

Some Aspects of Plasma Polymerization Investigated by Pulsed R.F. Discharge

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Synopsis

The polymerization of organic compounds in glow discharge (plasma polymerization) was investigated by using pulsed R.F. discharge (100 μ sec on, 900 μ sec off). The effects of pulsed discharge on polymer deposition rate, pressure change in plasma, ESR signals of free spins in both plasma polymer and substrate, and the contact angle of water on the plasma polymer surface were investigated for various organic compounds. The results are correlated to the mechanisms of polymer formation in plasma (plasma polymerization) which has been postulated as repeating processes of stepwise (propagation) reactions. The effect of the pulse is different from one group of organic compounds to another depending on whether or not they contain an olefinic double bond and/or a triple bond. The main difference seems to be the addition polymerization which can occur exclusively during the off-period of pulsed discharge. Ultraviolet emission from pulsed discharge is much less than from continuous discharge. Consequently, the fragmentation of the monomer and the free-radical formation in the substrate are less with the pulsed discharge. Properties of polymers from some organic compounds formed in continuous and in pulsed discharge were found to be significantly different, and the differences were postulated from the changes of polymerization mechanisms in the pulsed discharge.

INTRODUCTION

The polymerization of an organic compound in plasma (glow-discharge polymerization) is quite different from the conventional chemically initiated polymerizations or radiation-initiated polymerization. For instance, polymerization of styrene in plasma and those by other means of initiation can be distinguished in the following manner. In conventional polymerizations, including radiation-induced polymerizations which utilize relatively low dose rate such as γ -rays, various means of initiation are used to produce various kinds of reactive species, but the propagation step of the styrene polymerization is essentially the addition reaction of those reactive species onto the vinyl double bond of styrene. Therefore, the reactivity of the vinyl double bond toward the reactive species created in the initiation step is an important factor which influences the overall polymerization rate. A typical example may be seen in polymerization rates of styrene and α -methylstyrene in free-radical-initiated polymerization. In any case, however, the presence of vinyl double bond is necessary for all conventional (radiation-induced) polymerizations, and the absence of the vinyl double bond (i.e., ethylbenzene) means no polymerization.

In the case of the plasma polymerization, ethylbenzene not only polymerizes,

but also its polymer deposition rate is similar to that of styrene.¹ Furthermore, the deposition rates observed with various organic compounds are, by and large, similar (within two orders of magnitude when the molecular weights of monomers are taken into consideration).²

These facts indicate that plasma polymerization is an entirely different process of forming polymers. The properties of plasma-polymerized polymers are also quite different from those of the conventional polymers, and it is best to consider that they are not the same polymers formed from the corresponding monomers by conventional means (e.g., plasma-polymerized styrene is not a kind of polystyrene).

The mechanism of plasma polymerization of organic compounds is very complex. The overall polymer formation is the consequence of many complex reactions, and the polymer deposition rate as well as the properties of polymers are dependent on many experimental factors such as types of electric discharge, conditions of the discharge, geometrical factors of the reaction vessel, and the properties of substrate upon which a polymer deposits. Consequently, the plasma polymerization cannot be specifically described for the general case. However, a series of recent studies has projected reasonable overall mechanisms of the plasma polymerization of organic compounds, which seem to be able to apply in many cases.^{3,4}

The overall mechanisms can be represented by eqs. (1)–(2),

Initiation:



Propagation:



where i and k are numbers of repeating units (i.e., $i = k = 1$ for the monomer) and the M^* are reactive species which can be ions of either charge, an excited molecule, and a free radical. The important point is that these are stepwise reactions, and no chain reaction is involved at least as a major reaction. Furthermore, the product of a reaction is not immune to the initiation and is subjected to repeated initiation processes.

Although the kind of reactive species that play predominant roles in the plasma polymerization has been a subject of debate for past years, there seems to be no conclusive evidence which enables us to exclude any specific species. Therefore, it seems most reasonable to assume that any energetic and/or reactive species being created in plasma can contribute to the overall polymer formation in plasma.

In studies of plasma polymerization by use of the tail-flame portion of inductively coupled R.F. discharge, it was found that free radicals seem to play an important role.⁵ Furthermore, the concentration of trapped free radicals in plasma polymers is closely related to the chemical structure of monomers and consequently to the mechanism of plasma polymerization. It seems that the trapped free radicals in plasma polymer are caused by the unbalance between the production rate and consumption rate of free radicals. This is an important aspect of the polymerization mechanism described above. In conventional

free-radical polymerization, the rate of free-radical production (initiation) is identical to the rate of free-radical consumption due to the chain termination, which leads to no trapped free radicals in the formed polymer. However, in plasma polymerization postulated by the mechanism described above, the rate of free-radical production and the rate of free-radical consumption are not directly related, and they can be considered as two independent factors.

