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Feature article

Fluorinated poly(meth)acrylate: Synthesis and properties

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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.

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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

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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.

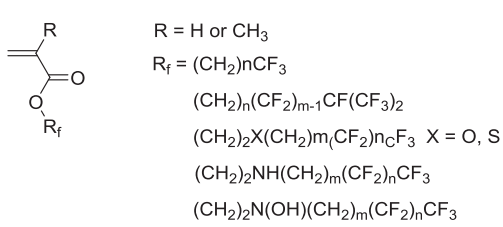


Fig. 1. Commercially available fluorinated alkyl (meth)acrylates.

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 ([2π + 2π] 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].

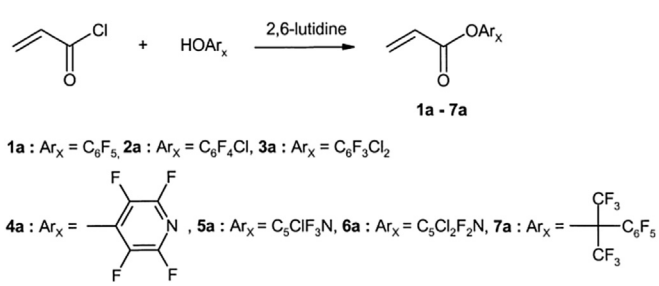


Fig. 2. Synthesis of fluorinated aryl acrylates. Reprinted with permission from Ref. [23].

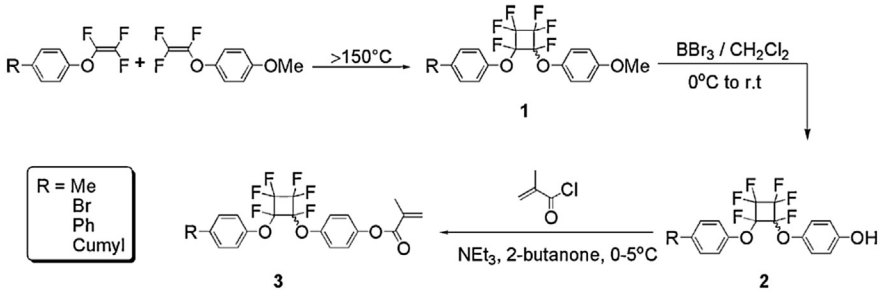


Fig. 3. Synthesis of PFCB-containing methacrylates. Reprinted with permission from Ref. [26].

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.

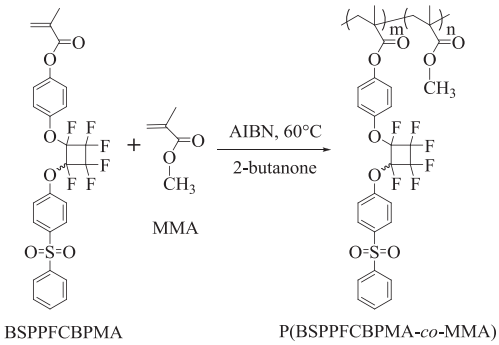


Fig. 4. Synthesis of P(BSPPFCBPMA-*co*-MMA) random copolymer. Reprinted with permission from Ref. [27].

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-

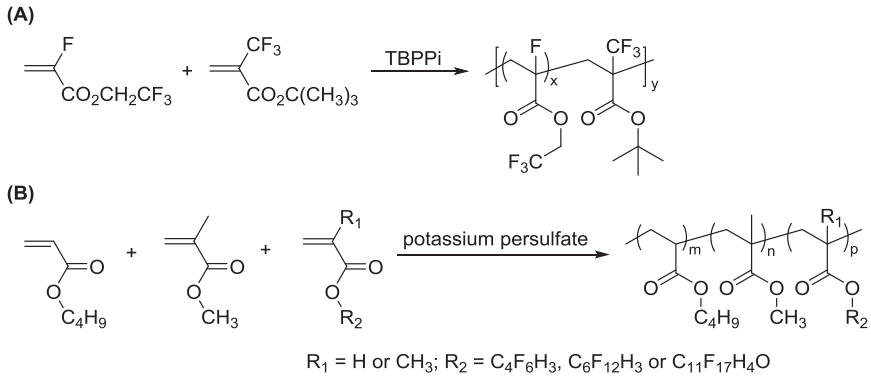


Fig. 5. Random copolymerization initiated by peroxide and persulfide initiators. Reprinted with permission from Refs. [36,39].

