NOTES

Anionic Polymerization of Fluoroalkyl 2-Trifluoromethylacrylate

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Fluorine-containing acrylate polymers have recently come to attract much attention in the fields of X-ray and electron beam lithography. The reactivity of fluorine-containing acrylates toward carbanions may be increased since fluoroalkyl substituents possess a high electron-withdrawing effect which reduces the electron density of vinyl groups. The high e values of fluoroalkyl acrylates, methacrylates and methyl 2-trifluoromethylacrylate have been reported.^{1,2} It has recently been pointed out that fluoroalkyl acrylates and methacrylates are polymerized anionically with initiators of low basicity.³⁻⁷ The anionic polymerization of alkyl 2-trifluoromethylacrylates have been reported by two research groups.⁸⁻¹⁰ Since the e value of methyl 2-trifluoromethylacrylate is as high as 2.9, the anionic polymerization of alkyl 2-trifluoromethylacrylate is expected to take place with initiators of low basicity; that is, the polymers of ethyl 2-trifluoromethylacrylate are obtained with lithium *tert*-butoxide, potassium *tert*-butoxide, triethylaluminum, and diethyl(ethyl cyanoacetato)aluminum as initiator. Ito *et al.* have also reported that methyl 2-trifluoro-

methylacrylate is polymerized with alkali metal salts complexed with 18-crown-6.¹¹

The present paper deals with the anionic polymerization of the acrylates possessing two fluoroalkyl groups such as 2,2,2-trifluoroethyl 2-trifluoromethylacrylate (TFTFA) and 2,2,2-trifluoro-1-trifluoromethylethyl 2-trifluoromethylacrylate (HxFTFA) with several initiators.

EXPERIMENTAL

Experiments were carried out under a purified nitrogen atmosphere to preclude oxygen and atmospheric moisture.

Reagents

2,2,2-Trifluoroethyl 2-trifluoromethylacrylate (TFTFA) and 2,2,2-trifluoro-1-trifluoromethylethyl 2-trifluoromethylacrylate (HxFTFA) (from Central Glass Co.) were refluxed over calcium hydride and then distilled; TFTFA, bp 52°C/53 mmHg; HxFTFA, bp 41°C/50 mmHg. Commercial *n*-butyllithium (hexane solution) and *n*-butylmagnesium chloride (ether solution) were used after

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determination of the concentrations of the active species by alkalimetry. Lithium *tert*-butoxide and potassium *tert*-butoxide were synthesized from corresponding metals with *tert*-butanol, respectively. $\text{Zn}(\text{C}_2\text{H}_5)_2$ and $\text{Al}(\text{C}_2\text{H}_5)_3$ were distilled under reduced pressure. $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ and $\text{LiAlC}_4\text{H}_9(\text{C}_2\text{H}_5)_3$ were synthesized from *n*-butyllithium and $\text{Zn}(\text{C}_2\text{H}_5)_2$ or $\text{Al}(\text{C}_2\text{H}_5)_3$, respectively. Ethyl-(acetylacetonato)zinc ($\text{C}_2\text{H}_5\text{Znacac}$), ethyl-(ethyl cyanoacetato)zinc ($\text{C}_2\text{H}_5\text{ZnECA}$) and diethyl(ethyl cyanoacetato)aluminum ($(\text{C}_2\text{H}_5)_2\text{AlECA}$) were synthesized according to the literature.¹² Toluene, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were purified by usual methods.

Procedures

Polymerization was carried out in a glass ampule charged with monomer (5 mmol), ini-

tiator (0.1 mmol) and solvent (5 ml) under nitrogen. The ampule was sealed and kept at 60°C. After an appropriate time interval, the polymer was isolated by precipitation with methanol and dried to constant weight. When a precipitate was not obtained, methanol was removed under reduced pressure and the residue was extracted with benzene. The solution was washed with diluted hydrochloric acid in order to get rid of initiator residue and the polymer was obtained by removing benzene by lyophilization.