In order to see the balance between these two factors, the pulsed R.F. discharge is utilized. It is expected that the production of free radicals will be proportional to the duration of R.F. discharge. While the discharge is off, no free radicals are created; but during this off-period, the free radicals already created can either react to each other or react to a neutral molecule. Consequently, it may be possible to change the balance between the free radical production rate and their consumption rate, as in continuous plasma, by using this technique.

It is mainly intended to see the differences observed in the polymerizations by continuous and pulsed R.F. discharge under a set of conditions arbitrarily chosen for this study. The analysis of the differences correlated to the chemical structures of the monomers would enable us to gain more insight into the mechanism of plasma polymerization.

EXPERIMENTAL

The apparatus and method used in this study are identical to those described in the previous studies.^{1,2} For ESR study, a glass tube of 4 mm O.D. and 15 cm in length was joined to the monomer inlet by use of a glass joint. A length of about 10 cm of glass tube was exposed to plasma. The monomer was fed into the reaction tube through this glass tube, and the polymer deposition rate was measured by placing underneath this glass tube a glass slide upon which two 2.2 cm $\times$ 2.2 cm cover glasses were used to receive the plasma coating for determination of weight increase. Since the monomer feed-in passway is different from previous studies, some minor differences may show up in the deposition rate and other parameters. After the weight increase or deposition rate had been measured, the cover glass was used to determine the contact angle of water. The ESR signals were obtained by placing the plasma polymer-coated glass tube into the cavity of a Varian Model V4502 ESR spectrometer about 10 min after the discharge was terminated. In the case of a composite signal, i.e., a polymer free-radical signal superimposed on a glass radical signal, the composite signal was recorded first. The glass radical signal was then recorded after the plasma polymer coating was wiped off.

A programmed pulse generator (Model 612AT, Wang Laboratories, Inc., Natick, Mass.) was used in the experiments with pulsed plasma during which a continuous power from an R.F. transmitter was pulsed through this programmed pulse generator to a pulsed power with an on-off alternate period of 100 and 900 μ sec, respectively. The pulsed signal was simultaneously displayed on the screen of an oscilloscope (type 585, Tektronix, Inc., Portland, Oregon) to ensure the power was pulsed to the designated on-off time scale.

The intensity of an ESR resonance may be approximated by eq. (3)

$$I = KW^2H \quad (3)$$

where peak width W is peak separation of the first derivative and peak height H is the height of the resonance. The constant K , as determined by the line

shape, is 0.52 and 2.73 for Gaussian line and pitch in KCl, respectively. By comparing with the intensity of a standard pitch, the intensity of an unknown sample can be calculated by eq. (4)

$$I_s = I_p K_s W_s^2 H_s A_p L_p / K_p W_p^2 H_p A_s L_s \quad (4)$$

where modulation amplitude A and signal level L are instrument parameters. The subscripts s and p represent sample and standard pitch, respectively. The standard pitch sample used in this work is a 0.1% sample with a spin concentration of 3×10^{15} spins/cm. By substituting appropriate values into eq. (4) and assuming a Gaussian line shape, the polymer signal intensity (spins/cm) can be expressed as

$$I_s = 0.23 \times 10^{21} W_s^2 H_s / H_p A_s L_s. \quad (5)$$

The total volume of plasma polymer coated outside of a 1-cm length ESR tube is $0.4\pi Z$, where Z is the coating thickness and is assumed to be the same as the coating thickness on the cover glass as determined from weight gain. Therefore, the spin concentration in plasma polymer (spins/cm³), C_s , will be

$$C_s = I_s / 1.257Z \quad (6)$$

In the calculation of C_s , the H_s is obtained by subtracting the background signal, if only a polymer signal is presented, and appropriate glass signal, if a composite signal showed up, from the polymer signal peak height.

A typical glass signal has been integrated. By comparing with the standard pitch sample, the relationship between the glass spin concentration (spins/cm²), C_g , and the peak height, H_g , may be expressed by

$$C_g = 1.56 \times 10^{21} H_g / H_p A_g L_g \quad (7)$$

where subscript g represents a glass signal. Since the distribution of glass spins is unknown, the glass spin concentration can only be expressed by spins/cm².

Both initial spin concentration in plasma polymer, C_s^0 , and half-life time of initial decay are obtained from a plot of $\log C_s$ versus measuring time t . The normalized peak heights are calculated from C_s^0 by assuming that ESR spectra of 1-cm³ plasma polymers are recorded under identical experimental parameters and against the same standard pitch signal. The normalized peak heights of ESR signals with similar peak width will, therefore, be directly proportional to the spin concentrations.

