in view of Coulson-122 and Badyal.

1. Claim 1

181. Francesch taught the plasma copolymerization of a fluorine-containing methacrylate monomer (pentafluorophenyl methacrylate (PFM)) with two different crosslinkers, one of which was BDVE



in order to deposit crosslinked polymer coatings with improved solvent resistance onto silicon substrates. Ex. 1009 at 606-07, 610. The BDVE crosslinker taught by Francesch was also described by Holliday and fit the all the structural requirements given in claim 1 for the Formula A crosslinker, as I previously explained above.

A POSA would have used Francesch's BDVE crosslinker in the coatings described by Coulson-122 and Badyal

182. In my view, several factors would have motivated a POSA to use

BDVE as a crosslinker in combination with PFAC8 or PFMAC8 to prepare protective coatings on electronics in view of Coulson-122, Badyal, and Francesch. As I explained earlier when discussing Holliday, BDVE fit the structural requirements of Badyal's generic description of suitable crosslinking reagents known in the polymer field for copolymerizing with monomers like PFAC8 and PFMAC8, including two double bonds separated by an alkyl bridging group containing interposed oxygen atoms in the preferred embodiments. Ex. 1005 at 5:1-5, 5:18-6:20. Because BDVE contained interposed oxygen atoms in its alkyl bridging group, a POSA considering Francesch in view of Badyal would have preferred BDVE over the other crosslinker described by Francesch (1,7-octadiene). A POSA would have known that 1,7-octadiene lacks the interposed oxygen atoms in its alkyl bridging group as called out by Badyal.

183. Because Francesch described using BDVE as a crosslinker to create plasma polymer coatings by co-polymerizing with a fluorinated methacrylate (PFM), a POSA would have understood that BDVE was suitable for copolymerizing with such monomers belonging to the family of acrylate and methacrylate by plasma polymerization. Ex. 1009 at 606-10. That would have reinforced the POSA's understanding that BDVE would be compatible or plasma polymerizing with other fluorinated (meth)acrylates—including PFAC8 and PFMAC8—based on its qualifying as a "suitable" crosslinker structure under the criteria set forth by

Badyal. Ex. 1005 at 5:1-23.

184. Francesch taught that co-polymerizing BDVE with PFM under pulsed plasma yielded a copolymer film with improved solvent resistance and a continuous, pinhole-free surface covering the silicon wafer substrate. Ex. 1009 at 609-610, Fig. 3(b). A POSA would have wanted to achieve solvent resistance and a pinhole-free film surface when preparing a protective coating to provide a continuous barrier because solvent resistance provides added protection and improves polymer durability, and pinholes provide gaps in the polymer through which electrical current or corrosive substances like water vapor can pass. Francesch described plasma conditions that resulted in depositing the PFM/BDVE copolymer at a rate of 8 nm per hour. Ex. 1009 at 608. Francesch also described performing plasma deposition for 2-8 hours (Ex. 1009 at 607), so a POSA would have understood that deposition time multiplied by the disclosed deposition rate meant that Francesch described depositing films containing BDVE at a thickness of approximately 16-64 nm. A POSA would have recognized that coating thicknesses in that range were suitable for providing a protective coating on electronics. Ex. 1014 at 28:23-25; Ex. 1008 at [0053]. As a result, a POSA would also be aware that BDVE could be delivered as a vapor phase reagent into a vacuum chamber used for plasma polymerization. Ex. 1009 at 606-07, 610.

185. A POSA also would have reasonably expected to succeed in using the

proposed combination of BDVE and PFAC8 or PFMAC8 to prepare protective plasma polymer coatings based on Coulson-122, Badyal, and Francesch. As I have explained, plasma polymerization was routine by 2015. Both Badyal and Francesch taught that plasma copolymerization from a mixture containing a crosslinking monomer having two double bonds and a fluorine-containing monomer from the family of acrylate and methacrylate monomers, increased the durability of the resulting protective layer, so a POSA would have expected the combination of BDVE and PFAC8 or PFMAC8 (both fluorinated, acrylate-based monomers similar to PFM) to work together for plasma polymerization. Ex. 1005 at 7:4-9:26; Ex. 1009 at 606-07, 610. A POSA would have known that BDVE has a normal boiling point near and less than PFAC8 and PFMAC8, so the POSA would have expected that BDVE vapors could be readily supplied to a plasma chamber with vapors of PFAC8 or PFMAC8. A POSA also would have expected the resulting polymer coatings to exhibit protective properties. That would have included water repellence based on the properties associated with PFAC8- and PFMAC8-based coatings reported by Coulson-122 and Badyal as well as the hydrocarbon-based bridging group of BDVE. That also would have included barrier properties because Francesch described achieving smooth, continuous, pinhole-free upon crosslinking with BDVE. Ex. 1009 at 609-10, Fig. 3(b).

186. Finally, Francesch taught successfully applying plasma-polymer coat-

ings crosslinked with BDVE to silicon wafers (Ex. 1009 at 607), which a POSA would have recognized as a similar solid surface to many electronic components and devices. A POSA would have reasonably expected to succeed in coating electronic devices with a plasma polymer based on BDVE and PFAC8 and PFMAC8 due to the success with the solid surfaces of silicon substrates in Francesch combined with the extensive disclosures about protecting electronics using monomers like PFAC8 and PFMAC8 in Coulson-122 (Ex. 1004 at 1:3-7) and the teachings in Badyal about the substrate versatility of crosslinked PFAC8 or PFMAC8 coatings (Ex. 1005 at 9:28-34, 11:22-24).

2. Claims 2, 3

187. Claims 2 and 3 identify physical properties of the polymer coatings in claim 1. I discuss claims 2 and 3 in Section G below.

3. Claims 5 and 6

188. As I explained above under Ground 2, the BDVE crosslinker described by Francesch meets the structural limitations of claims 5 and 6.

4. Claim 7

"The device or component according to claim 5, wherein each Y_{12} is fluoro and each Y_{13} is fluoro."

189. As I explained above under Ground 2, it is my opinion that it would have been obvious to modify BDVE to obtain a fluorinated bridging group structure as specified in claim 7 in view of Badyal's disclosures of the increased hydro-

phobicity that can be achieved using perfluoroalkyl groups.

5. Claim 8

"The device or component claim 5, wherein n is from 4 to 6."

190. As I explained above under Ground 2, a POSA would have considered it obvious to modify BDVE to obtain the longer, more flexible and hydrophobic hydrocarbon chain in the bridging group to improve the properties of the resulting protective coatings.

6. Claims 11-15

191. In claim 11, BDVE is stated as a specified crosslinking reagent. Ex. 1001 at 20:67, 21:3-4.

192. As I've already described, Coulson-122 and Badyal taught PFAC8 and PFMAC8 as monomers that would be used in the proposed combination of Francesch, Coulson-122, and Badyal, and those monomers meet the requirements set forth in claims 12-15

F. Ground 5: Coulson-122, Badyal, and Tropsch

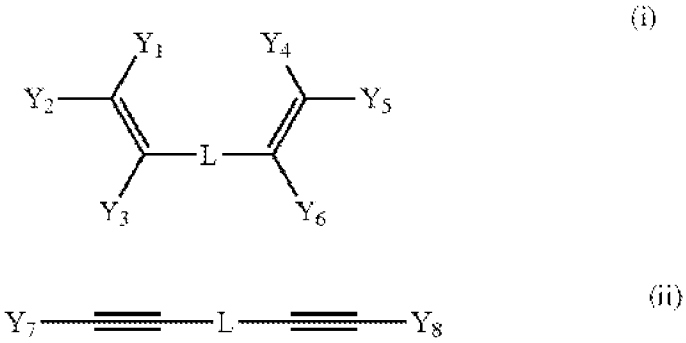
193. In my opinion, as explained in more detail below, claims 1-3, 5-8, and 12-15 of the '876 patent would have been obvious over Coulson-122 and Badyal combined with Tropsch.

194. As previously explained, Coulson-122 and Badyal would have prompted a POSA to seek known crosslinkers that fit Badyal's generic crosslinker structure with two double bonds and a bridging group and properties beneficial for

preparing protective coatings for electronics. Tropsch described a known crosslinking reagent that a POSA would have used for preparing crosslinked coatings in view of Coulson-122 and Badyal: 1,6-hexanediol divinyl ether (HDVE). Ex. 1011 at 4:34-38.

1. Claim 1

[*Element 1c*] "and wherein the crosslinking reagent comprises two or more unsaturated bonds attached by means of one or more linker moieties and has a boiling point of less than 500° C. at standard pressure, the crosslinking reagent having one of the following structures:



where Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7 and Y_8 are each independently selected from hydrogen, optionally substituted cyclic, branched or straight chain C_1-C_6 alkyl or aryl; and L is a linker moiety;"

195. Tropsch described using HDVE as a preferred crosslinking reagent for producing polymers. Ex. 1011 at 3:48-54, 4:34-38. As a POSA would have known, the structure of HDVE is as shown below:



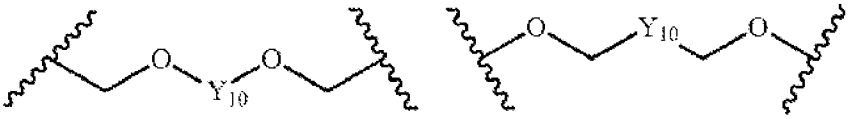
HDVE fit the structure (i) shown above in '876 claim 1, with two unsaturated

bonds having hydrogen at each of the Y1-Y6 positions and a bridging group between the two double bonds. A POSA would have known that the normal boiling point of HDVE is approximately 233°C (verified on chemspider.com using CAS No. 19763-13-4) (Ex. 1039 at 9). A POSA would have known that boiling point of HDVE, or would have been able to look it up using standard chemistry reference materials or determine it experimentally using basic laboratory techniques like measuring the temperature of a boiling sample of HDVE at standard pressure. A POSA also would have been able to accurately estimate the normal boiling point of HDVE using the Joback method (Ex. 1037) as I've shown below:

HDVE			
Group	*Contribution*	*No.*	*Total*
$=CH_2$	18.18	2	36.36
=CH-	24.96	2	49.92
$-CH_2-$	22.88	6	137.28
O nonring	22.42	2	44.84
Total			268.4
Boiling Point (K)			466.6
Boiling Point (°C)			193.45

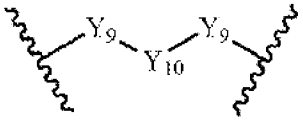
A POSA thus would have estimated the normal boiling point of HDVE to be approximately 193°C. That estimated value would have been well below 500°C, close to the actual normal boiling point, and lower than but near the normal boiling points of PFAC8 and PFMAC8.

[*Element 1d*] [*Formula A*] "wherein for compound (i) L is of formula A having one of the following structures:



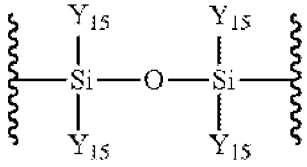
and Y_{10} is selected from optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene and a siloxane group; or

[*Formula B*] wherein for compound (i) L is of formula B having the following formula:



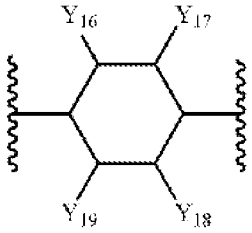
where each Y_9 is independently selected from, a bond, —O—, —O—C(O)—, —C(O)—O—, —Y_{11}—O—C(O)—, —C(O)—O—Y_{11}—, —OY_{11}—, and —Y_{11}O—, where Y_{11} is an optionally substituted cyclic, branched or straight chain C_1-C_8 alkylene; and

[*Formula B1*] wherein Y_{10} has the following formula:



and each Y_{15} is independently selected from optionally substituted branched or straight chain C_1-C_6 alkyl; or

[*Formula B2*] wherein Y_{10} has the following formula:



and Y_{16} to Y_{19} are each independently selected from H and optionally substituted branched or straight chain C_1-C_8 alkyl or alkenyl."

196. HDVE fit the structure shown on the right side of Formula A in claim 1. For HDVE, Y_{10} is a linear alkenyl chain having four carbon atoms (C4).

A POSA would have used Tropsch's HDVE crosslinker in the coatings described by Coulson-122 and Badyal

197. Tropsch described preparing polymers containing peroxycarboxyl groups. Ex. 1011 at 1:1-7. A disclosed preferred crosslinker in Tropsch was HDVE. Ex. 1011 at 3:48-54, 4:34-38. A POSA would have been motivated to use HDVE as a crosslinker in crosslinked Coulson-122/Badyal coatings for several reasons. HDVE was a crosslinker known in the polymer art, and HDVE's structure fell within Badyal's group of suitable crosslinkers, having two double bonds, R1-R6 being hydrogen, and a bridging group interposed with oxygen atoms separating the double bonds. Ex. 1005 at 5:1-23. In addition, based on the teachings of Tropsch, crosslinking building blocks can form a multitude of copolymers with one family of comonomers being the family acrylate and methacrylate monomers (Ex. 1011 at 3:1-8), which would have motivated at POSA to use HDVE as a crosslinker for the fluorine-containing monomers of Coulson-122 and Badyal include PFAC8 and PFMAC8 because those too are an acrylate and a methacrylate, respectively. A POSA also would have believed that the relatively long hydrophobic hydrocarbon chain of the HDVE bridging group would be suitable for preparing hydrophobic

polymer coatings, as would be preferred for protective coatings for use on electronics. A POSA would be aware that the normal boiling points of HDVE is approximately 233°C. That value would have suggested to a POSA that HDVE would have sufficient volatility for use as a reactant vapor for plasma co-polymerization with PFAC8 or PFMAC8, which have similar normal boiling points. Altogether, those various factors known to a POSA would have motivated combining Coulson-122, Badyal, and Tropsch to prepare electronics with a protective plasma polymer coating made using PFAC8 or PFMAC8 and HDVE as a crosslinker.

198. In my opinion, a POSA also would have reasonably expected to succeed with the proposed combination using HDVE as a crosslinker. Plasma polymerization was routine by 2015. Tropsch taught using various initiation techniques for polymer production using the disclosed crosslinkers, such as suspension polymerization and free-radical initiation using hydrogen peroxide. Ex. 1011 at 5:7-30. A POSA would have expected HDVE could be similarly polymerized with plasma methods given that activation methods could typically be substituted for one another when using reagents that can be polymerized, and especially given the similar polymerization processes that occur in free-radical and plasma polymerization. A POSA further would have recognized that HDVE is structurally similar to BDVE (the alkenyl chain in HDVE's bridging group is two carbons longer than BDVE), which was known to be suitable for crosslinking a fluorinated acrylate by

plasma polymerization (Ex. 1009 at 606-07), so a POSA would have expected similar results with HDVE.

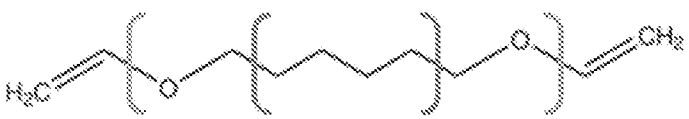
199. A POSA also would have expected compounds like HDVE that fit Badyal's generic crosslinker structure to successfully co-polymerize with the PFAC8/PFMAC8 monomers of Coulson-122 and Badyal because Badyal taught that such crosslinkers would work. Ex. 1005 at 4:17-5:19. In addition, Tropsch taught that its crosslinkers, which included HDVE as preferred, could be polymerized with acrylates (Ex. 1011 at 3:1-10, 4:34-38), which would have supported a reasonable expectation that HDVE could successfully crosslink other acrylate and methacrylate monomers like PFAC8 and PFMAC8.

2. Claims 2, 3

200. Claims 2 and 3 identify physical properties of the polymer coatings in claim 1. I discuss claims 2 and 3 in Section G below.

3. Claims 5, 6, and 8

201. The bridging group of HDVE met every additional limitation specified for the bridging group in claims 5, 6, and 8. I have provided the structure of HDVE below, with the bridging group bracketed in blue and the Y10 group bracketed in red:



202. Claim 5 specifies that Y_{10} takes the form of a carbon chain with between 1 and 10 carbon atoms in the chain, and the Y_{12} and Y_{13} groups bound to each carbon in the chain can be a number of substituents, including hydrogen. Ex. 1001 at 20:18-33. In HDVE, the Y_{10} carbon chain (red bracket) has four carbon atoms, which is an integer between 1 and 10 as claimed. In addition, each carbon in the Y_{10} carbon chain is $–CH_2–$ meaning that all of the Y_{12} and Y_{13} groups are hydrogen. Claim 6 limits each Y_{12} and Y_{13} groups to being hydrogen, which is again satisfied by the structure of HDVE.

203. Claim 8 specifies that the Y_{10} carbon chain must have a backbone of between 4 and 6 carbon atoms (n = 4, 5, or 6). In HDVE, the Y_{10} carbon chain is $(–CH_2–)_4$ (i.e., n = 4), so HDVE satisfies claim 8 as well.

4. Claim 7

"The device or component according to claim 5, wherein each Y_{12} is fluoro and each Y_{13} is fluoro."

204. A POSA would have known that perfluorinated alkyl chains confer strong hydrophobicity. Ex. 1005 5:18-23, 10:32-11:1; Ex. 1019 at 2031. In addition, Badyal taught that the bridging group in a suitable crosslinker could be perfluorinated. Ex. 1005 at 5:18-23. And a POSA would have known that water-repellency was desirable when making protective coatings for electronics. Ex. 1004 at 4:9-15. In my opinion, a POSA considering Tropsch, Coulson-122, and Badyal therefore would have been motivated to substitute fluorine at every Y_{12} and

Y_{13} position in HDVE to improve hydrophobicity in the resulting protective coatings. A POSA would have retained HDVE's alkylene (CH_2) groups separating the Y_{12} and Y_{13} groups from the oxygen of the ether groups to maintain a spacer between the oxygen and fluorocarbon moieties to promote stability of the resulting fluorine-substituted crosslinking reagent. Ex. 1038 at [0005-06]. In addition, a POSA in 2015 would have reasonably expected to succeed in obtaining and using the fluorine-substituted version of HDVE because methods to prepare fluorine-substituted divinyl ethers were known, Ex. 1038, and because Badyal taught that the crosslinker's bridging group could include perfluoroalkyl groups, Ex. 1005 at 5:18-6:13.

5. Claims 12-15

205. As I've already described, Coulson-122 and Badyal taught PFAC8 and PFMAC8 as monomers that would be used in the proposed combination of Tropsch, Coulson-122, and Badyal, and those monomers meet the requirements set forth in claims 12-15.

G. All Grounds: Claims 2 and 3

206. In my opinion, as explained in more detail below, claims 2 and 3 of the '876 patent would have been obvious over Coulson-122 and Badyal combined with any of Cohen, Holliday, Padiyath, Francesch, and Tropsch.

1. Claim 2

"The device or component according to claim 1, wherein the protective cross-linked polymeric coating is a physical barrier to mass and electron transport."

207. Claim 2 specifies that the coating is a physical barrier to mass and electron transport. To a POSA, a barrier to electron transport is something that impedes electrical conductance, often referred to as an electrical insulator (Ex. 1012 at 1:9-18), and that is consistent with the '876 patent's description of the coatings as able to provide electrical insulation. Ex. 1001 at 3:41, 4:7, 4:14-15. Providing electrically insulating coatings on electrical components and devices has long been known and desired to protect such components from short circuits and other electrical damage. Ex. 1007 at 1:10-52, 2:17-35; Ex. 1012 at 7:8-10; Ex. 1018 at 1:6-28; Ex. 1033 at [0001-04], [0015-16]. Similarly, a barrier to mass transport impedes passage of molecules having mass such as liquids and gases, consistent with the '876 patent's discussion of restricting the passage of water, oxygen, and ions. Ex. 1001 at 3:1-6. It was also well known that providing protective coatings for electronics that could restrict passage of such molecules was helpful for preventing corrosion by preventing those molecules from contacting the underlying electronics. Ex. 1008 at [0023-24]; Ex. 1013 at [0004]; Ex. 1007 at 1:50-52; Ex. 1014 at 1:14-17; Ex. 1029 at 6207-08, 6210.

208. A POSA would have known that plasma polymer coatings applied us-

ing fluorinated acrylate-based monomers including PFAC8 and PFMAC8 taught by Coulson-122 and Badyal provided electrically insulating and barrier properties. Ex. 1012 at 7:3-21, 13:3-14; Ex. 1014 at 4:22-55, 16:7-27. In general, a POSA would have expected crosslinking to improve the barrier and insulating properties of coatings made with those fluoroacrylates because crosslinking was known to yield more amorphous (less crystalline) polymer structure, reducing surface roughness and thus the incidence of channels or gaps (pinholes) forming in the coating. Ex. 1026 at 6550-53. A POSA would have known that channels typically present in crystalline coatings with rough, irregular surfaces could allow corrosive molecules like oxygen or water vapor to pass through to the substrate or provide a pathway for electrical conductance across the coating.

209. Consistent with those expectations, a POSA also would have known that many crosslinkers also including DVTMDS, DCHD, BDVE, and CDMDA had been associated with barrier and/or insulating properties when used in polymer coatings. DVTMDS had been used in electrically insulating coatings. Ex. 1006 at 5:1-12; Ex. 1018 at 1:6-11, 3:50-4:25; Ex. 1017 at 3:27-4:20; Ex. 1033 at [0002], [0040]. DVTMDS had also been used in barrier coatings. Ex. 1017 at 3:27-4:20. DCHD and BDVE had been used in coatings provided to achieve electrical insulation, reduced permeability, and chemical or solvent resistance. Ex. 1007 at 5:48-54, 1:10-51; Ex. 1009 at 610. CDMDA had been taught for use in preparing polymer

layers to provide a barrier against water and oxygen. Ex. 1008 at [0023-24]. Accordingly, a POSA would have expected coatings prepared using PFAC8 or PFMAC8 and a crosslinking reagent as in Grounds 1-5 to exhibit barrier and insulating properties at least as effective as those provided by coatings based on PFAC8 or PFMAC8 alone.

210. A POSA who desired to prepare a plasma-polymer coating with barrier properties using those materials also would have known that, as a basic principle, the ability of a coating to provide insulation and block the passage of contaminants from the environment typically increases as the thickness of the coating increases. Ex. 1013 at [0039]. The POSA would have known that the thickness of a plasma polymer coating can be increased by increasing the polymerization time. Ex. 1014 9:15-17, 28:23-25; Ex. 1009 at 608. It therefore would have been straightforward for a POSA seeking to enhance barrier properties in a crosslinked coating based on the combinations of monomers and crosslinkers described in Grounds 1-5 to do so by increasing the substrate's plasma exposure time to provide a coating with greater thickness and testing the resulting coatings at various thicknesses to verify that the desired barrier properties had been achieved.

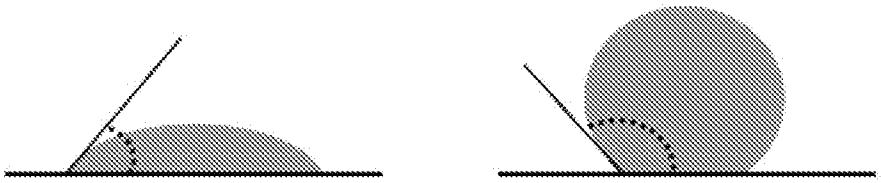
211. In addition, a POSA would have known that the properties of a copolymer depend on its components. Both the monomers, PFAC8 or PFMAC8, and crosslinkers, including at least DVTMDS, DCHD, BDVE, and CDMDA, were

known to yield units in polymeric coatings with the barrier properties in claim 2. Therefore, a POSA would have expected that co-polymer coatings produced using those components in combination would necessarily exhibit the properties in claim 2.

2. Claim 3

"The device or component according to claim 1, wherein the protective cross-linked polymeric coating forms a liquid repellent surface defined by a static water contact angle (WCA) of at least 90°."

212. Claim 3 specifies that the coating has a static water contact angle (WCA) of at least 90°C. A POSA would have known WCA as a standard metric for measuring the hydrophobicity of a surface. In general, the test is performed by placing a droplet of a liquid, such as water, on a surface to be tested and then measuring the angle formed by the liquid where it contacts the surface, as I've shown below:



A POSA would have understood that, generally speaking, the larger the contact angle, the more liquid-repellent the surface is considered to be. Ex. 1013 at [0041]; Ex. 1015 at [0011-17], Figs. 1-2; Ex. 1012 at 11:4-11; Ex. 1014 at 12:4-5; Ex. 1029 at 6204-06 and Fig. 19. Thus, a POSA would have concluded that the surface

illustrated on the right in the diagram above is more water-repellent that the surface on the left. As a general benchmark, a 90° contact angle was often considered a cutoff between hydrophobic and non-hydrophobic surfaces. Ex. 1013 at [0041]. A high WCA manifests in the commonly observed phenomenon of water beading on a hydrophobic surface, such as a lotus leaf or a newly waxed finish on a car.

213. As I have discussed, fluorinated monomers like the PFAC8 and PFMAC8 monomers described by Coulson-122 and Badyal were well known to yield surfaces that have hydrophobic properties and form water-repellent coatings when applied to a surface by plasma polymerization. Ex. 1004 at 3:14-4:3, 12:7-22, 13:30-14:23; Ex. 1019 at 2037-38; Ex. 1012 at 10:13-11:11; Ex. 1014 at 13:30-14:23; Badyal; Ex. 1029 at 6204-06. A POSA looking at the known bridging structures of the crosslinkers in Ground 1-5 (DVTMDS, DCHD, BDVE, CDMDA, and HDVE) would have expected that those compounds would exhibit hydrophobicity. The bridging structures for DCHD, BDVE, CDMDA, and HDVE are made up primarily of alkyl hydrocarbon groups, which were well known to be hydrophobic. Ex. 1005 at 4:21-23. The siloxane bridging group in DVTMDS with its four methyl substituents also would have been well known to a POSA as being associated with hydrophobicity. Ex. 1014 at 4:5-5:13, 16:7-14. A POSA therefore would have found hydrophobicity, with a WCA of at least 90° to be an obvious an expected property when preparing plasma coatings made with the perfluorinated PFAC8 or

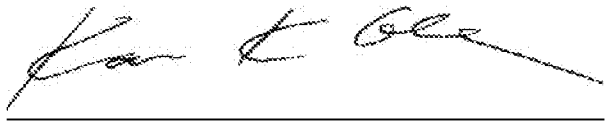
PFMAC8 monomers in combination with any of the organic crosslinkers specified in Grounds 1-5.

214. The molecular composition of a polymer determines its hydrophobicity. Because PFAC8 and PFMAC8 are inherently hydrophobic due to their perfluorinated chains (Ex. 1029 at 6204-06; Ex. 1005 at 4:23-25, 9:10-26, 8:15-19; Ex. 1016 at 4:41-44), and because the crosslinking reagents cited in Grounds 1-5 also consisted primarily of hydrophobic bridging groups, combining those reagents naturally and necessarily would have resulted in a co-polymer with hydrophobic properties, as characterized by a WCA of at least 90°.

I hereby declare that all the statements made in this Declaration are of my own knowledge and true; that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I declare under the penalty of perjury that all statements made in this declaration are true and correct.

Date: July 9, 2020



Karen K. Gleason, Ph.D.

Curriculum Vitae
Karen K. Gleason

Massachusetts Institute of Technology (MIT)
Department of Chemical Engineering
77 Massachusetts Avenue, Room 3-240
Cambridge, MA 02139-4307

T: 617-253-5066
E: kkg@mit.edu

Education

Ph.D. Chemical Engineering, University of California, 1987
M.S. Chemical Engineering, Massachusetts Institute of Technology, 1982 (simultaneous with B.S.)
B.S. Chemistry, Massachusetts Institute of Technology, 1982

Professional Experience

1/16/2020-present	Alexander and I. Michael Kasser Professor of Chemical Engineering, MIT, Emerta
7/2006–1/15/2020	Alexander and I. Michael Kasser Professor of Chemical Engineering, MIT
42014–62018	Associate Provost, MIT, with primary responsibilities for space allocation, planning, and management of the renovation budget, along with oversight of MIT's industrial engagements, Technology Licensing Office (TLO), and Industrial Liaison Program (ILP). Co-chair of the Information Technology Governance Committee (ITGC).
4/2008–1/2011	Associate Dean of Engineering for Research, MIT
7/2005–4/2008	Associate Director, Institute for Soldier Nanotechnologies, MIT
7/2001–6/2004	Executive Officer (Vice-chair), Department of Chemical Engineering, MIT
7/2000–6/2006	Professor, MIT
7/1993–6/2000	Associate Professor, MIT
6/1991–5/1995	Esther and Harold E. Edgerton Career Development Professor, MIT
9/1987–6/1993	Assistant Professor, MIT
9/1987–6/1990	Herman P. Meissner Career Development Professor in Chemical Engineering, MIT
11/2014-present	Co-founder and Principle Scientist, DropWise (drop-wise.com), Cambridge, MA. DropWise won the Gold Prize at MassChallenge in 2014 for technology to improve the efficiency and reduce the carbon emissions of power plants by controlling the mechanism by which steam condenses on surfaces.
5/2001–present	Co-founder and Chief Scientific Advisor, GVD Corporation (gvdcorp.com), Cambridge, MA (headquarters) and Greenville, SC (manufacturing). GVD offers custom surface modification services and equipment. Products in include RapidRelease™ coatings applied to the molds used in the manufacture of tires, Enduro™ hydrophobic release layers on advanced gaskets, and Excilis™ encapsulation layers for the protection of printed circuit boards,

Honors

ICI Canada Distinguished Lectureship Series, University of Calgary, 2020 (upcoming)
John M. Prausnitz American Institute of Chemical Engineering Institute Lecturer Award, 2019
Elected to the National Academy of Engineering, 2015
Charles M.A. Stine Award, American Institute of Chemical Engineers, 2015
International Union of Pure and Applied Chemistry, Distinguished Women in Chemistry or Chemical Engineering Award, 2015
Adel Sarofilm Distinguished Lecture, University of Utah, 2015
Fellow, American Institute of Chemical Engineering, 2013
American Institute of Chemical Engineering Process Development Research Award, 2012
ID TechEx Printed Electronics Europe Best Technical Development Materials Award, 2011
Tis Lahiri Lectureship, Department of Chemical Engineering, Vanderbilt University, 2013

Favored Ex. 1003

Mawson Lectureship, University of South Australia, December 2009

Visiting Professor, Donders Chair, Utrecht University, Netherlands, 2006

Excellence Award for Research in Manufacturing and Environment, Safety and Health, sponsored by Semiconductor Research Corporation and International SEMATECH, 2000

Van Ness Lectureship, Department of Chemical Engineering, Rensselaer Polytechnic Institute, 2000

Keynote Speaker, Dielectrics for ULSI Multilevel Interconnection Conference, San Jose, CA 1999

National Science Foundation Presidential Young Investigator Award, 1990–1995

Office of Naval Research Young Investigator Program, 1990–1993

Materials Research Society Graduate Student Award, 1986

Amoco Foundation Fellowship, 1982–1985

National Collegiate Athletic Association (NCAA) Postgraduate Fellowship, 1982–1983

MIT Outstanding Scholar Athlete, 1982

Warren K. Lewis Fellowship, 1981–1982

Corning's Women in Engineering Fellowship, 1981

Captain, MIT Women's Swimming Team, 1980–1982

All-American NCAA Division III Swimming, 1978–1982

National Merit Scholarship, 1978

Westinghouse Science Talent Search Semifinalist, 1978

Professional Society Memberships

American Chemical Society

American Institute of Chemical Engineers

American Vacuum Society

Electrochemical Society

Materials Research Society

Professional Service Activities

9/2018-present	Deputy Editor, *Science Advances* (AAAS)
12/2019	Co-organizer Symposium FF05: Materials Research Society Meeting, Boston, MA
4/2017	Lead organizer for Rising Stars in Chemical Engineering, October 4 & 5, 2018, MIT (https://cheme.mit.edu/rising-stars/)
5/2018	Co-organizer Symposium S: European Materials Research Society Meeting, Strasbourg, France.
9/2015-8/2018	American Institute of Chemical Engineering (AIChE) Awards Selection Committee
9/2015-8/2018	American Institute of Chemical Engineering (AIChE) Braskem Award Selection Committee
9/2015-present	MIT Deshpande Center Steering Committee
5/2015-6/2018	University Advisory Board of the HKUST-MIT Alliance
4/2015-6/2018	MIT-Philips Alliance Steering Committee
11/2014-10/2015	Massachusetts Competitive Partnership Academic Committee
4/2014-6/2018	Ragon Institute Steering Committee
4/2014-3/2016	Dupont-MIT Alliance Steering Committee
6/2013–present	Executive Advisory Board, *Advanced Materials Interfaces* (Wiley)
2012–2014	Scientific Committee, International Conference on Desalination using Membrane Technology
2009–2014	External Advisory Board, Center for Hierarchical Manufacturing, University of Massachusetts–Amherst
6/2009	Guest Editor, Special Issue on CVD of Polymeric Materials in *Chemical Vapor Deposition*
8/2008	Chair, 5th International Conference on Hot-Wire Chemical Vapor Deposition
2007–present	Editorial Board, *Chemical Engineering Communications* (Taylor and Francis)
2005–2013	Editorial Board, *Plasma Processes and Polymers* (Wiley)
2004–present	International Organizing Committee, International Conference on Hot-Wire CVD
1998	Chair, Gordon Conference on Diamond Synthesis, Oxford, UK

Issued US Patents

1. Gleason KK, Limb SJH, Gleason EF, Sawin HH, Edell DJ. 1999. "Chemical vapor deposition of fluorocarbon polymer thin films," US Patent No. 5,888,591, issued 03/30/1999.
2. Gleason KK, Kwan MC. 2000. "Pyrolytic chemical vapor deposition of silicone films," US Patent No. 6,045,877, issued 04/04/2000.
3. Gleason KK, Limb SJH, Gleason EF, Sawin HH, Edell DJ. 2000. "Chemical vapor deposition of fluorocarbon polymer thin films: 1st divisional application," US Patent No. 6,153,269, issued 11/28/2000.
4. Gleason KK, Limb SJH, Gleason EF, Sawin HH, Edell DJ. 2000. "Chemical vapor deposition of fluorocarbon polymer thin films: 2nd divisional application," US Patent No. 6,156,435, issued 12/05/2000.
5. Gleason KK, Ober C, Herr D. 2003."Solventless, resistless, direct dielectric patterning," US Patent No. 6,509,138, issued 01/21/2003.
6. Gleason KK, Murthy SK. 2005. "Fluorocarbon-organosilicon copolymers and coatings prepared by hot-filament CVD," US Patent 6,887,578, issued 05/03/2005.
7. Gleason KK, Ober C, Herr D. 2005." "Electrical device including dielectric layer formed by direct patterning process," US Patent No. 6,946,736, issued 09/20/2005.
8. Gleason KK, Loo LSS, Lipson M, Kimerling LC. 2007. "Air gaps for optical applications," US Patent No. 7,227,678, issued 06/05/2007.
9. Gleason KK, Lock J, Kimerling LC. 2007. "Polysilane thin films for directly patternable waveguides," US Patent No. 7,190,871, issued 03/13/2007.
10. Gleason KK, Wu Q, Ross A. 2006. "Porous material formation by chemical vapor deposition onto colloidal crystal templates," US Patent No. 7,112,615, issued 09/26/2006.
11. Gleason KK, Chan K. 2008. "Chemical vapor deposition of hydrogel films," US Patent No. 7,431,969, issued 10/07/2008.
12. Gleason KK, Martin TP, Chan K. 2009. "Chemical vapor deposition of antimicrobial polymer coatings," US Patent No. 7,563,734, issued 07/21/2009.
13. Gleason KK, Lock J. 2009. "Oxidative chemical vapor deposition of electrically conductive and electrochromic polymers," US Patent No. 7,618,680, issued 11/17/2009.
14. Gleason KK, Rutledge GC, Gupta M, Ma M, Mao Y. 2010. "Superhydrophobic fibers produced by electrospinning and chemical vapor deposition," US Patent No. 7,651,760, issued 01/26/2010.
15. Gleason KK, Vanddiraju S. 2012. "Light emitting device including semiconductor nanocrystals," US Patent No. 8,106,420, issued 01/31/2012.
16. Gleason KK, Xu J. 2013. "Hard, impermeable, flexible, and conformal organic coatings," US Patent No. 8,372,928, issued 02/12/2013.
17. Gleason KK, Arora WJ, Barbasthathis G, Tenhaeff WE. 2013. "Electro-mechanical switches and methods of use thereof," US Patent No. 8,441,081, issued 05/14/2013.
18. Gleason KK, Clark HA, Baxamusa S, Dubach JM. 2013. "Coated sensors and methods related thereto," US Patent No. 8,470,300, issued 06/25/2013.
19. Gleason KK, Bhattacharyya D. 201. "Biosensors," US Patent No.9034659, issued 5/19/2015.
20. Gleason KK, Kong J, Park H, Howden RM. "Devices comprising graphene and a conductive polymer and related systems and methods, 2012." US Patent No. 9136488, issued 9/15/2015.
21. Gleason KK, Petruczok CD, "Three-Dimensional Photoresists via Functionalization of Polymer Thin Films Fabricated by iCVD", US Patent No. 9163307, issued 10/20/2015.
22. Gleason KK, Bulovic V, Barr MC, Rowehl J. "Conductive Polymer on a Textured or Plastic Substrate", US Patent No. 9214639, issued 12/15/2015.
23. Handy ES, White AJ, O'Shaughnessy WS, Pryce Lewis HG, Bansal NP, Gleason, KK, "Methods for coating articles" United States Patent 9,387,508, issued 7/12/2016.

24. Arora, W.J.; Gleason, K.K.; Barbastathis, G.; Tenhaeff, W.E.; "Electro-mechanical switches and methods of use thereof", United States Patent 9,448,219, issued September 20, 2016.
25. Paxton, A.T.; Yague, J.L.; Varanasi, K.K.; Gleason, K.K. Liu, A. "Grafted polymer surfaces for dropwise condensation, and associated methods of use and manufacture", United States Patent 9,498,934, issued November 22, 2016.
26. Gleason, K.K.; Im, S.G. "Conductive polymer films grafted on organic substrates", United States Patent 9,530,965, issued December 27, 2016.
27. Barr M.C.; Gleason, K.K. Carbonera, C., Po, R., Bulovic, V. "Cathode buffer materials and related devices and methods", United States Patent 9,553,268, issued January 24, 2017
28. Gleason, K.K.; Khan, Z.; Shafi, H.Z.; Yang, R.; "Development of zwitterionic coatings that confer ultra anti-biofouling properties to commercial reverse osmosis membranes", United States Patent 9,598,598, issued March 21, 2017.
29. Gleason, K.K.; Yang, R.; Segal, Y.; Buonassisi, T.; Jayan, B.R.; "Fabrication and passivation of silicon surfaces", United States Patent 9,656,294, issued May 23, 2017.
30. White, A.J.; O'Shaughnessy, W.S.; Handy, E.S.; Lewis, H.G.P.; Gleason, K.K. "Coatings for electrowetting and electrofluidic devices", United States Patent 9,714,463, issued July 25, 2017.
31. Gleason, K.K.; Bulovic, V.; Barr, M.C.; Borrelli, D.C. "Methods for fabricating devices including photovoltaic devices", United States Patent 9,793,479, issued October 17, 2017.
32. Colton, C.K.; Gleason, K.K.; Coclite, Anna M.; Dilenno, Amanda R. "Articles and methods for stem cell differentiation", United States Patent 9,816,070, issued November 14, 2017.
33. Gleason, Karen K.; Coclite, A.M. Methods of coating surfaces using initiated plasma-enhanced chemical vapor deposition", United States Patent 9,884,341, issued February 6, 2018
34. Bhattacharyya D; Gleason K; Barr MC, "Single-unit reactor design for combined oxidative, initiated, and plasma-enhanced chemical vapor deposition", United States Patent 9,957,618, issued May 1, 2018
35. Hart, Anastasios John; Kim, Sanha; Sojoudi, Hossein; Gleason, Karen K.;" Nanoporous stamp for flexographic printing" 10,118,426, issued November 6, 2018
36. Gleason, Karen K.; Wang, Minghui; Boscher, Nicolas D.; Choquet, Patrick, "Ultra-thin, Pinholes-free, Flexible Metal-Organic Films" United States Patent 10,155,843, issued December 18, 2018
37. Liu, Andong, Gleason Karen K, Wang, Minghui, "Vapor-deposited nanoscale ionic liquid gels as gate insulators for low-voltage high-speed thin film transistors", United States Patent 10,510,971, issued December 17, 2019
38. Gleason, Karen K; Yang, Rong, "Antifouling and chlorine-resistant ultrathin coatings on reverse osmosis membranes", United States Patent 10,519,326, issued December 31, 2019
39. White, Aleksandr J.; O'Shaughnessy, William Shannan; Johnson, Seth; Gleason, Karen K; "Liquid-impregnated coatings and devices containing the same", United States Patent 10,519,326, issued January 28, 2020.

Books and Book Chapters

1. Matsumura H., Umemoto H., Gleason KK, and Schropp R.E.I. (2019*) Catalytic Chemical Vapor Deposition: Technology and Applications of Cat-CVD*, Wiley, ISBN 9783527818662
2. Wang X, Gleason KK (2019) oxidative Chemical Vapor Deposition for Conjugated Polymers: Theory and Applications, chapter for *Conjugated Polymers: Perspective, Theory, and New Materials*, CRC Press, edited by Reynold JR Thompson BC, and Skotheim TA.
3. Gleason KK (2019) Organic Surface Functionalization by initiated Chemical Vapor Deposition (iCVD), chapter for *Surface Modification of Polymers: Methods and Applications* (Wiley) ISBN: 9783527345410, edited by Thiery D. and Pinson J.
4. Gleason KK, editor (2015). *CVD Polymers. Fabrication of Organic Surfaces and Devices* (Wiley) ISBN-13: 978-3527337996 ISBN-10: 3527337997\

5. Gleason KK (2015). Overview of Chemically Vapor Deposited (CVD) Polymers, chapter for *CVD Polymers. Fabrication of Organic Surfaces and Devices* (Wiley), edited by Gleason KK, p. 1-9.
6. Yague J, Gleason KK (2014). Vapor Deposition of Fluoropolymer Surfaces, chapter for *Handbook of Fluoropolymer Science and Technology*, Wiley, edited by Smith DW, Iacono ST, and Iyer SS, p. 133-149.
7. McNamara KM and Gleason KK (1998). Characterization of Diamond, chapter for *Industrial Handbook for Diamond and Diamond Films*, Marcel Dekker, edited by Bigelow K, p. 413-480
8. Gleason KK (1996). Multiple Quantum NMR in Solids, chapter for *Encyclopedia of Nuclear Magnetic Resonance*, Wiley, edited by Grant DM and Harris RK, vol. 5, p. 3163-3172.
9. Gleason KK (1996). Diamond Thin Films, chapter for *Encyclopedia of Nuclear Magnetic Resonance*, Wiley, edited by Grant DM and Harris RK, vol. 5, p. 1592-1599.

Publications in Refereed Journals

1. Gharahcheshmeh MH, Tavakoli MM, Gleason EF, Robinson MT, Kong J, Gleason, KK (2019) tuning, optimization, and perovskite solar cell device integration of poly(3,4-ethylene dioxythiophnene) films via a single-step all-dry process, *Science Advances*, 5(11) eaay0414 doi:10.1126/sciadv.aay0414.
2. Gharahcheshmeh MH, Gleason, KK (2019) Hall of Fame Article: Device Fabrication Based on Oxidative Chemical Vapor Depostion (oCVD) Synthesis of Conducting Polymers and Related Conjugated Organic Materials, *Adv. Mater. Interfaces*, 6, 1801564 doi: 10.1002/admi.201970016
3. Zhou Y, Wang X, Acauan L, Kalfon-Cohen E, Ni X, Stein Y, Gleason KK, Wardle BL (2019) Ultrahigh-Areal-Capacitance Flexible Supercapacitor Electrodes Enabled by Conformal P3MT on Horizontally Aligned Carbon-Nanotube Arrays, *Adv. Mater.* 31(30), 1901916 doi: 10.1002/adma.201901916
4. Schroder S, Strunskus T, Rehders D, Gleason KK, Faupel F (2019) Tunable polytetrafluoroethylene electret films with extraordinary charge stability synthesized by initiated chemical vapor deposition for organic electronics applications, Scientific Reports 9, 2237 doi: 10.1038/s41598-018-38390-w.
5. Aktas, OC, Schroder S, Veziroglu S, Ghori MZ, Haidar A, Polonskyi O, Strunskus T, Gleason K, Faupel F (2019) Superhydrophobic 3D Porous PTFE/TiO2 Hybrid Structures, *Adv. Mater. Interfaces*, 6(4) 1801967, doi: 10.1002/admi.201801967
6. Khalil K, Soto D, Farnham T, Paxson A, Katmis AU, Gleason KK, Varanasi, KK, Grafted Nanofilms Promote Dropwise Condensation of Low-Surface-Tension Fluids for High-Performance Heat Exchangers, *Joule*, 3, 1377-1388, doi: 10.1016/j.joule.2019.04.009
7. Sojoudi H, Nemani SK, Mullin KM, Wilson MG, Aladwani, H, Lababidi H, Gleason, KK (2019) Micro-Nanoscale Approach for Studying Scale Formation and Developing Scale-Resistant Surfaces, *ACS Appl. Mater. & Interfaces*, 11(7), 7330-7337, doi: 10.1021/acsami.8b18523
8. Zhao J, Wang M, Jebuti M, Zhu M, Gleason KK (2019) Fundamental nanoscale surface strategies for robustly controlling heterogeneous nucleation of calcium carbonate, *J. Mater. Chem. A*, 7, 17242-17247 doi: 10.1039/C9TA04341A
9. Dolejsi M, Moni P, Bezik CT, Zhou C, de Pablo JJ, Gleason KK, Nealey PF (2019) Ultrathin initiated chemical vapor deposition polymer interfacial energy control for directed self-assembly hole-shrink applications, *J. Vacuum Sci. Technol. B*, 37, 061804 doi:10.1116/1.5121541
10. Wang XX, Zhang X, Sun L, Lee D, Lee S, Wang MH, Zhao JJ, Shao-Horn Y, Palacios T, Gleason KK (2018) High electrical conductivity and carrier mobility in oCVD PEDOT thin films by engineered crystallization and acid treatment, *Science Advances*, **4**, article no. eaat5780 doi: 10.1126/sciadv.aat5780

11. Xu Y, Wang XX, Zhou J, Song B, Zhang J, Lee EMY, Huberman S, Gleason KK, Chen G (2018) Molecular Engineered Conjugated Polymer with High Thermal Conductivity, *Science Advances*, **4**, article no. eaar3031 doi: 10.1126/sciadv.aar3031
12. Mao XM, Lui AD, Tian WD, Wang XX, Gleason KK, Hatton TA (2018) Enhancing Performance Stability of Electrochemically Active Polymers by Vapor-Deposited Organic Networks, *Advanced Functional Materials*, **28**, article no. 1706028 doi: 10.1002/adfm.201706028.
13. Sojoudi H, Arabnejad H, Raiyan A, Shirazi, SA, McKinley GH, Gleason KK (2018) Scalable and Durable Polymeric Icephobic and Hydrate-Phobic Coatings, 14, 3443-3464 *Soft Matter* doi: 10.1039/C8SM00225H
14. Zhao JJ, Wang MH, Lababadi HMS, Al-Adwani H, Gleason KK (2018) A review of heterogeneous nucleation of calcium carbonate and control strategies for scale formation in multi-stage flash (MSF) desalination plants, *Desalination*, **442**, 75-88 doi: 10.1016/j.desal.2018.05.008
15. Moni P, Suh HS, Dolejsi M, Kim DH, Mohr AC, Nealy PF, Gleason KK (2018) Ultrathin and Conformal Initiated Chemical-Vapor-Deposited Layers of Systematically Varied Surface Energy for Controlling the Directed Self-Assembly of Block Copolymers, *Langmuir*, **34**, 4494-4502 doi: 10.1021/acs.langmuir.8b00173
16. Soto D, Ugur A, Farnham TA, Gleason KK, Varanasi KK (2018) Short-Fluorinated iCVD Coatings for Nonwetting Fabrics, *Advanced Functional Materials*, **28**, article no. 1701355 doi: 10.1002/adfm.201707355
17. Moni P, Mohr AC, Gleason KK (2018) Growth Rate and Cross-Linking Kinetics of Poly(divinyl benzene) Thin Films Formed via Initiated Chemical Vapor Deposition, *Langmuir*, **34**, 6687-6696 doi: 10.1021/acs.langmuir.8b00624
18. Mao XM, Lui AD, Tian WD, Wang XX, Gleason KK, Hatton TA (2018) Enhancing Performance Stability of Electrochemically Active Polymers by Vapor-Deposited Organic Networks, *Advanced Functional Materials*, vol. 28, no. 10, article no. 1706028 doi: 10.1002/adfm.201706028.
19. Lee S, Borrelli DC, Jo WJ, Reed AS, Gleason KK (2018) Nanostructured Unsubstituted Polythiophene Films Deposited using oxidative Chemical Vapor Deposition: Hopping Conduction and Thermal Stability, *Advanced Materials Interfaces doi: 10.1002/admi.201701513*
20. Sojoudi H, Arabnejad H, Raiyan A, Shirazi, SA, McKinley GH, Gleason, KK (2018) Scalable and Durable Polymeric Icephobic and Hydrate-Phobic Coatings, *Soft Matter* doi: 10.1039/C8SM00225H
21. Suh HS, Kim DH, Moni P, Xiong SS, Ocola LE, Zaluzec NJ, Gleason KK, Nealey PF (2017) Sub-10-nm patterning via directed self-assembly of block copolymer films with a vapour-phase deposited topcoat, *Nature Nanotechnology*, 13, 575-581, doi:10.1038/NNANO.2017.34 eISSN: 1748-3395
22. Liu AD, Kovacik P, Peard N, Tian WD, Goktas H, Lau J, Dunn B, Gleason KK (2017) Monolithic Flexible Supercapacitors Integrated into Single Sheets of Paper and Membrane via Vapor Printing, *Advanced Materials*, vol. 29, article no. 1606091 doi:10.1002/adma.201606091
23. Wang MH, Wang XX, Moni P, Liu AD, Kim DH, Jo WJ, Sojoudi H, Gleason KK (2017) CVD Polymers for Devices and Device Fabrication, *Advanced Materials*, 28, article no. UNSP 1604606 doi:10.1002/adma.201604606
24. Warsinger DM, Servi A, Conners GB, Mavukkandy MO, Arafat HA, Gleason KK, Lienhard JH (2017) Reversing membrane wetting in membrane distillation: comparing dryout to backwashing with pressurized air, *Environmental Science-Water Research & Technology*, 3, 930 doi: 10.1039/c7ew00085e
25. Sojoudi, H, Kim, S, Zhao, HB, Annavarapu RK, Mariappan D, Hart AJ, Gleason KK (2017) Stable Wettability Control of Nanoporous Microstructures by iCVD Coating of Carbon Nanotubes, *ACS Applied Materials and Interfaces*, 49, 43287-43299 doi: 10.1021/acsami.7b13713
26. Wang M, Kovacik P, Gleason, KK (2017) Chemical Vapor Deposition of Thin, Conductive, and Fouling-Resistant Polymeric Films, *Langmuir* 33 10623-10631 doi: 10.1021/acs.langmuir.7b02646.
27. Wang MH, Zhao JJ, Wang XX, Liu AD, Gleason KK (2017). Recent progress on submicron gas-selective polymeric membranes, *Journal of Materials Chemistry A* 5 8860-8886, doi: 10.1039/c7ta01862b

28. Zhao JJ, Wang MH, Gleason KK (2017) Stabilizing the Wettability of Initiated Chemical Vapor Deposited (iCVD) Polydivinylbenzene Thin Films by Thermal Annealing, *Advanced Materials Interfaces*, 4, article no. 1700270, doi: 10.1002/admi.201700270

29. Bucs SS, Valladares L, Farhat N, Matin A, Khan Z, Loosdrecht CM, Yang R, Wang M, Gleason KK, Kruithof JC, Vrouwenvelder JS (2017) Coating of reverse osmosis membranes with amphiphilic copolymers for biofouling control, *Desalination and Water Treatment*, 68, 1-11 doi: 10.5004/dwt.2017.20369

30. Servi AT, Guillen-Burrieza E, Warsinger DM, Livernois W, Notarangelo K, Kharraz J, Lienhard JH, Arafat HA, Gleason KK (2017) The effects of iCVD film thickness and conformality on the permeability and wetting of MD membranes, *Journal of Membrane Science*, vol. 523, pp. 470-479, doi:10.1016/j.memsci.2016.10.008

31. Castillo ML, Ugar A, Soujoudi H, Nakamura N, Liu Z, Lin F, Brandt RE, Buonassissi T, Reeja-Jayan B, Gleason KK (2017) Organic passivation of silicon through multifunctional polymeric interfaces, *Solar Energy Materials and Solar Cells*, vol. 160, pp. 470-475, doi:10.1016/j.solmat.2016.10.050

32. Lachman N, Stein IY, Ugar A, Lidston DL, Gleason KK, Wardle BL (2017) Synthesis of polymer bead nano-necklaces on aligned carbon nanotube scaffolds, *Nanotechnology*, vol. 28, article no. 24LT01, doi:10.1088/1361-6528/aa71c5

33. Wang XX, Ermez S, Goktas H, Gradecak, S, Gleason KK (2017) Room Temperature Sensing Achieved by GaAs Nanowires and oCVD Polymer Coating, Macromolecular Rapid Communications, vol. 38, article no. 170055 doi:10.1002/marc.201700055

34. Shafi HZ, Matin A, Akhtar S, Gleason KK, Zubair SM, Khan Z (2017) Organic fouling in surface modified reverse osmosis membranes: Filtration studies and subsequent morphological and compositional characterization, *Journal of Membrane Science*, 527, 152-163 doi:10.1016/j.memsci.2017.01.017

35. Wang M, Boscher ND, Heinz K, Gleason KK (2017) Gas Selective Ultrathin Organic Covalent Networks Synthesized by iPECVD: Does the Central Metal Ion Matter? Advanced Functional Materials, 27, article no. 1606652, doi: 10.1002/adfm.201606652

36. Moni P, Al-Obeidi A, Gleason KK (2017) Vapor deposition routes to conformal polymer thin films, Beilstein *Journal of Nanotechnology*, 8, 723--735, doi:10.3762/bjnano.8

37. Kim S, Sojoudi H, Zhao H, Mariappan D, McKinley GH, Gleason KK, and Hart AJ (2016). Ultrathin high-resolution flexographic printing using nanoporous stamps, *Science Advances*, article no. ne1601660, doi: 10.1126/sciadv.1601660o

38. Boscher ND, Wang M, Perrotta A, Heinze K, Creatore M, Gleason KK (2016) Metal-Organic Covalent Network Chemical Vapor Deposition for Gas Separation, *Advanced Materials*, 28 7479-7485, doi:10.1002/adma.201601010 ***(Frontispiece)***

39. Boscher ND, Wang M, Gleason KK (2016) 'Chemical Vapor Deposition of metalloporphyins: a simple route towards the preparation of gas separation membranes, *Journal of Material Chemistry A*, 4, 18144-18154, doi:10.1039/c6ta08003k

40. Raayai-Ardakani S, Yague JL, Gleason KK, Boyce MC (2016) Mechanics of Graded Wrinkling, *Journal of Applied Mechanics-Transactions of the ASME*, 83, Article No. 121011 doi:10.1115/1.4034829

41. Goktas H, Wang XX, Boscher ND, Torosian S, Gleason KK (2016) Functionalizable and electrically conductive thin films formed by oxidative chemical vapor deposition (oCVD) from mixtures of 3-thiopheneethanol (3TE) and ethylene dioxythiophene (EDOT), *Journal of Materials Chemistry C*, 4, 3403-3414 doi:10.1039/c6tc00567e

