

Structure and ESR Investigation of Plasma-Polymerized Film of Hexafluoropropene

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SYNOPSIS

The structure and constitution of plasma-polymerized film of C_3F_6 (PPHFP) have been investigated by measuring its ESCA, ^{19}F -NMR, and IR spectra. It is found that the PPHFP film was a high degree of branching and 57% of quaternary carbons are linked to CF_3 groups. It is also found that the constitution of PPHFP film is changed greatly at high power and a large amount of Si and O atoms are linked to the PPHFP chains. Furthermore, using element analysis, ESCA, and theoretical calculation by electronegative model, we found that the nitrogen atoms get into the PPHFP chains when using N_2 as plasma gas. Besides, the radical concentration in the film is obtained to be 9.97×10^{19} spins/g and its half-life is about half a year at room temperature in Ar gas. Having investigated decay process of the radicals in two gases of air and Ar, we calculated the activation energies and rate constants of radical recombination and oxidation reactions at different temperatures.

INTRODUCTION

Plasma polymerization has been an active area of study interested both in academia and industry. The thin film has the characteristics of continuity, being well-distributed, nonhole, superthin, good stability and dielectric, and its structure is different from the traditional polymers. Usually the film is high degree of crosslinking,¹⁻³ so that its density is higher than that of traditional polymer.⁴ In the present study we characterized the structure of PPHFP film by using ^{19}F -NMR, ESCA, and IR techniques and found that the film has a high degree of branching. Yasada reported that the content of nitrogen in plasma polymer would increase when using N_2 as plasma gas, but no details and not enough evidence could be found.⁵ Although many reports have shown that there is high radical concentration in plasma polymer,^{6,7} there has been no literature on the investigation of decay process of plasma polymer radical by dynamics. We present a short report on the plasma polymer of C_3F_6 here.

EXPERIMENTAL

The reactor used was a capacitively coupled 13.56-MHz radio-frequency plasma apparatus with external electrodes. The ratio of plasma gas to monomer was regulated by controlling the partial pressure of gas. C_3F_6 was frozen three times before being introduced into the reactor. The polymer sample for IR and ESCA determination was deposited directly on the NaCl power and copper disc, respectively. The specimen for elementary analysis and ESR was gathered by scratching and mixing the polymers which had been deposited on the wall of the reaction chamber, and this process should be protected by the flowing Ar gas. The ESR tube which was pre-treated with Ar gas was closed after adding the sample into it to avoid touching air. The process of adding the sample is that the mouth of the ESR tube was inserted into the gathered polymers presented in the reaction chamber, which was protected by flowing Ar gas. The closed ESR tube was opened and the flowing air was poured into it, measuring the decay of free radicals in air. It requires a short time of exposing the samples to air during the process of handling samples in transfer from a closed tube to an element analysis and ESCA spectrometer.

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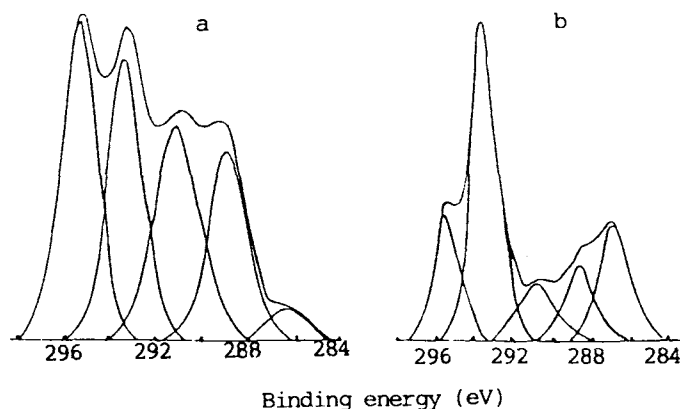


Figure 1 C_{1s} levels of PPHFP films obtained at 60 W, 0.05 torr, and 20 min: (a) glow discharge region; (b) nonglow discharge region.

ESCA spectra were recorded on an ESCA-650 spectrometer with an Mg- $K_{\alpha 1,2}$ photo source. Integration of the spectra was accomplished with a PAC-660 analog curve. The infrared spectra was carried out with NaCl powder on an FTS-20E infrared spectrometer. ^{19}F -NMR spectra were recorded on an Fx-100 spectrometer. The observed frequency was 93.66 MHz and pulse duration was 24 μs . The internal reference was trifluoroacetic acid. ESR measurement was carried out on a JMFE-A spectrometer.