The contact angle of water was measured with a drop of 50 μ l of triply distilled water and by using a cathetometer with goniometer eyepiece. For each sample, an average of 4–8 readings is reported.

The following monomers were studied: acetylene, ethylene, tetrafluoroethylene, and ethylene oxide (from Matheson), benzene (from Fisher Scientific Company), hexafluorobenzene and propionic acid (from Aldrich Chemical Company), styrene, acrylic acid, and vinyl acetate (from Monomer-Polymer Laboratories), cyclohexane (from Mallinckrodt Chemical Works), hexamethyldisilane (from PRC, Inc.), tetramethyldisiloxane and divinyltetramethyldisiloxane (from Silar Laboratories), and hexamethyldisiloxane (from K & K Laboratories).

All monomers were used as received without further purification. Nevertheless, the purity of a monomer was checked by the determination of its con-

densibility in cold finger after repeated degassing procedures. All monomers, except tetrafluoroethylene, showed a high condensibility of at least 99% which indicated a high purity. The condensibility of tetrafluoroethylene is about 95% which might be due to the contamination of some noncondensable gas (at 77°K) in the sample.

The pressure change in the reaction chamber was automatically recorded by a recorder through a Baratron (Type 170 M, MKS Instruments, Inc.). The instant change of pressure due to a breakdown step immediately after the glow started can be either increased or decreased, depending upon the nature of monomers.

RESULTS

Until now, not a great deal of research has been done on the effect of pulsed power in discharge. Shaw,⁶ using continuous and pulsed power at frequencies of 3000–9000 Mc and at average power of from 5–300 W, found no significant difference between them in the production of H atoms from hydrogen. This finding is not surprising, because the lifetime of atoms in a discharge is about 0.1–1.0 sec. With a pulse repetition of 1000 or more, there would be little change in the atomic concentration between pulses. On the other hand, Winkler and his colleagues⁷ obtained high concentration of atoms from N₂ using a pulse rate of 30–60/sec. It appears that the pulsed type of discharge is capable of giving a higher concentration of nitrogen atoms from pure nitrogen than any other system.

So far, no work has been reported on the effect of pulsed plasma on the plasma polymerization of organic compounds. The results of this study on the effect

TABLE I
Pressure Parameter δ of Various Monomers in the Continuous and the Pulsed R.F. Discharges

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

^bChanges are based on values of continuous discharge.

of pulsed plasma are analyzed in terms of the pressure change in glow discharge, deposition rate of plasma polymer, contact angle of plasma polymer surface, and ESR spectra of both plasma polymer and substrate. In addition, some fluorocarbons have been studied, and their results are compared with that of their counterparts in hydrocarbons.

Pressure Change

In dealing with reactions which involve a gaseous component, the pressure change associated with the reaction is an important parameter which can be used for elucidation of the reaction. In plasma polymerization of organic compounds, the change of pressure is caused by (1) the production of hydrogen (fluorine in the case of fluorocarbons), (2) decomposition of the monomer yielding nonpolymerizable gas, and (3) polymerization of the monomer.^{8,9} In the plasma polymerization of hydrocarbons in a closed system, the majority of gas residue is hydrogen, and the hydrogen abstraction (by plasma) seems to play an important role in the free-radical formation.⁸ The experiments in this study are carried out under the steady-state flow condition, and the change of steady-state flow pressure can be used as a parameter which may replace the hydrogen yield reported previously.⁸

The change of pressure (of steady-state flow) before and during the discharge is expressed by the pressure-change parameter

$$\delta = p_g/p_m \quad (8)$$

where p_m is the pressure of monomer before the discharge is initiated and p_g is the pressure of the steady-state flow system during the discharge.

For plasma polymerization of hydrocarbons in a closed system, the value of δ is nearly identical to the value of hydrogen yield.⁸ That is, the value of δ (in a closed system) indicates the number of hydrogen molecules liberated by the process of one monomer is incorporated into a polymer. The values of δ in the flow system may be used to indicate the extent of hydrogen or fluorine liberation associated with plasma polymerization. Results are shown in Table I.

TABLE II
Effect of Pulsed R.F. on Acetylene and Benzene in a Closed System

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

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

^b Fraction of residual vapor: $X = (p_\infty - p_{H_2})/p_0$, where p_{H_2} is the pressure after the cold finger is surrounded by liquid nitrogen.

^c Hydrogen yield: $y = p_{H_2}/p_0$.

The results indicate that the changes in δ values due to pulsed R.F. are relatively small except for a few monomers. For most organic compounds, the change of δ value is either negligibly small or changes toward unity when the pulsed R.F. is employed. Noteworthy exceptions are as follows: significant increases in δ values are observed for acetylene and aromatic compounds when the pulsed R.F. is employed (this trend is also seen for ethylene); significant decreases in δ values are found for acrylic acid and propionic acid.