Measurements

¹H NMR spectra were registered at 60 MHz on a HITACHI model R-600 FT-NMR spectrometer. Infrared (IR) spectra (KBr disk method) were measured on a SHIMADZU IR-400 spectrophotometer. Gel permeation chromatography (GPC) was measured with

Table I. Anionic polymerization of fluoroalkyl 2-trifluoromethylacrylates

Initiator	Solvent	Time/day	Poly(TFTFA) yield/%	Poly(HxFTFA) yield/%
<i>n</i> -C ₄ H ₉ Li	THF	7	54.3	25.2
	DME	7	59.0	11.1
<i>n</i> -C ₄ H ₉ MgCl	THF	7	7.6	41.1
	DME	7	11.5	14.2
LiZnC ₄ H ₉ (C ₂ H ₅) ₂	THF	10	68.5	12.5
	DME	7	69.0	16.1
	Toluene	10	0	0
LiAlC ₄ H ₉ (C ₂ H ₅) ₃	THF	10	0	7.2
	Toluene	10	0	0
	THF	10	37.1	10.1
<i>t</i> -C ₄ H ₉ OLi	DME	7	11.5	11.1
	Toluene	7	0	0
	THF	7	0	0.6
<i>t</i> -C ₄ H ₉ OK	DME	7	0	16.3
	THF	10	0	0
	Toluene	10	0	0
Zn(C ₂ H ₅) ₂	THF	7	34.2	5.0
	Toluene	7	0	2.7
C ₂ H ₅ Znacac	THF	7	0	0
	Toluene	7	0	0
C ₂ H ₅ ZnECA	THF	10	0	2.3
	Toluene	10	0	0
Al(C ₂ H ₅) ₃	THF	10	0	3.0
	Toluene	10	0	0
(C ₂ H ₅) ₂ AlECA	THF	10	0	0
	Toluene	10	0	0

^a Polymerization temperature, 60°C.

a TOYO SODA HLC-820A equipped with a TSK gel G4000HXL-G3000HXL-G2000HXL column series using THF as the eluent. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed with a RIGAKU DENKI TG-DSC calorimeter.

RESULTS AND DISCUSSION

Since the methyl and ethyl esters of 2-trifluoromethylacrylic acid are hardly polymerized with radical initiator,¹⁰ the polymerizations of 2,2,2-trifluoroethyl 2-trifluoromethylacrylate (TFTFA) and 2,2,2-trifluoro-1-trifluoromethylethyl 2-trifluoromethylacrylate (HxFTFA) were examined using anionic initiators. Table I shows the results of TFTFA

TFTFA: $\text{R}_f = \text{CH}_2\text{CF}_3$

HxFTFA: $\text{R}_f = \text{CH}(\text{CF}_3)_2$

and HxFTFA with several anionic initiators. *n*-Butyllithium and $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ are the most effective initiators for polymerization of TFTFA in THF and DME. HxFTFA is also polymerized with *n*-butyllithium, *n*-butylmagnesium chloride and $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$. These results are in contrast to those reported by Ito *et al.*,¹⁰ according to which *n*-butyllithium does not produce poly(methyl 2-trifluoromethylacrylate). Lithium *tert*-butoxide as initiator gives appreciable yields of poly(TFTFA) and poly(HxFTFA). Organozinc and organoaluminum compounds, by some of which it is possible to produce poly(ethyl 2-trifluoromethylacrylate),⁹ are inactive for polymerizations of TFTFA and HxFTFA but active for the $\text{C}_2\text{H}_5\text{Znacac-TFTFA}$ systems. THF and DME are found to be preferable solvent compared with toluene as far as polymer yields are concerned.

Table II. Solubility of poly(TFTFA) and poly(HxFTFA)^a

Solvent	Poly(TFTFA)	Poly(HxFTFA)
Methanol	++	—
Ethanol	++	—
1,2-Dimethoxyethane	++	—
1,4-Dioxane	++	—
Tetrahydrofuran	++	—
Chloroform	+	—
Acetone	++	—
Toluene	+	—
Benzene	++	—
Cyclohexane	+	—
Hexane	++	—
Hexafluorobenzene	++	—

^a ++, soluble; +, partially soluble; —, insoluble.

Figure 1. ^1H NMR of TFTFA (A) and poly(TFTFA) (B) produced with *n*- $\text{C}_4\text{H}_9\text{Li}$ in THF at 60°C for 7 days.