RESULTS AND DISCUSSION

Structure Characterization of PPHFP Film

The C_{1s} levels of PPHFP film formed in glow and nonglow discharge region are shown in Figure 1. Each C_{1s} level can be resolved into five peaks by using the computer, i.e., CF_3 , CF_2 , CF , C , and CH groups, respectively. It can be seen that the structure of PPHFP film formed in the glow region is different obviously from that formed in the nonglow region. The ordered structure of latter is much better than former's. On the other hand, the relative content of quaternary carbon in polymer is higher (Fig. 1). Supposing that the quaternary carbon can represent crosslinking degree, the polymer would be insoluble and nonmelt. But, in fact, even if the polymer film formed at high power dissolved easily in the solvent of 1,2-dibromo-1,1,2,2-tetrafluoroethane. This indicates that there is no crosslinking in the film. Figure 1 (a) also shows that the content of the CF_3 group is larger than that of the CF_2 group. This phenomenon will always occur at a polymerization condition of low power and high pressure, which is shown in

the latter system. In order to determine the distribution of the CF_3 group in the polymer and the branching degree of the PPHFP film, the ^{19}F -NMR spectrum was measured (Fig. 2).

The assignment of peaks in ^{19}F -NMR spectrum can be consulted in the literature.⁸ Their chemical displacements from low to high magnetic field are as follows: δ 30–10 ppm for $\text{CF}_3\text{-C}$; δ 10–0 ppm for $\text{CF}_3\text{-CF}$; δ 0–10 ppm for $\text{CF}_3\text{-CF}_2$; δ -10–-60 ppm for $\text{CF}_2 + \text{CF}$; δ -44 ppm for CF-CF_2 ; δ -49 ppm for $\text{CF}_2\text{-CF}_2$.

The molecular weight of PPHFP film is found to be 2998. The numbers of each group in one polymer chain can be obtained by theoretical calculation, supposing that each polymer chain is made of C and F atoms. The results are as follows: CF_3 , 22.3; C, 14.1; $\text{CF}_3\text{-C}$, 7.9; CF , 19.3; $\text{CF}_3\text{-CF}$, 8.4; $\text{CF}_2\text{-CF}_2$, 6.1.

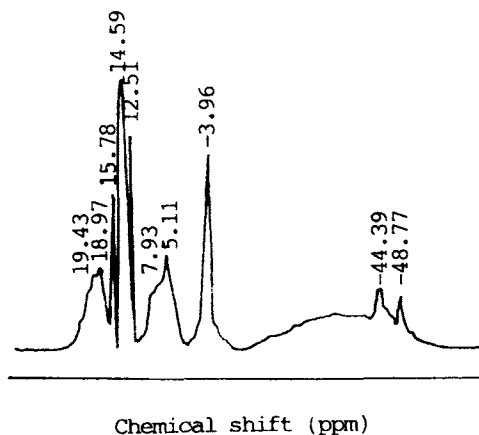


Figure 2 ^{19}F -NMR spectrum of PPHFP film obtained at 30 W, 0.1 torr, and $\text{C}_3\text{F}_6/\text{Ar} = 1:1$.

Table I Variety of Content for Groups at Different Power

| Power (W) | CF (%) | CF (%) | CF (%) | C (%) | F/C ^a |
|-----------|--------|--------|--------|-------|------------------|
| 10 | 31.36 | 30.34 | 20.62 | 17.68 | 1.75 |
| 30 | 29.61 | 28.55 | 23.27 | 18.55 | 1.69 |
| 50 | 27.85 | 30.04 | 24.13 | 17.95 | 1.67 |
| 70 | 25.22 | 30.01 | 25.93 | 18.81 | 1.60 |
| 120 | 23.93 | 29.40 | 26.97 | 19.61 | 1.58 |

^a The calculation of F/C ratio is as follows: $F/C = 3 CF + 2 CF + CF/3 CF + 2 CF + CF + C$, where CF ($x = 1-3$) represents its content in C_{1s} level.

