

Plasma Polymerization

H. Yasuda

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1985



ACADEMIC PRESS, INC.

(Harcourt Brace Jovanovich, Publishers)

Orlando San Diego New York London
Toronto Montreal Sydney Tokyo

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ACADEMIC PRESS, INC.
Orlando, Florida 32887

United Kingdom Edition published by
ACADEMIC PRESS INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Yasuda, H.
Plasma polymerization.

Includes index.
1. Polymers and polymerization. 2. Plasma chemistry.
I. Title.
QD381.8.Y37 1985 547.7 84-24350
ISBN 0-12-768760-2 (alk. paper)

PRINTED IN THE UNITED STATES OF AMERICA

85 86 87 88 9 8 7 6 5 4 3 2 1

Contents

Preface	ix
1 Introduction	
Text	1
References	3
2 Scope of Polymer Formation by Plasma Polymerization	
2.1 Preferred Form of Plasma Polymers	4
2.2 Plasma-State Polymerization versus Plasma-Induced Polymerization	5
2.3 Plasma Polymerization versus Graft Polymerization	7
2.4 Plasma Polymerization versus Radiation Polymerization	9
References	10
3 Fundamental Aspects of Gas-Phase Reactions	
3.1 Gas in a Closed System	11
3.2 Diffusion and Flow of Gas	15
3.3 Flow Rate and System Pressure of Flow	18
References	18
4 Fundamental Aspects of Ionized Gas	
4.1 Plasma for Plasma Polymerization	19
4.2 Macroscopic Treatment of Glow Discharge	20
4.3 Microscopic Treatment of Glow Discharge	23
4.4 Microscopic Treatment of Plasma	35
References	43
5 Fundamental Aspects of Polymerization	
5.1 Classification of Polymerization by Growth Mechanism	44
5.2 Addition Polymerization	49

5.3	Radiation Polymerization	59
5.4	Polymerization in a Vacuum	63
	References	71
6	Kinetic and Mechanistic Aspects of Plasma Polymerization	
6.1	Role of Ionization in Plasma Polymerization	73
6.2	Growth Mechanism of Plasma Polymerization	79
6.3	Reactive Species in Plasma Polymerization	82
6.4	Free Radicals in Plasma Polymers	86
6.5	Incorporation of Nonpolymerizable Gases in Plasma Polymers	115
6.6	Interpretation of Plasma Diagnostic Data	131
6.7	Interpretation of Polymer Properties	143
6.8	Atomic (Nonmolecular) Nature of Plasma Polymerization	166
	References	176
7	Competitive Ablation and Polymer Formation in Plasma	
7.1	Overall Reactions in a Plasma Polymerization System	178
7.2	Classification of Gases for Plasma	183
7.3	Ablation by Plasma	184
7.4	Dependence of Ablation on Operational Parameters	186
7.5	Simultaneous Sputter Coating and Plasma Polymerization	189
	References	195
8	Kinetic and Mechanistic Aspects of Polymer Deposition in Plasma Polymerization	
8.1	Polymerization and Deposition Mechanisms	196
8.2	Mass Balance in a Plasma Polymerization System	201
8.3	Distribution of Polymer Deposition	205
8.4	Dependence of Growth Reactions on Diffusional (Kinetic) Path Length	229
8.5	Polymer Deposition in a Closed System and in a Flow System	253
8.6	Overall Kinetics of Polymer Deposition	260
8.7	Simultaneous Polymerization–Deposition Mechanisms	273
	References	275
9	Operational Parameters of Plasma Polymerization	
9.1	Pressure of a Steady-State Flow System	277
9.2	System Pressure under a Glow Discharge	279
9.3	Factors That Determine Pressure under a Glow Discharge	281
9.4	Monomer Flow Rate	287
9.5	Determination of Flow Rate	288

9.6	Meaning of Flow Rate in a Plasma Polymerization System	290
9.7	Power Input of Plasma Polymerization	292
9.8	Effect of Power on the Volume and Intensity of Plasma	292
9.9	Plasma Energy Density and Input Power	295
9.10	Discharge Power for Polymer-Forming Plasma	298
9.11	Composite Power Parameter for Plasma Polymerization	301
9.12	Domains of Plasma Polymerization	309
9.13	Location of Polymer-Collecting Surface and Frequency of Electric Power Source	313
9.14	Stationary and Moving Substrates	315
9.15	Magnetron Discharge for Plasma Polymerization	319
	References	332
10	General Characteristics of Plasma Polymers	
10.1	Free Radicals in Plasma Polymers	334
10.2	Internal Stress in Plasma Polymers	337
10.3	Solubility and Fusibility of Plasma Polymers	344
10.4	Surface Properties of Plasma Polymers	344
10.5	Permeability Characteristics of Plasma Polymers	355
10.6	Adhesion of Plasma Polymers	359
	References	369
11	Electrical Properties of Plasma-Polymerized Thin Organic Films	
11.1	Historical Background	370
11.2	Dielectric Properties of Plasma-Polymerized Organic Films	372
11.3	Electrical Conduction in Plasma-Polymerized Organic Films	395
11.4	Concluding Remarks	414
	References	416
	Index	419

