

# POLYMERIZATION OF OCTAFLUOROCYCLOBUTANE IN GLOW DISCHARGE

## II. ESCA AND IR CHARACTERIZATION OF POLYMER STRUCTURE\*

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### ABSTRACT

In a capacitively coupled discharge with external electrodes, He, H<sub>2</sub>, N<sub>2</sub> or Ar were used as plasma gas, polymerization of octafluorocyclobutane was carried out under different conditions by varying discharge power, pressure, plasma gas and plasma-gas/monomer ratio. Structure of polymerized products was characterized by IR spectroscopy and ESCA measurement. It was found that there were six elements in the products, i.e. C, F, Si, O, N and H. The probably existed groups in polymers were investigated. By analyzing the resolved peaks of C<sub>1s</sub> region in ESCA spectra, effect of the reaction conditions on degree of branching of the polymerized products and the relationship of the polymer structure with the mechanism of the competitive ablation and polymerization process were studied. In addition, polymer deposition process occurring in glow discharge was discussed.

### INTRODUCTION

Plasma polymerization is a complicated chemical process. It is quite possible that all the materials existing in a system may be excited and activated, and also participated into reaction and eventually incorporated into polymer structure by input of higher energy. The active sites remaining in the polymer may retain great ability to continue the reaction out of plasma, which makes the polymer structure even more complicated. We have studied the mechanism of the competitive ablation and polymerization process of octafluorocyclobutane (OFCB) in glow discharge and discussed the dependence of that mechanism upon power, pressure, plasma gas and plasma-gas/monomer ratio<sup>[1]</sup>. On the basis of the above investigation, this paper further presents our study on the effect of reaction conditions on the structure of plasma-polymerized OFCB.

### EXPERIMENTAL

Octafluorocyclobutane used was a commercial product of the Experimental Plant of Shanghai Institute of Organic Chemistry. Its purity is 99.9%.

The substrates for ESCA measurement were aluminium foils and for IR spectroscopy NaCl and KBr crystals.

The reaction conditions of OFCB plasma polymerization for IR measurement are as follows:

\* Received May 15, 1984

power, 50W; pressure, 100  $\mu$ mHg; plasma-gas/monomer ratio, 1/1; reaction time, 7 hours.

Binding energy of each peak in ESCA spectra was corrected by  $\text{Au}_{4f\ 7/2}$  core level. Those listed in this paper are all corrected values.

The reaction equipments, experimental procedure and instruments for characterization may be referred to our previous work<sup>[2]</sup>. Plasma-gas/monomer ratio was regulated by controlling the partial pressure of gas.

## RESULTS AND DISCUSSION

### 1. Elemental composition and possible component groups of polymers

Figure 1 shows an ESCA spectrum of Ar plasma-polymerized OFCB with full scan. There are six elements C, F, Si, O, N and H in the polymer, in which only carbon and fluorine

