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# Plasma Polymerization Investigated by the Substrate Temperature Dependence

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## Synopsis

Plasma polymerization of tetrafluoroethylene (TFE), perfluoro-2-butyl-tetrahydrofuran (PFBTHF), ethylene, and styrene were investigated in various combinations of monomer flow rates and discharge wattages for the substrate temperature range of  $-50$  to  $80^{\circ}\text{C}$ . The polymer deposition rates can be generally expressed by  $k_0 = Ae^{-bt}$ , where  $k_0$  is the specific deposition rate given by  $k_0 = (\text{deposition rate})/(\text{mass flow rate of monomer})$ ,  $A$  is the preexponential factor representing the extrapolated value of  $k_0$  at zero absolute temperature, and  $b$  is the temperature-dependence coefficient. It was found that the value of  $b$  is not dependent on the condensibility of monomer but depends largely on the group of monomer; that is, perfluorocarbons versus hydrocarbons. The values of  $A$  are dependent on domains of plasma polymerization. In the energy deficient region  $A$  is given by  $A = a(W/FM)^n$ , where  $a$  is the proportionality constant,  $W$  is discharge wattage,  $FM$  is the mass flow rate, and  $n$  is close to unity. In the monomer deficient region  $A$  becomes a constant. The kinetic equation is discussed in view of the bicyclic rapid step-growth polymerization mechanisms.

## INTRODUCTION

Plasma polymerization is one of the rare cases in which deposition of a polymeric film occurs in a vacuum of less than 1 torr. Because of the extremely low ceiling temperature of polymerization at that low pressure, most monomers that polymerize by chain-growth polymerization do not yield polymers with molecular weights high enough for film deposition.

The fact that polymeric films are obtained by plasma polymerization of most organic compounds, many of which are not considered monomers of conventional polymerization reactions, suggests that the growth mechanisms are completely different from those of conventional polymerizations. A striking similarity between plasma polymerization and polymerization of *para*-xylene and its derivatives, which is believed to be the polymerization of diradicals created by the thermal cracking of vapor of cyclic dimers, has been pointed out by Yasuda.<sup>1</sup> An important aspects of vacuum polymer deposition is the effect of substrate temperature and gas-phase collisions which are related to the ceiling temperature of the growth reaction.

It has been observed by many investigators<sup>2-6</sup> that the polymer deposition rate decreases with increasing substrate temperature. Although some empirical equations that relate polymer deposition rates and substrate temperature have been proposed, the negative temperature-dependence has been dealt with as the consequence of the adsorption of "monomer" on the surface which subsequently polymerizes.

From the viewpoint of temperature of reactive species the effect of substrate temperature-dependence would provide important information rel-

evant to the growth and deposition mechanisms of plasma polymerization. In this study the temperature-dependence of polymer depositions was investigated for easily condensible and noncondensable monomers (within the temperature range studied) in various combinations of plasma polymerization. The authors wish to present some information that relate to the growth mechanisms of plasma polymerization which have been dealt with as a black box in most studies of the kinetic aspects of polymer deposition or plasma polymerization.

### EXPERIMENTAL

The plasma polymerization reactor used in this study is shown schematically in Figure 1 and is one in a tandem plasma polymerization reactor system reported earlier.<sup>7</sup> Glow discharge of monomer is created by parallel electrodes equipped with magnetic enhancement by a 10-kHz audiofrequency power source. A thickness monitor sensor (Inficon Model XTM) is placed at the projected circumference of an electrode intercepted by the midelectrode plane. The electrodes are 13.2 cm in diameter and 6.1 cm apart. The thickness of the monitor surface is perpendicular to the plane parallel to the electrodes.

The temperature of the crystal surface on which a plasma polymer deposits is controlled by circulating temperature-controlled liquid. For the higher temperature range (20–80°C) the circulating temperature-controlled bath is used. To measure the substrate temperature accurately two thermocouples are placed in the fluid circulating tubes (inlet and outlet) just outside the plasma reactor. The substrate temperature is estimated by the average of the thermocouple readings. No correction for the temperature-dependence of the thickness of the monitor reading was made in this study.

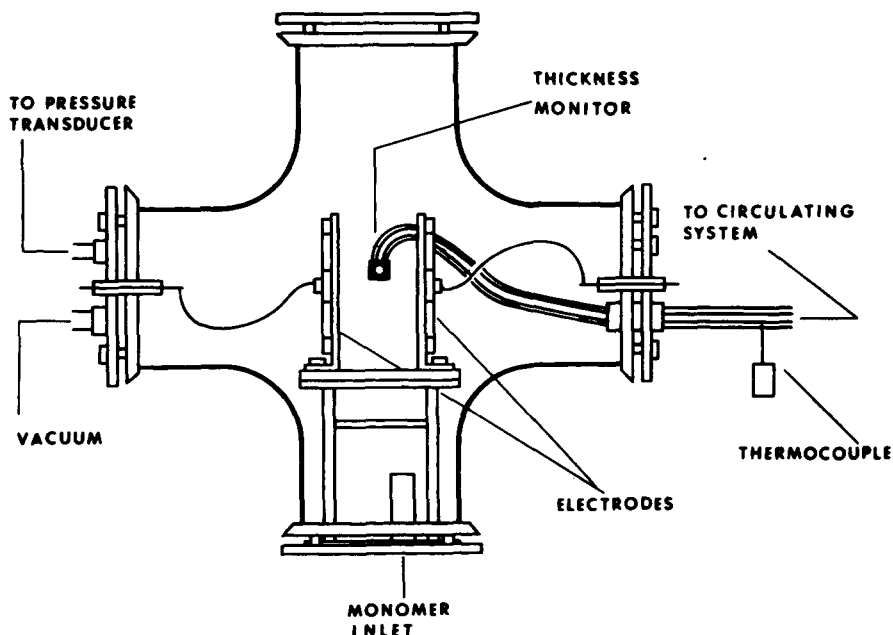


Fig. 1. Schematic representation of reactor.

The flow rates of monomers were measured by the conventional method based on a P-V relationship.<sup>8</sup> The flow rates of gaseous monomers were controlled by a Tylan mass-flow controller and those of liquid monomers were controlled by a micrometer metering valve and the temperature of the liquid in a reservoir. A gaseous monomer was fed directly from the gas cylinder. Liquid monomers are degassed by repeated freezing and thawing under evacuation.

