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On the Structure of Poly(hexafluoro-1,3-butadiene) Yielded by Anionic Polymerization

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ABSTRACT: The structure of the polymer obtained upon anionic polymerization of hexafluoro-1,3-butadiene (HFBD) was investigated by measuring solid-state ^{13}C NMR spectra, X-ray photoelectron spectra (XPS), and Raman spectra. ^{13}C NMR showed two peaks at 120 and 133 ppm which were assigned to the CF_3 carbon and the $>C=$ carbon, respectively. XPS also indicated the presence of these species which were observed at 293 and 287 eV, respectively. In the Raman spectra, the vibrations at 1675 and 1145 cm^{-1}, which were respectively assigned to C=C and C–C stretching, were detected. The peak at 770 cm^{-1} was attributed to the symmetric bending mode of the CF_3 group. Rocking and rotational vibrations assigned to the CF_3 group were also detected at 335 and 295 cm^{-1}, respectively. These spectral data basically agreed with those of poly(hexafluoro-2-butyne) [poly(HFBY)], which was produced under the same polymerization conditions as those used for the polymerization of HFBD. The structure of poly(HFBD) obtained here was concluded to be similar to that of poly(HFBY). The postulated polymerization mechanisms are (1) isomerization of HFBD to HFBY followed by polymerization and (2) an addition reaction of a propagating anion to the 2-carbon of HFBD followed by isomerization of the propagating end group to yield the poly(HFBY) structure.

Introduction

Fluorine-containing polymers are of industrial interest because of their excellent physical and chemical properties. Poly(tetrafluoroethylene), which is one of the typical fluoropolymers, is widely used as high-performance insulators and as highly efficient lubricants. However, perfluorocarbon polymers show poor dimensional stability at high temperature since they are thermoplastic.[1] A thermoplastic polymer generally exhibits a low glass transition temperature and a high thermal expansion coefficient. In order to improve these properties of perfluorocarbon polymers, the polymerization of hexafluoro-1,3-butadiene (HFBD) has been investigated with the purpose of developing a polymer possessing functional groups, which could bring about a cross-linking reaction between polymer chains. A polymer obtained from HFBD is expected to include carbon–carbon double bonds which are known to form cross-links. Cross-linked poly(HFBD) is expected to exhibit promising thermal properties such as a low thermal expansion coefficient and a high thermal decomposition temperature associated with an excellent chemical stability. Indeed, the chemical structure of the polymer is similar to poly(tetrafluoroethylene) and it would be a thermosetting resin. HFBD has been reported to hardly polymerize under radical or normal anionic conditions.[2] As previously reported, anionic polymerization of HFBD initiated by one of the initiators cesium fluoride, cesium *tert*-butoxide, cesium naphthalene, the dicesium salt of a living α-methylstyrene oligomer, rubidium fluoride, rubidium *tert*-butoxide, rubidium naphthalene, and the dirubidium salt of a living α-methylstyrene oligomer has successfully produced the expected polymer in high yield under mild conditions.[2,3] The poly(HFBD) obtained with CsF initiation in a toluene medium showed an excellent thermal stability as demonstrated by the thermal gravimetric analysis. The decomposition temperature of poly(HFBD) produced in toluene is about 360 °C, which is 200 °C higher than that of poly(HFBD) produced in tetrahydrofuran (THF). The thermal stability of poly(HFBD) is found to be affected by the solvent used upon polymerization. Poly(HFBD) behaves as a thermosetting polymer since its thermal expansion coefficient decreases with a heating treatment.[4] However, the structure of poly(HFBD) obtained here has not been clearly identified yet, because of the poor solubility of the polymer. From the ^{13}C NMR and the infrared spectra of the polymer, HFBD is tentatively concluded to undergo 1,4-addition polymerization.[2]

The present paper deals with a detailed study on the structure of poly(HFBD) in connection with that of poly(hexafluoro-2-butyne). Miller et al. have reported that the isomerization reaction of HFBD takes place in the presence of a large excess of CsF at 150 °C and ultimately yields hexafluoro-2-butyne (HFBY).[5] As has been reported in the previous paper,[3] poly(HFBD) can, however, be obtained in the presence of a small amount of CsF under much milder conditions.

In order to clarify the structure of poly(HFBD), which is insoluble in organic solvents, infrared spectra, ^{13}C NMR, X-ray photoelectron spectra (XPS), and Raman spectra of the polymer are discussed since these techniques are applicable to analyzing solid samples.