42. Wang M, Perrotta A, Heinze K, Creatore M, Gleason KK (2016). Metal–Organic Covalent Network Chemical Vapor Deposition for Gas Separation. *Advanced Materials* 28, 7479-7485, doi: 10.1002/adma.201601010

43. Jo WJ, Nelson JT, Chang, S, Bulović, V, Gradečak S., Strano MS, Gleason KK (2016). Oxidative Chemical Vapor Deposition of Neutral Hole Transporting Polymer for Enhanced Solar Cell Efficiency and Lifetime. *Advanced Materials* 28, 6399-6404, doi:10.1002/adma.201601221

44. Chen N, Reeja-Jayan B, Liu A, Lau J, Dunn B, Gleason KK (2016). iCVD Cyclic Polysiloxane and Polysilazane as Nanoscale Thin-Film Electrolyte: Synthesis and Properties *Macromolecular Rapid Communications* 37, 446-452, doi: 10.1002/marc.201500649

45. Servi A, Kharraz J, Klee D, Notarangelo K, Eyob B, Guillen-Burriezza E, Liu A, Hassan A, Gleason KK (2016). A systematic study of the impact of hydrophobicity on the wetting of MD membranes Journal of Membrane Science 520, 850-859, doi: 10.1016/j.memsci.2016.08.021

46. Chen N, Kim DH, Kovacik P, Sojoudi H, Wang M, Gleason KK (2016). Polymer Thin Films and Surface Modification by Chemical Vapor Deposition: Recent Progress *Annual Review of Chemical and Biomolecular Engineering* 7, 373-393, doi: 10.1146/annurev-chembioeng-080615-033524

47. Lee S, Borrelli D, Gleason KK (2016). Air-stable polythiophene-based thin film transistors processed using oxidative chemical vapor deposition: Carrier transport and channel/metallization contact interface *Organic Electronics* 33, 253-262, doi: 10.1016/j.orgel.2016.03.034

48. Warsinger, DM, Servi, A , Van Belleghem, S , Gonzalez, J , Swaminathan, J , Kharraz, J , Chung, HW , Arafat, HA, Gleason, KK , Lienhard, VJH (2016). Combining air recharging and membrane superhydrophobicity for fouling prevention in membrane distillation, *Journal of Membrane Science* 505, 241-252. doi: 10.1016/j.memsci.2016.01.018

49. Matin A , Shafi H, Wang M, Khan Z, Gleason KK, Rahman, F (2016). Reverse osmosis membranes surface-modified using an initiated chemical vapor deposition technique show resistance to alginate fouling under cross-flow conditions: Filtration & subsequent characterization, *Desalination* 379, 108-117 doi: 10.1016/j.desal.2015.11.003

50. McInnes SJP, Szili EJ, Al-Bataineh SA, Vasani RB, Xu JJ, Alf ME, Gleason KK, Short RD, Voelcker NH (2016). Fabrication and Characterization of a Porous Silicon Drug Delivery System with an Initiated Chemical Vapor Deposition Temperature-Responsive Coating, *Langmuir* 32, 301-308 doi: 10.1021/acs.langmuir.5b03794

51. Sojoudi H, Wang M, Boscher ND, McKinley GH, Gleason KK (2016). Durable and scalable icephobic surfaces: similarities and distinctions from superhydrophobic surfaces, *Soft Matter* 12, 1938-1963 doi: 10.1039/c5sm02295a

52. Goktas H, Wang X, Ugar A, Gleason KK (2015). Water-Assisted Vapor Deposition of PEDOT Thin Films *Macromolecular Rapid Communications* 36, 1286-1289, doi: 10.1002/marc.201500069

53. Jo WJ, Kang HJ, Kong KJ, Lee YS, Park H, Lee Y, Buonassisi T, Gleason KK (2015). Phase transition-induced band edge engineering of BiVO4 to split pure water under visible light *Proceedings of the National Academy of Sciences of the United States of America* 45, 13774-13778 doi:10.1021/acs.langmuir.5b02795

54. Jo, WJ, Borelli DC, Bulovic V, Gleason KK (2015). Photovoltaic effect by vapor-printed polyselenophene *Organic Electronics* 26, 55-60 doi: 10.1016/j.orgel.2015.07.017

55. Shafi HZ, Matin A, Khan Z, Khalil A, Gleason KK (2015). Surface modification of reverse osmosis membranes with zwitterionic coatings: A potential strategy for control of biofouling, *Surfaces & Coatings* 171-179 doi: 10.1016/j.surfcoat.2015.08.037

56. Wang XX, Hou SC, Goktas H, Kovacik, Yaul F, Paidimarri A, Ickes N, Chandrakasan A, Gleason KK (2015). Small-Area, Resistive Volatile Organic Compound (VOC) Sensors Using Metal-Polymer Hybrid Film Based on Oxidative Chemical Vapor Deposition (oCVD), *ACS Applied Materials & Interfaces* 7, 16213-16222 doi: 10.1021/acsami.5b05392

57. Hebert A, Bishop M, Bhattacharyya D, Gleason KK, Torosian S (2015). Assessment by Ames test and comet assay of toxicity potential of polymer used to develop field-capable rapid-detection device to analyze environmental samples, *Applied Nanoscience* 5, 763-769 doi:1007/s13204-014-0373-7

58. Yang R, Goktekin E, Gleason KK, Zwitterionic antifouling coatings for the purification of High-Salinity Shale Gas Produced Water (2015), *Langmuir* 31 11895-11903, doi: 10.1021/acs.langmuir.5b02795

59. Ugar A, Katmis F, Li MD, Wu LJ, Zhu YM, Varanasi KK, Gleason KK (2015). Low-dimensional conduction mechanisms in highly conductive and transparent conjugated polymers, *Advanced Materials* 31, 4604-4610, doi: 10.1002/adma.201502340

60. Reeja-Jayan B, Chen N, Lau J, Kattirtzi JA, Moni P, Liu AD, Miller IG, Kayser R, Willard AP, Dunn B, Gleason KK (2015) A group of cyclic siloxane and silazane polymer films as nanoscale electrolytes for microbattery architectures, *Macromolecules* 48, 5222-5229, doi: 10.1021/acs.macromol.5b00940

61. Kovacik P, del Hierro G, Livernois W, Gleason KK (2015) Scale-up of oCVD: large-area conductive polymer thin films for next-generations electronics, *Materials Horizons* 2, 221-227, doi: 10.1039/c4mh00222a

62. Sojoudi H, Walsh MR, Gleason KK, McKinley GH (2015). Investigation into the Formation and Adhesion of Cyclopentane Hydrates on Mechanically Robust Vapor-Deposited Polymeric Coatings, *Langmuir* 31, 6186-6196 doi: 10.1021/acs.langmuir.5b00413

63. Chen N, Reeja-Jayan B, Lau J, Moni P, Liu AD, Dunn B, Gleason KK (2015). Nanoscale, conformal polysiloxane thin film electrolytes for three-dimensional battery architectures, *Materials Horizons* 2, 309-314, doi: 10.1039/c4mh00246f

64. Guo F, Servi A, Liu AD, Gleason KK (2015). Desalination by Membrane Distillation using Electrospun Polyamide Fiber Membranes with Surface Fluorination by Chemical Vapor Deposition, *ACS Applied Materials & Interfaces* 7, 8225-8232 doi:10.1021/acsami.5b01197

65. Sojoudi H, Walsh MR, Gleason KK, McKinley GH (2015). Designing Durable Vapor-Deposited Surfaces for Reduced Hydrate Adhesion, *Advanced Materials Interfaces* 2, 1500003 doi: 10.1002/admi.201500003:

66. Shafi HZ, Khan Z, Yang R, Gleason KK (2015). Surface modification of reverse osmosis membranes with zwitterionic coating for improved resistance to fouling *Desalination* 362, 93-103 doi:10.1016/j.desal.2015.02.009

67. Sojoudi H, McKinley GH, Gleason KK (2015). Linker-free grafting of fluorinated polymeric cross-linked network bilayers for durable reduction of ice adhesion. *Materials Horizons* 2, 91–99 doi:10.1039/C4MH00162A

68. Yang R, Priya M, Gleason KK (2015). Ultra-thin zwitterionic coatings for roughness-independent underwater superoleophobicity and gravity-driven oil-water separation. *Advanced Materials Interfaces* 2, 1400489 doi:10.1002/admi.201400489

69. Sojoudi H, McKinley GH, Gleason KK (2015). Linker-free grafting of fluorinated polymeric cross-linked network bilayers for durable reduction of ice adhesion. *Materials Horizon* 2, 91–99. doi:10.1039/C4MH00162A

70. Chen N, Kovacik P, Howden RM, Wang X, Lee S, Gleason KK (2015). Low-substrate-temperature encapsulation for flexible electrodes and organic photovoltaics. *Advanced Energy Materials* 5, 1401442 doi: 10.1002/aenm.201401442

71. Lee S, Gleason KK (2014). Enhanced optical property with tunable band gap of cross-linked PEDOT copolymers via oxidative chemical vapor deposition. *Advanced Functional Materials 1, 85-93* doi: 10.1002/adfm.201402924

72. Liu A, Goktekin E, Gleason KK (2014). Cross-linking and ultra-thin grafted gradation of fluorinated polymers synthesized via initiated chemical vapor deposition to prevent surface reconstruction. *Langmuir* 30(47)14189–14194. doi: 10.1021/la503343x

73. Lee S, Paine DC, Gleason KK (2014). Heavily doped poly(3,4-ethylenedioxythiophene) thin films with high carrier mobility deposited using oxidative CVD: Conductivity stability and carrier transport. *Advanced Functional Materials* 24(45):7187–7196. doi:10.1002/adfm.201401282

74. Reeja-Jayan B, Kovacik, P, Yang R, Hossein S, Ugar A, Kim DH, Petruczok CD, Wang X, Liu A, Gleason KK (2014). A route towards sustainability through engineered polymeric interfaces. *Advanced Materials Interfaces*. 1(4), 1400117. doi:10.1002/admi.201400117 **(Invited review)**

75. Paxson AT, Yagüe JL, Gleason KK, Varanasi KK (2014). Stable dropwise condensation for enhancing heat transfer via the initiated chemical vapor deposition (iCVD) of grafted polymer films. *Advanced Materials* 26, 418–423. doi: 10.1002/adma.201303065 **(Cover)**

76. Yang R, Jang H, Stocker R, Gleason KK (2014). Synergistic prevention of biofouling in seawater desalination by zwitterionic surfaces and low-level chlorination. *Advanced Materials* 26, 1711–1718. doi: 10.1002/adma.201304386

77. Borelli DC, Lee S, Gleason KK (2014). Optoelectronic properties of polythiophene thin films and organic TFTs fabricated by oxidative chemical vapor deposition. *J. Materials Chemistry C* 35, 7223–7231, doi: 10.1039/c4tc00881b

78. Lachman N, Xu HP, Zhou Y, Ghaffari M, Lin M, Bhattacharyya D, Ugar A, Gleason, KK, Zhang QM, Wardle BL (2014) Tailoring thickness of conformal conducting polymer decorated aligned carbon nanotube electrodes for energy storage, *Advanced Materials Interfaces*, 1, Article no. 1400076, doi: 10.1002/admi.201400076

79. Zhou Y, Xu HP, Lachman N, Ghaffari M, Wu S, Liu Y, Ugur A, Gleason KK, Wardle BL, Zhang, QM (2014) *Nano Energy*, 9, 176-185, doi: 10.1016/j.nanoen.2014.07.007

80. Petruczok CD, Armagan E, Ince GO, Gleason KK (2014). Initiated chemical vapor deposition and light-responsive cross-linking of poly(vinyl cinnamate) thin films. *Macromolecular Rapid Communications* 35, 1345–1350. doi: 10.1002/marc.201400130

81. Zhou Y, Lachman N, Ghaffari M, Xu HP, Bhattacharya D, Fattahi P, Abidian MR, Wu S, Gleason KK, Wardle BL, Zhang QM (2014). A high performance hybrid asymmetric supercapacitor via nano-scale morphology control of graphene, conducting polymer, and carbon nanotube electrodes. *J Materials of Chemistry A* 26, 9964–9969. doi: 10.1039/c4ta01785d

82. Matin A, Shafi HZ, Khan Z, Khaled M, Yang R, Gleason K, Rehman F (2014). Surface modification of seawater desalination reverse osmosis membranes: Characterization studies & performance evaluation. *Desalination* 343, 128–139. doi: 10.1016/j.desal.2013.10.023

83. Petruczok CD, Chen N, Gleason KK (2014). Closed batch initiated chemical vapor deposition of ultrathin, functional, and conformal polymer films. *Langmuir* 16, 4830–4837. doi: 10.1021/la500543d

84. Amadei CA, Yang R, Chiesa M, Gleason KK, Santos S (2014). Revealing amphiphilic nanodomains of anti-biofouling polymer coatings. *ACS Applied Materials & Interfaces* 6(7), 4705–4712. doi: 10.1021/am405159f

85. Matin A, Khan Z, Gleason KK, Khaled M, Zaidi SMJ, Khalil A, Moni P, Yang R (2014). Surface-modified reverse osmosis membranes applying a copolymer film to reduce adhesion of bacteria as a strategy for biofouling control. *Separation and Purification Technology* 124, 117–123. doi:10.1016/j.seppur.2013.12.032

86. Yin J, Yague JJL, Boyce MC, Gleason KK (2014). Biaxially mechanical tuning of 2-D reversible and irreversible surface topologies through simultaneous and sequential wrinkling. *ACS Applied Materials & Interfaces* 6, 2850–2857. doi:10.1021/am4054207

87. Yang R, Goktekin E, Wang MH, Gleason KK (2014). Molecular fouling resistance of zwitterionic and amphiphilic initiated chemically vapor-deposited (iCVD) thin films. *J. Biomaterials Science–Polymer Edition* 25, 1687–1702. doi: 10.1080/09205063.2014.951245

88. Coclite AM, Howden RM, Borrelli DC, Petruczok CD, Yang R, Yagüe JL, Ugar A, Chen N, Lee S, Jo WJ, Liu A, Wang X, Gleason KK (2013). CVD polymers: A new paradigm for surface modification and device fabrication. *Advanced Materials* 25, 5392–5423. doi: 10.1002/adma.201301878 **(Invited review for the 25th anniversary of this Wiley journal.)**

89. Matin A, Shafi H, Khan Z, Khaled M, Yang R, Rehmand F (2014). Surface modification of seawater desalination reverse osmosis membranes: Characterization studies and performance evaluation. *Desalination* 343, 128–139. doi: 10.1016/j.desal.2013.10.023

90. Howden RM, Flores EJ, Bulovic V, Gleason KK (2013). The application of oxidative chemical vapor deposition (oCVD) PEDOT to textured and non-planar photovoltaic device geometries for enhanced light trapping. *Organic Electronics* 14, 2257–2268. doi: 10.1016/j.orgel.2013.05.004

91. Borelli DC, Gleason KK (2013). Tunable low bandgap polyisothianaphthene via oxidative chemical vapor deposition. *Macromolecules* 46, 6169–6176. doi: 10.1021/ma400890a

92. Yagüe JL, Yin J, Boyce MC, Gleason KK (2013). Design of ordered wrinkled patterns with dynamically tuned properties. *Physics Procedia* 46, 40–45. doi: 10.1016/j.phpro.2013.07.043

93. Howden RM, McVay ED, Gleason KK (2013). oCVD poly(3,4-ethylenedioxythiophene) conductivity and lifetime enhancement via acid rinse dopant exchange. *Journal of Materials Chemistry A* 1(4), 1334–1340. doi: 10.1039/c2ta00321j

94. Yagüe JL, Gleason KK (2013). Enhanced cross-linked density by annealing on fluorinated polymers synthesized via initiated chemical vapor deposition to prevent surface reconstruction. *Macromolecules* 246, 6548–6554. doi: 10.1021/ma4010633

95. Zhou Y, Lachman N, Lin M, Bhattacharya D, Gleason KK, Wardle BL, Zhang QM (2013). Hybrid supercapacitor materials from poly(3,4-ethylenedioxythiophene) conformally coated aligned carbon nanotubes. *Electrochimica Acta* 112, 522– 528. doi: 10.1016/j.electacta.2013.08.191

96. Petruczok CD, Choi HJ, Yang SY, Asatekin A, Gleason KK, Barbastathis G (2013). Fabrication of a microscale device for detection of nitroaromatic compounds. *Journal of Microelectromechanical Systems* 22(1), 54–61. doi: 10.1109/jmems.2012.2212421

97. Petruczok CD, Yang R, Gleason KK (2013). Controllable cross-linking of vapor-deposited polymer thin films and impact on material properties. *Macromolecules* 46(5), 1832–1840. doi: 10.1021/ma302566r

98. Yagüe JL, Coclite AM, Petruczok C, Gleason KK (2013). Chemical vapor deposition for solvent-free polymerization at surfaces. *Macromolecular Chemistry and Physics* 214(3), 302–312. doi: 10.1002/macp.201200600 **(Cover)**

99. Yang R, Buonassisi T, Gleason KK (2013). Organic vapor passivation of silicon at room temperature. *Advanced Materials* 25(14), 2078–2083. doi: 10.1002/adma.201204382 **(Frontispiece)**

100. Barr MC, Carbonera C, Po R, Bulovic V, Gleason KK (2012). Cathode buffer layers based on vacuum and solution deposited poly(3,4-ethylenedioxythiophene) for efficient inverted organic solar cells. *Applied Physics Letters* 100(18). doi: 10.1063/1.4709481

101. Barr MC, Howden RM, Lunt RR, Bulovic V, Gleason KK (2012). Top-illuminated organic photovoltaics on a variety of opaque substrates with vapor-printed poly(3,4-ethylenedioxythiophene) top electrodes and MoO3 buffer layer. *Advanced Energy Materials* 2(11), 1404–1409. doi: 10.1002/aenm.201200112

102. Bhattacharyya D, Gleason KK (2012). Low band gap conformal polyselenophene thin films by oxidative chemical vapor deposition. *Journal of Materials Chemistry* 22(2), 405–410. doi: 10.1039/c1jm13755g

103. Bhattacharyya D, Howden RM, Borrelli DC, Gleason KK (2012). Vapor phase oxidative synthesis of conjugated polymers and applications. *Journal of Polymer Science Part B—Polymer Physics* 50(19), 1329–1351. doi: 10.1002/polb.23138

104. Bhattacharyya D, Yang R, Gleason KK (2012). High aspect ratio, functionalizable conducting copolymer nanobundles. *Journal of Materials Chemistry* 22(33), 17147–17152. doi: 10.1039/c2jm32473c

105. Bong KW, Xu JJ, Kim JH, Chapin SC, Strano MS, Gleason KK, Doyle PS (2012). Non-polydimethylsiloxane devices for oxygen-free flow lithography. *Nature Communications* 3:805. doi: 10.1038/ncomms1800

106. Borrelli DC, Barr MC, Bulovic V, Gleason KK (2012). Bilayer heterojunction polymer solar cells using unsubstituted polythiophene via oxidative chemical vapor deposition. *Solar Energy Materials and Solar Cells* 99, 190–196. doi: 10.1016/j.solmat.2011.11.040

107. Coclite AM, De Luca F, Gleason KK (2012). Mechanically robust silica-like coatings deposited by microwave plasmas for barrier applications. *Journal of Vacuum Science & Technology A* 30(6). doi: 10.1116/1.4748804

108. Coclite AM, Gleason KK (2012). Global and local planarization of surface roughness by chemical vapor deposition of organosilicon polymer for barrier applications. *Journal of Applied Physics* 111(7). doi: 10.1063/1.3702428

109. Coclite AM, Gleason KK (2012). Initiated PECVD of organosilicon coatings: A new strategy to enhance monomer structure retention. *Plasma Processes and Polymers* 9(4), 425–434. doi: 10.1002/ppap.201100167

110. Coclite AM, Shi YJ, Gleason KK (2012). Controlling the degree of crystallinity and preferred crystallographic orientation in poly-perfluorodecylacrylate thin films by initiated chemical vapor deposition. *Advanced Functional Materials* 22(10), 2167–2176. doi: 10.1002/adfm.201103035

111. Coclite AM, Shi YJ, Gleason KK (2012). Grafted crystalline poly-perfluoroacrylate structures for superhydrophobic and oleophobic functional coatings. *Advanced Materials* 24(33), 4534–4539. doi: 10.1002/adma.201200682

112. Jain RM, Howden R, Tvrdy K, Shimizu S, Hilmer AJ, McNicholas TP, Gleason KK, Strano MS (2012). Polymer-free near-infrared photovoltaics with single chirality (6,5) semiconducting carbon nanotube active layers. *Advanced Materials* 24(32), 4436–4439. doi: 10.1002/adma.201202088

113. Macko JA, Lunt RR, Osedach TP, Brown PR, Barr MC, Gleason KK, Bulovic V (2012). Multijunction organic photovoltaics with a broad spectral response. *Physical Chemistry Chemical Physics* 14(42), 14548–14553. doi: 10.1039/c2cp43000b

114. McInnes SJP, Szili EJ, Al-Bataineh SA, Xu JJ, Alf ME, Gleason KK, Short RD, Voelcker NH (2012). Combination of iCVD and porous silicon for the development of a controlled drug delivery system. *ACS Applied Materials & Interfaces* 4(7), 3566–3574. doi: 10.1021/am300621k

115. Montero L, Gabriel G, Guimera A, Villa R, Gleason KK, Borros S (2012). Increasing biosensor response through hydrogel thin film deposition: Influence of hydrogel thickness. *Vacuum* 86(12), 2102–2104. doi: 10.1016/j.vacuum.2012.06.002

116. Ozaydin-Ince G, Coclite AM, Gleason KK (2012). CVD of polymeric thin films: Applications in sensors, biotechnology, microelectronics/organic electronics, microfluidics, MEMS, composites and membranes. *Reports on Progress in Physics* 75(1). doi: 10.1088/0034–4885/75/1/016501 **(Invited review)**

117. Park H, Howden RM, Barr MC, Bulovic V, Gleason K, Kong J (2012). Organic solar cells with graphene electrodes and vapor printed poly(3,4-ethylenedioxythiophene) as the hole transporting layers. *ACS Nano* 6(7), 6370–6377. doi: 10.1021/nn301901v

118. Petruczok CD, Gleason KK (2012). Initiated chemical vapor deposition-based method for patterning polymer and metal microstructures on curved substrates. *Advanced Materials* 24(48), 6445–6450. doi: 10.1002/adma.201201975

119. Raghunathan V, Yagüe JL, Xu JJ, Michel J, Gleason KK, Kimerling LC (2012). Co-polymer clad design for high performance athermal photonic circuits. *Optics Express* 20(19), 20808–20813. Doi: 10.1364/OE.20.020808

120. Sreenivasan R, Bassett EK, Cervantes TM, Hoganson DM, Vacanti JP, Gleason KK (2012). Solvent-free surface modification by initiated chemical vapor deposition to render plasma bonding capabilities to surfaces. *Microfluidics and Nanofluidics* 12(5), 835–839. doi: 10.1007/s10404-011-0913-3

121. Xu JJ, Asatekin A, Gleason KK (2012). The design and synthesis of hard and impermeable, yet flexible, conformal organic coatings. *Advanced Materials* 24(27), 3692–3696. doi: 10.1002/adma.201201197

122. Yagüe JL, Gleason KK (2012). Systematic control of mesh size in hydrogels by initiated chemical vapor deposition. *Soft Matter* 8(10), 2890–2894. doi: 10.1039/c2sm07137a

123. Yang R, Asatekin A, Gleason KK (2012). Design of conformal, substrate-independent surface modification for controlled protein adsorption by chemical vapor deposition (CVD). *Soft Matter* 8(1), 31–43. doi: 10.1039/c1sm06334k

124. Yang R, Gleason KK (2012). Ultrathin antifouling coatings with stable surface zwitterionic functionality by initiated chemical vapor deposition (iCVD). *Langmuir* 28(33), 12266–12274. doi: 10.1021/la302059s

125. Yin J, Yagüe JL, Eggenspieler D, Gleason KK, Boyce MC (2012). Deterministic order in surface micro-topologies through sequential wrinkling. *Advanced Materials* 24(40), 5441–5446. doi: 10.1002/adma.201201937 **(Frontispiece)**

126. Alf ME, Hatton TA, Gleason KK (2011). Initiated chemical vapor deposition of responsive polymeric surfaces. *Thin Solid Films* 519(14), 4412–4414. doi: 10.1016/j.tsf.2011.01.286

127. Alf ME, Hatton TA, Gleason KK (2011). Insights into thin, thermally responsive polymer layers through quartz crystal microbalance with dissipation. *Langmuir* 27(17), 10691–10698. doi: 10.1021/la201935r

128. Alf ME, Hatton TA, Gleason KK (2011c). Novel *N*-isopropylacrylamide based polymer architecture for faster LCST transition kinetics. *Polymer* 52(20), 4429–4434. doi:10.1016/j.polymer.2011.07.051

129. Asatekin A, Gleason KK (2011). Polymeric nanopore membranes for hydrophobicity-based separations by conformal initiated chemical vapor deposition. *Nano Letters* 11(2), 677–686. doi: 10.1021/nl103799d

130. Barr MC, Rowehl JA, Lunt RR, Xu JJ, Wang AN, Boyce CM, Im SG, Bulovic V, Gleason KK (2011). Direct monolithic integration of organic photovoltaic circuits on unmodified paper. *Advanced Materials* 23(31), 3500–3505. doi: 10.1002/adma.201101263 **(Frontispiece)**

131. Bhattacharyya D, Gleason KK (2011). Single-step oxidative chemical vapor deposition of -COOH functional conducting copolymer and immobilization of biomolecule for sensor application. *Chemistry of Materials* 23(10), 2600–2605. doi: 10.1021/cm2002397

132. Im SG, Gleason KK (2011). Solvent-free modification of surfaces with polymers: the case for initiated and oxidative chemical vapor deposition (CVD). *AIChE Journal* 57(2), 276–285. doi: 10.1002/aic.12522

133. Matin A, Ozaydin-Ince G, Khan Z, Zaidi SMJ, Gleason K, Eggenspiler D (2011). Random copolymer films as potential antifouling coatings for reverse osmosis membranes. *Desalination and Water Treatment* 34(1–3), 100–105. doi: 10.5004/dwt.2011.2804

134. Ozaydin-Ince G, Dubach JM, Gleason KK, Clark HA (2011). Microworm optode sensors limit particle diffusion to enable in vivo measurements. *Proceedings of the National Academy of Sciences of the United States of America* 108(7), 2656–2661. doi: 10.1073/pnas.1015544108

135. Ozaydin-Ince G, Gleason KK, Demirel MC (2011). A stimuli-responsive coaxial nanofilm for burst release. *Soft Matter* 7(2), 638–643. doi: 10.1039/c0sm00922a

136. Sreenivasan R, Bassett EK, Hoganson DM, Vacanti JP, Gleason KK (2011). Ultra-thin, gas permeable free-standing and composite membranes for microfluidic lung assist devices. *Biomaterials* 32(16), 3883–3889. doi: 10.1016/j.biomaterials.2011.02.017

137. Tekin H, Ozaydin-Ince G, Tsinman T, Gleason KK, Langer R, Khademhosseini A, Demirel MC (2011). Responsive microgrooves for the formation of harvestable tissue constructs. *Langmuir* 27(9), 5671–5679. doi: 10.1021/la200183x

138. Xu JJ, Gleason KK (2011). Conformal polymeric thin films by low-temperature rapid initiated chemical vapor deposition (iCVD) using tert-butyl peroxybenzoate as an initiator. *ACS Applied Materials & Interfaces* 3(7), 2410–2416. doi: 10.1021/am200322k

139. Yang R, Xu JJ, Ozaydin-Ince G, Wong SY, Gleason KK (2011). Surface-tethered zwitterionic ultrathin antifouling coatings on reverse osmosis membranes by initiated chemical vapor deposition. *Chemistry of Materials* 23(5), 1263–1272. doi: 10.1021/cm1031392

140. Alf ME, Asatekin A, Barr MC, Baxamusa SH, Chelawat H, Ozaydin-Ince G, Petruczok CD, Sreenivasan R, Tenhaeff WE, Trujillo NJ, Vaddiraju S, Xu J, Gleason KK (2010). Chemical vapor deposition of conformal, functional, and responsive polymer films. *Advanced Materials* 22(18), 1993–2027. doi: 10.1002/adma.200902765 **(Invited review)**

141. Alf ME, Godfrin PD, Hatton TA, Gleason KK (2010). Sharp hydrophilicity switching and conformality on nanostructured surfaces prepared via initiated chemical vapor deposition (iCVD) of a novel thermally responsive copolymer. *Macromolecular Rapid Communications* 31(24), 2166–2172. doi: 10.1002/marc.201000452

142. Asatekin A, Barr MC, Baxamusa SH, Lau KKS, Tenhaeff W, Xu JJ, Gleason KK (2010). Designing polymer surfaces via vapor deposition. *Materials Today* 13(5), 26–33. **(Invited review)**

143. Baxamusa SH, Montero L, Borros S, Gleason KK (2010). Self-aligned micropatterns of bifunctional polymer surfaces with independent chemical and topographical contrast. *Macromolecular Rapid Communications*, 31(8) 735–739. doi: 10.1002/marc.200900815

144. Chelawat H, Vaddiraju S, Gleason K (2010). Conformal, conducting poly(3,4-ethylenedioxythiophene) thin films deposited using bromine as the oxidant in a completely dry oxidative chemical vapor deposition process. *Chemistry of Materials* 22(9), 2864–2868. doi: 10.1021/cm100092c

145. Coclite AM, Ozaydin-Ince G, Palumbo F, Milella A, Gleason KK (2010). Single-chamber deposition of multi layer barriers by plasma enhanced and initiated chemical vapor deposition of organosilicones. *Plasma Processes and Polymers* 7(7), 561–570. doi: 10.1002/ppap.200900139

146. Gleason KK (2010). A chemical engineering perspective on "Views on macroscopic kinetics of plasma polymerisation." *Plasma Processes and Polymers* 7(5), 380–381. doi: 10.1002/ppap.201000012

147. Ince GO, Demirel G, Gleason KK, Demirel MC (2010). Highly swellable free-standing hydrogel nanotube forests. *Soft Matter* 6(8), 1635–1639. doi: 10.1039/c000569j

148. Kramer NJ, Sachteleben E, Ozaydin-Ince G, van de Sanden R, Gleason KK (2010). Shape memory polymer thin films deposited by initiated chemical vapor deposition. *Macromolecules* 43(20), 8344–8347. doi: 10.1021/ma101644w

149. Ozaydin-Ince G, Gleason KK (2010). Thermal stability of acrylic/methacrylic sacrificial copolymers fabricated by initiated chemical vapor deposition. *Journal of the Electrochemical Society* 157(1), D41–D45. doi: 10.1149/1.3251308

150. Ozaydin-Ince G, Gleason KK (2010). Tunable conformality of polymer coatings on high aspect ratio features. *Chemical Vapor Deposition* 16(1–3), 100–105. doi: 10.1002/cvde.200906821

151. Sedransk KL, Tenhaeff WE, Gleason KK (2010). Grafting CVD of poly(vinyl pyrrolidone) for durable scleral lens coatings. *Chemical Vapor Deposition* 16(1–3), 23–28. doi: 10.1002/cvde.200906760

152. Tenhaeff WE, McIntosh LD, Gleason KK (2010). Synthesis of poly(4-vinylpyridine) thin films by initiated chemical vapor deposition (iCVD) for selective nanotrench-based sensing of nitroaromatics. *Advanced Functional Materials* 20(7), 1144–1151. doi: 10.1002/adfm.200901890

153. Trujillo NJ, Barr MC, Im SG, Gleason KK (2010). Oxidative chemical vapor deposition (oCVD) of patterned and functional grafted conducting polymer nanostructures. *Journal of Materials Chemistry* 20(19), 3968–3972. doi: 10.1039/b925736e

154. Trujillo NJ, Wu QG, Gleason KK (2010). Ultralow dielectric constant tetravinyltetramethylcyclotetrasiloxane films deposited by initiated chemical vapor deposition (iCVD). *Advanced Functional Materials* 20(4), 607–616. doi: 10.1002/adfm.200900999

155. Vaddiraju S, Gleason KK (2010). Selective sensing of volatile organic compounds using novel conducting polymer-metal nanoparticle hybrids. *Nanotechnology* 21(12). doi: 10.1088/0957-4484/21/12/125503

156. Xu JJ, Gleason KK (2010). Conformal, amine-functionalized thin films by initiated chemical vapor deposition (iCVD) for hydrolytically stable microfluidic devices. *Chemistry of Materials* 22(5), 1732–1738. doi: 10.1021/cm903156a

157. Arora WJ, Tenhaeff WE, Gleason KK, Barbastathis G (2009). Integration of reactive polymeric nanofilms into a low-power electromechanical switch for selective chemical sensing. *Journal of Microelectromechanical Systems* 18(1), 97–102. doi: 10.1109/jmems.2008.2008529

158. Baxamusa SH, Gleason KK (2009). Initiated chemical vapor deposition of polymer films on nonplanar substrates. *Thin Solid Films* 517(12), 3536–3538. doi: 10.1016/j.tsf.2009.01.032

159. Baxamusa SH, Gleason KK (2009). Random copolymer films with molecular-scale compositional heterogeneities that interfere with protein adsorption. *Advanced Functional Materials* 19(21), 3489–3496. doi: 10.1002/adfm.200900943

160. Baxamusa SH, Im SG, Gleason KK (2009). Initiated and oxidative chemical vapor deposition: A scalable method for conformal and functional polymer films on real substrates. *Physical Chemistry Chemical Physics* 11(26), 5227–5240. doi: 10.1039/b900455f

161. Chen GH, Lau KKS, Gleason KK (2009). iCVD growth of poly(N-vinylimidazole) and poly (N-vinylimidazole-co-N-vinylpyrrolidone). *Thin Solid Films* 517(12), 3539–3542. doi: 10.1016/j.tsf.2009.01.053

162. Coclite AM, Ozaydin-Ince G, d'Agostino R, Gleason KK (2009). Flexible cross-linked organosilicon thin films by initiated chemical vapor deposition. *Macromolecules* 42(21), 8138–8145. doi: 10.1021/ma901431m

163. Gleason KK (2009). Special issue on CVD and polymeric materials. *Chemical Vapor Deposition* 15(4–6), 75–76. doi: 10.1002/cvde.200904001

164. Gupta M, Gleason KK (2009). Surface modification of high aspect ratio structures with fluoropolymer coatings using chemical vapor deposition. *Thin Solid Films* 517(12), 3547–3550. doi: 10.1016/j.tsf.2009.01.037

165. Im SG, Bong KW, Lee CH, Doyle PS, Gleason KK (2009). A conformal nano-adhesive via initiated chemical vapor deposition for microfluidic devices. *Lab on a Chip*, 9(3), 411–416. doi: 10.1039/b812121d

166. Im SG, Kim BS, Tenhaeff WE, Hammond PT, Gleason KK (2009). A directly patternable click-active polymer film via initiated chemical vapor deposition (iCVD). *Thin Solid Films* 517(12), 3606–3611. doi: 10.1016/j.tsf.2009.01.040

167. Lee CH, Tenhaeff W, Gleason KK (2009). Nano-patterning of an iCVD polymer, followed by covalent attachment of QDs. *Thin Solid Films* 517(12), 3619–3621. doi: 10.1016/j.tsf.2009.01.036

168. Mari-Buye N, O'Shaughnessy S, Colominas C, Semino CE, Gleason KK, Borros S (2009). Functionalized, swellable hydrogel layers as a platform for cell studies. *Advanced Functional Materials* 19(8), 1276–1286. doi: 10.1002/adfm.200801561

169. Montero L, Baxamusa SH, Borros S, Gleason KK (2009). Thin hydrogel films with nanoconfined surface reactivity by photoinitiated chemical vapor deposition. *Chemistry of Materials* 21(2), 399–403. doi: 10.1021/cm802737m

170. O'Shaughnessy WS, Edell DJ, Gleason KK (2009). Initiated chemical vapor deposition of a siloxane coating for insulation of neural probes. *Thin Solid Films* 517(12), 3612–3614. doi: 10.1016/j.tsf.2009.01.192

171. Ozaydin-Ince G, Gleason KK (2009). Transition between kinetic and mass transfer regimes in the initiated chemical vapor deposition from ethylene glycol diacrylate. *Journal of Vacuum Science & Technology A* 27(5), 1135–1143. doi: 10.1116/1.3168553

172. Sreenivasan R, Gleason KK (2009). Overview of strategies for the CVD of organic films and functional polymer layers. *Chemical Vapor Deposition* 15(4–6), 77–90. doi: 10.1002/cvde.200800040

173. Tenhaeff WE, Gleason KK (2009). Crosslinking of copolymer thin films by initiated chemical vapor deposition for hydrogel applications. *Thin Solid Films* 517(12), 3543–3546. doi: 10.1016/j.tsf.2009.01.052

174. Tenhaeff WE, Gleason KK (2009). Surface-tethered pH-responsive hydrogel thin films as size-selective layers on nanoporous asymmetric membranes. *Chemistry of Materials* 21(18), 4323–4331. doi: 10.1021/cm9023474

175. Trujillo NJ, Baxamusa S, Gleason KK (2009). Grafted polymeric nanostructures patterned bottom-up by colloidal lithography and initiated chemical vapor deposition (iCVD). *Thin Solid Films* 517(12), 3615–3618. doi: 10.1016/j.tsf.2009.01.034

176. Trujillo NJ, Baxamusa SH, Gleason KK (2009). Grafted functional polymer nanostructures patterned bottom-up by colloidal lithography and initiated chemical vapor deposition (iCVD). *Chemistry of Materials* 21(4), 742–750. doi: 10.1021/cm803008r

177. Vaddiraju S, Cebeci H, Gleason KK, Wardle BL (2009). Hierarchical multifunctional composites by conformally coating aligned carbon nanotube arrays with conducting polymer. *ACS Applied Materials & Interfaces* 1(11), 2565–2572. doi: 10.1021/am900487z

178. Baxamusa SH, Gleason KK (2008). Thin polymer films with high step coverage in microtrenches by initiated CVD. *Chemical Vapor Deposition* 14(9–10), 313–318. doi: 10.1002/cvde.200806713

179. Baxamusa SH, Montero L, Dubach JM, Clark HA, Borros S, Gleason KK (2008). Protection of sensors for biological applications by photoinitiated chemical vapor deposition of hydrogel thin films. *Biomacromolecules* 9(10), 2857–2862. doi: 10.1021/bm800632d

180. Gupta M, Kapur V, Pinkerton NM, Gleason KK (2008). Initiated chemical vapor deposition (iCVD) of conformal polymeric nanocoatings for the surface modification of high-aspect-ratio pores. *Chemistry of Materials* 20(4), 1646–1651. doi: 10.1021/cm702810j

181. Im SG, Bong KW, Kim BS, Baxamusa SH, Hammond PT, Doyle PS, Gleason KK (2008). Patterning nanodomains with orthogonal functionalities: solventless synthesis of self-sorting surfaces. *Journal of the American Chemical Society* 130(44), 14424–14425. doi: 10.1021/ja806030z

182. Im SG, Kim BS, Lee LH, Tenhaeff WE, Hammond PT, Gleason KK (2008). A directly patternable, click-active polymer film via initiated chemical vapor deposition. *Macromolecular Rapid Communications* 29(20), 1648–1654. doi: 10.1002/marc.200800404

183. Im SG, Kusters D, Choi W, Baxamusa SH, de Sanden M, Gleason KK (2008). Conformal coverage of poly(3,4-ethylenedioxythiophene) films with tunable nanoporosity via oxidative chemical vapor deposition. *ACS Nano* 2(9), 1959–1967. doi: 10.1021/nn800380e

184. Karaman M, Kooi SE, Gleason KK (2008). Vapor deposition of hybrid organic-inorganic dielectric Bragg mirrors having rapid and reversibly tunable optical reflectance. *Chemistry of Materials* 20(6), 2262–2267. doi: 10.1021/cm703107d

185. Lau KKS, Gleason KK (2008). Applying HWCVD to particle coatings and modeling the deposition mechanism. *Thin Solid Films*, 516(5), 674–677. doi: 10.1016/j.tsf.2007.06.045

186. Lau KKS, Gleason KK (2008). Initiated chemical vapor deposition (iCVD) of copolymer thin films. *Thin Solid Films*, 516(5), 678–680. doi: 10.1016/j.tsf.2007.06.046

187. Lee LH, Gleason KK (2008). Cross-linked organic sacrificial material for air gap formation by initiated chemical vapor deposition. *Journal of the Electrochemical Society* 155(4), G78–G86. doi: 10.1149/1.2837838

188. Martin TP, Chan K, Gleason KK (2008). Combinatorial initiated chemical vapor deposition (iCVD) for polymer thin film discovery. *Thin Solid Films*, 516(5), 681–683. doi: 10.1016/j.tsf.2007.06.113

189. O'Shaughnessy WS, Edell DJ, Gleason KK (2008). Initiated chemical vapor deposition of biopassivation coatings. *Thin Solid Films*, 516(5), 684–686. doi: 10.1016/j.tsf.2007.06.112

190. Tenhaeff WE, Gleason KK (2008). Initiated and oxidative chemical vapor deposition of polymeric thin films: iCVD and oCVD. *Advanced Functional Materials* 18(7), 979–992. doi: 10.1002/adfm.200701479 **(invited review)**

191. Vaddiraju S, Senecal K, Gleason KK (2008). Novel strategies for the deposition of -COOH functionalized conducting copolymer films and the assembly of inorganic nanoparticles on conducting polymer platforms. *Advanced Functional Materials* 18(13), 1929–1938. doi: 10.1002/adfm.200800196

192. Bakker R, Verlaan V, van der Werf CHM, Rath JK, Gleason KK, Schropp REI (2007). Initiated chemical vapour deposition (iCVD) of thermally stable poly-glycidyl methacrylate. *Surface & Coatings Technology* 201(22–23), 9422–9425. doi: 10.1016/j.surfcoat.2007.03.058

193. Chen GH, Gupta M, Chan K, Gleason KK (2007). Initiated chemical vapor deposition of poly(furfuryl methacrylate). *Macromolecular Rapid Communications* 28(23), 2205–2209. doi: 10.1002/marc.200700466

194. Im SG, Gleason KK (2007). Systematic control of the electrical conductivity of poly(3,4-ethylenedioxythiophene) via oxidative chemical vapor deposition. *Macromolecules* 40(18), 6552–6556. doi: 10.1021/ma0628477

195. Im SG, Gleason KK, Olivetti EA (2007). Doping level and work function control in oxidative chemical vapor deposited poly (3,4-ethylenedioxythiophene). *Applied Physics Letters* 90(15). doi: 10.1063/102721376

196. Im SG, Olivetti EA, Gleason KK (2007). Systematic control of the electrical conductivity of poly (3,4-ethylenedioxythiophene) via oxidative chemical vapor deposition (oCVD). *Surface & Coatings Technology*, 201(22–23), 9406–9412. doi: 10.1016/j.surfcoat.2007.04.081

197. Im SG, Yoo PJ, Hammond PT, Gleason KK (2007). Grafted conducting polymer films for nano-patterning onto various organic and inorganic substrates by oxidative chemical vapor deposition. *Advanced Materials* 19(19), 2863–2867. doi: 10.1002/adma.200701170

198. Lau KKS, Gleason KK (2007). All-dry synthesis and coating of methacrylic acid copolymers for controlled release. *Macromolecular Bioscience* 7(4), 429–434. doi: 10.1002/mabi.200700017

199. Lau KKS, Gleason KK (2007). Particle functionalization and encapsulation by initiated chemical vapor deposition (iCVD). *Surface & Coatings Technology*, 201, 9189–9194. doi: 10.1016/j.surfcoat.2007.04.045

200. Lock JP, Lutkenhaus JL, Zacharia NS, Im SG, Hammond PT, Gleason KK (2007). Electrochemical investigation of PEDOT films deposited via CVD for electrochromic applications. *Synthetic Metals* 157(22–23), 894–898. doi: 10.1016/j.synthmet.2007.08.022

201. Ma ML, Gupta M, Li Z, Zhai L, Gleason KK, Cohen RE, Rubner MF, Rutledge GC (2007). Decorated electrospun fibers exhibiting superhydrophobicity. *Advanced Materials* 19(2), 255–259. doi: 10.1002/adma.200601449

202. Martin TP, Kooi SE, Chang SH, Sedransk KL, Gleason KK (2007). Initiated chemical vapor deposition of antimicrobial polymer coatings. *Biomaterials* 28(6), 909–915. doi: 10.1016/j.biomaterials.2006.10.009

203. Martin TP, Sedransk KL, Chan K, Baxamusa SH, Gleason KK (2007). Solventless surface photoinitiated polymerization: Grafting chemical vapor deposition (gCVD). *Macromolecules* 40(13), 4586–4591. doi: 10.1021/ma070150v

204. Martin TP, Lau KKS, Chan K, Mao Y, Gupta M, O'Shaughnessy WS, Gleason KK (2007). Initiated chemical vapor deposition (iCVD) of polymeric nanocoatings. *Surface & Coatings Technology* 201, 9400–9405. doi: 10.1016/j.surfcoat.2007.05.003

205. O'Shaughnessy WS, Baxamusa SH, Gleason KK (2007). Additively patterned polymer thin films by photo-initiated chemical vapor deposition (piCVD). *Chemistry of Materials* 19(24), 5836–5838. doi: 10.1021/cm071381j

206. O'Shaughnessy WS, Mari-Buye N, Borros S, Gleason KK (2007). Initiated chemical vapor deposition of a surface-modifiable copolymer for covalent attachment and patterning of nucleophilic ligands. *Macromolecular Rapid Communications* 28(18–19), 1877–1882. doi: 10.1002/marc.200700333

207. O'Shaughnessy WS, Murthy SK, Edell DJ, Gleason KK (2007). Stable biopassive insulation synthesized by initiated chemical vapor deposition of poly(1,3,5-trivinyltrimethylcyclotrisiloxane). *Biomacromolecules* 8(8), 2564–2570. doi: 10.1021/bm070242s

208. Tenhaeff WE, Gleason KK (2007). Initiated chemical vapor deposition of alternating copolymers of styrene and maleic anhydride. *Langmuir* 23(12), 6624–6630. doi: 10.1021/la070086a

209. Tenhaeff WE, Gleason KK (2007). Initiated chemical vapor deposition of perfectly alternating poly(styrene-alt-maleic anhydride). *Surface & Coatings Technology*, 201(22), 9417–9421. doi: 10.1016/j.surfcoat.2007.04.024

210. Casserly TB, Gleason KK (2006). Effect of substrate temperature on the plasma polymerization of poly(methyl methacrylate). *Chemical Vapor Deposition* 12(1), 59–66. doi: 10.1002/cvde.200506409

211. Chan K, Gleason KK (2006). A mechanistic study of initiated chemical vapor deposition of polymers: Analyses of deposition rate and molecular weight. *Macromolecules* 39(11), 3890–3894. doi: 10.1021/ma051776t

212. Chan K, Gleason KK (2006). Air-gap fabrication using a sacrificial polymeric thin film synthesized via initiated chemical vapor deposition. *Journal of the Electrochemical Society* 153(4), C223–C228. doi: 10.1149/1.2168297

213. Chan K, Kostun LE, Tenhaeff WE, Gleason KK (2006). Initiated chemical vapor deposition of polyvinylpyrrolidone-based thin films. *Polymer* 47(20), 6941–6947. doi: 10.1016/j.polymer.2006.07.068

214. Choi HG, Amara JP, Martin TP, Gleason KK, Swager TM, Jensen KF (2006). Structure and morphology of poly(isobenzofuran) films grown by hot-filament chemical vapor deposition. *Chemistry of Materials* 18(26), 6339–6344. doi: 10.1021/cm0616331

215. Gorga RE, Lau KKS, Gleason KK, Cohen RE (2006). The importance of interfacial design at the carbon nanotube/polymer composite interface. *Journal of Applied Polymer Science* 102(2), 1413–1418. doi: 10.1002/app.24272

216. Gupta M, Gleason KK (2006). Initiated chemical vapor deposition of poly(1H,1H,2H,2H-perfluorodecyl acrylate) thin films. *Langmuir* 22(24), 10047–10052. doi: 10.1021/la061904m

217. Gupta M, Gleason KK (2006). Large-scale initiated chemical vapor deposition of poly(glycidyl methacrylate) thin films. *Thin Solid Films* 515(4), 1579–1584. doi: 10.1016/j.tsf.2006.05.021

218. Lau KKS, Gleason KK (2006). Initiated chemical vapor deposition (iCVD) of poly(alkyl acrylates): An experimental study. *Macromolecules* 39(10), 3688–3694. doi: 10.1021/ma0601619

219. Lau KKS, Gleason KK (2006). Initiated chemical vapor deposition (iCVD) of poly(alkyl acrylates): A kinetic model. *Macromolecules* 39(10), 3695–3703. doi: 10.1021/ma0601621

220. Lau KKS, Gleason KK (2006). Particle surface design using an all-dry encapsulation method. *Advanced Materials* 18(15), 1972–1977. doi: 10.1002/adma.200600896

221. Lau KKS, Mao Y, Lewis HGP, Murthy SK, Olsen BD, Loo LS, Gleason KK (2006). Polymeric nanocoatings by hot-wire chemical vapor deposition (HWCVD). *Thin Solid Films* 501(1–2), 211–215. doi: 10.1016/j.tsf.2005.07.208

222. Lock JP, Im SG, Gleason KK (2006). Oxidative chemical vapor deposition of electrically conducting poly(3,4-ethylenedioxythiophene) films. *Macromolecules* 39(16), 5326–5329. doi: 10.1021/ma060113o

223. Mao Y, Felix NM, Nguyen PT, Ober CK, Gleason KK (2006). Positive- and negative-tone CVD polyacrylic electron-beam resists developable by supercritical CO_2. *Chemical Vapor Deposition* 12(5), 259–262. doi: 10.1002/cvde.200506416

224. Mao Y, Gleason KK (2006). Positive-tone nanopatterning of chemical vapor deposited polyacrylic thin films. *Langmuir* 22(4), 1795–1799. doi: 10.1021/la0521701

225. Mao Y, Gleason KK (2006). Vapor-deposited fluorinated glycidyl copolymer thin films with low surface energy and improved mechanical properties. *Macromolecules* 39(11), 3895–3900. doi: 10.1021/ma052591p

226. Martin TP, Gleason KK (2006). Combinatorial initiated CVD for polymeric thin films. *Chemical Vapor Deposition* 12(11), 685–691. doi: 10.1002/cvde.200606495

227. O'Shaughnessy WS, Gao ML, Gleason KK (2006). Initiated chemical vapor deposition of trivinyltrimethylcyclotrisiloxane for biomaterial coatings. *Langmuir* 22(16), 7021–7026. doi: 10.1021/la0607858

228. Ross AD, Gleason KK (2006). The CVD of nanocomposites fabricated via ultrasonic atomization. *Chemical Vapor Deposition* 12(4), 225–230. doi: 10.1002/cvde.200506368

229. Casserly TB, Gleason KK (2005). Chemical vapor deposition of organosilicon thin films from methylmethoxysilanes. *Plasma Processes and Polymers* 2(9), 679–687. doi: 10.1002/ppap.200500055

230. Casserly TB, Gleason KK (2005). Density functional theory calculation of Si-29 NMR chemical shifts of organosiloxanes. *Journal of Physical Chemistry B* 109(28), 13605–13610. doi: 10.1021/jp044385+

231. Casserly TB, Gleason KK (2005). Enthalpies of formation and reaction for primary reactions of methyl- and methylmethoxysilanes from density functional theory. *Plasma Processes and Polymers* 2(9), 669–678. doi: 10.1002/ppap.200500054

232. Chan K, Gleason KK (2005). Initiated chemical vapor deposition of linear and cross-linked poly(2-hydroxyethyl methacrylate) for use as thin-film hydrogels. *Langmuir* 21(19), 8930–8939. doi: 10.1021/la051004q

233. Chan K, Gleason KK (2005). Initiated CVD of poly(methyl methacrylate) thin films. *Chemical Vapor Deposition* 11(10), 437–443. doi: 10.1002/cvde.200506381

234. Chan K, Gleason KK (2005). Photoinitiated chemical vapor deposition of polymeric thin films using a volatile photoinitiator. *Langmuir* 21(25), 11773–11779. doi: 10.1021/la051469g

235. Lock JP, Gleason KK (2005). Tunable waveguides via photo-oxidation of plasma-polymerized organosilicon films. *Applied Optics* 44(9), 1691–1697.

236. Ma ML, Mao Y, Gupta M, Gleason KK, Rutledge GC (2005). Superhydrophobic fabrics produced by electrospinning and chemical vapor deposition. *Macromolecules* 38(23), 9742–9748. doi: 10.1021/ma0511189

237. Mabboux PY, Gleason KK (2005). Chemical bonding structure of low dielectric constant Si:O:C:H films characterized by solid-state NMR. *Journal of the Electrochemical Society* 152(1), F7–F13. doi: 10.1149/1.1830353

238. Poliskie GM, Cohen RE, Gleason KK (2005). Static uniaxial compression of polyisoprene-montmorillonite nanocomposites monitored by ^{1}H spin-lattice relaxation time constants. *Journal of Applied Polymer Science* 98(4), 1806–1813. doi: 10.1002/app.22328

239. Poliskie GM, Gleason KK (2005). Stress relaxation of polyisoprene-laponite nanocomposites monitored by magic angle spinning ^{1}H NMR and optical microscopy. *Polymer Composites 26*(6), 799–805. doi: 10.1002/pc.20150

240. Poliskie GM, Haddad TS, Blanski RL, Gleason KK (2005). Characterization of the phase transitions of ethyl substituted polyhedral oligomeric silsesquioxane. *Thermochimica Acta* 438(1–2), 116–125. doi: 10.1016/j.tca.2005.08.028

241. Ross AD, Gleason KK (2005). Effects of condensation reactions on the structural, mechanical, and electrical properties of plasma-deposited organosilicon thin films from octamethylcyclotetrasiloxane. *Journal of Applied Physics* 97(11). doi:10.1063/1.1923163

242. Ross AD, Gleason KK (2005). Enhancement of mechanical properties of organosilicon thin films deposited from diethylsilane. *Journal of Vacuum Science & Technology A* 23(3), 465–469. doi: 10.1016/1.1881636

243. Sparacin DK, Hong CY, Kimerling LC, Michel J, Lock JP, Gleason KK (2005). Trimming of microring resonators by photo-oxidation of a plasma-polymerized organosilane cladding material. *Optics Letters* 30(17), 2251–2253.

244. Wu QG, Ross AD, Gleason KK (2005). Nanoporous organosilicate glass films via chemical vapor deposition onto colloidal crystal templates. *Plasma Processes and Polymers* 2(5), 401–406. doi: 10.1002/ppap.200500024

245. Burkey DD, Gleason KK (2004). Organosilicon thin films deposited from cyclic and acyclic precursors using water as an oxidant. *Journal of the Electrochemical Society* 151(5), F105–F112. doi: 10.1149/1.1688801

246. Burkey DD, Gleason KK (2004). Temperature-resolved Fourier transform infrared study of condensation reactions and porogen decomposition in hybrid organosilicon-porogen films. *Journal of Vacuum Science & Technology A* 22(1), 61–70. doi: 10.1116/1.1627766

247. Loo LS, Gleason KK (2004). Investigation of polymer and nanoclay orientation distribution in nylon 6/montmorillonite nanocomposite. *Polymer* 45(17), 5933–5939. doi: 10.1016/j.polymer.2004.06.025

248. Mao Y, Felix NM, Nguyen PT, Ober CK, Gleason KK (2004). Towards all-dry lithography: Electron-beam patternable poly(glycidyl methacrylate) thin films from hot filament chemical vapor deposition. *Journal of Vacuum Science & Technology B* 22(5), 2473–2478. doi: 10.1116/1.1800351

249. Mao Y, Gleason KK (2004). Hot filament chemical vapor deposition of poly(glycidyl methacrylate) thin films using tert-butyl peroxide as an initiator. *Langmuir* 20(6), 2484–2488. doi: 10.1021/la0359427

250. Murthy SK, Olsen BD, Gleason KK (2004). Effect of filament temperature on the chemical vapor deposition of fluorocarbon-organosilicon copolymers. *Journal of Applied Polymer Science* 91(4), 2176–2185. doi: 10.1002/app.13342

251. Murthy SK, Olsen BD, Gleason KK (2004). Peptide attachment to vapor deposited polymeric thin films. *Langmuir* 20(11), 4774–4776. doi: 10.1021/la036102v

252. Burkey DD, Gleason KK (2003). Structure and mechanical properties of thin films deposited from 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane and water. *Journal of Applied Physics* 93(9), 5143–5150. doi: 10.1063/1.1562744

253. Burkey DD, Gleason KK (2003). Structure and thermal properties of thin film poly(alpha-methylstyrene) deposited via plasma-enhanced CVD. *Chemical Vapor Deposition* 9(2), 65–71.

