Novel Polymerization of THF Introducing Fluoroformyl Group as a Polymer End Group Utilizing the Reaction between HFPO and THF for the Initiation — The Effect of $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ as a Catalyst

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ABSTRACT: Novel poly(THF) with fluoroformyl group at a polymer end was prepared by the reaction of HFPO and THF. Using $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ as a catalyst fairly higher polymer yields were obtained compared with no catalyst polymerization. The end group of obtained polymer was easily able to be modified to hydroxy or methoxy group.

KEY WORDS Hexafluoropropylene Oxide / THF / $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ /

Hexafluoropropylene oxide (HFPO) is one of important source chemicals for the development of fluorine containing polymeric materials. HFPO has not given high polymer but only oligomer due to its low reactivity with ionic initiators.¹ HFPO oligomers are, however, widely utilized as thermally stable materials such as lubricants in various fields. Study on the reactivity of HFPO, — especially on its nature in the polymerization reaction — is thus a key for the development of new fluorine containing materials.

A few reports on the polymerization of cyclic ethers in the system consisting of HFPO and cyclic ether have been found only for ethylene oxide² and THF.³ In the previous works,^{4,5} we found novel initiation reaction for the ring-opening polymerization of cyclic ethers in which HFPO was involved. Initiation, propagation, and termination reaction of ring-opening polymerization of cyclic ether initiated with the reaction between HFPO and the cyclic ether were investigated in detail using 3, 4, 5 and 6 membered cyclic ethers, such as propylene oxide, oxetane, THF and THP.^{4,5} In that study, it was revealed that propylene oxide which has a substituent at 2-position showed different reactivity to HFPO from THF having no substituent, and that thus the polymerized products from the PO/HFPO system were the different from those from THF/HFPO system.⁴

Although HFPO reacts with THF without a catalyst and the resulting product initiates the polymerization of THF as described above, THF has been frequently used as a solvent polymerization or oligomerization of HFPO.^{6,7} This is because the reaction of HFPO with THF — by-reaction of the polymerization — is negligible compared with the polymerization of THF in the usual polymerization condition. The reaction of HFPO with THF has been, thus, little noted in the studies of

ring-opening polymerization of THF as yet. To study and utilize the reaction of HFPO with cyclic ethers would be, however, quite important and interesting for the synthesis of fluorine containing polymeric materials having polyether structure as a soft segment, especially for modification or functionalization of the polymer ends possessing fluorine atoms, because this reaction could introduce the modifiable polymer end at the initial end of polyether. The polymers with fluorine containing modifiable polymer end can be expected to prepare new materials for contact lens⁸ and for medical or dental use.⁹ In this paper, we describe that ring-opening polymerization of THF initiated by the reaction of HFPO with THF with $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ catalyst that was developed by our group. $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ catalyst involving copper as a 'soft' metal and organoaluminum with acidic nature can be expected to enhance the ring-opening polymerization reaction of THF in the system consisting of THF and HFPO.

EXPERIMENTAL

All experiments related to the polymerization reaction were carried out under nitrogen or argon atmosphere to exclude oxygen and moisture.

Reagents

CuF_2 were used as received. Hexafluoropropylene oxide was dried purified by distillation by calcium sulfate and molecular sieves 4A just before use. $(\text{C}_2\text{H}_5)_3\text{Al}$ was purified by distillation under reduced pressure. Tetrahydrofuran (THF) were dried by refluxing over calcium hydride and potassium and then distilled before use.

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Table I. Polymerization of THF initiated by the reaction of THF with HFPO^a

Run	Cat.	[HFPO]/[THF]	Temp. (°C)	Time (h)	Yield (%) ^b	$\bar{M}_n$ $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1	CuF ₂ /(C ₂ H ₅) ₃ Al	7/93	-30	24	14.7	8.0	1.4
2			20	6	56.1	4.7	1.5
3			20	24	44.5	4.0	1.7
4			50	24	57.8	0.6	1.4
5	None	17/83	20	24	44.0	2.5	1.9
6		43/57	20	24	32.8	1.0	1.4
7		7/93	-30	24	—	—	—
8		14/86	20	24	37.0	1.1	1.3
9			50	24	34.1	0.5	1.4
10			20	24	42.0	1.1	1.4
11			20	24	42.0	0.6	1.4

^aPolymn. time: 24 h., [monomer]/[catalyst] = 20/1, without solvent. ^bYield (%) = (polymer obtained, g)/(total amount of monomer fed, g) $\times$ 100.

Polymerization

Polymerization was carried out under dry nitrogen in a sealed ampoule which was carefully flame dried. In the ampoule, CuF₂/(C₂H₅)₃Al system was prepared first by addition of (C₂H₅)₃Al to CuF₂. The reaction mixture prepared was a homogeneous dark solution. Then THF and HFPO were introduced there and the ampoule was fused and sealed. The reaction mixture was poured into a large amount of water. The resulting precipitate which was contaminated with copper, was extracted with chloroform, and washed three times with diluted HNO₃ and then water, respectively. The extracted solution was concentrated by evaporation and dried *in vacuo*. For the polymerization of catalyst free system, the polymer was isolated by precipitation from a large amount water, extracted with chloroform. The extracted solution was washed with water and then dried over magnesium sulfate anhydride. After filtration, chloroform was removed and dried under reduced pressure.

