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Copolymerization of 3,3,3-Trifluoro-1,2-epoxypropane with 1,2-Epoxypropane Using Organozinc Compounds

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ABSTRACT: The copolymerization of 3,3,3-trifluoro-1,2-epoxypropane (TFEP) with 1,2-epoxypropane (EP) using organozinc compounds, $[Zn(OMe)_2(EtZnOMe)_6]$, $[Zn(OMe)_2]_n$, and Et_2Zn-H_2O (1:0.8), was studied. The molar ratio of TFEP and EP in the resulting copolymer was estimated by ^{1}H-NMR analysis and elemental analysis. The copolymerization that started with equimolar amounts of TFEP and EP produced an EP-rich copolymer in moderate yield when $[Zn(OMe)_2(EtZnOMe)_6]$ or $[Zn(OMe)_2]_n$ was used as the initiator. On the other hand, copolymerization initiated using Et_2Zn-H_2O (1:0.8) produced TFEP–EP copolymers with various molar ratios in high yield. ^{1}H-NMR and DSC analyses indicated that the copolymerization proceeded in a block manner. When the molar ratio of TFEP in the copolymer obtained using $[Zn(OMe)_2(EtZnOMe)_6]$ approached approximately 90%, the T_m, T_g, and contact angle to water of the copolymer were close to those of the TFEP homopolymer.

Introduction

The polymerization of fluorine-containing epoxides has been paid much attention because resulting polymers are expected to possess interesting mechanical, thermal, optical, surface physical, and chemical properties that are different from non-fluorinated ones.[1] However, most of fluorine-containing monomers have been proved to have different reactivities toward polymerization compared to non-fluorinated ones.[1] For instance, tetrafluoroethylene cannot be polymerized with a Ziegler–Natta catalyst which can easily produce a high density polyethylene.

For the ring-opening polymerization of epoxides, several polymerization and copolymerization methods have been developed for the usual non-fluorinated epoxides,[2] and many types of polyethers have been prepared as needed. For the fluorine-containing epoxides, however, it was difficult to obtain high molecular weight polymers.[3–5] Hexafluoropropylene oxide or tetrafluoroethylene oxide gave only a greasy or oily low molecular weight polymer.[6–8] The polymerization of 3,3,3-trifluoro-1,2-epoxypropane (TFEP) using $FeCl_3$, which is fairly active as a cationic catalyst for ring-opening polymerization, afforded only a wax-like polymer with a rather medium to low molecular weight.[9,10]

Recently, we found that the ring-opening polymerization of TFEP with organozinc compounds, such as $[EtZnOMe]_4$, $[Zn(OMe)_2(EtZnOMe)_6]$, $[Zn(OMe)_2]_n$, and Et_2Zn-H_2O, which are known as catalysts for anionic coordination polymerization,[2,11,12] gave the corresponding polymer with high molecular weight: M_w by GPC was beyond 10^4.[13,14] This was the first example of a high molecular weight fluorine-containing polyether.

Copolymerization is a highly useful way to improve the properties of polymeric materials. For fluorine-containing polymers such as poly(tetrafluoroethylene), copolymerization using a radical intermediate was utilized for improving its thermoprocessability and/or its surface nature. During the ring-opening polymerization of epoxides in which radical polymerization rarely occurs, modification of the polymeric material was attempted by ionic copolymerization. TFEP has been reported to be copolymerized with 1,2-epoxypropane (EP) using $FeCl_3$.[15] However, the copolymerization gave a copolymer only in low yield, and the copolymer involved EP in a higher molar ratio than TFEP regardless of the molar ratio of the starting monomers. If copolymerization of TFEP is achieved in high yield, novel polymeric materials with a high functionality can be obtained.

This paper describes the copolymerization of TFEP with EP using organozinc compounds as anionic coordination catalysts. The properties of the resulting copolymers are also surveyed.

Experimental Section

Materials. (*S*)-3,3,3-Trifluoro-1,2-epoxypropane (TFEP: 75% ee) was prepared from 3,3,3-trifluoropropene by fermentation with *Nocardia corallina*[16] and purified by distillation after refluxing over calcium hydride. 1,2-Epoxypropane (EP: racemic) was distilled after refluxing over calcium hydride. Commercial toluene was successively treated with concentrated sulfuric acid, water, diluted NaOH, and water and then dried over $CaCl_2$. Toluene was refluxed over Na and distilled. Commercial dibutyl ether (DBE) was successively washed with aqueous Na_2SO_3, diluted NaOH, and water and then dried over calcium hydride. DBE was distilled after refluxing over Na. Commercial methanol was dried over Linde type 4A molecular sieves and warmed with clean dry magnesium turnings and iodine. After refluxing, methanol was distilled off. Diethylzinc in hexane (Kanto Chemical Co., Inc) was used without further purification.