The increase of δ value in a flow system may indicate either an increase of hydrogen yield or an increase of unreacted monomer (or condensible gas-phase products in the case of $\delta < 1$). In order to examine these possibilities, the analysis of gas phase was carried out for acetylene and benzene in a closed system. The closed-system experiments were carried out according to the procedures described previously⁸ by use of both continuous and pulsed discharge. Some polymerization parameters which have been described in detail⁸ are summarized in Table II. The results indicate that the characteristic reactions of polymer formation are essentially identical in both types of discharge. The only significant difference is in the rates of polymer formation (or rate of monomer dissipation rate) as indicated by half-time of reactions $t_{1/2}$. The pulsed R.F. reduces the rate of polymer formation of acetylene to $1/5$ and of benzene to $1/8$. According to this result, it is anticipated that the higher δ value in a flow system with pulsed discharge is, at least in part, due to the higher concentration of nonpolymer components in the vapor phase at steady-state flow.

Therefore, a similar analysis was applied to the flow system in order to ascertain the contribution of nonpolymer components to the higher δ values observed in a pulsed discharge. The results, summarized in Table III, show an increase of condensible vapor in the steady-state flow with a pulsed discharge as expected from the above analysis. The significant increases in δ values of acetylene and aromatic compounds in a pulsed discharge are thus probably due to the decrease of polymer formation rate.

Significant decreases in δ values for acrylic acid and propionic acid are due to the reduced detachment of substituent groups in a pulsed discharge as will be discussed later in the text.

Deposition Rates

Data summarized in Table IV show the change of deposition rates due to a pulsed discharge. The deposition rate is based on the total time, not on the

TABLE III
Vapor-Phase Analysis in a Flow System at Steady State

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

on-period of the pulsed discharge.

The deposition rate generally decreases with the pulsed discharge (100 μ sec on, 900 μ sec off); however, the decrease in deposition rate is not proportional to the "on"-time of the pulsed discharge. On the other hand, significant increases in the deposition rate has been found for acrylic acid, propionic acid, and tetrafluoroethylene when the pulsed discharge is employed.

Electron Spin Resonance (ESR) Spectroscopy

The first derivative ESR spectra of plasma polymers studied in this work can be categorized into two different groups: polymer signal only without glass signal, and polymer signal superimposed on glass signal. Representative spectra of each group are shown in Figures 1–5. It is interesting to note that free radicals of various plasma polymers always give a relatively broad singlet spectra. Similar singlet spectra have been observed previously by Ohnishi et al.,¹⁰ when they irradiated various polymer samples with high doses. For example, polyethylene gives the sextet spectrum when lightly irradiated ($\sim 10^6$ rad); on further irradiation (10^7 – 10^8 rad), the spectrum becomes a complex one involving a septet. At higher doses ($\sim 10^9$ rad), polyethylene gives only a singlet spectrum. The singlet spectra have been interpreted as unpaired electron in some conjugated double-bond system. In the case of polyethylene, the radical has been suggested to be the polyenyl type:



When n becomes larger, the number of hyperfine lines becomes larger and the hyperfine separation becomes smaller due to the greater delocalization of radical. As a result, the spectral shape might become a singlet as the hyperfine structure is being unresolved.

TABLE IV
Deposition Rates of Various Monomers in the Continuous and Pulsed R.F. Discharges

Monomer	Deposition rate $\times 10^8$, g/cm ² -min		
	Continuous	Pulsed	Change ^a
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 Changes are based on values of continuous discharge.

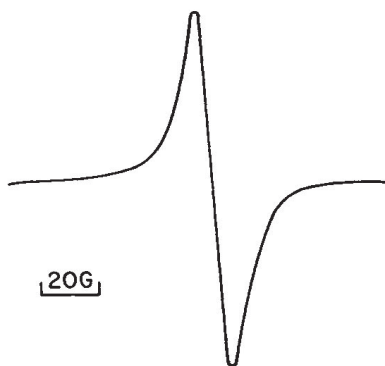


Fig. 1. ESR signal of a plasma polymer of acetylene (without glass signal).



Fig. 2. ESR signal of a plasma polymer of tetramethyldisiloxane (without glass signal).