The temperature-dependence of plasma polymer deposition is measured by the following procedure: plasma polymerization of a monomer is investigated by starting at the highest temperature, that is, 80°C. After the constant temperature of the crystal surface is confirmed a constant flow of monomer is established. To avoid the influence of the transient state of the plasma at the beginning of plasma polymerization<sup>9</sup> the deposition rate and temperature of the crystal are recorded. Discharge power is adjusted every 10 min by reading the current and voltage until a steady glow discharge is established, and checked (and readjusted if necessary) during the entire duration of a run.

When the steadiness of the deposition rate and system pressure shown on the recorder is confirmed the deposition-rate reading is recorded as the deposition rate at the temperature. The temperature of crystal is then lowered by changing the thermostat control of the circulating bath, whereas plasma polymerization is kept in the steady state. The deposition rate at the next temperature is read after the steady-state readings are obtained at that temperature. In this way the deposition rate versus substrate temperature can be obtained at a set flow rate and power. A similar procedure is repeated for another set of flow rate and power.

Monomers used in this study are

Monomer	Molecular weight	Boiling point (°C)
Perfluoro-2-butyltetrahydrofuran (PFBTHF)	416	107
Tetrafluoroethylene (TFE)	100	-76
Styrene	104	145
Ethylene	28	-104

## EXPERIMENTAL RESULTS

The deposition rates are expressed by the following parameters:

$k_1$  = deposition rate given by  $\text{kg/m}^2 \cdot \text{s}$ ,  $\text{mg/cm}^2 \cdot \text{s}$ , etc.

$k_2$  = thickness growth rate in  $\text{m/s}$ ,  $\text{Å/s}$ , etc.

$k_2$  is related to  $k_1$  by  $k_2 = k_1/\rho$  where  $\rho$  is the specific weight ( $\text{kg/m}^3$ ) of polymer.

$k_0$  = specific deposition rate, which is given by  $k_0 = k_1/(FM)$  in  $\text{m}^{-2}$  or  $\text{cm}^{-2}$ , where  $F$  is molar flow rate and  $M$  is the molecular weight of monomer; that is,  $(FM)$  is the mass flow rate and  $k_0$  is the polymer conversion ratio per unit area. The overall polymer conversion ratio is given by  $k_0 \times (\text{total surface area})$ .

The temperature-dependence of a polymer deposition of various monomers (with different molecular weights) under different discharge conditions is best expressed in terms of a specific deposition rate,  $k_0$ , rather than a deposition rate  $k_1$  or  $k_2$ , because the actual deposition rate observed under a set of conditions is dependent on the mass flow rate. In Figure 2  $k_2$ s (in Å/s) versus temperature are shown for two sets of flow rates and discharge wattages that give the same value of composite parameter  $(W/FM)^{10}$  ( $1.28 \times 10^8$  J/kg). When the same data are plotted in  $k_0/\rho$  (Å/kg) the two lines shown in Figure 2 converge into a single line (Fig. 3). The data in Figure 3 also show that the specific deposition rate is identical on both sets of conditions, indicating that various combinations of flow rates and wattages can be simplified by the composite parameter  $(W/FM)$ .

The specific deposition rates at various temperatures are shown in Figures 4 through 7 as plots of  $\ln(k_0/\rho)$  versus the absolute temperature  $T$ , which was found to give the best fits by regression analysis for all monomers studied. As shown in these figures, the temperature-dependence of  $k_0$  is given by

$$k_0 = Ae^{-bT} \quad (1)$$

where  $A$  represents the extrapolated specific deposition rate at  $T = 0$ .

Thus the polymer deposition rate can be expressed by the two parameters; that is the extrapolated specific deposition rate at  $T = 0$  and the temper-

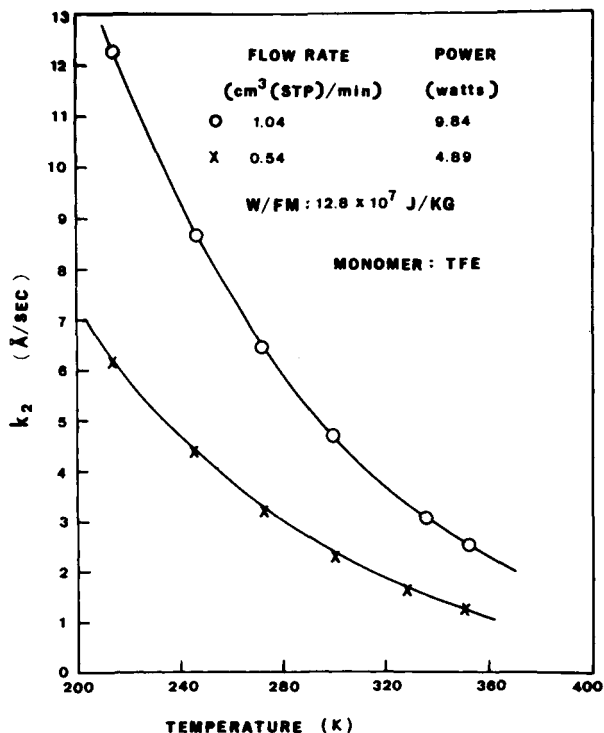


Fig. 2. Temperature-dependence of  $k_2$  for tetrafluoroethylene.

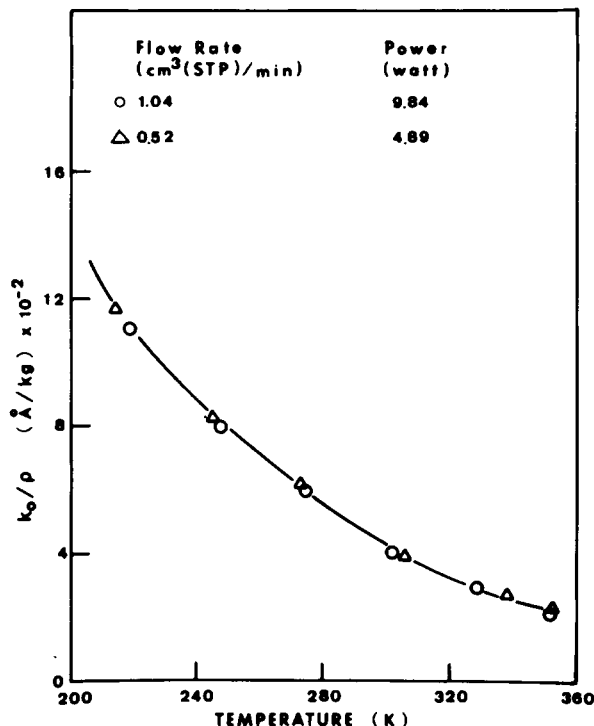


Fig. 3. Temperature-dependence of  $k_0/\rho$  for tetrafluoroethylene at the same  $W/FM$  ( $1.3 \times 10^8$  J/kg).