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

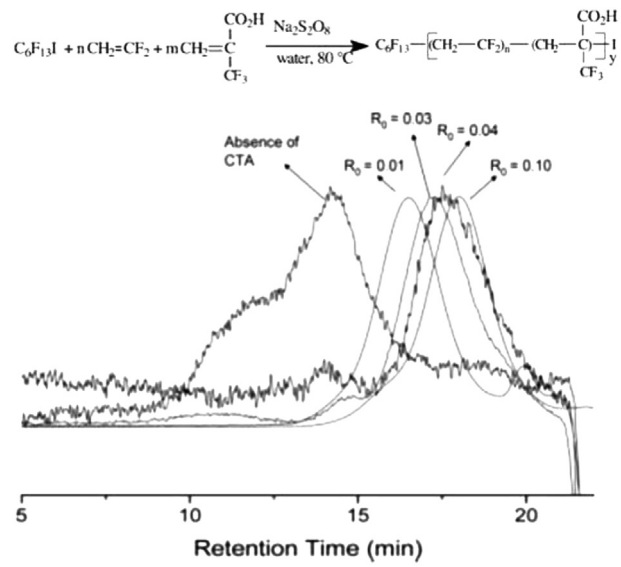


Fig. 6. SEC chromatograms of poly(TFMA-*co*-VDF) random copolymers obtained by ITP with different feeding ratios (R_0 = $[CTA]_0$)/($[VDF]_0$+$[TFMA]_0$). Reprinted with permission from Ref. [49].

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

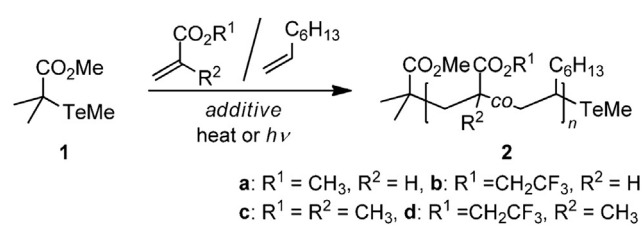


Fig. 7. Random copolymerization of (meth)acrylates and 1-octene. Reprinted with permission from Ref. [51].

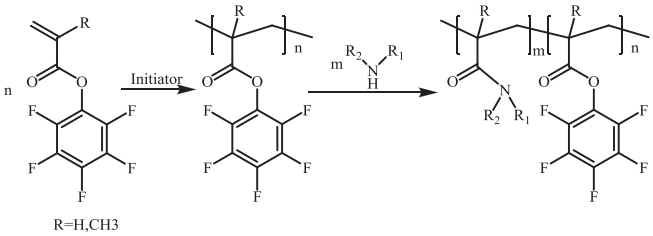


Fig. 8. Synthesis of fluorinated random copolymers from active ester polymers. Reprinted with permission from Ref. [22].

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. [55] 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.

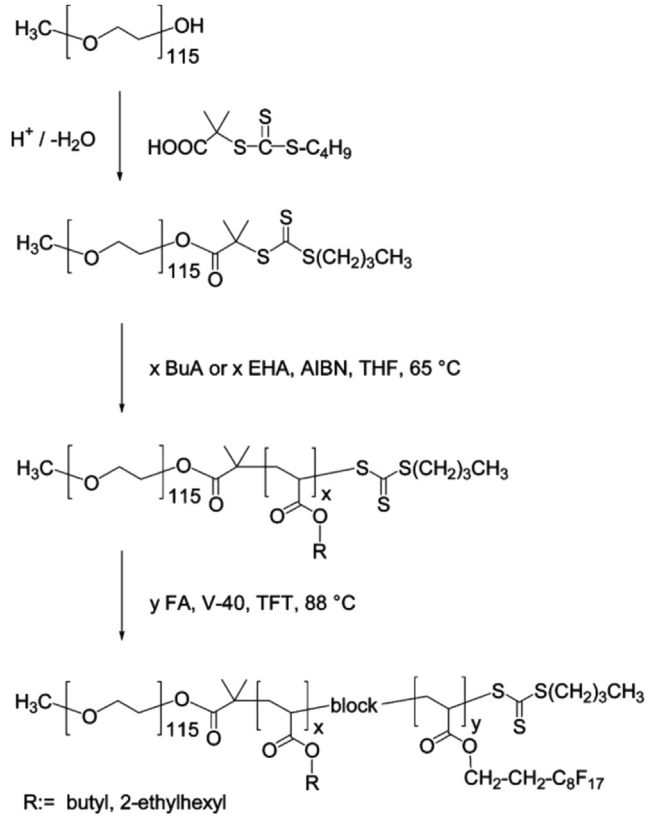


Fig. 10. Synthesis route of PEO-*b*-PBA-*b*-PFA and PEO-*b*-PEHA-*b*-PFA. Reprinted with permission from Ref. [56].