Preparation of Initiator. All organozinc compounds were prepared from diethylzinc and methanol or water. $[Zn(OMe)_2(EtZnOMe)_6]$ was prepared using the previously reported methods[17,18] and used as a toluene solution. $[Zn(OMe)_2]_n$[11] and Et_2Zn-H_2O (1:0.8)[14,19] were prepared in a Pyrex tube under nitrogen just before use and used as a solid after removing the solvent in vacuo.

Copolymerization and Isolation of Copolymer. A typical procedure was as follows: Solvent (6.3 mL), 0.70 mL

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Table 1. Copolymerization of TFEP with EP in Various Mole Ratios Initiated by Organozinc Compounds[a]

entry	initiator	solv	starting molar ratio TFEP:EP	temp (°C)	time (h)	yield[b] (%)	molar ratio (TFEP:EP) in copolymer	
							^{1}H-NMR[c]	elemental anal.[d]
1	$[Zn(OMe)_2(EtZnOMe)_6]$	toluene	50:50	80	48	33	22:78	24:76
2	$[Zn(OMe)_2(EtZnOMe)_6]$	toluene	50:50	80	24	16	11:89	18:82
3	$[Zn(OMe)_2(EtZnOMe)_6]$	DBE[e]	50:50	80	48	63	37:63	42:58
4	$[Zn(OMe)_2(EtZnOMe)_6]$	DBE	50:50	80	24	34	20:80	46:54 ~36:64
5	Et_2Zn-H_2O (1:0.8)	no solv	50:50	rt[f]	478	98	50:50	74:26 ~68:32
6	Et_2Zn-H_2O (1:0.8)	no solv	50:50	rt	16	25	0:100	24:76
7	$[Zn(OMe)_2]_n$	toluene	50:50	80	24	12	15:85	18:82
8	$[Zn(OMe)_2(EtZnOMe)_6]$	DBE	60:40	80	48	48	39:61	41:59
9	$[Zn(OMe)_2(EtZnOMe)_6]$	DBE	70:30	80	48	41	49:51	50:50
10	$[Zn(OMe)_2(EtZnOMe)_6]$	DBE	80:20	80	48	53	86:14	92:8
11	Et_2Zn-H_2O (1:0.8)	no solv	60:40	rt	24	99	60:40	63:37
12	Et_2Zn-H_2O (1:0.8)	no solv	80:20	rt	24	100	77:23	83:27

[a] Copolymerization conditions: [initiator]/[epoxides] = 2/100; [epoxides] = 2.6 mmol/mL. [b] Yield = weight of the isolated copolymer/total weight of comonomers. [c] The molar ratios in the copolymers were estimated from the integration ratios of [(methylene + methine) for TFEP and EP]/[methyl for EP] in the ^{1}H-NMR spectra. [d] The molar ratios in the copolymers were calculated from carbon and hydrogen content by elemental analysis. [e] Dibuthyl ether. [f] Room temperature.

(8.17 mmol) of TFEP, 0.55 mL (8.15 mmol) of EP, and an organozinc compound (containing 0.33 mmol of an initiator species) were placed in a Pyrex tube under a nitrogen atmosphere and sealed. The copolymerization was carried out at a constant temperature with stirring for a specified time. The reaction mixture was poured into a mixture of methanol and water (1:1) containing a small quantity of concentrated hydrochloric acid. The polymer which precipitated was collected by filtration, washed with a mixture of methanol and water (1:3), and then dried in vacuo at 60 °C. When the polymer did not precipitate, the reaction mixture was dissolved in toluene, washed successively with diluted hydrochloric acid and water. After removal of the solvent, the resulting polymer was dried in vacuo at 60 °C.

Measurement. Gel-permeation chromatography (GPC) was carried out at 55 °C with a Shodex KF-80M-KF-80M series using THF as the eluent (flow rate: 0.5 mL/min). Molecular weight was calibrated using polystyrene standard samples.

