Polymer Bulletin 7, 65–70 (1982)

Polymer Bulletin

Glow Discharge Polymerization in the CF_3Br/CH_4 System

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Summary

Glow discharge polymerization in the system of the CF_3Br/CH_4 mixture was investigated by infrared spectroscopy and ESCA.

Surface energies of polymers from the CF_3Br/CH_4 mixture decrease as increasing the concentration of CF_3Br in the mixture, but the value of surface energy is not as low as that of polymers from CF_4/CH_4 mixture and from $CF_2{=}CF_2$. Polymers from the CF_3Br/CH_4 mixture possess a large amount of bromine as well as fluorine, and consist of five structural features which was determined by deconvolution of the C_{1s} level spectra. A relative concentration of each structural feature was also discussed in comparison with that for polymers from the CF_4/CH_4 mixture and $CF_2{=}CF_2$.

Introduction

Glow discharge polymerization is an unique technique to form polymeric materials from almost all compounds which include even compounds having no functional groups such as double bonds. If utilized this polymerization technique hydrophobic and fluorine-containing polymers can be easily obtained from perfluorocarbons (YASUDA, et al. 1977). Similar polymers can be also yielded from the mixture of CF_4 and CH_4 (INAGAKI, et al. 1981).

Evidently in glow discharge polymerization of hydrocarbons the addition of CH_3Br leads to enhanced polymer formation, and the added CH_3Br is considered to play as a radical source to form polymers because of low bond energy of C-Br bonds (KOBAYASHI, et al. 1974).

This study focuses on glow discharge polymerization in the system of CF_3Br/CH_4 mixture, and the formed polymers are examined by infrared spectroscopy and ESCA.

0170-0839/82/0007/0065/$01.20

Experimental

Materials

Chemicals used for glow discharge polymerization in this study were bromotrifluoromethane (Daiflon 13B1) (provided from Daikin Industries) and methane (provided from Matheson).

Glow Discharge Polymerization

The apparatus and experimental procedures for glow discharge polymerization are essentially the same as those reported elsewhere (INAGAKI, et al. in press). The reaction chamber is a tubular reactor (35 mm inner diameter, 400 mm long) which is made of Pyrex glass, 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 radio frequency source. The glow discharge polymerization was performed under following operating conditions: the flow rate of monomer gas, 0.5 cm^3(STP)/min; the pressure in the reaction chamber before initiating glow discharge, 10 mTorr; the level of a r. f. power, 25 W.

Elemental Analysis

Polymers which were deposited on a glass plate and which were scraped with a knife were provided for C, H, N, Br and F analyses. The C, H and N contents in the deposited polymers were determined using a CHN corder MT-2 (Yanagimoto Co.). The Br and F contents were also determined by potentiometry and colorimetric analysis (alizarine complex method), respectively (UKI BIRYO BUN SEKI 1969).

Surface Energy

The contact angle of polymer films which were deposited on glass plates against water, glycerol, formamide, diiodomethane and tricresyl phosphate was 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 (KAELBLE 1971).

Infrared Spectra

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

ESCA Spectra

Polymer films (approximately 0.1 μm thickness) deposited on glass plates (10 X 10 mm) which were placed just under the monomer inlet were provided for measurement of ESCA spectra. Spectra were recorded with a

Hewlett-Packard 5950A spectrometer employing monochromatic $AlK_{\alpha 1,2}$ exciting radiation. To alleviate charging of samples by a 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-flat-gun, 1mA, 1eV.

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 binding energy arising from extraneous hydrocarbon contamination.

Spectra of the C_{1s} level were deconvoluted by nonlinear root mean square method. A Gaussian curve was assumed, and resolved curves which were mostly fitted to the observed spectra were determined by variation of three parameters, i. e., position and height of peak, and full width at half-maximum (FWHM). A typical FWHM value of resolved curves was less than 2 eV.