It should be pointed out that both the Si and O atoms in the polymer here are neglected in previous treatment. This is because their contents are too small to be considered in the system, i.e., at high pressure and low power, although these two elements obviously appear in IR spectra in other systems. It can be found from the results that almost 57% of quaternary carbons in PPHFP film are linked to the CF₃ group; thereby the film is high degree of branching. In order to investigate the changes in structure with power, we chose five kinds of different power to prepare PPHFP film. The relative contents of the groups in C_{1s} levels and F/C ratios of the polymers are shown in Table I. It can be seen that defluoridation in the PPHFP film increased quickly with the increase of power. This led to more active points to form branching bonds.

To illustrate the above change in defluoridation (representing etching reaction to some extent) in the film, a series of IR spectra of the film formed at different powers were measured. Figure 3 is a representative spectrum among these. The peak at 1250 cm⁻¹ is the vibration of C—F bonds (or the products of plasma polymerization of C₃F₆). The peak at 740 cm⁻¹ is the vibration of Si—F bonds caused by the reaction of SiF₄ and NaCl (or representing etching reaction). The ratio of peak area of Si—F to that of C—F can be considered to represent approximately the ratio of the polymerization rate to the etching rate.

It has been seen from the results listed in Table II that the defluoridation (or etching rate) increases and the polymerization rate decreases with the increase of power. It should be noticed that there is an interesting phenomenon in IR spectra of PPHFP film at different power, i.e., the peak at 1090 cm⁻¹ is hard to see at low power, but it gets bigger, and resolves into three peaks as increasing power (Fig. 4). According to the literature,⁹ the spectrum line of Si—O—Si bonds is between 1120 and 1000 cm⁻¹, and only one peak appears at 1090 cm⁻¹ or so for a

short chain compound. But with increasing the length of chain this peak will resolve into two or three peaks, which are very complex, strong, and wide. This is right in accord with our experimental results. It can be inferred that the peak at this region is caused by Si—O—Si bonds. To confirm this inference, the ESCA measurement of the film was made (Fig. 5), and the two spectra prove powerfully the existence of Si and O atoms in PPHFP film. This indicates that the constitution of the film changes greatly and confirms the existence of etching reaction in plasma polymerization.

Because of the high energy of electrons or F atoms created at high power, the SiF₄ molecule will be produced when F atoms impact the glass wall; then the SiF₄ molecule reacts with NaCl on disk to form NaSiF₆. When electrons impact the glass wall, Si—O—Si parts will be etched down from the glass wall. These Si—O—Si parts are deposited on the disk and rebegin polymerization after high energy species further impact the disk surface. This makes IR spectra have peaks at 1120–1000 cm⁻¹.

Confirmation of Nitrogen Getting into the PPHFP Chains

Table III shows the element analysis data of PPHFP film obtained using Ar/N₂ as plasma gas at the same

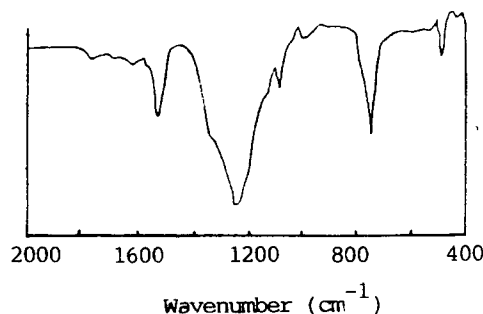


Figure 3 IR spectrum of PPHFP film obtained at 50 W, 0.05 torr, C₃F₆/Ar = 1 : 1, and 20 min.