Measurement

¹H, ¹³C and ¹⁹F NMR spectra were recorded on a JEOL JNM-ECP 500 NMR spectrometer using CDCl₃ as a solvent. ¹³C NMR spectrum was measured under proton irradiated condition. Chemical shifts are given in ppm with plus value for downfield shift (δ -scale) from tetramethylsilane (TMS) for ¹H and ¹³C NMR as well as trichlorofluoromethane for ¹⁹F NMR. Gel permeation chromatography (GPC) was conducted with RI- and UV-detectors with TSK gel GMHXL $\times$ 2–Shodex KF-802 column. The molecular weight calibration was carried out with polystyrene standard samples. The molecular weight estimated from GPC was in fairly good agreement with that from NMR data. Thermogravimetric analysis (TGA) was carried out with TA Instruments TGA 51 thermogravimeter (sample weight *ca.* 10 mg), with Thermal Analyst 2000

(TA Instruments), under argon atmosphere with heating rates of 10 k/min.

RESULTS AND DISCUSSION

Polymerization

Results of the polymerization of THF in the system consisting of HFPO and THF with CuF₂/(C₂H₅)₃Al and without the catalyst are shown in Table I. When initial molar ratio of HFPO/THF is 7/93, polymer was obtained in 37% yield for no catalyst system at 20 °C, 24 h. For the polymerization system with CuF₂/(C₂H₅)₃Al, the yield was much improved to be, 56.1% for 6 h and 44.5% for 24 h under the same polymerization condition. These results suggest that CuF₂/(C₂H₅)₃Al works as a catalyst which promotes the polymerization of THF initiated by the reaction of HFPO with THF in the polymerization system consisting of HFPO and THF.

The temperature effect on the polymer yield is very interesting. For the usual THF polymerization systems, high temperature is not so preferable to obtaining high polymer yield.¹⁰ In the polymerization of [HFPO]/[THF] = 7/93, the polymer yields at 50 °C were slightly lowered compared with those at 20 °C and molecular weights of the obtained polymer were considerably lowered from 1.1×10^3 (at 20 °C) to 0.5×10^3 (at 50 °C) for the polymerization without CuF₂/(C₂H₅)₃Al. For the polymerization involving CuF₂/(C₂H₅)₃Al the decline of the polymer yield is not observed, though molecular weights of the obtained polymer were also significantly decreased from 4.0×10^3 (at 20 °C) to 0.6×10^3 (at 50 °C). Very low temperature is also unfavored for the polymerization. At -30 °C, no polymer was obtained without using the catalyst while 14.7% yield was obtained in the polymerization system with CuF₂/(C₂H₅)₃Al. Significant influence of the initial molar ratio of HFPO/THF

on the polymer yields was not observed for no catalyst system (yield: *ca.* 40% at 20 °C), but observed on the molecular weight of polymer. In the case of $[\text{HFPO}]/[\text{THF}] = 43/57$, the molecular weight of the polymer was about half as much as those in the other cases. On the other hand, for the system with $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$, the influence of the initial molar ratio of HFPO/THF was observed on both yield and molecular weight. When initial molar ratio of HFPO/THF was close to equal, both yield and molecular weight were lowered compared with those obtained from the polymerization in the lower initial molar ratio.

Characterization of Obtained Polymer and Mechanistic Aspect of Polymerization

Figure 1a shows the typical ^{13}C NMR spectrum of the obtained polymer (run 3 in Table I). The signals at 25 and 70 ppm can be assigned to methylene carbons of THF units. The absorptions observed at 100–105 and 115–125 ppm are assignable to fluoromethylene and trifluoromethyl carbons of HFPO units, respectively. The doublet signals observed at 80–90 ppm are derived from monofluoromethyl carbon and the singlet signal at 160 ppm is an absorption of carbonyl carbon. The interesting fact that no signal from di-

fluoromethylene carbon being originally in HFPO is observed should be noted. Figure 1b shows the ^{19}F NMR spectrum of the same sample. The peaks at -78 and -130 ppm are able to be assigned to trifluoromethyl and fluoromethylene groups of HFPO units, respectively. The signal at -218 ppm can be assigned to monofluoromethyl group. As well as in the ^{13}C NMR spectrum, the signals from difluoromethylene group are not found. These NMR results indicate that difluoromethylene group in HFPO unit disappears in the process of polymerization. This implies that this polymerization reaction does not proceed through usual ring opening mechanism. The disappearance of difluoromethylene group in HFPO unit can be explained by the specific initiation mechanism of this polymerization as shown in Scheme 1: the initiation reaction takes place, at first, by the reaction of HFPO which can coordinate to $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ complex with THF, and the initiating species produced releases fluoride anion ((I), (II) in Scheme 1).