It is apparent that the polymer yields are lower compared to those in the usual polymerization of alkyl acrylates and methacrylates,

Figure 2. IR spectra of HxFTFA (A) and poly(HxFTFA) (B) produced with $n\text{-C}_4\text{H}_9\text{MgCl}$ in THF at 60°C for 7 days.

probably because the electron density of the carbanions at propagating end groups may be also decreased by the electron-withdrawing effect of fluoroalkyl groups.

Produced poly(TFTFA) was soluble or partly soluble in the such solvents as alcohols, ethers, hydrocarbons and hexafluorobenzene, but no solvent was found for poly(HxFTFA), which behaved similarly as poly(tetrafluoroethylene), as shown in Table II. The polymerization system of HxFTFA, therefore, becomes gelatinous as the reaction proceeds.

Figure 1 shows the ¹H NMR spectra of TFTFA and poly(TFTFA) produced with $n\text{-C}_4\text{H}_9\text{Li}$ in THF. Signals at $\delta=4.6$ and 2.65 in

Figure 3. GPC eluogram of poly(TFTFA) obtained with $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ in DME at 60°C for 7 days.

Figure 1(B) are assigned to the methylene protons of trifluoroethyl group and the main chain, respectively, with an intensity ratio of

1:1. No peak assignable to vinylic protons is observed. Figure 2 shows the IR spectra of HxFTFA and poly(HxFTFA) produced with $n\text{-C}_4\text{H}_9\text{MgCl}$ in THF since the polymer is insoluble in any solvent for measuring the ^1H NMR spectrum. The absorptions at 870 cm^{-1} and 1650 cm^{-1} assignable to vinyl group of HxFTFA disappeared in the spectrum of poly(HxFTFA). The spectra in Figures 1(B) and 2(B) lead to the tentative conclusion that addition polymerization of the vinyl group takes place predominantly without appreciable side reactions.

According to the GPC eluogram of poly(TFTFA) obtained with $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ in DME, as shown in Figure 3, the molecular weight distribution is unimodal and the molecular weight of the peak based on the standardized poly(styrene) calibration is 3.5×10^4 . It is of interest that the refractive index of a solution of poly(TFTFA) is lower than that of the solvent, THF, as has been found in the case of poly(2,2,2-trifluoro-1-trifluoromethyl-ethyl methacrylate).⁵

The thermal character of poly(HxFTFA) was analyzed by TG-DSC. The polymer began to decompose at 250°C . No peak or onset corresponding to T_g or T_m was observed below the decomposition temperature.

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REFERENCES

1. T. Narita, T. Hagiwara, and H. Hamana, *Makromol. Chem., Rapid Commun.*, **6**, 5 (1985).
2. S. Iwatsuki, A. Kondo, and H. Harashima, *Macromolecules*, **17**, 2473 (1984).
3. T. Narita, T. Hagiwara, and H. Hamana, *Makromol. Chem., Rapid Commun.*, **6**, 175 (1985).
4. T. Narita, T. Hagiwara, and H. Hamana, *Nippon Kagaku Kaishi*, 1945 (1985).
5. T. Narita, T. Hagiwara, H. Hamana, and M. Goto, *Makromol. Chem.*, **187**, 731 (1986).
6. T. Narita, T. Hagiwara, H. Hamana, H. Yanagisawa, and Y. Akazawa, *Makromol. Chem.*, **187**, 739 (1986).
7. T. Narita, T. Hagiwara, H. Hamana, T. Miyasaka, A. Wakayama, and T. Hotta, *Makromol. Chem.*, **188**, 273 (1987).
8. T. Narita, T. Hagiwara, H. Hamana, and T. Nara, *Makromol. Chem., Rapid Commun.*, **6**, 301 (1985).
9. T. Narita, T. Hagiwara, H. Hamana, and T. Nara, *polym. J.*, **20**, 277 (1988).
10. H. Ito, D. C. Miller, and C. G. Willson, *Macromolecules*, **15**, 915 (1982).
11. H. Ito and R. Schwalm, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **27**, 196 (1986).
12. Y. Kawakami and T. Tsuruta, *Bull. Chem. Soc. Jpn.*, **44**, 247 (1971).