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Anionic copolymerization of hexafluoroacetone with epoxides

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Abstract

The anionic copolymerizations of hexafluoroacetone (HFA) with epoxyethane (EO) and epoxypropane (PO) have been undertaken with a view to obtaining fluorine-containing polyethers. Hexane-insoluble solid copolymer was obtained from the copolymerization of HFA with EO initiated with t-C_4H_9OCs or t-C_4H_9OK. The copolymer derived from HFA with PO was an oily oligomer. Alternating copolymerization was confirmed in the HFA–EO copolymerization.

Introduction

Fluorine-containing polymers are generally prepared by radical polymerization and copolymerization of fluorinated vinyl monomers such as tetrafluoroethylene, chlorotrifluoroethylene and fluoroalkyl acrylates. The main chains of these polymers consist chiefly of carbon–carbon bonds. The properties and functionalities of these polymers usually depend on the fluorine contents. Fluorine-containing polyethers, on the other hand, are expected to show different properties from vinyl polymers since the main chains consist of carbon–oxygen–carbon bonds. Fluorine-containing polyethers of low molecular weight are used as high-performance lubricants and vacuum oils.

Fluorinated polyethers are generally synthesized by the ring-opening polymerization of fluorinated epoxides, but it is difficult to obtain polyethers of high molecular weight in this way. Anionic copolymerizations of fluorinated ketones with epoxides take place readily to yield fluorinated polyethers, although homopolymers of fluorinated ketones are generally hard to produce [1]. Systematic studies on the anionic copolymerizations of hexafluoroacetone (HFA) with epoxides are scarce, although many patents have claimed the

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anionic copolymerization of HFA with EO or PO initiated by cesium fluoride [2].

In this paper the anionic copolymerizations of HFA with EO or PO are reported, initiated mainly with alkali metal t-butoxides, some of which were found to be excellent initiators for the anionic polymerization of hexafluoro-1,3-butadiene [3, 4].

Experimental

All polymerization reactions were carried out under a purified nitrogen atmosphere in order to preclude oxygen and atmospheric moisture.

HFA (Central Glass Co.) was purified by passing through molecular sieves and calcium sulfate columns in the vapour phase. Epoxyethane was purified by the same method. Epoxypropane was purified by distillation over calcium hydride under nitrogen. Cesium t-butoxide was synthesized from cesium metal and 2-methyl-2-propanol. Commercial potassium t-butoxide was purified by sublimation under reduced pressure.

$[Zn(OCH_3)_2 \cdot (C_2H_5ZnOCH_3)_6]$ was synthesized according to a literature method [5]. 'Ate' complexes such as $LiAlC_4H_9(C_2H_5)_3$ and $LiZnC_4H_9(C_2H_5)_2$ were synthesized by the reactions of equimolar amounts of butyllithium and triethylaluminium or diethylzinc, respectively. Toluene and tetrahydrofuran (THF) were purified by the usual methods. 1,2-Dimethoxyethane (DME) was refluxed over calcium hydride and then distilled. The distillate was further purified by refluxing with triethylaluminium followed by distillation under nitrogen.

Polymerization was carried out in a sealed glass ampoule which was charged with an initiator (0.4 mmol), HFA (20 mmol), epoxide (20 mmol) and solvent. The total volume was 15 ml. After a fixed time, polymerization was ceased by the addition of hydrochloric acid/methanol. Solid polymer was separated by filtration and the oily product was isolated by removing the solvent by evaporation.

Gel permeation chromatography (GPC) was undertaken with a Tosoh HLC-822A apparatus at 38 °C using a TSK gel G4000HXL–G3000HXL–G2000HXL column series with THF as the eluent. The molecular weights of the copolymers were estimated by calibrated against standardized polystyrene. ^{13}C NMR spectra were registered on a JEOL JNM-GX270 FT-NMR spectrometer at 67.80 MHz using THF-d_8 as the solvent and tetramethylsilane as an internal standard.

