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Structural Interpretation of Plasma-polymerized Tetrafluoroethylene

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Structural interpretation of plasma-polymerized tetrafluoroethylene produced in a glow discharge chamber is given by referring to ^{19}F-NMR and IR spectroscopy, elemental analysis, and number-average molecular weight determination. The polymer is hardly soluble in the usual organic solvents because of its highly branched structure, making NMR spectroscopy and molecular weight determination impossible. However, the polymer is soluble in 1,2-dibromo-1,1,2,2-tetrafluoroethane and the following structural interpretation could be obtained. The number-average molecular weight is 3600 for the majority of the polymer, consisting of 96 carbon and 129 fluorine atoms within a unit molecule. The IR spectrum shows evidence of some C=C groups and the ^{19}F-NMR spectrum a highly branched and cross-linked structure in which a large number of quaternary carbons are involved in the polymer matrix as compared with CF_2 and CF carbons. The plasma-polymerized tetrafluoroethylene has been characterized in a somewhat different way from the plasma-polymerized ethylene, involving a small number of quaternary carbons.

Polymer thin films deposited on solid substrates by means of plasma polymerization in which monomer gases are exposed to glow discharge have a highly branched and cross-linked structure, uniform film thickness, and are pinhole free. By selective use of the monomer gases we can alter the physico-chemical properties of the polymer films, such as surface free energy, optical transmittance, and electric specificities.[1-3)]

Plasma-polymerized fluorocarbons have an extraordinarily low surface free energy and a good optical transparency throughout the visible and infrared regions. Deposition of the plasma-polymer was successfully applied to the hydrophobic coating of ion-crystal windows installed in various infrared instruments and the anti-reflection coating of certain organic lenses.[4-6)] We recently reported the use of tetrafluoroethylene (TFE) as a monomer gas by which solid materials of fine and complicated structure such as ashed residue of biological specimens were effectively coated by the hydrophobic plasma-polymer eliminating the initial hygroscopic nature and preserving the three-dimensional microstructures.[7)] The results suggest further application of the plasma-polymer to the hydrophobic coating of porous surfaces or granular materials.

We have undertaken to obtain structural interpretation of plasma-polymerized tetrafluoroethylene (PPTFE) mainly by means of ^{19}F-NMR spectroscopy, also by infrared and ESR spectroscopy, elemental analysis, and number-average molecular weight determination. This paper reports a hypothetical model of the atom configration within the polymer molecule having average molecular weight.

Experimental

Monomer Gas. TFE was stored in a pressure tank and supplied to the plasma chamber through a flow meter and a needle valve. The purity was confirmed by a gas chromatograph incorporated with a Porapack column giving no signal of impurity.

Plasma System. A schematic diagram of the apparatus for the plasma polymerization, which is the same as reported[7)] is shown in Fig. 1. A valve introducing air was incorporated with the system for occasional cleaning of the polymer film deposited on the inside wall of the plasma chamber by plasma oxidation. The gas pressure in the system was monitored by a MacLeod gauge attached to a three-way manifold located between the plasma chamber and a rotary pump. The plasma in the chamber was initiated and sustained by controlling high-frequency electric power supplied from a 100 W generator operating at 13.56 MHz. Typical operating conditions for the film deposition were 2—3 ml(1 atm)/min for the TFE flow, 20 W for the effective input power, and 0.2—0.4 Torr (13.322 Pa) for the gas pressure. Vapor pressure osmometer, Knauer Dampfdruck Osmometer; IR spectrometer, Shimadzu Model IR-400; ESR spectrometer, JEOL Model JES-FE-3X; ^{19}F-NMR spectrometer, Varian Model EM-390.