254. Lau KKS, Bico J, Teo KBK, Chhowalla M, Amaratunga GAJ, Milne WI, McKinley GH, Gleason KK (2003). Superhydrophobic carbon nanotube forests. *Nano Letters* 3(12), 1701–1705. doi: 10.1021/nl034704t

255. Lau KKS, Murthy SK, Lewis HGP, Caulfield JA, Gleason KK (2003). Fluorocarbon dielectrics via hot filament chemical vapor deposition. *Journal of Fluorine Chemistry* 122(1), 93–96. doi: 10.1016/s0022-1139(03)00099-x

256. Lin J, Murthy SK, Olsen BD, Gleason KK, Klibanov AM (2003). Making thin polymeric materials, including fabrics, microbicidal and also water-repellent. *Biotechnology Letters* 25(19), 1661–1665.

257. Loo LS, Gleason KK (2003). Fourier transform infrared investigation of the deformation behavior of montmorillonite in nylon-6/nanoclay nanocomposite. *Macromolecules* 36(8), 2587–2590. doi: 10.1021/ma0259057

258. Loo LS, Gleason KK (2003). Insights into structure and mechanical behavior of alpha and gamma crystal forms of nylon-6 at low strain by infrared studies. *Macromolecules* 36(16), 6114–6126. doi: 10.1021/ma034213v

259. Qi HJ, Teo KBK, Lau KKS, Boyce MC, Milne WI, Robertson J, Gleason KK (2003). Determination of mechanical properties of carbon nanotubes and vertically aligned carbon nanotube forests using nanoindentation. *Journal of the Mechanics and Physics of Solids* 51(11–12), 2213–2237. doi: 10.1016/j.jmps.2003.09.015

260. Wu QG, Gleason KK (2003). Plasma-enhanced chemical vapor deposition of low-*k* dielectric films using methylsilane, dimethylsilane, and trimethylsilane precursors. *Journal of Vacuum Science & Technology A* 21(2), 388–393. doi: 10.1116/1.1539086

261. Wu QG, Gleason KK (2003). Plasma-enhanced CVD of organosilicate glass (OSG) films deposited from octamethyltrisiloxane, bis(trimethylsiloxy) methylsilane, and 1,1,3,3-tetramethyldisiloxane. *Plasmas and Polymers* 8(1), 31–41.

262. Cruden BA, Gleason KK, Sawin HH (2002). Optical emission spectroscopy of pulsed hexalfuoropropylene oxide and tetrafluoroethylene plasmas. *Journal of Applied Physics* 91(12), 9547–9555. doi: 10.1063/1.1471386

263. Cruden BA, Gleason KK, Sawin HH (2002). Relationship of CF_2 concentration to deposition rates in the pyrolytic chemical vapor deposition process. *Journal of Vacuum Science & Technology B* 20(2), 690–695. doi: 10.1116/1.1459726

264. Cruden BA, Gleason KK, Sawin HH (2002). Ultraviolet absorption measurements of CF_2 in the parallel plate pyrolytic chemical vapour deposition process. *Journal of Physics D—Applied Physics* 35(5), 480–486.

265. Mabboux PY, Gleason KK (2002). ^{19}F NMR characterization of electron beam irradiated vinylidene fluoride-trifluoroethylene copolymers. *Journal of Fluorine Chemistry* 113(1), 27–35.

266. Murthy SK, Gleason KK (2002). Fluorocarbon-organosilicon copolymer synthesis by hot filament chemical vapor deposition. *Macromolecules* 35(5), 1967–1972. doi: 10.1021/ma011286a

267. Murthy SK, Olsen BD, Gleason KK (2002). Initiation of cyclic vinylmethylsiloxane polymerization in a hot-filament chemical vapor deposition process. *Langmuir* 18(16), 6424–6428. doi: 10.1021/la025815v

268. Cruden BA, Gleason KK, Sawin HH (2001). Time resolved ultraviolet absorption spectroscopy of pulsed fluorocarbon plasmas. *Journal of Applied Physics* 89(2), 915–922.

269. Gleason KK, Hill DJT, Lau KKS, Mohajerani S, Whittaker AK (2001). The use of ^{19}F NMR for new structure determination in the radiolysis of FEP. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* 185, 83–87. doi: 10.1016/s0168-583x(01)00749-2

270. Labelle CB, Gleason KK (2001). Pulsed plasma deposition from 1,1,2,2-tetrafluoroethane by electron cyclotron resonance and conventional plasma enhanced chemical vapor deposition. *Journal of Applied Polymer Science* 80(11), 2084–2092.

271. Lau KKS, Gleason KK (2001). Thermal annealing of fluorocarbon films grown by hot filament chemical vapor deposition. *Journal of Physical Chemistry B* 105(12), 2303–2307.

272. Lau KKS, Lewis HGP, Limb SJ, Kwan MC, Gleason KK (2001). Hot-wire chemical vapor deposition (HWCVD) of fluorocarbon and organosilicon thin films. *Thin Solid Films* 395(1–2), 288–291. doi: 10.1016/s0040-6090(01)01287-1

273. Lewis HGP, Casserly TB, Gleason KK (2001). Hot-filament chemical vapor deposition of organosilicon thin films from hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane. *Journal of the Electrochemical Society* 148(12), F212–F220. doi: 10.1149/1.1415723

274. Lewis HGP, Caulfield JA, Gleason KK (2001). Perfluorooctane sulfonyl fluoride as an initiator in hot-filament chemical vapor deposition of fluorocarbon thin films. *Langmuir* 17(24), 7652–7655.

275. Lewis HGP, Weibel GL, Ober CK, Gleason KK (2001). E-beam patterning of hot-filament CVD fluorocarbon films using supercritical CO_2 as a developer. *Chemical Vapor Deposition* 7(5), 195–197.

276. Loo LS, Gleason KK (2001). Hot filament chemical vapor deposition of polyoxymethylene as a sacrificial layer for fabricating air gaps. *Electrochemical and Solid State Letters* 4(11), G81–G84. doi: 10.1149/1402496

277. Labelle CB, Gleason KK (2000). Fourier transform infrared spectroscopy study of thermal annealing behavior of ECR pulsed plasma deposited fluorocarbon thin films from 1,1,2,2-tetrafluoroethane. *Journal of the Electrochemical Society* 147(2), 678–681.

278. Labelle CB, Gleason KK (2000). Overhang test structure deposition profiles of pulsed plasma fluorocarbon films from hexafluoropropylene oxide, 1,1,2,2-tetrafluoroethane, and difluoromethane. *Chemical Vapor Deposition* 6(1), 27–32.

279. Lau KKS, Caulfield JA, Gleason KK (2000). Structure and morphology of fluorocarbon films grown by hot filament chemical vapor deposition. *Chemistry of Materials* 12(10), 3032–3037.

280. Lau KKS, Caulfield JA, Gleason KK (2000). Variable angle spectroscopic ellipsometry of fluorocarbon films from hot filament chemical vapor deposition. *Journal of Vacuum Science & Technology A—Vacuum Surfaces and Films* 18(5), 2404–2411.

281. Lau KKS, Gleason KK (2000). Pulsed plasma enhanced and hot filament chemical vapor deposition of fluorocarbon films. *Journal of Fluorine Chemistry* 104(1), 119–126. doi: 10.1016/s0022-1139(00)00234-7

282. Lau KKS, Gleason KK, Trout, B. L. (2000). Thermochemistry of gas phase CF_2 reactions: A density functional theory study. *Journal of Chemical Physics* 113(10), 4103–4108.

283. Lewis HGP, Edell DJ, Gleason KK (2000). Pulsed-PECVD films from hexamethylcyclotrisiloxane for use as insulating biomaterials. *Chemistry of Materials* 12(11), 3488–3494.

284. Loo LS, Cohen RE, Gleason KK (2000). Chain mobility in the amorphous region of nylon 6 observed under active uniaxial deformation. *Science* 288(5463), 116–119.

285. Loo LS, Cohen RE, Gleason KK (2000). Deuterium nuclear magnetic resonance of deuterium oxide in nylon 6 under active uniaxial deformation. *Polymer* 41(21), 7699–7704.

286. Winder EJ, Gleason KK (2000). Growth and characterization of fluorocarbon thin films grown from trifluoromethane (CHF_3) using pulsed-plasma enhanced CVD. *Journal of Applied Polymer Science* 78(4), 842–849. doi: 10.1002/1097-4628(20001024)78:4<842::aid-app180>3.0.co;2-j

287. Banerjee I, Harker M, Wong L, Coon PA, Gleason KK (1999). Characterization of chemical vapor deposited amorphous fluorocarbons for low dielectric constant interlayer dielectrics. *Journal of the Electrochemical Society* 146(6), 2219–2224.

288. Cruden B, Chu K, Gleason K, Sawin H (1999). Thermal decomposition of low dielectric constant pulsed plasma fluorocarbon films: I. Effect of precursors and substrate temperature. *Journal of the Electrochemical Society* 146(12), 4590–4596.

289. Cruden B, Chu K, Gleason K, Sawin H (1999). Thermal decomposition of low dielectric constant pulsed plasma fluorocarbon films: II. Effect of postdeposition annealing and ambients. *Journal of the Electrochemical Society* 146(12), 4597–4604.

290. Labelle CB, Gleason KK (1999). Pulsed plasma-enhanced chemical vapor deposition from CH_2F_2, $C_2H_2F_4$, and $CHClF_2$. *Journal of Vacuum Science & Technology A* 17(2), 445–452.

291. Labelle CB, Gleason KK (1999). Surface morphology of PECVD fluorocarbon thin films from hexafluoropropylene oxide, 1,1,2,2-tetrafluoroethane, and difluoromethane. *Journal of Applied Polymer Science* 74(10), 2439–2447.

292. Labelle CB, Karecki SM, Reif R, Gleason KK (1999). Fourier transform infrared spectroscopy of effluents from pulsed plasmas of 1,1,2,2-tetrafluoroethane, hexafluoropropylene oxide, and difluoromethane. *Journal of Vacuum Science & Technology A* 17(6), 3419–3428.

293. Lau KKS, Gleason KK (1999). Solid-state nuclear magnetic resonance spectroscopy of low dielectric constant films from pulsed hydrofluorocarbon plasmas. *Journal of the Electrochemical Society* 146(7), 2652–2658.

294. Loo LS, Cohen RE, Gleason KK (1999). Deuterium nuclear magnetic resonance of Phenol-d_5 in nylon 6 under active uniaxial deformation. *Macromolecules* 32(13), 4359–4364.

295. Lau KKS, Gleason KK (1998). High-resolution ^{19}F MAS NMR spectroscopy of fluorocarbon films from pulsed PECVD of hexafluoropropylene oxide. *Journal of Physical Chemistry B* 102(31), 5977–5984.

296. Limb SJ, Edell DJ, Gleason EF, Gleason KK (1998). Pulsed plasma-enhanced chemical vapor deposition from hexafluoropropylene oxide: Film composition study. *Journal of Applied Polymer Science* 67(8), 1489–1502.

297. Loo LS, Cohen RE, Gleason KK (1998). Correlation times of motion of deuterium oxide in polyamide 6 rods. *Macromolecules* 31(25), 8907–8911.

298. Chang WK, Gleason KK (1997). Relationship of processing parameters to photoluminescence intensity and mechanical failure in thick porous silicon layers. *Journal of the Electrochemical Society* 144(4), 1441–1446.

299. Kwan MC, Gleason KK (1997). Pyrolytic CVD of poly(organosiloxane) thin films. *Chemical Vapor Deposition* 3(6), 299–301.

300. Labelle CB, Limb SJ, Gleason KK (1997). Electron spin resonance of pulsed plasma-enhanced chemical vapor deposited fluorocarbon films. *Journal of Applied Physics* 82(4), 1784–1787.

301. Lau KKS, Gleason KK (1997). Structural correlation study of pulsed plasma-polymerized fluorocarbon solids by two-dimensional wide-line separation NMR spectroscopy. *Journal of Physical Chemistry B* 101(35), 6839–6846.

302. Limb SJ, Gleason KK, Edell DJ, Gleason EF (1997). Flexible fluorocarbon wire coatings by pulsed plasma enhanced chemical vapor deposition. *Journal of Vacuum Science & Technology A—Vacuum Surfaces and Films* 15(4), 1814–1818.

303. Chang WK, Liao MY, Gleason KK (1996). Characterization of porous silicon by solid-state nuclear magnetic resonance. *Journal of Physical Chemistry* 100(50), 19653–19658.

304. Kwan MC, Gleason KK (1996). Method for achieving high selectivity and resolution in selectively deposited diamond films. *Diamond and Related Materials* 5(9), 1048–1050.

305. Limb SJ, Labelle CB, Gleason KK, Edell DJ, Gleason EF (1996). Growth of fluorocarbon polymer thin films with high CF2 fractions and low dangling bond concentrations by thermal chemical vapor deposition. *Applied Physics Letters* 68(20), 2810–2812.

306. Roy AK, Gleason KK (1996). Analytical solutions for multiple-quantum-coherence dynamics among two or three dipolar-coupled, spin-1/2 nuclei. *Journal of Magnetic Resonance Series A* 120(2), 139–147.

307. Rutledge KM, Gleason KK (1996). Hydrogen in CVD diamond films. *Chemical Vapor Deposition* 2(2), 37–43.

308. Wolden CA, Gleason KK (1996). On the pressure limits of diamond chemical vapor deposition. *Diamond and Related Materials* 5(12), 1503–1508.

309. Gleason KK (1995). Applications of solid-state multiple-quantum NMR. *Trends in Analytical Chemistry* 14(3), 104–112.

310. Mukai U, Gleason KK, Argon AS, Cohen RE (1995). Poly(dimethylsiloxane)/nylon-6 block-copolymers: Molecular mobility at the interface. *Macromolecules* 28(14), 4899–4903.

311. Okano K, Gleason KK (1995). Electron-emission from phosphorus-doped and boron-doped polycrystalline diamond films. *Electronics Letters* 31(1), 74–75.

312. Rutledge KMM, Scruggs BE, Gleason KK (1995). Influence of hydrogenated defects and voids on the thermal-conductivity of polycrystalline diamond. *Journal of Applied Physics* 77(4), 1459–1462.

313. Lathrop DA, Handy ES, Gleason KK (1994). Multiple-quantum NMR coherence growth in single-crystal and powdered calcium-fluoride. *Journal of Magnetic Resonance Series A* 111(2), 161–168.

314. McNamara KM, Gleason KK (1994). Radial distribution of hydrogen in chemical vapor deposited diamond. *Chemistry of Materials* 6(1), 39–43.

315. McNamara KM, Scruggs BE, Gleason KK (1994). The effect of impurities on the IR absorption of chemically vapor deposited diamond. *Thin Solid Films* 253(1–2), 157–161.

316. McNamara KM, Williams BE, Gleason KK, Scruggs BE (1994). Identification of defects and impurities in chemical-vapor-deposited diamond through infrared spectroscopy. *Journal of Applied Physics* 76(4), 2466–2472.

317. Roy AK, Gleason KK (1994). Application of proton multiple-quantum NMR to the study of dynamics in bulk chloral polycarbonate. *Journal of Polymer Science Part B—Polymer Physics* 32(13), 2235–2240.

318. Scruggs BE, Gleason KK (1994). The role of proton nuclear magnetic resonance spin-lattice relaxation centers in the strong absorption transition at 210 nm in fused silica. *Journal of Applied Physics* 76(5), 3063–3067.

319. Wolden C, Gleason KK, Howard JB (1994). A reduced reaction mechanism for diamond deposition modeling. *Combustion and Flame* 96(1–2), 75–79.

320. Burum DP, Cory DG, Gleason KK, Levy D, Bielecki A (1993). Quadrature detection of cramps NMR data for maximum resolution and sensitivity. *Journal of Magnetic Resonance Series A* 104(3), 347–352.

321. Lathrop DA, Gleason KK (1993). Effects of polymeric motion on ^{19}F NMR multiple quantum coherences: signal refocusing in poly(tetrafluoroethylene). *Macromolecules* 26(17), 4652–4657.

322. Levy DH, Gleason KK (1993). ^{1}H nuclear magnetic resonance of thermally grown silicon dioxide films. *Journal of the Electrochemical Society* 140(3), 797–800.

323. Levy DH, Gleason KK (1993). Nuclear magnetic resonance probe for low level hydrogen detection. *Journal of Vacuum Science Technology A—Vacuum Surfaces and Films* 11(1), 195–198.

324. Levy DH, Gleason KK, Rothschild M, Sedlacek JHC (1993). The role of hydrogen in excimer-laser-induced damage of fused silica. *Journal of Applied Physics* 73(6), 2809–2815.

325. Limb SJ, Scruggs BE, Gleason KK (1993). Distribution and motion of trifluoromethanesulfonate anions in poly(p-hydroxystyrene) and polystyrene films studied by multiple-quantum NMR. *Macromolecules* 26(15), 3750–3757.

326. McNamara KM, Gleason KK (1993). Comparison of tantalum and rhenium filaments in diamond CVD using selective carbon-13 labeling. *Journal of the Electrochemical Society* 140(2), L22–L24.

327. Mitra S, Gleason KK (1993). ^{1}H NMR studies on the effects of annealing on chemical-vapor-deposited (CVD) diamond. *Diamond and Related Materials* 2(2–4), 126–129. doi: 10.1016/0925-9635(93)90042-z

328. Mitra S, Gleason KK, Jia H, Shinar J (1993). Effects of annealing on hydrogen microstructure in boron-doped and undoped rf-sputter-deposited amorphous silicon. *Physical Review B* 48(4), 2175–2182.

329. Scruggs BE, Gleason KK (1993). Analysis of fluorocarbon plasma-treated diamond powders by solid-state fluorine-19 nuclear magnetic resonance. *Journal of Physical Chemistry* 97(36), 9187–9195.

330. Wolden C, Gleason KK (1993). Heterogeneous formation of atomic hydrogen in hot-filament diamond deposition. *Applied Physics Letters* 62(19), 2329–2331.

331. Levy DH, Gleason KK (1992). Multiple quantum nuclear magnetic resonance as a probe for the dimensionality of hydrogen in polycrystalline powders and diamond films. *Journal of Physical Chemistry* 96(20), 8125–8131.

332. Levy DH, Gleason KK, Rothschild M, Sedlacek JHC, Takke R (1992). Reactions of hydrogenated defects in fused silica caused by thermal treatment and deep ultraviolet irradiation. *Applied Physics Letters* 60(14), 1667–1669.

333. McNamara KM, Gleason KK (1992). Selectively ^{13}C-enriched diamond films studied by nuclear magnetic resonance. *Journal of Applied Physics* 71(6), 2884–2889.

334. McNamara KM, Gleason KK, Robinson CJ (1992). Quantitative correlation of infrared absorption with nuclear magnetic resonance measurements of hydrogen content in diamond films. *Journal of Vacuum Science & Technology A—Vacuum Surfaces and Films* 10(5), 3143–3148. doi: 10.1116/1.577834

335. McNamara KM, Gleason KK, Vestyck DJ, Butler JE (1992). Evaluation of diamond films by nuclear magnetic resonance and Raman spectroscopy. *Diamond and Related Materials* 1(12), 1145–1155. doi: 10.1016/0925-9635(92)90088-6

336. McNamara KM, Levy DH, Gleason KK, Robinson CJ (1992). Nuclear magnetic resonance and infrared absorption studies of hydrogen incorporation in polycrystalline diamond. *Applied Physics Letters* 60(5), 580–582.

337. Scruggs BE, Gleason KK (1992). Computer-simulation of the multiple-quantum dynamics of one-dimensional, two-dimensional and three-dimensional spin distributions. *Chemical Physics* 166(3), 367–378.

338. Scruggs BE, Gleason KK (1992). Multiple-quantum NMR coherence growth in polycrystalline salts containing ^{19}F. *Journal of Magnetic Resonance* 99(1), 149–160.

339. Scruggs BE, Gleason KK (1992). Photosensitive salt distribution in polymer films studied by ^{19}F multiple-quantum NMR. *Macromolecules* 25(7), 1864–1869.

340. Wolden C, Mitra S, Gleason KK (1992). Radiative heat transfer in hot-filament chemical vapor deposition diamond reactors. *Journal of Applied Physics* 72(8), 3750–3758.

341. Gleason KK, Petrich MA, Reimer JA (1987). Hydrogen microstructure in amorphous hydrogenated silicon. *Physical Review B* 36(6), 3259–3267.

342. Gleason KK, Wang KS, Chen MK, Reimer JA (1987). Monte Carlo simulations of amorphous hydrogenated silicon thin-film growth. *Journal of Applied Physics* 61(8), 2866–2873.

343. Petrich MA, Gleason KK, Reimer JA (1987). Structure and properties of amorphous hydrogenated silicon carbide. *Physical Review B* 36(18), 9722–9731.

344. Baum J, Gleason KK, Pines A, Garroway AN, Reimer JA (1986). Multiple-quantum NMR-study of clustering in hydrogenated amorphous silicon. *Physical Review Letters* 56(13), 1377–1380

345. Klincewicz KM (*maiden name*), Reid RC (1984). Estimation of critical properties with group contribution methods. *AIChE Journal* 30(1), 137–142. doi: 10.1002/aic.690300119

Invited Lectures

1. John M. Prausnitz AICH Institute Lecture, AIChE Annual Meeting, Orlando FL; November 13, 2019.
2. Durable Surface Energy Control with Initiated Chemical Vapor Deposition (iCVD) Polymers, American Vacuum Society (AVS), Columbus OH; October 23, 2019
3. Vapor Deposited Polymers: from Fundamentals to Commercialization, University of Illinois, Department of Chemical & Biomolecular Engineering, Urbana, IL; September 24, 2019.
4. Chemical Vapor Deposition of Zwitterionic Surfaces, 4th Int'l Conf. on Bioinspired and Zwitterionic Materials, Kerkrade, The Netherlands; June 18, 2019 ***Plenary address***
5. Vapor Deposited Polymers: from Fundamentals to Commercialization, American Physical Society March Meeting, Boston, MA, March 4, 2019.
6. Vapor Deposited Polymers: from Fundamentals to Commercialization, AIChE Women in Chemical Engineering (WIC) 20th Anniversary Symposium, Pittsburgh, PA; October 30, 2018.
7. Initiated Plasma-Enhanced CVD of Ultrathin Gas-Selective Polymers Films, American Vacuum Society (AVS) 65th International Symposium & Exhibition, Long Beach, CA; October 22, 2018 .
8. Vapor Deposited Polymers: from Fundamentals to Commercialization, 2018 STAMI Industrial Partners Day and Exposition, Georgia Tech, Atlanta, GA; September 27, 2018. ***Keynote address***
9. Stable Wettability Control of Nanoporous Microstructures by Ultrathin Polymers for Applications in Electronics, European Materials Research Symposium (EMRS), Strasbourg, France; June 19, 2018.
10. Initiating Polymers from Monomer Vapors via Heat, Light, and Plasma, Physics Dept. Colloquium, Graz University of Technology (TU Graz), Graz, Austria; June 14, 2018.
11. Ultrathin and Conformal Polymer Films for Organic Surfaces and Devices, 17th Congress of the Asian-Pacific Confederation of Chemical Engineering, Hong Kong, August 24, 2017. ***Plenary address***
12. Welcoming Address, History and Future of Massachusetts Innovation, HUBweek MIT, Cambridge, MA, September 27, 2017.
13. Synthesizing Polymers by iCVD for Organic Surfaces & Devices, 9th International Conference on Hot Wire and Initiated CVD, Philadelphia, PA, September 6 2016. ***Keynote address***
14. Panelist for Clean Energy session, Conference of New England Governors & Eastern Canadian Premiers, Boston, MA, August 29, 2016.
15. Synthesizing Polymers from Monomer Vapors for Organic Surfaces & Devices, St. Gobain, Northboro, MA, June 10, 2016.
16. Philips MIT alliance: Introduction to the MIT Innovation ecosystem, Eindhoven, Netherlands, May 12, 2016
17. Moderator for Panel Discussion:At the Crossroads of Collaboration: How the MIT Campus will change by 2030, a launch activity for MIT's Campaign for a Better World, May 7th, 2016.
18. Opening Remarks, MIT J-WAFS Food and Water Conference, Cambridge, MA, April 27th, 2016.
19. Food and Water-borne Pathogen Detection, MIT J-WAFS Food and Water Conference, Cambridge, MA, April 27th, 2016.
20. Synthesizing Polymers from Monomer Vapors for Organic Surfaces & Devices, UCLA, Chemical Engineering Departmental Seminar, Los Angeles, CA, April 15th, 2016.
21. Panelist Analog Devices Women's Forum, Boston, MA, April 12, 2016
22. Synthesizing Polymers from Monomer Vapors for Organic Surfaces & Devices, University of Washington, Chemical Engineering Departmental Seminar, Seattle, April 4th, 2016.
23. Engineering the Vapor Deposition of Organic Surfaces & Devices, Microsystems Technology Laboratory Industrial Advisory Board Meeting, January 22, 2016.
24. Ultrathin and Durable Fluoropolymer Networks by initiated Chemical Vapor Deposition, Pacific Polymer Conference, ACS Pacific Polymer Conference, Kauai, HI, Dec 12, 2015.

25. Synthesizing Polymers from their Monomer Vapors for Organic Surfaces and Devices Synthesizing Polymers from their Monomer Vapors for Organic Surfaces and Devices, National Academy of Engineering, Section 3, Washington DC, Oct. 5, 2015.
26. AIChE Stine Award Lecture, Engineering the Vapor Deposition of Organic Thin Films and Devices, AIChE National Meeting, Salt Lake City, UT, Nov 11, 2015. ***Award Lecture.***
27. Synthesizing Polymers from their Monomer Vapors for Organic Surfaces and Devices, Department of Material Science, Georgia Institute of Technology, Sept. 14, 2015.
28. Science Talent Search Alumni Reception, hosted by Akamai: panelist with Eric Lander, Erika Ebbeel Angle, Frank Wilczek, Tom Leighton, Sept 9, 2015.
29. The Accidental Entrepreneur: the Road to Commercialization of Ultrathin Vapor Deposited Polymer Films, MIT Brazil Challenge of Innovation Conference, San Paulo, Brazil May 13, 2015.
30. Chemically Vapor Deposited (CVD) Polymers for Device Fabrication, Spring MRS Meeting, San Francisco, April 8, 2015
31. All in the Life of a Chemical Engineer: from Spectroscopist to Accidental Entrepreneur', Adel F. Sarofim Distinguished Lecture, University of Utah Department of Chemical Engineering, March 24, 2015. ***Named lectureship.***
32. Durable Water Shedding Surfaces, Solve for X (Google X). San Martin, CA, February 5, 2014.
33. Solvent-free Polymerization for Surface Design. Materials Research Society, Boston, MA, December 2, 2013.
34. Vapor Printed Surface and Devices on Fiber-based Substrates. Harvard Science Symposium "Smart Clothes," Cambridge, MA, November 15, 2013.
35. Solvent-free Polymerization at Surfaces by initiated Chemical Vapor Deposition (iCVD). Japan Society of Applied Physics and Materials Research Society Joint Symposium, Kyoto, Japan, September 16, 2013.
36. Chemically Vapor Deposited Polymers: A New Paradigm for Surface Modification and Device Fabrication. Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, September 2013.
37. Vapor Printed Organic Electrodes. 14th SPIE Conference on Organic Photovoltaics, San Diego, CA, August 25, 2013.
38. Vapor Printed Electrodes. 6th International Symposium on Flexible Organic Electronics, Thessaloniki, Greece, June 28, 2013. **Keynote speaker.**
39. Initiated and Oxidative CVD Polymers for Paper PV. Society of Vacuum Coaters, Providence, RI, April 24, 2013.
40. Chemically Vapor Deposited Polymers: A New Paradigm for Surface Modification and Device Fabrication. Tis Lahiri Lecture, Department of Chemical Engineering, Vanderbilt University, Nashville, TN, April 15, 2013. **Named lectureship.**
41. Vapor Deposited Polymers for Membrane Applications. Masdar Institute, Abu Dhabi, United Arab Emirates, January 10, 2013.
42. Paper Photovoltaics. Microfluidics 2.0 Conference, Boston University, Boston, MA, November 30, 2012.
43. Chemical Vapor Deposition for Ultrathin and Conformal Fluoropolymer Surfaces. Fluoropolymer 2012 Conference, Las Vegas, NV, October 15, 2012.
44. Designing Novel Devices with Chemically Vapor Deposited Polymers. Department of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, September 17, 2012.
45. Designing Novel Devices with Chemically Vapor Deposited Polymers. 14th International Conference on Organized Molecular Films, Paris, France, July 12, 2012.
46. Designing Novel Devices with Chemically Vapor Deposited Polymers. IUPAC MACRO 2012, Blacksburg, VA, June 27, 2012.
47. Designing Novel Devices with Chemically Vapor Deposited Polymers. Canadian Society of Chemistry, Calgary, Canada, May 29, 2012.

48. Designing Novel Devices with Chemically Vapor Deposited Polymers. Institut Químic de Sarrià, Barcelona, February 23, 2012.
49. Paper PV. Printed Electronics USA 2011 Conference, Santa Clara, CA, December 1, 2011.
50. Ultrathin and Conformal Biopassivation CVD Polymers. 2011 MIT Research and Development Conference, Cambridge, MA, November 16, 2011.
51. Paper PV. MIT Energy Initiative Advisory Board, Cambridge, MA, November 11, 2011.
52. Designing Novel Devices with Chemically Vapor Deposited Polymers. Department of Chemical, Materials, and Biomolecular Engineering, University of Connecticut, Storrs, CT, September 27, 2011.
53. CVD Polymers. PerkinElmer NanoSymposium, Museum of Science, Boston, MA, August 25, 2011.
54. CVD Polymers for Biosensing. US Food and Drug Administration, Winchester, MA, August 11, 2011.
55. Designing Surfaces with Chemically Vapor Deposited (CVD) Polymers. Center for Advanced Materials and Membranes, Pall Corporation, Port Washington, NY, July 13, 2011. **Inaugural lecture.**
56. CVD Polymers. Aixtron, Herzogenrath, Germany, April 7, 2011.
57. Paper PV. Printed Electronics Europe 2011 Conference, Dusseldorf, Germany, April 5–6, 2011. **Keynote address.**
58. CVD Polymers. Henkel, Dusseldorf, Germany, April 4, 2011.
59. Designing Novel Devices with Chemically Vapor Deposited Polymers. ACS Award in Chemistry Materials: Symposium in Honor of Debra Rolison, Anaheim, CA, March 28, 2011.
60. CVD Polymers. Presentation to Dr. Thomas Russell, Director, Air Force Office of Scientific Research, MIT, March 25, 2011.
61. Designing Novel Devices with Chemically Vapor Deposited Polymers. Chemical Engineering Seminar, MIT, Cambridge, MA, March 18, 2011.
62. Designing Novel Devices with Chemically Vapor Deposited Polymers. 6th International Smart Coatings Symposium, Orlando, FL, February 24, 2011.
63. Designing Novel Devices with Chemically Vapor Deposited Polymers. International Microelectronics and Packaging Society, Cambridge, MA, January 18, 2011.
64. Polymers by Chemical Vapor Deposition, featuring GVD Corporation. MIT's Technology Breakfast Series, Cambridge, MA, December 2, 2010.
65. Designing Novel Devices with Chemically Vapor Deposited Polymers. Epoch Foundation, MIT, Cambridge, MA, November 4, 2010.
66. Responsive and Conducting Polymers by Chemical Vapor Deposition. Mechanical, Materials and Structures Technical Network Symposium, Burlington, MA, October 6, 2010.
67. CVD Polymers. Aixtron AG, Aachen, Germany, September 21, 2010.
68. Initiating Hot Wire Chemical Vapor Deposition for Conformal and Responsive Polymeric Layers. 6th International Conference on Hot-Wire Chemical Vapor Deposition, Paris, France, September 13, 2010.
69. Patterning Nanodomains with Orthogonal Functionalities: Solventless Synthesis of Self-sorting Surfaces. NanoOptics Plasmonics Conference, Rockville, MD, April 21, 2010.
70. Functional and Conducting Polymer Thin Films by Vapor Deposition. Department of Chemical and Biological Engineering Seminar, Tufts University, Medford, MA, January 25, 2010.
71. Engineering the Chemistry of Vapor Deposited Functional and Responsive Polymeric Surfaces. 11th Pacific Polymer Conference, Cairns, Australia, December 7, 2009. **Keynote address.**
72. Functional and Conducting Polymer Thin Films by Vapor Deposition. American Vacuum Society, San Jose, CA, November 10, 2009.
73. Initiated and Oxidative Chemical Vapor Deposition (CVD) of Conformal and Functional Polymers. EuroCVD16, Vienna, Austria, October, 2009.

74. Functional and Conducting Polymer Thin Films by Vapor Deposition. 23rd International Conference on Amorphous and Nanocrystalline Semiconductors, Utrecht, Netherlands, August 25, 2009. **Keynote address**.
75. Designing Functional and Responsive Organic Surfaces by Chemical Vapor Deposition (with S.G. Im). 13th International Conference on Surface and Colloid Science and the 83rd ACS Colloid and Surface Science Symposium, New York, NY, June 17, 2009.
76. Functional and Conducting Polymer Thin Films by Vapor Deposition. Raytheon, Tewksbury, MA, June 9, 2009.
77. Patterning Nano-domains with Orthogonal Functionalities: Solventless Synthesis of Self-sorting Surfaces. 2009 Optical Data Storage Topical Meeting (IEEE sponsored), Orlando, FL, May 12, 2009.
78. Designing Functional and Responsive Organic Surfaces by Chemical Vapor Deposition. Department of Chemical Engineering Seminar, University of Colorado, Boulder, CO, March 31, 2009.
79. Designing Functional and Responsive Organic Surfaces by Chemical Vapor Deposition. Department of Chemical Engineering Seminar, University of Rochester, Rochester, NY, February 25, 2009.
80. Designing Functional and Responsive Organic Surfaces by Chemical Vapor Deposition. Polymer Technology and Fiber Engineering Seminar, Georgia Institute of Technology, Atlanta, GA, February 9, 2009.
81. Designing Functional and Responsive Organic Surfaces by Chemical Vapor Deposition. Department of Chemical Engineering Seminar, University of Massachusetts, Amherst, MA, February 6, 2009.
82. Functional and Responsive Organic Surfaces by Chemical Vapor Deposition. MIT Industrial Liaison Program (ILP) Annual Symposium, Cambridge, MA, October 28, 2008.
83. Functional Vapor Deposited Polymers for Ligand Attachment and Patterning. Fluoropolymer 2008 (ACS sponsored), Charleston, SC, October 20, 2008.
84. Designing Functional and Responsive Organic Surfaces by Chemical Vapor Deposition. Department of Chemical Engineering Seminar, University of Texas, Austin, TX, September 30, 2008.
85. Surface Modification by Vapor Deposited Polymeric Nanocoatings. Army Research Lab, Adelphi, MD, March 18, 2008.
86. Engineering the Vapor Deposition of Conducting Polymer Nanocoatings. Chemical Engineering Department, Drexel University, Philadelphia, PA, February 1, 2008.
87. Design of Chemical Vapor Deposition Processes for Low-k Dielectrics and Air Gap Formation. IMEC, Leuven, Belgium, January 23, 2008.
88. Surface Modification by Vapor Deposited Polymeric Nanocoatings. MIT in Japan: 10th Annual Symposium, Tokyo, Japan, January 18, 2008.
89. Surface Modification by Vapor Deposited Polymeric Nanocoatings. Teijin, Tokyo, Japan, January 17, 2008.
90. Air Gap Fabrication. Tokyo Electron, Ltd. Tokyo, Japan, January 17, 2008.
91. Surface Modification by Vapor Deposited Polymeric Nanocoatings. Hitachi, Tokyo, Japan, January 16, 2008.
92. Surface Modification by Vapor Deposited Polymeric Nanocoatings. MIT ILP-Epoch Taiwan Symposium, Taipei, Taiwan, January 14, 2008.
93. Engineering Polymeric Nanocoatings by Vapor Deposition. 31st Annual Symposium of the Macromolecular Science and Engineering Program at the University of Michigan, Ann Arbor, MI, October 25, 2007.
94. Conformal Polymeric Thin Films via Initiated Chemical Vapor Deposition. American Vacuum Society, Seattle, WA, October 15, 2007.
95. Chemical Vapor Deposition of Polymeric Nanocoatings. Department of Chemical Engineering, University of Calgary, Calgary, Canada, October 5, 2007.

96. Initiated CVD of Polymeric Nanocoatings. 16th European Conference on Chemical Vapor Deposition, The Hague, Netherlands, September 20, 2007.
97. Sensing Science at the Institute for Soldier Nanotechnologies. ACS National Meeting, Boston, MA, August 21, 2007. **Invited panelist.**
98. The Institute for Soldier Nanotechnologies. Emerging Defense Technologies Conference, Paris, France, June 14, 2007.
99. Engineering the Chemistry of Vapor Deposition. Raytheon, Andover, MA, May 9, 2007.
100. Polymeric Nanocoatings by Chemical Vapor Deposition. Presstek, Cambridge, MA, April 24, 2007.
101. Polymeric Nanocoatings by Chemical Vapor Deposition. St. Gobain, Northboro, MA, April 13, 2007.
102. Biopassivation Coatings by Initiated CVD from Trivinyltrimethylcyclotrisiloxane. 2007 Materials Research Society Spring Meeting: Symposium, San Francisco, CA, April 11, 2007.
103. Design of CVD Processes for Low-k Dielectrics and Air Gap Formation. 2007 Materials Research Society Spring Meeting: Symposium B, San Francisco, CA, April 11, 2007.
104. Polymeric Nanocoatings by Chemical Vapor Deposition. CIBA, by webcast, March 22, 2007.
105. Polymeric Nanocoatings by Chemical Vapor Deposition. Millipore, Bedford, MA, January 16, 2007.
106. Nonfouling iCVD Coatings for Optodes. Draper Laboratory, Cambridge, MA, January 9, 2007.
107. Strategies for Frugal Vacuum Processing. Defense Advanced Research Projects Agency/Microsystems Technology Office Workshop on Low-Volume N/MEMS Manufacturing for Defense Applications, Chantilly, VA, November 29, 2006.
108. Initiated Chemical Vapor Deposition of Fluorinated Acrylate Homopolymer and Copolymer Thin Films. Fluoropolymer 2006 (sponsored by the ACS), Charleston, SC, October 16, 2006.
109. The Institute for Soldier Nanotechnologies. University Affiliated Research Center Director's Meeting, Salt Lake City, UT, September 12, 2006.
110. Polymeric Nanocoatings by Chemical Vapor Deposition. Debye Lecture, Utrecht University, Netherlands, June 14, 2006.
111. Initiated Chemical Vapor Deposition of Polymeric Thin Films. Ornstein Colloquium, Utrecht University, Netherlands, June 9, 2006.
112. Mechanistic Aspects of initiated Chemical Vapor Deposition for Polymeric Films. 209th Electrochemical Society Meeting, Denver, CO, May 9, 2006.
113. Initiated Chemical Vapor Deposition of Polymeric Thin Films. Chemical Engineering Department, City College of New York, New York, NY, April 24, 2006.
114. Fundamentals of Chemically Vapor-deposited Organosilicate Glass (OSG) Low-*k* Dielectrics. MIRAI Workshop on Interconnect Technology, Tsukuba, Japan, 2006. **Keynote address.**
115. From Prototype to Product with the Help of SBIR [Small Business Innovation Research] Funding. American Institute of Chemical Engineers, October 2005.
116. Initiated Chemical Vapor Deposition of Flexible Polymeric Coatings. Plastic Electronics, Frankfurt, Germany, October 6, 2005.
117. Polymer Nanocoating by initiated Chemical Vapor Deposition. Medtronics, Minneapolis, MN, September 21, 2005.
118. Microsphere Encapsulation with Polymers by Chemical Vapor Deposition. Dupont, Wilmington, DE, May 20, 2005.
119. Polymeric Nanocoatings by initiated Chemical Vapor Deposition. Nanotech 2005, Anaheim, CA, May 10, 2005.
120. Chemical Vapor Deposition of Porous Organosilicon Low-k Dielectrics. American Chemical Society National Meeting, San Diego, CA, March 14, 2005.
121. Polymeric Nanocoatings by Chemical Vapor Deposition. Michelin, Greenville, SC, February 11, 2005.

122. Engineering the Vapor Deposition of Polymers. Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH, November 4, 2004.
123. Fluoropolymers by Chemical Vapor Deposition. Fluoropolymer 2004 (ACS Sponsored), Savannah, GA, October 9, 2004.
124. Polymeric Nanocoatings by Hot Wire Chemical Vapor Deposition. 3rd International Conference on Hot Wire CVD, Utrecht, Netherlands, August 26, 2004.
125. Chemical Strategies for Structural Retention and Rapid Growth of Vapor-deposited Organic Films. Gordon Conference on Plasma Processing, Holderness, NH, August 18, 2004.
126. Polymeric Nanocoatings by Chemical Vapor Deposition. Bakaert, Buffalo, NY, July 14, 2004.
127. Polymeric Nanocoatings by Chemical Vapor Deposition. Xerox, Webster, NY, July 13, 2004.
128. Silicone Nanocoatings by Chemical Vapor Deposition. Silicon Symposium, Philadelphia, PA, May 2004.
129. Polymeric Nanocoatings by Hot Filament Chemical Vapor Deposition. Department of Materials Science and Engineering, Cornell University, Ithaca, NY, April 29, 2004.
130. Engineering Surfaces for Nanotechnology. MIT on the Road, Detroit, MI, November 2002.
131. Status of Women Faculty at MIT. American Institute of Chemical Engineers National Meeting, Indianapolis, IN, November 6, 2002.
132. Fluorinated Dielectrics via CVD. 224th American Chemical Society National Meeting, Boston, MA, August 22, 2002.
133. Thin Film Characterization by Solid State NMR. Rocky Mountain Conference on Analytical Chemistry, Denver, CO, August 1, 2002.
134. Engineering the Chemistry of Vapor Deposition. Department of Chemical Engineering, Penn State, University Park, PA, April 2002.
135. Engineering the Chemistry of Vapor Deposition. Chemical Engineering Seminar, Georgia Tech, Atlanta, GA, April 2002.
136. Low Dielectric Constant Films. Dupont Experimental Station, Wilmington, DE, January 2002.
137. Air Gap Technology. TEL Corporate Research Center, Yamanashi, Japan, December 10, 2001.
138. New Paradigms for Low Dielectric Constant Films. Semicon Japan, Tokyo, Japan, December 7, 2001.
139. New Paradigms for Low Dielectric Constant Films. TMS/SPE Polymer Materials Conference, Indianapolis, IN, November 3, 2001. **Keynote address**.
140. Pulsed-plasma Deposition of Organosilicon Films. CIP'2001-13th International Colloquium on Plasma Processes, Antibes-Juan les Pins, France, June 10, 2001.
141. Mechanical Properties of Fluorocarbon Polymer Thin Films Grown by PECVD. International Conference on Metallurgical Coatings and Thin Films Meeting, San Diego, CA, June 3, 2001.
142. Low Dielectric Constant Films. IEEE International Interconnect Technology Conference, Santa Clara, CA, June 1, 2001.
143. Engineering the Chemistry of Vapor Deposition. Chemical Engineering Colloquium, University of Arizona, Tucson, AZ, April 17, 2001.
144. New Paradigms for Low Dielectric Constant Films. TEL Advanced Technology Forum, Tokyo, Japan, April 13, 2001.
145. Patternable CVD Thin Films. Materials Research Society, San Francisco, CA, April 1, 2001.
146. Low-k Dielectrics for Pulsed-plasma CVD of Organosilicon Precursors. Materials Research Society, San Francisco, CA, April 1, 2001.
147. Porous and Directly Patternable PTFE Films Grown by Hot-filament Chemical Vapor Deposition. Fluorine in Coatings IV, Brussels, Belgium, March 3, 2001.
148. Pulsed-plasma–Enhanced Deposition of Low-k Materials. Sematech Workshop on Low-k Materials. Austin, Texas, February 20, 2001.
149. Chemical Vapor Deposition of Low-k Materials. Atofina, King of Prussia, PA, February 16, 2001.

150. Pulsing or Eliminating the Plasma Enhancement of Chemically Vapor-deposited Organic Thin Films. Center for Plasma-Aided Manufacturing Colloquium, University of Wisconsin, Madison, WI, January 26, 2001.

151. Fast Magic Angle Spinning ^{19}F NMR of Fluorocarbon Polymers and Thin Films. Winter Fluorine Conference, St. Petersburg, FL, January 15, 2001.

152. Elucidating the Molecular Architecture of Chemically Vapor-deposited (CVD) Fluorocarbons. PACIFICHEM 2000, Honolulu, HI, December 14, 2000.

153. HWCVD [Hot-wire Chemically Vapor-deposited] Fluorocarbon & Organosilicon Thin Films. Japan, November 2000.

154. Low Dielectric Constant Materials for Microelectronics. Van Ness Lectures, Rensselaer Polytechnic Institute, Troy, NY, October 16–26, 2000.

155. Engineering the Chemistry of Vapor Deposition. Van Ness Lectures, Rensselaer Polytechnic Institute, Troy, NY, October 16–26, 2000.

156. CVD Films as Directly Patternable Low-k Dielectrics. American Vacuum Society National Meeting, Boston, MA, October 2, 2000.

157. Pulsed-plasma and Hot-Filament CVD Dielectrics. Semicon West, San Francisco, CA, July 10, 2000.

158. Chemical Vapor Deposition for Nanotechnology. Defense Advanced Research Projects Agency: Applied Physics of Nanostructures, Arlington, VA; May 8, 2000.

159. Fluorocarbon Films Vapor Deposited in the Absence of a Plasma. Polymers for Microelectronics, Winterthur, DE, May 1, 2000.

160. Patternable Low-k Dielectrics Developed by Supercritical CO_2. Semiconductor Safety Association Meeting; Washington, DC, April 26, 2000.

161. *In Situ* Deformation of Nylon 6 Monitored by ^{2}H NMR. American Chemical Society National Meeting, San Francisco, CA, March 27, 2000.

162. Pulsed-plasma and Hot Filament Organosilicon CVD. American Chemical Society National Meeting, San Francisco, CA, March 27, 2000.

163. CVD of Fluorocarbon Low-K Dielectric Films. Fluorocarbon Plasma Workshop, Grenoble, France, March 20, 2000.

164. Chemical Vapor Deposition of Low Dielectric Films. American Vacuum Society, New England Chapter, Cambridge, MA, February 16, 2000.

165. Hot-Wire CVD Flurocarbon and Organosilicon Thin Films. Japan, January 2000.

166. Fluorocarbon Low Dielectric Constant Chemical Vapor Deposition. American Chemical Society Workshop on Low-k Materials, Monterey, CA, November 1999.

167. Low Dielectric Constant CVD Fluorocarbon Films, American Chemical Society National Meeting. PMSE-Symposium on Micro- and Nano-Patterning Science and Technology, New Orleans, LA, August 1999.

168. CVD of Fluorocarbon Low-k Dielectric Films. Gordon Research Conference on Electronic Materials, New England College, Henniker, NH, July 1999.

169. The History and Future of Fluorocarbon CVD Dielectric Thin Films. Dielectrics for ULSI Multilevel Interconnection Conference (DUMIC), San Jose, CA, February 1999. **Keynote Address.**

170. Controlling and Characterizing the Molecular Architecture of Pulsed Plasma and Pyrolytic Chemical Vapor Deposition (CVD) Fluorocarbons and Organosilicones. 1st Alpine International Symposium on Plasma Processing of Polymers, Campitello di Fassa, Italy, January–February 1999.

171. Controlling and Characterizing the Molecular Architecture of Fluorocarbon Thin Films by Chemical Vapor Deposition (CVD). Department of Chemical Engineering, Stanford University, , Stanford, CA, January 1999.

172. Controlling and Characterizing the Molecular Architecture of Fluorocarbon Thin Films by Chemical Vapor Deposition (CVD). Department of Chemical Engineering, Colorado State University, Fort Collins, CO, January 1999.

173. Controlling and Characterizing the Molecular Architecture of Fluorocarbon Thin Films by Chemical Vapor Deposition (CVD). Department of Chemical Engineering, Colorado School of Mines, Golden, CO, January 1999.

174. Fast MAS and Multidimensional NMR of Fluorocarbon Chemically Vapor Deposited Thin Films. International Symposium on the NMR Spectroscopy of Polymers (sponsored by the Polymer Division of the ACS), Breckenridge, CO, January 1999.

175. Pulsed Plasma Enhanced and Pyrolytic Chemical Vapor Deposition of Fluorocarbon Films. Fluorine in Coatings III Conference, Orlando, FL, January 1999.

176. Low Dielectric Constant Fluorocarbon Films. Materials Research Society Fall Meeting, Boston, MA, December 1998.

177. Pulsed Plasma and Pyrolytic CVD of Fluorocarbon and Organosilicone Films. Naval Research Laboratory, Washington, DC, November 1998.

178. Pulsed Plasma Enhanced Chemical Vapor Deposition form $C_2H_2F_4$, CH_2F_2, and $CHC1F_2$. Materials Research Society Spring Meeting, San Francisco, CA, April 1998.

179. NMR of Pulsed Plasma and Pyrolytic CVD Fluorocarbon Films. 1997 Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI, October 1997.

180. ES&H Issues Related to Low-k Materials, Processing Advanced Metallization and Interconnect Systems for ULSI Applications. San Diego, CA, September 1997.

181. Pulsed Plasma and Pyrolytic CVD of Low Dielectric Constant Fluorocarbon Films. Tokyo Electron Ltd., Tokyo, April 1997.

182. Pulsed Plasma Enhanced and Pyrolytic CVD of "Teflon-like" Thin Films. DuPont, Wilmington, DE, March 1997.

183. Pulsed Plasma Enhanced and Pyrolytic CVD of Low Dielectric Constant Fluorocarbon Films. Intel, Santa Clara, CA, February 1997.

184. Novel CVD of Polymeric Thin Films. Applied Biosystems, Perkin-Elmer, Foster City, CA, February 1997.

185. Pulsed Plasma Enhanced and Pyrolytic CVD of "Teflon-like" Thin Films. Department of Chemical Engineering, North Carolina State University, Raleigh, NC, February 1997.

186. Pulsed Plasma Enhanced and Pyrolytic CVD of "Teflon-like" Thin Films. Becton Dickinson Research Center, Research Triangle Park, NC, February 1997.

187. Theory and Modelling of Processes and Process Redesign: Design for the Environment. Panel Discussion, Materials Research Society, Boston, MA, December 1996.

188. CVD of Teflon-like Thin Films, Lam Research, Fremont, CA, October 1996.

189. Novel CVD of "Teflon"-like Insulating Biomaterials. American Vacuum Society 43rd Annual Meeting, Philadelphia, PA, October 1996.

190. Pulsed-Plasma Polymer Deposition. Defense Sciences Research Council, La Jolla, CA, July 1996.

191. NMR of Diamond Films. Department of Chemistry, University of Illinois, Chicago, IL, February 1996.

192. Solid-State Multiple Quantum NMR of Polymer Mixtures. ACS, Honolulu, HI, December 1995.

193. Solid-State NMR of Polymeric Blends. Program in Polymer Science and Technology Seminar, MIT, October 1995.

194. Relating Defect Structure to Growth Processes in Solids. Department of Chemical Engineering Seminar Series, University of California, Berkeley, CA, May 1995.

195. Deposition and Defect Studies of Diamond Thin Films. Department of Materials Science, University of California, Berkeley, CA, May 1995.

196. Nuclear Magnetic Resonance of Optical Materials. Spire, Bedford, MA, March 1995.

197. Diamond Deposition and Defects. Department of Chemical Engineering Seminar Series, Rice University, Houston, TX, March 1995.

198. Pulsed Plasma Fluorocarbon Films. AT&T Bell Laboratories, February 1995.

199. Creating Multiple-Quantum NMR Coherences in Solids. Department of Chemistry, Sherbrooke University, Quebec, Canada, September 1994.

200. Proton and ^{19}F NMR of Solid Thin Films and Interfaces. 36th Rocky Mountain Conference in Analytical Chemistry, Denver, CO, August 1994.

201. Multiple Quantum NMR Studies of Microstructure in Solids. 14th Blue Hen NMR Symposium, University of Delaware, Newark, DE, June 1994.

202. Applications of Solid-State Multiple Quantum NMR. Exxon Research and Development, Annandale, NJ, June 1994.

203. Application of ^{1}H, ^{13}C and ^{19}F to Diamond Thin Films. Gordon Conference on Diamond Synthesis, Henniker, NH, June 1994.

204. Probing Molecular Dynamics in Solids via Multiple Quantum Coherences. 35th Experimental Nuclear Magnetic Resonance Conference, Asilomar, CA, April 1994.

205. NMR of Hydrogen in Bulk and Thin Film Silicon Dioxide. Physical Chemistry Seminar, Brown University, Providence, RI, April 1994.

206. Diamond Deposition and Defect Chemistry Studied by Solid-State NMR. Department of Chemical Engineering Seminar, University of California at Davis, Davis, CA, March 1994.

207. Multiple Quantum NMR in Solids. Department of Chemistry, Physical Chemistry Seminar, University of California, San Diego, San Diego, CA, November 1993.

208. Molecular Motion Studied by ^{19}F Multiple-Quantum NMR. Gordon Conference on Magnetic Resonance, Henniker, NH, July 1993.

209. Diamond Defect Detection by NMR. Condensed Matter/Surface Science Seminar, Ohio University, Athens, OH, June 1993.

210. Molecular Dynamics in Polymeric Systems Studied by ^{19}F Multiple Quantum NMR Coherences. Naval Research Laboratory, Washington, DC, April 1993.

211. Application of NMR to Diamond Surfaces. Surface Science and Catalysis Seminar, Department of Chemistry, University of California, Berkeley, Berkeley, CA, April 1993.

212. The Deposition and Microstructure of Diamond Thin Films. Department of Chemical Engineering, Iowa State University, Ames, IA, September 1992.

213. NMR of Chemical Vapor Deposited Diamond Including ^{1}H Multiple Quantum Studies. 34th Rocky Mountain Conference in Analytical Chemistry, Denver, CO, August 1992.

214. The Relationship of Hydrogen to the Optical Properties of Thin Films. 6th International Symposium on Magnetic Resonance in Colloid and Interface Science, Florence, Italy, June 1992.

215. Diamond Films: Towards Larger Areas and Fewer Defects. MIT ILP Symposium on Electronics, Cambridge, MA, May 1992.

216. Multiple Quantum Dynamics in Polycrystalline Powders and Diamond Films. 33rd Experimental Nuclear Magnetic Resonance Conference, Asilomar, CA, March 1992.

217. Revolutions in Solid-Carbon. 11th International Chemical Symposium at Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Mexico, March 1992.

218. NMR of CVD Diamond Films. Lockheed Missiles and Space Co., Livermore, CA, March 1992.

219. Diamond Deposition and Defects. Department of Chemical Engineering, University of Wisconsin–Madison, Madison, WI, February 1992.