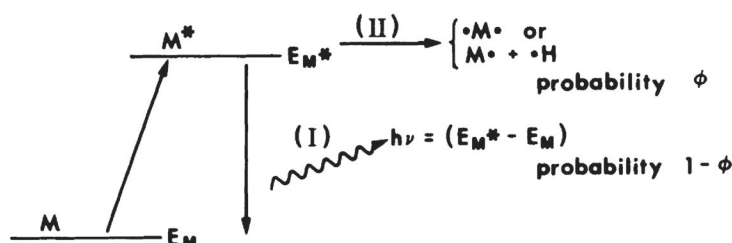


Fig. 6.12 Schematic representation of the dissipation of the excess energy of an excited molecule M^* .

If we take the probability of M^* following the second process (chemical reactions to form reactive species) to be ϕ , the probability of photon emission is given by $1 - \phi$. Then the intensity I_0 of photon emission can be given by

$$I_0 = (h\nu)n(1 - \phi) = n(1 - \phi)(E^* - E), \quad (6-10)$$

where n is the number of monomer molecules excited to M^* in unit time. Thus, the intensity of photon emission and the consequential irradiation effect are greater when the excited-state energy is larger, the number of excited molecules is larger, and the probability of free radical formation by the dissociation is smaller.

Assuming that n is proportional to p in the gas phase, according to the empirical relationship used to derive Eq. (6-9),

$$I_0 = K \Delta E p(1 - \phi), \quad (6-11)$$

where K is a proportionality constant and ΔE the energy level difference between an excited state and the ground state of a monomer, that is, $\Delta E = E^* - E$.

Because the quantity of free radicals trapped in the plasma polymer is proportional to the total quantity of free radicals produced, it should be proportional to ϕ . When ϕ increases, $1 - \phi$ decreases; thus, when the free radicals trapped in the plasma polymer increase, the free radicals formed in the substrate decrease.

6.4.3 STRUCTURE OF MONOMERS AND FREE RADICALS IN PLASMA POLYMERS

The structure of a monomer plays an important role in determining the quantity of free radicals trapped in the plasma polymer. For instance, when group III monomers polymerize, producing free radicals mainly by hydrogen detachment, the number of species in the gas phase that do not yield free radicals increases, which leads to a lower overall probability ϕ . Therefore,

Table 6.9**ESR SPIN CONCENTRATION IN PLASMA POLYMERS AND GLASS SUBSTRATES^a**

Monomer	$C_s^0 \times 10^{-19}$ (spins/cm ³)			$C_g \times 10^{-15}$ (spins/cm ²)		
	Continuous	Pulsed	Change ^b	Continuous	Pulsed	Change ^b
C ₂ H ₂	8.6	15.6	7 (81)	0	0	0
C ₆ H ₆	3.2	1.6	−1.6 (−50)	0	0	0
C ₆ F ₆	7.4	5.4	−2.0 (−27)	0	0	0
Styrene	3.8	0.54	−3.26 (−86)	0	0	0
C ₂ H ₄	1.36	14.5	13.1 (970)	4.0	0.85	−3.15 (−79)
C ₂ F ₄	13.0	8.4	−4.6 (−35)	11.2	1.8	−9.4 (−84)
Cyclohexane	0.84	0	−0.84 (−100)	1.1	0	−1.1 (−100)
Ethylene oxide	0.75	0.5	−0.25 (−33)	6.6	1.6	−5.0 (−76)
Acrylic acid	0.76	1.85	1.09 (140)	4.4	0	−4.4 (−100)
Propionic acid	1.0	1.0	0 (0)	6.3	1.6	−4.7 (−75)
Vinyl acetate	0.42	0.33	−0.09 (−21)	6.1	1.8	−4.3 (−71)
Methyl acrylate	0.31	0.15	−0.16 (−52)	6.4	1.5	−4.9 (−77)
Hexamethyldisilane	0.5	0.24	−0.26 (−52)	0	0	0
Tetramethyldisiloxane	0.49	0.05	−0.44 (−90)	0	0	0
Hexamethyldisiloxane	0.21	0	−0.21 (−100)	0	0	0
Divinyltetramethyldisiloxane	0.15	0.05	−0.10 (−67)	0	0	0

^a From Yasuda and Hsu (11).^b Changes are based on values of continuous discharge. Numbers in parentheses are percentages.

group III monomers yield plasma polymers containing the least number of free radicals, but the substrate contains the highest concentration of free radicals; that is, the irradiation effect associated with the plasma polymerization is the highest.