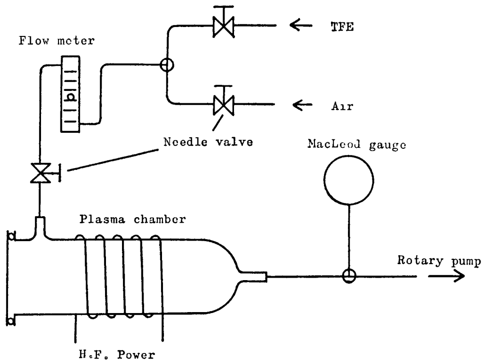

Fig. 1. Schematic diagram of plasma-polymerization apparatus.

Results and Discussion

Solubility of PPTFE in Organic Solvents. TFE monomer gas was polymerized for 60 min in an empty chamber. Solid film was always deposited on the inside wall of the chamber under the plasma conditions employed without forming other types of polymer such as oil or powder. The solid film deposited in the chamber was scraped off and extracted with acetone. However, a large portion of the polymer, obviously of higher degree polymer, remained insoluble. Various other polar or nonpolar organic solvents were examined for removal of the insoluble substance. No usual organic solvent was found to be more effective than acetone.

1,2-Dibromo-1,1,2,2-tetrafluoroethane($DF114B_2$) was found to be an effective solvent, supposedly because of the chemical analogy within the two. TFE could be prepared simply by reacting sodium hydroxide with DF114B$_2$.

DF114B$_2$ still left a small fraction of insoluble substance which suggested an extremely high degree of cross-linking. The fraction was rejected from further application to NMR or molecular weight determination.

The acetone and DF114B$_2$ extracts were vacuum-evaporated at room temperature. The dried extracts together with the insoluble residue were weighed in order to determine the weight percent compositions of the initial polymer substance; acetone extract=15%, DF114B$_2$ extract=81%. Only 4% was left as insoluble residue. The acetone extract was dark brown, the DF114B$_2$ extract and the insoluble residue being amber colored.

The acetone and DF114B$_2$ dissolved the respective fractions of the polymer in high concentrations until forming viscous fluid, no quantitative solubility could be obtained. The solubility was therefore determined by use of organic solvents having much less solubility to the individual fractions. The powder sample was put in a centrifuge tube with an organic solvent. The mixture was stirred at room temperature and the resulting suspension was centrifuged (3500 rpm) for 5 min. 5 ml of the supernatant layer was transferred to a weighed beaker which was then vacuum-evaporated at room temperature. The beaker was weighed and the solubility calculated. The solubility data are given in Table 1.

The acetone extract was practically insoluble in nonpolar solvents, but somewhat soluble in polar solvents. On the other hand, the DF114B$_2$ extract was insoluble in all the solvents examined. The difference in behavior between the two extracts is probably due to the shape of the molecules, *i.e.*, the acetone extract consisting of smaller molecules is more or less polarized due to the branched structure of the plasma-polymer, while the DF114B$_2$ extract of larger molecules exhibits no orientation of the branching effects which were dispersed in all directions resulting in a perfectly nonpolar characteristic. It is understandable that the acetone extract is somewhat soluble in the polar solvents.

Thermal Property and Average Molecular Weight. Each of the three fractions of the polymer was powdered and the individual melting point was measured on a hot stage. Melting took place in a wide range of temperature, half-liquified point being taken as the melting point. The results are given in Table 2.

Table 1. Solubility data of two solvent extracts of PPTFE in different organic solvents

Solvent	Acetone extract (%)	DF114B$_2$ extract (%)
Petroleum ether	0.01	0.00
Carbon tetrachloride	0.01	0.00
Hexane	0.01	0.00
Toluene	0.01	0.00
Benzene	0.00	0.00
Chloroform	0.02	0.00
Diethyl ether	1.29	0.00
Ethanol	2.71	0.01
Methanol	1.23	0.00

Table 2. Physical and chemical properties of three fractions derived from PPTFE

Item of determination		Fractions		
		Acetone extract	DF114B$_2$ extract	Insoluble residue
Melting point/°C		80—105	141—150	190—225
Average molecular weight		900	3600	—
Elemental composition	F (%)	56.4	67.8	64.0
	C (%)	—	32.0	—

The insoluble residue showed the highest melting point but lower than that of the conventional Teflon resin by *ca.* 100 °C. This is understandable if we assume that the PPTFE we obtained has a lower molecular weight than that of the conventional Teflon and/or the intermolecular force was reduced by the three-dimensional molecular structure resulting from the high branching of carbon chain developed during the course of plasma polymerization.