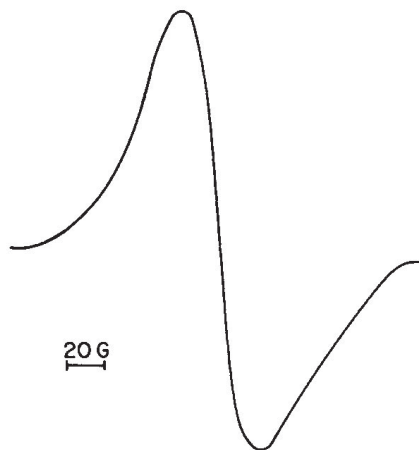


Fig. 3. ESR signal of a plasma polymer of hexafluorobenzene (without glass signal).

The calculated glass radical concentration, C_g (in spins/cm²), and the initial polymer radical concentration, C_s^0 (in-spins/cm³), are listed in Table V. Two parameters of the first-derivative ESR spectrum, normalized peak height H (in cm) and line width W (in gauss), as well as half-life of the initial decay of polymer radicals, are listed in Table VI. The initial polymer radical concentration and the half-life time of the initial decay of polymer radicals are obtained from a plot of $\log C_s$; C_s is the polymer radical concentration, as a function of time. A typical plot is shown in Figure 6 for hexamethyldisilane.

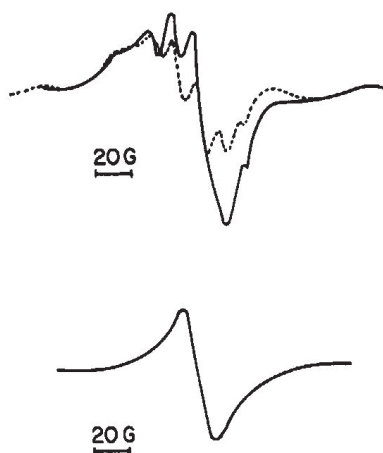


Fig. 4. ESR signal of plasma polymer of cyclohexane: (above) polymer signal superimposed on glass signal; (below) polymer signal only after subtracting glass signal.

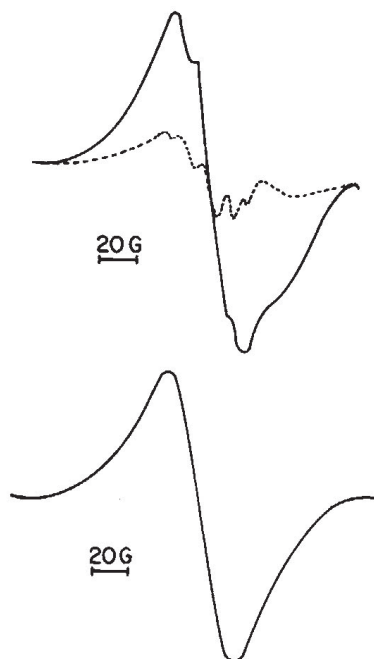


Fig. 5. ESR signal of plasma polymer of tetrafluoroethylene (by pulsed discharge): (above) polymer signal superimposed on glass signal; (below) polymer signal only after subtracting glass signal.

It has been shown recently⁵ that unpaired spins are generated on substrates, designated as glass radicals in this study, by ultraviolet emission from the plasma. This ultraviolet energy is emitted from such processes as the capture of free electrons into various excited states of molecules and ions and the acceleration of electrons during collisions with ions or molecules. For a particular plasma, the amount of glass radical generated will depend upon the amount of ultraviolet energy emitted from the plasma which in turn will depend on the number of excited species or the energy absorbed by the plasma. In general, less energy has been supplied to the system in pulsed plasma than in continuous plasma. Consequently, less ultraviolet energy is expected to be emitted from the pulsed

TABLE V
ESR Spin Concentration in Plasma Polymers and Glass Substrates

Monomer	$C_s^o \times 10^{-19}$, spins/cm ³			$C_g \times 10^{-15}$, spins/cm ²		
	Continuous	Pulsed	Change ^a	Continuous	Pulsed	Change ^a
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

^aChanges are based on values of continuous discharge.