ature-dependence parameter  $b$ . As shown in Figures 4 through 7, the value of  $b$  for a monomer is independent of discharge conditions, that is, flow rate and discharge wattage, and may be considered as a characteristic parameter of a monomer. The values of  $b$  for these four monomers are listed in Table I. It is important to note that the temperature-dependence is nearly the same for easily condensible monomer (PFBTHF) and gas monomer (TFE), as well as for styrene and ethylene, but is dependent on the type of monomers, that is, perfluorocompounds versus hydrocarbons. The fact that the temperature-dependence (Table I) and the specific deposition rate at a given temperature, for example, at 273 K and at a given value of  $W/FM$  (Table II) are not directly related to the condensibility of monomers clearly indicates that the adsorption of monomer plays only a small part in the plasma polymerization investigated under the conditions of this study.

As pointed out above, the temperature-dependence of polymer deposition is not dependent on the condition of plasma polymerization, that is, flow rate and discharge power. On the other hand, because polymer deposition can generally be expressed by eq. (1), it is important to examine the effect of plasma polymerization conditions on the value of the preexponential factor  $A$  in eq. (1).

In Figure 8 the values of  $A$  for PFBTHF and TFE are plotted against the composite parameter ( $W/FM$ ). A similar plot for ethylene is shown in Figure 9. The leveling off of the deposition rate as  $W/FM$  increases, a trend noted

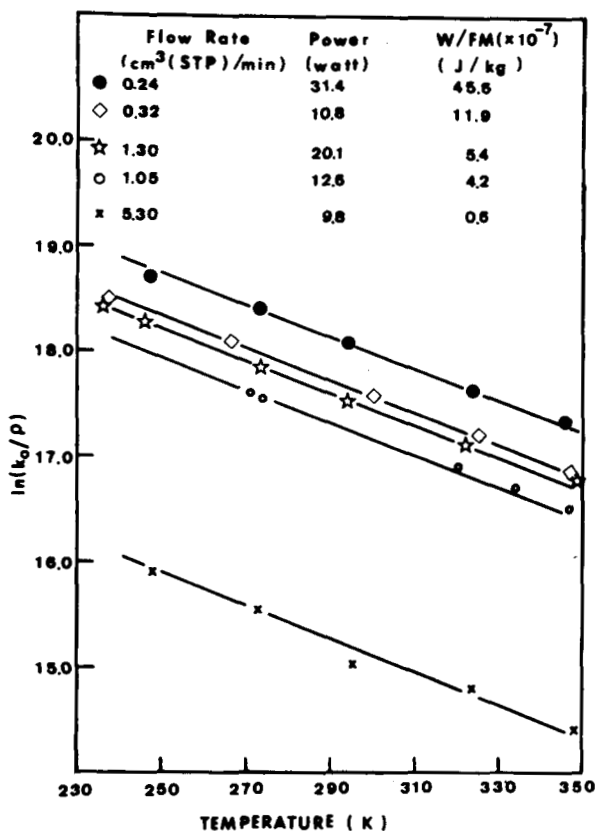


Fig. 4. Effect of substrate temperature on  $(k_0/\rho)$  for PFBTFH.

for many monomers by many investigators, is clearly seen here. Based on the dependence on  $W/FM$ , it is possible to distinguish domains of plasma polymerization conditions. Two major domains can be identified: (1) a  $W/FM$  dependent region at lower  $W/FM$ ; (2) a  $W/FM$  independent (plateau) region at higher  $W/FM$ . The first is an energy-deficient region, the second is a monomer-deficient region.

### Energy Deficient Region

Let us first determine how  $W/FM$  would affect the specific deposition rate at  $T = 0$ ,  $A$ , in the energy-deficient region by assuming that  $A$  is proportional to  $(W/FM)^n$ . In Figure 10  $\ln A/\rho$  is plotted against  $\ln (W/FM)$ . The values of  $n$  can be estimated from the slopes of lines. By regression analysis the value of  $n$  is 0.98 for PFBTFH, 0.92 for TFE, and 0.92 for ethylene. In the energy deficient region, therefore,  $A$  can be given by

$$A = a(W/FM)^n \quad (2)$$

and  $n$  is close to unity. For the first approximation of  $n = 1$  the effect of molecular weight of monomer can be estimated by plotting  $A/\rho$  against  $(W/FM)$ , as shown in Figure 11. The value of  $A/\rho$  increases almost linearly

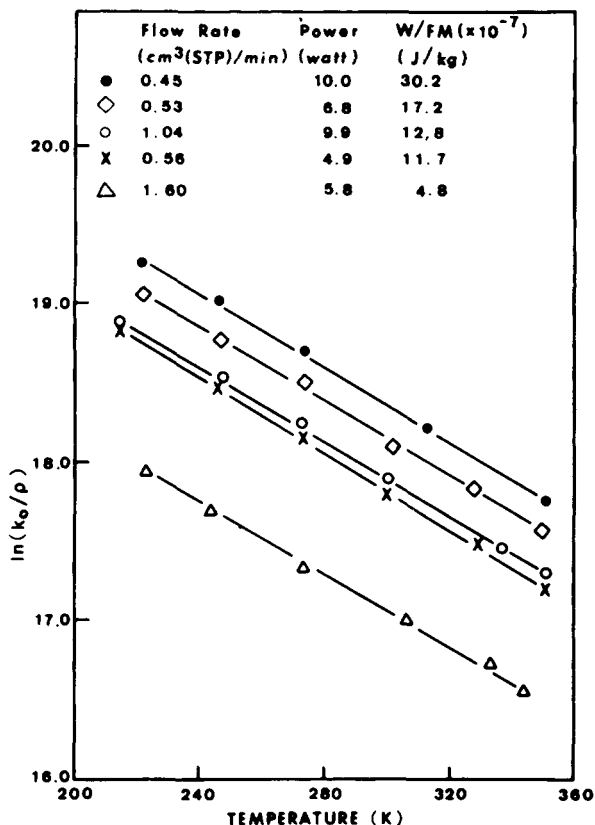


Fig. 5. Effect of substrate temperature on  $(k_0/\rho)$  for TFE.

