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Glow Discharge Polymerization of CF_4/CH_4 Mixture Investigated by Infrared Spectroscopy and ESCA

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ABSTRACT

The glow discharge polymerization of a CF_4/CH_4 mixture was investigated by using infrared spectroscopy and ESCA in comparison to the glow discharge polymerization of tetrafluoroethylene. The polymers prepared from a CF_4/CH_4 mixture (70/30 molar ratio) as well as from tetrafluoroethylene possess low surface energy compared with that of conventionally polymerized polytetrafluoroethylene. The infrared spectrum of the polymer from a CF_4/CH_4 mixture was fairly different from that of the polymer prepared from tetrafluoroethylene by glow discharge polymerization, which had an almost identical spectrum to that of conventionally polymerized polytetrafluoroethylene. Unanticipated residues included C≡C, C=CF,  $\underset{\underset{O}{\|}}{C}-F$, NO_2 and C–O groups, in addition to the expected C–F groups. The formation of these residues was discussed.

INTRODUCTION

Glow discharge polymerization generally involves a simultaneous polymer-forming process and a degradation process of the polymers formed by electron radiation, activated molecules, and vacuum ultraviolet light created by plasma. Accordingly, polymers which we get by glow discharge polymerization are products subjected to degradation to some extent. This concept has been named CAP (Compatitive Ablation and Polymerization) mechanism by Yasuda [1]. This balance between a polymer-forming process and a degradation process can be shifted by operational conditions, e.g., pressure in the reactor, rf power, monomer flow rate [1].

Glow discharge polymerization of fluorine-containing compounds such as tetrafluoroethylene offers polymers like Teflon. Yasuda has reported that the chemical structure of the polymers formed is easily altered by changing the operational condtions to sustain a glow discharge [1]. This indicates that fluorine-containing compounds are easily susceptible to plasma, and that the balance between the polymer-forming process and the degradation process is shifted. Accordingly, to obtain polymers like Teflon by glow discharge polymerization it is important to examine the effects of the operational conditions on the chemical structure of the polymers formed. A change in the form of the reactor used can also be important because there are frequently changes in the physical properties of polymers formed by glow discharge polymerization in different forms of a reactor, even if the polymerization has been performed under exactly the same operating conditions.

We have already reported that the glow discharge polymerization of a CF_4/CH_4 mixture yields polymers like Teflon possessing low surface energy when using an inductive coupling system [2]. This study focuses on the chemical structure of polymers formed from a CF_4/CH_4 mixture by glow discharge polymerization as well as a preliminary search for a reactor design and operational conditions for the preparation of polymers like Teflon.

EXPERIMENTAL

Materials

The chemicals used for glow discharge polymerization in this study were tetrafluoromethane, methane (provided by Matheson Co.), and tetrafluoroethylene (provided by Ideal Gas Co.).

Glow Discharge Polymerization

The apparatus and experimental procedures for glow discharge polymerization are essentially the same as those reported elsewhere

[2, 3]. The reaction chamber is a tubular reactor (35 mm i.d., 400 mm long) which is made of Pyrex and is constructed with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for inductive coupling of a 13.56 MHz rf source.

Substrates were horizontally placed in the reaction chamber, and the system was evacuated to approximately 0.1 mTorr using a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber. To eliminate the water adsorbed on the surfaces of the substrates, the surfaces were exposed to argon plasma for 15 min. The flow rate of argon gas was 0.46 cm^3 (STP)/min at 80 mtorr, and the level of rf power was 25 W. The system was again evacuated to 0.1 mtorr. A monomer gas, the flow rate of which was adjusted to 1.0 cm^3 (STP)/min at a pressure of 10 mtorr in the reaction chamber, was injected into the reaction chamber. The rf power was turned on, glow discharge polymerization was initiated, and the polymerization was kept at a rf level of 25 W for an adequate time. The flow rate was calculated from the slope of the pressure increase vs the time when the outlet valve of the reaction chamber was closed.

The polymer deposition rate was calculated from weight increase of aluminum foils (5 × 22 mm, 0.007 mm thickness) which were horizontally placed in the reaction chamber. The aluminum foils were lined with a cover glass (5 × 22 mm, 0.13 mm thickness) and mounted on a glass plate (35 × 250 mm) at 10 mm interval with Scotch tape.