^{1}H-NMR spectra were recorded on a JEOL JNM-GSX 270 FT-NMR spectrometer at 50 °C using deuterated acetone as a solvent. The molar ratio of TFEP to EP was estimated on the basis of the area ratio of methylene + methine and methyl signals in the ^{1}H-NMR spectra.

Elemental analyses of carbon and hydrogen were measured on a Perkin-Elmer 240C instrument.

Differential scanning calorimetric (DSC) measurements were performed under nitrogen using a Seiko Denshi DSC-200 at a heating rate of 10 °C/min after preheating from −80 to +220 °C at a rate of 10 °C/min, followed by cooling to −115 °C at a rate of −10 °C/min, and then kept at that temperature for 1 min. The sample weight for the DSC measurements was about 5 mg.

The contact angles to water were measured using a Kyowa Kaimen Kagaku CA-D instrument. The values were estimated from the angles of 2 mm diameter water drops on the surfaces of the copolymer films, which were prepared by casting 2% THF solutions on glass.

Results and Discussion

Copolymerization and Reactivity of TFEP with EP. As previously reported, TFEP showed high reactivity during the polymerization initiated with $[Zn(OMe)_2(EtZnOMe)_6]$,[13] $[Zn(OMe)_2]_n$,[13] or Et_2Zn-H_2O.[14] When $[Zn(OMe)_2(EtZnOMe)_6]$ was used as the initiator during the polymerization of TFEP, the yield of the resulting polymer was higher in dibutyl ether than in toluene. EP was also highly reactive during the polymerization initiated with $[Zn(OMe)_2(EtZnOMe)_6]$[20] or Et_2Zn-H_2O,[21] while it showed rather low reactivity when $[Zn(OMe)_2]_n$ was used as an initiator.[11,21]

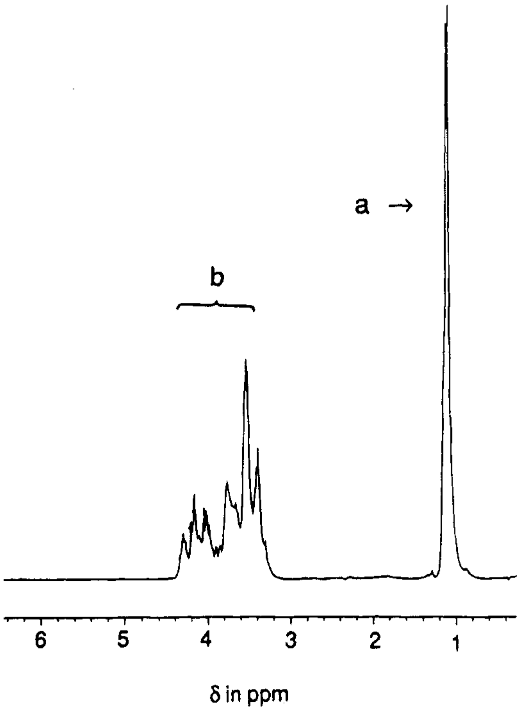

Figure 1. ^{1}H-NMR spectrum of the copolymer of TFEP with EP $[-(TFEP)_m-(EP)_n-]$. The molar ratio of TFEP to EP was calculated from the area ratio of (methylene + methine)/methyl; $m/n = (b - a)/a$.

Referring to these results, the copolymerization of TFEP with EP was carried out using several kinds of organozinc compounds as initiators. The results are shown in Table 1. The molar ratio of TFEP to EP in the resulting copolymer was estimated by ^{1}H-NMR and elemental analysis. The ^{1}H-NMR spectrum showed methylene and methine signals for TFEP and EP units at 4.4−3.2 ppm and a methyl signal for the EP unit at 1.2−0.9 ppm (Figure 1). The carbon and hydrogen contents in the copolymer were determined by elemental analysis. The molar ratios of TFEP to EP in the resulting copolymers calculated from the carbon content were in fair agreement with those using the hydrogen content, except for entries 4 and 5. Furthermore, the molar ratios in the copolymer estimated from the integration ratios of [(methylene + methine)/methyl] in the ^{1}H-NMR spectra showed a lower TFEP content than those estimated from the carbon and hydrogen contents.