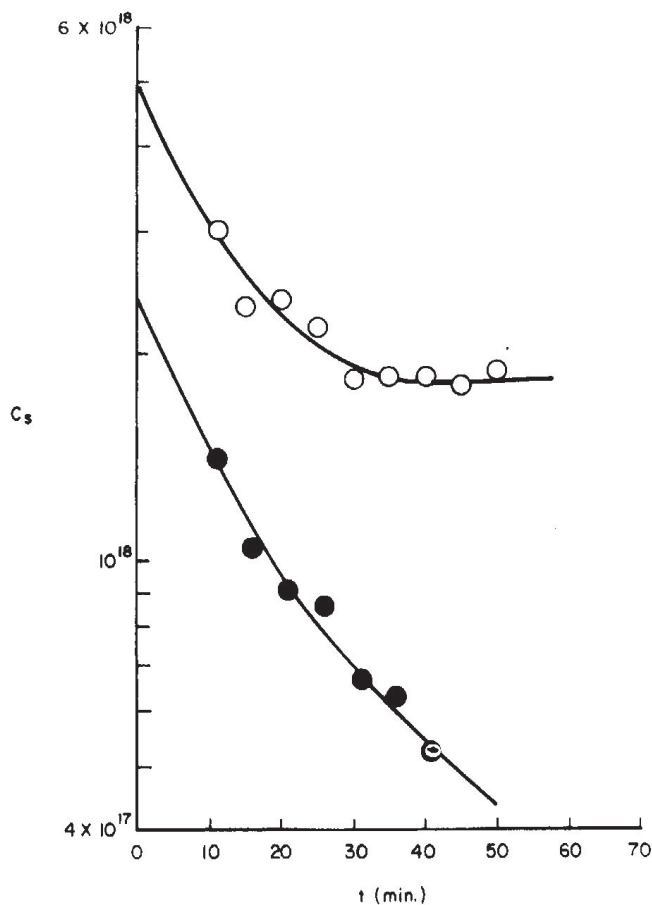


Fig. 6. Change of ESR signal of plasma polymer of hexamethyldisilane with time: (○) continuous; (●) pulsed.

plasma, which in turn will generate less glass radicals as indicated by data listed in Table V. Since the glass radicals do not increase with time and probably are generated in the first few minutes, the limiting glass radical concentration as listed in Table V may be expressed by eq. (9),

$$C_g = kI_0/aR \quad (9)$$

where k is a constant relating the rate of glass radical generation to the ultraviolet intensity impinging on the glass, I_0 is the ultraviolet intensity, a is the absorption coefficient, and R is the deposition rate of plasma polymer on the glass surface.⁵

It may be interesting to note that no glass radicals have been generated from the plasma of siloxane compounds and the hydrocarbons with aromatic structure and triple bond. It has been observed^{8,9} that compounds with triple bonds or conjugated double bonds polymerize in plasma with a very small hydrogen yield, which has been given the interpretation that the plasma polymerization of these compounds must proceed by the opening of double bonds or triple bonds. If this is true, then most of the energy absorbed by the plasma is consumed to break the multiple bonds for polymerization instead of being consumed to excite the molecule.³ Consequently, no ultraviolet emission and no glass radicals will be generated in the substrate. This is exactly what we have observed here from ESR study.

The generation of plasma polymer radicals in both continuous and pulsed plasmas is more complicated than the generation of glass radicals, since the plasma polymer radicals formed represent a final balance between the production of free radicals and the consumption of free radicals.^{3,4} With continuous plasma, the high concentration of plasma polymer radicals is found in polymers from compounds containing aromatic, heteroaromatic structure, and triple bonds, less radicals with compounds containing cyclic structure, double bond (except tetrafluoroethylene), and silicones. Apparently, the high-polymer radicals produced from compounds such as aromatic and heteroaromatic result from the favorable radical production compared to radical consumption due to the formation of diradicals by the opening of multiple double bonds in these structures. In the case of triple bond-containing compounds, such as acetylene, the reason for higher polymer radical concentration compared to that from the double bond-containing compound can be clearly seen from the above-proposed mechanisms. The unusual high-polymer radicals observed in plasma polymer of tetrafluoroethylene may be due to the easy detachment of fluorine atoms from the monomer.

Under the condition of pulsed plasma, the production of free radicals (based on the duration of plasma) decreases to $\frac{1}{10}$ of continuous plasma and allows free radicals more time to complete coupling. In this case, the free-radical concentration in plasma polymer should be less in most compounds but not all, as indicated by the data in Table V. It is rather surprising that free radicals in plasma polymer of ethylene increase by an order of magnitude by pulsed plasma. A modest increase of free radicals by pulsed plasma has been found in acetylene and acrylic acid. This may be due to either the high susceptibility of these monomers toward the breakdown step which occurs repeatedly in pulsed plasma or the participation of vinyl polymerization without radical coupling.

TABLE VI
Characteristics of Spin Signals

Monomer	Normalized peak ^a height, arbitrary units		Peak width, gauss		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	a	17.6	a	36	a
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	a	5.9	a	20	a
Divinyltetramethyl- disiloxane	1.6	0.5	7.5	7.5	19	21

^aSignal cannot be detected.

The ESR spectrum of siloxane compound, which shows a narrow line width of 5 gauss and no indication of any kind of hyperfine splitting, suggests that there is no magnetic interaction of the free radicals with the immediate neighbors in the sample. The infrared spectrum of plasma-polymerized hexamethyldisiloxane shows a broad Si—O stretching frequency indicating the retention of Si—O bond in the plasma polymer.⁴ Based on those observations, the formation of polymer radicals in plasma polymers of siloxanes may come from the abstraction of hydrogen or methyl group attached on silicone.