Results and discussion

Copolymerization of HFA with epoxypropane

The results of the anionic copolymerization of hexafluoroacetone (HFA) with epoxypropane (PO) are summarized in Table 1. The highest yield of

TABLE 1

Copolymerization of hexafluoroacetone with epoxypropane[a]

Initiator	Solvent	Temp. (°C)	Yield (wt.%)
t-C_4H_9OCs	toluene	0	18.5
		40	17.1
		60	34.7
	THF	0	8.7
		40	23.1
		60	11.0
	DME	−20	51.8
		−20	25.0[b]
		0	97.3
		0	71.9[b]
		40	58.7
		60	2.7
t-C_4H_9OCs/18-crown-6	DME	0	92.1[c]
		0	88.8[c]
CsF	toluene	40	39.9
C_2H_5Cs	DME	0	0
t-C_4H_9OK	toluene	40	18.9
$LiAlC_4H_9(C_2H_5)_3$		40	9.1
$LiZnC_4H_9(C_2H_5)_2$			41.1

[a] $[HFA]_0 = 20$ mmol; HFA/PO/initiator = 50:50:1 in feed; polym. time, 10 d.
[b] HFA/PO/initiator = 100:100:1 in feed.
[c] t-C_4H_9OCs/18-crown-6 = 1:1 in feed.
[d] t-C_4H_9OCs/18-crown-6 = 1:2 in feed.

copolymer, obtained by the initiation of t-C_4H_9OCs in DME at 0 °C, was 97.3%. When the HFA/PO/initiator feed ratio was 100:100:1, the yield was as high as 71.9%. The addition of crown ether seemed to have no effect on the polymerization activity of t-C_4H_9OCs as far as the polymer yields were concerned. The yields increased with increasing polymerization temperature in toluene although the polymerization temperature showed no regular effect on the polymer yields in ethereal solvents.

Polymerization systems initiated with CsF and $LiZnC_4H_9(C_2H_5)_2$ produced the copolymers in fairly good yields.

GPC analyses of the copolymers obtained with t-C_4H_9OCs in DME at 0 °C at feed ratios of 50:50:1 (A) and 100:100:1 (B) are depicted in Fig. 1. The molecular weights of the polymers were 7.8×10^3 and 1.2×10^4, respectively.

The ^{13}C NMR spectrum of the HFA–PO copolymer is shown in Fig. 2. The peaks at *c.*16–18 ppm are attributed to the carbon of CH_3, the peaks at *c.* 67–70 ppm to the carbon of CH_2, the peaks at *c.* 70–72 ppm to the carbon of CH, the multiplet peaks at *c.* 95–99 ppm to the tertiary carbon of the HFA units, and the peaks at *c.* 119–127 ppm to the carbons of CF_3 ($J = 292$ Hz), respectively. The peaks at 29.9 or 30.7 ppm may be assignable

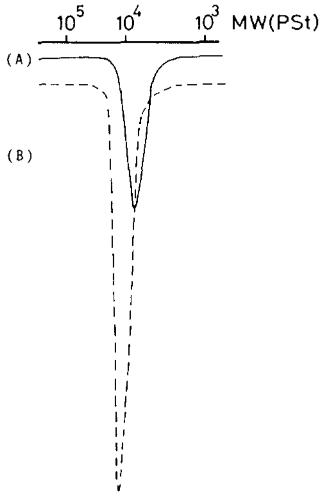

Fig. 1. GPC of HFA–epoxypropane copolymers obtained with t-C_4H_9OCs in DME at 0 °C in feed ratios of (A) 50:50:1 and (B) 100:100:1.