In this reaction process, CuF_2 and $(\text{C}_2\text{H}_5)_3\text{Al}$ is considered to form an ate complex type species, which would work as a catalyst. As shown in Table I, the polymerization system involving $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ gives poly(THF) with a fluoroformyl end group at -30 °C, while no polymer is obtained without $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$. Furthermore, the acceleration of the polymerization reaction is observed for the polymerization system with $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ in the low initial molar ratio of HFPO to THF ($[\text{HFPO}]/[\text{THF}] = 7/93$) at 20 °C (run 2, run 3 and run 8). In the polymerization at higher ratios of $[\text{HFPO}]/[\text{THF}]$, significant difference of the polymerization behavior is not observed for polymerization systems — with or without $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$. These results apparently suggest that $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ participates in the initiation process of the polymerization in which HFPO would play an important role rather than propagation in which HFPO does not take part.

The propagation reaction of the polymerization is considered to proceed through oxonium ion mechanism with the $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ complex ((III) and (IV) in Scheme 1).

According to Scheme 1, the polymer produced should have fluoroformyl (CFO) group at one end of the polymer chain due to the initiation reaction. On the NMR spectra shown in Figure 1, however, the signal assignable to CFO group could not be found while ordinary carbonyl group is detected in ^{13}C NMR. This is due to hydrolysis of CFO group to $-\text{OH}$ group by treatment with water in the isolation process of the polymer (see Experimental section). In fact, when obtained polymer was dipped into methanol before treatment with water, the end group of the polymer was changed to $-\text{OCH}_3$ group. This was confirmed by

Figure 1. ^{13}C NMR (A) and ^{19}F NMR (B) spectra of the polymer obtained with the reaction of HFPO and THF (run 8 in Table I).

Scheme 1.

NMR analysis.

Figure 2 shows the ^1H NMR spectra of the polymers obtained from the polymerization above room temperature treated with water (a) and methanol (b). In Figure 2a, the absorption of hydroxy group is observed around 10.3 ppm as a broadened signal. For the methanolysis polymer, the signal of methoxy group is clearly observed at 3.91 ppm in Figure 2b, and the intensity ratio of the $-\text{OCH}_3$ signal which was introduced by methanolysis of $-\text{CFO}$ generated in the initiation step to $-\text{CH}_2\text{F}$ given as a termination end by the termination with fluoride anion is 3:2. This result indicates that the all polymerization reaction initiated with the species from HFPO is terminated with only fluoride anion in the polymerization system with $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ above room temperature ((V) in Scheme 1).

On the other hand, in the polymerization system at -30°C , the signal intensity ratio of $-\text{OCH}_3$ to CH_2F is 9:2 for the polymer obtained after methanolysis as illustrated in Figure 3a. This polymer is confirmed to have the HFPO initiating unit by ^{19}F NMR spectrum (Figure 3b) as well as the other resulting polymers, *i.e.* this polymer also has fluoroformyl group at initiating end quantitatively. This means that termination reaction other than that with fluoride anion would occur in the polymerization reaction at -30°C with $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ complex: for instance, termination with ethyl group which can migrate from

triethylaluminium ((VI) in Scheme 1). In fact, the signals assignable to ethyl group are observed on Figure 3a as triplet (1.34 ppm) and quartet (1.48 ppm) signals, respectively. The polymerization of THF in the presence of HFPO as an initiating species generator gives the poly(THF) with a fluoroformyl end group for each polymer chain whether $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ is in the polymerization system or not. As mentioned above, the fact that the fluoroformyl group can be introduced quantitatively at one end of each polymer chain and easily transformed other functional groups by simple post-treatment suggests that the polymer obtained from these polymerization systems consisting of HFPO and THF have versatile potentiality for the reactivity polymeric material.

The polymers which were obtained from different post-treatment showed different thermal property. Figure 4 shows TGA curves of the polymers treated with water (a) and methanol (b). For the TGA curve of the polymer treated with water, thermal decomposition starts around 200°C . The temperature of 10% weight loss is 215°C , which is slightly more stable than that of the polymer treated with methanol. This higher thermal property observed in the TGA profile for the polymer with hydroxyl end group may be due to the hydrogen bond formed by hydroxyl groups.

Figure 2. ^1H NMR spectrum of the polymer obtained with the reaction of HFPO and THF in the presence of $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ at 20°C treated with water (A) and methanol (B) (run 3 in Table I).

Figure 4. TGA profiles of the water-treated (a) and methanol-treated (b) polymers.

Figure 3. ^1H NMR (A) and ^{19}F NMR (B) spectra of the polymer obtained with the reaction of HFPO and THF in the presence of $\text{CuF}_2/(\text{C}_2\text{H}_5)_3\text{Al}$ at -30°C treated with methanol (run 1 in Table I).

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