The results of the investigation on the anionic polymerization reactivity of HFBY will be reported elsewhere.[6]

Experimental Section

Reagents. Poly(HFBD) was synthesized according to the literature reported previously.[3] Poly(HFBY) was obtained under similar polymerization conditions.[6]

Measurements. Infrared spectra were measured on Jasco Model FT/IR-8000 and Hitachi Model I-5040 Fourier transform infrared spectrometers. Solid-state pulse saturation ^{13}C NMR spectra were registered at 67.8 MHz on a JEOL JNM-GX400 at 25 °C. Chemical shifts of each carbon in ppm were transformed from the peak of silicone rubber. X-ray photoelectron spectroscopy (XPS) was performed by a VG Model ESCALAB5 with Mg $K\alpha_{1,2}$ in vacuo of 1×10^{-9} Torr. XPS spectra were recorded

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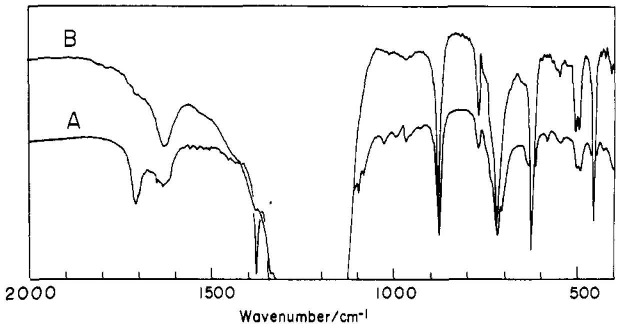

Figure 1. Infrared spectra of poly(HFBD) (A) and poly(HFBY) (B) obtained with *tert*-C_4H_9OCs in THF at 60 °C for 3 h.

at the takeoff angle of photoelectrons of 90°. The values of charge up were estimated from the F 1s peak, which is located at 688.7 eV. Raman spectra were recorded with a Jasco R-500 Raman spectrophotometer using the 514.5-nm line from an Ar^+ laser as an excitation beam.

Results and Discussion

Infrared and ^{13}C NMR Spectra of Poly(HFBD) and Poly(HFBY). The structure of poly(HFBD) has tentatively been concluded to be a 1,4-addition sequence from the results obtained by infrared and ^{13}C NMR analyses, as reported in a previous paper.[2,3] A more detailed study on infrared and ^{13}C NMR spectra of poly(HFBD) was carried out to further substantiate the above statement. Figure 1 shows the infrared spectra of poly(HFBD) and poly(HFBY) obtained with *tert*-C_4H_9OCs in THF at 60 °C for 3 h. Both spectra show very strong broad bands between 1100 and 1300 cm^{-1} assignable to C–F absorption. The spectrum of poly(HFBD) in Figure 1A exhibits a small absorption at 1710 cm^{-1}, whereas Toy et al. have reported the existence of two characteristic absorption peaks at 1786 and 1724 cm^{-1} assignable to a pendant perfluorovinyl group and a perfluorovinylene group in the main chain, respectively.[7] On the contrary, the spectrum of poly(HFBY) in Figure 1B shows no peaks around 1700 cm^{-1} assignable to C═C bonds. Poly(HFBY) should include a polyene sequence since HFBY is polymerized by the addition polymerization of triple bonds. The polyene sequence has two configurations, which are the trans form and the cis form. The symmetric vibration of the trans form C═C stretching of the main chain should be inactive for infrared measurement. It is, therefore, concluded that poly(HFBD) possesses a small amount of the 1,4-addition sequence and that the structure of poly(HFBY) is a *trans*-polyene sequence without a 1,4-addition structure. The spectrum of the low-frequency region of poly(HFBD) coincides with that of poly(HFBY). The presence of the CF_3 group could not be confirmed from the data obtained by infrared.

Solid-state ^{13}C NMR of poly(HFBD) and poly(HFBY), which were produced by *tert*-C_4H_9OCs as the initiator in THF, are shown in Figure 2. ^{13}C NMR of poly(HFBD) and poly(HFBY) show simply two peaks. The peaks at 133 and 120 ppm in the spectrum of poly(HFBD) were predicted to be assignable to the carbons of ═CF and of CF_2, respectively. However, the same peaks are observed in the spectrum of poly(HFBY). It is difficult to distinguish the CF_3 carbon from the CF_2 carbon in terms of the chemical shift in solid-state ^{13}C NMR due to peak broadening. In order to compare the spectra of poly(HFBD) with those of the compounds having similar structures, ^{13}C NMR spectra of model compounds which possess the CF_3 group were measured. Figure 3 shows ^{13}C NMR spectra of perfluoroheptene-1 ($CF_2{=}CFCF_2CF_2CF_2CF_2CF_3$) and octafluorotoluene ($CF_3C_6F_5$) in carbon tetrachloride. In the spectrum of perfluoroheptene-1, the peaks around 110, 120, and 155 ppm are observed and the intensity ratio of these absorptions is 4:2:1. The peaks at about 110 and 155 ppm are assigned to the CF_2 and $CF_2{=}$ carbons, respectively. The peaks at about 120 ppm are assignable to the CF_3 and $CF{=}$ carbons. In the spectrum of octafluorotoluene, the quartet peaks observed at about 120 ppm are assignable to the CF_3 carbon. The peak at 120 ppm in the spectra of poly(HFBD) and poly(HFBY) are probably assignable to the CF_3 carbon in accordance with the results of model compounds. These results strongly suggest the presence of a polyene sequence in poly(HFBD).