The half-life time of free radicals relates to the mobility of radicals. The shortest half-life of radicals studied in this work is that of propionic acid, being less than 15 min. It is interesting to note that parameters of vinyl acetate and propionic acid listed in Table VI are not consistent with other members in their series. The half-life time of initial free radicals of plasma polymer, both continuous and pulsed, of acrylic acid and methyl acrylate are of the order of 1–2 hr, but vinyl acetate and propionic acid have a rather short half-life time of 25 min or less.

According to the suggested polyenyl radical structure for polyethylene irradiated to high doses, the line width H of the singlet spectrum becomes smaller as the delocalization increases. All line widths of plasma polymer radicals listed in Table VI, except some fluorocarbon and siloxane plasma polymers, are quite close to that observed by Ohnishi et al.¹⁰ of approximately 17 gauss. The relatively narrow line width and long half-life time of both continuous and pulsed plasma polymer of acetylene indicate that the radicals are associated with a highly delocalized conjugated system as should be expected from this system.

The ESR spectra of plasma-polymerized perfluorinated compounds show an ESR line width of approximate 40 gauss, which is much wider than the other polymers investigated. The half-life of the decay of initial free spins in plasma polymer of fluorocarbons is usually longer than that of their corresponding hydrocarbons. This may be due to their low mobility because of the difficulty of fluorine abstraction from neighboring molecules in the movement of free radicals.

TABLE VII
Contact Angles of Water with Plasma Polymers

Monomer	Cos θ (H ₂ O)		
	Continuous	Pulsed	Change
C ₂ H ₂	0.82	0.81	−0.01
C ₆ H ₆	0.94	0.18	−0.76
C ₆ F ₆	0.05	0.01	−0.04
Styrene	0.29	0.20	−0.09
C ₂ H ₄	0.15	0.06	−0.09
C ₂ F 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

Contact Angle of Water

Contact angles θ of water at the surfaces of plasma polymers are shown in Table VII by $\cos \theta$. The following trends seem to be quite evident from these data. Plasma polymers of some hydrocarbons have unexpectedly high hydrophilicity (e.g., acetylene, benzene). Pulsed discharge produces surfaces which are more hydrophobic than those by the continuous discharge with the exception of acrylic acid and propionic acid. The surfaces of plasma polymers of acrylic acid and propionic acid by the continuous discharge are unexpectedly hydrophobic, and the pulsed discharge seems to produce very hydrophilic surfaces, as expected from their chemical nature.

DISCUSSION

As mentioned in the Introduction, any reactive species can contribute to the polymer formation in plasma. However, for the convenience of discussion, the polymerization mechanisms may be represented by a free-radical scheme, since very high concentrations of trapped free radicals are found in many plasma polymers. It has been shown that the following types of reaction contribute to the formation of free radicals:^{3,5,8} detachment of hydrogen and/or halogen atoms; detachment of substituent groups; opening of cyclic structures; opening of double bonds; opening of triple bonds; and opening of aromatic and hetero-aromatic structures.

It should be emphasized that all these reactions occur simultaneously and in a competitive manner, depending on the chemical structure of monomers. The effects of pulsed discharge on some parameters of typical monomers, as well as types of reaction involved, are summarized in Table VIII.

TABLE VIII
Effect of Pulsing on Plasma Polymers of Some Typical Monomers

Monomer	Types of reaction involved ^a	Changes due to pulsed discharge ^b				
		δ	Deposition rate	C_s°	C_g	$\cos \theta$
Hexamethyl-disiloxane	Detachment H, X	-(23)	-(82)	-(100)	0	-0.11
Propionic acid	Detachment H, X, substituent	-(18)	-(110)	(0)	-(81)	+0.53
Acrylic acid	Detachment H, X, substituents	-(29)	+(120)	+(140)	-(100)	+0.49
Cyclohexane	Opening double bonds					
	Detachment H, X	+(21)	-(90)	-(100)	-(100)	-0.09
Ethylene	Opening cyclics					
	Detachment H, X	+(19)	+(2)	+(970)	-(79)	-0.09
Acetylene	Opening double bonds					
	Detachment H, X	+(200)	-(23)	+(81)	0	-0.01
Benzene	Opening triple bonds					
	Detachment H, X	+(150)	-(8)	-(50)	0	-0.76
	Opening aromatic					

^aReactions in continuous plasma; see text.

^bNumbers in parentheses are percent changes based on values of continuous discharge; $\delta = p_g/p_m$; C_s° = spin concentration in plasma polymer; C_g = spin concentration in glass substrate; θ is the contact angle of water.

