Anionic polymerization of fluorine-containing vinyl monomers. 11. α-Fluoroacrylates

Tadashi Narita*, Tokio Hagiwara, Hiroshi Hamana, Hideo Arai and Yogo Okajima

Department of Environmental Engineering, Saitama Institute of Technology, 1690 Okabe-machi, Osato-gun, Saitama 369-02 (Japan)

Abstract

The polymerization conditions of methyl α-fluoroacrylate ($H_2C=CFCOOCH_3$) and 2,2,2-trifluoroethyl α-fluoroacrylate ($H_2C=CFCOOCH_2CF_3$) have been investigated by systematically surveying the typical anionic polymerization initiators and solvents in order to obtain preliminary information on the general trend of the anionic polymerization of fluorinated acrylates. It is concluded that α-fluoroacrylates are polymerized by initiators of relatively low basicity which are incapable of producing polymers of non-fluorinated acrylates and methacrylates. No remarkable side reactions occurred since the molecular weight distributions were unimodal and no peaks assignable to vinyl protons or other additional signals were observed in the ^1H NMR spectra. The polymerization took place in an anionic fashion as established from an investigation of the initiation reaction.

Introduction

In previous papers [1–3] it has been pointed out that α-trifluoromethylacrylates ($H_2C=C(CF_3)COOR$) such as methyl α-trifluoromethylacrylate, trifluoroethyl α-trifluoromethylacrylate and hexafluoroisopropyl α-trifluoromethylacrylate, which are virtually unaffected under radical polymerization conditions, readily undergo anionic polymerization to produce the corresponding homopolymers in high yield. It has thus been concluded that the effect of the trifluoromethyl substituent is quite important in determining the polymerization reactivity of vinyl monomers. Although a similar effect on the vinyl group should be expected in the polymerization of α-fluoroacrylates ($H_2C=CFCOOR$), since the σ-value of CF_3 is similar to that of F [4], only a few studies on the polymerization of these monomers with anionic initiators have been reported [5]. As far as radical polymerizations are concerned, some detailed studies have been carried out on methyl α-fluoroacrylate ($H_2C=CFCOOCH_3$) (MFA) [6] and ethyl α-fluoroacrylate [7] (EFA), the Q,e-values being reported to be 0.47 and 0.73 for MFA, and 0.49 and 0.68 for EFA, respectively. It is probable these high e-values indicate that α-fluoroacrylates should show high anionic polymerization reactivity.

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*To whom all correspondence should be addressed.

To obtain preliminary information on the general trend of the anionic polymerization of fluorinated acrylates, this study has been directed towards an investigation of the polymerization conditions of MFA and 2,2,2-trifluoro-ethyl α-fluoroacrylate ($H_2C=CFCOOCH_2CF_3$) (TFEFA) by systematically surveying the typical anionic polymerization initiators and solvents.

Experimental

Reagents

Methyl α-fluoroacrylate (MFA) and 2,2,2-trifluoroethyl α-fluoroacrylate (TFEFA) (from Daikin Industries Ltd.) were refluxed over CaH_2 and then distilled under reduced pressure; b.p., MFA, 32 °C/60 mmHg; TFEFA, 45 °C/77 mmHg. Toluene and tetrahydrofuran (THF) were purified by the usual methods. 1,2-Dimethoxyethane (DME) was purified by the same method and further purification was carried out by refluxing with $Al(C_2H_5)_3$ followed by distillation. Commercial $n-C_4H_9Li$ and C_2H_5MgBr were used after determination of their concentrations. $LiZnC_4H_9(C_2H_5)_2$ and $LiAlC_4H_9(C_2H_5)_3$ were synthesized via the equimolar reactions of $n-C_4H_9Li$ with $Zn(C_2H_5)_2$ or $Al(C_2H_5)_3$, respectively; $t-C_4H_9OK$ was purified by sublimation under reduced pressure.

$(C_2H_5)_2Al(NCCHCOOC_2H_5)$ (Et$_2$AlECA), $(C_2H_5)_2Al(CH_3OCOCHCOOCH_3)$ (Et$_2$AlDMM) and $(C_2H_5)_2Al(CH_3COCHCOCH_3)$ (Et$_2$Alacac) were synthesized via the equimolar reactions of $Al(C_2H_5)_3$ with ethyl cyanoacetate, dimethyl malonate or acetylacetone, respectively. Organozinc compounds were synthesized according to literature methods [8]. Commercial $Zn(C_2H_5)_2$ and $Al(C_2H_5)_3$ were purified by distillation under reduced pressure.