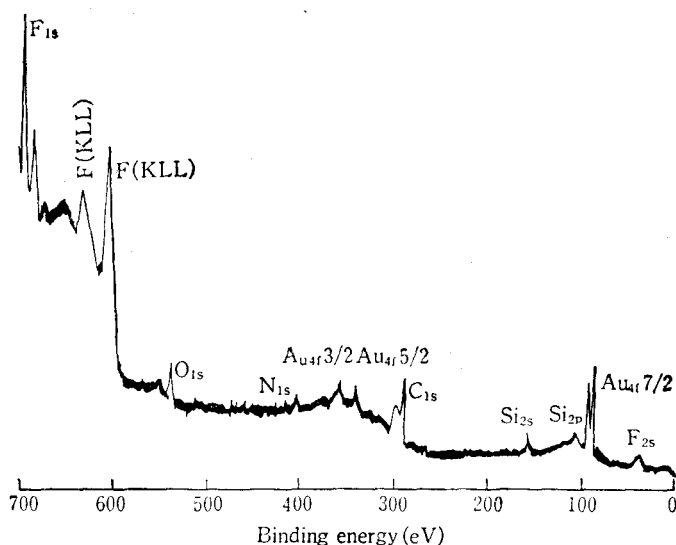


Fig. 1 ESCA spectra of Ar plasma-polymerized OFCB with full scan

are component elements of the original monomer. In Figure 2,  $\text{C}_{1s}$  region with binding energy from 296 to 284 eV, which were corrected by  $\text{Au}_{4f\ 7/2}$  core level, shows an overlapping line shape with various components, which could be resolved into five separate peaks by a deconvolution technique. Arranged in the order from higher to lower binding energy, those

peaks could be attributed to  $-\text{CF}_3$ ,  $-\text{CF}_2-$ ,  $-\text{CF}-$ ,  $-\text{C}-$  and  $-\text{CH}_2-$  groups respectively<sup>[3,5]</sup>.

Half-width of  $-\text{CF}$  and  $-\text{C}-$  peaks is wider than that of  $-\text{CF}_3$  and  $-\text{CF}_2-$  peaks, this obviously indicates overlapping with other groups. Carbons with lower binding energy such as  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$  and the others just fall in the above regions.  $\text{F}_{1s}$  region with binding energy from 696 to 686 eV could be deconvoluted into two separate peaks. The one with higher binding energy corresponds to CF group and the other one is related to SiF group<sup>[1]</sup>. As shown in

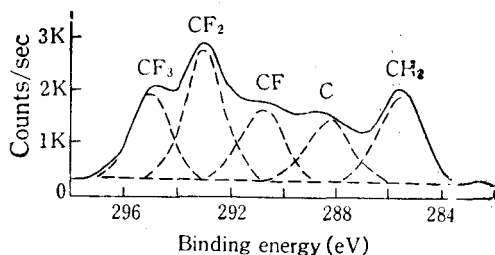


Fig. 2 ESCA spectrum of  $C_{1s}$  region of Ar plasma-polymerized OFCB  
Power, 90W; pressure,  $100\mu\text{mHg}$ ; Ar/M, 1/1; time, 15 minutes

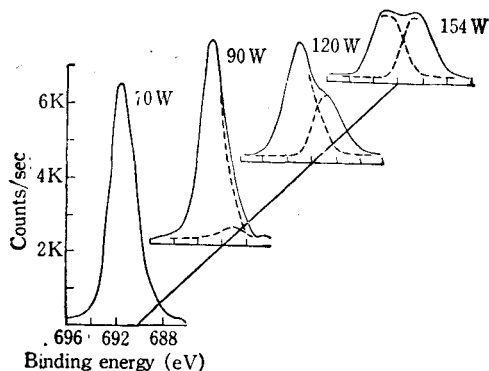


Fig. 3 ESCA spectra of  $F_{1s}$  region of Ar plasma-polymerized OFCB at different power  
Pressure,  $100\mu\text{mHg}$ ; Ar/M, 1/1; time, 15 minutes

Figure 3, with the increase of power, SiF content increases with corresponding decrease in CF content, meanwhile the area and the intensity of  $F_{1s}$  peak decreases in proper order, which is in good accordance with the discussion about the mechanism of the competitive ablation and polymerization process of OFCB in glow discharge. It can be seen in Figure 4, binding energy of  $Si_{2p}$  region is around 101.2 eV, which is 4 eV lower than that of 105.1 eV for silicon in  $Na_2SiF_6$ . This suggests that Si in the polymer is fluorine-deficiency in comparison with that in  $Na_2SiF_6$ . It is possible that  $SiF_4$  formed after the etching of reactor walls by reactive fluorine species is incorporated into polymer structure as end-groups in the forms of  $C-SiF_3$  or  $C-O-SiF_3$ , or as a part of the polymer skeleton in the forms of  $C-SiF_2-C$  or  $C-O-SiF_2-O-C$ . However, just one of the above groups could exist dominantly in polymer structure because  $Si_{2p}$  region does not show an evident overlapping line shape as  $C_{1s}$  region, although it is not specific. ESCA spectra of  $O_{1s}$  and  $N_{1s}$  regions of Ar plasma-polymerized OFCB are shown in Figure 5 respectively. Half-width of  $O_{1s}$  peak with binding energy around 533 eV is wider, which indicates the existence of more than one kind of oxygen-containing groups in  $O_{1s}$  region. Incorporation of oxygen is partially due to the termination of the reactive sites on sample surface by oxygen after exposing to atmosphere. It may also be the case that the polymer surface or the organic vapour in the reaction system react with dissociated  $O_2$  through etching of  $SiO_2$  from the reactor walls. Binding energy of  $N_{1s}$  region is around 402 eV. Since there was no nitrogen in reaction system, incorporation of nitrogen can only