Results and Discussion

Surface energies of polymers formed from the CF_3Br/CH_4 mixture by glow discharge polymerization are listed in TABLE 1 in comparison with those of polymers from the CF_4/CH_4 mixture and from $CF_2{=}CF_2$ which have been reported previously (INAGAKI et al. in press). Surface energies of polymers from the CF_3Br/CH_4 mixture decrease as increasing the concentration of CF_3Br in the mixture, but the value of surface energy is not as low as that of polymers from the CF_4/CH_4 mixture and from $CF_2{=}CF_2$. The CF_3Br/CH_4 mixture, consequently, is not a favouring system to form hydrophobic polymer surfaces by glow discharge polymerization.

TABLE 1
Surface Energies of Polymers Prepared by Glow Discharge Polymerization

Polymers from	Mixing ratio	Surface energies γ_s	γ_s^d	γ_s^p
CF_3Br/CH_4	3/7	37.3	37.0	0.3
	5/5	36.0	36.0	0
	7/3	29.6	29.6	0
CF_4/CH_4	3/7	39.1	38.9	0.2
	5/5	38.0	38.0	0
	7/3	17.4	16.5	0.9
$CF_2{=}CF_2$		12.8	12.1	0.7

TABLE 2 shows elemental composition of polymers prepared by glow discharge polymerization. Polymers from the CF_3Br/CH_4 mixture are distinguished in elemental composition with those from the CF_4/CH_4 mixture. Although the quantity of fluorine is comparable between polymers from the CF_3Br/CH_4 and from the CF_4/CH_4 mixtures, the polymers from the former mixture possess

TABLE 2

Elemental Composition of Polymers Prepared by Glow Discharge Polymerization

Polymers from	Mixing ratio	Empirical formular of polymers
CF_3Br/CH_4	7/3	$CH_{1.18}N_{0.11}O_{0.15}Br_{0.41}F_{0.73}$
CF_4/CH_4	7/3	$CH_{0.06}N_{0.17}O_{0.09}F_{0.68}$
$CF_2{=}CF_2$		$CH_{0.08}N_{0.06}O_{0.09}F_{1.26}$

a large amount of hydrogen and bromine. This is primary difference between the two polymers. The incorporation of bromine into the polymers formed from the CF_3Br/CH_4 mixture seems to assist ascending surface energy. This result indicates that glow discharge polymerization has a capability that any element which is constituent in monomers injected into a glow discharge can be incorporated into the resulting polymers in more or less quantity.

On infrared spectrum of polymers from the CF_3Br/CH_4 mixture (7/3 mixing ratio), although the spectrum is not illustrated here for the sake of brevity, there were strong absorptions at 2100 (C≡C), 1520 (NO_2), 1260, 1130, 1090, 1050 (C-F) and 750 cm^{-1} (SiF_6^{2-}); and weak absorptions at 2930, 2850 (CH_2, CH) and 1295 cm^{-1} (NO_2). This spectrum is different from that of polymers from CF_4/CH_4 mixture and from $CF_2{=}CF_2$ in appearance of absorptions at 2930 and 2850 cm^{-1}, and intensity of absorptions at 1130, 1090 and 1050 cm^{-1} (INAGAKI et al. in press, submitted). This suggests that the polymers from the CF_3Br/CH_4 mixture contain a large amount of CH_2 and CH groups, and different types of fluorinated carbons Accordingly, polymer structure is examined in detail by ESCA.