Elemental Analysis

Polymers which deposited on the glass plate were used for C, H, N, O, and F analyses. The C, H, N, and O contents were determined using a CHN corder MT-2 (Yanagimoto Co.) and the F content was determined by the alizarine complexon method [4].

Surface Energy

The contact angles of polymer films which were deposited on a glass plate in water, glycerol, formamide, diiodomethane, and tricresyl phosphate were measured by a drop-on-plate method using a Kyowa Kagaku contact angle meter CA-1. The contact angle data were analyzed to estimate a dispersive contribution, γ_s^d, and a polar contribution, γ_s^p, according to Kaelble's method [5].

Infrared Spectra

KBr powder ground to approximately 150 mesh was thinly sprinkled on a glass plate, and glow discharge polymerization was performed according to the same procedures mentioned above. The KBr powder coated with a polymer film was used for the preparation of a KBr disk. The spectrometer used was a Nihon Bunko spectrometer A-3.

ESCA Spectra

Polymer films (~ 1 μm thickness) deposited on glass plates (10 × 10 mm) were placed under the monomer inlet and at a distance of 100 mm from the monomer inlet in the direction of the monomer flow to measure the ESCA spectra. Spectra were recorded with a Hewlett-Packard 5950A spectrometer employing monochromatic $AlK_{\alpha 1,2}$ exciting radiation. To alleviate charging by x-ray radiation, an electron-flat-gun was employed. Typical operating conditions were: x-ray gun, 800 W; pressure in the sample chamber, 2×10^{-9} torr; electron-exchange-gun, 1 mA, 1 eV.

Under the experimental conditions employed, the F_{1s} level at 690.0 eV was temporarily used for calibration of the energy scale because of the very weak signal at 285.0 eV binds the energy arising from extraneous hydrocarbon contamination.

Spectra of the C_{12} level were deconvoluted by the nonlinear root-mean-square method. A Gaussian curve was assumed, and resolved curves, which were mostly fitted to the observed spectra, were determined by variations of three parameters; position of peak, height of peak, and full width at half-maximum (FWHM). A typical FWHM value of the resolved curves was less than 2 eV.

RESULTS AND DISCUSSION

Surface Energy and Polymer Deposition Rate

Preliminary experiments examined the effects of the form of a reactor as well as operational conditions for the sustenance of a glow discharge in the CF_4/CH_4 mixture and tetrafluoroethylene systems. This examination showed the preferred form of a reactor to obtain polymers like Teflon in these monomer systems. The relative orientation of the rf supply, the monomer inlet, and the polymer deposition zone are shown in Fig. 1. Operating conditions were determined at a rf level of 25 W, a flow rate of 1 cm^3 (STP)/min, and a pressure of 30 mtorr in the reactor before glow discharge.

Table 1 shows the surface energy of polymer films prepared from the CF_4/CH_4 mixture and tetrafluoroethylene under the preliminarily determined operating conditions using the designed reactor. Polymer films formed from the CF_4/CH_4 mixture which contained 30 mol% of methane possessed a surface energy as low as conventionally

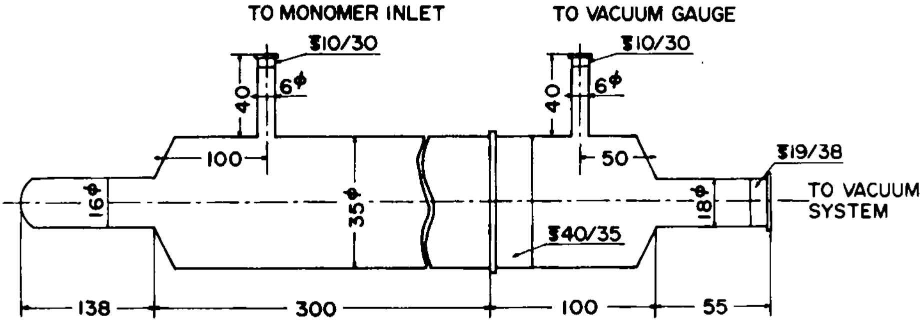


FIG. 1. Schema of reaction chamber. Unit: mm.