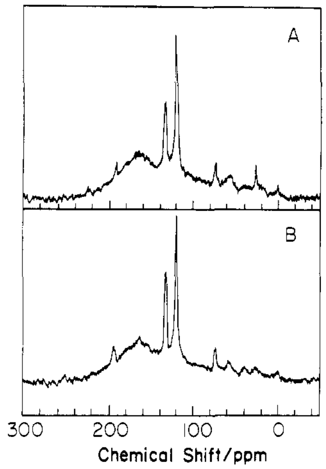

Figure 2. Solid-state ^{13}C NMR of poly(HFBD) (A) and poly(HFBY) (B) produced with *tert*-C_4H_9OCs in THF at 60 °C for 3 h.

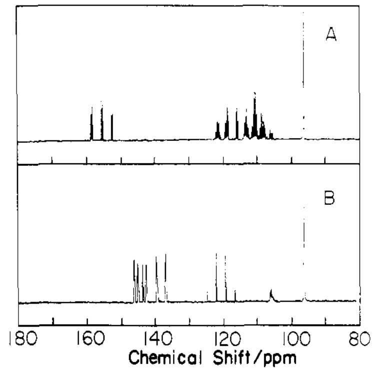

Figure 3. ^{13}C NMR spectra of perfluoroheptene-1 (A) and octafluorotoluene (B) in carbon tetrachloride.

XPS Spectra of Poly(HFBD) and Poly(HFBY). XPS is the most sensitive method for analyzing the structure of fluorocarbon polymers in the solid state since the C 1s binding energy shifts largely in terms of the number of fluorine atoms which bind to the observing carbon atom and adjacent carbon atoms. Several evaluation methods of the C 1s binding energy of fluoropolymers were reported.[8,9] Chen et al. have reported the analysis of plasma-polymerized poly(tetrafluoroethylene).[8] They estimated the C 1s binding energy in terms of the electrostatic potential model based on CNDO/2 calculation and electronegativity parameters. Takahagi and Ishitani reported the analysis of the sputtering process of fluoropolymers.[9] They evaluated the chemical shift values on the basis of experimental data of the fluoropolymer series, taking the diad effect of the fluorine atom into account. According to their evaluation, the C 1s binding energy shifts 2.9 eV for the observing carbon and 0.35 eV

Table I
Elemental Composition and Carbon Composition of Poly(HFBD) and Poly(HFBY) Estimated from C 1s XPS Spectra

			composition of carbon species, %					
sample	F/C	O/C	293 eV	292 eV	288 eV	287 eV	284 eV	283 eV
poly(HFBD)	1.42	0.007	41	6	5	34	12	3
poly(HFBY)	1.37	0.04	38	4	2	36	16	4
assignment			CF_3	CF_2	CF=	>C=	contaminant	
calcd value, eV			293.3	291.5	288.6	286.7		

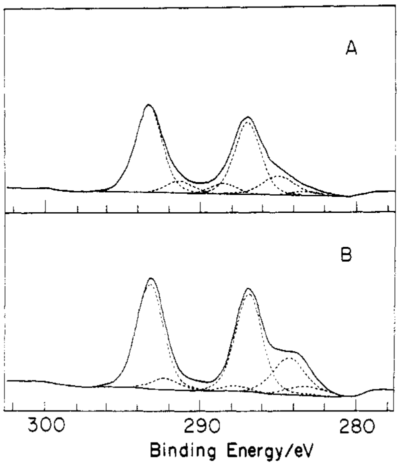

Figure 4. XPS C 1s spectra of poly(HFBD) (A) and poly(HFBY) (B) yielded by *tert*-C_4H_9OCs in THF at 60 °C for 3 h.