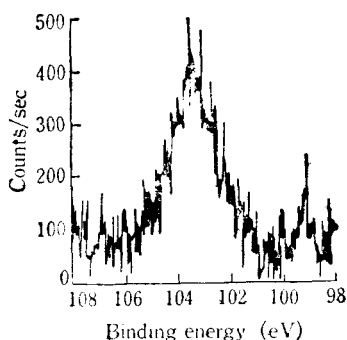


Fig. 4 ESCA spectrum of  $\text{Si}_{2p}$  region of Ar plasma-polymerized OFCB  
Power, 90W; pressure, 100  $\mu\text{mHg}$ ; Ar/M, 1/1; time, 15 minutes

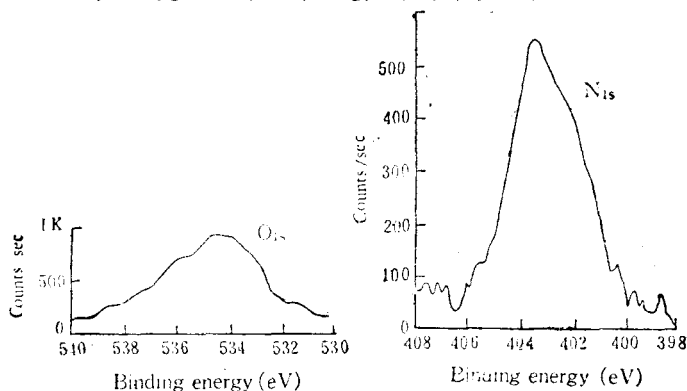


Fig. 5 ESCA spectra of  $\text{O}_{1s}$  and  $\text{N}_{1s}$  regions of Ar plasma-polymerized OFCB  
Power, 90W; pressure, 100  $\mu\text{mHg}$ ; Ar/M, 1/1; time, 15 minutes

be caused by the reaction between active sites on sample surface and  $\text{N}_2$  after exposing in the atmosphere. Owing to the stability of  $\text{N}_2$ , it is suggested that some very reactive sites existing on the fresh surface of sample. Binding energy of  $\text{N}_{1s}$  region for  $\text{N}_2$  plasma-polymerized is nearly similar to that for polymers prepared in a non- $\text{N}_2$  system. Therefore it is inferable that none of nitrogen atoms links with fluorine atoms directly.

IR spectra of polymerized OFCB in Ar,  $\text{N}_2$ ,  $\text{H}_2$ , He discharge are shown in Figure 6—9