220. NMR of Thin Films for Microelectronics Processing. 18th Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Anaheim, CA, October 1991.

221. ^{1}H and ^{19}F NMR Studies of Segregation in Diamond and Polymer Thin Films. Goodyear Tire and Rubber Co., Akron, OH, October 1991.

222. ^{19}F Multiple-Quantum NMR of Salt/Polymer Mixtures. Max Planck Institute for Polymer Research, Mainz, Germany, August 1991.

223. Characterizing Diamond Films and Deposition Chemistry via Solid-State NMR. Naval Undersea Warfare Center, Newport, RI, July 1990.

224. Solid-State NMR Studies of Thin Films. MIT ILP Symposium on "Chemical Engineering of Materials," Cambridge, MA, May 1990.

225. Solid State NMR Studies of Thin Films Used in the Fabrication of Integrated Circuits. Magnetic Resonance Seminar, MIT, Cambridge, MA, May 1990.

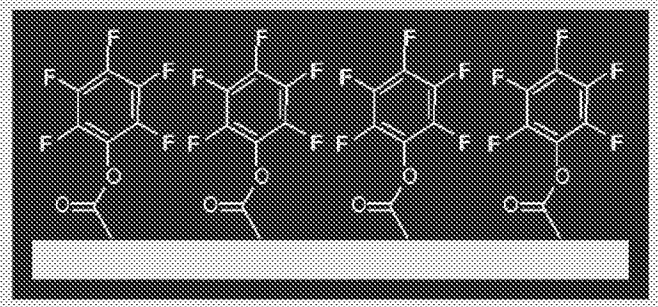
226. Hydrogen in Amorphous Silicon-Containing Thin-Films Studied by Solid-State NMR. IBM, Fishkill, NY, August 1989.

227. Solid-State NMR of Amorphous Thin-Film Processing: Semiconductors and Photoresists. IBM, Almaden Research Center, San Jose, CA, May 1989.

228. The Effect of Hydrogen on PECVD Thin-Film Properties Studied using Solid-State NMR. Digital Equipment Co., Hudson, MA, May 1989.

229. NMR Investigation of Atomic Microstructure in Amorphous Semiconductors. Experimental NMR Conference, Asilomar, CA, March 1987.

Summary: Material coating of surfaces can enhance receptivity for cells and biological compounds. Existing plasma coating technologies and possible materials are limited. A new polymer from pentafluorophenyl methacrylate (PFM) monomer was synthesized, and was plasma enhanced chemical vapor deposited on silicon wafers. The optimal plasma polymerization parameters for the PFM monomer and its copolymerization with the cross-linking agents 1,7-octadiene and 1,4-butanediol divinyl ether co-monomers were established. All the resulting polymer coatings leave the labile pentafluorophenyl group on the surface, enabling a rapid reaction with an amino-terminated biotin ligand and allowing layer-by-layer self-assembly of biotin-streptavidin. In addition, the deposited polymer layers showed an extremely flat morphology with a nanoscale average roughness. This approach provides an easy means of obtaining functionalized surfaces which can enhance and control the biocompatibility of bulk materials. Merging the versatility of plasma polymerization processes, via simple monomers and reaction conditions, with biological platforms that enable target of cell adhesion brings us closer to the ultimate goal of controlling cell function through structured surfaces for their application in tissue engineering.



Schematic representation of a functionalized surface obtained by plasma polymerization of the PFM monomer, showing labile pentafluorophenyl groups on the surface.

Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived Monomer

Laia Francesch,[1] *Elena Garreta,*[1] *Mercedes Balcells,*[1,2] *Elazer R. Edelman,*[2,3] *Salvador Borrós**[1]

[1] Laboratori de Ciència dels Materials, Barcelona Bioengineering Center, Institut Químic de Sarriá-Universitat Ramon Llull, Via Augusta 390, Barcelona 08017, Spain
Fax: +34-932-056-266; E-mail: s.borros@iqs.url.edu
[2] Harvard University-Massachusetts Institute of Technology, Division of Health Sciences and Technology, Cambridge, MA 02139, USA
[3] Cardiovascular Division, Brigham and Women's Hospital and Harvard Medical School, Boston, MA 02115, USA

Received: April 27, 2005; Revised: August 6, 2005; Accepted: August 22, 2005; DOI: 10.1002/ppap.200500042

Keywords: biomaterials; biotin-streptavidin; immobilization of molecules; pentafluorophenyl methacrylate; plasma polymerization

Introduction

Targeting materials to specific cells,[1] designing materials that can sense biochemical signals[2] and developing materials with improved biocompatibility remain challenges in biomaterials development.[3] Significant effort remains in increasing the cell recognition and attractiveness of biomaterial surfaces. Modified materials stimulate cell adhesion, growth and proliferation,[4] while maintaining the mechanical attributes of the bulk material.[5–7] Cell attachment to bioactive surfaces may be enhanced through linkage of biological ligands specific for cell-substrate

 DOI: 10.1002/ppap.200500042 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Favored Ex. 1009

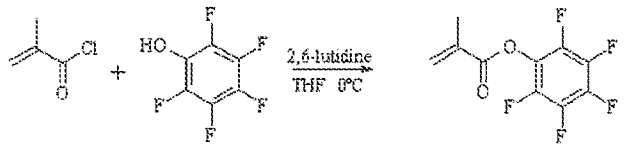
interactions.[8,9] One broadly used approach to immobilizing ligand motifs on biomaterial surfaces consists of creating covalent attachments to reactive polymer side chains.[10] To this goal, plasma polymerization allows deposition of thin films onto substrates of complex geometry with a uniform distribution of functional groups.[11,12] The integrity of the functional groups, however, remains a challenge in any plasma polymerization process. Additionally, the adhesion between the film obtained and the substrate needs to be taken into account.[13]

Biotin-streptavidin technology, a valuable tool in modern biotechnology, is used for immobilization of molecules to solid phases,[14] signal amplification in bioaffinity assays,[15,16] and targeted drug delivery.[17,18] In this context, microcontact printing (μ-CP) offers relatively simple, easy to implement, and attractive methods for micropatterning of such biomolecules.[19] The target surfaces must however be extremely reactive for a successful covalent linkage of biomolecules. In other words, the presentation of labile groups, such as voluminous active esters, is a requisite for the substitution of such groups by the biomolecule of interest.[20–23] Classically plasma vapor deposition utilizes derivatives of parylene, and yet the synthesis processes involved are complex and lengthy.[24] This study sought to develop a feasible alternative to complex functionalized monomers. A new acrylate-type monomer, pentafluorophenyl methacrylate (PFM), was synthesized and used for plasma polymerization. Although methacrylate derivatives of pentafluorophenol are well known,[25] their use as monomers for plasma polymerization has not been studied in depth. We established the different parameters needed to maintain the monomer functionality under pulsed radio-frequency (RF) plasma polymerization. Plasma polymerized films presented the labile pentafluorophenyl group on the surface, which was optimum for subsequent biotin binding.

Experimental Part

Materials

Fiorosil® (60–100 mesh), methacryloyl chloride (+98%), 2,6-dimethylpyridine (2,6-lutidine, 97%), 2,3,4,5,6-pentafluorophenol (99%), 1,7-octadiene (98%), 1,4-butanediol divinyl ether (98%) were obtained from Aldrich (Milwaukee, USA) and used as supplied. (+)-Biotinyl-3,6,9-trioxaundecanediamine, streptavidin, fluorescein-conjugated streptavidin and Tween 20 detergent were obtained from Pierce (IL, USA). Phosphate buffered saline (PBS, pH 7.4) and bovine serum albumin (BSA) were obtained from Gibco (New York, USA) and Fluka (Switzerland), respectively. Tetrahydrofurane (THF) was obtained form Aldrich (Milwaukee, USA).



Scheme 1. Chemical synthesis of pentafluorophenyl methacrylate (PFM).

PFM Synthesis

Methacryloyl chloride (8 ml, 82 mmol) was added drop-wise to a stirred solution of pentafluorophenol (7.6 g, 41 mmol) and 2,6-dimethylpyridine (6.6 g, 62 mmol) in THF (100 ml) at 0 °C (see Scheme 1). After 10 min stirring at the same temperature, the precipitate was filtrated and washed with THF (50 ml). After solvent removal under reduced pressure, the PFM residue was purified by chromatography on a Florosil® column, using pentane as eluent, and obtained as colorless oil (7.0 g, 85%). The monomer was stored at 4 °C until use.

^{1}H NMR and ^{13}C NMR spectra of PFM were determined in $CDCl_3$ as solvent on a Gemini 300 Varian spectrometer.

^{1}H NMR ($CDCl_3$/TMS, 300 MHz, ppm): δ = 6.454 (1H, dq, H_b), 5.914 (1H, dq, H_a), 2.093 (3H, CH_3, dd).

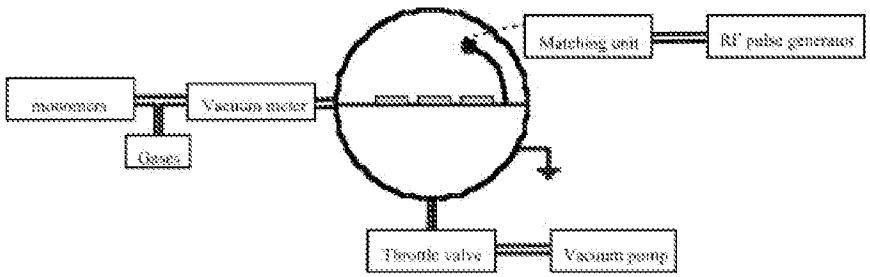
^{13}C NMR ($CDCl_3$/TMS, 75 MHz, ppm): δ = 162.910 (1C, s, C=O), ca. 139.6 (5C, m, C–F), 133.626 (1C, s, H_2C=C), 129.786 (1C, s, H_2C=*C*), 18.272 (1C, s, C–CH_3).

IR spectra were obtained using a Nicolet Magna 5600 spectrophotometer.

IR (KBr, cm^{-1}): ν = 2 950 (m), 1 764 (s), 1 625 (m), 1 475 (m), 1 100 (m).

Plasma Polymerization

The plasma deposition apparatus consisted of a stainless steel discharge vessel (diameter: 26 cm, length: 24 cm) parallel plate reactor (Scheme 2). The ground electrode was the reactor chamber, and the RF electrode was a stainless steel plate. The



Scheme 2. Scheme of the reactor.

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

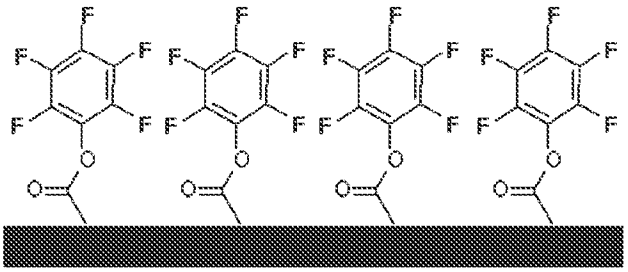
samples were located on this plate for polymerization. The RF electrode was connected to a RF pulse generator (13.56 MHz) through a matching network.

The gases or monomers were supplied via a standard manifold with gas fluxes adjusted with needle valves. The system pressure was determined using a Pirani type vacuum meter (MKS, USA), positioned between the reactor and a cold trap. The two stage mechanical pump (RV12 903, Edwards, GB), positioned after the cold trap, evacuated the vessel to a reactor chamber pressure of 0.1 mbar. All polymers were deposited on 100 oriented silicon wafers. All polymerizations were performed under pulsed plasma. The pulsed RF power setting was 10 W, with a duty cycle of 50% with a frequency of 15 Hz. Deposition times ranged from 2 to 8 h. PFM was used as synthesized. The monomer was preheated to reach the desired polymerization pressure. The monomer flow rate was set so that the pressure within the reactor was 0.3 mbar. PFM was also copolymerized with 1,7-octadiene (liquid, boiling point: 115.5 °C at 760 mmHg) and with 1,4-butanediol divinyl ether (liquid, boiling point 95 °C at 20 mmHg) as crosslinkers. Crosslinker/PFM ratios used were 3:1 and 6:1 for octadiene/PFM and 3:1 and 4:1 for divinyl ether/PFM.

All thin films obtained were characterized by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). XPS analysis was carried out using a Perkin Elmer PHI 5500 spectrometer (USA), equipped with a 350 W monochromatic Alk(alpha) X-rays source. Pass energy for the acquisition of C1s photoelectrons narrow scans was 23.5 eV. All XPS spectra were recorded at a take off angle of 45° relative to the surface normal under high vacuum conditions (the pressure in the main UHV chamber was maintained below 5×10^{-9} mmHg). Data analyses were carried out using Multipax software (PHI) using for calibration the C1s component of the unfunctionalized aliphatic hydrocarbon at a binding energy of 285.0 eV. AFM analysis was performed in tapping mode using a Nanoscope III Instrument (Digital Instruments, Santa Barbara, CA, USA). The roughness of the coatings was measured in terms of and root mean square roughness (R_q) and maximum roughness height (R_{max}). Film thickness was used as a measure of growth rate and determined after 2 h of deposition using a Dektak 6M profilometer (Veeco, USA).

Biotin and Streptavidin Linkage

Thin films previously obtained by polymerization of PFM (see Scheme 3), octadiene/PFM and divinyl ether/PFM were immersed for 2 h while shaking in a 10×10^{-3} M solution of (+)-biotinyl-3,6,9-trioxaundecanediamine in distilled water. Subsequently, samples were washed for 30 min in buffer A consisting of PBS with 0.02% (v/v) Tween 20 and 0.1% (w/v) BSA. The detergent Tween 20 is a blocking agent composed of polyoxyethylene sorbitan monostearate that preferentially adsorbs to the background. It was used to wash away non-covalently bound biotin and to avoid non-specific adsorption of streptavidin.[26] Then, samples were immersed for 1 h in in a 10×10^{-3} M solution of fluorescein-conjugated streptavidin in buffer A while shaking. The surfaces were rinsed several times with PBS before examination done using an epifluorescence microscope (Nikkon, New York). The streptavidin is labeled with a fluorescent die (in our case fluorescein 5′-isothiocyanate (FITC)) which emits fluorescent light when excited at a certain wavelength. Therefore, if the streptavidin is bonded to the biotin, we can prove that by irradiating the sample at the characteristic wavelength of the fluorescent die. The emission of fluorescence by the sample indicates the presence of the biotin-streptavidin complex. In an epifluorescence microscope both the excitation and emission light travel through the objective. The key to the optics in an epifluorescence microscope is the separation of the illumination (excitation) light from the fluorescence emission emanating from the sample. In order to obtain either an image of the emission without excessive background illumination, or a measurement of the fluorescence emission without background "noise", the optical elements used to separate these two light components must be very efficient.



Scheme 3. Schematic representation of a functionalized surface obtained by plasma polymerization of the PFM monomer, showing labile pentafluorophenyl groups on the surface.

Results and Discussion

Pentafluorophenyl Methacrylate Synthesis

The synthesis of the PFM followed a general synthesis pathway for acrylate derivatives with a yield of 85% which represents a 2.5 fold increase compared to yields previously reported using *p*-cyclophane derivatives.[27] Sterically hindered pyridine was used as proton acceptor to limit the extent of an undesired side reaction: Michael addition of the pyridine to the acrylate. Moreover, an excess of the base was used to prevent the addition of hydrogen chloride to the activated double bond of the acrylate. The high basic pH of the 2,6-lutidine compared to pyridine increased the extent of deprotonation of the phenol.[25] The reaction product was purified using a Florosil® chromatography column, resulting into a very pure form, as suggested by the NMR spectra. The IR spectrum of the pure PFM showed some characteristic bands (Figure 1a). Bands in accordance with with alkane C–H stretching absorptions were present around 2 950 cm^{-1}, while the band at 1 764 cm^{-1} indicated a carbonyl stretching absorption of a carboxylate ester. Aromatic system stretching vibrations between 1 625 and 1 475 cm^{-1} and typical bands for C–F stretching around 1 100–1 000 cm^{-1} could also be clearly distinguished in the spectrum. In addition, the NMR spectra (Figure 1b) also confirmed the chemical structure of the synthesized monomer.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

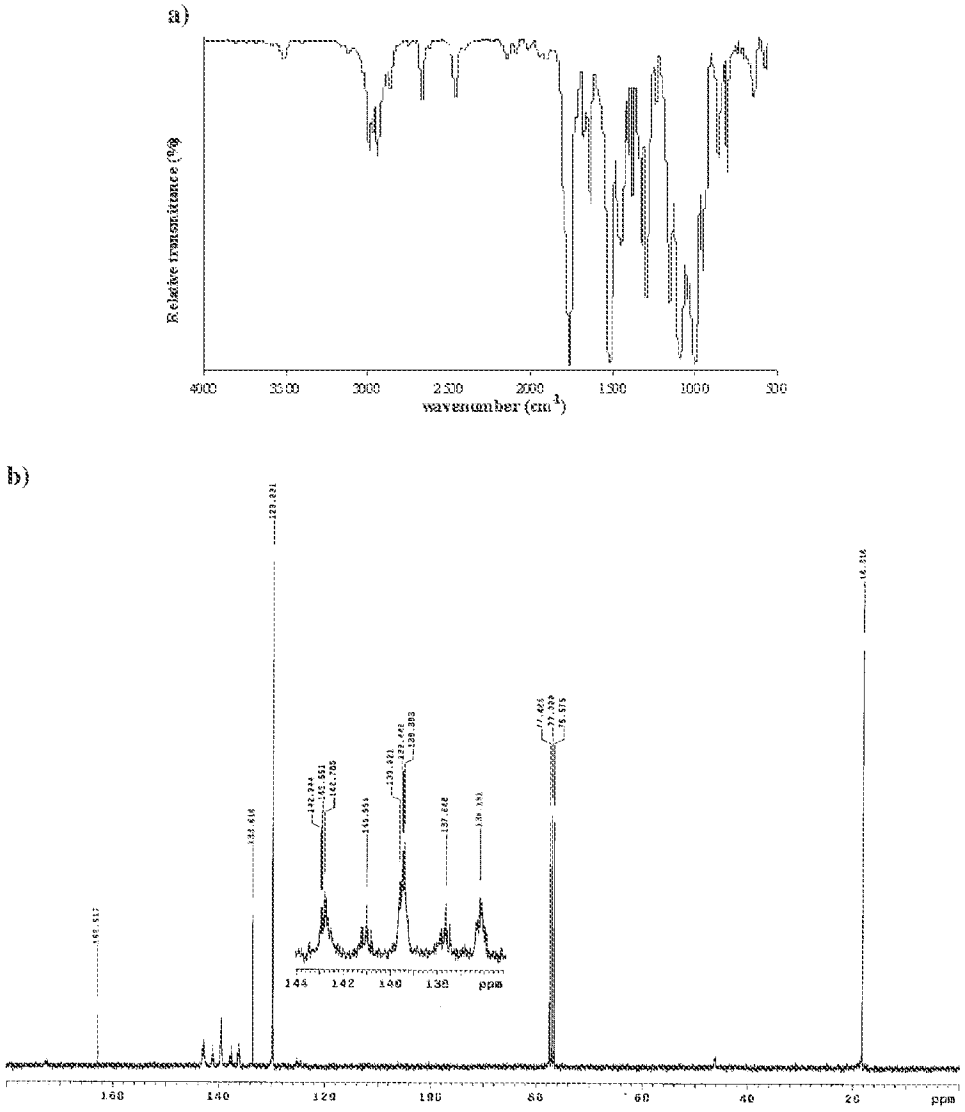


Figure 1. (a) IR and (b) ^{13}C NMR spectrum of the synthesized PFM.

The proton spectrum showed a decoupled signal at $\delta = 2.03$ corresponding to the methyl group of the acrylated part of PFM and two signals at $\delta = 5.9$ and 6.4 from protons in the *cis* and *trans* position within this group. The carbon spectrum was set in accordance with those reported in the literature[25] with a signal at 162.910 ppm that reflected formation of the ester bond between the acrylate and the phenol, a signal at ca. 139.6 ppm showing the C–F bond in the ring, two signals at 133.626 and 129.786 ppm that illustrate the presence of the double bond, and a signal at 18.272 ppm that reflects the presence of the CH_3 group.

Plasma Polymerization and Characterization of the Films

The deposition rate for bare PFM was 25 nm · h^{-1}. The deposition rate was 16 nm · h^{-1} for the octadiene/PFM (6:1) copolymer and 8 nm · h^{-1} for the divinyl ether/PFM (3:1) copolymer, suggesting the different reactivity of the products used.

XPS widescan spectra of the PFM (10 W, duty cycle of 1/215 Hz, 2 h deposition) revealed the presence of oxygen, carbon, fluorine, and nitrogen. The C1s core level signals were fitted on various oxygen-containing functionalities and on fluorine-containing functionalities. Nitrogen functionalities were not considered, since Cl and N were found only in limited amount at the surface coating. Spectra were corrected for sample charging, setting the hydrocarbon signal to 285.0 eV, and the position of the others centroids accordingly adjusted. The XPS survey spectrum of the PFM polymer showed retention of fluorinated functionalities, but in levels below the theoretical ones, probably caused by fragmentation of the monomer during the polymerization. The XPS C1s spectrum of the polymer PFM showed the expected carbon environments such as C–R, COOR (R = C or H), and C–F, each exhibiting a characteristic chemical

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

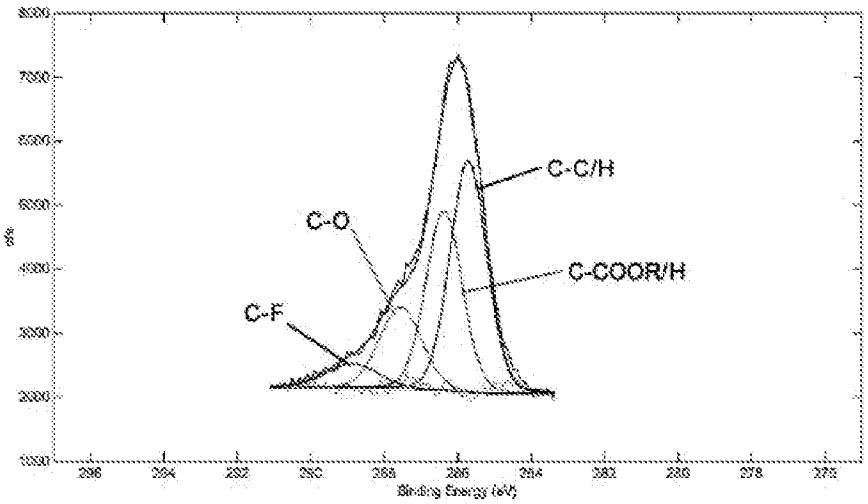


Figure 2. C1s core line fit for the PFM film, **A** C–C/H, **B**, C–COOH/R, **C** C–CO, **D** C–F.

shift (Figure 2). The spectrum was fit with four signals corresponding to hydrocarbon (C–C/H, A in the figure) set at 285.0 eV (see above), an α-ester carbon (C–COOH/R, B in the figure) at 285.6 eV, an ether carbon at 286.8 eV (C in the figure) and fluorinated carbon (C–F, D in the figure) at 288.2 eV. The existence of other oxygen-containing functionalities in addition to carboxylates constituted a further indication of monomer-oxygen reaction and fragmentation of the monomer in the plasma giving rise to the formation of side products during polymerization. A reaction between the film and the water desorbed from the walls of the plasma vessel (during polymerization), and atmospheric oxygen and water (after polymerization) might also have contributed.[26,28]

XPS spectra of the PFM copolymerization with the two cross-linking copolymers (Table 1) showed the expected carbon environments, such as C–R, COOR and C–F, each exhibiting their characteristic chemical shift.

Carbon environments of the form C–R, C–O, C=O and COOR (R = C or H) and C–F were present in the XPS spectrum obtained from the polymer of PFM and 1,7-octadiene copolymerization, each exhibiting a characteristic chemical shift.[28] This spectrum was fit with signals corresponding to hydrocarbon (C–C/H) set at 285 eV, an α-ester carbon (C–COOH/R) at 285.6 eV, an alcohol or ether carbon (C–O) at 286.7 eV, carbonyl (C=O) at 287.9 eV and carboxyl/carboxylate COOH/R at 289.2 eV. As expected, the amount of carbon was slightly higher than in the case of bare PFM (see Table 1), due to the presence of the two co-monomers that are formed mainly by a hydrocarbon structure. Again in all cases, the existence of oxygen-containing functionalities in addition to carboxylates constituted a further indication of monomer-oxygen reaction and fragmentation of the monomer in the plasma, giving rise to the formation of side products during polymerization. A reaction between the film and the water desorbed from the walls of the plasma vessel (during polymerization), and atmospheric oxygen and water (after polymerization) have contributed to the composition of the coating.[26,28] In the same way, the film obtained by copolymerization of PFM and divinyl ether showed a higher amount of oxygen (32.5% vs. 30.9% for bare PFM, see Table 1), attributed to the ether functionality in the molecule. Even in the case of the octadiene/PFM copolymer, the amount of oxygen compared to the bare PFM (33.1% vs. 30.9% for bare PFM, see Table 1) was higher. These results suggest that the use of the cross-linkers, octadiene and divinyl ether, promotes a higher oxygen incorporation into the film. The high loss of F amount in the divinyl ether/PFM polymer indicates the possibility of different polymerization mechanisms compared with the other polymerizations.

AFM Imaging

AFM analysis was performed for all samples. The AFM image of octadiene/PFM copolymer (Figure 3) showed flat, homogeneous surfaces, pinhole free with an average roughness of less than 0.5 nm (R_q) and a maximum

Table 1. Elemental analysis by XPS of the plasma polymerized monomers.

Monomer	%C	%O	%F	%N	C/F theoretical	C/F experimental
PFM	55.8	30.9	12.5	0.8	2.0	4.4
PFM/octadiene (1:6)	60.9	33.1	4.3	1.7	11.6	14.2
PFM/divinyl ether (1:3)	60.7	32.5	0.6	6.0	6.8	101.0

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

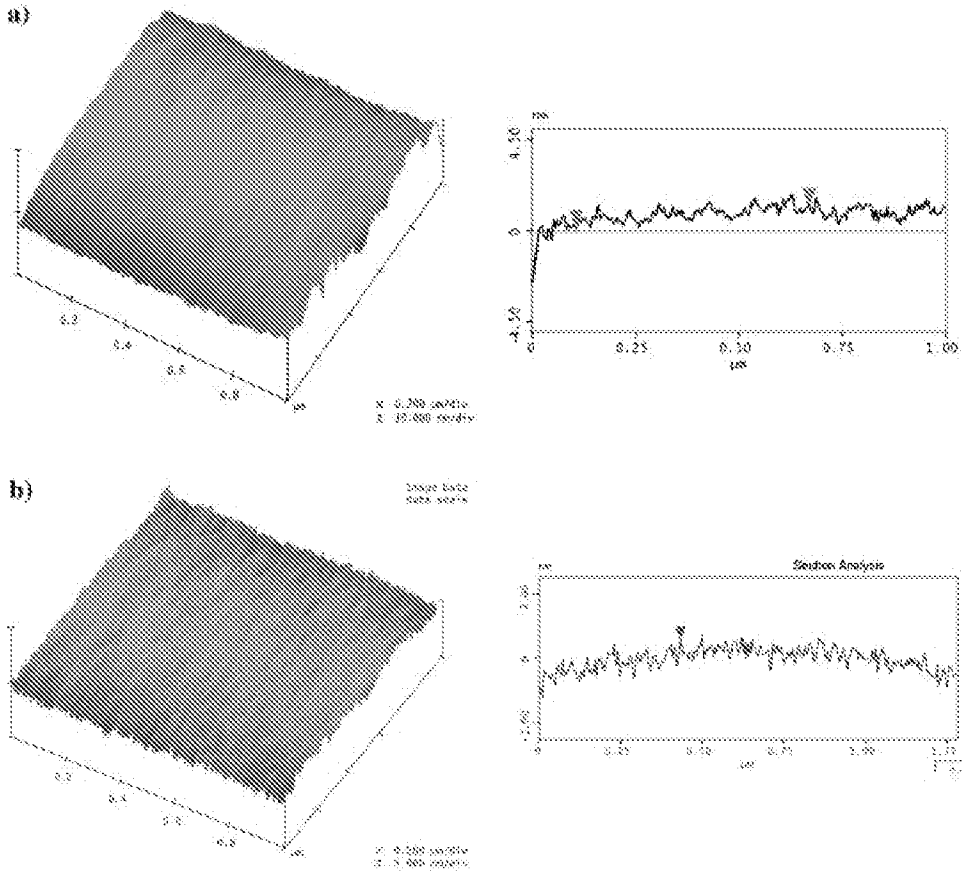


Figure 3. (a) AFM image and roughness profilometry corresponding to the octadiene/PFM copolymer film with a crosslinker/PFM ratio of 6:1, obtained under pulse plasma at 10 W, 15 Hz and a deposition time of 2 h. (b) AFM image and roughness profilometry corresponding to the divinyl ether/PFM copolymer film with a crosslinker/PFM ratio of 4:1, obtained under pulse plasma at 10 W, 15 Hz and a deposition time of 2 h.

roughness of 4 nm (R_{max}). This low roughness is likely from a combination of two factors: pulsed plasma conditions, through which it is possible to control the ratio between nucleation and growth of the film with a slow deposition rate, and the geometry of the reactor. In fact, our research group has already reported this level of roughness in thiophene and pyrrole plasma polymerized films using conditions similar to those described in this paper.[29]

Biotin and Streptavidin Linkage

A control sample (non-treated silicon wafer, Figure 4a) and PFM/octadiene-activated surfaces (Figure 4b) were exposed to a solution of fluorescein-conjugated streptavidin for microscopic fluorescence detection. Tween 20, a blocking agent composed of polyoxyethylene sorbitan monostearate that preferentially adsorbs to the background, was used to wash non-covalently bound biotin and to avoid non-specific adsorption of streptavidin.[26] Compared to control sample (non-polymerized, Figure 4a), PFM/octadiene-activated surfaces effectively bound biotin, allowing self-assembly of streptavidin, as shown by the fluorescence detection. This procedure establishes the basis for further attachment of other biotinylated biomolecules that enable control of cell attachment and proliferation.

Conclusion

PFM has been synthesized following a simple approach based on a general derivatization method for acrylates with a yield of 85%. The derivatized methacrylate was successfully used as monomer for plasma polymerization alone and copolymerized with different cross-linkers to improve the solvent resistance of the resulting deposited thin films. XPS analysis confirmed that labile ester groups remained on the functionalized surfaces. Such active esters enabled a fast reaction with amino-PEG biotin and subsequent self-assembly of streptavidin, a well-established platform for further immobilization of biomolecules that promote substrate-cell interaction.

Merging the versatility of plasma polymerization processes, via simple monomers and easy reaction conditions,

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

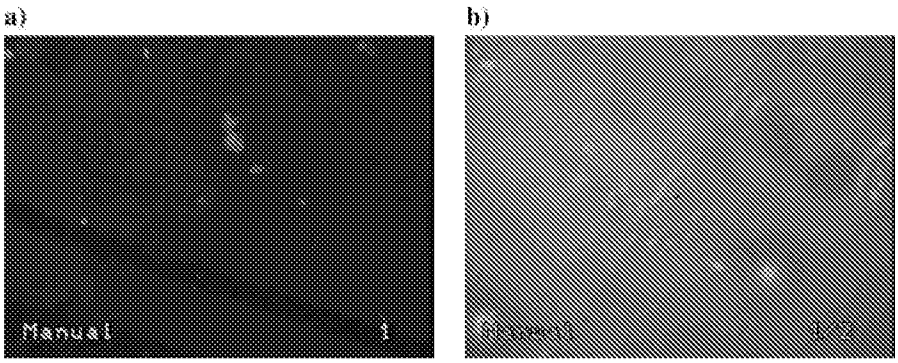


Figure 4. Fluorescence micrographs of a silicon wafer (a) and a silicon wafer after plasma polymerization of octadiene/PFM (ratio 6:1, obtained under pulse plasma at 10 W, 15 Hz, deposition time of 2 h) (b), both submitted to the treatment with biotin and fluorescein-conjugated streptavidin. Magnification is 50×.

with biological platforms that enable guidance of cell adhesion brings us closer to the ultimate goal of controlling cell function through structured surfaces for their application in tissue engineering.

Acknowledgements: E. E. and M. B. thank the *National Institutes of Health* (grants HL60407 and HL49039). E. G. thanks *Institut Químic de Sarria* for a Ph. D. fellowship.

[1] A. Quintana, E. Raczka, L. Piehler, I. Lee, A. Myc, I. Majoros, A. K. Patri, T. Thomas, J. Mule, J. R. Baker, Jr., *Pharm. Res.* **2002**, *19*, 1310.
[2] S. S. Mark, N. Sandhyarani, C. Zhu, C. Campagnolo, C. A. Batt, *Langmuir* **2004**, *20*, 6808.
[3] R. Langer, D. A. Tirrell, *Nature* **2004**, *428*, 487.
[4] S. F. Long, S. Clarke, M. C. Davies, A. L. Lewis, G. W. Hanlon, A. W. Lloyd, *Biomaterials* **2003**, *24*, 4115.
[5] S. I. Jeong, S. H. Kim, Y. H. Kim, Y. Jung, J. H. Kwon, B. S. Kim, Y. M. Lee, *J. Biomater. Sci., Polym. Ed.* **2004**, *15*, 645.
[6] H. H. Xu, D. T. Smith, C. G. Simon, *Biomaterials* **2004**, *25*, 4615.
[7] T. Kokubo, H. M. Kim, M. Kawashita, *Biomaterials* **2003**, *24*, 2161.
[8] Y. Liu, K. de Groot, E. B. Hunziker, *Ann. Biomed. Eng.* **2004**, *32*, 398.
[9] J. Tessmar, A. Mikos, A. Gopferich, *Biomaterials* **2003**, *24*, 4475.
[10] F. E. Black, M. Hartshorne, M. C. Davies, C. J. Roberts, S. J. B. Tendler, P. M. Williams, K. M. Shakesheff, S. M. Cannizzaro, I. Kim, R. Langer, *Langmuir* **1999**, *15*, 3157.
[11] J. D. Whittle, N. A. Bullett, R. D. Short, C. W. Ian Douglas, A. P. Hollander, J. Davies, *J. Mater. Chem.* **2002**, *12*, 2726.
[12] P. K. Chu, J. Y. Chen, L. P. Wang, N. Huang, *Mater. Sci. Eng., R: Reports* **2002**, *R36*, 143.
[13] U. Vohrer, D. Hegemann, C. Oehr, *Anal. Bioanal. Chem.* **2003**, *375*, 929.
[14] H. Schetters, *Biomol. Eng.* **1999**, *16*, 73.
[15] A. Scorilas, A. Bjartell, H. Lilja, C. Moller, E. P. Diamandis, *Clin. Chem.* **2000**, *46*, 1450.
[16] Q. P. Qin, T. Lövgren, K. Pettersson, *Anal. Chem.* **2001**, *73*, 1521.
[17] D. S. Wilbur, P. M. Pathare, D. K. Hamlin, P. S. Stayton, R. To, L. A. Klumb, K. R. Buhler, R. L. Vessella, *Biomol. Eng.* **1999**, *16*, 113.
[18] K. Ohno, B. Levin, D. Meruelo, *Biochem. Mol. Med.* **1996**, *58*, 227.
[19] Z. Yang, A. M. Belu, A. Liebmann-Vinson, H. Sugg, A. Chilkoti, *Langmuir* **2000**, *16*, 7482.
[20] G. W. Cline, S. B. Hanna, *J. Am. Chem. Soc.* **1987**, *109*, 3087.
[21] G. W. Anderson, J. E. Zimmermann, F. M. Callahan, *J. Am. Chem. Soc.* **1964**, *86*, 1839.
[22] P. Ferruti, A. Betteli, A. Feré, *Polymer* **1972**, *13*, 462.
[23] M. C. Tanzi, L. Rusconi, C. Barozzi, P. Ferruti, L. Angiolini, M. Nocentini, V. Barone, R. Barbucci, *Polymer* **1984**, *25*, 863.
[24] J. Lahann, M. Balcells, T. Rodon, J. Lee, I. S. Choi, K. F. Jensen, R. Langer, *Langmuir* **2002**, *18*, 3632.
[25] J. C. Blazejewski, J. W. Hofstraat, C. Lequesne, C. Wakselman, U. E. Wiersum, *J. Fluorine Chem.* **1998**, *91*, 175.
[26] J. Hyun, Y. Zhu, A. Liebmann-Vinson, T. P. Beebe, Jr., A. Chilkoti, *Langmuir* **2001**, *17*, 6358.
[27] T. Lahtinen, E. Weselim, K. Rissonen, *New J. Chem.* **2001**, *25*, 905.
[28] S. Fraser, R. D. Short, D. Barton, J. W. Bradley, *J. Phys. Chem., B* **2002**, *106*, 5596.
[29] L. Martin, J. Esteve, S. Borros, *Thin Solid Films* **2004**, *74–80*, 451.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Macromolecules

Article

pubs.acs.org/Macromolecules

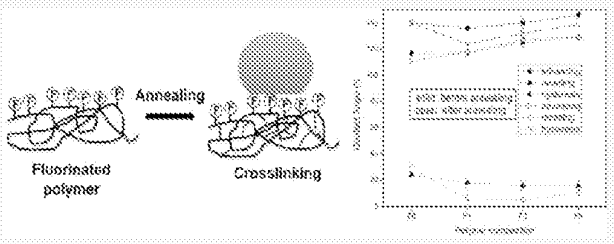
Enhanced Cross-Linked Density by Annealing on Fluorinated Polymers Synthesized via Initiated Chemical Vapor Deposition To Prevent Surface Reconstruction

Jose Luis Yagüe and Karen K. Gleason*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Thin films of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate copolymerized with the cross-linker divinylbenzene (p(PFDA-*co*-DVB)) were synthesized via initiated chemical vapor deposition (iCVD). The vapor deposited approach is significant as the fluorinated monomer and hydrocarbon cross-linker lack a common solvent. Changes in physical and chemical properties in the copolymers before and after an annealing treatment were characterized by Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), contact angle (CA) measurements with water and mineral oil, X-ray diffraction (XRD), and nanoindentation. Cross-linking results in lower CA hysteresis than measured for the iCVD p(PFDA) homopolymer. Furthermore, annealing improves the extent of reaction of the vinyl bonds on the DVB units incorporated into the film. This further enhancement in the cross-linking density is correlated with an additional reduction in the CA hysteresis observed after annealing of the p(PFDA-*co*-DVB) films. CA hysteresis values with water as low as 5° were achieved while maintaining advancing angles $\theta > 130°$. For mineral oil, CA hysteresis was found to be lower than 1° with $\theta > 85°$. The cross-linking is concluded to provide a steric barrier to the reconstruction of the surface fluorinated groups when switching between dry and wet conditions and is a primary factor in the observed reduction in CA hysteresis.



1. INTRODUCTION

Fluorinated polymers are desired for their outstanding chemical and physical properties, including a low coefficient of friction, low dielectric constant, high thermal stability, high gas permeability, and flame-retardant behavior.[1−5] Nonetheless, the primary application of fluorinated polymers derives from their hydrophobic character due to the low energy surface of the $-CF_2-$ and $-CF_3$ groups, 18 and 6 mN/m respectively.[6] The wetting properties of the fluorinated coating depend on the molecular ordering at the surface.[7,8] In the dry state, fluorine groups segregate to the surface to lower the surface energy. Angle-resolved XPS experiments have confirmed that the F/C ratio at the surface is higher than in the bulk.[9] Exposure of the surface to water is a driving force for the fluorinated groups to reorder into the bulk of the film, which reduces the hydrophobic character of the surface and thus contributes to increase the hysteresis in the contact angle (CA) behavior of water.[10] Hysteresis is the difference between the advancing and the receding CA and can be caused by surface roughness, heterogeneity of the solid surface, dissolved substances into the liquid, line tensions, and/or energy dissipation.[11] Obtaining surfaces with low CA hysteresis is desirable for many applications, including self-cleaning surfaces, ice adhesion reduction, or water condensation.[12−14] Creating chemical and physical heterogeneities are the most common approaches to modify the hysteresis. Microtextured surfaces can result in superhydrophobic surfaces. However, hysteresis depends on the wetting state of the system. Wenzel state enhances pinning of the droplet, while Cassie state reduces the CA hysteresis.[15] Additionally, crystallization can act as a barrier for surface reconstruction for fluorinated films and thus decreasing the hysteresis.[16] Enhancing the crystallinity and controlling the surface topography in fluorinated films has resulted in CA hysteresis as low as 5°.[17] Nonetheless, not all the polymers happen to crystallize, nor in all applications is crystallinity desirable. Therefore, obtaining surfaces with low CA hysteresis behavior independently of the roughness and without requiring crystallinity represents an important milestone to develop materials with improved water shedding properties.

Initiated chemical vapor deposition (iCVD) of the 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate (PFDA) monomer has successfully been used to develop fluorinated coatings with superhydrophobic properties.[18] iCVD is a variant of hot-wire chemical vapor deposition (HWCVD), in which an initiator decomposes at the filaments inducing a free radical polymerization, which can lead to a significant increase in the film deposition rate.[19] The iCVD method is a solvent-free technique which yields homogeneous, conformal polymer coatings with full retention of the pendant functionality of the monomeric

Received: May 22, 2013
Revised: July 18, 2013
Published: August 13, 2013

Downloaded via Chris Moua on June 22, 2020 at 14:50:57 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

Favored Ex. 1026

species.[20−22] Coclite et al. demonstrated that the experimental conditions for iCVD pPFDA films can both tune the degree of crystallinity and switch the preferred orientation of the perfluorinated side chain between parallel to or perpendicular to the substrate.[23] Further studies showed that grafting PFDA polymer chains to the substrate enhances the crystallinity and alignment of the side chains perpendicular to the surface.[17] The iCVD approach enables copolymerization of two or more monomeric species. Adjusting the flow rates of monomer vapors allows for systematic control in the final composition of the copolymer.[24] While lack of a common solvent for both monomers can be a synthesis challenge for traditional polymerization, solubility characteristics are not a limited factor when the monomers are delivered through the vapor phase. Thus, iCVD can produce novel compositions. Indeed in the present work, we readily synthesize copolymers by iCVD from the fluorinated monomer PFDA with the hydrocarbon monomer divinylbenzene (DVB) (p(PFDA-*co*-DVB)) over the entire compositional range. The DVB acts as a cross-linker when both vinyl bonds are reacted. Since complete reaction of the DVB is not observed upon iCVD growth,[25] the chemical and physical properties in the current study are compared before and after annealing. We demonstrate that the DVB cross-linker and the annealing lower the CA hysteresis of the copolymers by creating a steric barrier to the surface reconstruction of the fluorinated iCVD films between their dry and wet states without inducing a crystalline state and independently of the surface roughness.

2. EXPERIMENTAL PART

2.1. Materials. *tert*-Butyl peroxide (TBPO) (98%, Aldrich), 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate (PFDA) (97%, Aldrich), and divinylbenzene (DVB) (80%, Aldrich) were used as received.

2.2. Experimental Setup. The polymerizations were conducted in a custom-design cylindrical reactor (diameter 24.6 cm and height 3.8 cm). On top of the reactor laid a quartz top that allowed laser interferometry (633 nm He−Ne laser, JDS Uniphase) for in-situ film thickness monitoring. Inside the reactor, 14 parallel ChromAlloy filaments (Goodfellow) were resistively heated to 230 °C, and the stage was back-cooled at a constant temperature of 30 °C by water using a recirculating chiller/heater (Neslab RTE-7). Reactor pressure was maintained at 200 mTorr using a throttle valve (MKS Instruments). The radical initiator, TBPO, and N_2 were delivered inside the reactor through mass flow controllers (MKS Instruments). The monomers PFDA and DVB were heated in a glass jar to a temperature of 80 and 60 °C, respectively, and their flows were controlled by needle valves. The flow rates of TBPO and PFDA were kept constant at 3.2 and 0.2 sccm. For the different experiments, the flow rate of DVB was varied to 0, 0.2, 0.6, and 1 sccm, and a patch flow of N_2 was introduced to keep a total flow of 5 sccm. These samples are denoted as F0, F1, F3, and F5, respectively, where integer in the label represents the ratio of DVB to PFDA in the inlet reactants (Table 1). After deposition samples were annealed at 80 °C for 30 min.

Table 1. Nomenclature and Details of the Flow Rates during the Polymerizations

	flow rate (sccm)			
sample	PFDA	DVB	TBPO	N_2
F0	0.2	0	3.2	1.6
F1	0.2	0.2	3.2	1.4
F3	0.2	0.6	3.2	1.0
F5	0.2	1.0	3.2	0.6

2.3. Characterization. Variable-angle ellipsometric spectroscopy (VASE, M-2000, J.A. Woollam) was used to measure film thicknesses. All thickness measurements were performed at a 70° incidence angle using 190 wavelengths from 315 to 718 nm. A nonlinear least-squares minimization was used to fit ellipsometric data of dry films to the Cauchy−Urbach model. The thickness was obtained upon convergence of the algorithm. The films were grown up to a thickness of 400 nm. FTIR measurements were performed on a Nicolet Nexus 870 ESP spectrometer in normal transmission mode equipped with a MCT (mercury cadmium tellurium) detector and KBr beamsplitter. Spectra were acquired over the range of 400−4000 cm^{-1} with a 4 cm^{-1} resolution for 256 scans. All spectra were baseline-corrected. CA measurements were performed using a goniometer equipped with an automated dispenser (Model 500, Rame-Hart). Advancing and receding were measured using the sessile drop method, depositing a droplet of 1 μL on the surface. The advanced CA was the largest angle obtained and the receding CA the smallest one. AFM images were acquired using a scanning probe microscope (Digital Instruments, Dimension 3100) in tapping mode using a conical gold-coated silicon tip. Crystallinity of the samples was studied by XRD. The XRD measurements were carried out on a Scintag $\theta-\theta$ diffractometer with a Cu Kα radiation (1.541 867 Å) at 40 kV and 44 mA. Data were collected in continuous mode at 3° min^{-1}, with a step size of 0.02°. The scans were taken in symmetrical reflection geometry. Mechanical properties of the film were measured by nanoindentation (Nanovea) on 1 μm thick coatings deposited on silicon substrates. The nanoindentation depth was limited to the first 10% of the overall coating thickness in order to avoid substrate effects. A Berkovich-type tip was used having a radius <10 nm. The elastic moduli were calculated from the slope of the unloading curve of the load−displacement graph, while the hardness values were calculated from the ratio of the depth at maximum load to the indent area as the tip penetrate into the coating with knowledge of the exact tip shape.

3. EXPERIMENTAL RESULTS

Figure 1 shows the FTIR spectra of the pPFDA and pDVB homopolymer and the p(PFDA-*co*-DVB) copolymer. pPFDA

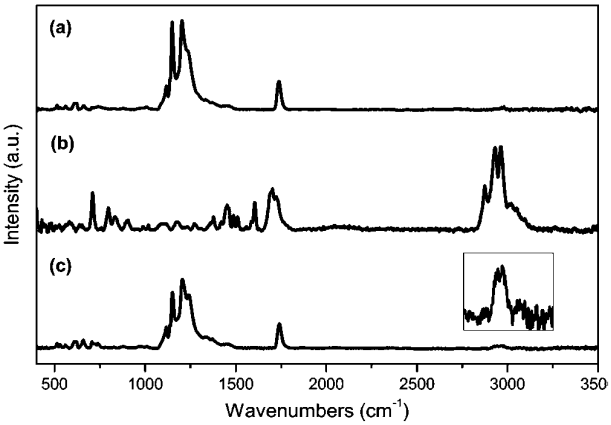


Figure 1. FTIR spectra of the pPFDA homopolymer (a), the pDVB homopolymer (b), and the p(PFDA-*co*-DVB) copolymer (c). The inset graph shows the region between 2750 and 3250 cm^{-1} of the copolymer film at expanded intensity of 220×. The bands observed resemble to the bands of the pDVB homopolymer in the same region.

homopolymer (Figure 1a) is characterized by a sharp band corresponding to the carbonyl group at 1741 cm^{-1}. In addition, the fluorinated moieties present three strong, sharp absorbance bands. The two bands at 1246 and 1207 cm^{-1} are caused by the asymmetric and symmetric stretching of the $-CF_2-$ moiety, respectively. The sharp band at 1153 cm^{-1} belongs to the

dx.doi.org/10.1021/ma4010633 | *Macromolecules* 2013, 46, 6548−6554

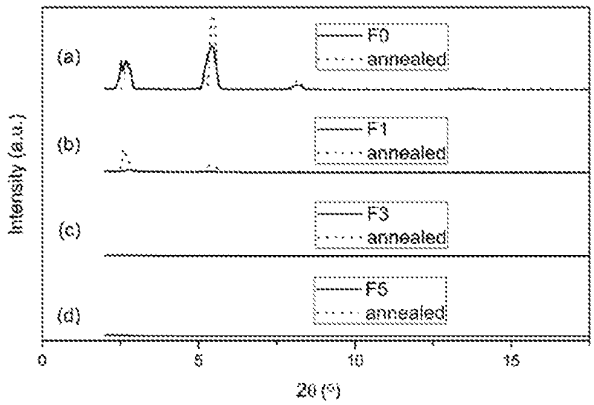


Figure 2. XRD spectra of the PFDA homopolymer, F0 (a), and the p(PFDA-*co*-DVB) copolymers F1 (b), F3 (c), and F5 (d). Solid line corresponds to the sample before annealing and dashed line after annealing. Only F0 and F1 display an increase in the crystallinity after the annealing. All the spectra were normalized to the sample thickness.

$-CF_2-CF_3$ end group.[26] Regarding the pDVB homopolymer (Figure 1b), the FTIR spectrum shows the aromatic −CH− bands between 3000 and 3100 cm^{-1}, the $-CH_2-$ stretching bands between 2810 and 2890 cm^{-1}, and some other characteristic bands related to the substituted phenyl group that appear in the range 700−1000 cm^{-1}.[27−30] The band at 710 cm^{-1} is assigned to the typical stretching vibration of the phenyl group. The bands at 795 and 838 cm^{-1} correspond to the meta- and para-disubstituted aromatic ring, respectively. The copolymer (Figure 1c) presents all the characteristic bands associated with its components. It should be noted that bands corresponding to DVB are less intense than PFDA bands but can be seen readily when the CH stretching region intensity is expanded (Figure 1 inset). Thus, the FTIR results show the incorporation of the two monomers into the copolymer film and the retention of the chemical functionality from both reactants after the polymerization.

Films with four different compositions were iCVD synthesized: F0, F1, F3, and F5. Figure 2 shows the crystallinity of the as-deposited and postannealed samples. The pPFDA homopolymer, F0 (Figure 2a), presents a characteristic lamellar structure, classified as smectic B type. This aggregation involves the arrangement of bilayers with perfluorinated side chains perpendicular to the substrate, facing each other, and forming the lamellar structure parallel to the substrate.[31] The crystalline peaks at 2.8° and 5.6° at 2θ in the X-ray diffraction (XRD) spectrum correspond to a spacing of 32.4 and 16.2 Å, respectively. These distances match with the length of a double layer and a single layer of the perfluorinated side chain, respectively, corroborating the smectic B aggregation.[17] Annealing increases the intensity of peaks observed in the XRD data for F0. The observed increase can be attributed to reorganization of the polymer chain due to the thermal process,

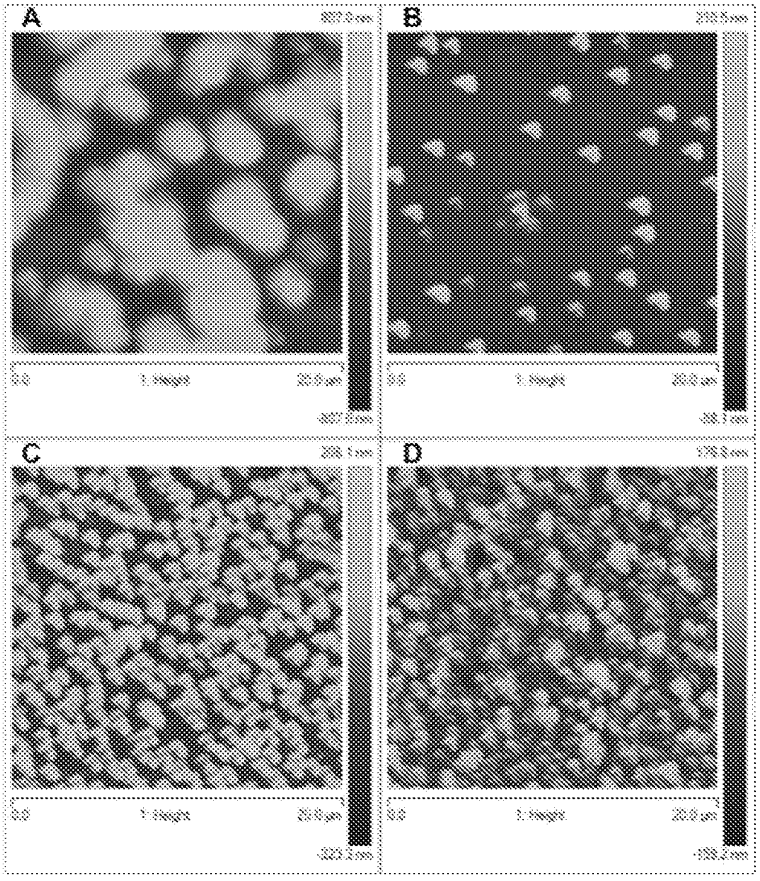


Figure 3. AFM images of the PFDA homopolymer, F0 (A), and the p(PFDA-*co*-DVB) copolymers F1 (B), F3 (C), and F5 (D) as-deposited.

dx.doi.org/10.1021/ma4010633 | *Macromolecules* 2013, 46, 6548−6554

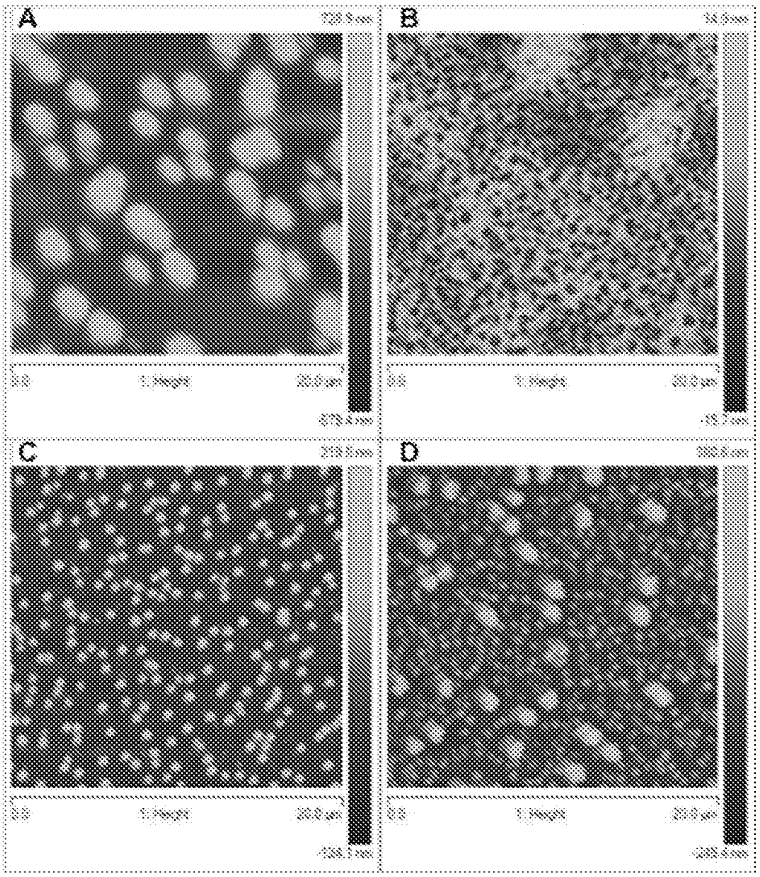


Figure 4. AFM images of the PFDA homopolymer, F0 (A), and the p(PFDA-*co*-DVB) copolymers F1 (B), F3 (C), and F5 (D) after annealing.