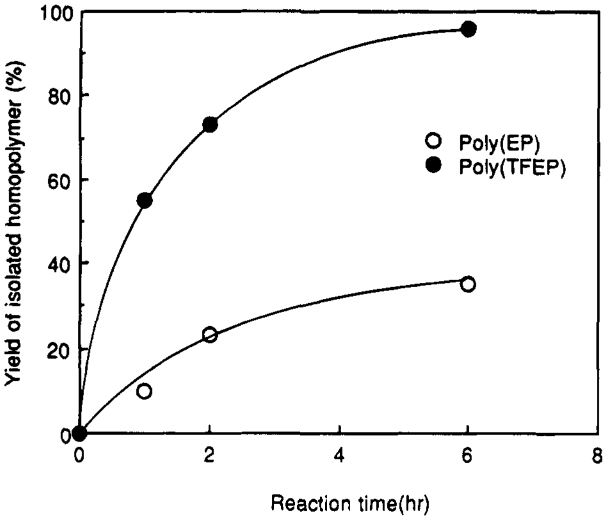

Figure 2. Yield of isolated homopolymer obtained using Et_2Zn-H_2O (1:0.8) as an initiator. [initiator/[epoxide] = 2/100, bulk polymerization.

Because the ^1H-NMR was measured in a deuterated acetone solution of the polymer, the TFEP-rich part, which is hardly soluble in acetone, may not be observed. As can be seen from the results of the reactions carried out using TFEP and EP in a molar ratio of 50:50 (entries 1−7), TFEP and EP were found to copolymerize with all of the organozinc initiators examined in the present study. The molar ratio in the resulting copolymer varied depending on the initiator, reaction time, and solvent. $[Zn(OMe)_2(EtZnOMe)_6]$ gave white or yellow wax-like copolymers after a 24 and 48 h reaction with approximately the same molar ratio. A higher EP-containing copolymer was obtained during the copolymerization in toluene as compared to that in DBE. Copolymerization reactivity using $[Zn(OMe)_2]_n$ in toluene was equivalent to that with $[Zn(OMe)_2(EtZnOMe)_6]$. Et_2Zn-H_2O (1:0.8) gave an EP-rich copolymer after only a 16 h reaction, similar to the copolymerization using $[Zn(OMe)_2(EtZnOMe)_6]$ and $[Zn(OMe)_2]_n$. However, for the 48 h reaction, the molar ratio of the copolymer was changed to a higher TFEP content, and white rubber with a surface similar to that of the TFEP homopolymer was obtained in high yield. This indicated that during the copolymerization initiated by Et_2Zn-H_2O (1:0.8), EP was more easily incorporated into the polymer chain than TFEP at the early stage, and TFEP was more easily incorporated at the late stage. When $[Zn(OMe)_2(EtZnOMe)_6]$ was used as an initiator, the liability of the monomer incorporation into the polymer chain was approximately constant during the 48 h reaction. Copolymerization of TFEP with EP for various starting molar ratios was also performed (entries 8−12). Et_2Zn-H_2O (1:0.8) produced a rubber-like copolymer having the same molar ratio as that started in high yield in the 24 h reaction. However, $[Zn(OMe)_2(EtZnOMe)_6]$ produced a copolymer in moderate yield with a molar ratio different from that at the start even in the 48 h reaction. Although the copolymer obtained using $[Zn(OMe)_2(EtZnOMe)_6]$ was wax when the EP content is higher than that of TFEP, an extremely high content of TFEP changed the polymer form to rubber.

The rate of the homopolymerization of TFEP initiated with Et_2Zn-H_2O (1:0.8) was larger than that of EP, as shown in Figure 2. The yield of poly(TFEP) reached 98% after 6 h, while that of poly(EP) was only 35% under the same conditions. In contrast, as can be seen from the result that the EP-rich copolymer was obtained during the early stage of the copolymerization initiated by organozinc compounds, EP was more reactive than TFEP during the copolymerization, independent of the rate of homopolymerization and the molar ratio of the starting comonomers (entries 8 and 9). The polymerization of TFEP or EP initiated with an organozinc compound is considered to be an anionic coordination type reaction as described in previous reports.[14,22−25] Because an organozinc compound prefers to coordinate to the electron-rich oxygen in EP, the copolymer involves EP more than TFEP during the early stage of copolymerization. Polymerization of TFEP proceeds during the late stage in which the EP concentration becomes very low, because TFEP has a very high polymerization reactivity using organozinc compounds.