Procedures

A glass ampoule was charged with monomer (10 mmol), initiator (0.2 mmol) and solvent (10 ml) using a syringe under an atmosphere of purified nitrogen. The ampoule was sealed and kept at constant temperature. The reaction mixture was stirred magnetically. The polymer was isolated by reprecipitation with methanol and dried to a constant weight.

[1]H (at 270 MHz), [13]C (at 67.9 MHz) and ^{19}F NMR (at 254 MHz) spectra were obtained by means of a JEOL GSX-270 FT-NMR spectrometer, using tetramethylsilane as a reference for ^{1}H and ^{13}C NMR measurements and $CFCl_3$ for ^{19}F NMR, with $CDCl_3$ or acetone-d_6 as the solvent. Gel permeation chromatography (GPC) was undertaken with a TOSOH HLC-802A instrument equipped with a TSK gel G4000HXL–G3000HXL–G2000HXL column series using THF as an eluent. Vapor-phase chromatography was measured by a Hewlett-Packard 5890A instrument equipped with FID.

Results and discussion

The results of the anionic polymerization of MFA with several initiators are summarized in Table 1. Although $n-C_4H_9Li$ and C_2H_5MgBr (which are

TABLE 1

Anionic polymerization of methyl α-fluoroacrylate[a]

Initiator	Solvent	Temp. (°C)	Yield (%)
n-C$_4$H$_9$Li	Tol	40	2.5
	THF	40	11.6
C$_2$H$_5$MgBr	Tol	40	trace
	THF	40	trace
	DME	40	0
LiZnC$_4$H$_9$(C$_2$H$_5$)$_2$	Tol	40	29.6
	THF	40	29.8
	DME	40	74.1
LiAlC$_4$H$_9$(C$_2$H$_5$)$_3$	Tol	40	31.4
	THF	40	28.4
	DME	40	25.7
t-C$_4$H$_9$OK	Tol	40	0
	THF	40	0
	DME	40	0
Zn(C$_2$H$_5$)$_2$	Tol	40	9.6
	THF	40	6.6
	DME	40	33.8
[Zn(OCH$_3$)$_2$·(C$_2$H$_5$ZnOCH$_3$)$_6$]	Tol	40	7.0
	THF	40	35.5
	DME	40	48.1
Al(C$_2$H$_5$)$_3$	Tol	40	68.5
	DME	40	49.9
(C$_2$H$_5$)$_2$Al(NCCHCOOC$_2$H$_5$)	Tol	40	92.3
	DME	60	28.6
		40	84.0
		0	14.7
		−78	4.6
(C$_2$H$_5$)$_2$Al(CH$_3$OCOCHCOOCH$_3$)	Tol	40	92.5
	DME	40	23.7
(C$_2$H$_5$)$_2$Al(CH$_3$COCHCOCH$_3$)	Tol	40	23.7
	DME	40	32.0

[a]Monomer, 10 mmol; initiator, 0.2 mmol; solvent, 10 ml; polymerization time, 7 d.

well-known initiators of non-fluorinated methyl acrylate and methacrylate polymerizations) produce poly(MFA) in very low yield, ate complexes such as LiZnC$_4$H$_9$(C$_2$H$_5$)$_2$ and LiAlC$_4$H$_9$(C$_2$H$_5$)$_3$, which are active initiators for the anionic polymerization of ethyl α-trifluoromethylacrylate [1, 2] and 2,2,2-trifluoroethyl α-trifluoromethylacrylate [3], produce poly(MFA) in appreciable yield. Organoaluminum compounds generally show higher activity relative to organozinc initiators. Et$_2$AlECA and Et$_2$AlDMM, which are well-known initiators of the anionic polymerization of vinyl ketones [9], show the highest polymerization reactivity listed in Table 1. Organozinc compounds such as Zn(C$_2$H$_5$)$_2$ and [Zn(OCH$_3$)$_2$·(C$_2$H$_5$ZnOCH$_3$)$_6$] were also found to produce the polymer in fairly high yield.

A similar tendency was observed in the anionic polymerization of TFEFA, as shown by the results listed in Table 2, although it took longer to obtain fairly high yields of polymer. It is apparent that the polymer yields are generally lower relative to those for MFA, probably because the electron density of the carbanions at propagating end-groups may have been reduced by the electron-withdrawing effect of the fluoroalkyl groups, although the electron density of the vinyl group of the monomer would also be diminished by the same effect.