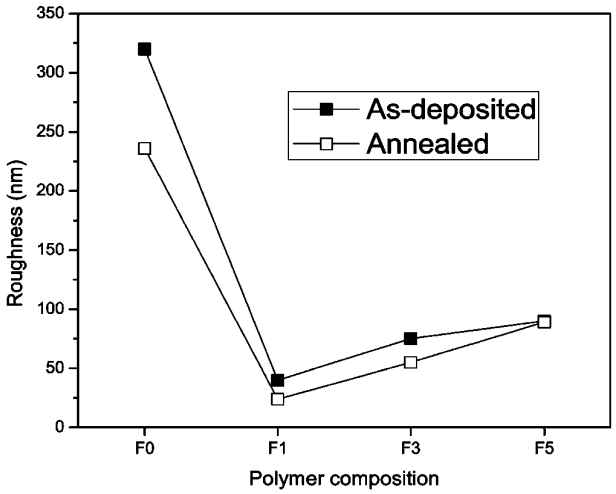


Figure 5. Roughness evolution (nm) of the polymer films as-deposited (solid symbols) and after the annealing treatment (open symbols).

which improves the crystalline structure.[32] In all as-deposited copolymer films, F1, F3, and F3, no XRD peaks are observed (Figures 2b, 2c, and 2d, respectively), indicating that these films are amorphous. Thus, the addition of the DVB cross-linker to pPFDA eliminates crystallinity in the as-deposited films. After annealing, only the copolymer with the lowest DVB content, F1, displays any crystallinity (Figure 2b). The degree of crystallinity of the annealed F1 sample is lower than that of the F0 homopolymer. Thus, incorporation of the DVB hinders the arrangement of the perfluorinated side chains into the Smetic B aggregation, leading to a loss of crystallinity.

Surface morphologies of the as-deposited films were studied by atomic force microscopy (AFM) (Figure 3). The F0 homopolymer (Figure 3a) presents large islands, characteristic of previously reported pPFDA films with crystallinity achieved at high initiator/monomer (I/M) ratio.[23] Conversely, the morphology of the copolymer samples is rather different (Figures 3b–d). The polymer aggregations found on the surface are smaller and their density increases with increasing DVB flow rate. This could be due to the formation of a higher number of nucleation sites. Nucleation is intimately related to the monomers adsorption on the surface, which in turn, depends on the P_M/P_{sat} parameter, the ratio of the vapor pressure of the monomer to the saturation vapor pressure of the monomer, equivalently to the monomer surface concentration.[33] Thus, working at the same total gas pressures, raising the flow rate of DVB increases its P_M/P_{sat} which is observed to correlate with the formation of more nucleation sites during the polymerization process. Furthermore, annealing of the films results in a decrease of the grain size depending on the DVB incorporated in the polymer chain, as observed in Figure 4. The more cross-linked are the films, the less variation in the grain size. It could be hypothesized that the DVB cross-linker density hinders the reorganization of the polymer chains and therefore

dx.doi.org/10.1021/ma4010633 | *Macromolecules* 2013, 46, 6548–6554

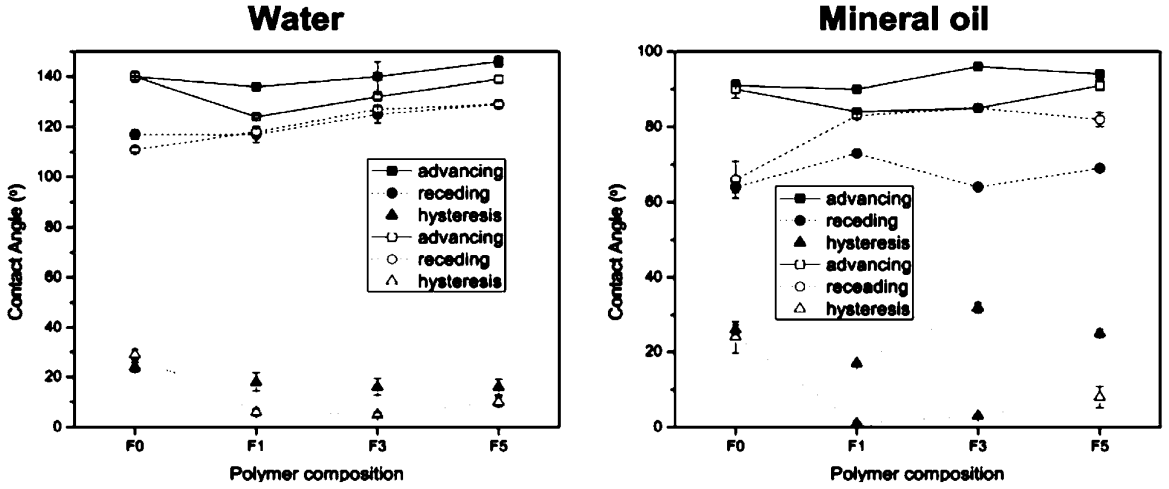


Figure 6. Advancing, receding and hysteresis of water (left) and mineral oil (right) CA of the PFDA homopolymer, F0, and the p(PFDA-*co*-DVB) copolymers corresponding to F1, F3, and F5. Solid symbols correspond to the sample before annealing and open symbols after annealing.

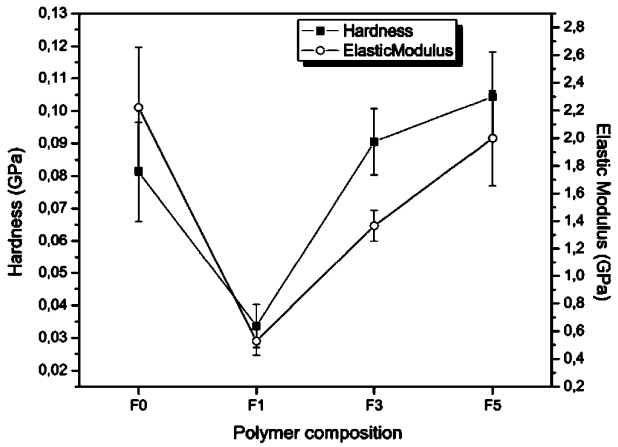


Figure 7. Hardness and elastic modulus as a function of the DVB cross-linker.

the decrease of the grain size. The change in the surface topography was also studied following the roughness variation for the different samples (Figure 5). The main difference is observed between the homo- and the copolymer samples, where the roughness decreases abruptly. The transition from the crystalline to the amorphous state entails the loss of the crystalline domains, which are characterized by large island-shape aggregations. However, as seen in the AFM images, the copolymer films show smaller and more numerous aggregations, which confers a lower roughness to the film. These results are in agreement with the change in crystallinity observed in the XRD experiments.

The cross-linking and the annealing effects on the surface wettability were evaluated by CA measurements using water and mineral oil (Figure 6). Homo- and copolymer samples present a similar hydrophobic behavior, with an advancing CA > 130°, before and after annealing. This finding suggests that both materials have a comblike structure leading to CF_3 enrichment on the surface when in contact with air. The hydrocarbon nature of the cross-linker, which would increase the surface energy,[34] is not detected at the surface layer leading to similar advancing CA measurements. It should be noted, however, the decrease on the CA hysteresis due to the annealing process in the copolymerized samples. Whereas annealed copolymerized films show a CA hysteresis lower than 10°, the rest of samples present a hysteresis higher than 20°. Low CA hysteresis on fluorinated surfaces is related to the fluorine concentration on the surface. It is known that the pendant fluorinated groups of polymer chains segregate of the surface under dry conditions and reorient into the bulk when the surface is exposed to water. The reduction in the surface fluorine concentration in the wet state decreases the value of the receding CA.[35] The cross-linking of the DVB units, which is enhanced upon annealing, fixes the fluorine concentration on top of the surface. Additionally, only in the homopolymer film, F0, and in the copolymer polymer film with the lowest degree of DVB incorporation, F1, does the degree of crystallinity increases with annealing. This crystallinity represents an additional steric barrier to the reorientation of the perfluorinated functional groups.[23] Note that for copolymer sample F1 crystallinity is observable only after annealing, as no diffraction peaks are seen in the as-deposited film. Thus, the annealed sample F1 is unique in having both cross-linking and crystallinity. This annealed sample also provides the lowest CA hysteresis values for both water and mineral oil.

The degree of cross-linking in pDVB can be quantified by determining the area in the FTIR spectrum of two characteristic bands: one band at 903 cm^{-1} corresponding to the vinyl bound and the other one at 710 cm^{-1} belonging to the meta-substituted DVB ring.[25] Since these bands are not intense enough in the copolymer spectrum, the cross-linking measurement was performed over a pDVB homopolymer film (see spectra in Supporting Information, Figure S1). Cross-linking before annealing was 55% and after 68%, which corroborates the increase of cross-linking density due to the thermal treatment. Similar behavior can be observed for the mineral oil CA measurements. All samples show an advancing CA with mineral oil of around 90°. Copolymerized annealed samples present a decrease of 20° in the hysteresis obtaining values lower than 1°. Moreover, as observed in Figure 5, the roughness before and after the annealing can be considered to be within the same order for the copolymers, which means

dx.doi.org/10.1021/ma4010633 | *Macromolecules* 2013, 46, 6548−6554

that the decrease of the CA hysteresis is independent of the surface morphology. Thus, the driving force to obtain this low hysteresis is based primarily on the improvement of the reduction in the surface reconstruction of the fluorine groups, which is due to the formation of a steric barrier against molecular reorientation produced by the incorporation of cross-linkable groups.

Mechanical properties of the thin films were studied using nanoindentation (Figure 7). Contrary to expectations, the pPFDA homopolymer shows high values for the Young's modulus (Y) and hardness (H) in comparison to p(PFDA-*co*-DVB) copolymers. This result may be explained by the fact that the homopolymer presents a highly crystalline structure.[36,37] The secondary bonds formed due to the orientation of the polymer chains create a cross-linked effect increasing the stiffness and strength of the polymer. The introduction of DVB leads to a loss of crystallinity and, thus, a decrease in the Y and H values for the F1 sample. Nonetheless, increasing the amount of DVB cross-linker in the polymer background causes the boost of the mechanical properties of the thin films because of the bonds formed among chains.

4. CONCLUSIONS

In this work, we have demonstrated the synthesis of p(PFDA-*co*-DVB) copolymer thin films via iCVD showing hydrophobic and oleophobic properties. In the as-deposited films, the introduction of the DVB cross-linker entails a loss of crystallinity in comparison with the pPFDA homopolymer as well as a reduction in the grain size of the particles aggregated on the surface, resulting in films with lower roughness. The mechanical properties of the films increase with the amount of cross-linker incorporated in the copolymer; however, the homopolymer shows comparable values due to its crystallinity state. Furthermore, an annealing treatment has been performed to the films. The annealing produced crystallinity in only one of the copolymer samples, F1, which possesses the lowest amount of DVB cross-linker. The CA hysteresis after the annealing process for the copolymer films has decreased significantly, obtaining values as low as 5° for water and lower than 1° for mineral oil droplets. The annealing leads to a higher cross-linking density through reaction of the pendant vinyl bonds of pDVB. Cross-linking acts as a steric barrier for the reorganization of the fluorinated groups on the surface. The introduction of the cross-linker and the annealing in the polymerization process of fluorocompounds result in low-energy surfaces showing no or little segregation without the need of inducing crystallinity. These smooth, chemically stable, and low-hysteresis thin films are excellent candidates for applications demanding low CA hysteresis with fluids having surface energies between those for water and those for mineral oil.

ASSOCIATED CONTENT

Supporting Information

FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kkg@mit.edu (K.K.G.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Masdar Institute for funding this research.

REFERENCES

(1) Suzuki, M.; Saotome, Y.; Yanagisawa, M. *Thin Solid Films* **1988**, *160*, 453−462.
(2) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3−65.
(3) Kang, J. W.; Kim, J. P.; Lee, W. Y.; Kim, J. S.; Lee, J. S.; Kim, J. J. *J. Lightwave Technol.* **2001**, *19*, 872−875.
(4) Tanaka, K.; Kita, H.; Okano, M.; Okamoto, K. *Polymer* **1992**, *33*, 585−592.
(5) Errifai, I.; Jama, C.; Le Bras, M.; Delobel, R.; Gengembre, L.; Mazzah, A.; De Jaeger, R. *Surf. Coat. Technol.* **2004**, *180*, 297−301.
(6) Zisman, W. A. In *Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution*; American Chemical Society: Washington, DC, 1964; Vol. *43*, pp 1−51.
(7) Genzer, J.; Sivaniah, E.; Kramer, E. J.; Wang, J. G.; Korner, H.; Xiang, M. L.; Char, K.; Ober, C. K.; DeKoven, B. M.; Bubeck, R. A.; Chaudhury, M. K.; Sambasivan, S.; Fischer, D. A. *Macromolecules* **2000**, *33*, 1882−1887.
(8) Corpart, J. M.; Girault, S.; Juhue, D. *Langmuir* **2001**, *17*, 7237−7244.
(9) Mao, Y.; Gleason, K. K. *Macromolecules* **2006**, *39*, 3895−3900.
(10) Synytska, A.; Appelhans, D.; Wang, Z. G.; Simon, F.; Lehmann, F.; Stamm, M.; Grundke, K. *Macromolecules* **2007**, *40*, 297−305.
(11) Butt, H.-J.; Graf, K.; Kappl, M. In *Contact Angle Phenomena and Wetting*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2004; pp 118−144.
(12) Bhushan, B.; Jung, Y. C.; Koch, K. *Philos. Trans. R. Soc., A* **2009**, *367*, 1631−1672.
(13) Kulinich, S. A.; Farzaneh, M. *Appl. Surf. Sci.* **2009**, *255*, 8153−8157.
(14) Wier, K. A.; McCarthy, T. J. *Langmuir* **2006**, *22*, 2433−2436.
(15) Lafuma, A.; Quere, D. *Nat. Mater.* **2003**, *2*, 457−460.
(16) Wang, J. G.; Mao, G. P.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1997**, *30*, 1906−1914.
(17) Coclite, A. M.; Shi, Y. J.; Gleason, K. K. *Adv. Mater.* **2012**, *24*, 4534−4539.
(18) Ma, M. L.; Gupta, M.; Li, Z.; Zhai, L.; Gleason, K. K.; Cohen, R. E.; Rubner, M. F.; Rutledge, G. C. *Adv. Mater.* **2007**, *19*, 255−259.
(19) Martin, T. P.; Lau, K. K. S.; Chan, K.; Mao, Y.; Gupta, M.; O'Shaughnessy, A. S.; Gleason, K. K. *Surf. Coat. Technol.* **2007**, *201*, 9400−9405.
(20) Tenhaeff, W. E.; Gleason, K. K. *Adv. Funct. Mater.* **2008**, *18*, 979−992.
(21) Ozaydin-Ince, G.; Coclite, A. M.; Gleason, K. K. *Rep. Prog. Phys.* **2012**, *75*, 016501.
(22) Yagüe, J. L.; Coclite, A. M.; Petruczok, C.; Gleason, K. K. *Macromol. Chem. Phys.* **2013**, *214*, 302−312.
(23) Coclite, A. M.; Shi, Y. J.; Gleason, K. K. *Adv. Funct. Mater.* **2012**, *22*, 2167−2176.
(24) Yagüe, J. L.; Gleason, K. K. *Soft Matter* **2012**, *8*, 2890−2894.
(25) Petruczok, C. D.; Yang, R.; Gleason, K. K. *Macromolecules* **2013**, *46*, 1832−1840.
(26) Gupta, M.; Gleason, K. K. *Langmuir* **2006**, *22*, 10047−10052.
(27) Bartholin, M.; Boissier, G.; Dubois, J. *Makromol. Chem.* **1981**, *182*, 2075−2085.
(28) Boguslavsky, Y.; Margel, S. *J. Colloid Interface Sci.* **2008**, *317*, 101−114.
(29) Ji, H. F.; Wang, S. P.; Yang, X. L. *Polymer* **2009**, *50*, 133−140.
(30) Hasegawa, J.; Kanamori, K.; Nakanishi, K.; Hanada, T. *C. R. Chim.* **2010**, *13*, 207−211.
(31) Honda, K.; Morita, M.; Otsuka, H.; Takahara, A. *Macromolecules* **2005**, *38*, 5699−5705.
(32) Rottele, A.; Thurn-Albrecht, T.; Sommer, J. U.; Reiter, G. *Macromolecules* **2003**, *36*, 1257−1260.

(33) Lau, K. K. S.; Gleason, K. K. *Macromolecules* **2006**, *39*, 3688−3694.
(34) Kim, B. G.; Sohn, E. H.; Lee, J. C. *Macromol. Chem. Phys.* **2007**, *208*, 1011−1019.
(35) Synytska, A.; Appelhans, D.; Wang, Z. G.; Simon, F.; Lehmann, F.; Stamm, M.; Grundke, K. *Macromolecules* **2007**, *40*, 1774−1774.
(36) Cadek, M.; Coleman, J. N.; Barron, V.; Hedicke, K.; Blau, W. J. *Appl. Phys. Lett.* **2002**, *81*, 5123−5125.
(37) Starkweather, H. W.; Moore, G. E.; Hansen, J. E.; Roder, T. M.; Brooks, R. E. *J. Polym. Sci.* **1956**, *21*, 189−204.

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 457 (2004) 26–33
thin solid films
www.elsevier.com/locate/tsf

Detection of deposition rate of plasma-polymerized acrylate and methacrylate derivatives using quartz crystal microbalance

Shigeru Kurosawa[a,b,*], Björn Atthoff[a,c], Hidenobu Aizawa[a,d], Jöns Hilborn[c]

[a]National Institute of Advanced Industrial Science and Technology (AIST), 1-1 Higashi, Tsukuba 305-8565, Japan
[b]Institut de Physique et de Chimie des Materiaux de Strasbourg, CNRS, 23, rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France
[c]The Ångström Laboratory, Uppsala University, P.O. Box 538, SE-751 21 Uppsala, Sweden
[d]New Energy and Industrial Technology Development Organization, 3-1-1 Higashi-Ikebukuro, Tokyo 170-6028, Japan

Abstract

The deposition rates of plasma-polymerized (pp-)films of 12 acrylate derivatives ($CH_2=CHCOOR$: substitution R is –H, $–CH_3$, $–CH=CH_2$, $–CH_2CH_3$, $–CH_2CH_2CH_3$, $–(CH_2)_3CH_3$, $–C(CH_3)_3$, $–CH_2CH(CH_3)_2$, $–CH_2(CH_2)_4CH_3$, $–CH_2CF_3$, $–CH_2CF_2CF_3$, $–CH_2(CF_2)_2CF_3$), and 12 methacrylate derivatives ($CH_2=CCH_3COOR'$: substitution R′ is –H, $–CH_3$, $–CH=CH_2$, $–CH_2CH_3$, $–CH_2CH_2CH_3$, $–(CH_2)_3CH_3$, $–C(CH_3)_3$, $–CH_2CH(CH_3)_2$, $–CH_2(CH_2)_4CH_3$, $–CH_2CF_3$, $–CH_2CF_2CF_3$, $–CH_2(CF_2)_2CF_3$) are determined by the quartz crystal microbalance technique. Using the same polymerization conditions (100 W RF and 100 Pa vapor pressure) for the various monomers, it is found that the deposition rates were proportional to the polymerization time. The average deposition rate of pp-acrylate derivatives is larger than that of pp-methacrylate derivatives without pp-hexylacrylate. The average deposition rate of pp-fluoroalkylacrylates was higher than 7–25 times that of pp-alkylacrylate, and the average deposition rate of pp-fluoroalkylmethacrylates was higher than 10–31 times that of pp-alkylmethacrylates, respectively. The average deposition rate of pp-film depends on the chemical structure of the monomer suggesting different mechanisms under plasma-polymerization.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Plasma processing and deposition; Quartz crystal microbalance; Acrylate derivatives; Plasma polymers; Deposition rate

1. Introduction

Plasma-polymerization has been widely used to fabricate thin films of a variety of volatile compounds without chemical solvents in coating process. These films adhere firmly to most substrates and are highly resistant to chemical and physical treatment. The plasma-polymerization technique has also been conventionally employed to fabricate thin functional films that facilitate the surface modification of materials [1,2]. Such films are expected to be useful as surface protection films rigidly fixed on the substrates [3,4]. Acrylate derivatives and methacrylate derivatives are one of the candidates of transparency coating materials. For the automobile industry and builder industry, the control of deposition rate of thin film on the body is one of the important problems [5]. The deposition rates in plasma-polymerization have been determined with a balance or by in situ measurement of the film thickness with a multi-interference thickness meter [6–10]. These methods cannot, however, detect the deposition rates of ultra-thin films. Piezoelectric quartz crystal is widely recognized as a useful microbalance (quartz crystal microbalance, QCM). Adsorption of material on the surface of a crystal changes its oscillation frequency. When an AT-cut quartz crystal with a fundamental oscillation frequency of 9 MHz is used, adsorption of approximately 1 ng of material decreases the oscillation frequency by 1 Hz [11,12]. Many attempts have been made to use these highly sensitive, convenient and portable devices as chemical sensors and biosensors [13–16]. The QCM has also been used to monitor the thickness of films during vapor deposition and plasma processes. The deposition rates of gaseous monomers in plasma-polymerization have been thoroughly investigated [6–10], whereas few of liquid monomers have been reported. It is well known that liquid monomer having high boiling point is easily liquefied in the reaction

*Corresponding author. Tel./fax: +81-298-61-4746.
E-mail address: shigeru-kurosawa@aist.go.jp (S. Kurosawa).

0040-6090/04/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2003.12.008

Favored Ex. 1035

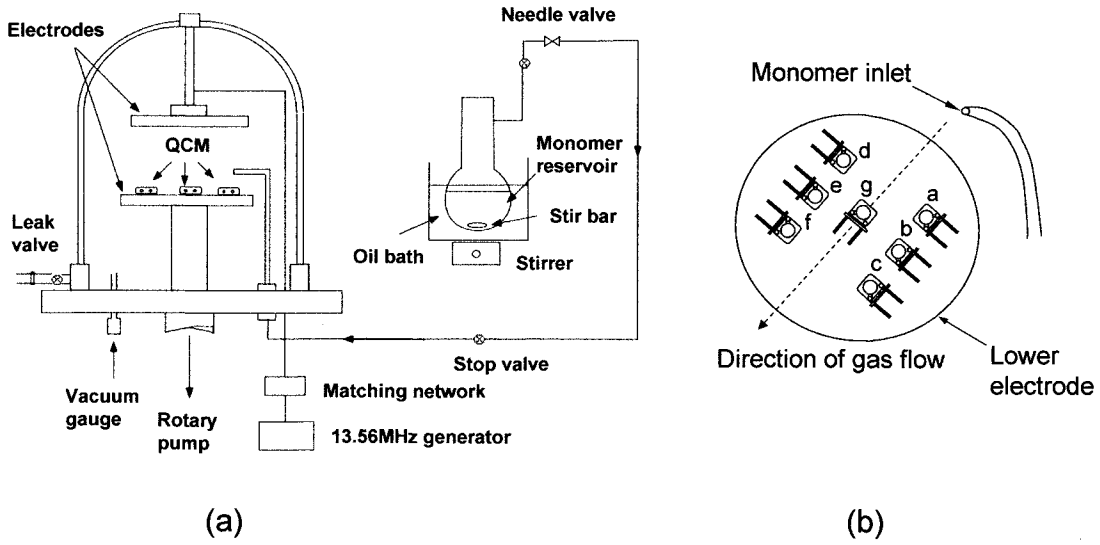


Fig. 1. (a) Schematic diagram of plasma-polymerization equipment. (b) Position settings (a–g) of seven QCMs on the lower electrode.

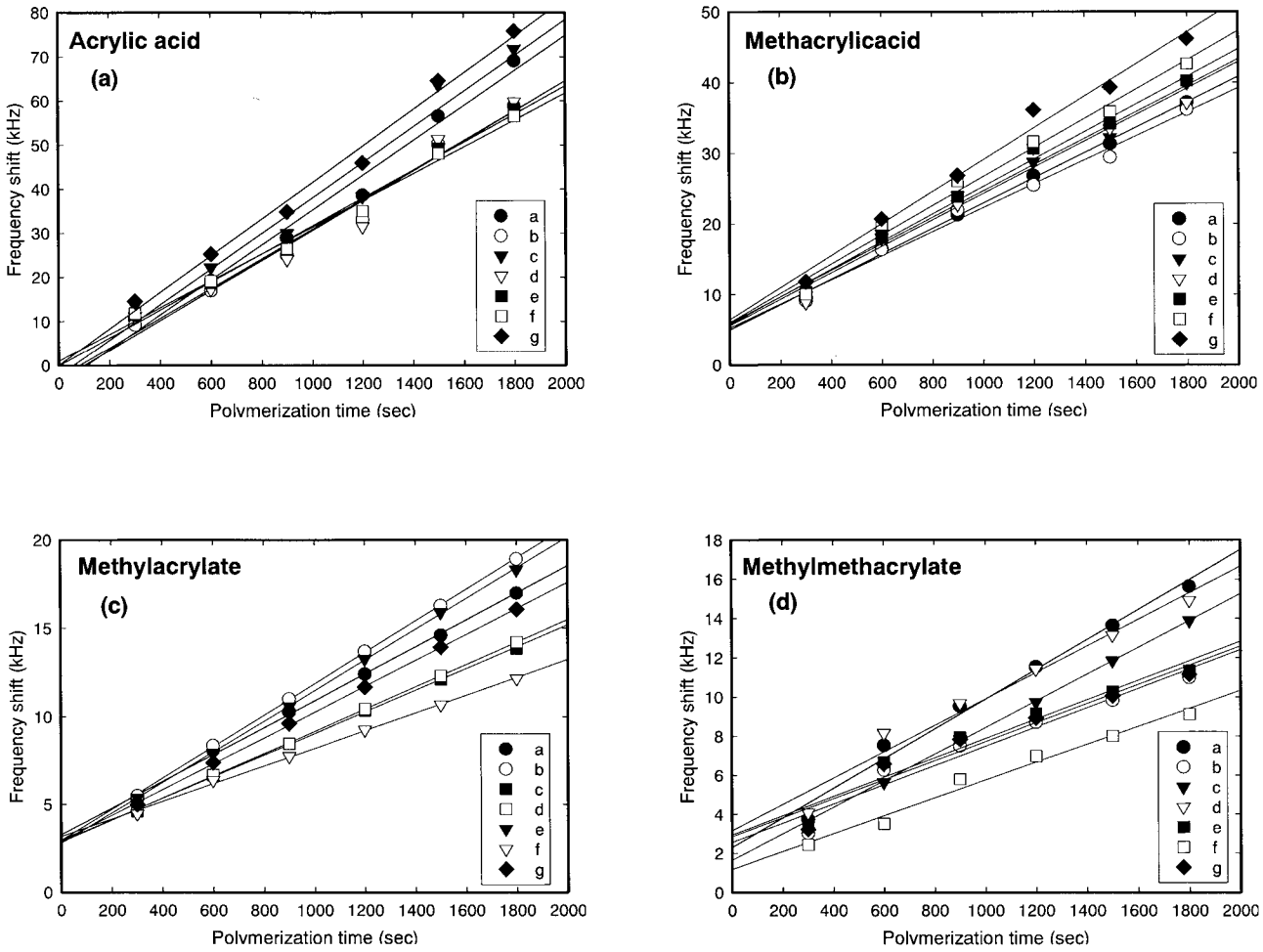


Fig. 2. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) Acrylic acid, (b) methacrylic acid, (c) methylacrylate and (d) methylmethacrylate.

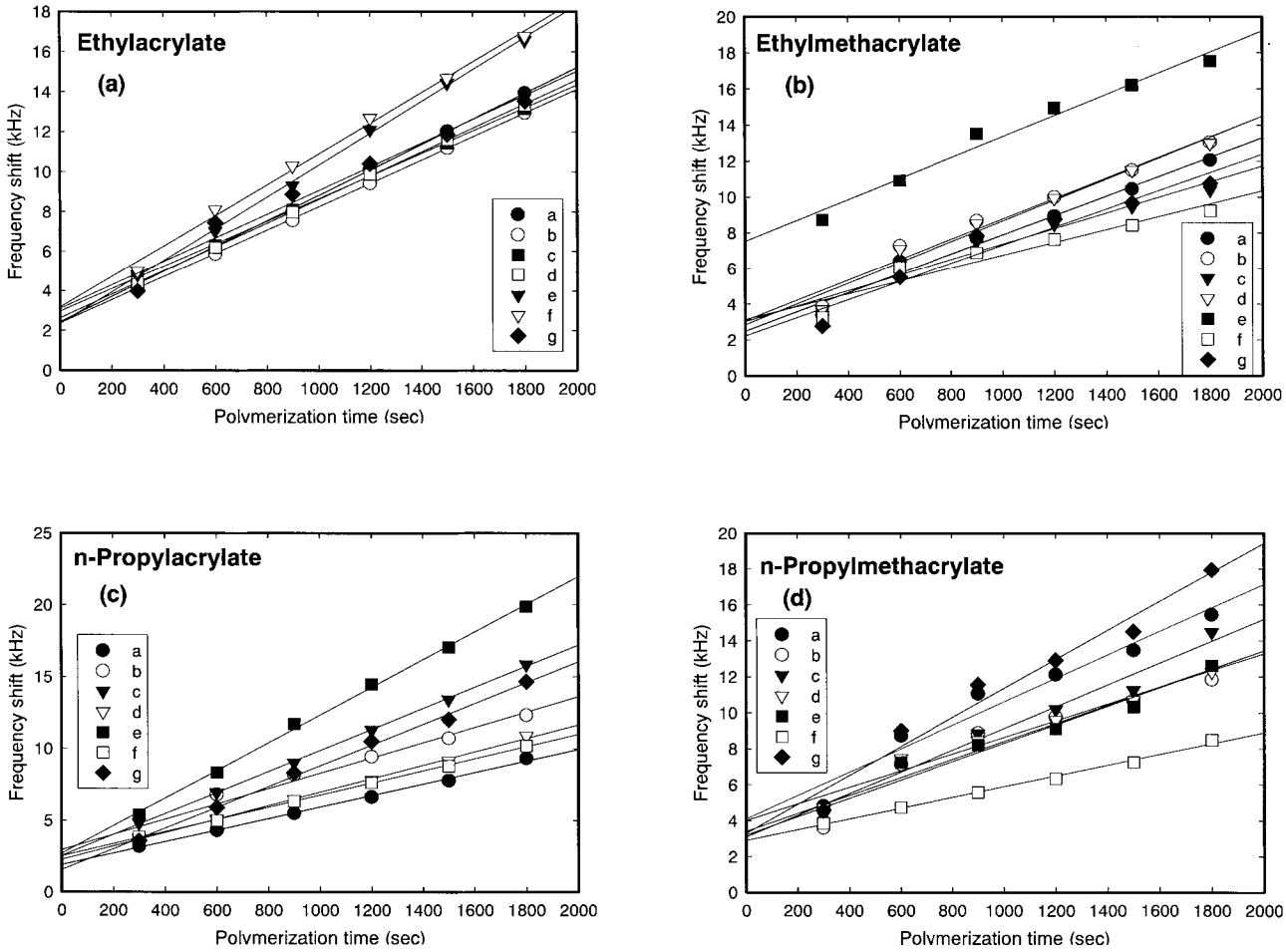


Fig. 3. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) Ethylacrylate, (b) ethylmethacrylate, (c) *n*-propylacrylate and (d) *n*-propylmethacrylate.

chamber. Therefore, the plasma-polymerization of liquid monomers has not been reported. We aim to construct polymer coating database for surface protection using plasma-polymers and to understand reaction mechanisms of plasma-polymerization.

In this paper, plasma-polymerized (pp-)films are prepared from 12 acrylate derivatives (acrylic acid, methylacrylate, vinylacrylate, ethylacrylate, *n*-propylacrylate, *n*-butylacrylate, *tert*-butylacrylate, *iso*-butylacrylate, *n*-hexylacrylate, 2,2,2-triflouroethylacrylate, 2,2,3,3,3-pentafluoropropylacrylate and 2,2,3,3,4,4,4-heptafluorobutylacrylate) and 12 methacrylate derivatives (methacrylic acid, methylmethacrylate, vinylmethacrylate, ethylmethacrylate, *n*-propylmethacrylate, *n*-butylmethacrylate, *tert*-butylmethacrylate, *iso*-butylmethacrylate, *n*-hexylmethacrylate, 2,2,2-triflouroethylmethacrylate, 2,2,3,3,3-pentafluoropropylmethacrylate and 2,2,3,3,4,4,4-heptafluorobutylmethacrylate). Each of these monomers is polymerized under the same polymerization condition at 100 Pa of monomer vapor pressure, 100 W of RF with 13.56 MHz of continuous wave (CW).

The present work is a preliminary study in using the QCM sensor array to detect the deposition rates of pp-films in order to investigate the deposition mechanism of acrylate and methacrylate monomers under plasma-polymerization.

2. Experimental section

The monomers used in this experiment were all of analytical or guaranteed grade and were purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan) or Kanto Chemical Co., Inc. (Tokyo, Japan) and used without further purification. For plasma-polymerization, the plasma-polymerization equipment Model BP-1 of Samco International Co. (Kyoto, Japan) was used [17,18]. Fig. 1a shows a schematic diagram of the plasma-polymerization equipment. The deposition rates of the pp-films were measured with the QCM during the polymerization process. The QCM had gold electrodes on both of its surfaces (AT-cut of 9 MHz; $8\times8\times0.15$ mm^3) and was purchased from Nihon Dem-

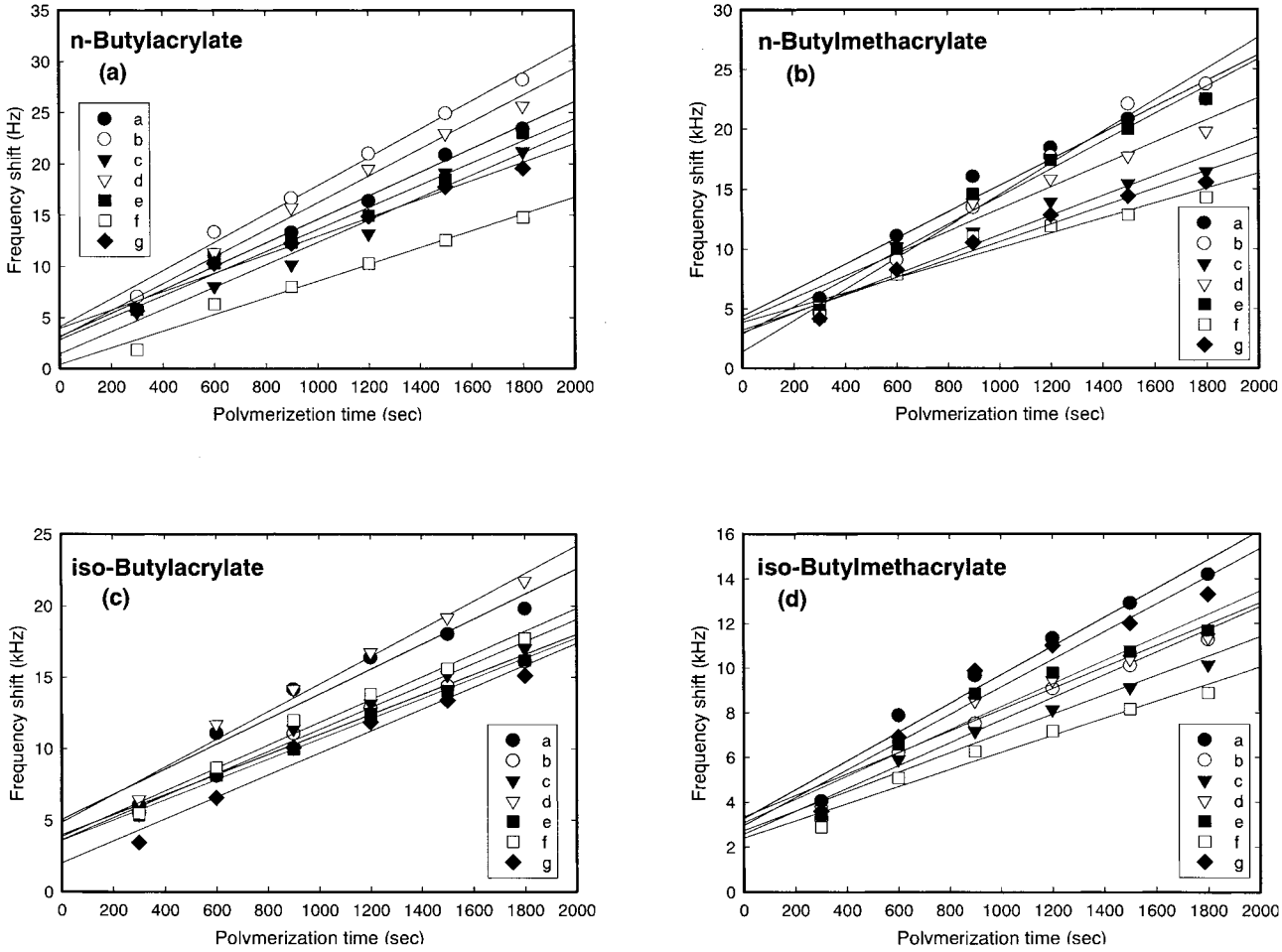


Fig. 4. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) *n*-Butylacrylate, (b) *n*-butylmethacrylate, (c) *iso*-butylacrylate and (d) *iso*-butylmethacrylate.

pa Kogyo Co. Ltd (Tokyo, Japan). The pp-films were deposited on one side of the QCM. The deposition rates of the pp-films depend on the positioning of the substrates. Therefore, the seven QCMs were placed on the lower electrode (diameter 100 mm) for the glow discharge. The position settings of the seven QCMs on the lower electrode are denoted in Fig. 1b. Prior to plasma-polymerization, the seven QCMs were treated by plasma sputtering for 5 s under 100 W RF power and 100 Pa of He pressure.

The plasma-polymerization conditions were controlled by two parameters: the vapor pressure of the monomer and the power of the glow discharge. We used the same polymerization conditions for all 12 acrylate monomers and 12 methacrylate monomers: a vapor pressure of 100 Pa and RF power of 100 W with 13.56 MHz of CW. The monomers were vaporized at a constant liquid temperature, which was maintained by an oil bath, and a controlled vacuum. The distance between the electrodes was 6.0 cm and the power of the glow discharge was set at 100 W. The plasma-polymerization was performed for 300–1800 s by 300-s intervals. We obtained an optimum film-state of the polymers under these conditions.

The apparatus and procedure for determining the deposition rate have been described previously [17,18]. The oscillating frequency of the QCM was measured with a universal counter (Iwatsu SC7201, Tokyo, Japan) using data stored in a microcomputer (NEC PC9821, Tokyo, Japan). The laboratory made transistor–transistor logic electronic circuit used is described in Ref. [19] (circuit II). The relationship between the weight of the pp-films and the frequency shift is expressed in units of ng/Hz [12]. All of the experiments were carried out at 25 ± 2 °C. The chemical structure of pp-films was characterized by FT-IR, XPS and contact angle. These results will be published elsewhere [20].

3. Results and discussion

The deposition rates of the pp-films onto the QCM were measured directly by the shift in the oscillation

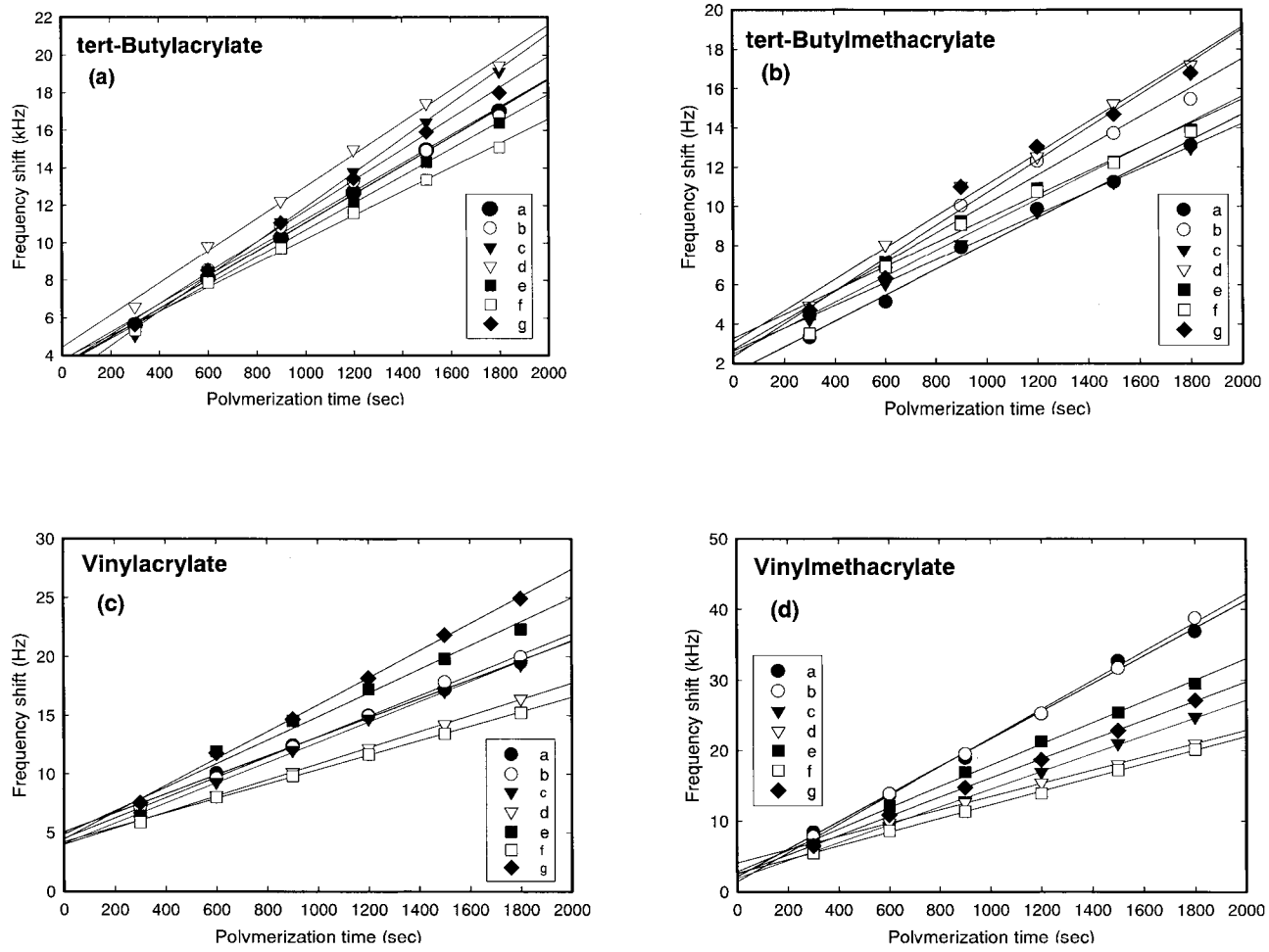


Fig. 5. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) *tert*-Butylacrylate, (b) *tert*-butylmethacrylate, (c) vinylacrylate and (d) vinylmethacrylate.

frequency. Fig. 2a shows the relationship between the deposition rates of pp-acrylic acid for the seven positions (a–g) of the lower electrode and the polymerization time. A linear relationship was observed up to a polymerization time of 1800 s. The correlation coefficient of each line (the polymerization time response for the positions a–g) is almost 1.0. We define the individual deposition rates of the pp-films using the slope of lines a–g for each sample. The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. The average of deposition rate for the pp-acrylic acid film is 2.15 μg/min. The value of the standard deviation (σ) and the coefficient of variation (CV) of pp-acrylic acid is 0.269 μg/min and 12.5%, respectively. The reproducibility of the deposition rate is high, in three independent experiments the CV within 15% (data not shown). Therefore, we confirm the accuracy of this technique.

Fig. 2b and Figs. 3–6d show the typical data between the frequency shift and polymerization time for pp-acrylic acid, pp-methylacrylate, pp-vinylacrylate, pp-ethylacrylate, pp-propylacrylate, pp-butylacrylate, pp-*tert*-butylacrylate, pp-*iso*-butylacrylate, pp-2,2,2-triflouroethylacrylate, pp-2,2,3,3,3-pentafluoropropylacrylate, pp-methacrylic acid, pp-methylmethacrylate, pp-vinylmethacrylate, pp-ethylmethacrylate, pp-propylmethacrylate, pp-butylmethacrylate, pp-*tert*-butylmethacrylate, pp-*iso*-butylmethacrylate, pp-2,2,2-triflouroethylmethacrylate and pp-2,2,3,3,3-pentafluoropropylmethacrylate, respectively. The range of linearity between frequency shift and the polymerization time is also included for the seven positions (a–g) of the lower electrode. Outside this range, or above the formed thickness, the QCM does not work as a microbalance.

Table 1 summarizes the averaged deposition rates for the 12-acrylate monomers of polymerization. The values are in the order of 2,2,3,3,4,4,4-heptafluorobutylacrylate > 2,2,3,3,3-pentafluoropropylacrylate > 2,2,2-triflouroethylacrylate > acrylic acid > *n*-hexylacrylate > vinylacrylate > *n*-butylacrylate > *iso*-butylacrylate > *tert*-butylacrylate > methylacrylate > ethylacrylate > *n*-propylacrylate. Table 2 summarizes the averaged deposition rates

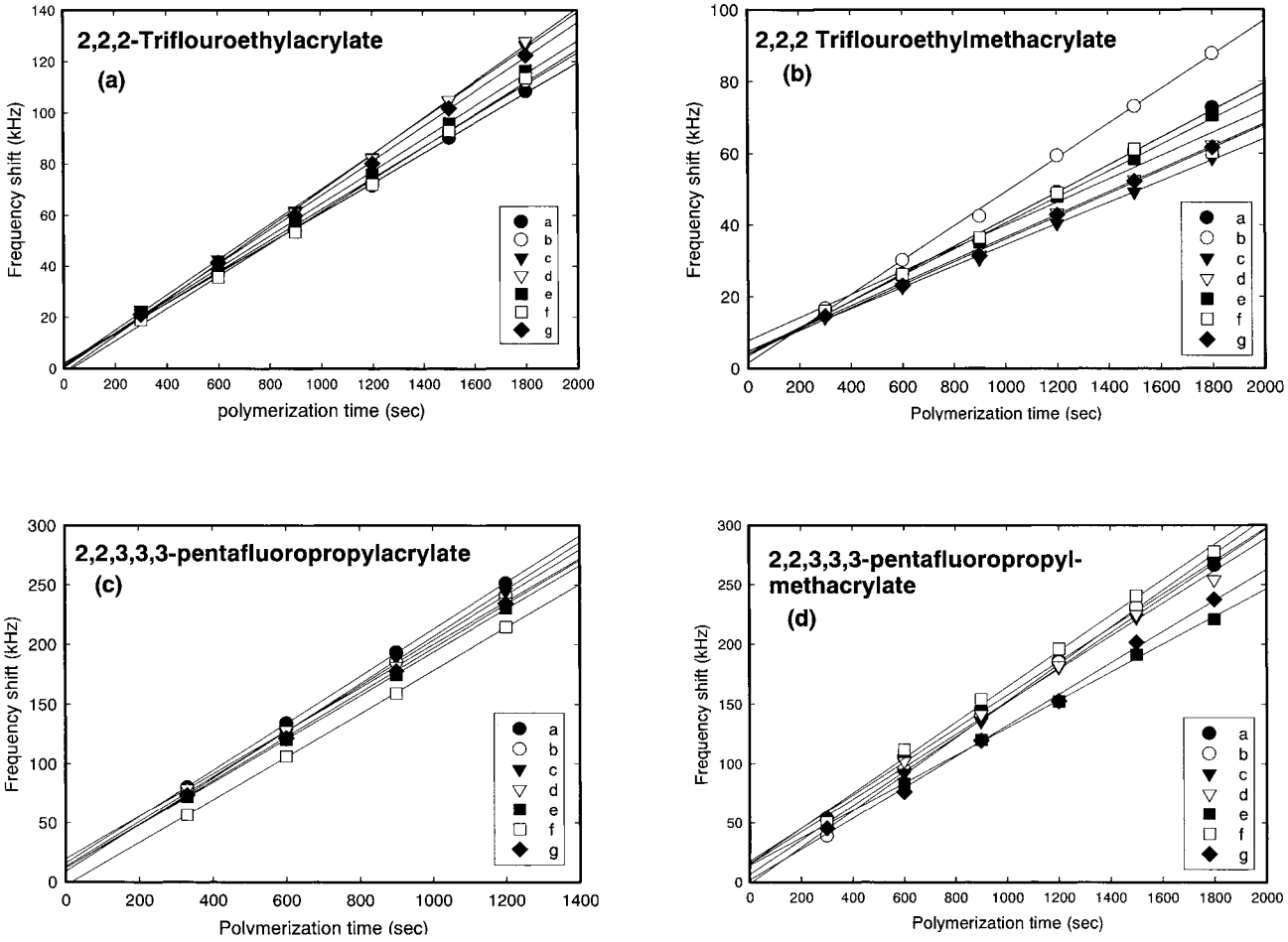


Fig. 6. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with (a) 2,2,2-trifluoroethylacrylate, (b) 2,2,2-trifluoroethylmethacrylate, (c) 2,2,3,3,3-pentafluoropropylacrylate and (d) 2,2,3,3,3-pentafluoropropylmethacrylate.

for the 12-methacrylate monomers of polymerization. The averaged deposition rates for the 12-methacrylate monomers are in the order of 2,2,3,3,4,4,4-heptafluorobutylmethacrylate > 2,2,3,3,3-pentafluoropropylmethacrylate, 2,2,2-triflouroethylmethacrylate > *n*-hexylmethacrylate > methacrylic acid > vinylmethacrylate > *n*-butylmethacrylate > *tert*-butylmethacrylate > methylmethacrylate > *n*-propylmethacrylate > ethylmethacrylate = *iso*-butylmethacrylate.

The average deposition rate of pp-acrylate derivatives is larger than that of pp-methacrylate derivatives without pp-hexylacrylate. The average deposition rate of pp-fluoroalkylacrylates was higher than 7–25 times that of pp-alkylacrylate, and the average deposition rate of pp-fluoroalkylmethacrylates was higher than 10–31 times that of pp-alkylmethacrylates, respectively. The differences of the order of deposition rate were occurred under the small deposition values. Accordingly, the deposition rate of the pp-films is affected by the chemical structure of the monomer and, hence, the reaction mechanism.

All of the polymerizations were conducted under identical settings of the equipment, which caused higher gas phase concentration of the monomers with lower boiling points. The reaction pathway of the different monomers, however, often canceled this concentration effect. Polymerization is assumed to proceed via a free radical mechanism initiated through the collision of an electron with a monomer molecule (Eq. (1)). Dissociation of this molecule results in the formation of free radicals, which may add to intact monomers (Eq. (2)) denoted as the initiation:

$$M + e^- \rightarrow R^\bullet \quad (1)$$

$$R^\bullet + M \underset{k_i}{\rightarrow} RM^\bullet \quad (2)$$

Polymerization (Eq. (3)) then proceeds in the gas phase and on the surface.

$$RM^\bullet + nM \underset{k_p}{\rightarrow} RM^\bullet_{n+1} \quad (3)$$

Table 1
Average of deposition rates of pp-films coated with 300 s of time intervals for the plasma-polymerization

Acrylates	Molecular formula	Adr	σ	CV
Acrylic acid	$CH_2=CHCOOH$	2.15	0.269	12.5
Methylacrylate	$CH_2=CHCOOCH_3$	0.43	0.085	19.7
Vinylacrylate	$CH_2=CHCOOCH=CH_2$	1.26	0.155	12.3
Ethylacrylate	$CH_2=CHCOOC_2H_5$	0.39	0.056	14.4
n-Propylacrylate	$CH_2=CHCOOCH_2CH_2CH_3$	0.36	0.124	34.1
n-Butylacrylate	$CH_2=CHCOO(CH_2)_3CH_3$	0.66	0.121	18.3
tert-Butylacrylate	$CH_2=CHCOOC(CH_3)_3$	0.47	0.055	11.9
iso-Butylacrylate	$CH_2=CHCOOCH_2CH(CH_3)_2$	0.48	0.057	11.9
n-Hexylacrylate	$CH_2=CHCOOCH_2(CH_2)_4CH_3$	1.31	0.147	11.2
2,2,2-Triflouroethylacrylate	$CH_2=CHCOOCH_2CF_3$	3.89	0.267	6.86
2,2,3,3,3-Pentafluoropropylacrylate	$CH_2=CHCOOCH_2CF_2CF_3$	11.2	0.446	3.97
2,2,3,3,4,4,4-Heptafluorobutylacrylate	$CH_2=CHCOOCH_2(CF_2)_2CF_3$	13.0	1.110	8.5

The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. σ and CV represent the standard deviation and the coefficient of variation, respectively. Adr, average deposition rate [μg/min]; σ, standarad deviation [μg/min]; CV, coefficient of variation [%].

Finally, collision between two radicals leads to termination of the reaction (Eq. (4)) by radical–radical coupling or disproportionation, as in the case of standard free radical polymerization.

$$R^{\bullet} + R' \xrightarrow[k_t]{} R - R' \tag{4}$$

If the monomers are polymerizable by conventional free radical polymerization, plasma-polymerization may proceed simultaneously with plasma-induced polymerization, resulting in high deposition rates. A unique feature of plasma-polymerization of 'normal' monomers is that the system may become starved of monomers. We assume that the rate of polymerization is mainly determined by the rate of initiation k_i, and not by the rate of propagation [21]. The termination of growing chains is suppressed by the immobility of the pp-layer, making the termination rate k_t low. In this study all monomers are prone to free radical polymerization and the rate of deposition is governed by the availability of surface radicals to propagate adsorbed monomers. For the alkylacrylates the differences are not significant. In general, a small difference is seen between the acrylates and the corresponding methacrylates, which can be attributed to differences in vapor pressure. A slight increase in deposition rate is observed with larger alkyl groups going from methyl to *n*-butyl and to hexyl. The reason for this is not clear but could be due to higher rate of formation of initiating radicals with larger alkyl groups or increased rate of monomer adsorption onto the surface. Vinylacrylate and vinylmethacrylate both give higher deposition rate than corresponding saturated monomers due to increase possibilities of reactions with surface radicals. By substitution of the alkyl to fluoroalkyl, a substantial increase in rate was observed. As earlier stated [22,23] halogen-containing monomers are more prone to form radicals in the plasma leading to higher concentration of propagating surface radicals and hence higher rate of deposition. We are well aware that although the proposed reaction pathway and rate-deter-

Table 2
Average of deposition rates of pp-films coated with 300 s of time intervals for the plasma-polymerization

Methacrylates	Molecular formula	Adr	σ	CV
Methacrylic acid	$CH_2=CCH_3COOH$	1.16	0.111	9.61
Methylmethacrylate	$CH_2=CCH_3COOCH_3$	0.35	0.073	21.1
Vinylmethacrylate	$CH_2=CCH_3COOCH=CH_2$	0.91	0.249	27.3
Ethylmethacrylate	$CH_2=CCH_3COOC_2H_5$	0.31	0.051	16.6
n-Propylmethacrylate	$CH_2=CCH_3COOCH_2CH_2CH_3$	0.33	0.095	29.1
n-Butylmethacrylate	$CH_2=CCH_3COO(CH_2)_3CH_3$	0.57	0.147	25.8
tert-Butylmethacrylate	$CH_2=CCH_3COOC(CH_3)_3$	0.42	0.058	13.9
iso-Butylmethacrylate	$CH_2=CCH_3COOCH_2CH(CH_3)_2$	0.31	0.056	18.3
n-Hexylmethacrylate	$CH_2=CCH_3COOCH_2(CH_2)_4CH_3$	1.32	0.123	9.3
2,2,2-Triflouroethylmethacrylate	$CH_2=CCH_3COOCH_2CF_3$	2.12	0.370	17.4
2,2,3,3,3-Pentafluoropropylmethacrylate	$CH_2=CCH_3COOCH_2CF_2CF_3$	8.33	0.760	9.12
2,2,3,3,4,4,4-Heptafluorobutylmethacrylate	$CH_2=CCH_3COOCH_2(CF_2)_2CF_3$	11.6	0.630	5.4

The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. σ and CV represent the standard deviation and the coefficient of variation, respectively. Adr, average deposition rate [μg/min]; σ, standard deviation [μg/min]; CV, coefficient of variation [%].

mining steps support the experimental findings, they are not direct proofs of these mechanisms. The contribution of the step-growth mechanism proposed by Yasuda [24] is certainly also important although not dominant for the conditions used here. Furthermore, ablation, which is especially important for fluorine-containing monomers, will certainly occur in parallel. Additional experimental support may be obtained by in situ determination of the reactive species in the plasma, in the gas phase, and the volatile products formed, together with careful characterization of the cross-linked film.