Vapor pressure osmometry was carried out for the acetone and DF114B$_2$ solutions of respective extracts. The number-average molecular weight was calculated for the individual polymer extracts employing benzyl as a standard (Table 2). The molecular weight of the DF114B$_2$ extract was 3600, the majority of PPTFE thus not being polymerized as highly as expected.[8–10] The insoluble residue was polymerized and cross-linked to a greater extent.

Elemental Analysis. Elemental analysis was carried out with a carbon-hydrogen-nitrogen analyzer and fluorine determination with an oxygen flask. Mean values are given in Table 2. Fluorine content of PPTFE was significantly lower than that of Teflon, supporting the highly branched structure.

The result of elemental analysis made it possible to determine the number of carbon and fluorine atoms in a unit molecule when a hypothetical molecule having the average molecular weight was assumed. For acetone extract we have C:F=30:30, and for DF114B$_2$ extract C:F=96:129. It is of interest that the F/C ratios of the two extracts were both much smaller than the H/C ratio of plasma-polymerized ethylene evaluated by Tibbit *et al.*[10] Higher concentrations of quaternary or tertiary carbons should be assumed for the former molecules.

IR Spectrum. A pressed KBr tablet was placed in the plasma chamber and coated with PPTFE in 10000 Å thickness. Each of the two extracts and the insoluble residue were powdered and mixed with KBr to form a tablet. The IR spectrum of the PPTFE film (Fig. 2) shows a strong resemblance to that of the other three fractions, indicating that the structural characteristics of the three fractions of the polymer are essentially the same.

The wide absorption band at 950—1500 cm^{-1} was

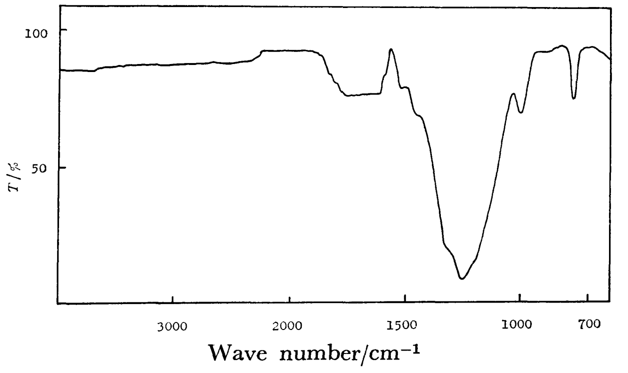

Fig. 2. IR spectrum of PPTFE.

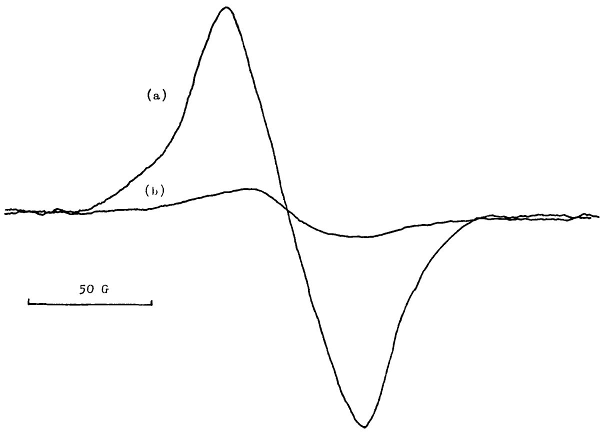

Fig. 3. Relative signal intensities of ESR spectra of freshly prepared PPTFE and its DF114B_2 extract.