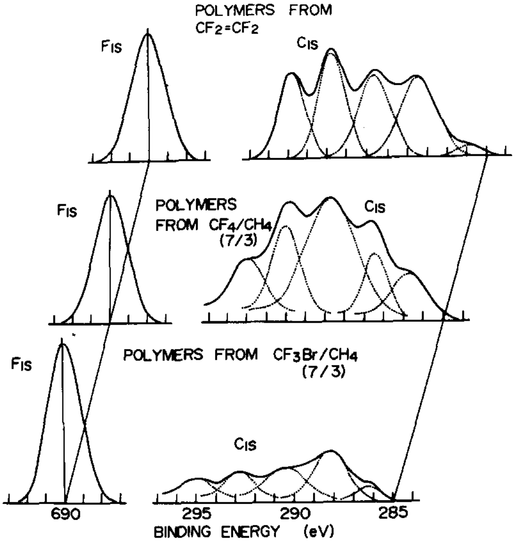

Fig. 1. ESCA (C_{1s}) spectra of polymers from CF_3Br/CH_4, CF_4/CH_4 and $CF_2{=}CF_2$ by glow discharge polymerization

The polymers from the CF_3Br/CH_4 mixture, as seen in Figure 1, shows complex C_{1s} level spectrum. The spectrum has great contribution arising from $\pi \rightarrow \pi^*$ shake-up satellite in the region of binding energy above 295 eV. Such great contribution has been also observed for the polymers from CF_4/CH_4 mixture (INAGAKI et al. in press), indicating the presence of unsaturated groups in these polymers.

On these C_{1s} level spectra there seem to be at least five different structural features. For the polymers from the CF_3Br/CH_4 mixture the spectrum was deconvoluted into five components centered at 286.2, 288.1, 290.4, 292.7 and 295.0 eV. These components can be tentatively assigned as $\underline{C}H_2\text{-}CF_2$; $\underline{C}F$, $\underline{C}F=$, $\underline{C}=O$ and $-\underline{C}-$; $\underline{C}F\text{-}CF_n$; $\underline{C}F_2$;and $\underline{C}F_3$ sites, respectively, with reference to report by Clark et al. (1975). These five structural features can be also observed on spectra of polymers from the CF_4/CH_4 mixture and from $CF_2=CF_2$ (INAGAKI et al. in press, submitted), and there is no difference among the 3 polymers in kind of structural features composing the C_{1s} level spectra. However, it is worth to notice that there is difference among the 3 polymers in relative peak area (TABLE 3).

TABLE 3
ESCA(C_{1s}) Spectra of Polymers Prepared by Glow Discharge Polymerization

Polymers from	Peak #1 centered at	Peak #2 centered at	Peak #3 centered at	Peak #4 centered at	Peak #5 centered at
CF_3Br/CH_4 (7/3)[a]	286.2eV (8%)[b]	288.1eV (37%)	290.4eV (28%)	292.7eV (15%)	295.0eV (12%)
CF_4/CH_4 (7/3)	286.0 (12)	288.5 (12)	290.8 (44)	292.9 (19)	295.0 (13)
$CF_2=CF_2$[c]	286.3 (3)	288.6 (23)	290.8 (26)	293.0 (23)	295.1 (25)

a) Mixing ratio, b) Relative peak area, c) Deposited at +8 cm

The polymers from the CF_3Br/CH_4 mixture possess a large amount of the $\underline{C}F$, $\underline{C}F=$, $\underline{C}=O$ and $-\underline{C}-$ sites (component #2); and $\underline{C}F\text{-}CF_n$ sites (component #3). The polymers from the CF_4/CH_4 mixture possess predominantly the $\underline{C}F\text{-}CF_n$ sites; and those from $CF_2=CF_2$ possess almost equivalent amount of four components except the $\underline{C}H_2\text{-}CF_2$ component. Such difference among three polymers in distribution of fluorinated carbons is to be noticed. This seems to indicate that rearrangement of fluorine atoms which occurs in a glow discharge depends strongly on nature of a starting material.

Results in this study seem to point out important aspects in application of glow discharge polymerization.

(1) Any element which was present in a glow discharge can be incorporated into the formed polymers in more or less quantity.

(2) Rearrangement of molecules to form polymers in a discharge state depends strongly on nature of a starting material.

Acknowledgement

Authors acknowledge Mitsubishi Chemical Industries for measurement of ESCA analysis, and also Daikin Industries for supplying bromotrifluoromethane.

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Received February 24, accepted March 8, 1982