In this system using an organozinc initiator, the polymerization of epoxides is considered to have living polymerization character; a block copolymer would be obtained by successively adding monomers. Actually, a complete TFEP−EP block copolymer was obtained by adding one monomer to the other homopolymer produced by the Et_2Zn-H_2O (1:0.8)-initiated polymerization. The ^1H-NMR spectrum and DSC curves for the complete TFEP−EP block copolymer, TFEP homopolymer, EP homopolymer, and TFEP−EP copolymer were compared in order to estimate the structure of the copolymers.

In the ^1H-NMR spectra of the copolymers obtained by the $[Zn(OMe)_2(EtZnOMe)_6]$- and Et_2Zn-H_2O (1:0.8)-initiated copolymerizations, the methylene and methine signals assignable to each homopolymer were observed at 4.4−3.9 ppm for poly(TFEP) and at 3.6−3.2 ppm for poly(EP). This indicates that these copolymers have a poly(TFEP) unit and a poly(EP) unit. Moreover, other methylene and methine signals at 3.9−3.6 ppm, attributed to the TFEP−EP sequence were also observed (Figure 3c), while those signals for the block copolymer were very small (Figure 3d). Therefore, the copolymer is not a blended polymer but undoubtedly a copolymer having repeating poly(TFEP) and poly(EP) units. The copolymers obtained using organozinc compounds are probably block-like.

In the DSC curve, the block copolymer showed two clear melting temperatures (T_m) of 59 and 123 °C and two glass transition temperatures (T_g) of −70 and −32 °C, which correspond to those of the homopolymers (Figure 4). The copolymer obtained using Et_2Zn-H_2O (1:0.8) also showed two melting temperatures in its DSC curve similar to the block copolymer. Such a DSC curve cannot be obtained if TFEP and EP are randomly copolymerized. These observations strongly support the fact that the copolymer obtained using Et_2Zn-H_2O (1:0.8) is a block-like copolymer. In the DSC curve of the copolymer obtained using $[Zn(OMe)_2(EtZnOMe)_6]$, the apparent T_m and T_g corresponding to those of the homopolymers were not observed. This result suggests that $[Zn(OMe)_2(EtZnOMe)_6]$ gave the copolymer having a shorter homopolymer unit compared to that obtained using Et_2Zn-H_2O (1:0.8).

In contrast to the copolymerization initiated with an organozinc compound, the anionic copolymerization of TFEP and EP initiated with potassium hydroxide gave only the TFEP homopolymer regardless of the molar ratio of the starting monomers. Because the coordination step is not important in KOH-initiated polymerization, the attack of an anion preferably occurs at the electron-deficient epoxy carbon in TFEP. Even when the TFEP concentration becomes very low, EP cannot

Table 2. Properties of Copolymers and Homopolymers Obtained with [$Zn(OMe)_2(EtZnOMe)_6$][a]

			mole ratio (TFEP:EP) in copolymer				
entry	starting molar ratio TFEP:EP	yield[b] (%)	^{1}H-NMR[c]	elemental[d] analysis	θ_w[e] (deg)	T_m[f] (°C)	T_g[g] (°C)
13	0:100	93	0:100	0:100	55	57	−69
3	50:50	63	37:63	42:58	64	(119)	−67
8	60:40	48	39:61	41:59	69	(121)	−67
9	70:30	41	49:51	50:50	69	(111)	−46
10	80:20	53	86:14	92:8	116	116	−32
14	100:0	80	100:0	100:0	111	120	−28

[a] Polymerization conditions: [initiator]/[epoxides] = 2/100; [epoxides] = 2.6 mmol/mL; solvent, dibutyl ether. [b] Yield = weight of the isolated copolymer/total weight of comonomers. [c] The molar ratios in the copolymers were estimated from the integration ratios of [(methylene + methine) for TFEP and EP]/[methyl for EP] in the ^{1}H-NMR spectra. [d] The molar ratios in the copolymers were calculated from carbon and hydrogen content by elemental analysis. [e] Contact angle to water of the polymer film coated on a glass. [f] Melting temperature observed by DSC as an endothermic peak upon heating at a rate of 10 °C/min after preheating and cooling. [g] Glass transition temperature observed by DSC as an endothermic peak upon cooling at a rate of 10 °C/min after the first heating.