Table II Peak Area and Their Ratios of C—F to Si—F at Different Powers

| Peak | Power (W) | | | | | |
|-----------------------|-----------|-----|-----|-----|-----|-----|
| | 30 | 50 | 70 | 90 | 120 | 140 |
| C—F ^a | 155 | 180 | 131 | 14 | 6 | 6 |
| Si—F ^a | 19 | 31 | 30 | 11 | 8 | 15 |
| C—F/Si—F ^b | 8.2 | 5.8 | 4.4 | 1.3 | 0.8 | 0.6 |

^a Peak area (cm²).^b Ratio of two peak areas.

condition. It can be seen that nitrogen atom does not get into the polymer chain in the case of using Ar as plasma gas. This can be confirmed by ESCA spectra of etched sample surface. A minute amount of nitrogen results from this when the sample was transferred from a closed tube to the element analysis spectrometer parts of the very reactive fragments on its surface absorb the N₂ from air. This phenomenon was also observed by Yasuda.⁵

The nitrogen content in PPHFP is very high and the N/C ratio reaches 1/3 at 30 W when N₂ was used as plasma gas. This indicates that there is one nitrogen atom for every three carbon atoms in the

polymer chain. Although Yasuda⁵ also found from ESCA spectra that with the N₂-plasma-treated polyethylene the significant level of nitrogen incorporation is evident, he could not explain it and no details could be found. It can be seen from the ESCA spectra of PPHFP films (Fig. 6) that the contents of CF₂ and quaternary carbons in PPHFP films for the N₂ plasma system are lower than that for Ar plasma system. The decrease of quaternary carbon can be explained by nitrogen into the polymer chain. And the decrease of CF₂ group can be illustrated by the theoretical calculation according to the electronegative model.^{10,11} Its formula is as follows:

$$\chi_c = \left[\left(\sum_{j=1}^4 \frac{1}{n_j} \chi_j \right) / \sum_{j=1}^4 \frac{1}{n_j} + 2.5 \right] / 2, \quad (1)$$

where χ_j is electronegativity on the j th adjacent atom and n_j is the number of the chemical bonds between the j th adjacent atom and its surrounding carbon atoms. After the electronegativity values on the carbon atoms from the farthest one to the nearest one along the polymer chain have been evaluated, the electronegativity values on the carbon atoms ad-

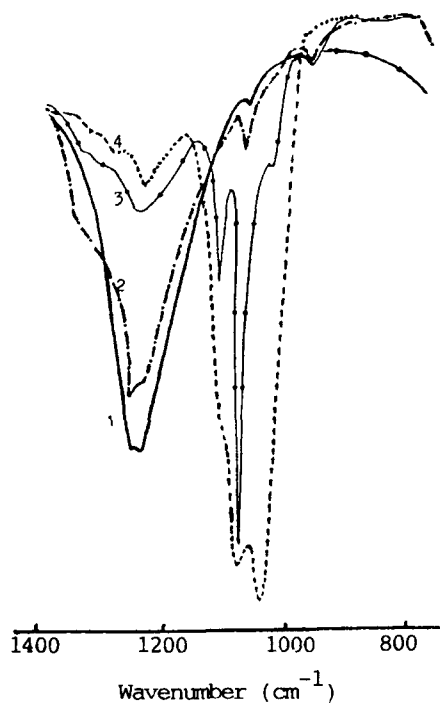


Figure 4 IR spectra of PPHFP film obtained at 0.05 torr, C₃F₆/Ar = 1 : 1, 20 min, and different power: (1) 30 W; (2) 70 W; (3) 90 W; (4) 140 W.

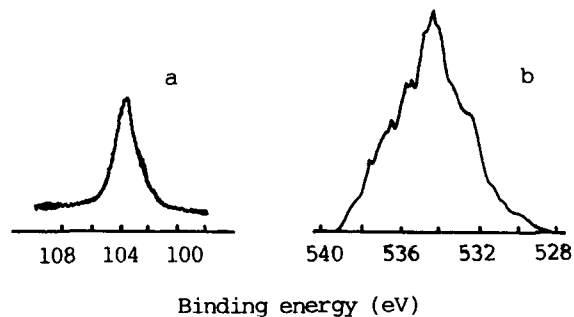


Figure 5 ESCA spectra of Si_{2p} and O_{1s} region of PPHFP film obtained at 100 W, 0.05 torr, C₃F₆/Ar = 1 : 1, and 20 min: (a) Si_{2p} region; (b) O_{1s} region.