assigned to C–F stretching vibration modified by various modes of neighboring atom groups. A weak absorption band at 1540—1800 cm^{-1} was tentatively assigned to C–C stretching vibration shifting considerably to higher wave number induced by the fluorinated carbon chain. Similarly the C=O absorption band appearing usually at *ca.* 1715 cm^{-1} is expected to shift towards much higher wave number for the same reason. The IR spectrum gave no signal of detectable C=O group. This is in line with the result of elemental analysis (Table 2). An intense and single band observed at 740 cm^{-1} is attributed to $-CF_2-$ bending vibration associated to adjacent $-CF_3$ terminal.

ESR Spectrum. Freshly prepared PPTFE was subjected to ESR spectroscopy. High concentration of unpaired spins, a characteristic of plasma-polymers, was observed as anticipated. The ESR spectrum of PPTFE was sealed in a standard 3.0 mm I.D. quartz tube filled with argon (Fig. 3(a)). The ESR signal showed a single and almost symmetrical wave form with a magnitude of 175 G having a *g*-value of 2.0038. The signal intensity decayed very slowly, reaching its half-intensity after 48 days at room temperature. A relative intensity of the ESR spectrum of the DF114B_2 extract is shown in Fig. 3-(b). A rough evaluation shows that the freshly prepared PPTFE contains *ca.* 20 folds higher concentration of free radicals than the DF114B_2 extract. This can be explained in terms of intense intermolecular collisions sustained during the course of extraction by the solvent DF114B_2 and the resulting rapid termination of free radicals in the polymer. No quantitative determination was possible because of the lack of standard material. One free radical would be involved in a few plasma-polymer molecules.[11] In such a large molecule the radical site could be ignored for determining the chemical structure of the polymer molecule.

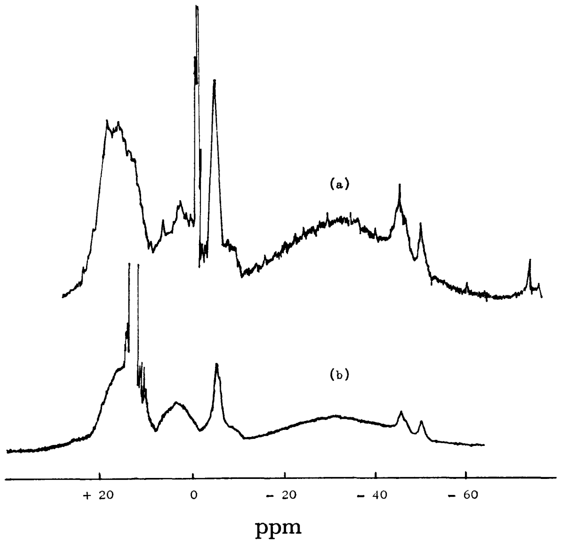

Fig. 4. ^{19}F-NMR spectra of PPTFE.

^{19}F-NMR Spectrum. ^{19}F-NMR spectra of the acetone extracts were measured with use of trifluoroacetic acid as an internal reference (Fig. 4(a)) and those of DF114B_2 extracts with the DF114B_2 itself (Fig. 4(b)).

The reference peaks are indicated at 0 and 16 ppm in the spectra (a) and (b), respectively. Eliminating these reference signals, the two spectra exhibit similar characteristics. It seems that the chemical structure of the two extracts are basically the same except for the difference in molecule size.