To obtain some information on the polymerization mechanism, initiation reactions of MFA with Et_2AlECA were carried out. The results are summarized in Fig. 1, which shows the conversion of the ECA moiety measured by vapor phase chromatography after a portion of the reaction mixture was added to acetic acid. The initiation reaction was found to be rather slow since only c. 35% of Et_2AlECA was consumed in 4 h. Initiation of the polymerization

TABLE 2

Anionic polymerization of 2,2,2-trifluoroethyl α-fluoroacrylate[a]

Initiator	Solvent	Temp. (°C)	Yield (%)
n-C_4H_9Li	Tol	40	0
	THF	40	0
C_2H_5MgBr	Tol	40	0
	THF	40	0
	DME	40	0
$LiZnC_4H_9(C_2H_5)_2$	Tol	40	6.8
	THF	40	trace
	DME	40	8.5
$LiAlC_4H_9(C_2H_5)_3$	Tol	40	13.1
	THF	40	11.6
	DME	40	10.8
t-C_4H_9OK	Tol	40	0
	THF	40	0
	DME	40	0
$Zn(C_2H_5)_2$	Tol	40	0
	THF	40	0
	DME	40	0
$[Zn(OCH_3)_2 \cdot (C_2H_5ZnOCH_3)_6]$	Tol	40	10.3
	THF	40	trace
	DME	40	13.8
$Al(C_2H_5)_3$	Tol	40	59.0
	DME	40	13.3
$(C_2H_5)_2Al(NCCHCOOC_2H_5)$	Tol	40	30.1
	DME	40	9.5
$(C_2H_5)_2Al(CH_3OCOCHCOOCH_3)$	Tol	40	8.4
	DME	40	11.3
$(C_2H_5)_2Al(CH_3COCHCOCH_3)$	Tol	40	7.5
	DME	40	24.9

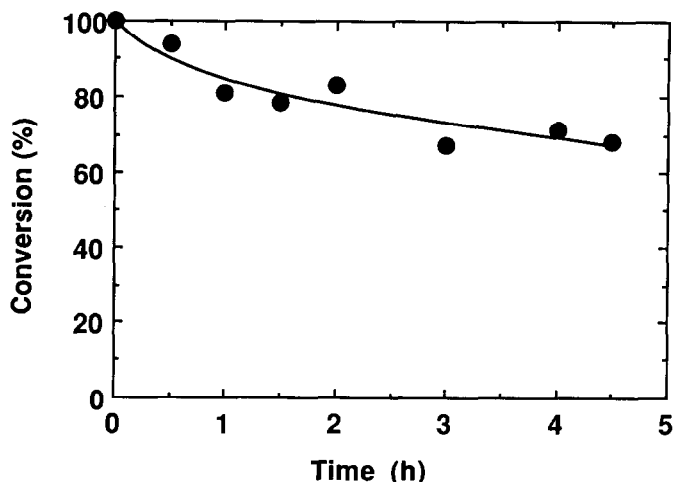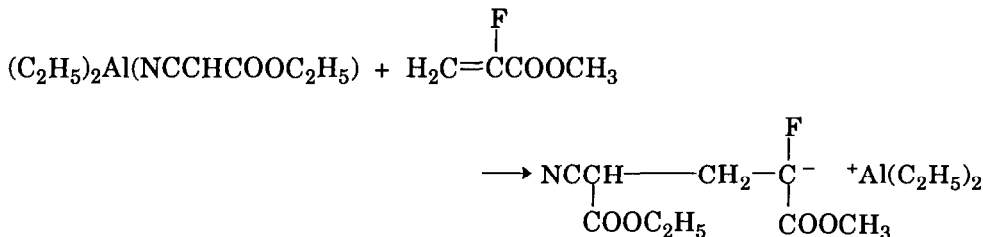[a]Monomer, 10 mmol; initiator, 0.2 mmol; solvent, 10 ml; polymerization time, 7 d.

Fig. 1. Time–conversion curve for the initiation reaction of $(C_2H_5)_2AlECA$ with MFA, calculated on the basis of the ethyl cyanoacetate moiety.

reaction of MFA with Et_2AlECA is thought to take place in an anionic fashion as reported by Kawakami and Tsuruta [9].

$$(C_2H_5)_2Al(NCCHCOOC_2H_5) + H_2C{=}\overset{\overset{\textstyle F}{\textstyle |}}{C}COOCH_3$$

$$\longrightarrow NC\underset{\underset{\textstyle COOC_2H_5}{\textstyle |}}{C}H{-\!\!\!-\!\!\!-}CH_2{-}\underset{\underset{\textstyle COOCH_3}{\textstyle |}}{\overset{\overset{\textstyle F}{\textstyle |}}{C}}{}^-\ {}^+Al(C_2H_5)_2$$

The poly(MFA) produced was soluble or partly soluble in such solvents as acetone, THF, toluene and chloroform, and insoluble in ethyl acetate, methanol, ethanol, n-hexane and cyclohexane. Poly(TFEFA) was soluble in acetone, ethyl acetate, THF and toluene, and insoluble in methanol, ethanol, n-hexane and cyclohexane.