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-

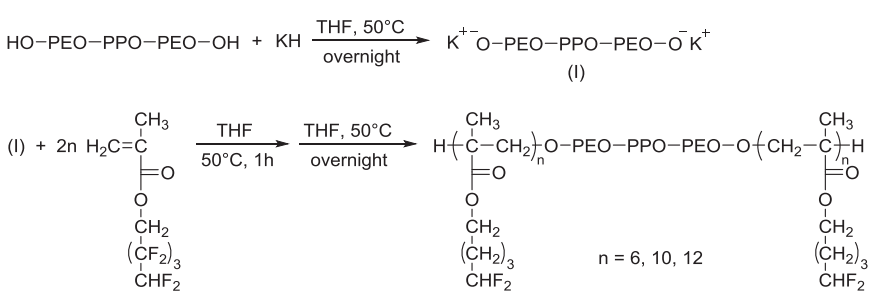


Fig. 9. Synthesis of fluorine-containing pentablock copolymer via oxyanion-initiated polymerization. Reprinted with permission from Ref. [55].

(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

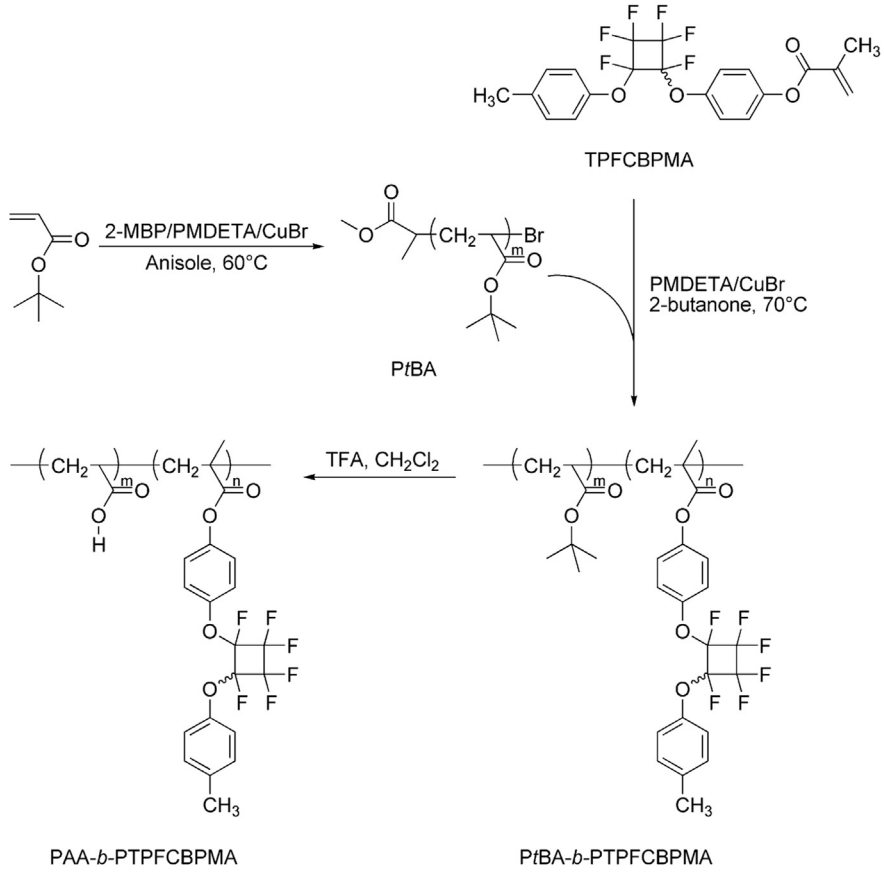


Fig. 11. Synthesis of PAA-*b*-PTPFCBPMA amphiphilic diblock copolymer by successive ATRP. Reprinted with permission from Ref. [66].