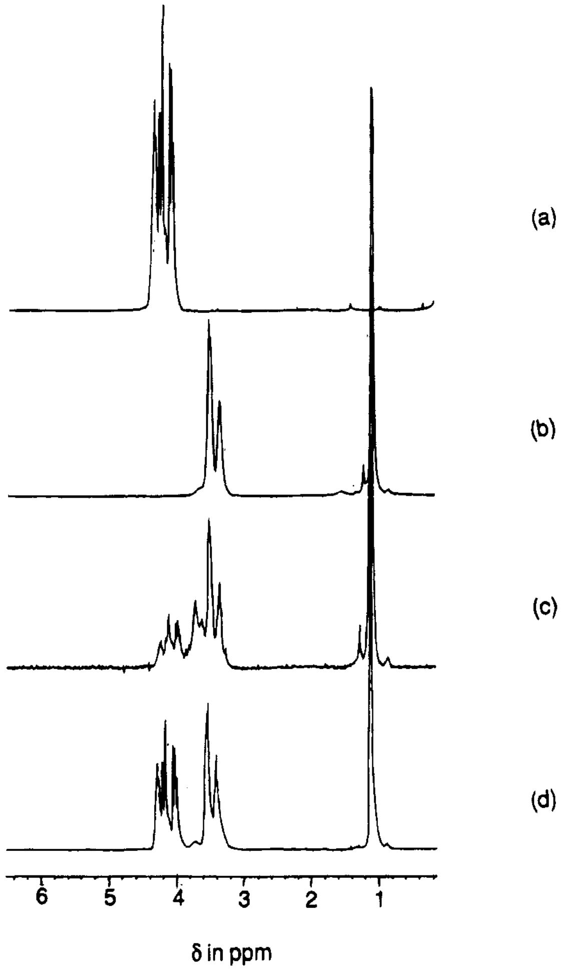

Figure 3. ^{1}H-NMR spectra of the copolymer of TFEP with EP and of homopolymers of TFEP and EP: (a) poly(TFEP) obtained by homopolymerization initiated with [$Zn(OMe)_2(EtZnOMe)_6$] (entry 14); (b) poly(EP) obtained by homopolymerization initiated with [$Zn(OMe)_2(EtZnOMe)_6$] (entry 13); (c) copolymer (TFEP:EP = 37:63 by ^{1}H-NMR) obtained by copolymerization initiated with [$Zn(OMe)_2(EtZnOMe)_6$] (entry 3); (d) complete block copolymer (TFEP:EP = 52:48 by ^{1}H-NMR) initiated with Et_2Zn-H_2O (1:0.8).