Table III Element Analysis Data of PPHFP Film Obtained Using Ar/N₂ Plasma Gas^a

| Plasma Gas | Plasma Power (W) | Content of Carbon (%) | Content of Nitrogen (%) |
|----------------|------------------|-----------------------|-------------------------|
| Ar | 30 | 28.43 | 0.75 |
| N ₂ | 30 | 27.93 | 9.97 |
| N ₂ | 90 | 28.43 | 7.75 |

^a Polymerization condition: 0.1 torr, C₃F₆/Ar(N₂) = 1 : 1, 6 h.

joining with the central carbon atom χ_j in eq. (1) can be obtained. The binding energy shift can be calculated according to the following formula:

$$\Delta E_c = \left[\sum_{i=1}^4 \frac{1}{n_i} (\chi_i - 2.5) \right] \times 1.57 + 1.50 \quad (2)$$

where n_i and χ_i has the same implication as above.

By designing different structure models, it can be seen from the calculation that when second carbon (two bonds are joined to carbon atoms) or even other carbon atoms in the PPHFP chains are linked to nitrogen atoms, the binding energy shift of the second carbon shifts obviously toward the CF region in the ESCA spectra. The results are shown in Table IV.

All the ESCA spectra of PPHFP films obtained using N₂ and Ar as plasma gas have N_{1s} and O_{1s} levels. Figure 7 shows the ESCA spectra of N_{1s} and O_{1s} region of PPHFP film obtained in Ar plasma

Table IV The Calculated Value of Binding Energy of C* in Different Model Compounds

| Model compounds | ΔE_c | E_c |
|---|--------------|--------|
| $\begin{array}{c} \\ -C-CF-CF_2-C- \\ \quad \\ *CF_3 \end{array}$ | 8.80 | 293.80 |
| $\begin{array}{c} CF_3 \\ \\ -CF_2-CF-C-CF_2-CF_3 \\ \quad \\ F_3C \quad *CF_2-C- \\ \end{array}$ | 7.40 | 292.40 |
| $\begin{array}{c} F_3C \quad CF_2 \\ \quad \\ -C-CF_2-*CF-C-CF_2-CF_3 \\ \quad \\ F_3C \quad CF_2 \end{array}$ | 5.44 | 290.44 |
| $\begin{array}{c} F_3C \quad CF_2-CF_3 \\ \quad \\ -N-C-*CF_2-C-N- \\ \quad \\ CF_3-CF_2 \quad CF_3 \end{array}$ | 6.47 | 291.47 |
| $\begin{array}{c} F_3C \quad \overset{\ominus}{N} \quad \\ \quad \quad \\ CF_3-CF_2-C-*CF-C-CF_2-CF_3 \\ \quad \\ -N- \quad CF_3 \end{array}$ | 5.01 | 290.01 |

gas. The content of oxygen in PPHFP film is higher than that of nitrogen. Figure 8 shows the treated results of ESCA spectra of O_{1s}, N_{1s}, C_{1s}, and F_{1s}

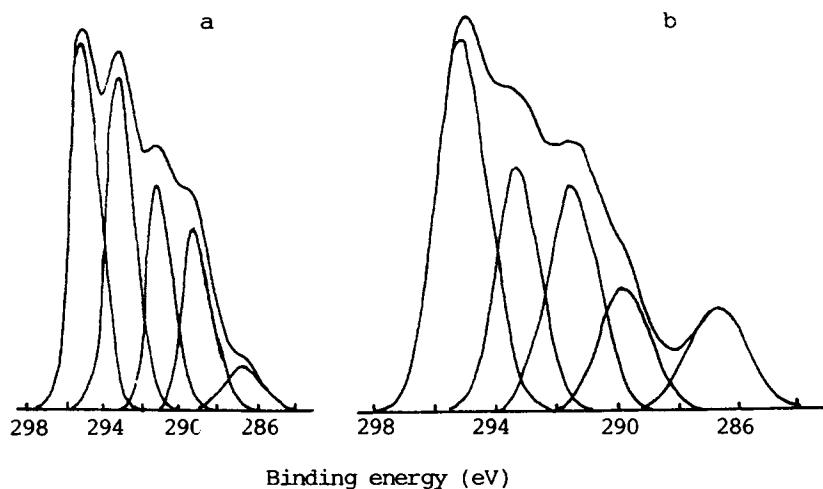


Figure 6 C_{1s} levels of PPHFP films obtained by using Ar and N₂ as plasma gases at 30 W, 0.1 torr, and C₃F₆/Ar(N₂) = 1 : 1: (a) Ar gas; (b) N₂ gas.