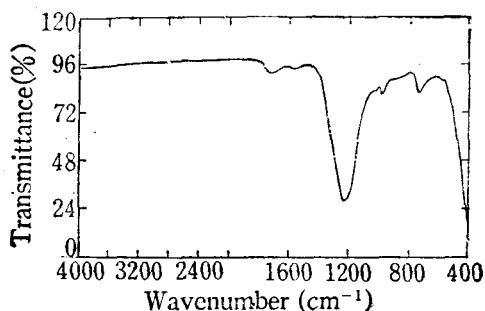


Fig. 6 IR spectrum of Ar plasma-polymerized OFCB

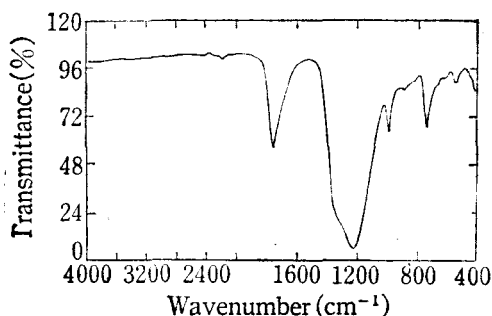
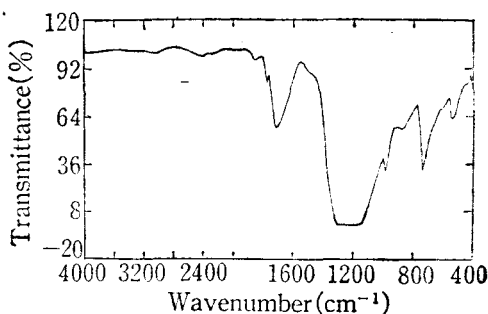
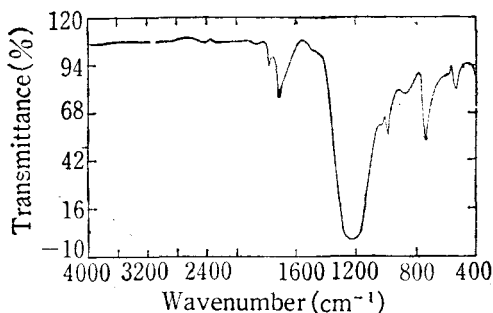
Fig. 7 IR spectrum of  $N_2$  plasma-polymerized OFCBFig. 8 IR spectrum of  $H_2$  plasma-polymerized OFCB

Fig. 9 IR spectrum of He plasma-polymerized OFCB

respectively. In general, the band appearing at  $1200\text{cm}^{-1}$  is characteristic of CF stretching and at  $740\text{cm}^{-1}$  of  $\text{SiF}_2^{[1]}$ . The absorption at  $1700\text{cm}^{-1}$  may be attributed to C=O, CF=CF or C=C groups<sup>[4]</sup>. The other two bands are observed at 990 and  $880\text{cm}^{-1}$ . The source of these peaks are not apparent. Perhaps they are caused by  $\text{CF}_3$  or Si—C groups. Observing in IR spectrum of  $H_2$  plasma-polymerized OFCB, it can be seen that at  $3000\text{cm}^{-1}$  absorption characterizing CH stretching in  $\text{CH}_3$  and  $\text{CH}_2$  groups appears and CF absorption band at  $1200\text{cm}^{-1}$  widens, which indicates that hydrogen was incorporated into polymer structure in a complicated form after substituting a part of fluorine atoms. As shown in IR spectrum of  $N_2$  plasma-polymerized OFCB, absorption at  $2200\text{cm}^{-1}$  is characteristic of  $\text{C}\equiv\text{N}$ , the weaker peak

shows the presence of only a few  $\text{C}\equiv\text{N}$  groups in the polymer. Band at  $1350\text{ cm}^{-1}$  overlaps with CF absorption partially and may be caused by  $-\text{N}-\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix}$ . Perhaps such groups were produced as a result of the reaction between the active sites on sample surface and  $\text{N}_2$  under the presence of  $\text{O}_2$ . It should be noted that an absorption shifts from  $1720$  to  $1760\text{ cm}^{-1}$ , which may be referred to the formation of  $-\text{O}-\text{N}=\text{O}$  in the polymer.