with  $(W/FM)$  and its dependency is largely dependent on molecular weight of the monomer; that is,

$$a = cM \tag{3}$$

The slopes of the initial linear portion of the plots in Figure 11 are plotted against the molecular weights of monomers in Figure 12. Thus in this region A can be given by

$$A = c(W/F) \tag{4}$$

Therefore in this region eq. (1) can be written as

$$k_0 = c(W/F)e^{-bT} \tag{5}$$

and the deposition rate  $k_1$  is given by

$$k_1 = cWMe^{-bT}. \tag{6}$$

At a given temperature



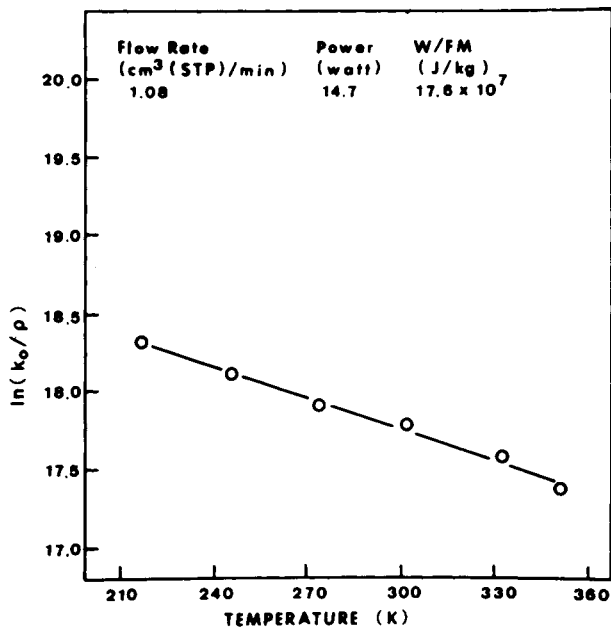
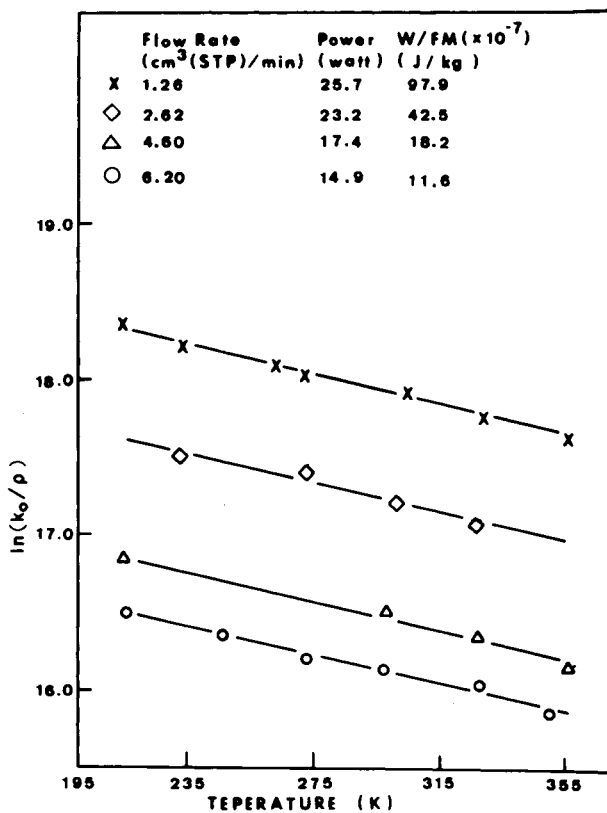
Fig. 6. Effect of substrate temperature on  $(k_0/\rho)$  for styrene.Fig. 7. Effect of substrate temperature on  $(k_0/\rho)$  for ethylene.

TABLE I  
Values of  $b$  for Monomers

Monomer	$b$
Ethylene	$0.0045 \pm 0.0003$
Styrene	$0.0060 \pm 0.0003$
TFE	$0.0112 \pm 0.0002$
PFBTHF	$0.0143 \pm 0.0004$

$$k_1 = c'WM \quad (7)$$

and the observed deposition rate is linearly proportional to discharge wattage ( $W$ ) and molecular weight of monomer ( $M$ ) but is independent of molar (or volume) flow rate ( $F$ ).

### Monomer Deficient Region

As shown in Figures 8 and 9, in the monomer-deficient region the value of  $A$  becomes independent of  $W/FM$ . Therefore eq. (1) for this region can be written as

$$k_0 = Be^{-bT} \quad (8)$$

where  $B$  is a constant that depends on the nature of the monomer. The observed deposition rate  $k_1$  in this region can be given by

$$k_1 = BFMe^{-bT} \quad (9)$$

and at a given temperature

$$k_1 = B'FM. \quad (10)$$

The deposition rate in this region is linearly proportional to the mass flow rate ( $FM$ ) or linearly proportional to the molar flow rate  $F$  and the molecular weight of monomer  $M$  but is independent of discharge power  $W$ .

Because of eq. (3), the value of  $b$  is expected to be larger when  $M$  is larger; however, an exact estimate of value of  $B$  is difficult to achieve because of the transition from the energy-deficient region to the monomer-deficient region. However, an interesting correlation is found between the value of  $(W/FM)_c$ , the critical  $(W/FM)$  value, above which plasma polymerizations become typically monomer-deficient, and the nature of the monomers. In Figure 13 the values of  $(W/FM)_c$  are plotted against values of (total bond

TABLE II  
Values of  $k_0/\rho$  at  $W/FM$  Approximately  $1.8 \times 10^8$  J/kg and Substrate Temperature 273 K

Monomer	$k_0/\rho$ ( $\text{\AA}/\text{kg}(\times 10^{-7})$ )
Ethylene	1.6
Styrene	6.0
TFE	10.8
PFBTHF	7.0