TABLE 1. Surface Energy of Polymer Films Prepared from CF_4/CH_4 Mixture and Tetrafluoroethylene by Glow Discharge Polymerization

Polymers from	Mixing ratio (mol% CF_4)	Surface energy (dyn/cm)		
		γ_s	γ_s^d	γ_s^p
CF_4/CH_4	30	39.1	38.9	0.2
	50	38.0	38.0	0
	70	17.4	16.5	0.9
$CF_2{=}CF_2$		12.8	12.1	0.7
Conventionally polymerized polytetrafluoroethylene[a]		19.1	18.6	0.5

[a] Taken from Ref. 6.

polymerized polytetrafluoroethylene ($\gamma_s = 19.1$, $\gamma_s^d = 18.6$, $\gamma_s^p = 0.5$) [6] although the polar contribution consisting of the surface energy was relatively high. Polymer films formed from tetrafluoroethylene by glow discharge polymerization had a lower surface energy than conventionally polymerized polytetrafluoroethylene. This result indicates that the reactor and the operational conditions employed in this study can be used for the preparation of polymer films possessing low surface energy like Teflon and that from a CF_4/CH_4 mixture as well as tetrafluoroethylene, polymer films having low surface energy can be created.

In practical applications of glow discharge polymerization for the

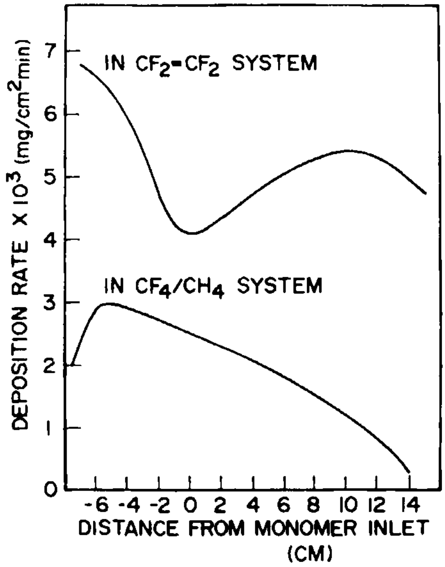


FIG. 2. Distribution of polymer deposition rate as a function of monomer system.

modification of polymer surfaces, the polymer deposition rate and the uniformity in the thickness of the polymers deposited must be considered. Figure 2 shows the polymer deposition rate in these systems as a function of the deposited position. The mark "+" denotes the downstream side of the monomer flow, and the mark "-" denotes the upstream side.

The polymer deposition rate, as shown in Fig. 2, is higher in the tetrafluoroethylene system than in the CF_4/CH_4 (70/30 molar ratio) mixture system by approximately 3 times, indicating that the tetrafluoroethylene system is advantageous for modification because of a shorter processing time required. However, the tetrafluoroethylene system seems to be inferior to the CF_4/CH_4 mixture system in respect to the uniformity of film thickness deposited.

Chemical Structure of Deposited Polymers

Elementary Composition

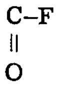
Contact angle measurement showed that polymers prepared from the CF_4/CH_4 mixture had low surface energy, almost identical to that of polytetrafluoroethylene polymerized conventionally. The chemical structure of the polymers formed was therefore examined.

TABLE 2. Elementary Composition of Polymers Formed from CF_4/CH_4 Mixture

Polymers from	Mixing ratio (mol% CF_4)	Elementary composition (wt%) C	H	N	O	F	Empirical formula
CF_4/CH_4	25	66.1	5.2	8.6	12.0	8.1	$CH_{0.93}N_{0.11}O_{0.14}F_{0.08}$
	75	41.8	0.2	8.6	4.8	44.8	$CH_{0.06}N_{0.17}O_{0.09}F_{0.68}$

Table 2 shows the elementary composition of polymers formed from the CF_4/CH_4 mixture as a function of the CF_4 concentration in the mixture. The composition of the polymers formed depends strongly on the composition of the monomer mixture injected. A low surface energy seems to be associated with a high fluorine content in the polymers formed because the polymers possessing low surface energy contain much fluorine while the polymers possessing fairly high surface energy contain less fluorine. Surprisingly, these polymers possess large amounts of nitrogen and oxygen which were not consciously injected into the reactor. The incorporation of these elements into the polymers is considered to arise from two sources: (1) an interaction of radicals created by plasma though the polymerization process with air when the polymers were taken out of the reactor, and (2) an interaction of the discharge of CF_4 with air still resident in the reactor although the reactor was evacuated to 10^{-4} torr before initiating the polymerization. This incorporation is discussed in the next section.