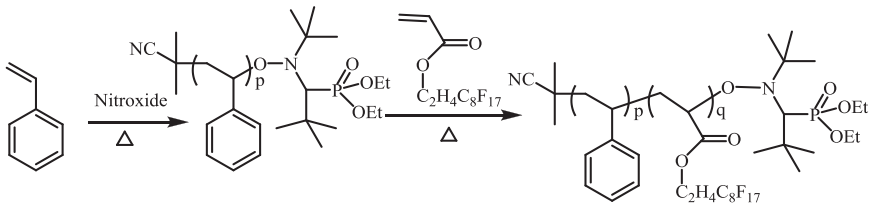


Fig. 12. Synthesis of PS-*b*-PFDA diblock copolymer by NMP. Reprinted with permission from Ref. [69].

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. [69] 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

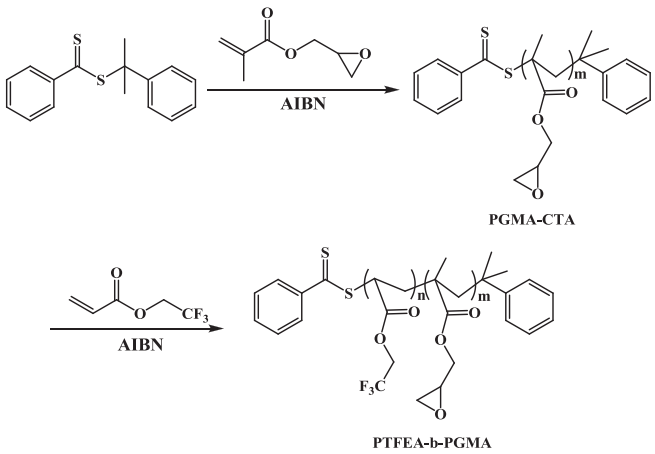


Fig. 13. Synthesis of PTFEA-*b*-PGMA diblock copolymer by successive RAFT polymerization. Reprinted with permission from Ref. [70].

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

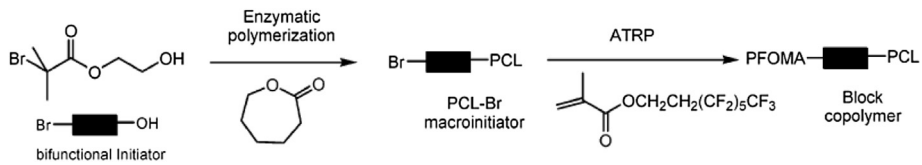


Fig. 14. Synthesis of fluorine-containing PFOMA-*b*-PCL diblock copolymer by sequential ROP and ATRP. Reprinted with permission from Ref. [80].

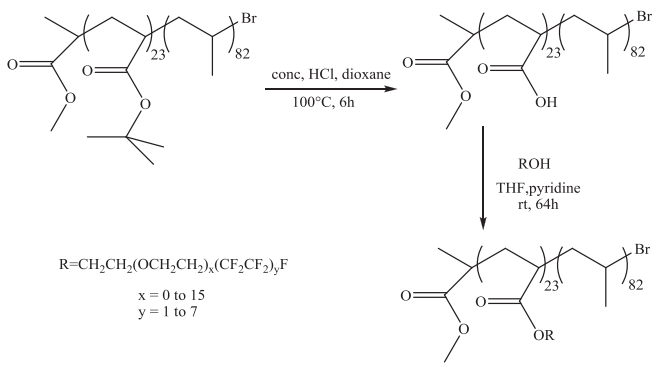


Fig. 15. Synthesis of poly(ethoxylated fluoroalkyl acrylate)-*block*-polystyrene. Reprinted with permission from Ref. [82].

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

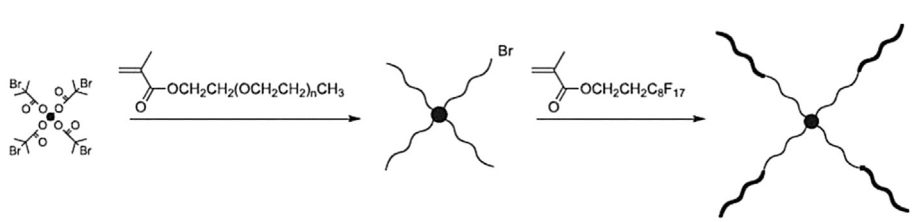


Fig. 16. Synthesis of 4-arm star-branched block copolymer by successive ATRP. Reprinted with permission from Ref. [83].