The formation of free radicals from monomers containing a triple bond, a double bond, or a cyclic structure proceeds by the cleavage of a covalent bond, which (1) forms a diradical and (2) does not increase the number of gas molecules (no H_2 is produced). Once diradicals are formed, polymer formation can proceed via cycle II in Fig. 6.1, which leads to the free radical "living polymer" without complete quenching of free radicals.

Thus, it can be easily understood that group I monomers yield plasma polymers with the highest level of trapped free radicals, and the irradiation effect associated with the plasma polymerization of these monomers is the lowest. Group II monomers yield plasma polymers with a moderate level of trapped free radicals, and the irradiation effect is also moderate.

This overall relationship is supported by experimental results obtained by using a pulsed radio frequency (rf) discharge (11). When similar experiments with glass substrates, as described earlier, were carried out by using a pulsed rf (100 μ sec on, 900 μ sec off) power source, the glass signal always decreased by a factor somewhat close to the duty cycle of the pulse (Table 6.9). With some monomers (e.g., ethylene, acetylene, acrylic acid, vinyl fluoride, and vinylidene fluoride), however, the trapped free radicals increased significantly when pulsed plasma was used. The reason for such a large increase in trapped free radicals is not quite clear; however, it provides strong proof that the free radicals trapped in plasma polymers are not produced by the irradiation mechanism. The increase in trapped free radicals due to the pulsed discharge found for double-bond-containing monomers can be explained, at least in part, by the following principle. Unlike the free radical chain-growth polymerization of vinyl monomers, the formation and dissipation (by recombination) of free radicals in plasma are not sequential, and they can be considered to be independent processes, which is a key principle in the RSGP mechanism for plasma polymerization discussed in the previous section. The effect of a pulsed rf discharge is discussed in more detail in the following section.

6.4.4 EFFECT OF PULSED RADIO FREQUENCY GLOW DISCHARGE

As shown in the previous section, a large quantity of the free radicals found in plasma polymers are due primarily to the mechanisms of polymer formation. According to the growth mechanisms of plasma polymerization shown in Fig. 6.1, there are two major cycles; cycle I consists of reactions of

monoradicals, and cycle II consists of reactions of diradicals. Because both kinds of radicals are formed simultaneously, reactions between monoradicals and diradicals also occur depending on the concentrations of both radicals; that is, reaction (6-3) is the cross-cycle reaction.

The results of ESR studies show that the presence of a triple bond, a double bond, and an aromatic structure in the monomer results in a large number of free radicals in the plasma polymer. Because the homolytic scission of the π bond of a double or a triple bond yields a diradical, polymer formation via diradicals would play an important, if not dominant, role in the plasma polymerization of such monomers. The reactions in cycle II do not terminate free radicals, and the cycle itself leads to a free radical "living polymer" that contains a large number of free radicals.

In contrast to those in cycle II, the reactions in cycle I are essentially the recombination reactions of free radicals, which dissipate free radicals and yield species that have no free spins. On the other hand, the completion of the termination reactions and the formation of free radicals by excitation and reexcitation occur independently. Therefore, the complete recombination of free radicals formed would not be realized even in a case in which only cycle I could take place; consequently, there would still be some free radicals in the plasma polymer. It is anticipated, however, that the concentration of free radicals would be much smaller than in the case where cycle II predominates.

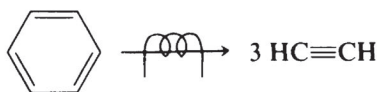
The effect of a pulsed rf discharge can be reviewed in terms of this growth mechanism. On the basis of the anticipated contribution of cycle I and cycle II, three representative cases might be chosen, that is, (1) primarily cycle I, (2) nearly equal contributions of cycle I and cycle II, and (3) predominantly cycle II with a small contribution of cycle I. Group I monomers are expected to belong to case (3), group II to case (2), and group III to case (1).

When a pulsed rf discharge is employed, cycle I ceases while the discharge is "off," whereas cycle II can keep going during the "off" period. Furthermore, during the "off" period, the cross-cycle reaction [(6-3)] also ceases, leading to a reduction in the dissipation of diradicals by the cross-cycle reaction. On the basis of the contribution of the cross-cycle reaction, the effect of the pulsed rf discharge would be most dramatic if the contributions of cycle I and cycle II were comparable. This is indeed the case, as shown by the experimental results in Table 6.9; that is, free radicals in the plasma polymer of ethylene increased nearly 10-fold when a pulsed rf discharge was employed. In the case of acetylene, which makes a relatively small contribution to cycle I (based on the detachment of hydrogen), the increase of free radicals in the plasma polymer is less pronounced (81% increase). In the case of tetramethyldisiloxane (primarily cycle I), the pulsed rf discharge decreases the free radical concentration in the plasma polymer, which can be explained by the more complete coupling of free radicals before new free radicals are formed by the subsequent "on" cycle of the pulsed rf discharge.