Infrared Spectra

Figure 3 shows the infrared spectra of polymers prepared from the CF_4/CH_4 mixture as a function of the CF_4 concentration in the mixture. The infrared spectrum of the polymer, as shown in Fig. 3, is strongly dependent on the composition of the mixture. On all the spectra of the polymers except that from pure methane, strong absorptions due to C–F groups appeared at 1260 and 1130 cm^{-1}, indicating that the polymers are fluorocarbon polymers. As the increase in the CF_4 concentration in the mixture injected into the reactor absorptions due to CH_2 and CH groups at 2950, 2930, 1460, and 1380 cm^{-1} became less intense, new absorptions appeared at 2100, 1850, 1720, 1620, 1530, 1050, 540, and 490 cm^{-1}. These absorptions can be assigned to $C\equiv C$ groups at 2100 cm^{-1},  $\underset{\underset{\displaystyle O}{\|}}{C}\text{–}F$ groups at 1850 cm^{-1}, C=CF and C=O groups at 1720 cm^{-1}, C=C groups at 1620 cm^{-1}, NO_2 groups at 1530 cm^{-1}, C–O groups at 1050 cm^{-1}, and

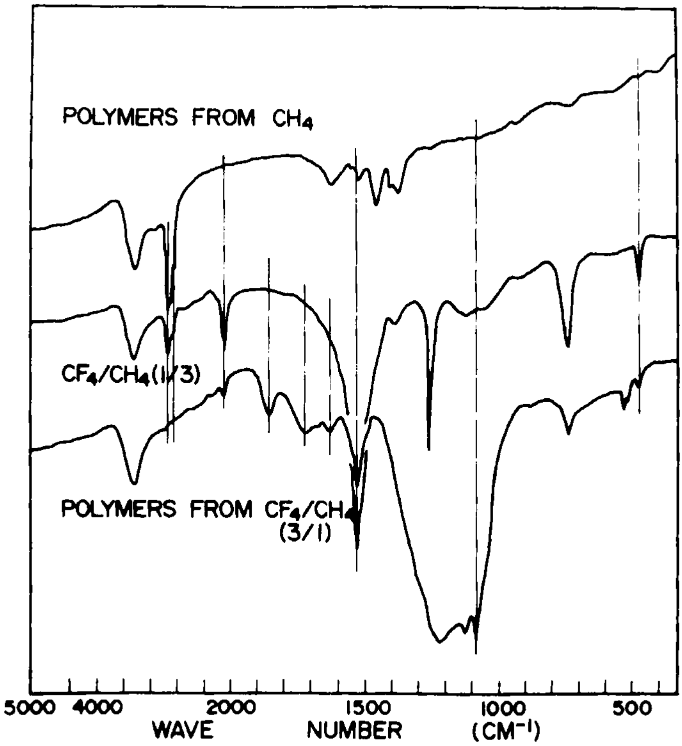


FIG. 3. Infrared spectra of polymers prepared from CF_4/CH_4 mixture and CH_4 by glow discharge polymerization.

SiF_6^{2-} groups at 540 and 490 cm^{-1} [7-9]. This indicates that the polymers formed from the CF_4/CH_4 mixture are conspicuously altered by changing the composition in the mixture, and also that the polymers from the mixture containing CH_4 of 25 mol%, which possess surface energy as low as that of conventionally polymerized polytetrafluoroethylene, involve unanticipated groups such as $C\equiv C$, $C=CF$, $C=C$, $C-F$, NO_2, $C-O$, and SiF_6^{2-} groups as well as $C-F$ groups.
||
O

Figure 4 shows a comparison of the infrared spectra of polymers prepared from the CF_4/CH_4 mixture and tetrafluoroethylene by glow discharge polymerization. The spectrum of the polymers from tetrafluoroethylene consists of main absorptions at 1235 and 740 cm^{-1} which can be assigned to C–F and SiF_6^{2-} groups, and of minor absorptions at 2930, 2335, 1720, 985, and 540 cm^{-1}. This spectrum, except minor absorptions at 2930, 2335, 1720, 985, and 540 cm^{-1}, resembles

