

Glow Discharge Polymerizations of Tetrafluoroethylene, Perfluoromethylcyclohexane and Perfluorotoluene Investigated by Infrared Spectroscopy and ESCA

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Summary

Glow discharge polymerizations of tetrafluoroethylene, perfluoromethylcyclohexane and perfluorotoluene were investigated by infrared spectroscopy and ESCA to clarify the contribution of olefinic double bonds and cyclic structures. The products formed from the three compounds were deposited as filmy polymers containing large amount of fluorine. Their polymeric chains are composed of CF, CF-CF_n, CF₂ and CF₃ groups and have less dependency on chemical structures of the starting compounds. The polymer-forming process involves not only chain reactions via addition reaction to double bonds and via ring-opening reaction but also the rupture of C-F bonds and the rearrangement of the ruptured fluorine atoms.

Introduction

Glow discharge polymerization which yields in most cases highly branched and crosslinked polymers has distinct features compared with conventional polymerization such as radical and ionic polymerization. One of them is no restriction of starting materials used as monomer for this polymerization, and even compounds having no functional group such as methane and ethane can be served. How such compounds are polymerized can not yet resolved in detail. It is considered that organic molecules in a discharge are in the state excited by interactions of electrons, ions, radicals etc.; and then, the activated species are fragmented.

Yasuda has pointed out that glow discharge polymerization involves essentially two different processes depending on the nature of the starting compounds. Those are chain reaction via addition to olefinic double bonds and via ring-opening reaction, and stepwise reaction by repetition of activation and recombination. This aspect is described in detail in the reference (YASUDA 1978). These two processes, if restricted to the compounds with functional groups as starting material, could occur simultaneously in a discharge. Either of the two processes proceeds predominantly is closely related to the properties of the formed polymers because linear polymers will be yielded by the chain reaction, and branched and crosslinked polymers will be yielded by the stepwise reaction.

This study focusses on the contribution of olefinic double bonds and cyclic structures in glow discharge polymeri-

zation. Tetrafluoroethylene (TFE), perfluoromethylcyclohexane (PFMCH) and perfluorotoluene (PFT) are used as monomer.

Experimental

Glow Discharge Polymerization: The reaction chamber is a tubular reactor of Pyrex glass (35 mm inner diameter, 400 long) with a monomer inlet, a pressure gauge, a vacuum system and a matching network for inductive coupling of a 13.56 MHz radio frequency source. The glow discharge polymerization was performed at a given flow rate of the monomer gas at a pressure of 0.13 Pa at a given level of the rf power from 50 to 70 W for an adequate duration. Detailed operations have been described in the previous paper (INAKAGI 1982). Chemicals used as monomer were tetrafluoroethylene (TFE) (purchased from Ideal Gas Co.), perfluoromethylcyclohexane (PFMCH) (from Aldrich Chemical Co.) and perfluorotoluene (PFT) (from Tokyo Kasei Co.).

ESCA Spectra: The polymer films (approximately 0.1 μm thickness) deposited on glass plates (10 X 10 mm) were provided for measurement of ESCA spectra. The spectra were recorded with a Hewlett-Packard 5950A spectrometer employing monochromatic $\text{Al K}_{\alpha 1,2}$ exciting radiation. To alleviate charging of the sample by a x-ray radiation an electron-flad-gun was employed. Typical operating conditions were: x-ray gun, 800 W; the pressure in the sample chamber, 2.7×10^{-7} Pa; the electron-flad-gun, 1 mA, 1 eV. The F_{1s} core level at 690.0 eV was temporarily used for calibration of the binding energy because of the very weak signal at 285.0 eV arising from extraneous hydrocarbon contamination. The complex C_{1s} spectra were deconvoluted by non-linear root mean square method. A Gaussian distribution was assumed, and the resolved curves mostly fitted to the observed spectra were determined by variation of three parameters i. e., the position and the height of the peak, and the full width at half-maximum (FWHM). The FWHM value of the each curve resolved was less than 2 eV.

The elemental composition, the surface energy and the infrared spectra of the formed polymers were examined according to the methods detailed in the previous paper (INAGAKI et al. 1982).