## 2. Degree of branching for polymers

In discussion about the effect of reaction conditions on the mechanism of the competitive ablation and polymerization process of OFCB in plasma, CF and SiF components of  $\text{F}_{1s}$  region in ESCA spectra have been studied<sup>[1]</sup>. on the basis of analysis from the resolved peaks of  $\text{C}_{1s}$  region in ESCA spectra of plasma-polymerized products, in the present work emphasis was put on the study of the effect of reaction conditions upon degree of branching of polymers, so as to reveal the internal relationship between polymer structure and the competition of ablation with polymerization process. Five resolved peaks of  $\text{C}_{1s}$  region in ESCA spectra of plasma-polymerized fluorocarbons could be attributed to  $-\text{CF}_3$ ,  $-\text{CF}_2-$ ,  $-\text{CF}-$ ,  $-\text{C}-$  and  $-\text{CH}_2-$  groups respectively<sup>[3]</sup>, with corresponding binding energy of 293.5, 291.3, 289.0, 286.8 and 284.0 eV (corrected values) in turn. With the exception of  $\text{H}_2$  plasma-polymerized fluorocarbons, the appearance of  $\text{CH}_2$  groups is generally attributed to the contamination by pump oil in measurement<sup>[5,6]</sup>. So the  $\text{CH}_2$  component could be excluded from discussion as groups existing in polymers. Furthermore, take into consideration of the presence of SiF component in  $\text{F}_{1s}$  region, therefore in the calculation of the F/C ratio of polymer structure, instead of using  $\text{F}_{1s}/\text{C}_{1s}$  ratio by area, we prefer to adopt percentage area of each resolved peak in  $\text{C}_{1s}$  region,

Table 1 ESCA results at different power and pressure

| Polymerization conditions |           |                              | Area of $\text{C}_{1s}$ peak* (%) |                 |               |              |                                    |      |
|---------------------------|-----------|------------------------------|-----------------------------------|-----------------|---------------|--------------|------------------------------------|------|
| Ar/M ratio                | Power (W) | Pressure ( $\mu\text{mHg}$ ) | $-\text{CF}_3$                    | $-\text{CF}_2-$ | $-\text{CF}-$ | $-\text{C}-$ | $2 \times -\text{C}- + -\text{CF}$ | F/C  |
| 1/1                       | 154       | 100                          | 17.82                             | 26.63           | 31.18         | 24.32        | 79.82                              | 1.38 |
|                           | 120       |                              | 18.27                             | 30.10           | 27.19         | 23.65        | 74.49                              | 1.42 |
|                           | 90        |                              | 22.07                             | 30.76           | 24.18         | 22.95        | 70.08                              | 1.52 |
|                           | 50        |                              | 24.00                             | 34.80           | 22.04         | 19.14        | 60.32                              | 1.64 |
| 0/1                       | 90        | 25                           | 23.15                             | 23.15           | 26.23         | 20.79        | 67.81                              | 1.55 |
|                           |           | 50                           | 25.44                             | 25.44           | 22.41         | 22.09        | 66.59                              | 1.58 |
|                           |           | 100                          | 23.60                             | 38.08           | 18.24         | 20.05        | 58.34                              | 1.65 |

\*  $-\text{CF}_3 + -\text{CF}_2- + -\text{CF}- + -\text{C}- = 100\%$ ; area of  $\text{CH}_2$  peak being excluded.

thus the formula  $F/C = (3 \times -CF_3 + 2 \times -CF_2- + -CF- + -C-)$  was adopted.

Percentage area and F/C ratios obtained from each of resolved peaks of  $C_{1s}$  region in ESCA spectra of plasma-polymerized OFCB are listed in Table 1 and 2. It is well known that  $-CF_3$  groups could represent the molecular end-groups and  $-CF_2-$  groups the linear degree of polymers. Because a carbon atom located in polymer skeleton should possess at least two bonds linking with the adjacent carbons, so C—C bonds in excess than two could be regarded as branching bonds for a certain carbon atom. It is assumed that a  $-C-$  has two branching bonds and a carbon in  $-CF$  group has one. Thus percentage area with  $(2 \times -C- + -CF-)$  could represent degree of branching. As shown in Table 1, with the increase of power or the