Acknowledgments

The authors wish to thank Mr T. Shima for his technical assistance of electronic measurements. This work was supported by the special funds for 'Study of chemical sensor of benzene and dioxins using quartz crystal microbalance' from Steel Industry Foundation for the Advancement of Environmental Protection Technology, for AIST grant on international collaborative research 'Synthesis of well-defined polymer and control of nanostructure by living radical polymerization' from AIST and for 'Study on monitoring of environmental risk compounds such as dioxins and endocrine disruptors using sensing system' from the Ministry of the Environment.

References

[1] H. Yasuda, Plasma Polymerization, Academic, New York, 1985, Chapters 1, 2 and 6.
[2] H. Biederman, Y. Osada, Plasma Polymerization Processes, Elsevier, New York, 1992, Chapter 7.
[3] N. Inagaki, Plasma Surface Modification and Plasma Polymerization, Technomic Publishing Co., Inc, Lancaster, 1996, Chapter 5 and 6.
[4] H. Mizuachi, M. Tobayama, Handbook of Surface Treatment Technologies, NTS Press, Tokyo, 2000, pp. 250–253, 575–597 (in Japanese).
[5] M. Ishizuka, High Performance Paints, Kogyo Chosakai Publ, Tokyo, 1988, pp. 15–92, in Japanese.
[6] S. Kurosawa, J. Jap. Oil Chem. Soc. 47 (1998) 1133, in Japanese.
[7] H. Kobayashi, A.T. Bell, M. Shen, J. Macromol. Sci. Chem. A 10 (1976) 491.
[8] H. Yasuda, T. Hirotsu, J. Polym. Sci. Polym. Chem. Ed. 16 (1978) 229.
[9] N. Morosoff, W. Newton, H. Yasuda, J. Vac. Sci. Technol. 15 (1978) 1815.
[10] N. Inagaki, H. Yasuda, J. Appl. Polym. Sci. 26 (1981) 3557.
[11] G. Sauerbrey, Z. Phys. 155 (1959) 206.
[12] W.D. Ward, D.A. Buttry, Science 249 (1990) 1000.
[13] S. Kurosawa, N. Kamo, D. Matsui, Y. Kobatake, Anal. Chem. 62 (1990) 353.
[14] S. Kurosawa, N. Kamo, T. Arimura, A. Sekiya, M. Muratsugu, Jap. J. Appl. Phys. 34 (7B) (1995) 3925.
[15] S. Kurosawa, E. Tawara-Kondo, N. Kamo, Anal. Chim. Acta 43 (1997) 175.
[16] H. Yasuda, C.R. Wang, J. Polym. Sci. Polym. Chem. Ed. 23 (1985) 87.
[17] S. Kurosawa, T. Hirokawa, K. Kashima, H. Aizawa, D.S. Han, Y. Yoshimi, Y. Okada, K. Yase, J. Miyake, M. Yoshimoto, J. Hilborn, Thin Solid Films 374 (2000) 262.
[18] S. Kurosawa, H. Aizawa, J. Miyake, M. Yoshimoto, J. Hilborn, Z.A. Talib, Thin Solid Films 407 (2002) 1.
[19] S. Kurosawa, E. Tawara, N. Kamo, Y. Kobatake, Anal. Chim. Acta 230 (1990) 41.
[20] Z.A. Talib, JICA Training Report 2001, in: Z.A. Talib, B. Atthoff, S. Kurosawa (Eds.), Tsukuba, Japan International Cooperation Agency, (2001) 50.
[21] J.M. Tibbitt, R. Jensen, A.T. Bell, M. Shen, Macromolecules 10 (1977) 647.
[22] R. Filler, Fluorine Chemistry Reviews, vol. 8, Marcel Dekker, New York, 1990, Chapter 1.
[23] N. Ishikawa, Y. Kobayashi, Kodanshya Sci., Tokyo, (1979) Chapter 5 (in Japanese).
[24] Y. Iriyama, H. Yasuda, Polym. Mater. Sci. Eng. 62 (1990) 162.

ELSEVIER

Thin Solid Films 407 (2002) 1–6

thin solid films

www.elsevier.com/locate/tsf

Detection of deposition rate of plasma-polymerized silicon-containing films by quartz crystal microbalance

Shigeru Kurosawa[a,b,*], Hidenobu Aizawa[a], Jun Miyake[c], Minoru Yoshimoto[d], Jöns Hilborn[e], Zainal Abidin Talib[a,f,1]

[a]*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1 Higashi, Tsukuba 305-8565, Japan*
[b]*Human Stress Signal Research Center, National Institute of Advanced Industrial Science and Technology (AIST), 1-1 Higashi, Tsukuba 305-8565, Japan*
[c]*Tissue Engineering Research Center, National Institute of Advanced Industrial Science and Technology (AIST), 1-1 Higashi, Tsukuba 305-8565, Japan*
[d]*Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan*
[e]*Uppsala University, SE-751 21 Uppsala, Sweden*
[f]*Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia*

Abstract

The deposition rates of plasma-polymerized (pp-) films of vinyltriethoxysilane, vinyltrimethylsilane, tetravinylsilane, diallyldimethylsilane, allyltrimethylsilane, 1,3-divinyltetramethyldisiloxane and 1,1,3,3-tetramethyl-1,3-divinyldisilazane were determined by the quartz crystal microbalance (QCM) technique. Using the same polymerization conditions (100 W RF and 100 Pa vapor pressure) for the various monomers, it was found that the deposition rates were proportional to the polymerization time. The average deposition rate of pp-vinyltrimethylsilane was 2.44 μg/min. The average deposition rate of pp-1,3-divinyltetramethyldisiloxane was five-fold higher and that of pp-tetravinylsilane was 13.5-fold higher than that of pp-vinyltrimethylsilane. The average deposition rate of pp-allyltrimethylsilane was 3.43 μg/min. The average deposition rate of pp-diallyldimethylsilane was 0.8-fold higher. The average deposition rate depended on the chemical structure of the monomer, giving rise to different mechanisms of polymerization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma processing and deposition; Quartz crystal microbalance; Coatings; Polymers

1. Introduction

It is well known that new lower dielectric-constant films are required for future generation integrated circuits (ICs). These materials are required to lower the RC time constants between interconnects, thus improving the overall IC response speeds. As future sizes are reduced below the 0.25 μm level, the need for lower dielectric constant materials becomes increasingly important. This reflects the fact that the interconnect delay times become increasingly dominant relative to gate-to-gate delays as the feature size is decreased [1,2].

Plasma polymerization has been widely used to fabricate thin films of a variety of volatile compounds. These films firmly adhere to most substrates and are highly resistant to chemical and physical treatment. The plasma polymerization technique has also been conventionally employed to fabricate thin functional films that facilitate the surface modification of materials [3,4]. Such films are expected to be useful as low dielectric-constant films rigidly fixed on the IC [5–7]. Silicon-containing compounds are candidates for low dielectric-constant materials. For the IC fabrication technology, control of the deposition rate of thin film is an important problem. The deposition rates in plasma polymerization have been determined with a balance or by in situ measurement of the film thickness with a multi-interference thickness meter [8–12]. These methods cannot, however, detect the deposition rates of ultra-thin films. Piezoelectric quartz crystal is widely recognized as a useful microbalance (quartz crystal microbalance, QCM). Adsorption of material on the

*Corresponding author. Tel./fax: +81-298-61-4746.
E-mail address: shigeru-kurosawa@aist.go.jp (S. Kurosawa), zainalat@fsas.upm.edu.my (Z. Abidin Talib).
[1] Tel.: +603-9486101.

0040-6090/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6090(02)00003-2

Favored Ex. 1036

surface of a crystal changes its oscillation frequency. When an AT-cut quartz crystal with a fundamental oscillation frequency of 9 MHz is used, adsorption of approximately 1 ng of material decreases the oscillation frequency by 1 Hz [13–15]. Many attempts have been made to use these highly sensitive, convenient and portable devices as chemical sensors and immunosensors [16–20]. The QCM has also been used to monitor the thickness of films during vapor deposition and plasma processes. Those reports used only one QCM settled in the vacuum chamber. The deposition rates of gaseous monomers in plasma polymerization have been thoroughly investigated [6–10], whereas those of liquid monomers have not yet been reported. It is well known that a liquid monomer with a high boiling point is easily liquefied in the reaction chamber. Therefore, the plasma polymerization of liquid monomers has not been reported.

In this study, plasma polymerized films were prepared from seven monomers: allyltrimethylsilane; vinyltrimethylsilane; vinyltriethoxysilane; 1,3-divinyltetramethyldisiloxane; 1,1,3,3-tetramethyl-1,3-divinyldisilazane; tetravinylsilane; and diallyldimethylsilane. Each of these monomers was polymerized under conditions of 100 W RF and 100 Pa of vapor pressure. The present work is a preliminary study in using a QCM sensor array to detect the deposition rates of plasma-polymerized films in order to gain an understanding of the deposition mechanism of silicon-containing monomers.

2. Experimental

The monomers used in this experiment were all of analytical or guaranteed grade and were purchased from Wako Pure Chemical Industries Ltd (Osaka, Japan) or Kanto Chemical Co Inc (Tokyo, Japan) and used without further purification. For plasma polymerization, Samco International Co (Kyoto, Japan) equipment, model BP-1, was used [20,21]. Fig. 1a shows a schematic diagram of the plasma polymerization equipment. The deposition rates of the pp-films were measured in situ with a QCM during the polymerization process. The QCM had silver electrodes on both of its surfaces (AT-cut of 9 MHz; $8\times8\times0.15$ mm) and was purchased from Seywa Crystal Co (Chiba, Japan). The pp-films were deposited on one side of the QCM. The deposition rate of a plasma-polymerized film is not dependent on the positioning of the substrate. Therefore, seven or five QCMs were placed on the lower electrode (diameter 100 mm) for the glow discharge. The position settings of the seven QCMs on the lower electrode are denoted in Fig. 1b, and the five QCMs on the lower electrode are denoted in Fig. 1c. Prior to plasma polymerization, the seven or five QCMs were treated by plasma sputtering for 5 s under 100 W RF power and 100 Pa of He pressure.

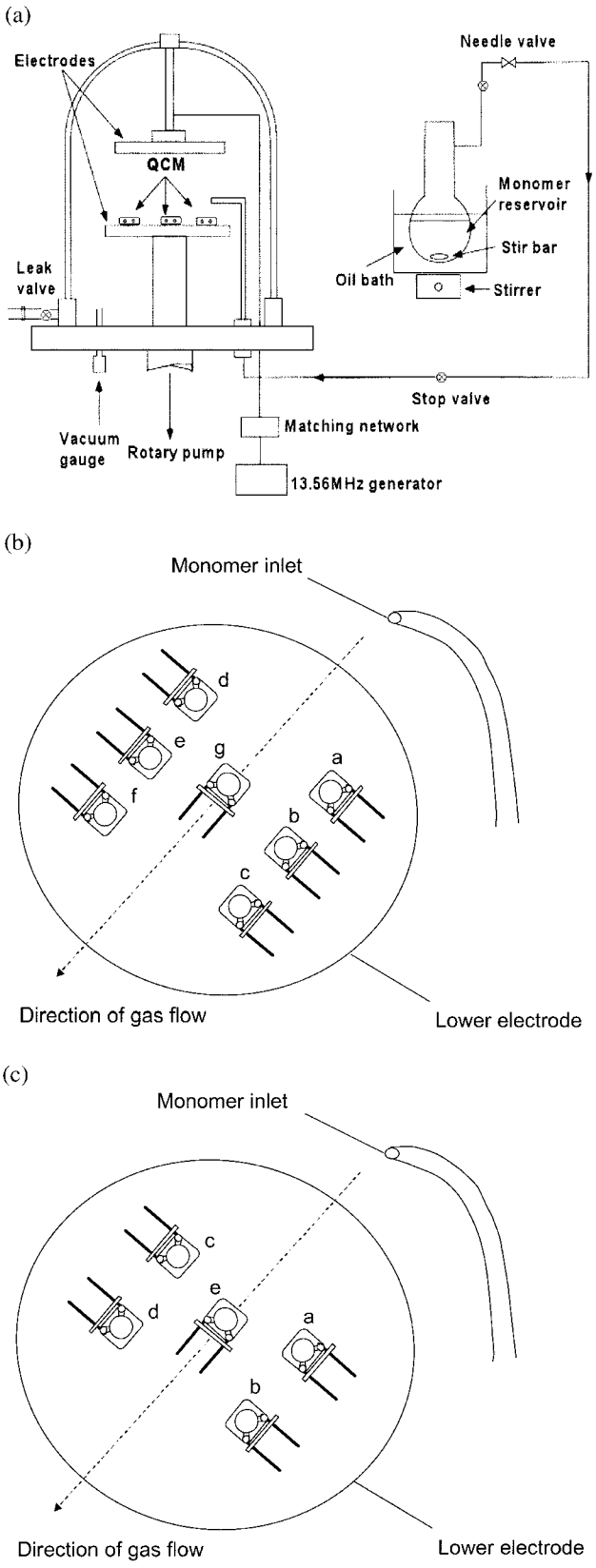


Fig. 1. (a) Schematic diagram of plasma-polymerization equipment. (b) Position settings (a–g) of seven QCMs on the lower electrode. (c) Position settings (a–e) of five QCMs on the lower electrode.

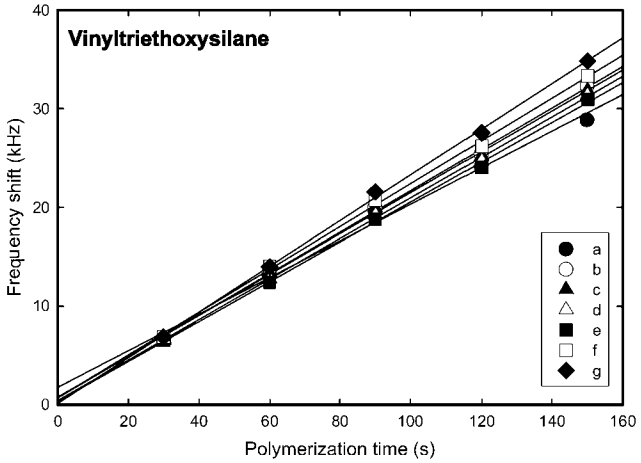


Fig. 2. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-vinyltriethoxysilane.

The plasma polymerization conditions were controlled by two parameters: the vapor pressure of the monomer and the power of the glow discharge. We used the same polymerization conditions for all seven monomers: a vapor pressure of 100 Pa and an RF power of 100 W. The monomers were vaporized at a constant liquid temperature, which was maintained by an oil bath, and under controlled vacuum. The distance between the electrodes was 6.0 cm and the power of the glow discharge was set at 100 W. The plasma polymerization was performed for 30–150 s at 30 s intervals and for 60–300 s at 60 s intervals. We obtained optimum polymer films under these conditions.

The apparatus and procedure for determining the deposition rate have been previously described [22,23]. The oscillating frequency of the QCM was measured with a universal counter (Iwatsu SC7201, Tokyo, Japan) using data stored in a microcomputer (NEC PC9821, Tokyo, Japan). The laboratory-made transistor–transistor logic (TTL) electronic circuit used is described in [15] (circuit II). The relationship between the weight of the pp-films and the frequency shift is expressed in units of ng/Hz [22,23]. All of the experiments were carried out at 25 ± 2 °C. The chemical structure of silicon-containing pp-films was measured by FT-IR, X-ray photoelectron spectroscopy (XPS) and the contact angle. These results are published elsewhere [24].

3. Results and discussion

The rate of deposition of the pp-films onto the QCM was directly measured by the shift in the oscillation frequency. Fig. 2 shows the relationship between the deposition rate of pp-vinyltriethoxysilane for the seven positions (a–g) of the lower electrode and the polymerization time. A linear relationship was observed up to a polymerization time of 150 s. The regression of the

Table 1
Deposition rates of pp-vinyltriethoxysilane

Position	Slope (kHz/s)	Intercept (kHz)	Correlation coefficient
a	0.185	1.780	0.996
b	0.210	0.691	0.999
c	0.207	0.733	0.999
d	0.205	0.403	1.000
e	0.202	0.368	0.999
f	0.217	0.696	0.999
g	0.232	0.092	0.999

polymerization time response for positions a–g is summarized in Table 1. The correlation coefficient of each line is almost 1.000. We define the individual deposition rate for plasma-polymerized films using the slope of lines a–g for each sample. The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. The average deposition rate for the pp-vinyltriethoxysilane film is 0.056 kHz/s (12.5 μg/min). The value of the standard deviation (σ) and the coefficient of variation (C.V.) of pp-vinyltriethoxysilane are 0.85 μg/min and 6.8%, respectively. The reproducibility of the deposition rate is high; in three independent experiments, the C.V. was within 8% (data not shown). This confirms the accuracy of this technique.

Figs. 3–8 show the same relationship for pp-allyltrimethylsilane, pp-vinyltrimethylsilane,pp-vinyltriethoxysilane, pp-1,3-divinyltetramethyldisiloxane, pp-1,1,3,3-tetramethyl-1,3-divinyldisilazane, pp-tetravinylsilane, and pp-diallyldimethylsilane, respectively. The linearity range is also included. Outside this range, or above the thickness formed, the QCM does not work as a microbalance.

Table 2 summarizes the average deposition rates for the seven monomers at a 30 s polymerization time

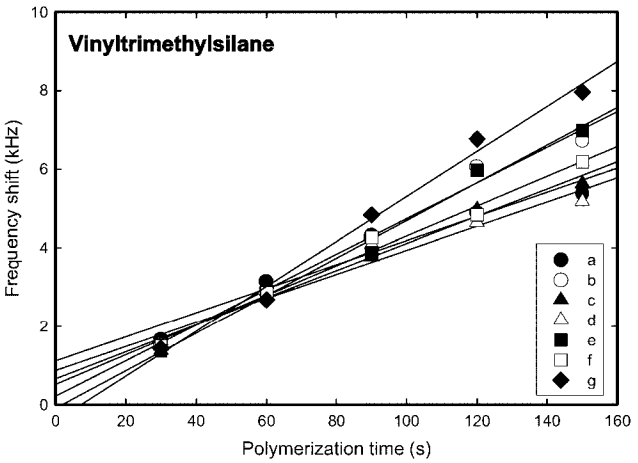


Fig. 3. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-vinyltrimethylsilane.

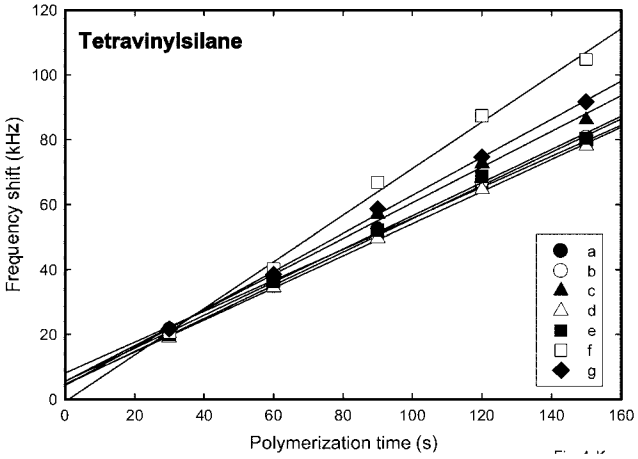


Fig. 4. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-tetravinylsilane.

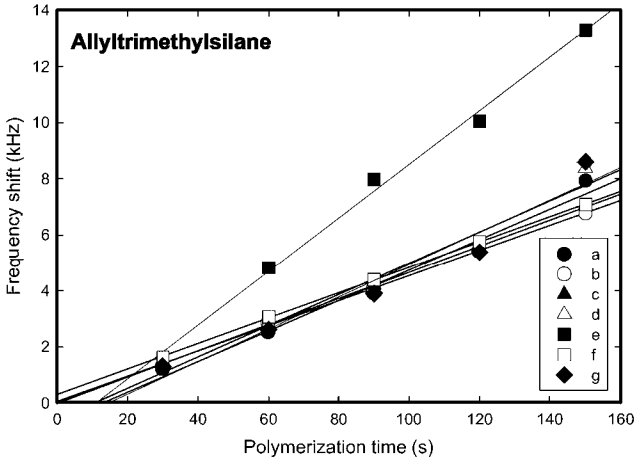


Fig. 6. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-allyltrimethylsilane.

interval. The values are in the order of tetravinylsilane > vinyltriethoxysilane > 1,3-divinyltetramethyldisiloxane > 1,1,3,3-teramethyl-1,3-divinyldisilazane > allyltrimethylsilane > diallyldimethylsilane > vinyltrimethylsilane.

Table 3 summarizes the averaged deposition rates for the seven monomers at a 60-s polymerization time interval. The values are in the order of tetravinylsilane > vinyltriethoxysilane > 1,1,3,3-teramethyl-1,3-divinyldisilazane > 1,3-divinyltetramethyldisiloxane > vinyltrimethylsilane > diallyldimethylsilane > allyltrimethylsilane. The difference in the order of deposition rate occurred for small deposition values.

The average deposition rate for a 300-s polymerization time interval for tetravinylsilane is 22.00 μg/min, and for diallyldimethylsilane, is 1.34 μg/min. Thus, the polymerization time interval affects the average deposition rate of pp-films. It is worth noting that for a high deposition rate, a very short polymerization time interval should be selected to detect the deposition rate of the pp-film. Accordingly, the deposition rate of the pp-films is affected by the chemical structure of the monomer, and hence the reaction mechanism.

All the polymerizations were conducted under identical equipment settings, which led to a higher gas-phase concentration of the monomers with lower boiling points. The reaction pathway of the different monomers, however, often canceled this concentration effect. Polymerization is assumed to proceed via a free-radical mechanism initiated through the collision of an electron with a monomer molecule [Eq. (1)]. Dissociation of this molecule results in the formation of free radicals,

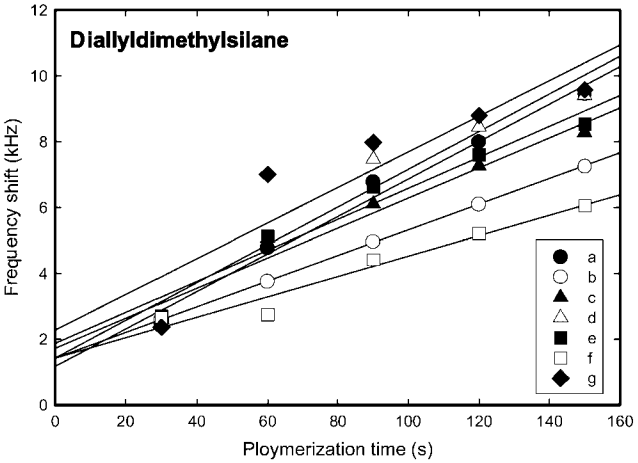


Fig. 5. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-diallyldimethylsilane.

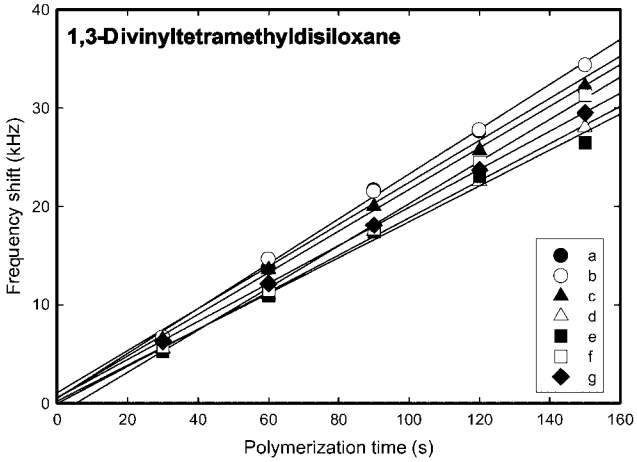


Fig. 7. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-1,3-divinyltetramethyldisiloxane.

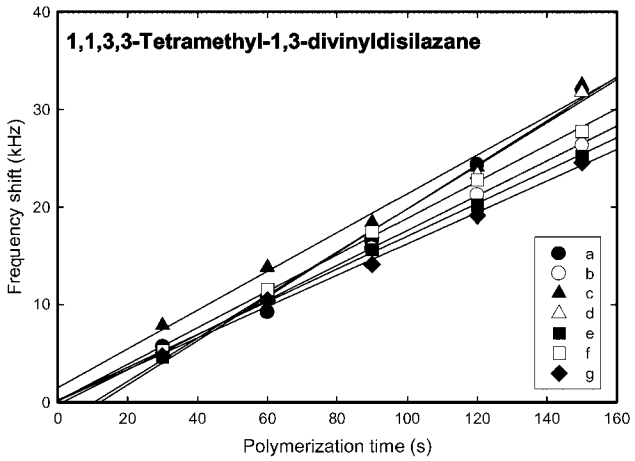


Fig. 8. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-1,1,3,3-tetramethyl-1,3-divinyldisilazane.

which may add to intact monomers [Eq. (2)]; this is denoted as the initiation.

$$M + e^- \rightarrow R^\bullet \quad (1)$$

$$R^\bullet + M \xrightarrow[k_i]{} RM^\bullet \quad (2)$$

Polymerization [Eq. (3)] then proceeds in the gas phase and on the surface.

$$RM^\bullet + nM \xrightarrow[k_p]{} RM^\bullet_{n+1} \quad (3)$$

Finally, collision between two radicals leads to termination of the reaction [Eq. (4)] by radical–radical coupling or disproportionation, as in the case of standard free-radical polymerization.

$$R^\bullet + {}^\bullet R' \xrightarrow[k_t]{} R - R' \quad (4)$$

If the monomers are polymerizable by conventional free-radical polymerization, plasma polymerization may simultaneously proceed with plasma-induced polymerization, resulting in high deposition rates. In our study, tetravinylsilane, 1,3-divinyltetramethyldisiloxane and 1,1,3,3-tetramethyl-1,3-divinyldisilazane were deposited at higher rates. The deposition rate of allyltrimethylsilane and diallyldimethylsilane, however, was not higher than the deposition rates of monomers containing allylic hydrogens. The monomers containing allylic protons, i.e. allyltrimethylsilane and diallyldimethylsilane, did not exhibit any significant plasma-induced polymerization. In this case, radical transfer to the allylic position

Table 2
Average of deposition rates of pp-films coated with 30 s of time intervals for the plasma-polymerization

Monomer	Deposition rate (μg/min)	σ (μg/min)	C.V. $\times 10^2$ (%)
Vinyltriethoxysilane	12.49	0.85	6.8
Vinyltrimethylsilane	2.44	0.59	24.4
Tetravinylsilane	33.02	4.96	15.0
Diallyldimethylsilane	2.84	0.59	20.7
Allyltrimethylsilane	3.43	1.06	30.9
1,3-Divinyltetramethyldisiloxane	12.26	0.99	8.1
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	11.48	1.50	13.1

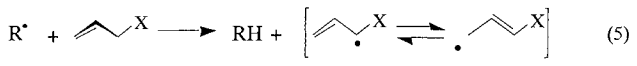
The average deposition rates of the pp-films were calculated from the slope of the seven lines (a–g) in the figures. σ and C.V. represent the standard deviation and the coefficient of variation, respectively.

Table 3
Average deposition rates of pp-films coated with 60-s time interval for the plasma polymerization

Monomer	Deposition rate (μg/min)	σ (μg/min)	C.V. $\times 10^2$ (%)
Vinyltriethoxysilane	11.14	2.39	21.4
Vinyltrimethylsilane	1.41	0.33	23.2
Tetravinylsilane	29.65	10.36	35.0
Diallyldimethylsilane	1.34	0.46	34.2
Allyltrimethylsilane	1.07	0.49	46.1
1,3-Divinyltetramethyldisiloxane	4.50	0.57	12.8
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	6.55	1.73	26.4

The average deposition rates of the pp-films were calculated from the slope of the five lines (a–e) in the figures (data not shown). σ and C.V. represent the standard deviation and the coefficient of variation, respectively.

[Eq. 5] was followed by radical–radical coupling [Eq. 6].



(5)



(6)

The reaction in Eq. 5 may be considered an 'initiation' that is promptly followed by termination [Eq. 6] without any intermediate steps of propagation. A unique feature of the plasma polymerization of 'normal' monomers is that the system may become starved of monomers. We assume that the rate of polymerization is mainly determined by the rate of initiation k_i and not by the rate of propagation [25,26]. The termination of growing chains is suppressed by the immobility of the plasma-polymerized layer, making the termination rate k_t low.

We are well aware that although the proposed reaction pathway and rate-determining steps are supported by the experimental findings, the results do not provide direct proof of these mechanisms. Additional experimental support may be obtained by in situ determination of the reactive species in the plasma and in the gas phase, as well as the volatile products formed. Precise characterization of the cross-linked film would also be a useful investigation.

Acknowledgments

This work has been supported in part by the Special Funds for 'Study of Molecular Conversion Technology for Greenhouse Gases' for the New Sunshine Project, National Institute of Advanced Industrial Science and Technology (AIST), Japan, and Japan International Cooperation Agency (JICA). One of the authors, Z.A. Talib, would like to express his gratitude to JICA for sponsoring his stay in Japan and to Universiti Putra Malaysia for granting leave of absence from his academic duties.

References

[1] S.P. Muraka, Solid-State Technol. 39 (1996) 83.
[2] C. Case, P. Kohl, W.W. Lee (Eds.), Mater. Res. Soc. Symp. Proc. 476 (1996).
[3] L.M. Han, R.B. Timmons, W.W. Lee, Y. Chen, Z. Hu, J. Appl. Phys. 84 (1998) 439.
[4] P. Laoharojanaphand, T.J. Lin, J.O. Stoffer, J. Appl. Polym. Sci. 40 (1990) 369.
[5] H. Yasuda, Plasma Polymerization, Academic, New York, 1985, Chapters 1, 2 and 6.
[6] H. Biederman, Y. Osada, Plasma Polymerization Processes, Elsevier Science, New York, 1992, Chapter 7.
[7] N. Inagaki, Plasma Surface Modification and Plasma Polymerization, Technomic Publishing Co. Inc, Lancaster, 1996, Chapters 5 and 6.
[8] H. Kobayashi, A.T. Bell, M. Shen, J. Macromol. Sci. Chem. A 10 (1976) 491.
[9] H. Yasuda, T. Hirotsu, J. Polym. Sci. Polym. Chem. 16 (1978) 229.
[10] N. Morosoff, W. Newton, H. Yasuda, J. Vac. Sci. Technol. 15 (1978) 1815.
[11] N. Inagaki, H. Yasuda, J. Appl. Polym. Sci. 26 (1981) 3557.
[12] H. Yasuda, C.R. Wang, J. Polym. Sci. Polym. Chem. 23 (1985) 87.
[13] G. Sauerbrey, Z. Phys. 155 (1959) 206.
[14] W.D. Ward, D.A. Buttry, Science 249 (1990) 1000.
[15] S. Kurosawa, E. Tawara, N. Kamo, Y. Kobatake, Anal. Chim. Acta 230 (1990) 41.
[16] S. Kurosawa, N. Kamo, T. Arimura, A. Sekiya, M. Muratsugu, Jpn. J. Appl. Phys. 34 (7B) (1995) 3925.
[17] D.B. Radloff, S. Kurosawa, K. Hirayama, T. Arimura, K. Otake, A. Sekiya, N. Minoura, M. Rapp, H.J. Ache, Mol. Cryst. Liq. Cryst. A 295 (1997) 141.
[18] S. Kurosawa, N. Kamo, T. Arimura, A. Sekiya, M. Muratsugu, Mol. Cryst. Liq. Cryst. 267 (1995) 447.
[19] S. Kurosawa, H. Aizawa, M. Yoshimoto, IEEE Trans. UFFC 47 (2000) 1256.
[20] S. Kurosawa, N. Kamo, M. Yoshimoto, J. Miyake, J. Hirayama, S. Sekiguchi, J. Photopolym. Sci. Technol. 11 (1998) 313.
[21] S. Kurosawa, K. Kobayashi, H. Aizawa, Y. Yoshimi, M. Yoshimoto, J. Photopolym. Sci. Technol. 12 (1999) 63.
[22] S. Kurosawa, T. Hirokawa, K. Kashima, H. Aizawa, D.-S. Han, Y. Yoshimi, Y. Okada, K. Yase, J. Miyake, M. Yoshimoto, J. Hilborn, Thin Solid Films 374 (2000) 262.
[23] S. Kurosawa, K. Kashima, T. Hirokawa, H. Aizawa, D.-S. Han, B. Atthoff, Y. Yoshimi, M. Yoshimoto, T. Hirotsu, J. Hilborn, J. Photopolym. Sci. Technol. 13 (2000) 33.
[24] Z.A. Talib, S. Kurosawa, B. Atthoff, H. Aizawa, K. Kashima, T. Hirokawa, Y. Yoshimi, M. Yoshimoto, T. Hirotsu, J. Miyake, J. Hilborn, J. Photopolym. Sci. Technol. 14 (2001) 129.
[25] J.M. Tibbitt, R. Jensen, A.T. Bell, M. Shen, Macromolecules 10 (1977) 647.
[26] Y. Iriyama, H. Yasuda, Polym. Mater. Sci. Eng. 62 (1990) 162.

CHEMICAL ENGINEERING COMMUNICATIONS

ISSN: 0098-6445 (Print) 1563-5201 (Online) Journal homepage: https://www.tandfonline.com/loi/gcec20

ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS

K.G. JOBACK & R.C. REID

To cite this article: K.G. JOBACK & R.C. REID (1987) ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS, CHEMICAL ENGINEERING COMMUNICATIONS, 57:1-6, 233-243, DOI: 10.1080/00986448708960487

To link to this article: https://doi.org/10.1080/00986448708960487

 Published online: 21 May 2007.

 Submit your article to this journal

 Article views: 2108

 View related articles

 Citing articles: 953 View citing articles

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=gcec20

Favored Ex. 1037

Chem. Eng. Comm. 1987, vol 57, pp. 233–243
Photocopying permitted by license only
© 1987 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS

K.G. JOBACK and R.C. REID

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

(*Received February 5, 1987*)

Simple group-contribution methods are proposed to estimate eleven important physical properties of pure materials. A common set of structural groups was employed. High accuracy is not claimed, but the proposed methods are often as accurate as or more accurate than techniques in common use today.

KEYWORDS Viscosity critical properties ideal gas group contributions estimation methods

In principle, properties of pure components are determined by the architecture of the molecules as well as, in certain instances, state variables such as temperature and pressure. For those properties which are unique (e.g., the critical temperature) or are functions of temperature only (e.g., the ideal-gas heat capacity), molecular group-contribution methods have been widely employed to estimate numerical values. Many such methods are described elsewhere [Reid *et al.*, 1987].

It was our objective to develop a family of group-contribution estimation methods using a consistent set of molecular groups that would cover a wide variety of organic compounds. The properties selected are listed in Table I.

Many different estimation equations requiring group contributions were examined, and those selected are given in Table II. Note we have assumed no interaction *between* groups, and structurally-dependent parameters (Σ) are thereby determined simply by summing the number frequency of each group times its group contribution. Clearly this is only a first-order approximation, but it is our experience that there rarely exist sufficient data to obtain reliable contributions between so-called "next-nearest neighbors." Also, introducing group interactions often leads to a significantly more complex estimation method.

We selected 41 molecular groups to allow one to treat many diverse types of organic compounds. These groups are the same as used earlier by Lydersen [1955] with the omission of >Si< and >B-, but with the inclusion of =N-(ring). Multiple linear regression techniques were employed to determine the group contributions for each structurally-dependent parameter. The contributions are shown in Table III. To obtain optimum values, in the regression procedure, we minimized the sum of the absolute errors found from the estimated and

TABLE I

Properties estimated

Property	Symbol	Units	Comments
Normal boiling point	T_b	K	$P = 1$ atm
Normal freezing point	T_f	K	
Critical temperature	T_c	K	
Critical pressure	P_c	bar	
Critical volume	V_c	cm^3/mole	
Enthalpy of formation, ideal gas at 298 K	$\Delta H^0_{f,298}$	kJ/mole	
Gibbs energy of formation, ideal gas, unit fugacity, at 298 K	$\Delta G^0_{f,298}$	kJ/mole	
Heat capacity, ideal gas	C^0_p	J/mole K	Function of T
Enthalpy of vaporization, at T_b	ΔH_{vb}	kJ/mole	
Enthalpy of fusion,	ΔH_f	kJ/mole	
Liquid viscosity	η_L	N s/m^2	Function of T

experimental property values, Y_{est} and Y_{exp}, i.e.,

$$\text{Minimize the objective function: } \sum |Y_{est} - Y_{exp}| \tag{1}$$

Minimizing the *sum-of-squares* of the errors was not done as we found this procedure weighted outliers too heavily. Thus our method will lead to slightly higher errors for such outliers, but will provide an improved estimation procedure for the majority of compounds.

TABLE II

Estimation equations[1]

$$T_b = 198.2 + \sum \tag{2}$$

$$T_f = 122.5 + \sum \tag{3}$$

$$T_c = T_b[0.584 + 0.965\sum - (\sum)^2]^{-1} \tag{4}$$

$$P_c = (0.113 + 0.0032n_A - \sum)^{-2} \tag{5}$$

$$V_c = 17.5 + \sum \tag{6}$$

$$\Delta H^0_{f,298} = 68.29 + \sum \tag{7}$$

$$\Delta G^0_{f,298} = 53.88 + \sum \tag{8}$$

$$C^0_p = \sum (a) - 37.93 + [\sum (b) + 0.210]T + [\sum (c) - 3.91 \times 10^{-4}]T^2 + [\sum (d) + 2.06 \times 10^{-7}]T^3 \tag{9}$$

$$\Delta H_{vb} = 15.30 + \sum \tag{10}$$

$$\Delta H_f = -0.88 + \sum \tag{11}$$

$$\eta_L = MW \times \exp\{[\sum (\eta_A) - 597.82]/T + \sum (\eta_B) - 11.202\} \tag{12}$$

[1] The notation $\sum$ signifies that, for the particular property of interest, one sums the product of the number of times a group appears in the compound and the group contributions in Table III. In cases where the property is a function of temperature, different $\sum(\ )$ terms are required.

TABLE III

Group contributions

	T_c	P_c	V_c
Non-ring increments			
—CH3	0.0141	−0.0012	65
—CH2—	0.0189	0	56
>CH—	0.0164	0.0020	41
>C<	0.0067	0.0043	27
=CH2	0.0113	−0.0028	56
=CH—	0.0129	−0.0006	46
=C<	0.0117	0.0011	38
═C═	0.0026	0.0028	36
≡CH	0.0027	−0.0008	46
≡C—	0.0020	0.0016	37
Ring increments			
—CH2—	0.0100	0.0025	48
>CH—	0.0122	0.0004	38
>C<	0.0042	0.0061	27
=CH—	0.0082	0.0011	41
=C<	0.0143	0.0008	32
Halogen increments			
—F	0.0111	−0.0057	27
—Cl	0.0105	−0.0049	58
—Br	0.0133	0.0057	71
—I	0.0068	−0.0034	97
Oxygen increments			
—OH (alcohol)	0.0741	0.0112	28
—OH (phenol)	0.0240	0.0184	−25
—O— (nonring)	0.0168	0.0015	18
—O— (ring)	0.0098	0.0048	13
>C═O (nonring)	0.0380	0.0031	62
>C═O (ring)	0.0284	0.0028	55
O═CH— (aldehyde)	0.0379	0.0030	82
—COOH (acid)	0.0791	0.0077	89
—COO— (ester)	0.0481	0.0005	82
═O (except as above)	0.0143	0.0101	36
Nitrogen increments			
—NH2	0.0243	0.0109	38
>NH (nonring)	0.0295	0.0077	35
>NH (ring)	0.0130	0.0114	29
>N— (nonring)	0.0169	0.0074	9
—N═ (nonring)	0.0255	−0.0099	—
—N═ (ring)	0.0085	0·0076	34
═NH	—	—	—
—CN	0.0496	−0.0101	91
—NO2	0.0437	0.0064	91
Sulfur increments			
—SH	0.0031	0.0084	63
—S— (nonring)	0.0119	0.0049	54
—S— (ring)	0.0019	0.0051	38

	T_b	T_f	$\Delta H^0_{f,298}$	$\Delta G^0_{f,298}$
Non-ring increments				
—CH3	23.58	−5.10	−76.45	−43.96
—CH2—	22.88	11.27	−20.64	8.42
>CH—	21.74	12.64	29.89	58.36

TABLE III (*contd.*)

	T_b	T_f	$\Delta H^0_{f,298}$	$\Delta G^0_{f,298}$
Non-ring increments (*contd.*)				
>C<	18.25	46.43	82.23	116.02
=CH2	18.18	−4.32	−9.63	3.77
=CH—	24.96	8.73	37.97	48.53
=C<	24.14	11.14	83.99	92.36
=C=	26.15	17.78	142.14	136.70
≡CH	9.20	−11.18	79.30	77.71
≡C—	27.38	64.32	115.51	109.82
Ring increments				
—CH2—	27.15	7.75	−26.80	−3.68
>CH—	21.78	19.88	8.67	40.99
>C<	21.32	60.15	79.72	87.88
=CH—	26.73	8.13	2.09	11.30
=C<	31.01	37.02	46.43	54.05
Halogen increments				
—F	−0.03	−15.78	−251.92	−247.19
—Cl	38.13	13.55	−71.55	−64.31
—Br	66.86	43.43	−29.48	−38.06
—I	93.84	41.69	21.06	5.74
Oxygen increments				
—OH (alcohol)	92.88	44.45	−208.04	−189.20
—OH (phenol)	76.34	82.83	−221.65	−197.37
—O— (nonring)	22.42	22.23	−132.22	−105.00
—O— (ring)	31.22	23.05	−138.16	−98.22
>C=O (nonring)	76.75	61.20	−133.22	−120.50
>C=O (ring)	94.97	75.97	−164.50	−126.27
O=CH— (aldehyde)	72.24	36.90	−162.03	−143.48
—COOH (acid)	169.09	155.50	−426.72	−387.87
—COO— (ester)	81.10	53.60	−337.92	−301.95
=O (except as above)	−10.50	2.08	−247.61	−250.83
Nitrogen increments				
—NH2	73.23	66.89	−22.02	14.07
>NH (nonring)	50.17	52.66	53.47	89.39
>NH (ring)	52.82	101.51	31.65	75.61
>N— (nonring)	11.74	48.84	123.34	163.16
—N= (nonring)	74.60	—	23.61	—
—N= (ring)	57.55	68.40	55.52	79.93
=NH	83.08	68.91	93.70	119.66
—CN	125.66	59.89	88.43	89.22
—NO2	152.54	127.24	−66.57	−16.83
Sulfur increments				
—SH	63.56	20.09	−17.33	−22.99
—S— (nonring)	68.78	34.40	41.87	33.12
—S— (ring)	52.10	79.93	39.10	27.76

	Ideal gas heat capacity			
	(a)	(b)	(c)	(d)
Non-ring increments				
—CH3	1.95E + 1	−8.08E − 3	1.53E − 4	−9.67E − 8
—CH2—	−9.09E − 1	9.50E − 2	−5.44E − 5	1.19E − 8
>CH—	−2.30E + 1	2.04E − 1	−2.65E − 4	1.20E − 7
>C<	−6.62E + 1	4.27E − 1	−6.41E − 4	3.01E − 7
=CH2	2.36E + 1	−3.81E − 2	1.72E − 4	−1.03E − 7
=CH—	−8.00	1.05E − 1	−9.63E − 5	3.56E − 8
=C<	−2.81E + 1	2.08E − 1	−3.06E − 4	1.46E − 7
=C=	2.74E + 1	−5.57E − 2	1.01E − 4	−5.02E − 8

TABLE III (*contd.*)

	Ideal gas heat capacity (a)	(b)	(c)	(d)
Non-ring increments (*contd.*)				
≡CH	2.45E + 1	−2.71E − 2	1.11E − 4	−6.78E − 8
≡C—	7.87	2.01E − 2	−8.33E − 6	1.39E − 9
Ring increments				
—CH2—	−6.03	8.54E − 2	−8.00E − 6	−1.80E − 8
>CH—	−2.05E + 1	1.62E − 1	−1.60E − 4	6.24E − 8
>C<	−9.09E + 1	5.57E − 1	−9.00E − 4	4.69E − 7
=CH—	−2.14	5.74E − 2	−1.64E − 6	−1.59E − 8
=C<	−8.25	1.01E − 1	−1.42E − 4	6.78E − 8
Halogen increments				
—F	2.65E + 1	−9.13E − 2	1.91E − 4	−1.03E − 7
—Cl	3.33E + 1	−9.63E − 2	1.87E − 4	−9.96E − 8
—Br	2.86E + 1	−6.49E − 2	1.36E − 4	−7.45E − 8
—I	3.21E + 1	−6.41E − 2	1.26E − 4	−6.87E − 8
Oxygen increments				
—OH (alcohol)	2.57E + 1	−6.91E − 2	1.77E − 4	−9.88E − 8
—OH (phenol)	−2.81	1.11E − 1	−1.16E − 4	4.94E − 8
—O— (nonring)	2.55E + 1	−6.32E − 2	1.11E − 4	−5.48E − 8
—O— (ring)	1.22E + 1	−1.26E − 2	6.03E − 5	−3.86E − 8
>C=O (nonring)	6.45	6.70E − 2	−3.57E − 5	2.86E − 9
>C=O (ring)	3.04E + 1	−8.29E − 2	2.36E − 4	−1.31E − 7
O=CH— (aldehyde)	3.09E + 1	−3.36E − 2	1.60E − 4	−9.88E − 8
—COOH (acid)	2.41E + 1	4.27E − 2	8.04E − 5	−6.87E − 8
—COO— (ester)	2.45E + 1	4.02E − 2	4.02E − 5	−4.52E − 8
=O (except as above)	6.82	1.96E − 2	1.27E − 5	−1.78E − 8
Nitrogen increments				
—NH2	2.69E + 1	−4.12E − 2	1.64E − 4	−9.76E − 8
>NH (nonring)	−1.21	7.62E − 2	−4.86E − 5	1.05E − 8
>NH (ring)	1.18E + 1	−2.30E − 2	1.07E − 4	−6.28E − 8
>N— (nonring)	−3.11E + 1	2.27E − 1	−3.20E − 4	1.46E − 7
—N= (nonring)	—	—	—	—
—N= (ring)	8.83	−3.84E − 3	4.35E − 5	−2.60E − 8
=NH	5.69	−4.12E − 3	1.28E − 4	−8.88E − 8
—CN	3.65E + 1	−7.33E − 2	1.84E − 4	−1.03E − 7
—NO2	2.59E + 1	−3.74E − 3	1.29E − 4	−8.88E − 8
Sulfur increments				
—SH	3.53E + 1	−7.58E − 2	1.85E − 4	−1.03E − 7
—S— (nonring)	1.96E + 1	−5.61E − 3	4.02E − 5	−2.76E − 8
—S— (ring)	1.67E + 1	4.81E − 3	2.77E − 5	−2.11E − 8

	ΔH_{vb}	ΔH_f	Liquid viscosity (η_A)	(η_B)
Non-ring increments				
—CH3	2.373	0.908	548.29	−1.719
—CH2—	2.226	2.590	94.16	−0.199
>CH—	1.691	0.749	−322.15	1.187
>C<	0.636	−1.460	−573.56	2.307
=CH2	1.724	−0.473	495.01	−1.539
=CH—	2.205	2.691	82.28	−0.242
=C<	2.138	3.063	—	—
=C=	2.661	4.720	—	—
≡CH	1.155	2.322	—	—
≡C—	3.302	4.151	—	—
Ring increments				
—CH2—	2.398	0.490	307.53	−0.798

TABLE III (*contd.*)

	ΔH_{vb}	ΔH_f	Liquid viscosity (η_A)	(η_B)
Ring increments (*contd.*)				
>CH—	1.942	3.243	−394.29	1.251
>C<	0.644	−1.373	—	—
=CH—	2.544	1.101	259.65	−0.702
=C<	3.059	2.394	−245.74	0.912
Halogen increments				
—F	−0.670	1.398	—	—
—Cl	4.532	2.515	625.45	−1.814
—Br	6.582	3.603	738.91	−2.038
—I	9.520	2.724	809.55	−2.224
Oxygen increments				
—OH (alcohol)	16.826	2.406	2173.72	−5.057
—OH (phenol)	12.499	4.490	3018.17	−7.314
—O— (nonring)	2.410	1.188	122.09	−0.386
—O— (ring)	4.682	5.879	440.24	−0.953
>C=O (nonring)	8.972	4.189	340.35	−0.350
>C=O (ring)	6.645	—	—	—
O=CH— (aldehyde)	9.093	3.197	740.92	−1.713
—COOH (acid)	19.537	11.051	1317.23	−2.578
—COO— (ester)	9.633	6.959	483.88	−0.966
=O (except as above)	5.909	3.624	675.24	−1.340
Nitrogen increments				
—NH2	10.788	3.515	—	—
>NH (nonring)	6.436	5.009	—	—
>NH (ring)	6.930	7.490	—	—
>H— (nonring)	1.896	4.703	—	—
—N= (nonring)	3.335	—	—	—
—N= (ring)	6.528	3.649	—	—
=NH	12.169	—	—	—
—CN	12.851	2.414	—	—
—NO2	16.738	9.679	—	—
Sulfur increments				
—SH	6.884	2.360	—	—
—S— (nonring)	6.817	4.130	—	—
—S— (ring)	5.984	1.557	—	—

Two properties treated are functions of temperature, i.e., the ideal-gas heat capacity and the liquid viscosity. For the former, the temperature range is from 273 to about 1000 K while, for the latter, from a value of T_f to a reduced temperature of about 0.7.

It should be noted in Table II the *total* number of atoms, n_A, appears in the equation for critical pressure, and the compound molecular weight, MW, in the liquid viscosity formulation. Also, in the estimation of T_c, it is preferable to employ an experimental value of T_b, but, if this is not available, it may be approximated separately.

The data used in the development of all the methods were obtained from the literature. Critical property values, T_c, P_c, and V_c, were obtained from Ambrose [1978, 1979] and Reid *et al.* [1987]. Values for the thermodynamic properties, $\Delta H^0_{f,298}$, $\Delta G^0_{f,298}$, and C^0_p were obtained from Reid *et al.* and Stull *et al.* [1969]. Values for T_b, T_f, ΔH_{vb}, and ΔH_f were obtained from Reid *et al.* and Stull *et al.*

TABLE IV

Summations of group contributions for use in the example

Property	—Cl		=CH— (ring)		=C< (ring)		Σ
	No. of groups	Group value	No. of groups	Group value	No. of groups	Group value	
T_b	2	38.13	4	26.73	2	31.01	245.20
T_f	2	13.55	4	8.13	2	37.02	133.66
T_c	2	0.0105	4	0.0082	2	0.0143	0.0824
P_c	2	−0.0049	4	0.0011	2	0.0008	−0.0038
V_c	2	58	4	41	2	32	344
$\Delta H^0_{f,298}$	2	−71.55	4	2.09	2	46.43	−41.88
$\Delta G^0_{f,298}$	2	−64.31	4	11.30	2	54.05	24.68
C^0_p, Σ (a)	2	33.3	4	−2.14	2	−8.25	41.54
Σ (b)	2	-9.63×10^{-2}	4	5.74×10^{-2}	2	1.01×10^{-1}	0.239
Σ (c)	2	1.874×10^{-4}	4	-1.64×10^{-6}	2	-1.42×10^{-4}	8.42×10^{-5}
Σ (d)	2	-9.96×10^{-8}	4	-1.59×10^{-8}	2	6.78×10^{-8}	-1.27×10^{-7}
ΔH_{vb}	2	4.532	4	2.544	2	3.059	25.36
ΔH_f	2	2.515	4	1.101	2	2.394	14.22
η_L, Σ (η_A)	2	625.45	4	259.65	2	−245.74	1798.0
Σ (η_B)	2	−1.814	4	−0.702	2	0.912	−4.612

TABLE V

Results from the example calculations

Compound: *p*-dichlorobenzene

Summation of group contributions from Table IV

Property	Eq. used	Estimated value	Experimental value
T_b	(2)	443.4 K	447.3 K
T_f	(3)	256 K	326 K
T_c	(4)[1]	681 K	685 K
P_c	(5)[2]	41.5 bar	39.0 bar
V_c	(6)	362 cm³/mole	372 cm³/mole
$\Delta H^0_{f,298}$	(7)	26.41 kJ/mole	23.01 kJ/mole
$\Delta G^0_{f,298}$	(8)	78.56 kJ/mole	77.15 kJ/mole
C^0_p(298)	(9)	112.3 J/mole K	113.9 J/mole K
(400)		139.2 J/mole K	143.3 J/mole K
(800)		206.8 J/mole K	210.7 J/mole K
(1000)		224.6 J/mole K	228.0 J/mole K
ΔH_{vb}	(10)	40.66 kJ/mole	38.79 kJ/mole
ΔH_f	(11)	13.3 kJ/mole	18.16 kJ/mole
η_L(333.8)	(12)[3]	7.26×10^{-4} N s/m²	7.22×10^{-4} N s/m²
(374.4)		4.92×10^{-4} N s/m²	4.95×10^{-4} N s/m²
(403.1)		3.91×10^{-4} N s/m²	3.98×10^{-4} N s/m²
(423.3)		3.40×10^{-4} N s/m²	3.48×10^{-4} N s/m²

[1] The experimental value of T_b (447 K) was employed in Eq. (4). If T_b had itself been estimated, a value of 443 K would have been obtained leading to a value for T_c of 675 K. In this case, the results are not too different. In other situations, large errors were found when using the estimated value of T_b.

[2] $n_A = 12$

[3] $MW = 147.0$ g/mole

TABLE VI

Statistical summary of regression testing

Property	No. of compounds used	Average absolute error	Standard deviation	Average per cent error
T_b	438	12.9 K	17.9 K	3.6
T_f	388	22.6 K	24.7 K	11.2
T_c	409	4.8 K	6.9 K	0.8
P_c	392	2.1 bar	3.2 bar	5.2
V_c	310	7.5 cm^3/mole	13.2 cm^3/mole	2.3
$\Delta H^0_{f,298}$	378	8.4 kJ/mole	18.0 kJ/mole	—
$\Delta G^0_{f,298}$	328	8.4 kJ/mole	18.3 kJ/mole	—
ΔH_{vb}	368	1.27 kJ/mole	1.79 kJ/mole	3.9
ΔH_f	155	2.0 kJ/mole	2.8 kJ/mole	39.

Values for η_L as a function of temperature were obtained from Orrick [1973] and Friend and Hargreaves [1945].

EXAMPLES AND DISCUSSION

To illustrate our proposed technique, we have estimated the values of each of the eleven properties in Table I using *p*-dichlorobenzene as an example substance. In Table IV, we show the group contribution summations for each property using the group values from Table III. In Table V, we summarize the results and compare them with experimental values.

In Table VI, we show an overall statistical summary of our regression results; a more detailed breakdown is given elsewhere [Joback, 1984].