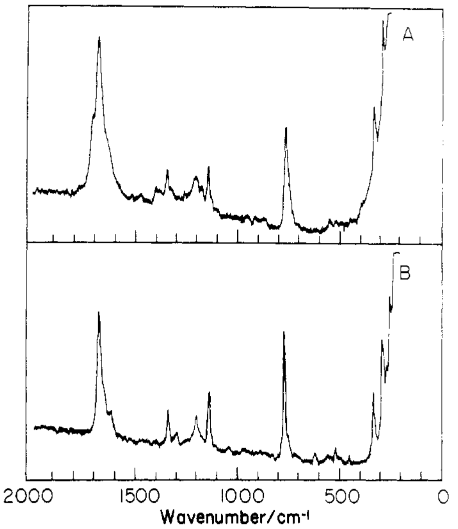

Figure 5. Raman spectra of poly(HFBD) (A) and poly(HFBY) (B) produced with *tert*-C_4H_9OCs in THF at 60 °C for 3 h.

for the adjacent carbon per fluorine atom from the value of a neutral carbon atom. On the other hand, Chambers et al. reported that XPS analysis of poly(HFBY) established its structure as a polyene sequence rather than a cross-linked system.[10] The 1,4-addition sequence (CF_2-CF=CFCF_2) and polyene sequence ((CF_3)C=C(CF_3)) are, therefore, expected to be clearly distinguished by the XPS analyses.

Figure 4 shows C 1s spectra of poly(HFBD) and poly(HFBY) yielded by *tert*-C_4H_9OCs initiation in THF. On the basis of the results of peak separation of these two spectra, both poly(HFBD) and poly(HFBY) exhibit two main peaks measured at 293 and 287 eV assignable to the CF_3 carbon and the >C= carbon of the polyene sequence, respectively. The results correspond with those of Chambers et al.[10] Four other peaks at 292, 288, 284, and 283 eV are observed. In order to clarify the assignment of these peaks, the binding energies of the each carbon species in the polyene sequence and in the 1,4-addition sequence were calculated using the parameters introduced by Takahagi and Ishitani.[9] The results of the observed and calculated values of the carbon species and the peak intensities are summarized in Table I. The two main peaks at 293 and 287 eV are assigned to CF_3 carbon and the >C= carbon, respectively. The peaks at 292 and 288 eV are assignable to CF_2 and CF=, respectively. The peak measured at 284 eV is assigned to hydrocarbons which might be contaminants. A satellite peak of the X-ray source is observed at 283 eV.

Table I also shows the elemental composition of these polymers. The results indicate that the ratios of fluorine to carbon in poly(HFBY) and poly(HFBD) are about 1.5, which appreciably agrees with the values calculated from the molecular formula of each polymer. The peak intensities of CF_3 and >C= in poly(HFBD) and poly(HFBY) are almost identical. Thus, the structure of poly(HFBD) is consistent with the polyene structure. Both polymers possess few percents of the 1,4-addition sequence since the peaks assignable to CF_2 and CF= are also detected.

The results of XPS spectra strongly confirm that poly(HFBD) and poly(HFBY) are primarily identical and contain a polyene sequence.

Raman Spectra of Poly(HFBD) and Poly(HFBY). Infrared spectra of poly(HFBD) and poly(HFBY) were discussed in a former section. The vibrations of CF_3 cannot be detected by infrared. For analysis of fluorocarbon polymers, Raman spectra should be much informative. In the case of poly(tetrafluoroethylene), complete analyses of vibration have been performed.[11] The vibrations of CF_2 bending or rocking are observed below 400 cm^{-1}, which is difficult to measure by infrared. The vibrations of the lower frequency region are also important for detection of the CF_3 group. In order to confirm the existence of the CF_3 group, Raman characterization was performed on both polymers. Figure 5 shows the Raman spectra of poly(HFBD) and poly(HFBY) produced with *tert*-C_4H_9OCs in THF. In both spectra, the vibrations of C=C in the main chain and the CF_3 group are detectable. The vibrations at 1675 and 1145 cm^{-1} are assigned to C=C and C–C stretching, respectively. The peak at 770 cm^{-1} is assignable to the symmetric bending mode of the CF_3 group. Rocking and rotational vibrations of the CF_3 group are detected at 335 and 295 cm^{-1}, respectively. In order to confirm this assignment, Raman spectra of the model compounds were also recorded. Figure 6 shows the Raman spectra of perfluoroheptene-1 and octafluorotoluene. The vibrations attributable to the CF_2, CF_3, and pendant vinyl groups can be observed in the Raman spectra of perfluoroheptene-1. The peaks at 775 and 315 cm^{-1} are assignable to symmetric bending and rotational vibrations of CF_3, respectively. The rocking mode of CF_3 is observed at 295 cm^{-1} as a shoulder. The vibrations of 725 and 380 cm^{-1} are expected to be assignable to the CF_2 bending and twisting modes, respectively. The presence of a pendant vinyl group is asserted by the peak at 1780 cm^{-1}, which is consistent with the infrared results reported by Toy et al.[7] In the spectrum of octafluorotoluene, the peak at 715 cm^{-1}