Reactions involving detachment of hydrogen or halogen atoms or detachment of substituent groups are essentially the same as far as the pressure change is concerned. The main differences are the size of the substituent and the possibility of further reactions of the detached substituent. For instance, when one carboxylic acid group is detached from one acrylic acid molecule, the weight loss is 62.5% of acrylic acid, whereas detachment of one hydrogen atom from an ethane molecule involves only a 3.3% weight loss. Furthermore, a carboxylic group may be split further to oxygen and hydrogen atoms. It is important to note that a pulsed discharge generally decreases the polymer deposition rate; however, a significant increase of the deposition rate by pulsed discharge has been observed in such monomers as acrylic acid, propionic acid, and tetrafluoroethylene. In the case of tetrafluoroethylene, reduced fluorine detachment may be partly responsible for this phenomenon, since the detachment of one fluorine atom represents a 19% weight loss of a repeating unit.

For the monomers which can polymerize by detachment reactions only, e.g., hexamethyldisiloxane, the effect of pulse seems to be straightforward. That is, the initiation step decreases in proportion to the duration of discharge. Consequently, the hydrogen yield ($\delta > 1$) decreases, and appreciable decrease in the deposition rate is found. The resting period of the pulsed discharge allows more complete reaction of free radicals formed, and consequently the trapped free radicals in the plasma polymers decrease beyond the sensitivity of the measurement. The relatively high surface energy (high $\cos \theta$ values) of plasma polymers are correlated to the carbonyl content which seems to be incorporated into the polymer by the postplasma reaction of free radicals with atmospheric oxygen and water.⁴ In this case, therefore, the pulsed discharge produces a more hydrophobic surface than that obtained by the continuous discharge.

Propionic acid illustrates the case where the main polymerization must proceed by the hydrogen detachment; however, the loss of carboxylic acid group occurs simultaneously. The pulsed discharge apparently decreases the extent of carboxylic acid detachment which is evidenced by the remarkable increases in the polymer deposition rate and in $\cos \theta$ (H_2O), indicating the hydrophilic group is retained in the polymer structure. Infrared spectra seem to support this interpretation.³

With monomers which contain polymerizable structure, i.e., vinyl double bond and triple bond, the possibility of regular addition polymerization during the off-period of the pulsed discharge should be recognized. It is interesting to note that all monomers which showed an increase in the trapped free-radical concentration by the pulsed discharge contain either vinyl double bond or triple bond (see Table V). During the process of conventional addition polymerization, which occurs during the off-period of the pulsed discharge, the concentration of free radicals does not decrease, and consequently the overall disappearance rate of the free radicals in a pulsed discharge decreases. Therefore, this decrease in the consumption rate of free radicals results in a net increase in the leftover free radicals, which seems to be the main cause of trapped free radicals in plasma polymers.^{3,5}

The significant increase in the deposition rate of acrylic acid by pulsed discharge may reflect the contributions of the addition polymerization, which increases the trapped free radicals, and of the retaining of the carboxylic acid group, which increases the molecular weight of the repeating unit (compared to that

in the continuous discharge). It should be noted that the increase of trapped free radicals is observed with acrylic acid but not with propionic acid.

The change of the pressure parameter δ by pulsed discharge should be interpreted with consideration of monomer type: monomers with $\delta < 1$ (type A) and monomers with $\delta > 1$ (type B) will behave differently in a pulsed discharge. It is generally observed that the effect of pulsed discharge is in the direction of increasing δ value for type A monomers, whereas for type B monomers, it is in the direction of decreasing δ value. The tendency of the δ values of both types of monomers changing toward unity indicates a reduced polymerization rate in a pulsed discharge system as shown by data in Table IV.

Therefore, it seems reasonable to consider that the changes of δ values are caused by the reduction in the polymer formation rate in a pulsed discharge, with some exceptions such as acrylic acid, propionic acid, and tetrafluoroethylene in which the reduced detachment of relatively large substituents overrides the decreases in the polymer formation rate by changing the molecular weight of the repeating units. The effect of plasma on the substrate material is minimal in pulsed discharge. This is in accordance with finding that most spins generated in substrates are caused by ultraviolet irradiation emitted from the plasma.^{3,5} These data also seem to support the polymerization mechanism of stepwise polymerization with repeated initiations^{3,4} as described in the Introduction.

The amount of trapped free radicals in plasma polymer can be reasonably explained by the concept of the balance between production and consumption (rates) of free radicals during the polymerization process. The use of pulsed discharge provides an additional experimental method to manipulate the free radical production rate as well as the consumption rate. Therefore, it can be utilized as a means of controlling the properties and deposition rates of plasma polymers.

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