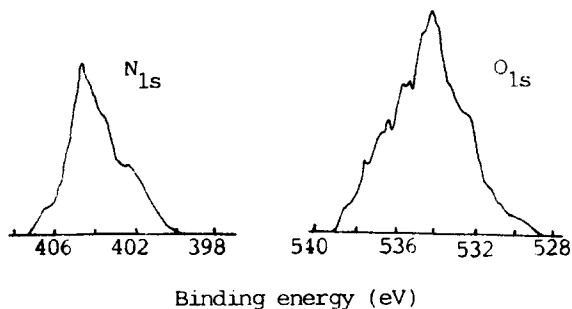


Figure 7 ESCA spectra of N_{1s} and O_{1s} region of PPHFP films obtained by using Ar as plasma gas.

regions for PPHFP films obtained at different plasma power and in Ar plasma gas. The calculation method of F/C ratio is just the same as described above. The O/C ratio is the ratio of the peak area of O_{1s} to that of C_{1s} (deducting the CH pollutant peak), and the N/C ratio is calculated using the same method. It can be seen from Figure 8 that the O/C and N/C ratios of PPHFP increase with the increase of plasma power. This can be explained by the fact that, on the polymer surface exposed to high power, many reactive points were created, thus absorbing more N and O atoms during the measurement of ESCA spectra.

It should be pointed out that the O/C ratio of PPHFP is much higher than the N/C ratio, and the difference between them will increase with the increase of plasma power. This indicates that O atoms are not only on surface of the polymer. Part of the O atoms are also caused by the etching reaction of reactive species with the glass wall. This means that the PPHFP film has more relative long Si—O—Si chains, which has been proved above. Comparing N_2 with Ar plasma gas, we can see that the N_{1s} peak

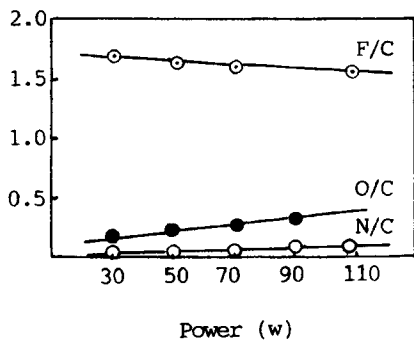


Figure 8 F/C, O/C, and N/C ratios of PPHFP films obtained by using Ar as plasma gas: $C_3F_6/Ar = 1 : 1$; 0.05 torr, and 20 min.

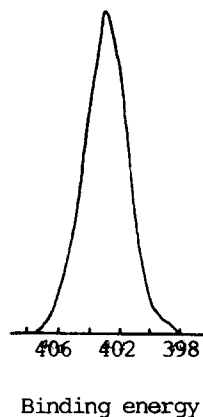


Figure 9 N_{1s} level of PPHFP film obtained in N_2 as plasma gas.

area of PPHFP obtained in the N_2 gas is much larger and more smooth than that in Ar gas at the same plasma power (Fig. 9). The N/C ratio of PPHFP also increases obviously, and it decreases with the increase of power (Fig. 10). This can be explained by the fact that the reactive species of N_2 get into the polymer chain in the form of order at low plasma power, but this order will be damaged at high power. All the results above can confirm that nitrogen atoms indeed get into the PPHFP chains when N_2 was used as plasma gas.

ESR Investigation of PPHFP Film

Because the ESR spectra of $CuSO_4 \cdot 5H_2O$ single crystal and PPHFP sample have almost the same line shape and width, so the radical concentration of PPHFP can be calculated by using $CuSO_4 \cdot 5H_2O$ as a standard sample, and the result is 9.97×10^{19} spins/g. Its half-life is about half a year at room temperature in Ar gas. The molecule weight of

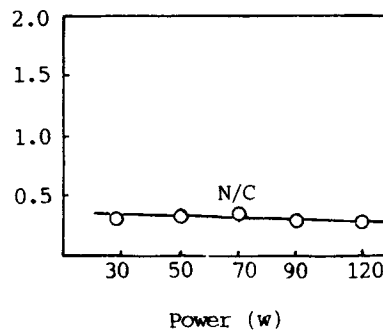


Figure 10 N/C ratio of PPHFP film obtained by using N_2 as plasma gas at different powers.