The unexpected and conspicuous increase of free radicals in plasma polymers of some monomers can be thus explained on the basis of the rapid step-growth mechanism. Examining why not all group I monomers showed an increase in free radicals by the pulsed rf discharge may provide further insight into the growth mechanism of plasma polymerization. A notable difference can be detected for monomers that contain certain aromatic structure (e.g., benzene and styrene showed a substantial decrease of free radicals in the plasma polymers by pulsed rf discharge).

6.4.4.1 AROMATIC STRUCTURE

Acetylene ($\text{HC}\equiv\text{CH}$) and benzene () are very similar in their plasma polymerization characteristics. Both compounds form plasma polymers with the least amount of hydrogen production (group I monomer), and their characteristics of copolymerization with N_2 and/or H_2O are nearly identical if we consider that one molecule of benzene is equivalent to three molecules of acetylene:



Analysis of the gas phase in both closed and flow systems is given in Tables 6.10 and 6.11. The most remarkable difference in these data is found

Table 6.10

EFFECT OF PULSED RADIO FREQUENCY ON ACETYLENE AND BENZENE IN A CLOSED SYSTEM^a

Polymerization parameter	Acetylene		Benzene	
	Continuous	Pulsed	Continuous	Pulsed
$t^{1/2}$ (sec)	1.0	5.0	2.5	18.5
Monomer type parameter γ^b	0.17	0.16	0.15	0.15
Fraction of residual vapor X^c	0.023	0.021	0.014	0.010
Hydrogen yield y^d	0.15	0.14	0.13	0.14
Polymer yield $Z = 1 - X$	0.98	0.98	0.99	0.99

^a From Yasuda and Hsu (11).

^b Monomer type parameter $\gamma = p_\infty/p_0$, where p_0 is initial monomer pressure in a closed system and p_∞ the pressure after glow discharge.

^c Fraction of residual vapor $X = (p_\infty - p_{\text{H}_2})/p_0$, where p_{H_2} is the pressure after the cold finger is surrounded by liquid N_2 .

^d Hydrogen yield $y = p_{\text{H}_2}/p_0$.

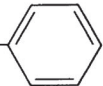
Table 6.11VAPOR-PHASE ANALYSIS IN A FLOW SYSTEM AT STEADY STATE^a

Parameter	Acetylene		Benzene	
	Continuous	Pulsed	Continuous	Pulsed
Total vapor pressure at steady state in glow discharge ($\mu\text{m Hg}$)	5.1	10.7	5.8	12.4
Vapor pressure after condensation with liquid N_2 (H_2 pressure) ($\mu\text{m Hg}$)	3.4	4.8	3.8	6.3
H_2 (%)	68	45	66	51
Condensable vapor (%)	32	55	34	49

^a From Yasuda and Hsu (11).

in the dissipation rates of monomer given by $t_{1/2}$ indicating that acetylene polymerizes (disappears from the gas phase) ~ 2.5 times faster than benzene. This difference is not very surprising if we recognize that we are measuring the rate of disappearance of the number of gas molecules. As far as the effect of pulsed rf discharge (on the gas-phase kinetic data) is concerned, these data indicate that the effect is nearly the same for acetylene and benzene.

In contrast, the concentration of ESR spins in plasma-polymerized polymers showed noteworthy differences between acetylene and benzene. Spin concentrations given in Table 6.9 are cited here for a comparison of acetylene, benzene, styrene, and ethylene.

Compound	$C_s^0 \times 10^{-19}$ (spins/ cm^3)	
	Continuous	Pulsed
$\text{HC}\equiv\text{CH}$	8.6	15.6
	3.2	1.6
$\text{H}_2\text{C}=\text{CH}$ - 	3.8	0.54
$\text{H}_2\text{C}=\text{CH}_2$	1.4	14.5

The effects of a pulsed rf discharge on the free radicals trapped in the plasma polymers of these monomers are most pronounced. When pulsed plasma is employed, the concentration of the trapped free radicals changes from that in continuous plasma. The ratio (free radicals by pulsed

plasma)/(free radicals by continuous plasma) for acetylene is 1.8, and the corresponding ratios for benzene and styrene are 0.5 and 0.14, respectively. Namely, an increase in trapped free radicals by the use of pulsed plasma is observed only with acetylene, and a decrease is observed with benzene and styrene. Consequently, the difference between acetylene and styrene becomes nearly 30 times that of the concentration in styrene, whereas this ratio for continuous plasma is only about 2.0.