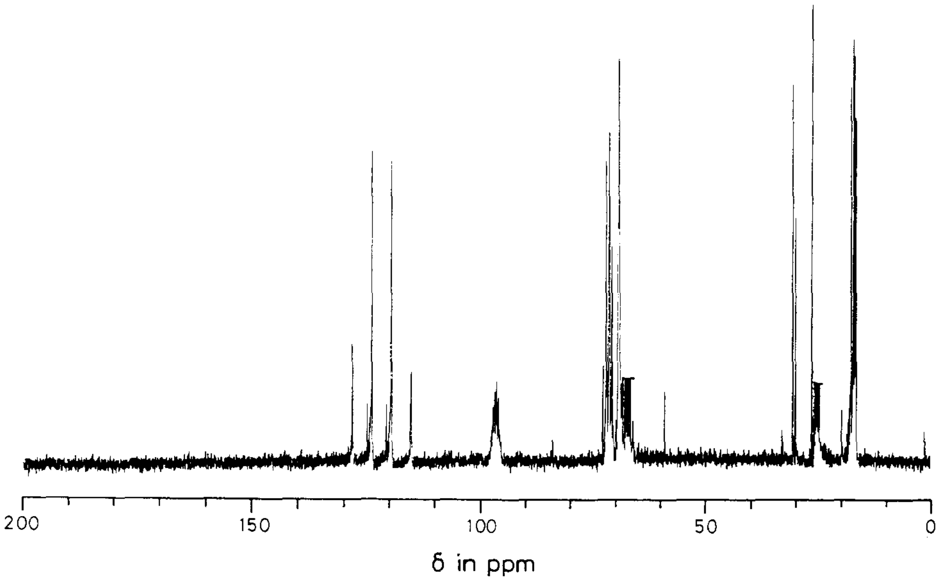

Fig. 2. ^{13}C NMR spectrum of HFA–epoxypropane copolymer obtained with t-C_4H_9OCs in DME at 0 °C in a feed ratio of 50:50:1.

to the carbon of CH_3 in the t-C_4H_9O group introduced by the initiation reaction. The product obtained in this case, therefore, possessed both HFA units and PO units.

As a tentative conclusion, the anionic copolymerization of HFA with PO produced an oily copolymer, probably because the microstructure of the PO units in the main chain was irregular.

Copolymerization of HFA with epoxyethane

In order to improve the properties of the HFA–epoxide copolymer, the anionic copolymerization of HFA with epoxyethane (EO) was investigated.

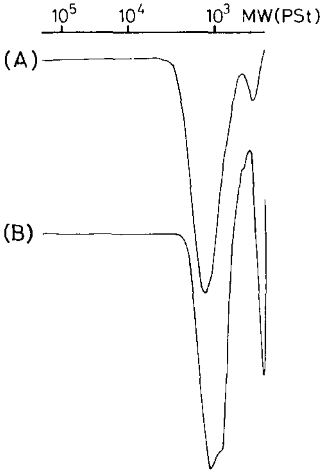

Fig. 3. GPC of HFA–epoxyethane copolymers obtained with (A) t-C_4H_9OK in toluene at 40 °C and (B) [$Zn(OCH_3)_2 \cdot (C_2H_5ZnOCH_3)_6$] in toluene at 60 °C.

TABLE 2

Anionic copolymerization of hexafluoroacetone with epoxyethane[a]

Initiator	Solvent	Temp. (°C)	Yield (wt.%)	
			Hexane insolub.	Hexane solub.
t-C_4H_9OCs	THF	0	7.0	–
		40	0	13.3
		60	6.6	0
		60	3.6	0
		80	1.9	0
	DME	0	0	–
		40	13.9	33.5
		60	0	2.6
	toluene	40	29.3	–
		60	45.3	–
t-C_4H_9OK	THF	40	4.8	35.5
		60	1.4	0
	THF/toluene	40	65.5	0
	THF/toluene	60	6.4	0
[$Zn(OCH_3)_2 \cdot (C_2H_5ZnOCH_3)_6$]	toluene	40	0.4	0
		60	0	55.0

[a] Hexafluoroacetone, 20 mmol; epoxyethane, 20 mmol; initiator, 0.4 mmol; total volume, 15 ml; polym. time, 10 d.

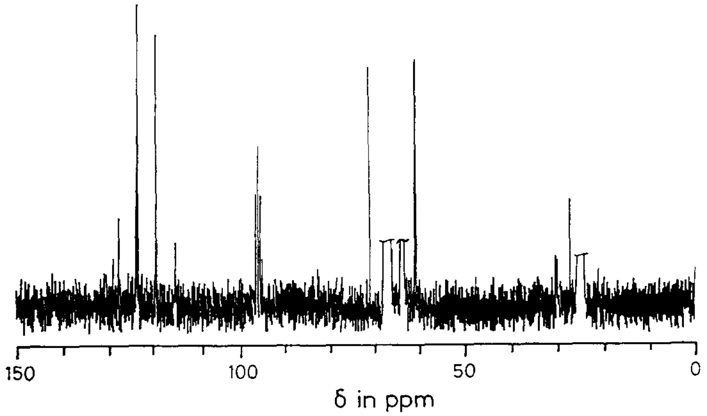

Fig. 4. ^{13}C NMR spectrum of HFA–epoxyethane copolymer obtained with t-C_4H_9OK in toluene at 40 °C.