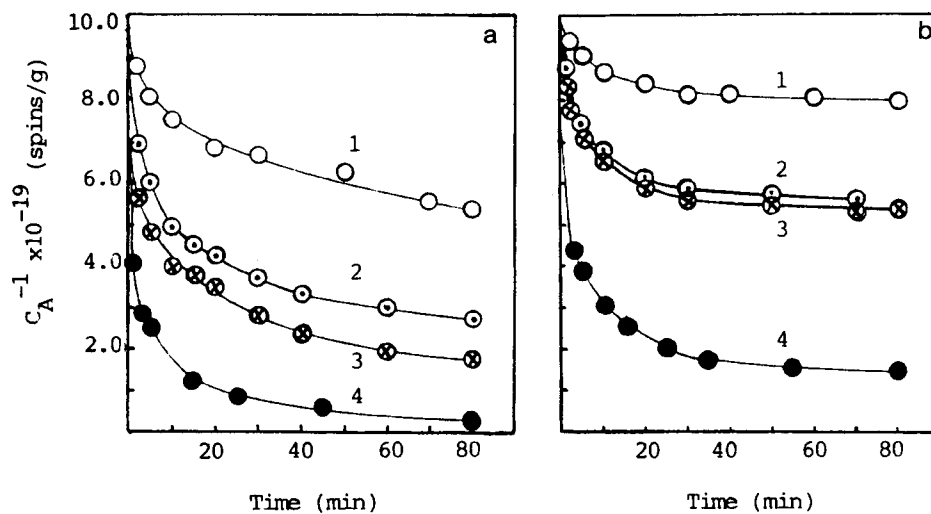


Figure 11 Decay curves of radicals in PPHFP film with different gases and at different temperatures: (a) in air; (b) in Ar gas; (1) 40°C; (2) 60°C; (3) 80°C; (4) 120°C.

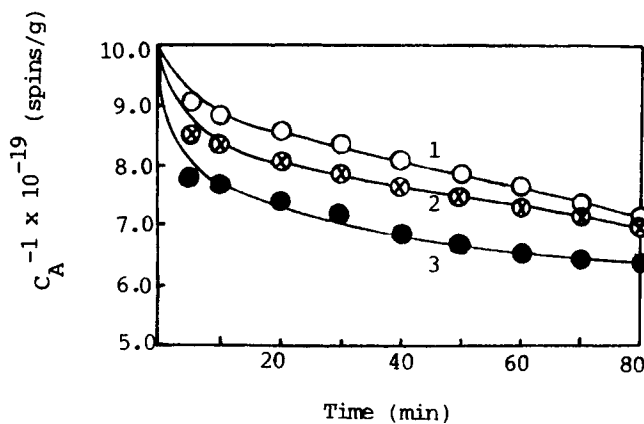


Figure 12 Decay curves of radicals in PPHFP film due to oxygen reaction (1) 40°C; (2) 60°C; (3) 80°C.

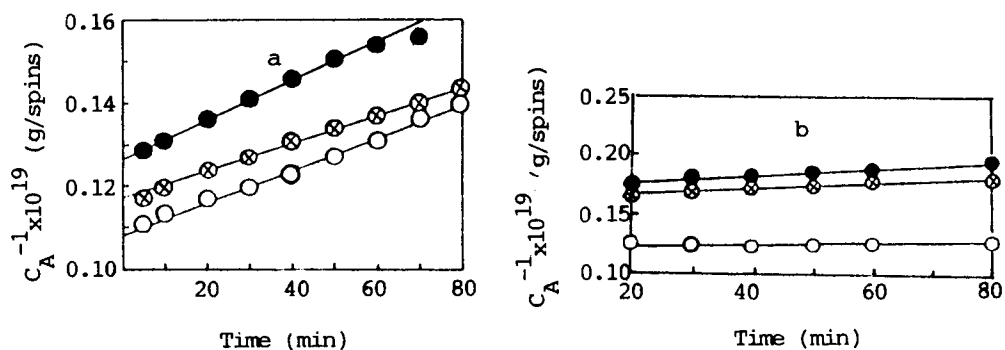


Figure 13 Relation curve of C_A^{-1} vs. t (a) radical oxidation; (b) radical recombination.