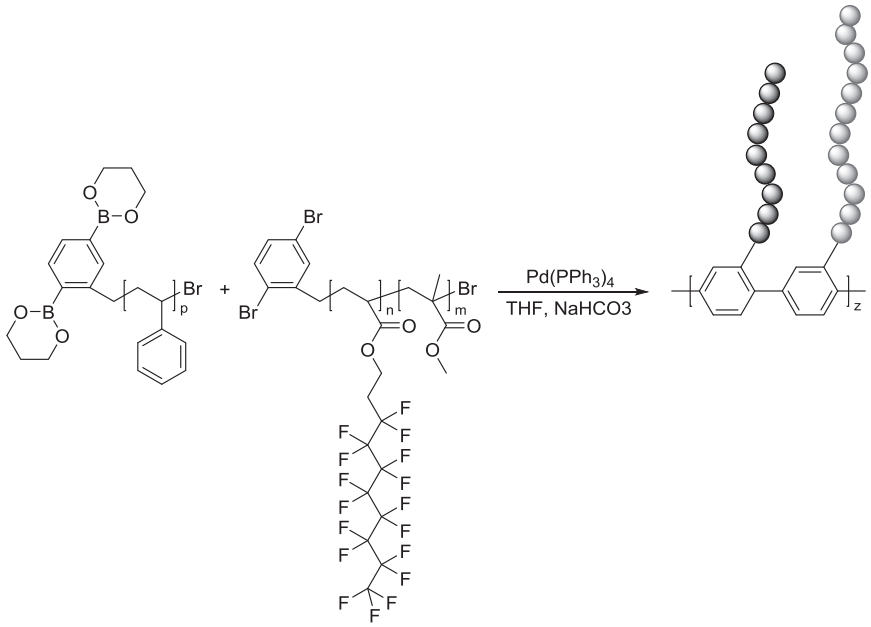


Fig. 17. Synthesis of graft copolymer by Suzuki polycondensation. Reprinted with permission from Ref. [84].

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.

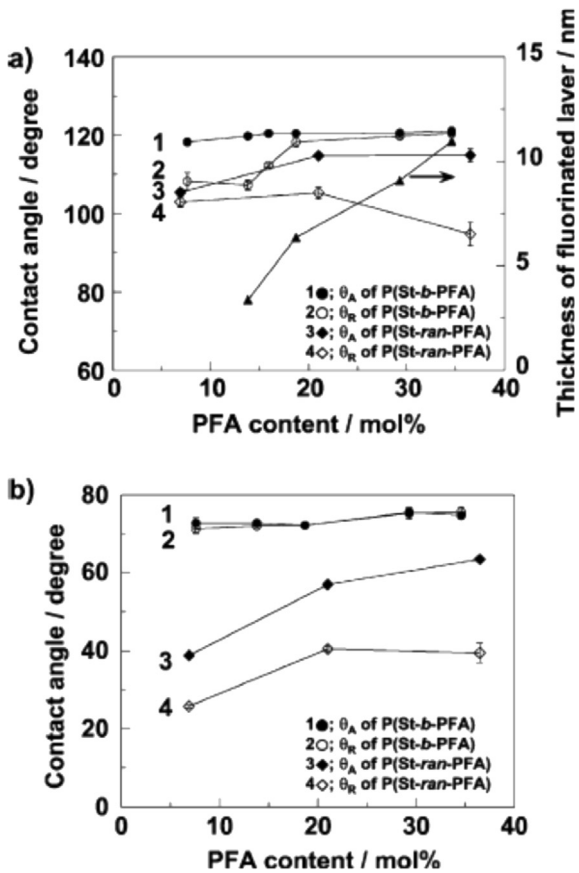


Fig. 18. Relation of dynamic contact angle to PFA content: (a) water and (b) dodecane. Reprinted with permission from Ref. [67].