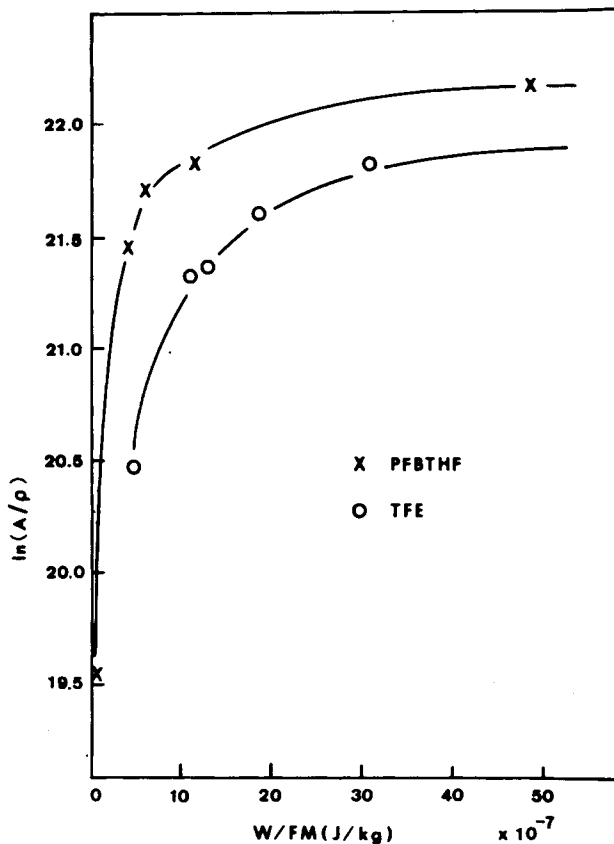


Fig. 8.  $\ln(A/\rho)$  versus  $W/FM$ .

energy)/(molecular weight for the corresponding monomer). Thus the necessary  $(W/FM)$  to bring the plasma polymerization system into the monomer deficient region is proportional to the value of (total bond energies)/(molecular weight). This dependence clearly indicates that in the monomer-deficient region nearly all bonds in a monomer are broken, and, because of this fact, the additional energy input does not influence the plasma polymerization. Plasma polymerization in this region can be recognized as a typical "atomic" polymerization<sup>11</sup> because the original monomer structure is nearly totally destroyed and what counts for polymer formation is the atoms that constituted the original monomer molecule.

Thus the value of  $(W/FM)_c$ , above which the preexponential term  $A$  becomes a constant  $B$ , characteristic of a monomer, can be given by

$$(W/FM)_c = \alpha\Phi \quad (11)$$

where

$$\Phi = \frac{\sum(\text{bond energy})}{M} \quad (12)$$

and  $\alpha$  is the proportionality constant of a given reactor.

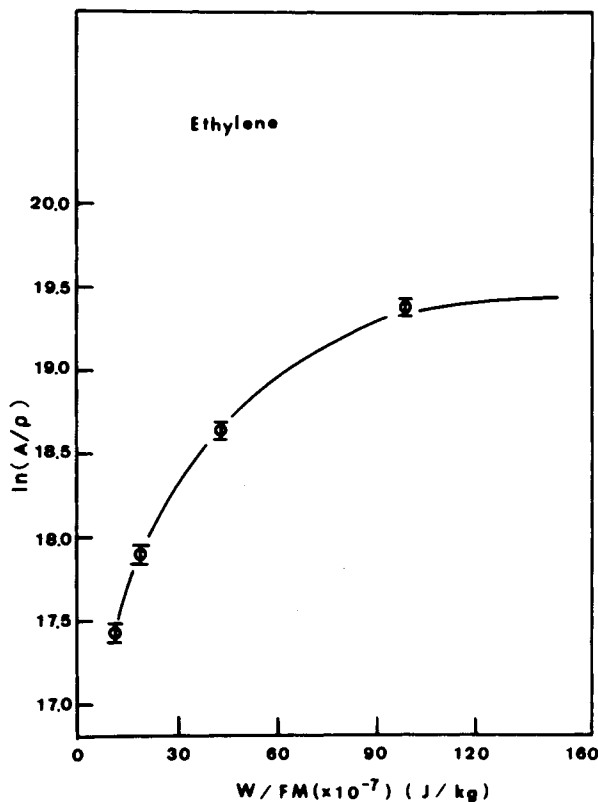


Fig. 9.  $\ln(A/\rho)$  versus  $W/FM$ .

Values of  $B/\rho$ ,  $(W/FM)_c$ , and  $\Phi$  are tabulated in Table III. From these values  $\alpha$  is approximately 19. Thus in the polymerization system used when the energy input in J/kg exceeds approximately 19 times that of the specific bond energy  $\Phi$ , in J/kg, the plasma polymerization becomes typically atomic.

It is important to recognize that a large molecule has a small specific bond energy. On the other hand, because of the larger mass, at a given discharge wattage the value of  $W/FM$  is also small for a large monomer. These trends clearly point out that plasma polymerization of various monomers cannot be compared at an arbitrarily chosen discharge power.

It is also important to recognize in what domain plasma polymerization is carried out under a given plasma polymerization condition. The value of  $(W/FM)$  alone does not determine whether plasma polymerization is in an energy-deficient region or monomer-deficient region. A crude estimate of domain might be made by the parameter  $(W/FM)/\alpha\Phi$  if the value of  $\alpha$  is known for the reactor. The following conditions may be used for this purpose:

- $(W/FM)/\alpha\Phi > 1$  – monomer deficient region
- $(W/FM)/\alpha\Phi < 0.5$  – energy deficient region
- $1 > (W/FM)/\alpha\Phi > 0.5$  – transient region

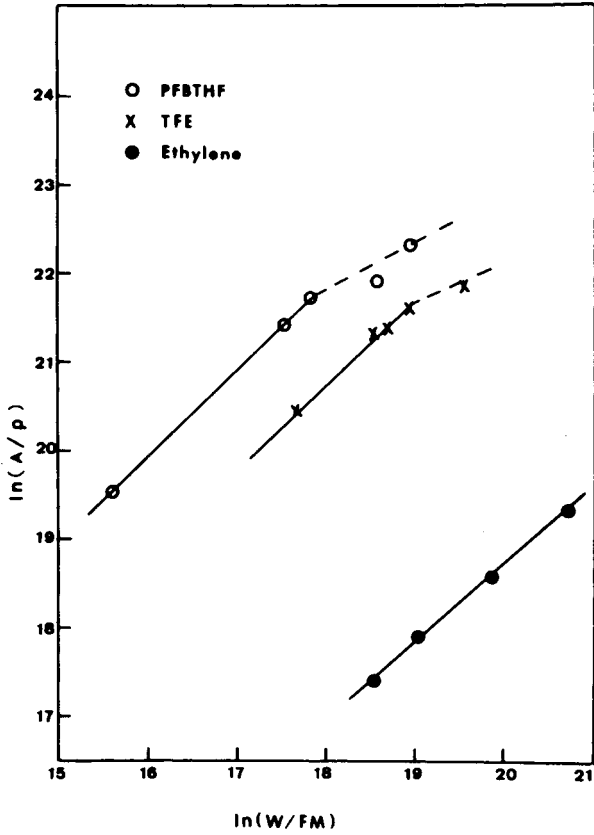


Fig. 10.  $\ln(A/\rho)$  versus  $\ln(W/FM)$ .

