

STRUCTURE OF PLASMA-POLYMERIZED OCTAFLUOROCYCLOBUTANE

YE Mu (叶牧) CHEN Jie (陈捷) LU Lizhen (卢丽珍)

HU Huizhen (胡慧贞) XIAO Yanwen (孝延文) and LIU Guizhen (刘桂珍)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

Plasma-polymerization of octafluorocyclobutane was carried out in a capacitively coupled tubular reactor with external electrodes. The number-average molecular weight, melting temperature, decomposition temperature and solubility in tetrafluorodibromoethane of the products was measured and the polymer structure was characterized by ESR, IR and ^{19}F -NMR methods. The experimental results show the absence of the highly crosslinked structure but a fluorine-deficient structure caused by free-radicals, carbonyl groups, double bonds and multicage-like segments in the polymer.

INTRODUCTION

It is generally believed that the plasma polymers are highly branched and crosslinked. The reasons are said to be: 1. fluorine-deficiency or hydrogen-deficiency of the polymer in comparison with monomers; 2. insolubility of plasma polymer in common solvents; 3. the amorphous structure of polymers; 4. the existence of the tertiary, quaternary carbons and end-groups structure in the polymer. We have previously characterized the plasma-polymerized octafluorocyclobutane prepared at different conditions by ESCA method and obtained the F/C ratios from 1.38 to 1.65^[1]. In the present work, the structure of that polymer is further studied by number-average molecular weight, melting temperature, decomposition temperature and solubility measurements and ESR, IR, ^{19}F -NMR characterization.

EXPERIMENTAL

Octafluorocyclobutane (OFCB), 99.9% in purity, was purchased from the Experimental Plant of Shanghai Institute of Organic Chemistry, Academia Sinica. Sodium hydrosulfite NaHSO_3 , analytical reagent, was produced by the Xinhua Chemical Plant of Tanggu, Tianjin.

Plasma polymerization of OFCB was carried out in a capacitively coupled tubular reactor with external electrodes. The system pressure was 0.1 Torr and plasma-gas/monomer ratio was 1/1, which was regulated by controlling the partial pressure of gases.

For NaHSO_3 nucleophilic addition reaction, the plasma-polymerized OFCB at first was ground into very fine powder, and put into the saturated aqueous solution of NaHSO_3 , and reacted for 4 hours at constant temperature of 50°C under stirring. The sample was rinsed

repeatedly with distilled water, the pressed tablet of the dried polymer with KBr was then used for IR analysis.

ESR measurement was taken on a TES-FE3AX ESR spectrometer (JEOL Corp. Japan) with operation frequency of 9.434 GHz and magnet modulation of 100 KHz. ^{19}F -NMR spectrum was obtained on a Fx-100 NMR spectrometer (Japanese Electronic Company) using tetrafluorodibromoethane as the solvent and CF_3COOH as the internal reference with an accumulation of 100 times and amplification of 100 times. Number-average molecular weight was measured on a KNAUER vapor phase osmometer at 37°C using tetrafluorodibromoethane as the solvent and formyl diphenyl as the standard. IR spectra were recorded on a FTS-20E IR spectrometer (DGLAR Corp. U.S.A.) with a scanning of 5 times.

RESULTS AND DISCUSSION

At room temperature, the plasma-polymerized OFCB was completely soluble in tetrafluorodibromoethane, an effective solvent for fluorocarbons. The number-average molecular weight of the polymer prepared in a Ar/OFCB discharge system with 40W power was 2003 by VPO method, which corresponds to that of 10 monomer units. And the molecular weight of polymer obtained with the power of 80W was 2736, corresponds to 14 monomer units. The melting temperature of plasma-polymerized OFCB was determined as from 120 to 140°C and the decomposition temperature from 200 to 240°C. The above results indicate the absence of highly crosslinked structure in the plasma-polymerized OFCB.

It was confirmed by ESR, IR and ^{19}F -NMR measurement that the fluorine-deficient structure of plasma-polymerized OFCB was due to the existence of trapped free-radicals, carbonyl groups, double bonds and some multicage-like structures.

The ESR spectrum of plasma-polymerized OFCB, an antisymmetrical spectroline with a line-width of 50 GHz and a g -value of 1.9874, was shown in Fig. 1 (A). A comparison was made to determine the radical concentration of the polymer. A $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ monocrystal with the concentration of 2.412×10^{21} spin/gram was used as internal standard, its ESR spectrum was shown in Fig. 1 (B). The radical concentration (n) of plasma-polymerized

OFCB could be obtained by using a formula $n = \frac{n_0 A L}{A_0 L_0}$, where A and A_0 are the peak area in

the ESR spectra of the polymer and standard respectively, L and L_0 are the line-width of the spectrum peaks. The calculated radical concentration of plasma-polymerized OFCB is 10^{19} spin/gram. It has been given that the number-average molecular weight of the polymer prepared in a Ar/OFCB discharge system with the power of 80W was 2736, and also has been determined that the radical concentration of the same sample was 4.454×10^{19} spin/gram, i.e. 1.219×10^{23} spin/mol, thus one free-radical per five molecules of plasma-polymerized OFCB could be given.