It is important to note that all of these monomers, excluding ethylene, are group I monomers, and their behavior in plasma polymerization, except under pulsed plasma conditions, is very similar to that described in previous sections and chapters. These conspicuous differences observed as a consequence of the use of pulsed plasma may be attributed to the behavior of the aromatic structure under the conditions of plasma polymerization.

Although numerous kinds of reactions could occur in plasma, as far as the dissipation of vapor-phase molecules (plasma polymerization) is concerned, one benzene molecule behaves as three acetylene molecules. Consequently, the final polymers formed (from acetylene and benzene) under the condition of relatively high W/FM [discharge-power-independent region; where W is discharge wattage, F volume or molar flow rate, and M molecular weight of monomer (details of this composite factor are described in Section 9.11)] are very similar. The transport characteristics of ultrathin films of plasma polymers and copolymers (with N_2 and/or H_2O) of acetylene and benzene are nearly identical.

However, with respect to the kinetics of polymer formation, benzene is one step behind acetylene, and in its original form (without the dissociation of the molecule in plasma) lacks reactions (6-1) and (6-4) of Fig. 6.1. Pulsed rf discharge highlights the difference in a dramatic way. Namely, the diradicals formed by plasma can react with acetylene during the “off” period of the pulsed discharge, although the addition is not a chain reaction with a long kinetic chain length, as discussed in Chapter 5. In contrast, the diradicals cannot react with benzene. Thus, although the olefinic double bonds or triple bonds may conserve the overall concentration of radicals that have built up during the “on” period by the addition onto these bonds during the “off” period of the pulsed discharge, the conjugated double bonds in the aromatic structure evidently do not behave in the same manner. In other words, the diradicals can be conserved by the reaction with the monomer during the “off” period in the case of acetylene and partially in the case of styrene; in the case of aromatic compounds, however, cycle II, the reactive species of which might be identical to those of acetylene, tends to cease during the “off” period because the diradicals cannot react with the original monomer.

Styrene can be viewed as a monomer that combines the effects of a double bond and an aromatic structure. In a continuous discharge, the dominating

factor is that of the phenyl group (styrene is a group I monomer). A large concentration of free radicals in the plasma polymer is due to this phenyl group. With a pulsed rf discharge, the dissociation of the phenyl group ceases during the "off" period, but the contribution of the vinyl double bond is much smaller than that of the triple bond of acetylene, which leads to the net loss. The large increase found with ethylene is due largely to the low value of trapped free radical concentration by the continuous discharge owing to the dissipation of free radicals via reaction (6-3).

Hydrocarbons that show a conspicuous increase of free radicals in plasma polymers upon the application of a pulsed rf glow discharge can be categorized as compounds having a double or triple bond but not an aromatic structure. It is important to note that, even with those monomers, the deposition rates of polymer generally decrease with the pulsed discharge, although the reduction is not as great as one might expect on the basis of the duty cycle of the pulsed discharge.

Table 6.12

PRESSURE PARAMETER δ OF VARIOUS MONOMERS IN CONTINUOUS AND PULSED RADIO FREQUENCY DISCHARGES^a

Monomer	δ^b		
	Continuous	Pulsed	Change ^c
C ₂ H ₂	0.10	0.30	0.2 (200)
C ₆ H ₆	0.13	0.33	0.2 (150)
C ₆ F ₆	0.10	0.15	0.05 (50)
Styrene	0.15	0.28	0.13 (87)
C ₂ H ₄	0.63	0.75	0.12 (19)
C ₂ F ₄	0.65	0.58	-0.07 (-11)
Cyclohexane	1.03	1.25	0.22 (21)
Ethylene oxide	1.45	1.38	-0.07 (-5)
Acrylic acid	2.00	1.43	-0.57 (-29)
Propionic acid	2.30	1.88	-0.42 (-18)
Vinyl acetate	2.25	2.13	-0.12 (-5)
Methyl acrylate	2.25	1.93	-0.32 (-14)
Hexamethyldisilane	1.50	1.20	-0.30 (-20)
Tetramethyldisiloxane	1.15	1.05	-0.10 (-9)
Hexamethyldisiloxane	1.50	1.15	-0.35 (-23)
Divinyltetramethyldisiloxane	0.73	0.75	0.02 (3)

^a From Yasuda and Hsu (11).

^b $\delta = p_g/p_m$, where p_g is the pressure of a steady-state flow in glow discharge and p_m the pressure of monomer before the discharge.

^c Changes are based on values of continuous discharge. Numbers in parentheses are percentages.