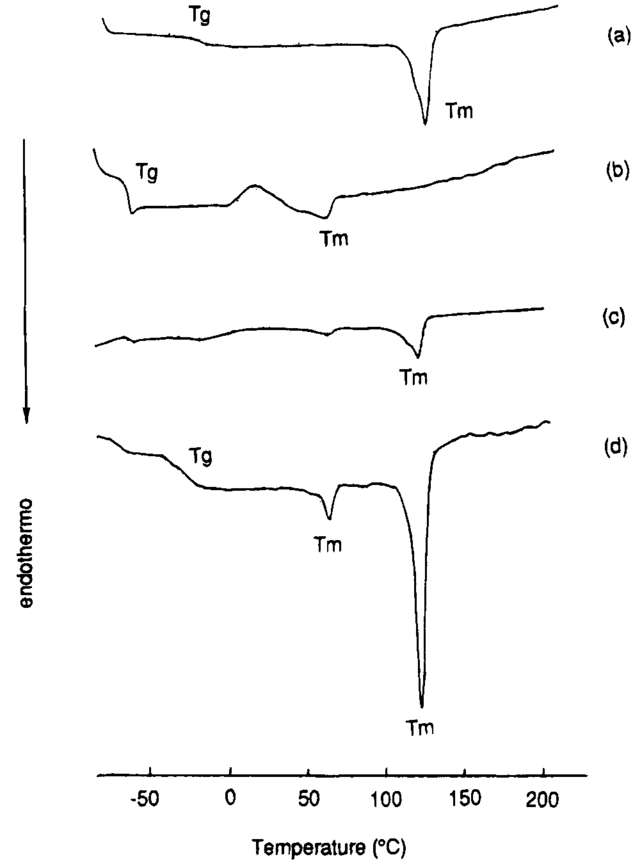

Figure 4. DSC thermograms of copolymers and homopolymers given during the second heating at a rate of 10 °C/min. Conditions: the first heating, −80 to +220 °C (10 °C/min); cooling, 220 to −115 °C (10 °C/min); the second heating, −115 to +220 °C (10 °C/min); sample weight, 5 mg; gas, N_2 (300 mL/min). (a) Poly(TFEP) obtained by homopolymerization initiated with [$Zn(OMe)_2(EtZnOMe)_6$] (entry 14). (b) Poly(EP) obtained by homopolymerization initiated with [$Zn(OMe)_2(EtZnOMe)_6$] (entry 13). (c) Copolymer (TFEP:EP = 50:50 by ^{1}H-NMR) obtained by copolymerization initiated with Et_2Zn-H_2O (entry 5). (d) Complete block copolymer (TFEP:EP = 52:48 by ^{1}H-NMR) initiated with Et_2Zn-H_2O (1:0.8).

be incorporated into the polymer chain, because EP has a low anionic polymerization reactivity accompanying the chain transfer reaction.

Properties of Copolymers. The solubility of the copolymers are somewhat affected by the initiator used. The copolymers obtained using Et_2Zn-H_2O (1:0.8) swelled a little in THF and DME, and those obtained using [$Zn(OMe)_2(EtZnOMe)_6$] were soluble in THF, acetone, ethyl acetate, DME, and DMF. The effect of the molar ratio of TFEP to EP on the solubility was observed for the copolymers produced with [$Zn(OMe)_2(EtZnOMe)_6$]; the copolymers involving a large amount of EP swelled even in acetonitrile and diethyl ether, although the TFEP-rich copolymers were insoluble in these solvents.

GPC chromatograms of the polymers in THF were recorded using a refractive index detector. When the molar ratio of TFEP to EP is close to 1:1, the refractive index of a THF solution of copolymer becomes similar to that of THF itself. The molecular weight of the copolymer obtained using [$Zn(OMe)_2(EtZnOMe)_6$] involving TFEP or EP in an extremely high molar ratio could be determined on the basis of the retention time of a peak in GPC. It GPC chromatogram showed a molecular weight of 10^4-10^7 with a very broad molecular weight distribution ($M_w/M_n = 5-30$).

Wettability of the copolymers toward water was estimated on the basis of the contact angle to water (θ_w) for the copolymer films coated on a glass, as shown in Table 2. The θ_w of poly(EP) showed a low value of 55°, while that of poly(TFEP) showed a high value of 111° similar to that of poly(tetrafluoroethylene). The copolymers, in which the molar ratio of EP was more than 50%, showed a low θ_w (<70°) close to that of poly(EP). In contrast, when the molar ratio of TFEP to EP in the copolymer was approximately 9:1 (entry 10), θ_w was 116°. This means that the water repellent effect due to fluorine appears only when the molar ratio of TFEP is extremely high; a large content of TFEP is necessary in order to orientate the CF_3 groups, which have a water repellent nature, on the surface of the copolymer film coated on a glass. The T_m and T_g of the copolymer involving TFEP and EP with a 9:1 molar ratio (entry 10) also approached those of the TFEP homopolymer.

Conclusions

The copolymers of TFEP with EP were prepared using organozinc compounds such as $[Zn(OMe)_2(EtZnOMe)_6]$, $[Zn(OMe)_2]_n$, and Et_2Zn-H_2O (1:0.8), which are known as anionic coordination catalyts. Especially, $[Zn(OMe)_2(EtZnOMe)_6]$ and Et_2Zn-H_2O (1:0.8) produced, for the first time, rubber-like TFEP/EP copolymers in moderate to high yields.

The copolymer obtained during the early stage involved EP more than TFEP. However, upon prolonging the reaction time, the Et_2Zn-H_2O (1:0.8) initiator incorporated TFEP into the polymer chain to give a block-like copolymer having the same molar ratio of TFEP to EP as initially started. The ^1H-NMR spectrum and DSC curves of the copolymers suggested that the copolymerization initiated by organozinc compounds proceeded in a block manner, because some signals and thermal peaks assignable to homopolymers were detected.

The difference in reactivity between TFEP and EP during the copolymerization was explained in terms of the effect of the epoxide substituents.

The effect of the CF_3 group on the properties of the copolymer—T_g, T_m, wettability toward water, and refractive index—appeared, but depended on the substantial content of TFEP.

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