Table V Activation Energy and Rate Constant of Radical Recombination and Oxidation

| | Rate Constant (mol spin g ⁻¹ min ⁻¹) | | | Activation Energy (kcal mol ⁻¹) |
|---------------|--|-------|-------|---|
| | 40°C | 60°C | 80°C | |
| Recombination | 4.17 | 10.84 | 16.56 | 7.96 |
| Oxidation | 23.82 | 19.88 | 27.93 | 1.84 |

PPHFP film is 2998, which was obtained by the VPO method. So the number of radicals in 1 mol PPHFP film is 2.99×10^{23} spins. Then it can be concluded that there is one radical every two polymer chains.

There are two factors affecting the decay process of the polymer radicals in air. One is the recombination between radicals; the other is the oxygen making the radicals terminate. But in Ar gas only the recombination of radicals plays a role. Figure 11 shows the decay process of radical concentration at different temperatures. It can be seen that the decay speed of radicals in air is much higher than in Ar gas.

In Ar gas only those reactive radicals (with small potential barrier) can gain enough recombination energy at low temperature. But for most of the radicals their energies are lower than the activation energy in the case. With the increase of temperature the motion of polymer chain increases; thus the number of reactive radicals increases, and it makes the decay rate increase. Even if the radicals with high potential barrier can move sufficiently, they would not recombine after certain reacting time. So the decay rate of radicals gets slower. In air there will be the oxidation reaction besides the above sit-

uation. The slow diffusion rate of O₂ at low temperature makes the decay rate slower. A curve can be gotten if the decay curve in Ar was subtracted from the decay curve in air at the same temperature (Fig. 12).

Supposing that recombination and oxidation reaction of the radicals are the dimolecule unit reaction, then the relation between radical concentration (C_A) and time (t) is as follows: $1/C_A = Kt + 1/C_{A0}$, where C_A is the original radical concentration; K is rate constant of the second-order reaction. Taking the C_A value of radical recombination corresponding to three different temperatures (40, 60, and 80°C)

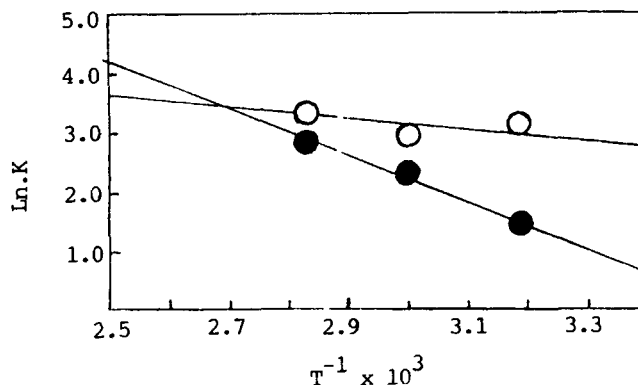
at different times, we can make a plot of $\frac{1}{C_A}$ vs. t

(Fig. 13). The rate constants of the radical recombination and oxidation at different temperatures, which were obtained from the slope of the straight line, are shown in Table V.

According to the Arrhenius equation $K = A \cdot e^{-E/RT}$, a plot of $\ln K$ vs. T^{-1} can be made (Fig. 14). The activation energies of the radical recombination and oxidation reaction can be calculated, which are shown also in Table V. It can be seen that the activation energy of recombination is higher than that of oxidation. This is probably due to the high degree of branching structure of the PPHFP film.

CONCLUSIONS

1. The plasma polymer film of hexafluoropropene has a high degree of branching; almost 57% of quaternary carbon are linked to the CF₃ group.
2. At high plasma power a large amount of Si and O atoms are linked to the PPHFP chains.

**Figure 14** Relation curve of $\ln K$ vs. T^{-1} .

3. Nitrogen atoms get into the PPHFP chains when N₂ is used as plasma gas.
4. Radical concentration of the PPHFP film is about 9.97×10^{19} spins/g. Its half-life is about half a year at room temperature in Ar gas. There is one radical every two polymer chains.
5. The rate constants at different temperatures and activation energies of radical recombination and oxidation reaction are also obtained.

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