Table 6.13DEPOSITION RATES OF VARIOUS MONOMERS IN CONTINUOUS AND PULSED RADIO FREQUENCY DISCHARGES^a

Monomer	Deposition rate $\times 10^8$ (g/cm ² ·min)		
	Continuous	Pulsed	Change ^b
C ₂ H ₂	31	24	-7 (-23)
C ₆ H ₆	110	101	-9 (-8)
C ₆ F ₆	190	149	-41 (-22)
Styrene	173	145	-28 (-16)
C ₂ H ₄	42	43	1 (2)
C ₂ F ₄	18	37	19 (110)
Cyclohexane	92	9	-83 (-90)
Ethylene oxide	15	14	-1 (-7)
Acrylic acid	28	61	33 (120)
Propionic acid	7	15	8 (110)
Vinyl acetate	31	16	-15 (-48)
Methyl acrylate	32	33	1 (3)
Hexamethyldisilane	251	65	-186 (-74)
Tetramethyldisiloxane	191	102	-89 (-47)
Hexamethyldisiloxane	233	43	-190 (-82)
Divinyltetramethyldisiloxane	641	277	-364 (-57)

^a From Yasuda and Hsu (11).^b Changes are based on values of continuous discharge. Numbers in parentheses are percentages.

Notable exceptions to this observation on deposition rates are found for acrylic acid and tetrafluoroethylene. In order to visualize the overall effect of a pulsed discharge, one should refer to the data given in the following tables: pressure parameters in Table 6.12, deposition rates of polymers in Table 6.13, characteristics of ESR spin signals in Table 6.14, and contact angles of water in Table 6.15.

6.4.4.2 POISONING EFFECT OF OXYGEN-CONTAINING FUNCTIONS

The increase in the deposition rate of acrylic acid by a pulsed rf discharge is due to the additional effect of oxygen-containing monomers, which is absent in the case of the other monomers. This effect can be visualized as a poisoning of the growth mechanism of cycle II (diradical cycles in Fig. 6.1), which is apparent from the data of polymer free radicals and glass free spin signals in Table 6.8.

The plasma polymerizations of acetylene and allene are characterized by a high concentration of free radicals trapped in the polymers and very low glass

Table 6.14
CHARACTERISTICS OF SPIN SIGNALS^a

Monomer	Normalized peak height (a.u.) ^b		Peak width (G)		Half-life of initial decay (min)	
	Continuous	Pulsed	Continuous	Pulsed	Continuous	Pulsed
C ₂ H ₂	20.6	56.5	15.7	12.7	60	90
C ₆ H ₆	4.9	2.7	19.6	18.6	32	15
C ₆ F ₆	2.2	2.3	44.1	37.2	60	64
Styrene	5.8	1.5	19.6	14.7	30	55
C ₂ H ₄	2.3	20.1	18.6	20.6	17	18
C ₂ F ₄	7.4	2.4	52.9	45.1	40	25
Cyclohexane	1.6	— ^c	17.6	— ^c	36	— ^c
Ethylene oxide	1.2	1.1	18.6	16.7	65	40
Acrylic acid	1.6	3.5	16.7	17.6	83	115
Propionic acid	1.9	2.4	17.6	15.7	13	10
Vinyl acetate	0.7	0.7	18.6	16.7	26	25
Methyl acrylate	0.5	0.3	18.6	17.6	100	110
Hexamethyldisilane	11.3	4.1	5.9	5.9	15	14
Tetramethyldisiloxane	5.2	1.1	7.5	5.1	28	20
Hexamethyldisiloxane	3.6	— ^c	5.9	— ^c	20	— ^c
Divinyltetramethyl-disiloxane	1.6	0.5	7.5	7.5	19	21

^a From Yasuda and Hsu (11).

^b Arbitrary units.

^c Signal not detected.

Table 6.15CONTACT ANGLES OF WATER WITH PLASMA POLYMERS^a

Monomer	$\cos \theta (\text{H}_2\text{O})$		
	Continuous	Pulsed	Change
C_2H_2	0.82	0.81	-0.01
C_6H_6	0.94	0.18	-0.76
C_6F_6	0.05	0.01	-0.04
Styrene	0.29	0.20	-0.09
C_2H_4	0.15	0.06	-0.09
C_2F_4	-0.22	-0.23	-0.01
Cyclohexane	0.01	-0.08	-0.09
Ethylene oxide	0.44	0.34	-0.10
Acrylic acid	0.50	0.99	0.49
Propionic acid	0.46	0.99	0.53
Vinyl acetate	0.39	0.36	-0.03
Methyl acrylate	0.39	0.37	-0.02
Hexamethyldisilane	-0.04	-0.12	-0.08
Tetramethyldisiloxane	0.23	-0.05	-0.28
Hexamethyldisiloxane	-0.18	-0.29	-0.11
Divinyltetramethyldisiloxane	0.03	0.03	0

^a From Yasuda and Hsu (11).

spin signals, which are typical features of group I monomers. When these monomers are copolymerized with H_2O , the characteristics of the plasma polymer based on the polymer free radicals change from those of group I to those of group III (i.e., low polymer signals and high glass signals). A more detailed discussion of copolymerization of H_2O is given in Section 6.5; only the effect on the trapped free radicals is discussed here.