It could be seen in Fig. 2, the radical concentration of the plasma-polymerized OFCB increased with the enhancement of discharge energy.

The plasma-polymerized OFCB was treated either in air or under Ar in quartz tubes at 80, 120 and 140°C. The radical concentration determined by ESR at different heating time

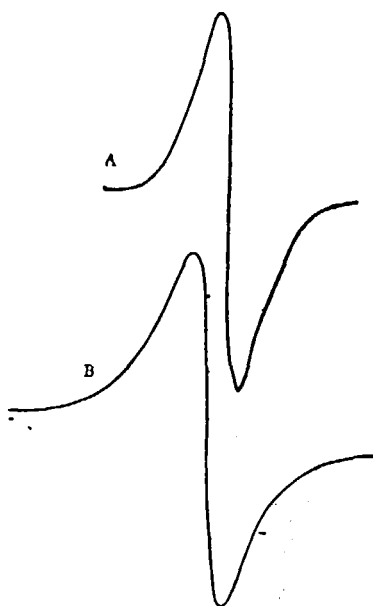


Fig. 1 ESR spectra of plasma-polymerized OFCB (A) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ monocrystal (B)

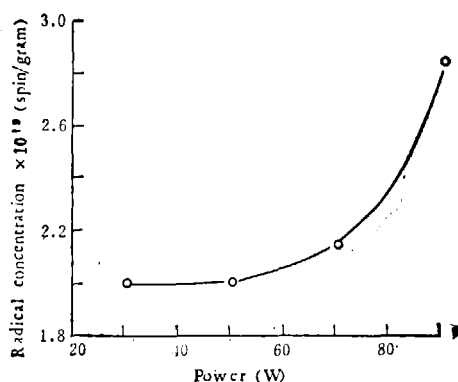


Fig. 2 Effect of the power on the radical concentration in the plasma-polymerized OFCB
Pressure, 0.1 Torr; He/OFCB , 1/1.

was shown in Fig. 3. The radicals in sample exposing in air attenuated much more quickly than that under Ar. For latter, the attenuation could only be performed via the combination between the molecular chain carrying radicals. On the other hand, the two competitive reactions, i.e. oxidation and combination could be carried out in air. As shown in Fig. 3 that at lower temperature, the oxidation was the main reaction, the carbonyl groups existing in polymer could be observed in IR, but at higher temperature the combination became dominant owing to the increase of the molecule motion.

It is difficult to study double bonds in the plasma-polymerized fluorocarbons. In the

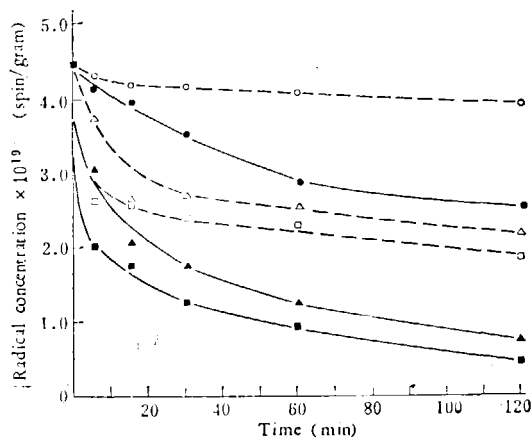


Fig. 3 Change of the radical concentration in plasma-polymerized OFCB at different temperatures

Power, 80W; Pressure, 0.1 Torr; Ar/OFCB, 1/1.

○● 80°C; △▲ 120°C; □■ 140°C.

---- in Ar; — in air.

ESCA spectra of C_{1s} region, shake up satellite peak characterizing $\pi-\pi^*$ transition of double bonds overlaps with CF_3 peak. The absorption bands of $C=O$, $CF=CF$ and $C=C$ groups in the IR spectra also overlap with each other, which was not easy to separate^[21]. Having performed the nucleophilic addition reaction of plasma-polymerized OFCB in the saturated aqueous solution of $NaHSO_3$, both untreated and treated samples were studied spectroscopically and the results were shown in Fig. 4. As shown in Fig. 4 (B), the absorption band at 1720 cm^{-1} was reduced, the band at 1640 cm^{-1} became obvious, and the overlapped peaks became separated. The absorption at 1720 cm^{-1} is generally attributed to carbonyl group and that at 1640 cm^{-1} to double bond^[21]. In the $NaHSO_3$ nucleophilic addition reaction, due to the strong electronegativity of fluorine, the positive charges at carbonyl carbon increased and the reactivity of the carbonyl carbon atom with nucleophilic reagents enhanced, the reaction resulted in the reduction of the absorption at 1720 cm^{-1} . The above results would indicate the existence of carbonyl groups and double bonds in plasma-polymerized OFCB. Furthermore, as can be seen from Fig. 4 (A), the content of double bonds is less than that of carbonyl groups. However, both carbonyl group and double bond are fairly less in content in the polymer when the absorption intensity at 1720 and 1640 cm^{-1} is compared to that at 1220 cm^{-1} . In addition, absence of 1789 cm^{-1} band attributed to $C=CF_2$ groups by Inagaki^[21] implies that there is no double bond as end-group existed in plasma-polymerized OFCB.