Estimations of the normal boiling point and, in particular, the normal freezing point are not accurate and should be considered as only very approximate. There is a strong dependence of the actual conformation of the molecule on T_f as shown, for example, in the large difference found for T_f between, say, cis- and trans-isomers. To illustrate, the difference in T_f between cis- and trans-1,2-

TABLE VII

Comparison of critical property estimation techniques

	Lydersen [1955]		Ambrose [1978, 1979]		Klincewicz [1984]		Proposed	
	AAE[1]	AAPE[2]	AAE	AAPE	AAE	AAPE	AAE	AAPE
T_c	8.1	1.4	4.3	0.7	7.5	1.3	4.8	0.8
P_c	3.3	8.9	1.8	4.6	3.0	7.8	2.1	5.2
V_c	10.0	3.1	8.5	2.8	8.9	2.9	7.5	2.3

[1] AAE = average absolute error.
[2] AAPE = average absolute percent error.
Average absolute errors have units of kelvins for T_c, bars for P_c, and cm^3/mole for V_c.

TABLE VIII

Comparison of enthalpy of formation estimation techniques

	Average absolute error, kJ/mole	Standard deviation kJ/mole
Benson *et al.* [1969]	4.6	5.4
Verma-Doraiswamy [1965]	10.5	13.4
Andersen, Beyer, and Watson [1944]	9.2	10.5
Franklin [1949]	18.8	27.2
Proposed	9.2	9.2

dimethylcyclopentane is about 64 K. Since our procedure does not differentiate between cis- and trans-isomers, the regression yields some medium value.

For the critical constants, other group-contribution methods have been proposed, [Lydersen, 1955; Ambrose, 1978, 1979; Klincewicz, 1982]. In Table VII we show a limited comparison between the results of the proposed method and those currently in use. The statistics for the earlier methods were obtained from Klincewicz [1982]. It is seen that the Ambrose method is somewhat more accurate than the proposed method for T_c and P_c, but it is also more complex and less readily implemented in computer-based estimation programs. For V_c, the proposed method yielded the least error.

For the standard enthalpy of formation at 298 K, the proposed method was compared to other group-contribution techniques now in use, and the results are shown in Table VIII. In this comparison, a sample of 29 compounds was used. The proposed method showed an average absolute error which is somewhat larger than Benson *et al.*'s [1969] method and about equal to that from the Verma-Doraiswamy [1965] technique. However, with Benson *et al.*'s method containing over 250 groups and 25 corrections for rings and next-nearest neighbors, we feel that a major advantage of our proposed method lies in its simplicity and accuracy only slightly less than significantly more complicated methods.

There are few other group-contribution methods to estimate the standard Gibbs energy of formation at 298 K. When we compared our procedure to that of van Krevelen and Chermin [1951, 1952] using a sample of 43 compounds, the

TABLE IX

Comparison of heat capacity estimation techniques

	Average absolute error, J/mole K	Standard deviation J/mole K
Benson *et al.* [1969]	4.6	6.7
Rihani-Doraiswamy [1965]	13.4	19.2
Thinh *et al.* [1976]	4.6	6.7
Proposed	5.9	8.4

TABLE X

Comparison of viscosity estimation techniques

	Average absolute percent error	Standard deviation
Thomas [1946]	20	24
Orrick [1973]	16	14
van Velzen *et al.* [1972]	15	23
Morris [1964]	15	15
Proposed	18	20

proposed technique yielded an average absolute error of 4.6 kJ/mole and a standard deviation of 6.7 kJ/mole. The van Krevelen and Chermin method gave an absolute average error of 13.0 kJ/mole and a standard deviation of 17.2 kJ/mole. The proposed method does not require a separate correction for symmetry number or for multiple optical isomers. While the accuracy of the proposed method is reasonable, the use of it to calculate chemical equilibrium constants may lead to large errors due to the exponentiation required to determine K.

For the ideal-gas heat capacity, we present a comparison between the proposed method and those of Benson *et al.* [1969], Rihani-Doraiswamy [1965], and Thinh *et al.* [1976] in Table IX. A sample of 28 compounds was employed and C_p^0 values at 298 and 800 K were used. The methods of Benson *et al.* and Thinh *et al.* both yielded lower errors than the proposed method, however, Benson's technique provides values of the heat capacity only at discreet temperatures while the Thinh *et al.* procedure is applicable only to hydrocarbons.

There are no group-contribution methods for the enthalpy of vaporization at the normal boiling point or for the enthalpy of fusion with which to compare the proposed method. Clearly, as shown in Table VI, the accuracy in estimating ΔH_f is poor; again, as with T_f, the value is sensitive to the exact conformation of the molecule. For ΔH_{vb}, errors are not particularly large, but if reliable values of T_b, T_c, and P_c are available, it is more accurate to estimate ΔH_{vb} from corresponding-states correlations [Reid *et al.*, 1987].

For the liquid viscosity we present a comparison between the proposed method and those of Thomas [1946], Orrick [1973], van Velzen *et al.* [1972], and Morris [1964] in Table X. A sample of 36 compounds was employed and η_L values at 3 to 5 temperatures were used. All methods yielded large errors.

REFERENCES

Ambrose, D., "Correlation and Estimation of Vapor–Liquid Critical Properties: I. Critical Temperatures of Organic Compounds," National Physical Laboratory, Teddington, NPL Rep. Chem. **92**, 1978, corrected 1980.

Ambrose, D., "Correlation and Estimation of Vapor–Liquid Critical Properties: II. Critical Pressures and Volumes of Organic Compounds," National Physical Laboratory, Teddington, NPL Rep. **98**, 1979.

Andersen, J.W., Beyer, G.H., and Watson, K.M., "Thermodynamic Properties of Organic Compounds. Estimation from Group Contributions," *Natl. Pet. News, Tech. Sec.* **36**: R476 (July 5, 1944).

Benson, S.W., Cruickshank, F.R., Golden, D.M., Haugen, G.R., O'Neal, H.E., Rogers, A.S., Shaw, R., and Walsh, R., "Additivity Rules for the Estimation of Thermochemical Properties," *Chem. Rev.* **69**, 279 (1969).

Franklin, J.L., "Prediction of Heat and Free Energies of Organic Compounds," *Ind. Eng. Chem.* **41**, 1070 (1949).

Friend, J.N., and Hargreaves, W.D., "Viscosity and the Hydrogen Bond—Hydroxyl and Ortho Effects," *Phil. Mag.* **36**, 731 (1945).

Joback, K.G., "A Unified Approach to Physical Property Estimation Using Multivariate Statistical Techniques," S.M. Thesis, Chem. Eng., Mass. Inst. of Tech., Cambridge, MA, 1984.

Klincewicz, K.M., "Prediction of Critical Temperatures, Pressures, and Volumes of Organic Compounds from Molecular Structure," S.M. Thesis, Chem. Eng., Mass. Inst. of Tech., Cambridge, MA, 1982; *AIChE J.* **30**, 137 (1984).

Lydersen, A.L., "Estimation of Critical Properties of Organic Compounds," Univ. Coll. Exp. Stn., Rept., Madison, WI, April, 1955.

Morris, P.S., "Estimation of Liquid Viscosity from Structure," M.S. Thesis, Department of Chemical Engineering, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., 1964.

Orrick, C., "Estimation of Viscosity for Organic Compounds," M.S. Thesis, Department of Chemical Engineering, Oklahoma State University, Stillwater, OK, 1973; Private communication, J.H. Erbar, 1975.

Reid, R.C., Prausnitz, J.M., and Poling, B.E., *The Properties of Gases and Liquids*, McGraw-Hill Book Co., New York, 4th ed., 1987.

Rihani, D.N., and Doraiswamy, L.K., "Estimation of Heat Capacity of Organic Compounds from Group Contributions," *Ind. Eng. Chem. Fundam.* **4**, 17 (1965).

Stull, D.R., Westrum, E.F., and Sinke, G.C., *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons Inc., New York (1969).

Thinh, T.-P., and Trong, T.K., "Estimation of Standard Heats of Formation ΔH_{fT}^*, Standard Entropies of Formation ΔS_{fT}^*, Standard Free Energies of Formation ΔF_{fT}^* and Absolute Entropies S_T^* of Hydrocarbons from Group Contributions: An Accurate Approach," *Can. J. Chem. Eng.* **54**, 344 (1976).

Thomas, L.H., "The Dependence of the Viscosities of Liquids on Reduced Temperature, and a Relation between Viscosity, Density, and Chemical Constitution," *J. Chem. Soc.*, 573, (1946).

van Krevelen, S.W., and Chermin, H.A.G., "Estimation of the Free Enthalpy (Gibbs Free Energy) of Formation of Organic Compounds from Group Contributions," *Chem. Eng. Sci.* **1**, 66 (1951).

van Krevelen, S.W., and Chermin, H.A.G., "Erratum: Estimation of the Free Enthalpy (Gibbs Free Energy) of Formation of Organic Compounds from Group Contributions," *ibid.*, **1**, 238 (1952).

van Velzen, D., Cardozo, R.L., and Langenkamp, H., "A Liquid Viscosity-Temperature-Chemical Constitution Relation for Organic Compounds," *Ind. Eng. Chem. Fundam.* **11**, 20 (1972).

Verma, K.K., and Doraiswamy, L.K., "Estimation of Heats of Formation of Organic Compounds," *Ind. Eng. Chem. Fundam.* **4**, 389 (1965).

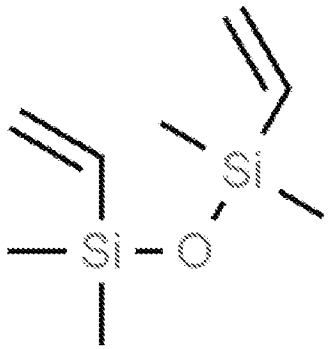
ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organization or local healthcare provider.

Simple Structure Advanced History

Found 1 result

Search term: **2627-95-4** (Found by approved synonym)



3D

JM9235250

Molecular Formula
$C_8H_{18}OSi_2$

Average mass
186.399 Da

Monoisotopic mass
186.089615 Da

More details:

Names Properties More

Experimental data Predicted - ACD/Labs Predicted - EPISuite Predicted - ChemAxon Predicted - Mobile

Experimental Physico-chemical Properties

Experimental Melting Point:

Experimental Boiling Point:

139-140 °C **Alfa Aesar**
139-140 °C **Alfa Aesar** A12463
139 °C **SynQuest** 52916.

Favored Ex. 1039

139 °C **Biosynth** J-503710

139 °C **LabNetwork** LN00239149

139 °C **SynQuest** 52916, 6390-1-01

139 °C **Sigma-Aldrich** ALDRICH-371904

139-140 °C **Strem** 93-1457

Experimental LogP:

Experimental Flash Point:

Experimental Refraction Index:

Experimental Density:

Miscellaneous

Safety:

Gas Chromatography

Retention Index (Kovats):

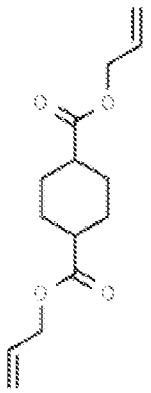
Retention Index (Linear):

ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organisation or local healthcare provision.

Found 1 result

Search term: **20306-22-3** (Found by synonym)



3D

Diallyl 1,4-cyclohexanedicarboxylate

Molecular Formula

$C_{14}H_{20}O_4$

Average mass

252.306 Da

Monoisotopic mass

252.136154 Da

More details:

Names Properties More

Predicted - ACD/Labs Predicted - EPISuite Predicted - ChemAxon

Predicted data is generated using the ACD/Labs Percepta Platform - PhysChem Module

Density:	1.1±0.1 g/cm^3
Boiling Point:	330.6±27.0 °C at 760 mmHg

Enthalpy of Vaporization:	57.3±3.0 kJ/mol
Flash Point:	156.9±22.1 °C
Index of Refraction:	1.480
Molar Refractivity:	67.6±0.3 cm^3
#H bond acceptors:	4
#H bond donors:	0
#Freely Rotating Bonds:	8
#Rule of 5 Violations:	0
ACD/LogP:	3.06
ACD/LogD (pH 5.5):	3.18
ACD/BCF (pH 5.5):	153.74
ACD/KOC (pH 5.5):	1279.10
ACD/LogD (pH 7.4):	3.18
ACD/BCF (pH 7.4):	153.74
ACD/KOC (pH 7.4):	1279.10
Polar Surface Area:	53 $Å^2$
Polarizability:	26.8±0.5 $10^{-24}cm^3$
Surface Tension:	36.9±3.0 dyne/cm
Molar Volume:	237.9±3.0 cm^3

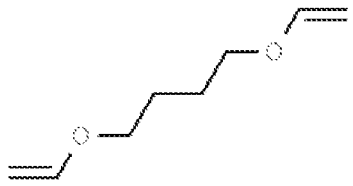
ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organization or local healthcare provider.

Simple Structure Advanced History

Found 1 result

Search term: **3891-33-6** (Found by approved synonym)



30

MFCD00026065

Molecular Formula

$C_8H_{14}O_2$

Average mass

142.196 Da

Monoisotopic mass

142.099380 Da

More details:

Names Properties More

Experimental data Predicted - ACD/Labs Predicted - EPISuite Predicted - ChemAxon Predicted - Mobile

Experimental Physico-chemical Properties

Experimental Melting Point:

Experimental Boiling Point:

62-64 °C **Parchem – fine & specialty chemicals** 71711

62-64 °C / 10 mmHg (199.4595-202.204 °C / 760 mmHg) **Sigma-Aldrich** ALDRICH-123315

Experimental LogP:

Experimental Refraction Index:

Experimental Density

Gas Chromatography

Retention Index (Kovats):

ChemSpider

Home
About us
Membership & professional community
Campaigning & outreach
Journals, books & databases
Teaching & learning
News & events
Locations & contacts
Careers
Awards & funding
Advertise
Help & legal
Privacy policy
Terms & conditions

© Royal Society of Chemistry 2020
Registered charity number: 207890

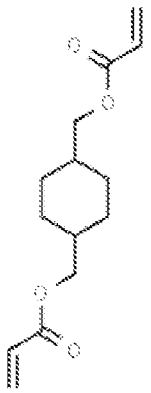
ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organisation or local healthcare provision.

Simple Structure Advanced History

Found 1 result

Search term: **67905-41-3** (Found by synonym)



3D

Cyclohexane-1,4-dimethanol, diacrylate

Molecular Formula
$C_{14}H_{20}O_4$

Average mass
252.306 Da

Monoisotopic mass
252.136154 Da

More details:

Names Properties More

Predicted - ACD/Labs Predicted - EPISuite Predicted - ChemAxon Predicted - Movia

Predicted data is generated using the ACD/Labs Percepta Platform - PhysChem Module

Density:	1.0±0.1 g/cm^3
Boiling Point:	332.7±15.0 °C at 760 mmHg

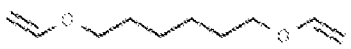
Enthalpy of Vaporization:	57.6±3.0 kJ/mol
Flash Point:	158.3±18.8 °C
Index of Refraction:	1.466
Molar Refractivity:	67.9±0.3 cm^3
#H bond acceptors:	4
#H bond donors:	0
#Freely Rotating Bonds:	8
#Rule of 5 Violations:	0
ACD/LogP:	3.38
ACD/LogD (pH 5.5):	3.43
ACD/BCF (pH 5.5):	237.31
ACD/KOC (pH 5.5):	1745.23
ACD/LogD (pH 7.4):	3.43
ACD/BCF (pH 7.4):	237.31
ACD/KOC (pH 7.4):	1745.23
Polar Surface Area:	53 $Å^2$
Polarizability:	26.9±0.5 $10^{-24} cm^3$
Surface Tension:	34.9±3.0 dyne/cm
Molar Volume:	244.8±3.0 cm^3

ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organization or local healthcare provision.

Simple Structure Advanced History

Found 2 results
Search term: **19763-13-4** (Found by synonym)



3D

1,6-Bis(vinyloxy)hexane

Molecular Formula
$C_{10}H_{18}O_2$

Average mass
170.249 Da

Monoisotopic mass
170.130676 Da

More details:

Names Properties More

Predicted - ACD/Labs Predicted - EPISuite Predicted - ChemAxon

Predicted data is generated using the ACD/Labs Percepta Platform - PhysChem Module

Density:	0.9±0.1 g/cm^3
Boiling Point:	233.6±23.0 °C at 760 mmHg
Vapour Pressure:	0.1±0.4 mmHg at 25°C
Enthalpy of Vaporization:	45.1±3.0 kJ/mol
Flash Point:	77.8±22.1 °C
Index of Refraction:	1.435

#H bond acceptors:	2
#H bond donors:	0
#Freely Rotating Bonds:	9
#Rule of 5 Violations:	0
ACD/LogP:	2.39
ACD/LogD (pH 5.5):	2.35
ACD/BCF (pH 5.5):	35.81
ACD/KOC (pH 5.5):	450.83
ACD/LogD (pH 7.4):	2.35
ACD/BCF (pH 7.4):	35.81
ACD/KOC (pH 7.4):	450.83
Polar Surface Area:	18 $Å^2$
Polarizability:	20.3±0.5 $10^{-24}cm^3$
Surface Tension:	26.9±3.0 dyne/cm
Molar Volume:	196.5±3.0 cm^3

ChemSpider

Home
About us
Membership & professional community
Campaigning & outreach
Journals, books & databases
Teaching & learning
News & events
Locations & contacts
Careers
Awards & funding
Advertise
Help & legal
Privacy policy
Terms & conditions

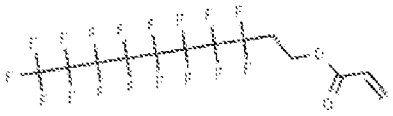
ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organisation or local healthcare provision.

Simple Structure Advanced History

Found 1 result

Search term: **27905-45-9** (Found by approved synonym)



3D

perfluorooctylethyl acrylate

Molecular Formula

$C_{13}H_7F_{17}O_2$

Average mass

518.166 Da

Monoisotopic mass

518.017456 Da

More details:

Names Properties More

Experimental data Predicted - ACDLabs Predicted - ChemAxon Predicted - Mpuls

Experimental Physico-chemical Properties

Experimental Melting Point:

89-90 deg C / 4 mm (266.723-268.1691 °C / 760 mmHg) **Alfa Aesar**

89-90 deg C / 4 mmHg (266.723-268.1691 °C / 760 mmHg) **Manchester Organics** E16773

90 ° / 4 mm (268.1691 °C / 760 mmHg) **Matrix Scientific**

89-90 °C / 4 mm (266.723-268.1691 °C / 760 mmHg) **Alfa Aesar** L11993

90 °C / 4 mm (268.1691 °C / 760 mmHg) **Matrix Scientific** 002217

90 °C / 4 mmHg (268.1691 °C / 760 mmHg) **SynQuest** 51978.

90 °C / 4 mm (268.1691 °C / 760 mmHg) **Oakwood** [019155]

90 °C / 4 mm (268.1691 °C / 760 mmHg) **LabNetwork** LN00115175

90 °C / 4 mmHg (268.1691 °C / 760 mmHg) **SynQuest** 51978, 2324-3-41

90 °C / 4 mmHg (268.1691 °C / 760 mmHg) **Sigma-Aldrich** ALDRICH-474487

Experimental Optical Rotation:

Experimental LogP:

Experimental Flash Point:

Experimental Refraction Index:

Experimental Density:

Miscellaneous

Safety:

Gas Chromatography

Retention Index (Kovats):

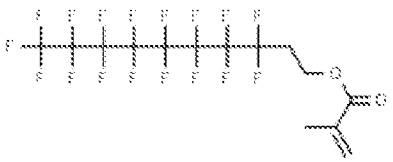
ChemSpider
Search and share chemistry

For medical information relating to Covid-19, please consult the World Health Organisation or local healthcare provision.

Simple Structure Advanced History

Found 1 result

Search term: **1996-88-9** (Found by approved synonym)



3D

HDFDMA

Molecular Formula

$C_{14}H_9F_{17}O_2$

Average mass

532.193 Da

Monoisotopic mass

532.033081 Da

More details:

Names Properties More

Experimental data Predicted - ACDLabs Predicted - ChemAxon Predicted - Mpuls

Experimental Physico-chemical Properties

Experimental Boiling Point:

120 °C / 4 mm (311.5088 °C / 760 mmHg) **Matrix Scientific** 002216

110 °C / 4 mmHg (297.0718 °C / 760 mmHg) **SynQuest** 18970,

120 °C / 4 mm (311.5088 °C / 760 mmHg) **Oakwood** [006503]

120 °C / 4 mm (311.5088 °C / 760 mmHg) **LabNetwork** LN00009720

110 °C / 4 mmHg (297.0718 °C / 760 mmHg) **SynQuest** 18970, 2324-3-42

110 °C / 4 mmHg (297.0718 °C / 760 mmHg) **Sigma-Aldrich** ALDRICH-474223

Experimental Optical Rotation:

Experimental LogP:

Experimental Flash Point:

Experimental Refraction Index:

Experimental Density:

Miscellaneous

Safety:

Home
About us
Membership & professional community
Campaigning & outreach
Journals, books & databases
Teaching & learning
News & events
Locations & contacts
Careers

Rachel Hradecky
Perkins Coie LLP
Librarian
131 S Dearborn, Suite 1700
Chicago, IL 60603
USA

29th November 2019

Dear Rachel

"Title: "Ultralow Surface Energy Plasma Polymer Films."
Chem. Mater. 2000, *12*, 2031-2038.
S. R. Coulson, I. S. Woodward, and J. P. S. Badyal
Published: Washington, DC: American Chemical Society, ©1989-
Shelfmark(s): Document Supply 3172.028000
Science, Technology & Business (P) JB 00 –E (153)".

According to our records, this item was receipted by The British Library on 31th July 2000 and would have been available for public use from that date.

A scan of the cover pages showing the date stamp on page one indicating the date of availability has been attached, together with the table of contents.

Please note that we can only provide the date that the British Library made this item available for public use; for the actual date of publication, please contact the publisher.

Yours sincerely

Ms S Rampersad

British Library Research Service
Tel: +44 (0) 20 7412 7903 bipc-research@bl.uk

Favored Ex. 1020

LOAN BAN EXPIRES

JULY 2000
VOLUME 12 NUMBER 7

CHEMISTRY OF MATERIALS

A PUBLICATION OF THE AMERICAN CHEMICAL SOCIETY

31-JUL-2000 BSDS BOSTON SPA LS23 7BQ
CHEMISTRY OF MATERIALS
*EDOC
3172.028000 VOL 12 PART 7
55
PB 1/1

http://pubs.acs.org/cm

CHEMISTRY OF MATERIALS

Chemistry of Materials (ISSN 0897-4756) is published monthly by the American Chemical Society at 1155 16th St., N.W., Washington, DC 20036. Periodicals postage paid at Washington, DC, and additional mailing offices. POSTMASTER: Send address changes to *Chemistry of Materials*, Member & Subscriber Services, P.O. Box 3337, Columbus, OH 43210.

American Chemical Society
1155 16th St., N.W.
Washington, DC 20036
(202) 872-4614
TDD (202) 872-6076
Fax (202) 776-8264

Publishing Operations
American Chemical Society
2540 Olentangy River Road
P.O. Box 3330, Columbus, OH 43210
(614) 447-3665
Fax (614) 447-3745; Telex 6842086
E-mail acsproof@acs.org

Member & Subscriber Services
American Chemical Society
P.O. Box 3337, Columbus, OH 43210
(614) 447-3776; (800) 333-9511
Fax (614) 447-3671
E-mail service@acs.org

Advertising Office
Centcom, Ltd.
676 East Swedesford Road
Suite 202, Wayne, PA 19087-1612
(610) 964-8061

Publications Division
Robert D. Bovenschulte, Director

Publishing Operations
Mary E. Scanlan, Director

Journal Publications
Anne C. O'Melia, Manager; Kathy E. Duffy, Journals Editing Manager; Margaret A. Winship, Associate Editor

Sales & Marketing
Justin R. Spence, Director
Dean J. Smith, Manager, Institutional Sales



Canadian GST Reg. No. 127571347
Printed in the USA

Copyright Permission: See copyright status form for certain rights (http://pubs.acs.org). Reprographic copying beyond that permitted by Section 107 or 108 of the U.S. Copyright Act is allowed, provided that $19.00 per article is paid to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923. Republication or reproduction for sale of articles or abstracts in this journal is permitted only by written permission from the Copyright Office, ACS, Washington, DC. Tel: (202) 872-4368. Fax: (202) 776-8112. E-mail: copyright@acs.org.

Subscription Donations: Members may donate/share their personal subscriptions to/with libraries but only after 5 years from publication.

Editorial Information

Instructions for Authors and Copyright Status Form: See the first issue of each volume or visit the Publications Division Web site (http://pubs.acs.org). Please conform to these instructions when submitting manuscripts.

Manuscript Submission: Send manuscripts to the Editor, Leonard V. Interrante, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180. Authors in Europe can send their manuscripts directly to our European office: Hellmut Eckert, Institut für Physikalische Chemie, Westfalische Wilhelms-Universität Münster, Schlossplatz 7, D-48149 Münster, Germany.

Accepted Papers and Proofs: Direct correspondence to Publishing Operations, Columbus, OH. Tel: (614) 447-3665. Fax: (614) 447-3745. E-mail: acsproof@acs.org.

Journal Policies: The American Chemical Society and its Editors assume no responsibility for the statements and opinions advanced by contributors. Registered names and trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

Document Number: At the end of each document is a 9-character code that serves as a link between the printed and electronic products and facilitates retrieval of the document in electronic form.

Digital Object Identifier (DOI): The DOI identification system for digital media has been designed to provide persistent and reliable identification of digital objects. Information on the DOI and its governing body, the International DOI Foundation, can be found at http://www.doi.org. In the Web editions of ACS journals, the DOI appears at the top of the HTML version of an article and at the bottom of the first page in its PDF version; in the print editions, the DOI appears in the same location as in the PDF version.

2000 Subscription and Ordering Information

		North America	Outside North America*
Printed Edition	Members	$ 83	$180
	Student Members	$ 62	$159
	Nonmembers	$229	$326
	Institutional	$804	$901
Web Edition†	Members	$ 50	$ 50
Print/Web Combination†	Members	$133	$230

* Air service included. † For Institutional rates, call Member & Subscriber Services.

Web Edition: This journal is available to subscribers via the Internet. Contact Member & Subscriber Services [Tel: (614) 447-3776 or (800) 333-9511. Fax: (614) 447-3671. E-mail: service@acs.org] or visit the Publications Division Web site (http://pubs.acs.org) for additional details.

New and Renewal Subscriptions: Send with payment to American Chemical Society, Department L-0011, Columbus, OH 43268-0011. Institutional subscribers in Japan must enter subscription orders with Maruzen Company Ltd., 3-10 Nihonbashi 2-chome, Chuo-ku, Tokyo 103, Japan. Tel: (03) 272-7211.

Change of Address: Notify Member & Subscriber Services, ACS, Columbus, OH. Tel: (614) 447-3776 or (800) 333-9511. Fax: (614) 447-3671. E-mail: address@acs.org. Include both old and new addresses and a mailing label from a recent issue.

Microfilm, Microfiche, Back Issue, and Printed Edition Single Issue Orders: Send requests to Publications Support Services, ACS, Washington, DC. Tel: (202) 872-4376. Fax: (202) 872-6325. E-mail: pss@acs.org. Printed edition not available prior to 1996.

Bulk Reprint Orders: For quotes and information, contact CJS Reprint Services. Tel: (888) 257-2134 or (410) 819-3991. Fax: (410) 820-9765.

Claims for Issues Not Received: Claims will be honored only if submitted within 90 days of the issue date (subscribers in North America) or within 180 days of the issue date (all other subscribers). Send requests to Member & Subscriber Services, ACS, Columbus, OH. Tel: (614) 447-3776 or (800) 333-9511. Fax: (614) 447-3671. E-mail: service@acs.org.

Supporting Information (SI): SI from 1995 to present is available free of charge via the Internet (http://pubs.acs.org) from the journal's home page. For information on electronic access, send E-mail to si-help@acs.org. SI prior to 1995 is available, for a fee, from Publications Support Services. Tel: (202) 872-4376. Fax: (202) 872-6325. E-mail: pss@acs.org.

© Copyright 2000 American Chemical Society

CHEMISTRY OF MATERIALS®

VOLUME 12, NUMBER 7
JULY 2000

CMATEX 12(7) 1807–2064 (2000)
ISSN 0897-4756

Registered in the U.S. Patent and Trademark Office
Copyright 2000 by the American Chemical Society

EDITORIAL

L. V. Interrante 1807 Special Issue on Organic–Inorganic Nanocomposite Materials

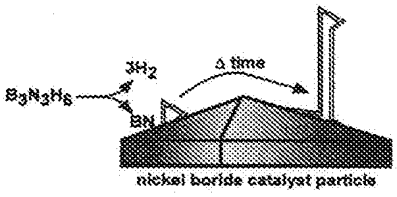
COMMUNICATIONS

Oleg R. Lourie, Carolyn R. Jones, Bart M. Bartlett, Patrick C. Gibbons, Rodney S. Ruoff,* and William E. Buhro*

Chem. Mater. **2000,** *12,* 1808 ■

CVD Growth of Boron Nitride Nanotubes

Multiwalled BN nanotubes are grown from nickel boride catalyst particles by chemical vapor deposition at 1000–1100 °C using borazine, $B_3N_3H_6$, as the precursor. This precursor is generated in situ from molten salt that forms from mixtures of $(NH_4)_2SO_4$, $NaBH_4$, and Co_3O_4 at 300–400 °C. The BN nanotubes have concentric-tube structures, are free of internal closures, have crystalline walls, and exhibit lengths of up to ~5 μm. The nanotubes often possess bulbous, flag-like, or club-like tip closures. A root-growth mechanism is proposed for the catalyzed process.

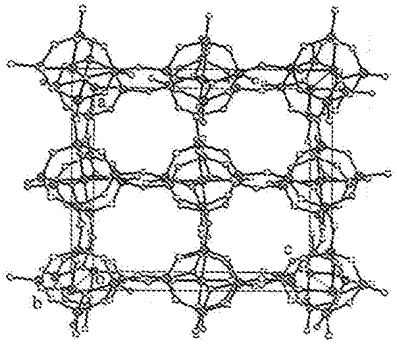


Xianhui Bu,* Pingyun Feng, and Galen D. Stucky*

Chem. Mater. **2000,** *12,* 1811 ■

First Open-Framework Zinc Germanates by a Molecular Templating Route

Despite the recent progress in the synthesis of new germanates, no zinc germanate has been synthesized by using a molecular templating route. A unique type of zincogermanate framework has now been prepared by using ethylenediamine as the structure-directing agent. The three-dimensional framework can be simply described as the face-centered packing of an elongated neutral cluster unit, Ge_9O_{18}.

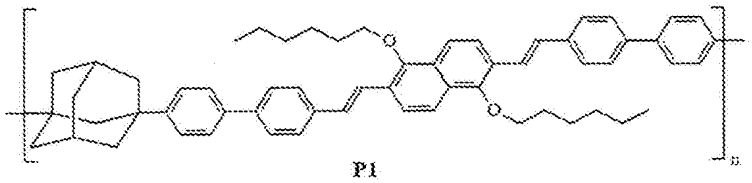


Shiying Zheng,* Jianmin Shi,* and Raphaele Mateu

Chem. Mater. **2000,** *12,* 1814 ■

Novel Blue Light Emitting Polymer Containing an Adamantane Moiety

A novel blue light emitting polymer **P1** containing a rigid adamantane moiety in the polymer main chain was synthesized. A similar green light emitting polymer was also prepared by effective control of the conjugation length. The incorporation of the adamantane units is an efficient π-conjugation interrupter. Blue light emission and low turn-on voltage were obtained from a single-layer LED fabricated from **P1**.



P1

ARTICLES

Seong-Ju Hwang, Hyo-Suk Park, Jin-Ho Choy,* and Guy Campet	1818	Evolution of Local Structure around Manganese in Layered $LiMnO_2$ upon Chemical and Electrochemical Delithiation/Relithiation
Dmitriy V. Soldatov and John A. Ripmeester*	1827 ■	Inclusion in Microporous β-Bis(1,1,1-trifluoro-5,5-dimethyl-5-methoxyacetylacetonato)copper(II), an Organic Zeolite Mimic
Leo van Wüllen,* Hellmut Eckert, and Georg Schwering	1840	Structure−Property Correlations in Lithium Phosphate Glasses: New Insights from $^{31}P \rightsquigarrow {}^{7}Li$ Double-Resonance NMR
C. M. Fang,* G. A. de Wijs, R. A. de Groot, H. T. Hintzen, and G. de With	1847	Bulk and Surface Electronic Structure of the Layered Sub-Nitrides Ca_2N and Sr_2N
Chun Yin, Yan-zhu Zhao, Chang-zheng Yang,* and Shu-yi Zhang	1853	Single-Ion Transport Light-Emitting Electrochemical Cells: Designation and Analysis of the Fast Transient Light-Emitting Responses
Carola Braunbarth, Hugh W. Hillhouse, Sankar Nair, Michael Tsapatsis,* Allen Burton, Raul F. Lobo,* Richard M. Jacubinas, and Steven M. Kuznicki	1857	Structure of Strontium Ion-Exchanged ETS-4 Microporous Molecular Sieves
Jeffrey W. Gilman,* Catheryn L. Jackson, Alexander B. Morgan, Richard Harris, Jr., Evangelos Manias, Emmanuel P. Giannelis, Melanie Wuthenow, Dawn Hilton, and Shawn H. Phillips	1866	Flammability Properties of Polymer−Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites
E. H. Lan, B. Dunn,* and J. I. Zink*	1874	Sol−Gel Encapsulated Anti-Trinitrotoluene Antibodies in Immunoassays for TNT
Hong Mei Jin, Yi Li, Hong Lin Liu, and Ping Wu*	1879	Study on the Behavior of Additives in Steel Hot-Dip Galvanizing by DFT Calculations
C. Tarducci, E. J. Kinmond, J. P. S. Badyal,* S. A. Brewer, and C. Willis	1884	Epoxide-Functionalized Solid Surfaces
Xiaoqiang Hou* and R. James Kirkpatrick	1890	Solid-State ^{77}Se NMR and XRD Study of the Structure and Dynamics of Seleno-Oxyanions in Hydrotalcite-like Compounds
Karine Heuzé, Cécile Mézière, Marc Fourmigué,* Patrick Batail,* Claude Coulon, Enric Canadell, Pascale Auban-Senzier, and Denis Jérome	1898 ■	An Efficient, Redox-Enhanced Pair of Hydrogen-Bond Tweezers for Chloride Anion Recognition, a Key Synthon in the Construction of a Novel Type of Organic Metal based on the Secondary Amide-Functionalized Ethylenedithiotetrathiafulvalene, β''-(EDT-TTF-CONHMe)$_2$[Cl·H_2O]
Alexander J. Norquist, Margaret E. Welk, Charlotte L. Stern, and Kenneth R. Poeppelmeier*	1905 ■	Synthesis of the Neutral $(CuF(NC_5H_5)_4)_2NbOF_5$ Cluster
Nobuhito Imanaka, Tomohiro Ueda, Yusuke Okazaki, Shinji Tamura, and Gin-ya Adachi*	1910	Trivalent Ion Conduction in Molybdates Having $Sc_2(WO_4)_3$-Type Structure
Kaupo Kukli,* Mikko Ritala, and Markku Leskelä	1914	Atomic Layer Deposition and Chemical Vapor Deposition of Tantalum Oxide by Successive and Simultaneous Pulsing of Tantalum Ethoxide and Tantalum Chloride
Sébastien Donze, Lionel Montagne,* and Gérard Palavit	1921	Thermal Conversion of Heavy Metal Chlorides ($PbCl_2$, $CdCl_2$) and Alkaline Chlorides (NaCl, KCl) into Phosphate Glasses
M. A. Monge,* E. Gutiérrez-Puebla, C. Cascales, and J. A. Campá	1926 ■	A Copper Germanate Containing Potassium in Its Two-Dimensional Channel Network
Anne Donat-Bouillud, Isabelle Lévesque,* Ye Tao, Marie D'Iorio, Serge Beaupré, Pierre Blondin, Maxime Ranger, Jimmy Bouchard, and Mario Leclerc	1931	Light-Emitting Diodes from Fluorene-Based π-Conjugated Polymers

Cédric Boissière, André Larbot, and Eric Prouzet*	1937	Synthesis of Mesoporous MSU-X Materials Using Inexpensive Silica Sources
Jeremy J. Harris, Jacqueline L. Stair, and Merlin L. Bruening*	1941	Layered Polyelectrolyte Films as Selective, Ultrathin Barriers for Anion Transport
G. S. Nolas,* B. C. Chakoumakos, B. Mahieu, Gary J. Long, and T. J. R. Weakley	1947	Structural Characterization and Thermal Conductivity of Type-I Tin Clathrates
D. R. Kammler, T. O. Mason,* and K. R. Poeppelmeier	1954	Phase Relationships, Transparency, and Conductivity in the Cadmium Indate−Cadmium Stannate System
Michal Kruk, Mietek Jaroniec,* Chang Hyun Ko, and Ryong Ryoo	1961	Characterization of the Porous Structure of SBA-15
Christopher M. Bender, James M. Burlitch,* Duane Barber, and Clifford Pollock	1969	Synthesis and Fluorescence of Neodymium-Doped Barium Fluoride Nanoparticles
Richard I. Walton, Franck Millange, Dermot O'Hare,* Capucine Paulet, Thierry Loiseau, and Gérard Férey*	1977	Synthesis, Structures, and Reactivity of Two Compounds Containing the Tancoite-like $[Ga(HPO_4)_2F]^{2-}_\infty$ Chain
Srikant Pathak, Marcia T. Greci, Raymond C. Kwong, Karine Mercado, G. K. Surya Prakash,* George A. Olah, and Mark E. Thompson*	1985	Synthesis and Applications of Palladium-Coated Poly(vinylpyridine) Nanospheres
Franck Millange, Richard I. Walton, Lixu Lei, and Dermot O'Hare*	1990	Efficient Separation of Terephthalate and Phthalate Anions by Selective Ion-Exchange Intercalation in the Layered Double Hydroxide $Ca_2Al(OH)_6{\cdot}NO_3{\cdot}2H_2O$
Markus Niederberger, Hans-Joachim Muhr, Frank Krumeich, Fabian Bieri, Detlef Günther, and Reinhard Nesper*	1995	Low-Cost Synthesis of Vanadium Oxide Nanotubes via Two Novel Non-Alkoxide Routes
M. A. Monge,* E. Gutiérrez-Puebla, J. L. Martínez, I. Rasines, and J. A. Campa	2001	Cation Distribution in Lithium Nickel Oxide Crystals
Mikhail Khoudiakov, Arthur B. Ellis,* John H. Perepezko,* Sungtae Kim, and Keith D. Kepler	2008	Low-Temperature, Mercury-Mediated Synthesis of Aluminum Intermetallics
Carmen I. Butoi, Neil M. Mackie, Lara J. Gamble, David G. Castner, Jeffrey Barnd, Anne M. Miller, and Ellen R. Fisher*	2014	Deposition of Highly Ordered CF_2-Rich Films Using Continuous Wave and Pulsed Hexafluoropropylene Oxide Plasmas
P. Audebert, F. Miomandre, S. G. Di Magno, V. V. Smirnov, and P. Hapiot	2025	Polymerization of 3,4-Difluoropyrrole: Electrochemical and Physicochemical Behavior of Poly(Difluoropyrrole)
S. R. Coulson, I. S. Woodward, J. P. S. Badyal,* S. A. Brewer, and C. Willis	2031	Ultralow Surface Energy Plasma Polymer Films
R. J. Waltman	2039	Experimental and Theoretical Investigation of the Effect of Lubricant Structure on the Bonding Kinetics of Perfluoroalkylpolyethers on CH_x Amorphous Hydrogenated Carbon
Alisa Bronshtein, Nadav Aharonson, Avner Turniansky, and Miriam Altstein*	2050	Sol−Gel-Based Immunoaffinity Chromatography: Application to Nitroaromatic Compounds
Young Kyu Hwang, Soo Yuen Woo, Jong Hyeon Lee, Duk-Young Jung,* and Young-Uk Kwon*	2059	Micropatterned CdS Thin Films by Selective Solution Deposition Using Microcontact Printing Techniques

ADDITIONS AND CORRECTIONS

Rupali Gangopadhyay and Amitabha De 2064 Conducting Polymer Nanocomposites: A Brief Overview

■ Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

* In papers with more than one author, the asterisk indicates the name of the author to whom inquiries about the paper should be addressed.

On the Cover

High magnification TEM image of a polypropylene-*graft*-maleic anhyhdride montmorillonite nanocomposite. The image shows a large multilayer stack of montmorillonite plates where polymer has intercalated into the galleries. At the edges of this stack, individual layers are beginning to exfoliate. (Artwork is courtesy of the National Institute of Standards and Technology.) See "Flammability Properties of Polymer–Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites" by Jeffrey W. Gilman, Catheryn L. Jackson, Alexander B. Morgan, Richard Harris, Jr., Evangelos Manias, Emmanuel P. Giannelis, Melanie Wuthenow, Dawn Hilton, and Shawn H. Phillips, p 1866.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D06M 14/18

A1

(11) International Publication Number: **WO 99/64662**

(43) International Publication Date: 16 December 1999 (16.12.99)

(21) International Application Number: PCT/GB99/01754

(22) International Filing Date: 3 June 1999 (03.06.99)

(30) Priority Data:
9812457.1 10 June 1998 (10.06.98) GB

(71) Applicant *(for all designated States except US)*: THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation and Research Agency, Ively Road, Farnborough, Hampshire GU14 0XL (GB).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: BADYAL, Jas, Pal, Singh [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). WILLIS, Colin, Robert [GB/GB]; CBDE Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BREWER, Stuart, Anson [GB/GB]; CBDE Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). COULSON, Stephen, Richard [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB).

(74) Agent: BOWDERY, A., O.; D/IPR, Formalities Section, Poplar 2, MOD Abbey Wood # 19, Bristol BS34 8JH (GB).

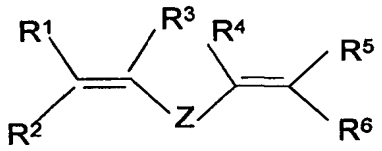
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: SURFACE COATINGS

(57) Abstract

A method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising one or more organic monomeric compounds, at least one of which comprises two carbon–carbon double bonds, so as to form a layer of cross–linked polymer on said surface. Suitable organic compounds include compounds of formula (I) where R^1, R^2, R^3, R^4, R^5, and R^6 are all independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group. The method is suitable for applying oil and/or water repellent coatings onto substrates such as fabrics.



(I)

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

Surface Coatings

The present invention relates to the coating of surfaces, in particular to the production of oil- and water-repellent surfaces, as well as to coated articles obtained thereby.

Oil- and water- repellent treatments for a wide variety of surfaces are in widespread use. For example, it may be desirable to impart such properties to solid surfaces, such as metal, glass, ceramics, paper, polymers etc. in order to improve preservation properties, or to prevent or inhibit soiling.

A particular substrate which requires such coatings are fabrics, in particular for outdoor clothing applications, sportswear, leisurewear and in military applications. Their treatments generally require the incorporation of a fluoropolymer into or more particularly, fixed onto the surface of the clothing fabric. The degree of oil and water repellency is a function of the number and length of fluorocarbon groups or moieties that can be fitted into the available space. The greater the concentration of such moieties, the greater the repellency of the finish.

In addition however, the polymeric compounds must be able to form durable bonds with the substrate. Oil- and water-repellent textile treatments are generally based on fluoropolymers that are applied to fabric in the form of an aqueous emulsion. The fabric remains breathable and permeable to air since the treatment simply coats the fibres with a very thin, liquid-repellent film. In order to make these finishes durable, they are sometimes co-applied with cross-linking resins that bind the fluoropolymer treatment to fibres. Whilst good levels of durability towards

laundering and dry-cleaning can be achieved in this way, the cross-linking resins can seriously damage cellulosic fibres and reduce the mechanical strength of the material. Chemical methods for producing oil- and water-repellent textiles are disclosed for example in WO 97/13024 and British patent No 1,102,903 or M. Lewin et al., 'Handbood of Fibre Science and Technology' Marcel and Dekker Inc., New York, (1984) Vol 2, Part B Chapter 2.

Plasma deposition techniques have been quite widely used for the deposition of polymeric coatings onto a range of surfaces. This technique is recognised as being a clean, dry technique that generates little waste compared to conventional wet chemical methods. Using this method, plasmas are generated from small organic molecules, which are subjected to an ionising electrical field under low pressure conditions. When this is done in the presence of a substrate, the ions, radicals and excited molecules of the compound in the plasma polymerise in the gas phase and react with a growing polymer film on the substrate. Conventional polymer synthesis tends to produce structures containing repeat units which bear a strong resemblance to the monomer species, whereas a polymer network generated using a plasma can be extremely complex.

The success or otherwise of plasma polymerisation depends upon a number of factors, including the nature of the organic compound. Reactive oxygen containing compounds such as maleic anhydride, has previously been subjected to plasma polymerisation (Chem. Mater. Vol. 8, 1, 1996).

US Patent No 5,328,576 describes the treatment of fabric or paper surfaces to impart liquid repellent properties by

subjecting the surfaces to a pre-treatment with an oxygen plasma, followed by plasma polymerisation of methane.

However, plasma polymerisation of the desirable oil and water repellent fluorocarbons have proved more difficult to achieve. It has been reported that cyclic fluorocarbons undergo plasma polymerisation more readily than their acyclic counterparts (H. Yasuda et al., J. Polym. Sci., Polym. Chem. Ed. 1977, 15, 2411). The plasma polymerization of trifluoromethyl-substituted perfluorocyclohexane monomers has been reported (A. M. Hynes et al., Macromolecules, 1996, 29, 18-21).

A process in which textiles are subjected to plasma discharge in the presence of an inert gas and subsequently exposed to an F-containing acrylic monomer is described in SU-1158-634. A similar process for the deposition of a fluroalkyl acrylate resists on a solid substrate is described in European Patent Application No. 0049884.

Co-pending patent applications based upon British Patent Application Nos. 9712338.4 and 9720078.6 describe and claim a improved method of producing polymer coatings which are water and/or oil repellent on surfaces. That application describes a method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising certain monomeric unsaturated organic compound which comprises an optionally substituted hydrocarbon group wherein any optional substituents are halogen; so as to form an oil or water repellent coating on said substrate.

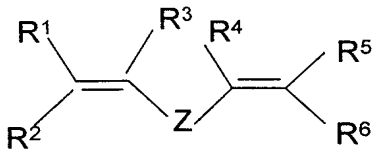
The applicants have found however that the durability of such coatings can be improved.

According to the present invention there is provided a method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising one or more organic monomeric compounds, at least one of which comprises two double bonds, so as to form a layer of cross-linked polymer on said surface.

Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by radiofrequencies (Rf), microwaves or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures as are known in the art.

Suitable compounds with more than one carbon-carbon double bond, or mixtures of such compounds with other monomeric organic compounds used in the plasma are suitably those which will yield cross-linked polymers having oil or water repellent properties. For water repellency, the presence of long chain hydrocarbon chains for example, alkyl chains is desirable. For oil-repellency or for water and oil repellency, the presence of haloalkyl chains, in particular perhaloalkyl side chains within the compound is preferable. The cross-linked polymeric coatings obtained thereby will have good durability. For example, when applied to substrates such as fabrics, the oil and/or water repellent coating would be better able to withstand washing.

Suitably the compound with more than one double bond comprises a compound of formula (I)



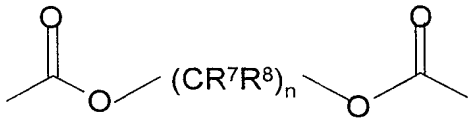
(I)

where R^1, R^2, R^3, R^4, R^5, and R^6 are all independently selected from hydrogen, halo, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group.

As used therein the term "halo" or "halogen" refers to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. The term "aryl" refers to aromatic cyclic groups such as phenyl or napthyl, in particular phenyl. The term "alkyl" refers to straight or branched chains of carbon atoms, suitably of up to 20 carbon atoms in length. The term "alkenyl" refers to straight or branched unsaturated chains suitably having from 2 to 20 carbon atoms. "Haloalkyl" refers to alkyl chains as defined above which include at least one halo substituent.

Examples of suitable bridging groups Z for use in the compound of formula (I) are those known in the polymer art. In particular they include optionally substituted alkyl groups which may be interposed with oxygen atoms. Suitable optional substituents for bridging groups Z include perhaloalkyl groups, in particular perfluoroalkyl groups.

In a particularly preferred embodiment, the bridging group Z includes one or more acyloxy or ester groups. In particular, the bridging group of formula Z is a group of sub-formula (II)



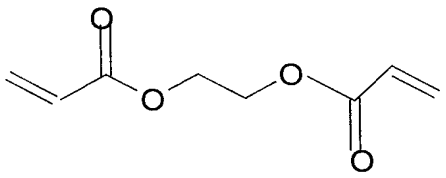
(II)

where n is an integer of from 1 to 10, suitably from 1 to 3, each R^7 and R^8 is independently selected from hydrogen, alkyl or haloalkyl.

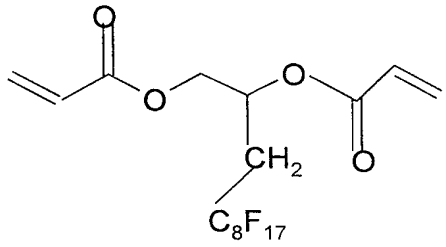
Suitably R^1, R^2, R^3, R^4, R^5, and R^6 are haloalkyl such as fluoroalkyl, or hydrogen. In particular they are all hydrogen.

Suitably the compound of formula (I) contains at least one haloalkyl group, preferably a perhaloalkyl group. This allows the formation oil repellent as well as water repellent coatings. This group is suitably located as a group R^7 or R^8 within the bridging group Z.

Thus particular examples of compounds of formula (I) include the following:



A



B

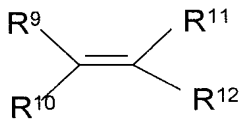
The compound of formula (I) is suitably mixed with another monomeric compound which may also contain a haloalkyl group. This may also contain a perhaloalkyl moiety, particularly

where the compound of formula (I) does not include such a group.

Where the compound of formula (I) is mixed with a further compound, these may comprise unsaturated organic compounds which contain at least one double bond which is capable of reacting to form a polymeric compound.

Perhalogenated compounds, whether saturated or unsaturated, may also give rise to oil and/or water repellent surfaces, particularly if they comprise long chains or rings, and these may form a further component of the plasma mixture. These compounds will suitably include perhaloalkyl or perhaloalkenyl groups having from 3 to 20, preferably from 8 to 12 carbon atoms.

Particularly suitable other organic compounds are those of formula (III)



(III)

where R^9, R^{10} and R^{11} are independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; and

R^{12} is a group X-R^{13} where R^{13} is an alkyl or haloalkyl group and X is a bond; a group of formula $-C(O)O(CH_2)_mY-$ where m is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(O)_pR^{14}(O)_q(CH_2)_t-$ where R^{14} is aryl optionally substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where q is 1, t is other than 0.

Preferably at least one of R^9, R^{10} or R^{11} is hydrogen.

Suitable haloalkyl groups for R^9, R^{10}, R^{11} and R^{13} are fluoroalkyl groups. The alkyl chains may be straight or branched and may include cyclic moieties.

For R^{13}, the alkyl chains suitably comprise 2 or more carbon atoms, suitably from 2-20 carbon atoms and preferably from 6 to 12 carbon atoms.

For R^9, R^{10} and R^{11}, alkyl chains are generally preferred to have from 1 to 6 carbon atoms.

Preferably R^{13} is a haloalkyl, and more preferably a perhaloalkyl group, particularly a perfluoroalkyl group of formula C_sF_{2s+1} where s is an integer of 1 or more, suitably from 1-20, and preferably from 6-12 such as 8 or 10.

Suitable alkyl groups for R^9, R^{10} and R^{11} have from 1 to 6 carbon atoms.

Preferably however, at least one of R^9, R^{10} and R^{11} is hydrogen and preferably R^9, R^{10}, R^{11} are all hydrogen.

Where X is a group $-C(O)O(CH_2)mY-$, m is an integer which provides a suitable spacer group. In particular, m is from 1 to 5, preferably about 2.

Suitable sulphonamide groups for Y include those of formula $-N(R^{14})SO_2^-$ where R^{14} is hydrogen or alkyl such as C_{1-4}alkyl, in particular methyl or ethyl.

In a preferred embodiment, the compound of formula (III) is a compound of formula (IV)

$$CH_2=CH-R^{13} \qquad (IV)$$

where R^{13} is as defined above in relation to formula (III).

In compounds of formula (II), X in formula (III) is a bond.

In an alternative preferred embodiment, the compound of formula (III) is an acrylate of formula (V)

$$CH_2=CR^{15}C(O)O(CH_2)_nR^{13} \qquad (V)$$

where m and R^{13} as defined above in relation to formula (III) and R^{15} is hydrogen or C_{1-6} alkyl, such as methyl.

Using these compounds, coatings with water hydrophobicity and oleophobicity values can be produced.

Other compounds of formula (III) are styrene derivatives as are well known in the polymer art.

All compounds of formulae (I) and (III) are either known compounds or they can be prepared from known compounds using conventional methods.

The surface coated in accordance with the invention may be of any solid substrate, such as fabric, metal, glass, ceramics, paper or polymers. In particular, the surface comprises a fabric substrate such as a cellulosic fabric, to which oil- and/or water-repellency is to be applied. Alternatatively, the fabric may be a synthetic fabric such as an acrylic/nylon fabric.

The fabric may be untreated or it may have been subjected to earlier treatments. For example, treatment in accordance with the invention can enhance the water repellency and confer a good oil-repellent finish onto fabric which already has a silicone finish which is water repellent only.

Precise conditions under which the plasma polymerization takes place in an effective manner will vary depending upon factors such as the nature of the polymer, the substrate etc. and will be determined using routine methods and/or the techniques illustrated hereinafter. In general however, polymerisation is suitably effected using vapours of the plasma compound or compounds at pressures of from 0.01 to 10 mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high frequency voltage, for example at 13.56MHz.

The applied fields are suitably of average power of up to 50W. Suitable conditions include pulsed or continuous fields, but are preferably pulsed fields. The pulses are applied in a sequence which yields very low average powers, for example in a sequence in which the power is on for 20μs and off for from 10000μs to 20000μs.

The fields are suitably applied from 30 seconds to 20 minutes, preferably from 2 to 15 minutes, depending upon the nature of the compounds used in the plasma chamber and the substrate etc.

Plasma polymerisation of compounds in accordance with the invention, particularly at low average powers may result in the deposition of highly fluorinated coatings which exhibit

super-hydrophobicity. In addition, a high level of structural retention of the compound occurs in the coating layer, which may be attributed to the direct polymerisation of the particular alkene monomers for instance a fluoroalkene monomer via its highly susceptible double bond.

Suitably, low power pulsed plasma polymerisation is used in order to produce well-adhered coatings which exhibit excellent water and oil repellency. This method leads to a greater level of structural retention, which can be attributed to free radical polymerisation occurring during the duty cycle off-time and less fragmentation during the on-time.

When the plasma compounds include a perfluoroalkylated tail or moiety, the process of the invention may have oleophobic as well as hydrophobic surface properties.

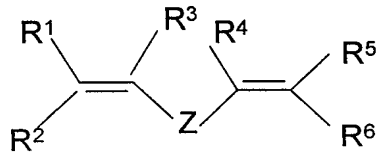
Thus the invention further provides a hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of a haloalkyl polymer which has been applied by the method described above. In particular, the substrates are fabrics but they may be solid materials such as biomedical devices.

Conventional plasma deposition apparatus, as is known in the art, can be used in the method of the present application.

Claims

1. A method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising one or more organic monomeric compounds, at least one of which comprises two carbon-carbon double bonds, so as to form a layer of cross-linked polymer on said surface.