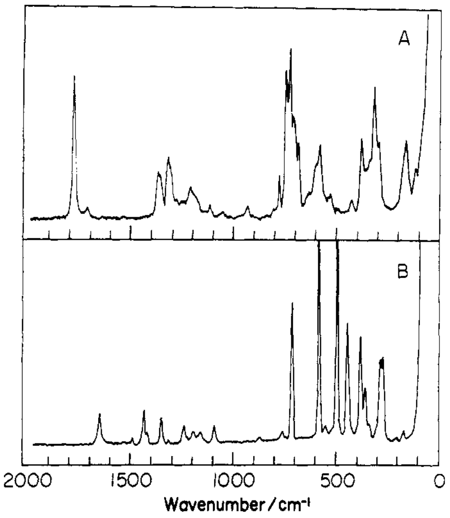

Figure 6. Raman spectra of perfluoroheptene-1 (A) and octafluorotoluene (B).

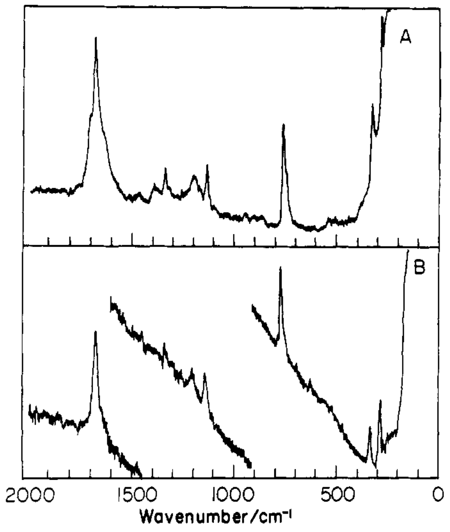

Figure 7. Raman spectra of poly(HFBD) yielded by *tert*-C_4H_9-OCs in THF (A) and in toluene (B).

is observed instead of 770 cm^{-1}. The symmetric bending mode of this compound might be Raman inactive. The Raman spectra of other compounds possessing a CF_3 group such as $N(SCF_3)_3$[12] and CF_3IF_2[13] showed the CF_3 symmetric bending mode at 760 cm^{-1}. As a tentative conclusion, the vibration at about 770 cm^{-1} was assigned to the symmetrical CF_3 bending mode.

Figure 7 shows the Raman spectra of poly(HFBD) yielded by *tert*-C_4H_9OCs in THF and in toluene. The structures of these two samples are basically identical since the identical vibrations are observed. Poly(HFBD) produced in toluene showed strong fluorescence during Raman measurement. It is attributable to the difference of the conjugation state of a polyene sequence. The peak at 1700 cm^{-1} is detected as a shoulder of the peak at 1675 cm^{-1}, which is assigned to the C=C stretching mode of a polyene sequence. The peak at 1700 cm^{-1} in the spectrum of poly(HFBD) produced in THF is stronger than that of poly(HFBD) yielded in toluene. Other peaks in Figure 7A are also accompanied by the shoulders at 1490, 1320, and 750 cm^{-1}. These shoulder peaks might be attributed to a 1,4-addition sequence which is contained in few percents in the polymer chain. Few percents of the CF_2 and CF= carbons of a 1,4-addition sequence are also detected by XPS spectra, as mentioned above. The solvent used as a polymerization media seems to affect the polymer structures such as the conjugation state of a polyene sequence and the content of a 1,4-addition structure.

Conclusion

In order to clarify the structure of poly(HFBD) produced upon using the initiators with cesium derivatives, the spectrophotometric analyses applicable to solid polymers are carried out. According to the results obtained from ^{13}C NMR, XPS, and Raman spectra, the presence of the CF_3 and C=C groups is evidenced. Poly(HFBD) is, therefore, concluded to possess a polyene structure which is the same as that of poly(HFBY). XPS and Raman spectra suggest that the structure of poly(HFBD) produced in THF as a polymerization solvent contains a 1,4-addition sequence, the content of which represents few percents. The postulated polymerization mechanisms are (1) isomerization of HFBD to HFBY followed by polymerization and (2) an addition reaction of a propagating anion to the 2-carbon of HFBD followed by isomerization of the propagating end group to yield the poly(HFBY) structure. An anionic polymerization mechanism of HFBD including isomerization of HFBD to HFBY is under way and will be reported elsewhere in the near future.

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