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 [89] 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

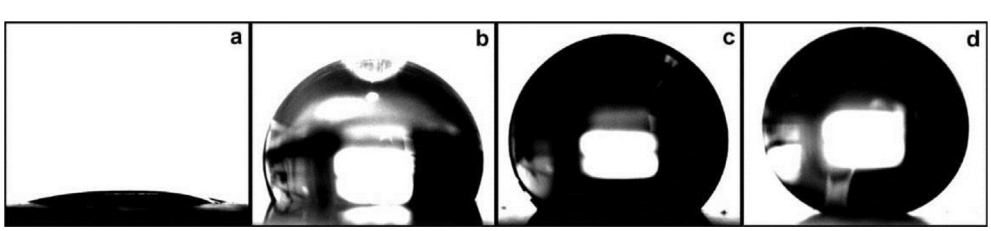
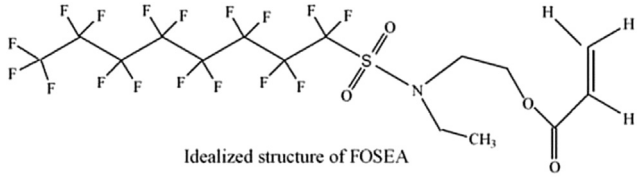


Fig. 19. Photographs of water droplets sitting on films prepared from Si (a) and Si bearing 1.2% (b), 4.8% (c), and 5.8% (d) of P1. Reprinted with permission from Ref. [78].



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

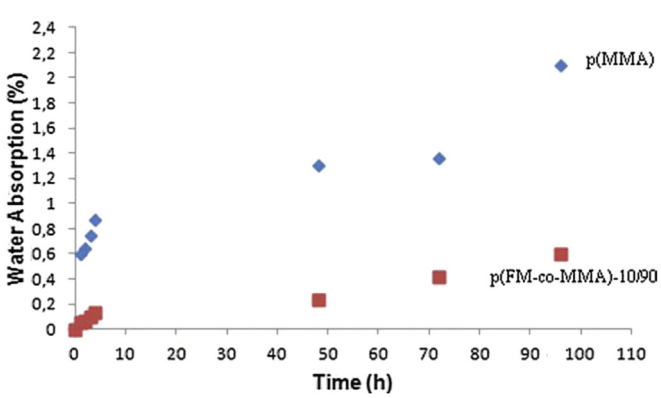


Fig. 21. Water absorption of pure PMMA and P(FM-*co*-MMA)-10/90. Reprinted with permission from Ref. [24].

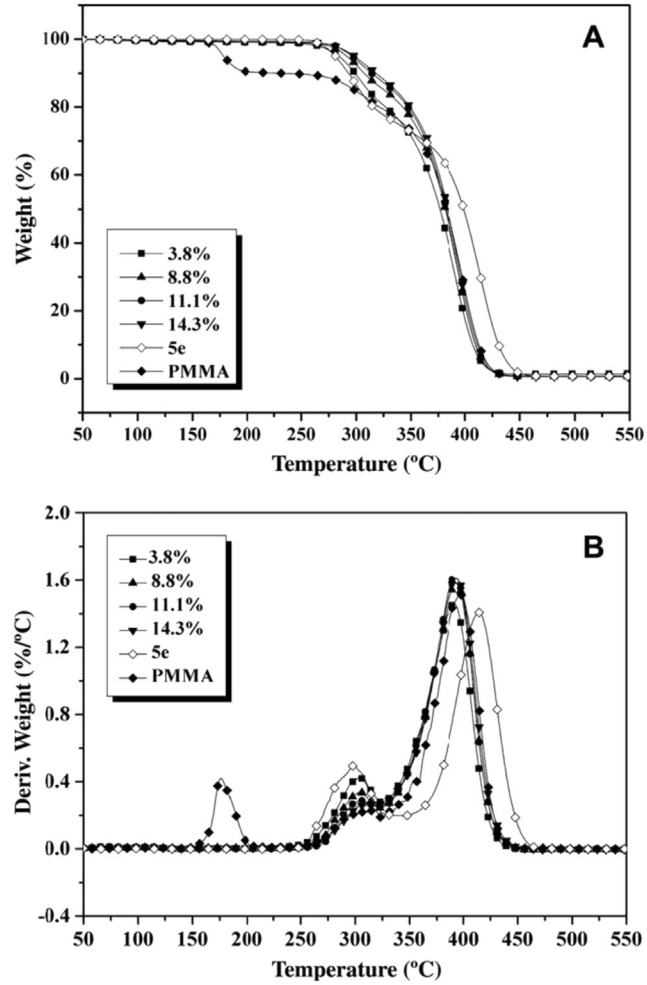


Fig. 22. TG (A) and DTG (B) curves of P(BSPPFCBPMA-*co*-MMA) with different compositions and PMMA (M_n = 35,000, M_w/M_n = 1.64). Reprinted with permission from Ref. [27].

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].