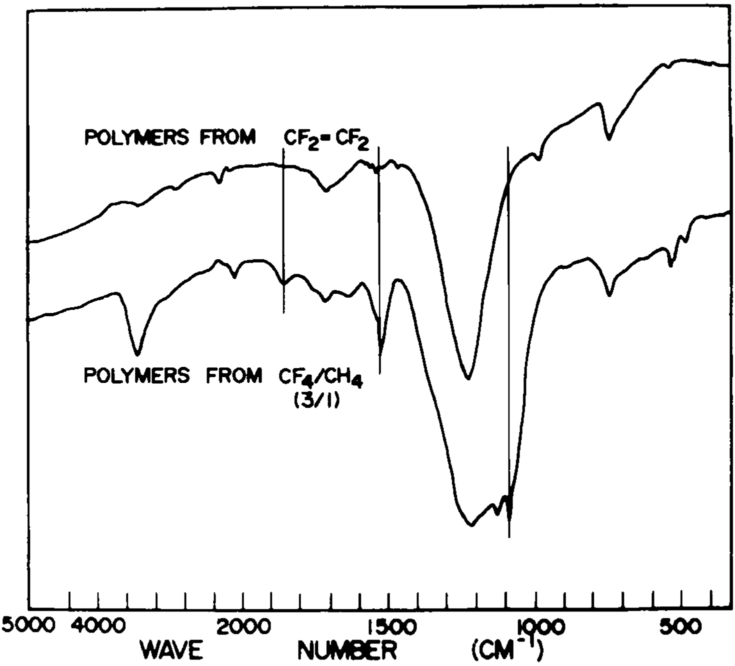


FIG. 4. Infrared spectra of polymers prepared from CF_4/CH_4 mixture and tetrafluoroethylene by glow discharge polymerization.

that of conventionally polymerized polytetrafluoroethylene. It can be concluded that the tetrafluoroethylene polymer formed by glow discharge polymerization is similar to conventional polymers, but that the polymers from the CF_4/CH_4 mixture are fairly different from that prepared from conventionally polymerized polytetrafluoroethylene.

How were the unanticipated residues such as $\underset{\underset{O}{\|}}{C}{-}F$, $C{=}CF$, and NO_2 groups generated in the CF_4/CH_4 mixture system by glow discharge polymerization? Smolinsky et al. [10, 11] have investigated the plasma chemistry of the CF_4/H_2 and CF_4/O_2 mixtures by mass spectroscopy, and have proposed a rf discharge chemistry of CF_4 as follows:

$$CF_4 \underset{M}{\overset{e}{\rightleftharpoons}} CF_3 + F \underset{M}{\overset{e}{\rightleftharpoons}} CF_2 + F \underset{M}{\overset{e}{\rightleftharpoons}} CF + F$$

This reaction is affected by adding hydrogen and oxygen gases. The

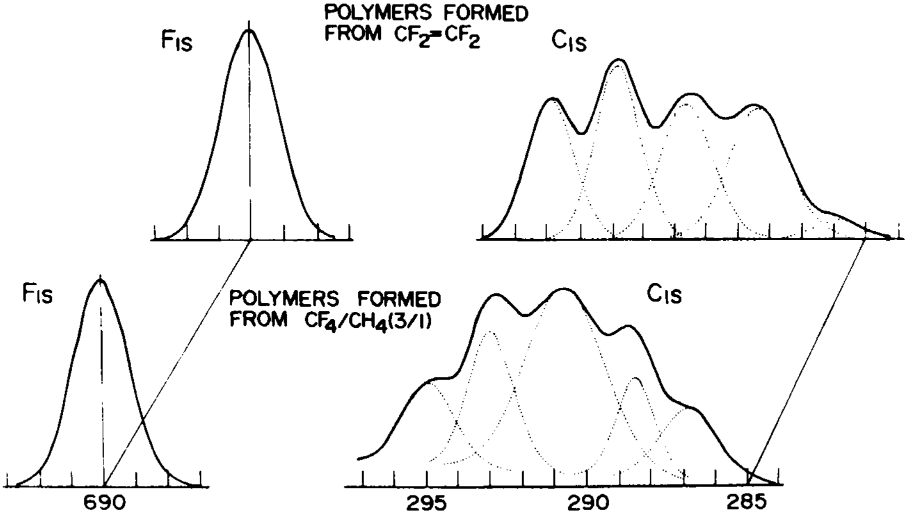


FIG. 5. ESCA spectra of polymers prepared from CF_4/CH_4 mixture and tetrafluoroethylene by glow discharge polymerization.