The change in the plasma polymerization characteristics of acetylene with the addition of H_2O is shown in Fig. 6.13, which depicts the pressure change due to the addition of the comonomer (H_2O), and in Fig. 6.14, which shows the decrease in trapped free radical concentration as a function of the added comonomers (H_2O and N_2).

This change due to the addition of H_2O can be explained by the relative contributions of cycle I and cycle II to the growth mechanisms of the plasma polymerization of the monomers. In the absence of H_2O , the polymer formation from these monomers depends heavily on cycle II (diradicals). The reversal of free radical characteristics by the addition of H_2O indicates that polymer formation in the presence of H_2O must depend on cycle I (based on monoradicals), because plasma-activated species of H_2O evidently block the diradical cycle. Because of the poisoning effect, most organic compounds with

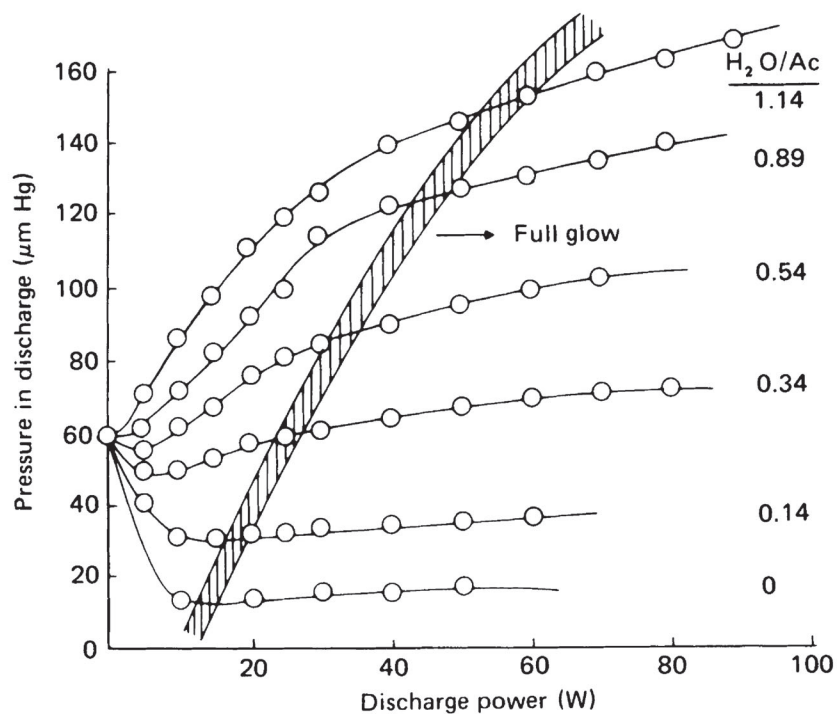


Fig. 6.13 Dependence of flow pressure in the discharge of acetylene/H₂O mixtures on discharge power. Adapted from Yasuda and Hirotsu (14).

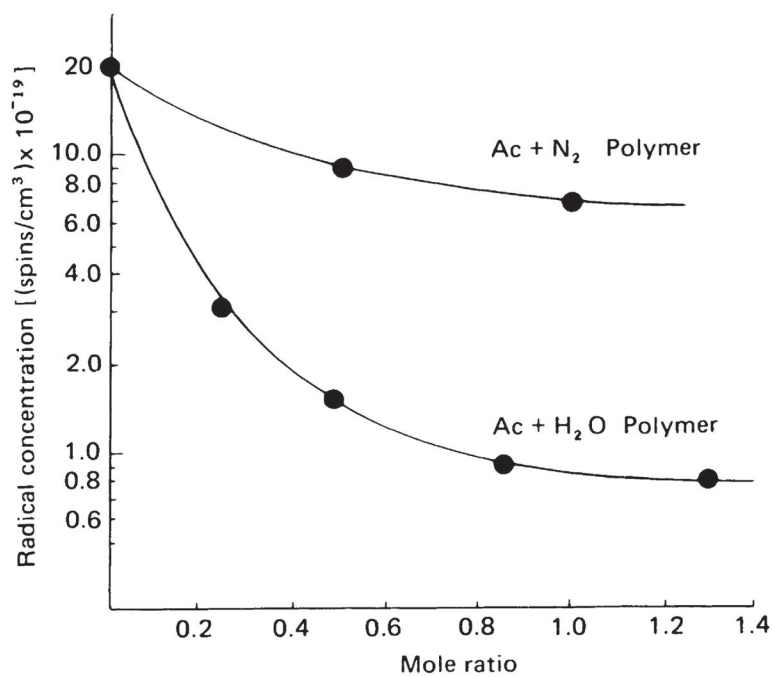


Fig. 6.14 Change in concentration of free radicals trapped in plasma polymers by copolymerization of acetylene with N₂ or H₂O. Adapted from Yasuda and Hirotsu (14).

oxygen-containing groups such as —COOH , —CO— , —OCO— , —OH , and —O— , are generally reluctant to form a polymer, and the plasma polymers rarely contain the original oxygen-containing groups.