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

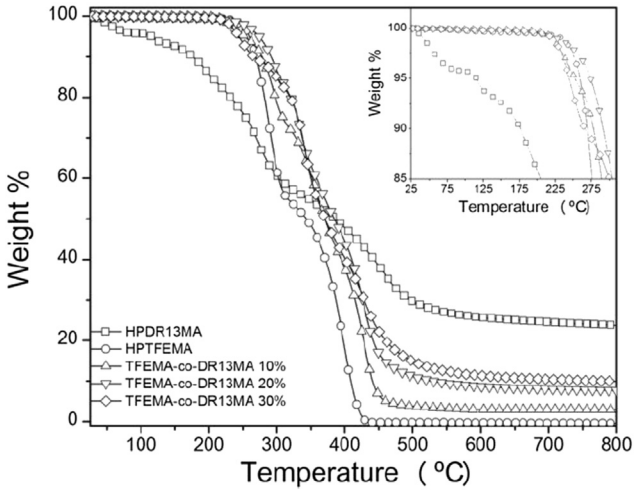


Fig. 23. TG curves of P(TFEMA-*co*-DR13MA) copolymers along with HPTFEMA and HPDR13MA homopolymers. Reprinted with permission from Ref. [29].

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. [53] 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.

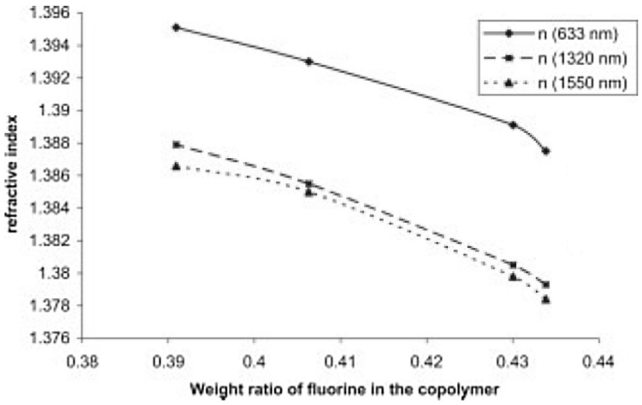


Fig. 24. Refractive index (20 °C) *vs.* weight content of fluorine in poly(FATRIFE-*co*-MAF-TBE) copolymers, measured at three different wavelengths: 633, 1320, and 1550 nm. Reprinted with permission from Ref. [36].

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-pentadecafluoroocanamide 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

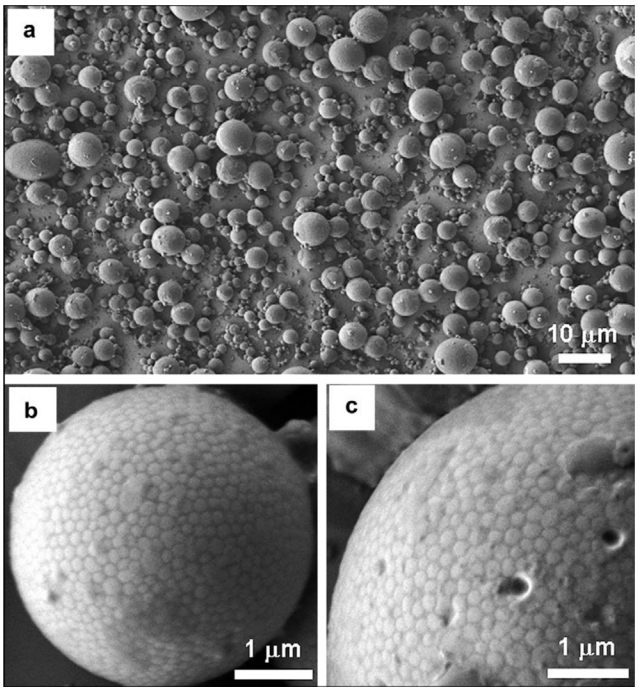


Fig. 25. SEM images of microspheres of P*t*BA-*b*-P(2-[(perfluorononenyl)oxy]ethyl methacrylate) copolymer. Reprinted with permission from Ref. [63].

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

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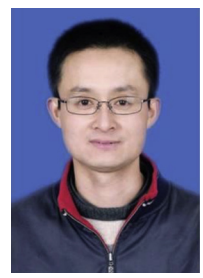

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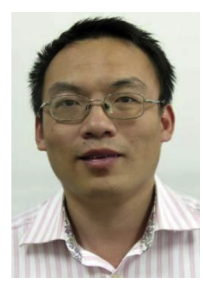

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