Table 2 ESCA results as using different plasma gas and plasma-gas/monomer ratio\*

| Plasma gas     | Plasma-gas/monomer | Area of $C_{1s}$ peak** (%) |          |        |       |          |                       |       |
|----------------|--------------------|-----------------------------|----------|--------|-------|----------|-----------------------|-------|
|                |                    | $-CF_3$                     | $-CF_2-$ | $-CF-$ | $-C-$ | $-CH_2-$ | $2 \times -C- + -CF-$ | F/C   |
| Ar             | 2/1                | 17.10                       | 28.50    | 28.80  | 24.97 | —        | 78.74                 | 1.39  |
|                | 1/1                | 22.07                       | 30.26    | 24.18  | 22.95 | —        | 70.08                 | 1.52  |
|                | 1/2                | 22.25                       | 36.30    | 22.90  | 18.53 | —        | 59.96                 | 1.62  |
| N <sub>2</sub> | 2/1                | 19.57                       | 26.70    | 27.96  | 25.71 | —        | 79.38                 | 1.40  |
|                | 1/1                | 22.71                       | 30.05    | 25.35  | 21.86 | —        | 69.07                 | 1.54  |
|                | 1/2                | 23.12                       | 37.27    | 20.29  | 19.30 | —        | 58.89                 | 1.64  |
| H <sub>2</sub> | 2/1                | 12.81                       | 27.54    | 24.12  | 24.82 | 10.67    | —                     | 1.32  |
|                | 1/1                | 22.20                       | 25.38    | 20.86  | 21.25 | 10.28    | —                     | 1.541 |
|                | 1/2                | 18.19                       | 23.05    | 15.49  | 18.70 | 24.55    | —                     | 1.540 |
| He             | 1/1                | 24.83                       | 29.30    | 23.68  | 22.28 | —        | 68.24                 | 1.55  |
| —              | 0/1                | 23.60                       | 38.80    | 18.24  | 20.03 | —        | 58.34                 | 1.65  |

\* Power, 90W; pressure, 100  $\mu$ mHg; substrate position, 7.5 cm.

\*\* Except for H<sub>2</sub> plasma-polymerized OFCB,  $-CF_3 + -CF_2- + -CF- + -C- = 100\%$ ; area of  $CH_2$  peak is excluded.

decrease of pressure,  $-\text{CF}_2-$  content decreases and  $(2 \times \text{---}\overset{|}{\underset{|}{\text{C}}}\text{---} + \text{---}\overset{|}{\underset{|}{\text{CF}}}\text{---})$  content increases,

which indicates less linear extent and enhancement of branching. At the same time, a decreasing trend is appearing for F/C ratios. These results are in good accordance with those discussed in our previous paper<sup>[1]</sup>, i.e. polymerization decreases and ablation increases under the same conditions. As shown in Table 2, as plasma-gas/monomer ratio decreases, excluding the

case of  $\text{H}_2$  plasma,  $-\text{CF}_2-$  content increases and  $(2 \times \text{---}\overset{|}{\underset{|}{\text{C}}}\text{---} + \text{---}\overset{|}{\underset{|}{\text{CF}}}\text{---})$  content decreases, which

indicates that linear extent of molecules increases and degree of branching decreases. Meanwhile, F/C ratios also increase gradually. The above results are also in good accordance with the trends of competitive changes between polymerization and ablation process under the same conditions. It is difficult to distinguish whether it is linked with another carbon or with a hydrogen by using ESCA spectra, as the chemical shifts for both are too small to be distinguished. When part of the fluorine atoms were substituted by hydrogen atoms, with the carbons remaining as the original primary, secondary, tertiary or quaternary carbon atoms, the contents of several kinds of carbons in ESCA spectra change quite prominently. On the basis of discussions about other plasma gases, perhaps there are similar effects.

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