Because of the poisoning effect of oxygen-containing groups, acrylic acid shows a lower deposition rate than one would expect from the molecular weight of the monomer, and the plasma polymer is rather hydrophobic, as seen in Table 6.15.

In a pulsed glow discharge, the poisoning effect is also reduced due to the low duty cycle of the pulse, but once-formed, the radicals can be conserved by the vinyl double bond during the “off” period of the pulse. Consequently, the net effects of a pulsed rf discharge on acrylic acid are the following:

1. Remarkable increase in the polymer deposition rate (Table 6.13)
2. Increase in the concentration of free radicals trapped in the plasma polymer (Table 6.9)
3. Decrease in the substrate glass signals (Table 6.9)
4. Significant increase in the wettability by water of the plasma polymer (Table 6.15).

For monomers with growth mechanisms in which cycle II mechanisms have a minor role, a pulsed glow discharge generally decreases the concentration of polymer signals, but the reduction is much less than what one might expect from the duty cycle of the pulsed discharge. The reduction of polymer signal in such cases can be explained by the more complete coupling of free radicals before new free radicals are created by the subsequent “on” cycle of the pulsed glow discharge.

6.4.4.3 PERFLUOROCARBONS

The effects of a pulsed rf discharge on the plasma polymerization of perfluorocarbons are more complicated due to the complex behavior of the detached fluorine under plasma conditions. Some aspects of the behavior of fluorine plasma are discussed in Chapter 7.

In general, the concentrations of free radicals in the plasma polymers of fluorine-containing monomers are higher than those of other organic compounds, with the exception of acetylene and ethylene. The free spin concentrations observed with glass substrates for both fluorine-containing monomers and hydrocarbons, however, are by and large the same. The effect of a pulsed rf discharge is generally a reduction in the polymer signals, with the exception of perfluoromethylcyclohexane, which exhibits a small increase (22%).

In view of the fact that the largest increase in polymer signal is observed with ethylene and that fluorohydrocarbons (e.g., vinyl fluoride and vinylidene

fluoride) show a conspicuous increase in polymer signal by a pulsed discharge, the decrease in polymer signal observed with tetrafluoroethylene and the generally observed decrease in polymer signal with most perfluorocarbons may indicate a significant difference between the plasma polymerization of hydrocarbons and that of perfluorocarbons. This difference can be seen in the behavior of hydrogen and of fluorine in plasma.

As evidenced by investigations with pulsed rf discharge, the detachment of hydrogen plays a significant role in the overall growth mechanisms of the plasma polymerization of ethylene. The detachment of fluorine, however, has a completely different effect on plasma polymerization. This situation can be visualized by a comparison of bond energies of C—H and C—F and the dissociation energies of H—H and C—F.

Energy (kcal/mol)	C—H	C—F	C—C
Bond	98.8	116	83
Dissociation	$\frac{\text{H—H}}{104.2}$	$\frac{\text{F—F}}{37.7}$	

The detachment of hydrogen to free H_2 is energetically favored, but the detachment of fluorine to free F_2 is not. In order for a polymeric molecule to be formed by plasma polymerization, a covalent bond must be broken to create a new covalent bond. In the case of hydrocarbons, the scission of C—H would provide an efficient route for building a polymer, because the scission of C—C is generally degradative. In the case of perfluorocarbons, however, the scission of C—C becomes the major route for building a large molecule because of the energetics just mentioned. Furthermore, if fluorine is detached from a perfluorocarbon under plasma conditions, because of the extremely high reactivity (evidenced by the very low dissociation energy of F—F) it participates in various chemical reactions much more actively than the detached hydrogen in the plasma of hydrocarbons. This means that the contribution of fluorine detachment to the growth mechanisms of plasma polymerization is considerably less than that of hydrogen detachment in hydrocarbon plasma. Thus, the plasma polymerization of perfluorocarbons depends heavily on cycle II growth mechanisms, whereas cycle I plays a significant role in the plasma polymerization of hydrocarbons. The rather heavy dependence on cycle II means that diradical-forming structures such as a double bond and a cyclic structure are needed for the efficient plasma polymerization of perfluorocarbons. The addition of H_2 , however, changes this situation significantly, as discussed in Chapter 7. The effects of a pulsed rf discharge on the plasma polymerization of some monomers representing different types of growth reaction are summarized in Table 6.16 (pp. 116–117).