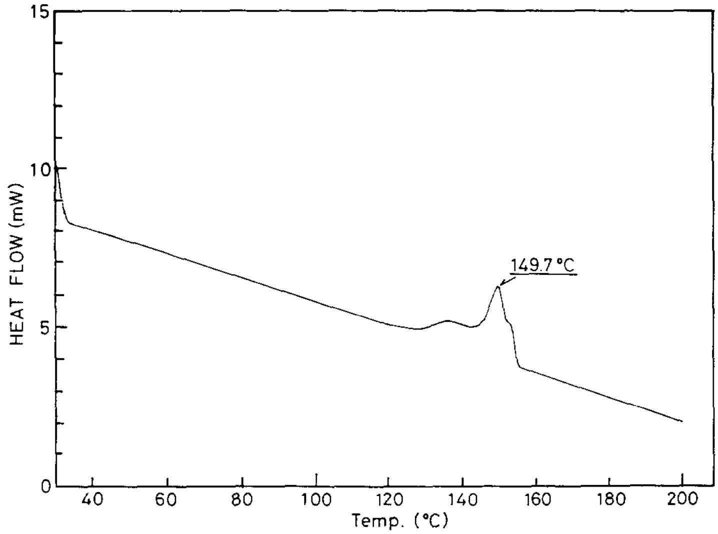

Fig. 5. Differential scanning calorimetric analysis of HFA-epoxyethane copolymer obtained with t-C_4H_9OK in toluene at 40 °C.

The results are summarized in Table 2. Solid copolymers insoluble in hexane were obtained with t-C_4H_9OK and t-C_4H_9OCs. The highest yield of solid copolymer, obtained with t-C_4H_9OK as initiator in toluene at 40 °C, was 65.5%. The molecular weight of the copolymer measured by GPC was 3.4×10^3 as shown in Fig. 3(A). The oily product produced with $[Zn(OCH_3)_2 \cdot (C_2H_5ZnOCH_3)_6]$ in fairly high yield had a molecular weight of 1.0×10^3 [Fig. 3(B)].

The ^{13}C NMR spectrum of copolymer obtained with t-C_4H_9OK in toluene at 40 °C is shown in Fig. 4. The peak at *c.* 71.3 ppm is assigned to the carbon of CH_2, the peaks at *c*. 95–97 ppm to the tertiary carbon of the HFA units ($J = 30$ Hz) and the absorptions at *c*. 114–128 ppm to the carbon of CF_3 ($J = 292$ Hz), respectively. The product obtained, therefore, possessed both HFA units and EO units.

The ratio of HFA units and EO units in the copolymer was 50.5:49.5 (mol%) calculated from the results of the elemental analysis of the carbon content (28.47 wt.%). The copolymer sequence may therefore be that of an alternating copolymer.

Figure 5 shows the differential scanning calorimetric analysis (DSC) of the copolymer. The melting point of the copolymer was 149 °C, which demonstrates its high crystallinity. However, the crystal structure of the copolymer is probably complex since the DSC spectrum shows three peaks.

It was difficult to prepare film from the polymer, probably because the molecular weight was not high enough to allow this. Rigid film was produced when the copolymer was treated with diisocyanate.

A more detailed study of the anionic copolymerization of HFA with epoxides is now under way.

References

1 C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, *1* (1967) 145.

2 F. S. Fawcett and E. G. Howard, *US Pat. 3 311 216* (1967).

3 T. Narita, T. Hagiwara, H. Hamana, M. Sezaki, A. Nagai, S. Nishimura and A. Takahashi, *Macromolecules*, *22* (1989) 3183.

4 T. Narita, T. Hagiwara, H. Hamana, M. Sezaki, N. Kezuka, K. Nakagawa, A. Nagai, S. Nishimura and A. Takahashi, *Makromol. Chem.*, *192* (1991) 351.

5 M. Ishimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, *49* (1976) 1165.