Results and Discussion

Prior to inquiry of chemical structures of the polymers formed from the three monomers the reproducibility of the glow discharge polymerization was appraised by measurement of contact angles of five liquids (water, glycerol, formamide, diiodomethane and tricresyl phosphate) at surfaces of the formed polymers. The good reproducibility was accomplished in the polymerizations conducted under following conditions: the pressure in the reaction chamber, 0.13 Pa; the flow rate of the monomer gas, 0.7 - 3.0 $\text{cm}^3(\text{STP})/\text{min}$, and the rf power, 50 to 70 W. The surface energy of typical polymers prepared from the three monomers under those conditions is tabulated in TABLE 1; indicating that changes of the W/FM value within 1 - 4 MJ/kg, which means the input rf power per mass of the monomer, where W is the rf power, F is the flow rate of the monomer,

and M is the molecular weight of the monomer; scarcely influence hydrophobicity of the formed polymers, and that the polymers formed from TFE and PFMCH possess fairly lower surface energy than conventionally polymerized polytetrafluoroethylene ($\gamma_s = 16.2$ dyn/cm).

TABLE 1
Surface Energy and Elemental Composition of Polymers
prepared from TFE, PFMCH and PFT

Polymers from	W/FM (MJ/kg)	Surface Energy(dyn/cm)			Empirical Formula
		γ_s	γ_s^d	γ_s^p	
CF ₂ =CF ₂	220	12.8	12.1	0.7	CF _{1.26} H _{0.08} N _{0.06} O _{0.09}
PFMCH	190	12.8	12.1	0.7	CF _{1.44} N _{0.04} O _{0.13}
	270	12.9	12.3	0.6	CF _{1.49} N _{0.07} O _{0.08}
PFT	290	22.4	22.3	0.1	CF _{0.79} H _{0.33} N _{0.21} O _{0.14}
	410	24.3	24.3	0	CF _{0.73} H _{0.52} N _{0.01} O _{0.14}

γ_s is surface energy. γ_s^d and γ_s^p are dispersive and polar contribution, respectively.

All the polymers formed from the three monomers, as listed in TABLE 1, possessed much quantities of fluorine and carbon with small amount of hydrogen, nitrogen and oxygen. Their atomic ratio of fluorine to carbon (F/C) was fairly lower than that of the starting materials used for the polymerization. This low F/C ratio indicates that the polymer-forming process in a discharge accompanies with the elimination of fluorine, and that the amount of the eliminated fluorine reaches to 25 - 37% of the total fluorine that the each starting compound initially possesses.

The polymers formed from TFE and PFMCH showed almost the same ir spectra. On their spectra, although the spectra are not represented here for the sake of brevity, there appeared absorptions at 3400 (OH), 1230 (C-F) and 735 cm^{-1} (SiF_6^{2-}) with minor absorptions at 2330 ($\text{C}\equiv\text{C}$), 1789 ($\text{CF}=\text{CF}_2$), 1720 and 1640 ($\text{C}=\text{O}$, $\text{CF}=\text{CF}$, $\text{C}=\text{C}$), 990 (unknown) and 540 cm^{-1} (SiF_6^{2-}). These spectra are different from those for conventionally polymerized polytetrafluoroethylene consisting of only absorptions at 1242, 1213 and 1152 cm^{-1} due to C-F₂ groups. On the spectra of the polymers formed from PFT there were main absorptions due to C-F (at 1220 and 1180 cm^{-1}), and $\text{CF}=\text{CF}$ and fluorinated phenyl groups (at 1740 - 1640 and 1500 cm^{-1}) with minor absorptions at 3440 (OH), 1000 (unknown) and 740 cm^{-1} (SiF_6^{2-}). These spectral results indicate that these polymeric chains contain residues such as $\text{CF}=\text{CF}$, $\text{CF}=\text{CF}_2$ and fluorinated phenyl groups that are unexpected from the chain reaction via addition to olefinic double bonds and via ring-opening reactions.

Although the ir spectra showed brief chemical structures of the polymers formed from TFE, PFMCH and PFT the results are not satisfying to clarify the details. Successively, ESCA spectra were examined. Fig. 1 shows typical C_{1s} core level spectra for the three polymers. The C_{1s} spectra, as seen in Fig. 1, are complex, and seem to contain at least five different structural features. These spectra were deconvoluted into five components. For example, the C_{1s} spectra for the polymers formed from TFE at a W/FM value of 220 MJ/kg were deconvoluted