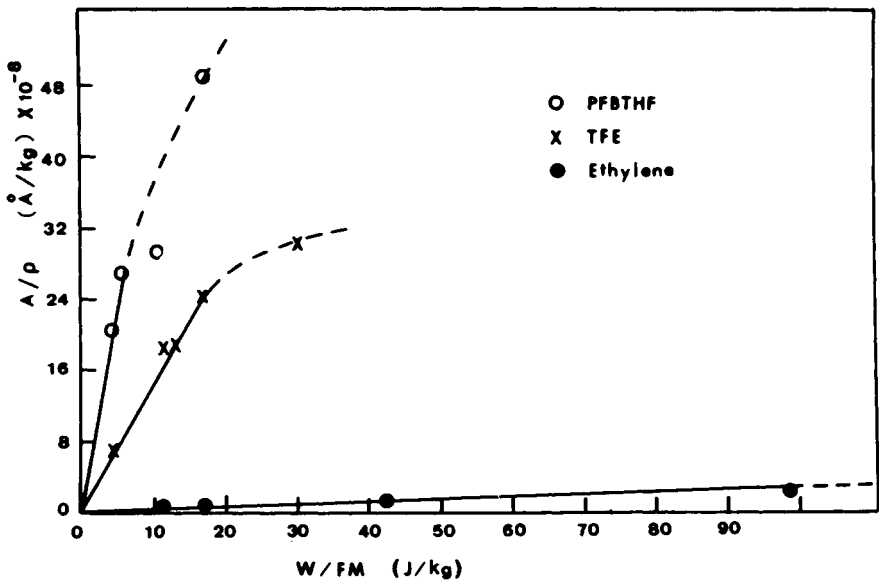


Fig. 11.  $(A/\rho)$  versus  $W/FM$ .

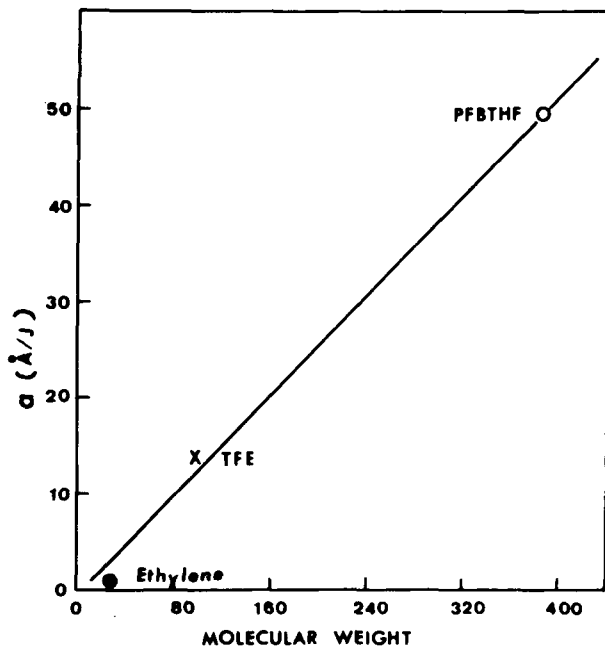


Fig. 12. Slopes of Figure 11 versus molecular weights.

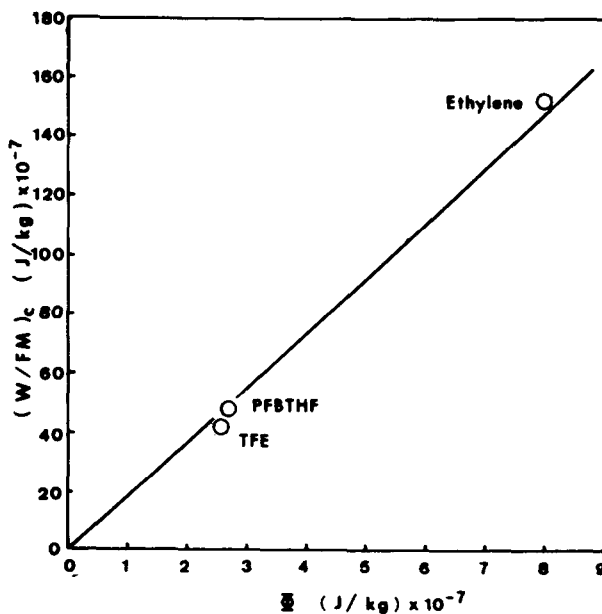


Fig. 13. Critical value of  $W/FM$  versus specific bond energy for each monomer.

TABLE III  
Values of  $B/\rho$ ,  $(W/FM)_c$ , and  $\Phi$  for Monomers

Monomer	$(B/\rho)$	$B/\rho$ ( $\text{\AA}/\text{kg}$ ) $\times 10^{-8}$	$(W/FM)_c$ ( $\text{J}/\text{kg}$ ) $\times 10^{-7}$	$\Phi = \Sigma BE/M$ ( $\text{J}/\text{kg}$ ) $\times 10^{-7}$
Ethylene	19.55	30.9	152	8.0
TFE	21.90	32.4	42	2.6
PFBTHF	22.15	41.6	48	2.7

### Discussion of Polymerization/Deposition Mechanisms

In the interpretation of the temperature-dependence of the polymer deposition described above it is important to recognize the following characteristic features of plasma polymerization:

(1) Plasma polymerization occurs under nonequilibrium conditions. No thermal equilibrium exists among the various reactive species involved in plasma; for instance, the temperature of electrons is in the order of 60,000 K, whereas the temperature of most neutrals and ions is less than 500 K.

(2) In the plasma state the overall average temperature of neutrals and ions is considerably higher than the ambient temperature and under such energetic states desorption rather than adsorption is favored. Consequently, condensed-phase polymerization of adsorbed "monomer" is unlikely to occur.