2. A method according to claim 1 wherein an organic monomeric compound comprises a compound of formula (I)

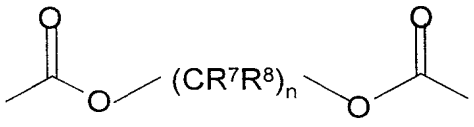


(I)

where R^1, R^2, R^3, R^4, R^5, and R^6 are all independently selected from hydrogen, halo, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group.

3. A method according to claim 2 wherein the bridging group Z comprises an optionally substituted alkyl group which may be interposed with oxygen atoms.

4. A method according to claim 3 wherein the bridging group Z is a group of sub-formula (II)



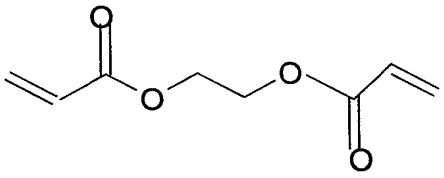
(II)

where n is an integer of from 1 to 10, suitably from 1 to 3, each R^7 and R^8 is independently selected from hydrogen, alkyl or haloalkyl.

5. A method according to any one of claims 2 to 4 wherein the compound of formula (I) contains at least one haloalkyl group.

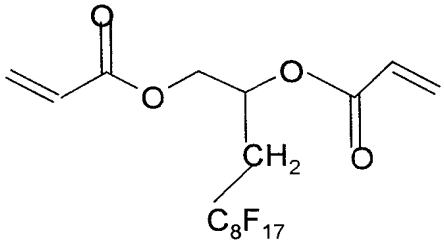
6. A method according to claim 5 wherein the haloalkyl group is a perhaloalkyl group.

7. A method according to any one of claims 2 to 6 wherein the compound of formula (II) is



A

or

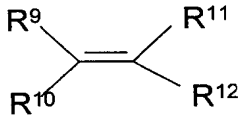


B

8. A method according to any one of claims 2 to 7 wherein the compound of formula (I) is mixed with a further monomeric compound.

9. A method according to claim 8 wherein said further monomeric compound comprises an unsaturated organic compounds which contain at least one double bond which is capable of reacting to form a polymeric compound, or a pehalogenated compound.

10. A method according to claim 9 wherein said further organic compound is a compound of formula (III)



(III)

where R^9, R^{10} and R^{11} are independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; and

R^{12} is a group X-R^{13} where R^{13} is an alkyl or haloalkyl group and X is a bond; a group of formula $-C(O)O(CH_2)_mY-$ where m is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(O)_pR^{14}(O)_q(CH_2)_t-$ where R^{14} is aryl optionally substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where q is 1, t is other than 0.

11. A method according to claim 10 wherein the compound of formula (III) is a compound of formula (IV)

$$CH_2=CH-R^{13} \qquad (IV)$$

where R^{13} is as defined in claim 10.

12. A method according to claim 10 wherein the compound of formula (III) is an acrylate of formula (V)

$$CH_2=CR^{15}C(O)O(CH_2)_nR^{13} \qquad (V)$$

where m and R^{13} as defined in claim 10 and R^{15} is hydrogen or C_{1-6} alkyl, such as methyl.

13. A substrate having a polymeric coating applied by a method according to any one of the preceding claims.

14. A substrate according to claim 13 which is a fabric.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01754

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D06M14/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D06M C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 120 316 A (MCNEELY) 3 October 1984 (1984-10-03) page 6, line 21 -page 24, last line	1-14
Y	EP 0 049 884 A (HATTORI ET AL.) 21 April 1982 (1982-04-21) cited in the application claims page 12 - page 16 : Tables	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 October 1999	15/10/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Hellemans, W

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/01754

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 120316 A	03-10-1984	ES 530104 A	01-04-1986
		JP 59168178 A	21-09-1984
EP 49884 A	21-04-1982	JP 1596594 C	27-12-1990
		JP 2022370 B	18-05-1990
		JP 58005734 A	13-01-1983
		JP 1596595 C	27-12-1990
		JP 2022371 B	18-05-1990
		JP 58005735 A	13-01-1983
		JP 57089753 A	04-06-1982
		US 4382985 A	10-05-1983
		US 4421842 A	20-12-1983
		US 4421843 A	20-12-1983

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 December 2012 (13.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/168440 A1

(51) International Patent Classification:
C09D 4/00 (2006.01)

(21) International Application Number:
PCT/EP2012/060914

(22) International Filing Date:
8 June 2012 (08.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

11004770.1	10 June 2011 (10.06.2011)	EP
61/495,756	10 June 2011 (10.06.2011)	US

(71) Applicant *(for all designated States except US)*: **EPPENDORF AG** [DE/DE]; Barkhausenweg 1, 22339 Hamburg (DE).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **TAESLER, Christian** [DE/DE]; Heitmanns Weg 9, 21614 Buxtehude (DE).

(74) Agent: **UEXKÜLL & STOLBERG**; Beselerstr. 4, 22607 Hamburg (DE).

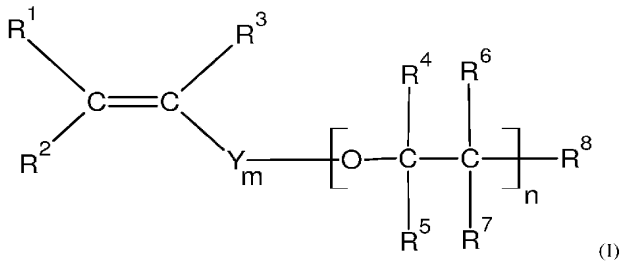
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: A COATED SUBSTRATE HAVING HYDROPHOBIC MOIETY-REPELLING SURFACE CHARACTERISTICS AND PROCESS FOR PREPARING THE SAME



(I)

(57) **Abstract**: The invention relates to a coated substrate comprising (i) a surface and (ii) a coating, said coating comprising a polymerization product of a monomer according to Formula (I) wherein m = 1 to 4; n = 1 to 5; wherein m = 1 to 4; n = 1 to 5; Y represents (CR^9R^{10}), R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^9 and R^{10} each independently represents: H, OH, halogen, C_1C_4 alkyl, C_1-C_4 alkenyl, C_1-C_4 alkynyl, C_1-C_4 dienyl, C_1-C_4 alkoxy or C_1-C_4 alkyl halide and R^8 represents H, halogen, C_1-C_4 alkyl, C_1-C_4 polyhydroxyalkyl or hydroxyalkyl, C_1-C_4 alkenyl, C_1-C_4 dienyl, C_1-C_4 alkynyl, C_1-C_4 haloalkyl, C_1-C_4 aldehyde, Ci-C4 ketone, C_1-C_4 epoxide, C_1-C_4 carboxylic acid, C_1-C_4 ester, $CH=CHR^{11}$, where R^{11} is H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 aldehyde, C_1-C_4 ketone, C_1-C_4 alkoxy, C_1-C_4 epoxide, C_1-C_4 carboxylic acid, or C1-C4 ester, or OR^{12}, where R is C1-C4 alkyl, C_1-C_4 alkenyl, C_1-C_4 dienyl, C_1-C_4 alkynyl, C_1-C_4 haloalkyl, C_1-C_4 aldehyde, C_1-C_4 ketone, C_1- C_4 epoxide, C_1-C_4 carboxylic acid, or C_1-C_4 ester.

WO 2012/168440 A1

A COATED SUBSTRATE HAVING HYDROPHOBIC MOIETY-REPELLING SURFACE CHARACTERISTICS AND PROCESS FOR PREPARING THE SAME

[0001] The present invention relates to a wide range of substrates such as a vessel for use in the laboratory or in larger scale operations filter media, foams, optical components, fabrics, solar panels, fuel cells, etc. where said substrate comprises a surface and a coating, as well as a process for preparing the coated substrate.

[0002] The ability to produce a protein-repelling coating on a substrate surface can have applications in a wide range of industries, including bioconsumables, filter media, foams, optical components, fabrics, solar panels, fuel cells, and in fact, any items that have problems due to protein-binding. Lipid-repelling coatings are of interest in the cosmetic industry, for example, to avoid undesired sticking of hydrophobic moieties of organic molecules of cosmetic formulations stored or handled in containers having surfaces with an affinity to such hydrophobic moieties, e.g. containers based on polyolefin materials. Furthermore, lipid-repelling coatings may serve the purpose of avoiding or reducing migration of ingredients of cosmetic formulations into the packaging material, a process which may negatively affect the mechanical properties of the packaging material.

[0003] In particular, for bioconsumables, the preparation and storage of biological samples are the basis for successful experiments and in particular quantitative analyses. When working with low volumes or concentrations, the purity of the sample and recovery after preparation are crucial. In these cases, losses are critical, as they may lead to incorrect or unreliable analytical results.

[0004] Working with protein-containing samples presents a specific challenge. Proteins consist of hydrophilic as well as hydrophobic domains, the latter being located on the inside of the globular protein structure in an aqueous environment. If the protein comes into contact with a solid surface of a sample vessel, the three-dimensional protein structure may become modified such that the hydrophobic regions move to the surface of the molecule and seek contact with the hydrophobic surface of the vessel. As a result, proteins in contact with a vessel surface may become immobilised or denatured, or undergo a conformational change, leading to the loss of valuable sample, or, in the case of enzyme

solutions, to a reduction in enzyme activity. These undesired effects on the sample increase with decreasing sample volume and concentration.

[0005] In general, the following methods have been employed in the laboratory to minimise adsorption of protein sample material:

1) The use of coated (e.g., siliconised) reaction vessels. This may result in leaching of the coating and interference with the sample.

2) The addition of bovine serum albumin (BSA) that will bind primarily to the vessel surface and thus protect the protein sample. However, the high BSA concentrations necessary may have an adverse effect on the precision of pipetting and may also influence further analyses.

[0006] US 6,765,069 B2 relates to a method for making a hydrophilic and lubricious coating for implantable medical devices. The coating includes a hydrophilic polymeric unit layer crosslinked with a plasma deposited double bond monomer. Examples for double bond monomers include allyl alcohol. Preferred implantable devices are stents, catheters and pacemakers. Coatings for laboratory vessels are not disclosed in this document.

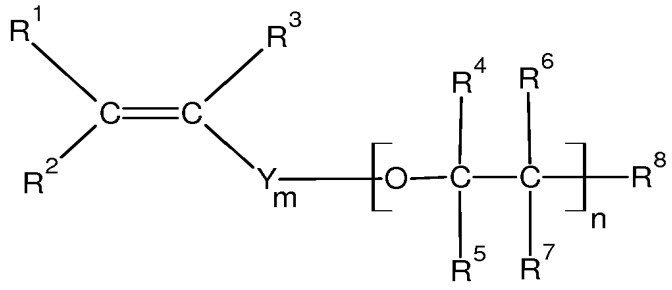
[0007] DE 195 48 152 A1 relates to a method for coating a surface to reduce the interaction with proteins, wherein the surface is exposed to the plasma deposition of an oligomeric ethylene glycol derivative.

[0008] US 6,482,531 B1 is directed to the coating of materials by gas phase or plasma polymerisation of a gas containing an organic compound or monomer. Specific substrates are contact lenses. The monomers are characterized by a generic formula which covers in particular vinyl ethers and acrylates of di(ethylene glycol).

[0009] When following the teachings of US 6,482,531 B1 and DE 195 48 152 A1, surfaces having a low affinity for proteins can be produced. However, the protein repelling surface characteristics may not be sufficiently stable under a variety of conditions, such as treatment with aqueous solutions of organic solvents (such as acetonitrile/water) and/or heating and pressurizing. This may render the coated surfaces unsuitable for the preparation and storage of biological samples containing proteins in a variety of applications, e.g. laboratory analytical processes or larger scale operations.

[0010] It is therefore an object of the invention to provide for a device such as a vessel for use in the laboratory or on a larger scale, said device having a surface showing protein- or lipid-repelling characteristics which are stable under a variety of conditions.

[0011] It has now surprisingly been found that this object can be achieved by the use of a monomer of formula I



(I),

where

m = 1 to 4;

n = 1 to 5;

Y represents (CR^9R^{10}),

R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^9 and R^{10} each independently represents:

H,

OH,

halogen,

C_1-C_4 alkyl,

C_1-C_4 alkenyl,

C_1-C_4 alkynyl,

C_1-C_4 dienyl,

C_1-C_4 alkoxy or

C_1-C_4 haloalkyl and

R^8 represents

H,

halogen,

C_1-C_4 alkyl,

C_1-C_4 polyhydroxyalkyl or hydroxyalkyl,

C_1-C_4 alkenyl,

C_1-C_4 dienyl,

C_1-C_4 alkynyl,

C_1-C_4 haloalkyl,

C_1-C_4 aldehyde,

C_1-C_4 ketone,

C_1-C_4 epoxide,

C_1-C_4 carboxylic acid,

C_1-C_4 ester,

$CH=CHR^{11}$, where R^{11} is H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 aldehyde, C_1-C_4 ketone, C_1-C_4 alkoxy, C_1-C_4 epoxide, C_1-C_4 carboxylic acid, or C_1-C_4 ester, or

OR^{12}, where R^{12} is C_1-C_4 alkyl, C_1-C_4 alkenyl, C_1-C_4 dienyl, C_1-C_4 alkynyl, C_1-C_4 alkyl halide, C_1-C_4 aldehyde, C_1-C_4 ketone, C_1-C_4 epoxide, C_1-C_4 carboxylic acid, or C_1-C_4 ester to form a polymeric coating on at least a portion of a surface of a device such as a laboratory vessel.

[0012] Thus, according to a first aspect, the present invention relates to a coated substrate comprising (i) a surface and (ii) a coating, said coating comprising a polymerisation product of a monomer according to Formula (I).

[0013] According to another aspect, the present invention relates to a process for the production of the coated substrate according to the first aspect and as defined in detail herein below, said process comprising:

i. providing a substrate comprising a surface and

ii. coating at least a portion of said substrate surface by means of chemical vapour deposition with a polymer derived from at least one monomer of Formula (I).

[0014] Preferred embodiments of the present invention are also disclosed in the dependent claims attached to this description. In one embodiment, the coating of the present invention consists of the various components disclosed herein.

[0015] Thus, the monomers of the present invention are based in particular on monoallyl ethers of certain polyols such as in particular glycerol. One or more different monomers can be used to prepare the coating for the laboratory vessel of the present invention. Thus, the present invention also relates to copolymers of one or more of the monomers as defined herein. Also, additional comonomers having a structure other than that defined by Formula (I) can be used, e.g. comonomers for cross-linking. Methods for making the monomers are well-known in the art. The methods for making the coatings according to the present invention are discussed in detail below.

[0016] In a group of preferred monomers, R^1 to R^7, R^9, R^{10} are as defined above and R^8 is C_1-C_4 polyhydroxyalkyl, e.g. a C_2 dihydroxyalkyl, a C_3 trihydroxyalkyl or a C_4 tetrahydroxyalkyl radical.

[0017] In another preferred embodiment of the present invention, R^1, R^2, R^3, R^9, and R^{10} each independently represent H or C_1-C_4 alkyl, m is 1; and R^4, R^5, R^6, R^7 each independently represent H or OH; and R^8 represents C_1-C_4 polyhydroxyalkyl or C_1-C_4 hydroxyalkyl, e.g. a C_2 dihydroxyalkyl, a C_3 trihydroxyalkyl or a C_4 tetrahydroxyalkyl radical.

[0018] A particularly preferred group of monomers is one where m = 1, each of R^1, R^2, R^3, R^4, R^6, R^9, and R^{10} is H; each of R^5 and R^7 is OH; and R^8 is C_1-C_4 polyhydroxyalkyl or hydroxyalkyl, in particular hydroxymethyl.

[0019] As noted above, a preferred monomer is the monoallyl ether of glycerol, also known as 3-allyloxy-1,2-propanediol. Other specific polyols which may be used to prepare the monoallyl ether monomers of the present invention are sugar alcohols such as tetroses, pentoses and hexoses, e.g. mannitol or sorbitol.

[0020] The coatings formed by the monomers of the present invention are in general obtained by chemical vapour deposition of monomers according to Formula (I) or a mix-

ture of different monomers according to Formula (I). Also, the process of the present invention may comprise the use of cross-linking agents such as 3-(Acryloyloxy)-2-hydroxypropyl methacrylate, 1,3-Butanediol dimethacrylate, 1,4-Butanediol diacrylate, Ethylene glycol diacrylate, Ethylene glycol dimethacrylate, Tetraethylene glycol dimethacrylate, Glycerol dimethacrylate, Pentaerythritol tetraacrylate, 2,4,6-Triallyloxy-1,3,5-triazine, Trimethylolpropane diallyl ether.

[0021] Substrates in accordance with the present invention can be bioconsumables, filter media, foams, optical components, cosmetic containers, fabrics, solar panels, fuel cells, and in fact, any items that have problems due to protein- or lipid-binding, *i.e.* binding of hydrophobic moieties. For bioconsumables, it can typically be a vessel for use in the laboratory or on a larger scale, e.g. on a plant scale. A substrate according to the present invention comprises one or more surfaces for coating. Such surface may also be called an operational surface.

[0022] As discussed above, lipid-repelling coatings may be used in the cosmetic industry, for example, to avoid undesired sticking of hydrophobic moieties of organic molecules of cosmetic formulations stored or handled in containers having surfaces with an affinity to such hydrophobic moieties, e.g. containers based on polyolefin materials or other materials such as in particular those materials which are described in more detail below.

[0023] Typically for bioconsumables, such vessels are used for the storing, handling, sampling, analyzing, collecting, isolating, incubating, transporting or other processing of liquids and fluids containing biological/chemical samples such as proteins. Specific examples for such vessels are given herein below.

[0024] Many vessels according to the invention have at least one interior wall which defines a reservoir portion for containing a volume of liquid, and at least one opening in communication with the reservoir portion. According to some embodiments of the invention, a laboratory vessel having an interior wall and an opening is coated on the interior wall and on the area surrounding and forming the opening, with a coating according to the invention. In other embodiments, a vessel according to the invention does not have an interior wall defining a reservoir portion but instead merely comprises a substrate surface partly or completely provided with a coating based on monomers of Formula (I), which

coated surface will be in contact with liquids or fluids of interest. For example, such "vessel" according to the present invention may be a microscope slide or a bead.

[0025] Particularly preferred vessels are selected from the group consisting of vials, flasks, dishes, test tubes, pipette tips, microcentrifuge tubes, syringes, microscope slides, microscope slide assemblies, sample chambers for analytical devices, tapes, laminates, plates, arrays, multi-titer plates and tubing.

[0026] Other preferred vessels are selected from the group consisting of bioreactors and elements thereof, fermentors, cultivation bags, beads, chromatography material; chromatographic carriers, membranes and filters.

[0027] Still other preferred vessels are selected from the group consisting a microtitre plate, a microcentrifuge tube, a cell culture consumable, a PCR (Polymerase Chain Reaction) consumable and a dispensing consumable.

[0028] Vessel materials may in general comprise plastic or sintered materials, glass, ceramic, metal and primed or pre-coated materials. The invention may also be used on operational surfaces which are porous, smooth, rough, pitted, grooved, cross-hatched, striated, or having patterned physical features.

[0029] Preferred examples of suitable materials for the laboratory vessels of the present invention include polyolefins, polyamides, polyesters, silicones, polyurethanes, epoxies, acrylics, polyacrylates, polyesters, polysulfones, poly(meth)acrylates, polycarbonates, PEEK, polyimides, polystyrenes, and fluoropolymers such as PTFE Teflon®, FEP Teflon®, Tefzel®, poly(vinylidene fluoride), PVDF, and perfluoroalkoxy resins. Glass products including silica glass are also used to manufacture laboratory vessels. Ceramic or oxide surfaces can be coated according to the invention. Cellulosic products such as paper and reinforced paper containers can be coated to form coated laboratory vessels according to the invention. Metal surfaces can be coated according to the invention, as can surfaces of glass, silicon, silicon compounds or ceramics that have or have not been primed with silane containing materials or other adhesion promoting materials. Primed metal, primed glass, primed ceramic and primed oxide surfaces can be coated according to embodiments of the invention. Vessel surfaces which have been pre-coated with epoxies, silicones, urethanes, acrylics, or other materials can also be coated according to the invention.

[0030] Plastic or glass is often used to manufacture low-cost laboratory vessels. Preferred materials used to manufacture laboratory vessels include polypropylene, polyethylene, poly-ethyleneterephthalate, polystyrene, polycarbonate and cellulosics. More expensive plastics such as polytetrafluoroethylene and other fluorinated polymers have been used. Because polypropylene is inexpensive and quite hydrophobic itself, it is a particularly preferred material for laboratory vessels, including pipette tips, used for handling and transporting minute and precise amounts of biological sample.

[0031] It will be understood that the above materials may comprise additives common in the art. For example, additives for providing antistatic performance are regularly incorporated in plastics such as polypropylene. Accordingly, a reference herein to the above materials such as polypropylene also includes those grades of materials, e.g. polypropylene, which contain those types of additives.

[0032] The thickness of the coating prepared in accordance with the present invention is generally in the range of nanometers, e.g. 10 to 300 nm; preferably below 100 nm, e.g. about 50 nm.

[0033] Although some wash-off of polymerised coating material or coating monomer might be expected after repeated usage, the coatings of the present invention do not considerably wash off most laboratory vessel surfaces. Little if any wash-off occurs from other vessel materials because of the extremely low solubility in most solvents of the coatings when prepared according to the present invention.

[0034] In addition, the following advantages are associated with the use of a coating in accordance with the present invention:

- high resistance against liquid media such as solvents (Without being bound by a specific theory, it is believed that this high resistance is due to the covalent binding (grafting) of the hydrogel functionality to the surface of the device and due to a sufficient degree of cross-linking within the coating.);
- high reproducibility and lack of defects;
- resistance against aging;

- lower costs as compared to monomers known in the art for preparing the same types of coating;
- no risk of contaminating a sample material (due to desorption of coating material from the surface in contact with the sample);
- good transparency since the thickness of the coating is in the nanometer range;
- no specific requirements with regard to the characteristics of the substrate material;
- advantages in biochemical assays: low enzyme/substrate bonding to the coated surface, thereby providing higher sensitivity;
- no need to use BSA as a "protector" in assays: the pipetting procedure is easier to control and less prone to errors;
- no need to use tensides such as Triton X or sodium dodecyl sulfate as a "protector" in assays: again the pipetting is easier to control and less prone to errors;
- higher sensitivity in methods directed to protein and/or DNA analysis;
- advantages in the processing and storage of samples of biomolecules (proteins, DNA, RNA etc.), in view of the minimized material losses;
- advantages in cell culture procedures: the cells grow un-differentiated in the medium;
- stable against steam sterilisation and organic solvents (acetonitrile).

[0035] The invention also relates to a process for preparing a coated substrate as described above. The process comprises the following steps:

(i) providing a substrate comprising a surface as defined herein above; and

(ii) coating at least a portion of said substrate surface by means of chemical vapour deposition (CVD) with a polymer derived from a monomer according to Formula (I).

[0036] In particular, the polymer coatings of the present invention can be prepared by plasma-enhanced chemical vapour deposition (PE-CVD) of a plurality of plasma-

polymerizable monomers comprising a monomer of Formula (I) as described hereinabove. Also, the PE-CVD process may comprise the use of multifunctional comonomers for promoting the formation of a more crosslinked structure in order to enhance the stability of the coating against solvents and chemicals. Suitable cross-linking agents are as described hereinabove. Thus, according to one embodiment, the polymerization product of the present invention has a structure comprising cross-linking units.

[0037] Other variants of chemical vapour deposition techniques such as hot filament induced CVD using an initiator (iCVD) or CVD enhanced by ultraviolet radiation (UV enhanced CVD) may also suitably be used to prepare the coated substrates of the present invention. With regard to iCVD, usually an initiator species, e.g. tert-butyl peroxide, is introduced together with the monomer of the invention into the vapour phase into a vacuum chamber maintained at a pressure of typically between 0.1 and 1 Torr. An array of filament wires is usually positioned 1 to 4 cm above the substrate to be coated and resistively heated to a temperature typically in the range of 200 to 500°C. The use of suitably low filament temperatures enables the synthesis of polymers with delicate functionalities. The substrate is generally backside cooled to a much lower temperature, typically less than 50°C, to promote adsorption of reactive species. The use of low substrate temperatures is also favourable for the coating of thermal sensitive objects.

[0038] Processes for preparing polymers on surfaces by means of plasma polymerization, in particular plasma enhanced chemical vapour deposition are known in the art, and those prior art processes can be used to apply the monomers on a surface of the laboratory vessel according to the invention. Preferred process parameters for PE-CVD are disclosed in e.g. US 6,482,531 B1; US 6,551,950 B1; US 5,853,894 B1; and DE 195 48 152 A1, which are fully incorporated herein for the purposes of US practice.

[0039] More specifically, plasma-enhanced chemical vapour deposition means any method wherein gaseous monomers are attached to the surface of a solid substrate such as an operational surface of a substrate such as a laboratory vessel to form a coating by polymerization and/or grafting of the monomers of the invention directly to the substrate. This includes plasma and photochemical-enhanced polymerizations. Plasma-induced polymerizations or shortly plasma depositions are polymerizations due to the generation of free-radicals caused by passing an electrical discharge through a gas. The electrical dis-

charge can be caused by high-voltage methods, either alternating current or direct current, or by electromagnetic methods such as radio frequency and microwave. Alternatively, a thermally generated plasma may be used.

[0040] Precise conditions under which the plasma polymerization takes place in an effective manner will vary depending upon factors such as the nature of the monomer, the substrate etc. The conditions will be determined using routine methods and/or the techniques illustrated in detail in the above-noted prior art. One or more plasma polymerization methods may be used to apply a coating. For example, a combination of a continuous and pulsed plasma polymerization may be used. Also, the process can be performed as a one-step or multi-step gas phase deposition.

[0041] In general, the substrate to be treated is placed within a plasma chamber together with the material to be deposited in a gaseous state, a glow discharge is ignited within the chamber and a suitable voltage is applied, which may be pulsed. However, atomisation techniques to deliver monomer into the chamber, such as those described in WO02/28548 (Dow Corning Ireland Ltd), WO2003101621 and WO2003097245 (Surface Innovations Limited), may also be used.

[0042] The polymeric coating may be produced under both pulsed and continuous-wave plasma deposition conditions but pulsed plasma may be preferred as this allows closer control of the coating, and so the formation of a more uniform polymeric structure.

[0043] As used herein, the expression "in a gaseous state" refers to gases or vapours, either alone or in mixture, as well as aerosols.

[0044] Precise conditions under which the plasma polymerization takes place in an effective manner will vary depending upon factors such as the nature of the polymer, the substrate treated and will be determined using routine methods and/or techniques.

[0045] Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by radiofrequencies (RF), microwaves or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures as known in the art. In particular however, they are generated by radiofrequencies (RF).

[0046] Various forms of equipment may be used to generate gaseous plasmas. Generally these comprise containers or plasma chambers in which plasmas may be generated.

Particular examples of such equipment are described for instance in WO2005/089961 and WO02/28548, but many other conventional plasma generating apparatus are available.

[0047] The gas present within the plasma chamber may comprise a vapour of the monomer alone, but it may be combined with a carrier gas, in particular, an inert gas such as helium or argon, if required. In particular helium is a preferred carrier gas as this can minimise fragmentation of the monomer.

[0048] When used as a mixture, the relative amounts of the monomer vapour to carrier gas are suitably determined in accordance with procedures which are conventional in the art. The amount of monomer added will depend to some extent on the nature of the particular monomer being used, the nature of the substrate being treated, the size of the plasma chamber etc. Generally, in the case of conventional chambers, monomer is delivered in an amount of from 50-250 mg/minute, for example at a rate of from 100-150 mg/minute. It will be appreciated however, that the rate will vary depending on the reactor size chosen and the number of substrates required to be processed at once, *i.e.* at the same time; this in turn depends on considerations such as the annual through-put required and the capital outlay.

[0049] Carrier gas such as helium is suitably administered at a constant rate for example at a rate of from 5-90 standard cubic centimetres per minute (sccm), for example from 15-30 sccm. In some instances, the ratio of monomer to carrier gas will be in the range of from 100:0 to 1:100, for instance in the range of from 10:0 to 1:100, and in particular about 1:0 to 1:10. The precise ratio selected will be so as to ensure that the flow rate required by the process is achieved.

[0050] In an embodiment of the present invention, a preliminary continuous power plasma may be applied. For example, this type of plasma may be applied for from 15 seconds to 10 minutes, for example from 2-10 minutes within the chamber. This may act as a surface pre-treatment step, ensuring that the monomer attaches itself readily to the surface, so that as polymerisation occurs, the coating "grows" on the surface. The pre-treatment step may be conducted before monomer is introduced into the chamber, in the presence of only an inert gas. In one embodiment, the inert gas comprises argon.

[0051] The plasma is then suitably switched to a pulsed plasma to allow polymerisation to proceed, at least when the monomer is present.

[0052] In general, a glow discharge is suitably ignited by applying a high frequency voltage, for example at 13.56 MHz. This is applied using electrodes, which may be internal or external to the chamber, but in the case of larger chambers are generally internal.

[0053] Suitably the gas, vapour or gas mixture is supplied at a rate of at least 1 standard cubic centimetre per minute (sccm) and preferably in the range of from 1 to 100 sccm.

[0054] If a monomer vapour is used, it may suitably be supplied at a rate of from 80-300 mg/minute, for example at about 120 mg/minute depending upon the nature of the monomer, the size of the chamber and the surface area of the product during a particular run whilst the pulsed voltage is applied. It may however, be more appropriate for industrial scale use to have a fixed total monomer delivery so that it is known how much monomer is used in total. This amount will vary with respect to the defined process time and will also depend on the nature of the monomer and the technical effect required.

[0055] Gases or vapours may be delivered into the plasma chamber using any conventional method. For example, they may be drawn, injected or pumped into the plasma region. In particular, where a plasma chamber is used, gases or vapours may be drawn into the chamber as a result of a reduction in the pressure within the chamber, caused by use of an evacuating pump, or they may be pumped, sprayed, dripped, electrostatically ionised or injected into the chamber as is common in liquid handling.

[0056] Polymerisation is suitably effected using vapours of compounds for example of formula (I), which are maintained at pressures of from 0.1 to 400 mtorr, suitably at about 10-100mtorr. Generally, the monomers of formula (I) are those which have a volatility which is such that the minimum vapour pressures required for the process of the present invention are provided at temperatures below the decomposition temperatures of the monomers.

[0057] The applied fields are suitably of power of from 5 to 500 W for example from 20 to 500W, suitably at about 100 W peak power, applied as a continuous or pulsed field. Where used, pulses are suitably applied in a sequence which yields very low average

powers, for example in a sequence in which the ratio of the time on : time off is in the range of from 1:100 to 1:1500, for example at about 1:650. Particular examples of such sequence are sequences where power is on for 20-50 μs, for example about 30 μs, and off for from 1000 μs to 30000 μs, in particular about 20000 μs. Typical average powers obtained in this way are 0.1 – 0.2 W.

[0058] The fields are suitably applied from 30 seconds to 90 minutes, preferably from 5 to 60 minutes, depending upon the nature of the compound of formula (I) and the substrates being treated.

[0059] Suitably a plasma chamber used is of sufficient volume to accommodate multiple substrates.

[0060] A particularly suitable apparatus and method for producing coated substrates in accordance with the invention is described in WO2005/089961, the content of which is hereby incorporated by reference for the purposes of US practice. More specifically, the apparatus comprises a plasma deposition chamber, a pumping system arranged to feed monomer in gaseous form into the chamber, at least two electrodes arranged so as to ignite a plasma within the chamber, and power control means programmed to pulse power supplied to the electrodes so as to produce a plasma at a power of from 0.001 to 500w/m^3 within a plasma zone within the chamber.

[0061] The pumping system is suitably one which can supply large amounts of vapours into the chamber, and to ensure that this remains in the chamber for the minimum adequate residence time, to achieve the desired effect. It may comprise a series of pumps, and large conductance pipes. The pumping system may also be arranged to draw gas out of the chamber to evacuate air, and/or reduce the pressure, as required.

[0062] In a particular embodiment, the pumping system comprises two pumps. A first pump or roots pump, which is suitably a high volume pump, is arranged to evacuate any vapours including water vapour or other contaminants from the chamber. In order to do this efficiently, and in a reasonable timeframe, bearing in mind the size of the chamber, the pump is suitably arranged close to the chamber, and connected to it by way of a single straight pipe, with as large a diameter as possible. A valve is provided in the pipe so that once the chamber has been evacuated, it can be sealed.

[0063] A second pump is suitably a lower volume pump, such as a dry-rotary pump. This is suitably connected to the chamber by the same opening as the first pump. It is arranged so that it can draw monomer, together with any carrier gas into the chamber at a suitable rate, and maintain the desired pressure and residence time of gas within the chamber.

[0064] The pumping means suitably vents to a furnace where any remaining monomer or fragments therefore, are incinerated before the gases safely pass into the atmosphere.

[0065] Preferably the apparatus further comprises heating means for the chamber. These may be integral with the walls of a chamber, or present in a casing surrounding the chamber. They may comprise electrical elements or recirculated, heated oil filled elements, suitably under the control of a temperature controller, to ensure that the desired temperature is maintained within the chamber.

[0066] Preferably also the apparatus comprises a container for monomer, which is connected to the chamber by a suitable pipe and valve arrangement. Preferably, this container is provided with a heater, which will allow the monomer to be heated above ambient temperature, if required, before being introduced, into the chamber. Preferably the container, the pipe leading from it to the chamber and the chamber itself are all heated, and the heating means are arranged to produce an increasing temperature gradient along the path of the monomer.

[0067] A supply of carrier gas may, if required, be connected to the container and gas from this supply can be passed into the container if required, in order to produce a sufficient flow of gas into the chamber to produce the desired result.

[0068] In use, in a batch process, the items to be coated are introduced into the chamber. In a particular embodiment, these are ready made garments, to which a water and/or oil repellent coating is to be applied. By depositing the polymer to the finished garment, rather than to the fabric used in the production, an "all over" coating is achieved, including areas such as zips, fasteners or stitched joints, which would otherwise remain uncoated.

[0069] The chamber is then evacuated, for instance using the entire pump suite, but in particular the large roots pump where provided. Once the chamber is evacuated, monomer

vapour, which is suitably warmed, is fed into it from the container. This is achieved for instance, by drawing using a second pump from a container in which a supply of liquid monomer is held. This container is suitably heated to a temperature sufficient to cause vaporisation of the monomer.

[0070] Preferably also the pipes and conduits which lead from the container to the chamber are also heatable. This means that it is possible to ensure that monomer is not lost through condensation in the feed pipes.

[0071] In particular, when using high volume chambers of the type discussed above, the plasma is created with a voltage as a pulsed field, at an average power of from 0.001 to 500 W/m^3, for example at from 0.001 to 100 W/m^3 and suitably at from 0.005 to 0.5 W/m^3.

[0072] These conditions are particularly suitable for depositing good quality uniform coatings, in large chambers, for example in chambers where the plasma zone has a volume of greater than 500 cm^3, for instance 0.1 m^3 or more, such as from 0.5 m^3-10m^3 and suitably at about 1 m^3. The layers formed in this way have good mechanical strength.

[0073] The dimensions of the chamber will be selected so as to accommodate the particular substrates being treated. For instance, generally cuboid chambers may be suitable for a wide range of applications, but if necessary, elongate or rectangular chambers may be constructed or indeed cylindrical, or of any other suitable shape.

[0074] The chamber may be a sealable container, to allow for batch processes, or it may comprise inlets and outlets for the substrate, to allow it to be utilised in a continuous process as an in-line system. In particular in the latter case, the pressure conditions necessary for creating a plasma discharge within the chamber are maintained using high volume pumps, as is conventional for example in a device with a "whistling leak". However it will also be possible to process substrates at atmospheric pressure, or close to, negating the need for "whistling leaks".

[0075] The advantages of the present invention will also become apparent from the following examples which are illustrative only and are not to be construed as limiting the scope of the present invention.

EXAMPLES

Example A: Coating Process

Plasma Polymerisation of 3-Allyloxy-1,2-propanediol

[0076] 3-Allyloxy-1,2-propanediol is used as supplied. The plasma deposition experiment is carried out in a plasma chamber of volume 40 litres. Test pieces of suitable size and shape are placed in the chamber and the pressure reduced to 5 mtorr. As a cleaning pre-treatment, argon is introduced to a pressure of 800 mtorr. RF power is then delivered to the chamber via a set of electrodes. A peak power of 100 W with a 10% duty cycle with 10 Hz frequency is applied for 5 minutes. After this stage the chamber is pumped down to < 5 mtorr.

[0077] 3-Allyloxy-1,2-propanediol vapour is then introduced to the chamber so that it reaches a pressure of 40 mtorr. 200 W RF power is applied for 5 minutes. For the next stage, the pressure conditions of the monomer are kept the same, but the power is now pulsed so a polymer is grown on the surface of the substrate with good retention of the monomer properties, i.e. those properties which are based on the functional groups and moieties of the monomers present in the monomer, which the functional groups and moieties are not consumed in the polymerization reaction. The peak power is 75 W and the on time of the pulse is 50 μs, and the off time is 20 ms. This pulsed plasma is applied for 60 minutes.

[0078] At the end of the process, the RF power is turned off, the chamber is pumped down to < 5 mtorr and then vented to atmosphere. The coated sample is then removed from the chamber.

Example B: Assay for Testing the Protein Repelling Effect

[0079] The experimental data shown below were obtained by using the following assay.

1. Basic operations

1.1. Marking of proteins using Iodine-131 (I-131)

Proteins:

Bovine Albumine (Sigma), Initial Fractionation by Cold Alcohol Precipitation, Approx. 99 %.;

Cytochrome C from bovine heart, Sigma;

Fibrinogen from bovine plasma, Fraction I, Type I-S, Sigma;

IgG from bovine serum, Sigma.

Reagents:

Chloramine T, 2 mg/ml

$Na_2S_2O_5$, 3 mg/ml

NaCl, 9 mg/ml (physiological)

Tris/HCl 0.1 M, pH 7.5

Protein solution in NaCl

Activity:

74 MBq Na131I starting activity (Amersham). Addition of 1.4 ml Tris buffer. Total volume ca. 2.0 ml.

Procedure:

Starting from 200 µl activity;

addition of 500 µl Tris buffer;

500 µl protein solution, carefully weighed;

200 µl Chloramine T;

5 minutes of swaying;

addition of 200 µl $Na_2S_2O_5$;

1 minute of swaying.

1.2. Determination of the specific counting rate of the reaction mixture

[0080] 20 µl reaction mixture are placed in a vial and weighed carefully. The counting rate is determined in a gamma counter (Cobra, Canberra-Packard). Measuring time: 10 minutes.

1.3. Determination of the marking yield

[0081] A small drop of reaction mixture is placed on a thin layer chromatography (tlc) plate (Polygram CEL 300, Macherey-Nagel) and chromatographed using methanol : water (85:15). The protein remains at the starting line, whereas free iodide travels with nearly the flow rate of the eluent. The ratio of the activities is determined using a autoradiographic method (PhosphorImager, Molecular Dynamics).

1.4. Cleaning of the proteins

[0082] A gel permeation column (PD-10, Amersham Pharmacia Biotech, filled with Sephadex G-25) is conditioned using 25 ml Tris buffer. The reaction mixture is placed on the column, and the eluate is discarded. Further 1 ml of Tris buffer is added, and the eluate is again discarded. After addition of further 3 ml Tris buffer, the eluate is collected ("cleaned protein solution").

1.5. Determination of the specific counting rates of the cleaned protein solution

[0083] 50 µl of reaction mixture are placed in a vial and weighed carefully. The counting rate is determined in a gamma counter (Cobra, Canberra-Packard). Measuring time: 10 minutes.

1.6. Determination of the protein proportion of the counting rate after cleaning

[0084] The cleaned protein solution still contains a small amount of free active iodide. A small drop of cleaned protein solution is placed on a tlc plate and chromatographed using methanol: water (85:15). The protein remains at the starting line whereas free iodide travels with nearly the flow rate of the eluent. The ratio of the activities is determined using a autoradiographic method (PhosphorImager, Molecular Dynamics).

1.7. Setting the concentration of protein at 1 µg/g

[0085] The following information is necessary so that the concentration of the protein solution can be brought to the desired value of 1 µg/g:

- specific counting rate of the reaction mixture;
- marking yield;
- specific counting rate of the cleaned protein solution;

– protein proportion of the counting rate after cleaning.

[0086] Dilution can therefore only be effected once the results of the autoradiographic analysis and the gamma counter are available.

1.8. Preparation of the vials

[0087] The projecting parts of the lid must be cut off so that the vial fits into the bore-hole geometry of the gamma counter. Likewise, the connection between the lid and the vial must be removed. The resulting difficulties when opening the vial are not substantial. The removal of the projecting parts must take place before filling the vial because upon agitation drops would be released from the surface of the liquid and would contaminate those parts of the vial which should not be wetted.

1.9. Filling the vials

[0088] The vial can be adjusted in height using a raising and lowering mechanism. It is filled using a multipette (Eppendorf). Care must be taken when filling: Areas above the normal liquid level can be wetted if the liquid shoots too quickly out of the opening of the pipette tip.

1.10. Measuring the counting rate

[0089] The vials of each series are brought together in the gamma counter. Measuring is stopped as soon as the counting error is below 0.1% on the required measuring time has been reached.

1.11. Controlled emptying of the vials

[0090] The liquid is siphoned off using a peristaltic pump. A yellow Eppendorf pipette tip is placed on the tube. The tip is fastened in downward position. The pump mechanism ensures that the depth of immersion is kept at 2-3 mm. One finally touches the bottom of the vial several times with the pipette tip to remove any liquid residue which can be mechanically caught.

1.12. Steps of a measuring series

[0091] The following steps were initially performed for a series of vials:

– preparation of the vials

- filling with 500 µl of cleaned protein solution
- 24 h waiting time
- determination of the gamma counting rate
- emptying of the vials and refilling with 500 µl Tris buffer
- emptying of the vials and refilling with 500 µl Tris buffer
- 24 h waiting time
- determination of the gamma counting rate
- emptying of the vials
- determination of the gamma counting rate.

[0092] This corresponds to the procedure which was followed in nearly all of the above measurements. Subsequently, a shortened procedure was followed for the following series since the in-between step after the first emptying was considered to provide little information.

- preparation of the vials
- filling with 500 µl of cleaned protein solution
- 24 h waiting time
- determination of the gamma counting rate
- emptying of the vials and refilling with 500 µl Tris buffer
- emptying of the vials
- determination of the income accounting rate.

[0093] When using vials having a filling volume of 2 ml, 1000 µl of liquid were used, in variation from the above described procedure.

1.13. Determination of the wetted surface

[0094] The measurements were made using three vials differing in size. The wetted surface therefore depends on the type:

[0095] Vials having a size of 500 µl are considered to be a combination of hemisphere and two frusta. A content of 500 µl corresponds to the following dimensions:

sphere diameter = small frustum1 diameter = 3 mm

large frustum1 diameter = small frustum2 diameter = 6 mm

length of the frustum1 mantle = 12 mm

large frustum2 diameter = 6.4 mm

length of frustum2 mantle = 9.6 mm

total volume: 500.4 µl

total wetted surface: 370.8 mm^2.

[0096] The vials having a volume of 1 ml are considered to be a combination of a hemisphere, a frustum and a cylinder. The following dimensions correspond to a content of 500 µl:

sphere diameter = small frustum diameter = 4 mm

large frustum diameter = 8 mm

length of the frustum mantle = 16 mm

The cylinder-shaped part is not wetted at 500 µl.

total volume: 499.0 µl

total wetted surface: 326.7 mm^2.

[0097] Vials having a volume of 2 ml are considered to be a combination of a hemisphere and a cylinder. The following dimensions correspond to a content of 1000 µl:

sphere diameter = cylinder diameter = 8.5 mm

height cylinder = 12.6 mm

total volume: 1037 µl

total wetted surface: 450.0 mm^2

1.14. Characterisation of a monolayer

[0098] Dimension of a protein molecule: 3.55 nm Stokes radius (as sphere) having a volume of 187 nm^3. A cube having the same volume has a side length of 5.7 nm and base of 33 nm^2.

[0099] At a content of 500 µl, the wetted surface of a vial having a volume of 500 µl is 371 mm^2 or 371 * 10^{12} nm^2. That is, a monolayer corresponds to 1.13 * 10^{13} molecules.

[00100] At a content of 500 µl, the wetted surface of a vial having a volume of 1 ml is 327 mm^2 or 327 * 10^{12} nm^2. That is, a monolayer corresponds to 9.98 * 10^{12} molecules.

[00101] At a content of 1 ml, the wetted surface of a vial having a volume of 2 ml is 450 mm^2 or 450 * 10^{12} nm^2. That is, a monolayer corresponds to 1.37 * 10^{13} molecules.

[00102] These values are a rough estimate.

1.15. Measurements with wells

[00103] A part of the samples consisted of sawn-up wells for which analogous measurements were to be made. Because of the size of the wells, the gamma counter "Cobra" could not be used. Instead, a device had to be used where all operations had to be performed manually. It turned out that the dimensions of the wells varied. Also, variations in the counting yield where encountered. Therefore, the counting rates were not put down to the number of monolayers. The results may be associated with an error in the magnitude of 50% of the measured value. The method described under 1.12 was followed. 1000 µl of liquid were used, respectively.

2. Results

[00104] The coverage is determined as counting rate and as the number of monolayers. The latter allows a comparison with earlier measurements and takes the differing wetted surface of the three types of vials into account. In addition, the activity of the protein solution is only partly localised on the protein. A small part (typically 7%) is present as free iodide, despite the cleaning by gel permeation chromatography. The proteins were marked in individual experiments. Therefore, a monolayer corresponds to an individual counting rate.

[00105] In the following results, the contact time was always 24 h, and the concentration of the proteins was 1 µg/ml. The experiments were performed with the proteins BSA, IgG, fibrinogen and cytochrome C.

[00106] The results given in the following table report the loss of protein in %, as obtained from a comparison of the coverages determined in accordance with the assay described above.

Table 1: Protein Loss in 1.5 ml Safe Lock Vessels

Samples	Composition	BSA Loss [%]			IgG Loss [%]		
		untreated	after aceto-nitrile/water	after 1X autoclaving at 121°C	untreated	after aceto-nitrile/water	after 1X autoclaving at 121°C
Comparison Example 1	Untreated hydrophobic polypropylene	60-75	60-75	60-75	50-65	50-65	50-65
Comparison Example 2	Hydrophobic polypropy-lene coated with diethylene glycol vinyl ether	2.5-3.6	4.0-4.4	4.2-7.2	0.6-1.0	2.4-5.5	4.2-7.2
Comparison Example 3	Hydrophobic polypropyl-ene coated with triethylene glycol allyl ether	3.8	---	---	---	---	---
Example according to the invention	Hydrophobic polypropyl-ene coated with glycerol monoallyl ether	0.3-2.0	3.9-4.1	0.3-0.6	0.3-0.5	3.1-3.4	0.3-0.6

--- = not measured

Table 1 continued: Protein Loss in 1.5 ml Safe Lock Vessels

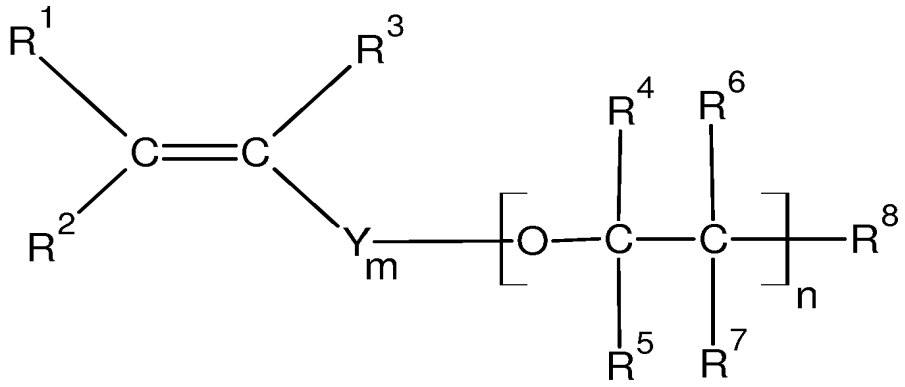
Samples	Composition	Cytochrome C Loss [%]			Fibrinogen Loss [%]		
		untreated	after aceto-nitrile/water	after 1X autoclaving at 121°C	untreated	after aceto-nitrile/water	after 1X autoclaving at 121°C
Comparison Example 1	Untreated hydrophobic polypropylene	45-60	45-60	45-60	75-90	75-90	79---
Comparison Example 2	Hydrophobic polypropyl-ene coated with diethylene glycol vinyl ether	2.1-16.6	6.4-9.2	4.2-7.2	5.2-7.1	18.4-24.4	20-30
Comparison Example 3	Hydrophobic polypropyl-ene coated with triethylene glycol allyl ether	---	---	---	---	---	---
Example according to the invention	Hydrophobic polypropyl-ene coated with glycerol monoallyl ether	0.3-0.4	6.7-7.5	0.3-0.6	0.5-1.2	11.3-12.9	1.8-2.7

--- = not measured

[00107] Comparison Examples 2 and 3 are vessels prepared in accordance with the teachings of DE 195 48 152 A1 and US 6,482,531 B1, respectively. Example 1 represents a vessel prepared in accordance with the teaching of the present invention using the monoallyl ether of glycerol as the monomer. The data in the table shows that protein loss is significantly reduced when using a coating in accordance with the present invention. This applies in particular to protein losses measured after the vessel had been subjected to contacting with acetonitrile/water or autoclaving at higher temperatures.

CLAIMS

1. A coated substrate comprising (i) a surface and (ii) a coating, said coating comprising a polymerization product of a monomer according to Formula (I)



(I),

wherein

m = 1 to 4;

n = 1 to 5;

Y represents (CR^9R^{10}),

R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^9 and R^{10} each independently represents:

H,

OH,

halogen,

C_1-C_4 alkyl,

C_1-C_4 alkenyl,

C_1-C_4 alkynyl

C_1-C_4 dienyl,

C_1-C_4 alkoxy or

C_1-C_4 alkyl halide and

R^8 represents

H,

halogen,

C_1-C_4 alkyl,

C_1-C_4 polyhydroxyalkyl or hydroxyalkyl,

C_1-C_4 alkenyl,

C_1-C_4 dienyl,

C_1-C_4 alkynyl,

C_1-C_4 haloalkyl,

C_1-C_4 aldehyde,

C_1-C_4 ketone,

C_1-C_4 epoxide,

C_1-C_4 carboxylic acid,

C_1-C_4 ester,

$CH=CHR^{11}$, where R^{11} is H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 aldehyde, C_1-C_4 ketone, C_1-C_4 alkoxy, C_1-C_4 epoxide, C_1-C_4 carboxylic acid, or C_1-C_4 ester, or

OR^{12}, where R^{12} is C_1-C_4 alkyl, C_1-C_4 alkenyl, C_1-C_4 dienyl, C_1-C_4 alkynyl, C_1-C_4 haloalkyl, C_1-C_4 aldehyde, C_1-C_4 ketone, C_1-C_4 epoxide, C_1-C_4 carboxylic acid, or C_1-C_4 ester.

2. A coated substrate according to claim 1, wherein R^1, R^2, R^3, R^9, and R^{10} each independently represent H or C_1-C_4 alkyl; m is 1; and R^4, R^5, R^6, R^7 each independently represent H or OH; and R^8 represents C_1-C_4 polyhydroxyalkyl or C_1-C_4 hydroxyalkyl.

3. A coated substrate according to claim 2, wherein the monomer is glycerol monoallyl ether.

4. A coated substrate according to any one of claims 1 to 3, wherein the coating comprises the polymerization product of at least two different monomers according to Formula (I).

5. A coated substrate according to any one of claims 1 to 4, wherein the coating comprises units derived from a comonomer effecting cross-linking.

6. A coated substrate according to any one of the preceding claims wherein the polymerization product is formed by chemical vapour deposition (CVD), in particular plasma enhanced CVD.

7. A coated substrate according to any one of the preceding claims wherein the substrate comprises a material selected from the group consisting of plastics, sintered materials, glass, ceramics, metals, filter media, surface finishes, primed and pre-coated materials.

8. A coated substrate according to claim 7 wherein the plastic is selected from the group consisting of polyolefins, polyamides, polyesters, silicones, polyurethanes, epoxies, acrylics, polyacrylates, polyesters, polysulfones, polyether-ketones, liquid crystalline polymers (LCP), poly(meth)-acrylates, polycarbonates, polyimides, polystyrenes (styrenics), vinylics, thermoplastic elastomers (TPE)and fluoropolymers.

9. A coated substrate according to claim 8 wherein the polyolefin is selected from the group consisting of polymers or copolymers of ethylene and propylene.

10. A coated substrate according to claim 7 wherein the glass is silica glass.

11. A coated substrate according to any of the preceding claims, wherein said substrate is selected from the group consisting of vials, flasks, dishes, test tubes, pipette tips, microcentrifuge tubes, syringes, microscope slides, microscope slide assemblies, sample chambers for analytical devices, tapes, laminates, plates, arrays, multi-titer plates and tubing.

12. A coated substrate according to any of the preceding claims, wherein said substrate is selected from the group consisting of bioreactors and elements thereof, fermentors, cultivation bags, beads, chromatography material; chromatographic carriers, membranes, and filters.

13. A coated substrate according to any of the preceding claims, wherein said substrate is selected from the group consisting of a microtitre plate, a microcentrifuge tube, a cell culture consumable, a PCR consumable and a dispensing consumable.

14. A process for the production of a coated substrate as defined in any of the preceding claims, said process comprising:

(i) providing a substrate comprising a surface; and

(ii) coating at least a portion of said substrate surface by means of chemical vapour deposition of a monomer of Formula (I).

15. Process according to claim 14, wherein the polymerization is conducted by plasma enhanced chemical vapour deposition.

16. Process according to claim 15, wherein a combination of plasma techniques is used.

17. Process according to any one of claims 14 to 16, wherein at least two different monomers according to Formula (I) are used.

18. Process according to any one of claims 14 to 16, wherein said process comprises the deposition of comonomers, in particular cross-linking agents.

19. Process according to any one of claims 14 to 18, wherein the chemical vapour deposition includes cross-linking and/or grafting of the monomers of Formula (I) to a surface of the substrate .

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/060914

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D4/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 195 48 152 A1 (BOEHRINGER MANNHEIM GMBH [DE]) 26 June 1997 (1997-06-26) cited in the application the whole document pages 2-3	1-19
X	JP 64 000109 A (NIPPON OILS & FATS CO LTD) 5 January 1989 (1989-01-05) abstract	1-6
X	JP 61 174256 A (NIPPON CATALYTIC CHEM IND) 5 August 1986 (1986-08-05) abstract	1-5
X	DE 103 11 163 A1 (ALBERT LUDWIGS UNI FREIBURG VE [DE]) 23 September 2004 (2004-09-23)	1-5
Y	abstract	1-19

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 July 2012	18/07/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Droghetti, Anna

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 482 531 B1 (TIMMONS RICHARD B [US] ET AL) 19 November 2002 (2002-11-19) cited in the application the whole document	1-19
Y	JP 11 181330 A (UNIV TEXAS [US]) 6 July 1999 (1999-07-06) the whole document	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/060914

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19548152 A1	26-06-1997	DE 19548152 A1	26-06-1997
		EP 0780423 A2	25-06-1997
		JP 9187727 A	22-07-1997
JP 64000109 A	05-01-1989	JP 2621308 B2	18-06-1997
		JP 64000109 A	05-01-1989
JP 61174256 A	05-08-1986	NONE	
DE 10311163 A1	23-09-2004	NONE	
US 6482531 B1	19-11-2002	US 6482531 B1	19-11-2002
		US 2003113477 A1	19-06-2003
JP 11181330 A	06-07-1999	CA 2243869 A1	08-02-1999
		JP 11181330 A	06-07-1999