Figure 2 shows the GPC eluograms for poly(MFA) (A) obtained with $Al(C_2H_5)_3$ in DME and poly(TFEFA) (B) obtained with $Et_2Alacac$. The molecular weight distributions are unimodal with the molecular weights at the peaks being 5.5×10^3 for A and 1.0×10^5 for B as calculated from monodisperse polystyrene standards. Other polymers obtained in this work also gave similar GPC eluograms.

The ^1H NMR spectra of MFA monomer (A) and poly(MFA) (B) produced with $Al(C_2H_5)_3$ are shown in Fig. 3. Absorptions assignable to methyl and methylene protons of poly(MFA) are observed at δ 3.7 ppm and 2.3–2.9 ppm, respectively, with an intensity ratio of 3:2.

Simple addition polymerization of the vinyl group is predominant in polymerizations of systems involving MFA and TFEFA, without any notable
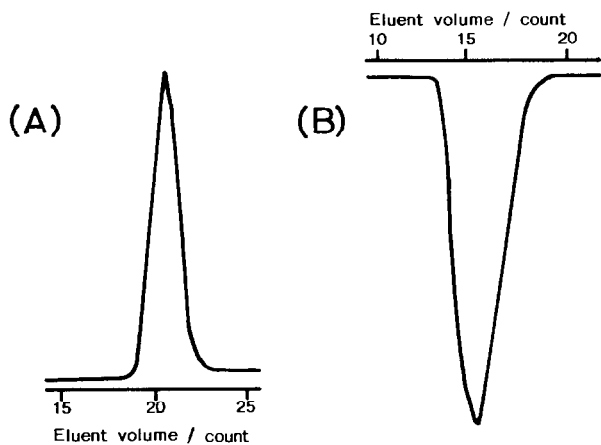
Fig. 2. GPC eluograms of poly(MFA) (A) obtained with $Al(C_2H_5)_3$ in DME and poly(TFEFA) (B) with $(C_2H_5)_2Alacac$ in DME at 40 °C for 7 d.
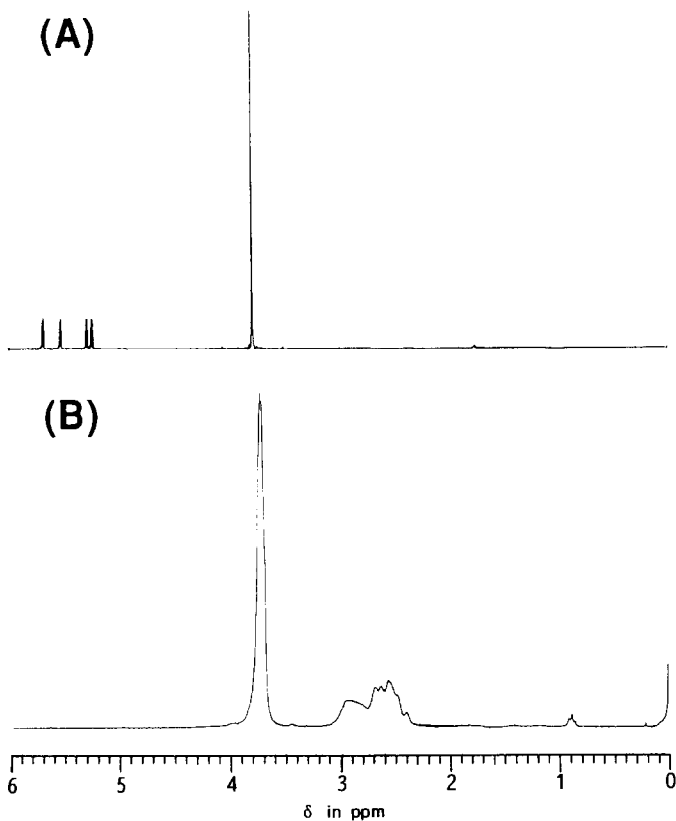

Fig. 3. ^1H NMR spectra of MFA monomer (A) and poly(MFA) (B) produced with $Al(C_2H_5)_3$.

side-reactions since the molecular weight distributions are unimodal and no peaks assignable to vinyl protons or other additional signals are observed in ^{1}H NMR spectra.