(3) Because of the extremely low ceiling temperature of polymerization under low pressure (vacuum), the chain-growth polymerization in the gas phase is unlikely to occur.

(4) Nearly all organic compounds, regardless of chemical structure, can be polymerized by plasma polymerization. The contribution of a polymerizable structure such as a double bond is relatively small.<sup>11</sup> Therefore plasma polymerization can be explained best by the rapid step-growth polymerization suggested by Yasuda.<sup>1</sup> This mechanism is explained here and is examined by virtue of experimental data presented in this article and also by some previously presented data on the trapped free radical concentration on plasma polymers.

Plasma polymerization may be explained by the bicyclic rapid step-growth polymerization shown schematically in Figure 14, in which the reactive species are represented by free radicals; however, any other reactive species can contribute each step. Step (1) and Step (4) are essentially the same as the addition of reactive species to the monomer; however, the kinetic chain length in vacuum is extremely short and in a practical sense these reactions can be considered as stepwise. Cycle 1 consists of reactions of monovalent reactive species and cycle 2 is based on divalent reactive species. Step (3) is essentially a cross-cycle reaction from cycles 1 and 2. Cycle 1 requires the reexcitation of the product species, whereas cycle 2 can proceed without reexcitation as long as divalent reactive species exist. Any of the species involved will collide with the substrate surface; however, not all of them would remain on the surface, depending on the kinetic energy of impinging species. The sticking coefficient may be defined as (number of particles remains on the surface)/(number of total impinging particles). The sticking coefficient will increase with the size of the particle and also at a

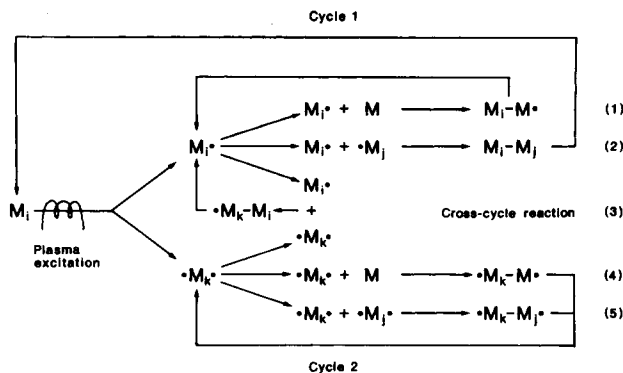


Fig. 14. Schematic representation of bicyclic step-growth mechanism of plasma polymerization.

lower substrate temperature. *The deposition occurs when an impinging particle fails to leave the surface by loss of kinetic energy or by formation of a chemical bond.*

In plasma polymerization, therefore, polymerization and deposition are inseparable aspects of polymerization/deposition mechanism. Each step considered in Figure 14 is not polymerization by itself, whereas repeating steps via cycle 1 or cycle 2 the species involved will deposit on the substrate surface.

The formation of reactive species from the monomer or from the (non-reactive) products of step (2) is essentially a destructive process; that is, it requires breaking the bond, C—H, C—F, C—C, etc. Consequently, how far these step reactions have progressed before the deposition occurs would influence the chemical nature of polymeric deposit. This situation may be visualized by the change in ESCA Cls spectra of plasma polymers of PFBTHF due to the change in substrate temperature. In Figure 15 Cls ESCA spectra of plasma polymer of PFBTHF deposited at two different temperatures, 75 and  $-25^{\circ}\text{C}$ , and at two different levels of  $(W/FM)$ ,  $0.65 \times 10^7 \text{ J/kg}$  and  $11.6 \times 10^7 \text{ J/kg}$ , are compared.

ESCA Cls peaks are deconvoluted by a computer. An example of deconvolution of Cls peak (shown at the upper left of Figure 15) is shown in Figure 16. The results of deconvolution, together with the assignment of peaks, are shown in Table IV.

At both levels of  $(W/FM)$  it is evident that polymers deposited at lower temperatures have higher contents of *F*-containing moieties. Peaks 1 and 2 steadily increase at the expense of peaks 4 and 5 as the substrate temperature decreases. A relatively small change is observed in No. 3 peak. It is also evident that at higher level of  $(W/FM)$  the *F*-containing moieties decrease and No. 5 peak increases significantly, indicating higher extent of fragmentation of *F* and a consequent increase in crosslinking and/or branching.

The most significant aspect here is the fact that the same trend is also found as a consequence of the change in substrate temperature at a given level of  $(W/FM)$ . It should be reiterated that the plasma polymerization conditions were kept constant and only the temperature of substrate surface



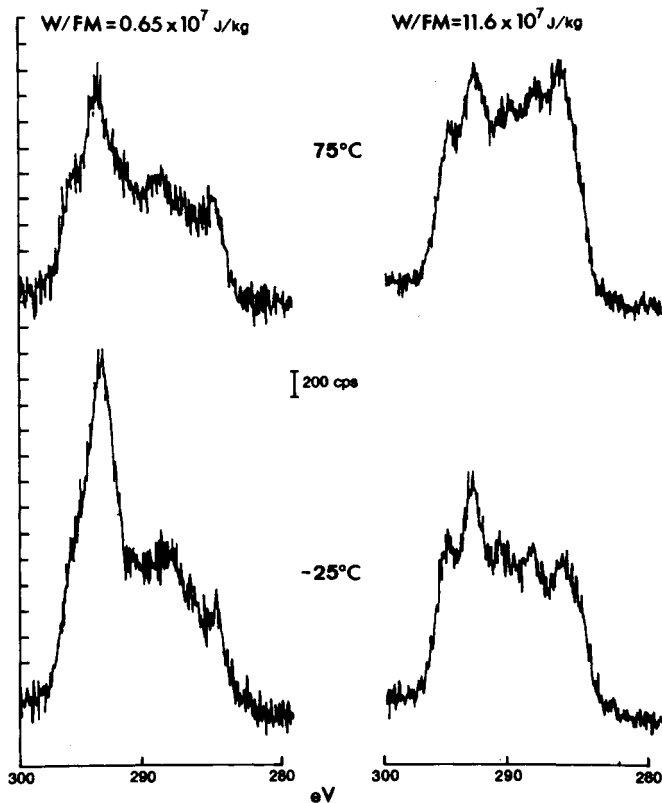


Fig. 15. ESCA Cls spectra of plasma polymers of PFBTHF obtained at different ( $W/FM$ ) and substrate temperature.