addition of hydrogen gas to the CF_4 discharge leads to the formation of HF and CF_3H. The addition of oxygen gas accelerates the elimination of fluorine from the CF_4 molecule and leads to the formation of oxidative products such as CO_2F, CO_2, and CO. This result seems to provide an idea of how the polymers prepared from the CF_4/CH_4 mixture by glow discharge polymerization contain unanticipated residues such as $\underset{\underset{\displaystyle O}{\|}}{C}$–F, NO_2 and C–O groups. According to this idea it is not unreasonable that these groups are created by the interaction between a CF_4 discharge and air which was not completely evacuated from the reactor. This interaction, as reported by Smolinsky et al., would occur predominantly at a high CF_4 concentration in the mixture.

ESCA Spectra

Although there is no doubt from the infrared spectroscopy results that the polymer created from the CF_4/CH_4 mixture by glow discharge polymerization is different in chemical structure from that from tetrafluoroethylene, differences of the two polymers in their chemical structures were reaffirmed by ESCA analysis. Figure 5 shows the C_{1s} level spectra of the two polymers which were formed from the CF_4/CH_4 mixture (70/30 molar ratio) and tetrafluoroethylene by glow discharge polymerization. The peak of the F_{1s} level at 690.0

eV was temporarily used to calibrate the binding energy scale although the FWHW was not satisfactorily narrow because of the very weak signal at 285.0 eV binding energy arising from extraneous hydrocarbon contamination.

Both polymers show similar C_{1s} level spectra, but the spectrum for the polymer prepared from the CF_4/CH_4 mixture has a large contribution arising from $\pi \rightarrow \pi^*$ shake-up satellites in the region of binding energy above 295 eV. This is a principal difference between the polymer prepared from the CF_4/CH_4 mixture and tetrafluoroethylene systems, corresponding with the infrared spectral result that the polymer from the CF_4/CH_4 mixture possesses a large number of unsaturated groups.

There seem to be at least five different structural features on these C_{1s} level spectra. The C_{1s} level spectrum for the polymer prepared from the CF_4/CH_4 mixture by glow discharge polymerization was deconvoluted into five components centered at 286.0, 288.5, 290.8, 292.9, and 295.0 eV. The C_{1s} level spectrum for the polymer from tetrafluoroethylene was also deconvoluted into five components centered at 285.8, 288.4, 290.6, 292.8, and 294.9 eV. These components can be tentatively assigned as $\underline{C}H_2{-}CHF$; $\underline{C}HF$, $-\underline{C}-$, and $\underline{C}{=}O$; $\underline{C}F_2{-}CH_2$ and $\underline{C}F$; $\underline{C}F_2$; and $\underline{C}F_3{-}CF_2$ sites, with reference to the primary and secondary effects of fluorine substituents on chemical shift by Clark et al. [12-14]. This deconvolution shows that the both polymers consist of similar structural features. The polymer from the CF_4/CH_4 mixture contains a large number of the structural feature of $CF_2{-}CH_2$ and CF sites, while the polymer from tetrafluoroethylene contains an almost equivalent amount of each structural feature except for the $CH_2{-}CHF$ site. This is also a difference between the polymers prepared from the CF_4/CH_4 mixture and tetrafluoroethylene. However, it should be noted that the relative intensity of these peaks is not exactly quantitative but rather semiquantitative because each deconvoluted peak appearing at high binding energy involves contributions arising from shake-up satellites.

This study points out an important aspect of glow discharge polymerization of fluorine-containing compounds. Glow discharge polymerization, as shown in the case of the CF_4/CH_4 mixture, causes not only polymerization of a monomer but also of a gas mixture, if these molecules are resident in a discharge, and gives polymers incorporating elements present in the mixture. In this sense, glow discharge polymerization is atomic polymerization as proposed by Yasuda [1]. However, the polymers from the CF_4/CH_4 mixture and those from tetrafluoroethylene in chemical structure, even when the polymerizations were performed under exactly the same operational conditions. This seems to arise from differences in the species activated by plasma: in the CF_4/CH_4 mixture system the activated species may be fluorine and in the tetrafluoroethylene system there are double bonds. The activated fluorine would induce some reactions with the resident air to form unanticipated groups. It is important to know what molecule is activated by a discharge, especially in a mixed gas system.

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