Figure 4 shows the ^{13}C and ^{19}F NMR spectra of poly(MFA). Absorptions corresponding to CH_3 carbon at 53.0 ppm, CH_2 carbon at 45 ppm, C–F carbon at 91.0–94.6 ppm and carbonyl carbon at 170 ppm, respectively, are observed. Absorptions corresponding to $=CH_2$ carbon at 102 ppm and $=C–F$ carbon at 151.2 and 155.1 ppm, which were observed in the ^{13}C NMR spectra of the MFA monomer, are missing. In the ^{19}F NMR spectrum, the peak assignable to the C–F fluorine is present at -160 to -170 ppm, while the absorption of the $=C–F$ fluorine in the monomer at -117.8 ppm is not detectable. These spectral measurements support the conclusions drawn from the ^{1}H NMR data. A more interesting feature is that the ^{13}C and ^{19}F NMR spectra of the polymer show fine structures. The intensity ratios of the absorptions at -160 to -163 ppm, -164 to -166 ppm and -166
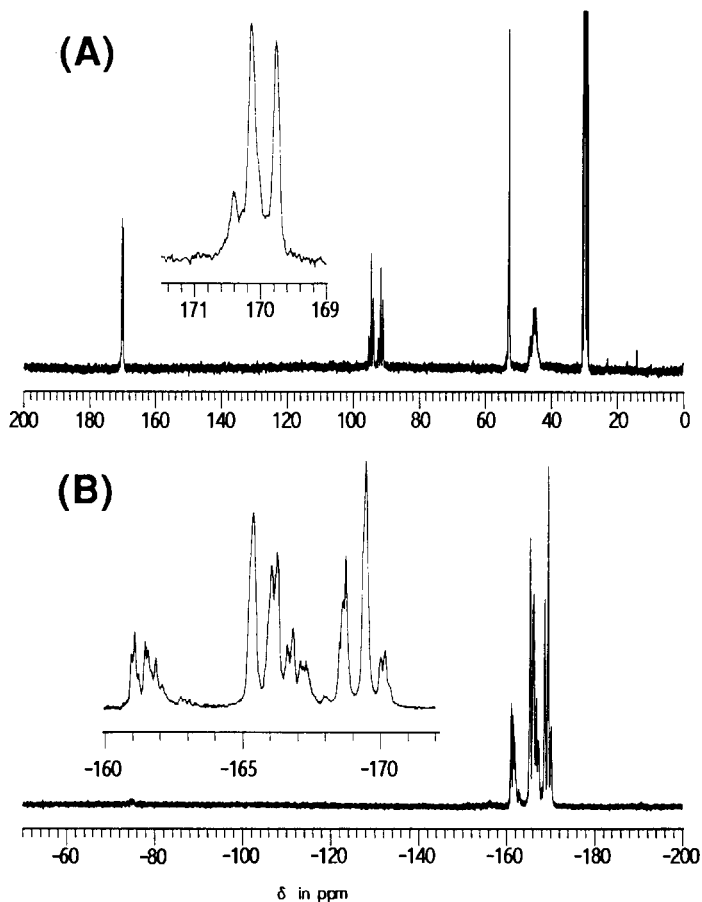

Fig. 4. ^{13}C (A) and ^{19}F NMR (B) spectra of poly(MFA).

to -171 ppm in the ^{19}F NMR spectrum correspond to the intensity ratios of the peaks at 170.419 ppm, 170.160 ppm and 169.771 ppm in the ^{13}C NMR spectra. These spectral fine structures may be attributed to the microstructure of the polymer, suggesting the possibility that the microstructure of fluorinated polymers could be analyzed by ^{19}F NMR spectra although analyses of the microstructure of polymers have hitherto been mainly carried out using ^{13}C NMR spectra. A more detailed study of the microstructure of poly(α-fluoroacrylate esters) is in progress.

In conclusion, α-fluoroacrylates are polymerized by initiators of relatively low basicity which are not capable of producing polymers of non-fluorinated acrylates and methacrylates. No destructive side-reactions occur since the molecular weight distributions are unimodal and no peaks assignable to vinyl protons or other additional signals are observed in the ^1H NMR spectra. Polymerization takes place in an anionic fashion as established from an investigation of the initiation reaction.

Acknowledgment

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