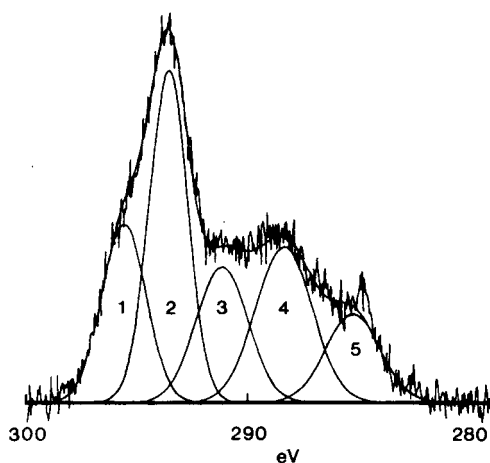

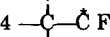



Fig. 16. An example of the deconvolution of ESCA Cls peaks of plasma polymer of PFBTHF;  $W/FM = 0.65 \times 10^7$  J/kg,  $T = 75^\circ\text{C}$ .

TABLE IV  
Change of ESCA Cls Peaks of Plasma Polymers of PFBTHF Due to the Change on  
Substrate Temperature and  $W/FM$

$W/FM$ (J/kg) $\times 10^{-7}$	Substrate temperature (°C)	Percent peak area of component peaks <sup>a</sup>				
		1	2	3	4	5
0.65	75	16.0	21.1	19.4	26.6	17.0
	50	16.5	26.8	18.5	22.9	15.2
	25	17.3	27.2	19.5	22.7	13.3
	0	18.5	27.8	14.9	22.1	16.7
	-25	19.1	30.9	16.8	21.4	11.8
11.6	75	14.9	18.1	18.8	19.3	28.9
	50	15.0	18.8	18.3	20.0	28.1
	25	16.6	20.0	17.7	18.8	27.2
	0	16.7	20.2	17.5	19.4	26.2
	-25	17.8	21.0	17.8	18.8	24.6
	-49.5	18.0	21.2	17.1	19.8	24.0

a

Peak	Approximate peak position (eV)	Approximate peak width (eV)
1 —CF <sub>3</sub>	295	2.0
2 —CF <sub>2</sub> —	293	1.9
3 	291	2.3
4 	288	2.3
5 $\text{>C-H}$ and 	286	2.8

was changed. Therefore the change in polymer structure is not due to the change in chemistry involved in the plasma phase but to the substrate temperature effect on plasma polymerization/deposition mechanisms, which can be explained best by the mechanisms described in Figure 14. The bicyclic rapid step-growth polymerization mechanism has an important implication in the interpretation of the diagnostic data of the plasma or gas phase; namely, species identified in the plasma phase are the intermediate species of the step-growth polymerization but not precursors or plasma-synthesized monomers of black-box plasma polymerization. In this sense the use of word "precursor," without identifying or specifying the growth mechanisms just because of seemingly highly reactive nature of the species, is misleading in the elucidation of plasma polymerization.

Other supporting evidence of the bicyclic rapid step-growth mechanism may be seen in the effect of pulsed glow discharge on plasma polymerization of various organic compounds reported earlier.<sup>12</sup> In the pulsed glow discharge study a peculiar phenomena which could not be clearly explained was observed; that is, when pulsed glow discharge was used certain types of monomer showed a conspicuous increase in their deposition rates compared with the continuous glow discharge. Those monomers also showed significantly a large increase in the trapped free radicals in the plasma polymers by the pulsed glow discharge. These groups of monomers all contained double or triple bonds in the monomer structure.

TABLE V  
ESR Spin Concentration in Plasma Polymers and Glass Substrates

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

<sup>a</sup> Changes are based on values of continuous discharge.

Now these peculiar phenomena can be explained by the bicyclic rapid step-growth mechanisms: when a double bond or triple bond containing monomer is subjected to glow discharge condition bifunctional reactive species, such as diradicals, carbene, or ion-radicals, are formed due to the presence of the multiple bond. At the same time, monovalent reactive species are formed by hydrogen abstraction and/or breaking of C—C bond formed by the preceding steps. Consequently, in most cases cycles 1 and 2 occur simultaneously in a competitive manner. Under such a circumstance step (3) acts as the breaking process of cycle 2.

When a pulsed glow discharge is used, during the off-duty period of pulsed glow discharge cycle 1 ceases while cycle 2 proceeds. Therefore the effect of pulsed glow discharge would be different, depending on which of the two cycles plays the dominant role.

In the case of saturated monomers cycle 1 plays the dominant role and the pulsed discharge decreases the deposition rate as well as the concentration of trapped free radicals. In contrast to this situation, in the case of unsaturated monomers, the cessation of cycle 1 during the off-duty period enhances the overall contribution of cycle 2 because of the absence of step (3) during this period. Consequently, increased deposition rates and increased concentration of trapped free radicals by the pulsed discharge result. This situation may be seen in data cited from the literature (Table V).

It is important to note that cycle 2 leads to unterminated "living" free radicals. *Para*-xylylene polymerization is a clear example of diradical polymerization which depends entirely on cycle 2. A well defined diradical is formed by the thermal cracking of cyclic dimer of *para*-xylylene and the overall situation is much simpler than in plasma polymerization. Nevertheless, in *para*-xylylene and plasma polymerization roughly equal amounts ( $10^{18} - 10^{20}$  spins/cm<sup>3</sup>) of free radicals are found in the product polymers.

Thus it appears that rapid step-growth polymerization is the key factor and bifunctional reactive species play important roles in the vacuum deposition of polymers. Without repeating the excitation, in the case of *para*-xylylene polymerization, rapid step-growth polymerization via bifunctional reactive species seems to be the only way by which polymeric film deposition can be achieved in an efficient manner.

In plasma polymerization the formation of bifunctional reactive species depends on the chemical structure of monomer and to a lesser extent on the glow discharge conditions. At high  $(W/FM)/\alpha\Phi$  ratio discussed in the preceding section plasma polymerization shifts more to the "atomic polymerization" and loses the specificity of the monomer. This aspect can also be clearly seen in ESCA data presented in Figure 15 and Table IV. In the monomer-deficient region the role of cycle 1 becomes dominant, even with a monomer that can easily form bifunctional reactive species in the energy deficient region.

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