^{19}F -NMR spectrum of tetrafluorodibromoethane solution of plasma-polymerized OFCB was shown in Fig. 5. As a reference, an attribution of the peaks in ^{19}F -NMR spectrum of plasma-polymerized TFE with the same solvent and standard used by Hozumi was listed as follows:

follows: δ 30—10 ppm, $CF_3-\overset{|}{C}-$; δ 10—0 ppm, CF_3-CF ; δ 0—-10 ppm, CF_3-CF_2 ; δ -10—-60 ppm, CF_2+CF ^[41]. Based on the above mentioned data and the relative ratio of the areas of each peak in ^{19}F -NMR spectrum, the relative ratio of various groups existed in the

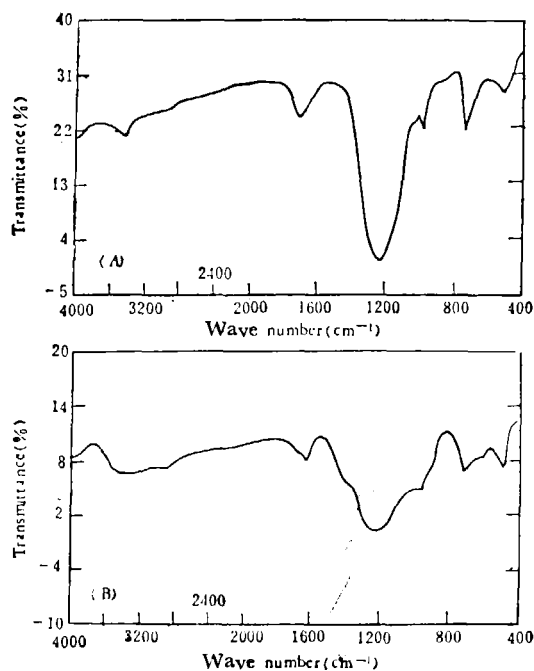


Fig. 4 IR spectra of the untreated (A) and NaHSO_3 treated (B) plasma-polymerized OFCB

polymer prepared in He/OFCB discharge system with the power of 90W is obtained as follows:

$\text{CF}_3-\text{C}-$: CF_3-CF : CF_3-CF_2 : $\text{CF}_2+\text{CF}=26:34:26:66$. By calculating the numbers of CF_3 , CF_2 and CF groups in one molecule, marked as X , Y and Z respectively, can be obtained, i.e. $X:Y:Z = \frac{26+34+26}{3} : \frac{66 \times 0.605}{2} : \frac{66 \times 0.395}{1} = 29:20:26$. When the molecular

weight of single molecule is taken as 2736 and F/C ratio as 1.60^[1], it is conceivable that there are 103 fluorine atoms and 64.5 carbon atoms in single polymer molecule and $3X+2Y+Z=103$. Solving the two equations, we get $X=20$, $Y=13.5$ and $Z=17.5$. The number of the quaternary carbons of 13.5 could be obtained from the difference between the sum of the carbon atoms and that of CF_3 , CF_2 and CF groups. From the ratio of the various groups in the polymer obtained from peak areas in ^{19}F -NMR spectrum, it can be calculated

that $\text{CF}_3-\text{C}-$ = 6.1, CF_3-CF = 7.9, CF_3-CF_2 = 6.1. Finally a group composition of single molecule in plasma-polymerized OFCB may be described as follows: CF_3-CF_2 = 6.1, CF_2 = 13.5; CF_3-CF = 7.9, CF = 17.5; $\text{CF}_3-\text{C}-$ = 6.1 and $-\text{C}-$ = 13.5. It can be in-

ferred that there is a dense multicage-like structure formed due to the high content of tertiary and quaternary carbons in the molecules of the plasma-polymerized OFCB.

Number of carbon atoms made the circles of each cage is uncertain and the arrangement of the circles is irregular in the three dimensions. In conclusion, plasma-polymerized OFCB is accumulated of multicage-like molecules with high degree of branches and some free-radicals, carbonyl groups and double bonds.

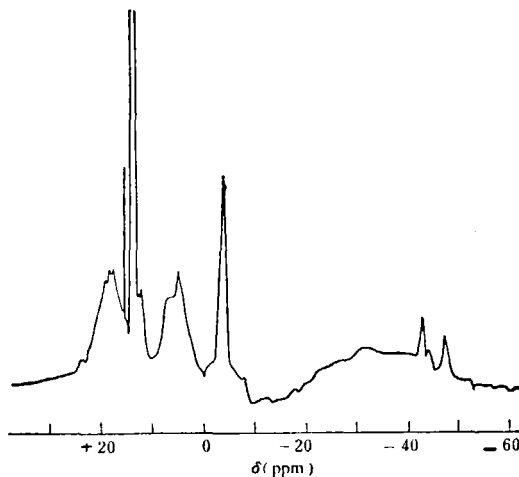


Fig. 5 ^{19}F -NMR spectrum of plasma-polymerized OFCB

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