The individual signals were assigned from the lower magnetic field to the higher as follows:[6]

δ 30— 10 ppm	$\underline{CF_3}$-C
δ 10— 10 ppm	$\underline{CF_3}$-CF
δ 0— −10 ppm	$\underline{CF_3}$-CF_2
δ −10— −60 ppm	CF_2 and CF_3
δ −44 ppm	-$\underline{CF_2}$-CF_3
δ −49 ppm	-$\underline{CF_2}$-CF_2-

Signal intensities of the CF_3 group derived from the DF114B_2 extract, the majority of PPTFE, were measured in order to calculate the relative abundance of different modes of adjacent carbon groups. From the result the following composition is obtained.

$$\underline{CF_3}\text{-C} : \underline{CF_3}\text{-CF} : \underline{CF_3}\text{-CF}_2 = 79 : 16 : 20$$

We see that the $\underline{CF_3}$–C group occupies a large majority of the overall CF_3 group within the polymer, in contrast to plasma-polymerized ethylene where the $\underline{CH_3}$–CH group is the major constituent, hardly any of the $\underline{CH_3}$–C group being found in the ^{13}C-NMR spectrum.[10] Thus it seems that the molecular structure of PPTFE consists of irregular sequences of very highly branched aliphatic chains.

Hypothetical Model of Molecular Structure. If we assume that a polymer molecule has the average molecular weight derived from the DF114B_2 extract, an interpretation of its chemical structure can be given in reference to spectral data and the elemental analysis. Atom constitution of a unit molecule was calculated to be 96 carbon and 129 fluorine atoms, the existence of some C=C groups being presumed by IR spectrometry.

^{19}F-NMR spectroscopy clarified the constitution of fluorocarbon groups in the molecule. The signal intensities of the following underlined groups gave the ratio:

$$\underline{CF}_3\text{-}C : \underline{CF}_3\text{-}CF : \underline{CF}_3\text{-}CF_2 : \underline{CF}_2 + \underline{CF} = 79 : 16 : 20 : 69$$

This indicates that equal numbers of CF_2 and CF groups are involved in one molecule. The signal intensity of CF_2+CF could be allocated to CF_2 and CF groups with 2/3 and 1/3 portions, respectively. If we denote the number of CF_3, CF_2, and CF groups within a unit molecule by x, y, and z, respectively, the relative abundance of these groups can be obtained.

$$x : y : z = \frac{79+16+20}{3} : \frac{69\times 2/3}{2} : \frac{69\times 1/3}{1}$$

$$= 38 : 23 : 23$$

Since the number of fluorine atoms in a unit molecule is 129, we have

$$3x + 2y + z = 129.$$

Solving the two equations, we get

$$x = 26.8, \quad y = 16.2, \quad z = 16.2.$$

The number of quaternary carbon is calculated by subtracting the number of carbons belonging to CF_3, CF_2, and CF groups from 96 the total number of carbon.

$$96 - (27+16+16) = 37$$

Rearranging the data, we get

$$CF_3 = 27, \ CF_2 = 16, \ CF = 16, \ C = 37.$$

Signal intensities of CF_3 groups adjacent to different carbon groups were allocated in proportion to the numbers of adjacent carbon groups.

$$\underline{CF}_3\text{-}CF_2 = 4.5 \quad \underline{CF}_3\text{-}CF = 4.5 \quad \underline{CF}_3\text{-}C = 19$$

The composition of the atom groups within a unit molecule is as follws:

$$\underline{CF}_3\text{-}CF_2 = 4\text{—}5, \ \underline{CF}_3\text{-}CF = 4\text{—}5, \ \underline{CF}_3\text{-}C = 19,$$
$$CF_2 = 16, \ CF = 16, \ C = 37.$$

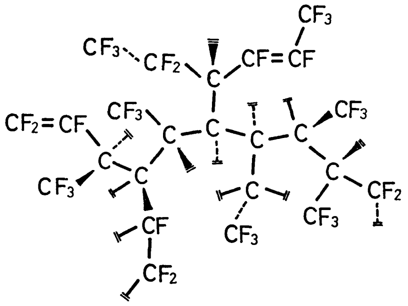

Fig. 5. Atom configuration of PPTFE depicted as 1/4 portion of unit molecule having average molecular weight.

A hypothetical model of a quarter of a unit molecule is shown in Fig. 5.

The structure is not yet established, since the abundance of the C–C group was roughly estimated by IR spectroscopy.

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