TABLE 2
ESCA Spectra (C1s) of Polymers prepared from TFE, PFMCH and PFT

Polymers from	W/FM (MJ/kg)	Location of Deconvoluted Component #1 centred at	(eV), (area)	24%	26%	26%	24%	26%	26%	26%
		Deconvoluted Component #2 centred at	(eV), (area)							
		Deconvoluted Component #3 centred at	(eV), (area)							
		Deconvoluted Component #4 centred at	(eV), (area)							
CF ₂ =CF ₂	220	-8 cm*	288.4, 26%	290.6, 24%	292.8, 26%	294.9, 21%				
		+8	288.6, 23	290.8, 26	293.0, 23	295.1, 25				
PFMCH	190	-8	288.6, 31	291.2, 24	293.0, 28	295.1, 17				
		+8	288.3, 19	290.6, 32	292.8, 24	294.8, 23				
	270	-8	288.0, 22	290.3, 27	292.4, 27	294.4, 22				
		+8	288.0, 22	290.3, 27	292.4, 27	294.4, 22				
PFT	290	0	287.9, 20	290.2, 50	292.8, 13	295.0, 8				
		+5	288.1, 24	290.4, 45	292.9, 14	295.0, 9				
	410	-5	288.1, 21	290.2, 45	292.8, 13	295.0, 8				
		0	288.2, 20	290.3, 47	292.9, 13	295.1, 7				
		+5	288.1, 28	290.4, 40	292.8, 15	295.0, 8				

*: The distance was taken from the monomer inlet. The remark "+" denotes a downstream side of a monomer flow, and the remark "-" denotes an upperstream side.

into five components centred at 285.8, 288.4, 290.6, 292.8 and 294.9 eV as illustrated in a dotted line in Fig. 1. These components can be assigned as $\text{CH}_2\text{-CHF}$; CF , C=O and -C- ; CF-CF_n ; CF_2 ; and CF_3 groups with reference to the primary and the secondary effects of fluorine substituents on the chemical shift (CLARK et al. 1975). Similar deconvolution and assignment were done for the other C_{1s} spectra. The position and the relative area of the four resolved peaks except the minor peak due to CH_2 groups appearing in the vicinity of 285.0 eV are summarized in TABLE 2 as function of the W/FM value and the location of polymer deposition.

The component #1 - #4 represented in TABLE 2 can be assigned as CF , C=O and -C- ; CF-CF_n ; CF_2 ; and CF_3 groups, respectively. TABLE 2 shows that the polymers; in spite of a kind of the used monomers, a magnitude of the W/FM, and a location of the polymer deposition; possess the same structural units. If the polymer-forming process was done predominantly by chain reactions via double bonds of TFE and ring-opening of PFMCH the $\text{CF}_2\text{-CF}_2$ units for the polymers formed from TFE and $\text{CF}_2(\text{CF}_2)_4$ CF units for the polymers from PFMCH should be a main structural CF_3

unit. The two polymers, as seen in TABLE 2, compose of CF , CF-CF_n , CF_2 and CF_3 groups, and each of them reaches approximately 25 mol% in content. The formation of CF_3 groups in glow discharge polymerization of TFE can not be possible without the rupture of C-F bonds. This indicates that the polymer-forming process involves not only chain reaction via addition to double bonds and via ring-opening but also the rupture of C-F bonds. Such assumption can be supported also in the system of PFT. The rupture of C-F bonds is recognized by the evidence that the polymers, as described on the ir spectra for the formed polymers, contained SiF_6^{2-} species which might be formed by the interaction between the eliminated fluorine atoms and glass walls of the reaction chamber.

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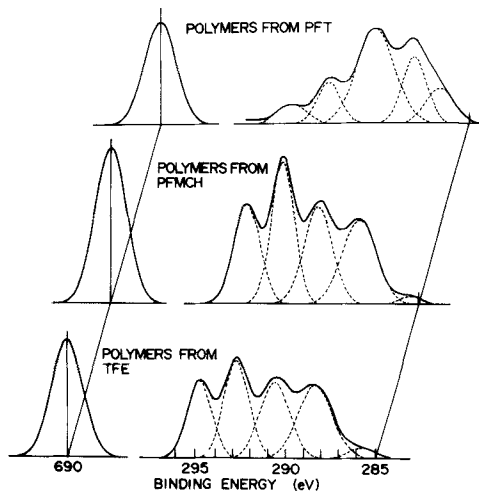


Fig. 1 ESCA Spectra of Polymers prepared from TFE, PFMCH and PFT at a W/FM value of 220 (for TFE), 270 (for PFMCH) and 290 MJ/kg (for PFT).