SHORT COMMUNICATIONS

**Anionic Polymerization of Ethyl 2-Trifluoromethylacrylate
with Organoaluminum and 'Ate' Complex Initiators**

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Fluorine-containing acrylate polymers have recently attracted much attention in the field of X-ray and electron beam lithography. It has recently been pointed out that the anionic polymerizations of ethyl 2-trifluoromethylacrylate (ETFMA) are successful by initiations of alkali metal *t*-butoxides, triethylaluminum and ethylzinc alkoxides.¹ Ito *et al.*² described the results of the radical homopolymerization and copolymerization of methyl 2-trifluoromethylacrylate (MTFMA), and they failed to obtain the homopolymer and *Q*, *e* values of the monomer since monomer reactivity ratio of MTFMA with methyl methacrylate was zero. According to the preliminary results of anionic polymerizations, *n*-butyllithium/18-crown-6 system and pyridine produced the polymer with insufficient yields.² They have recently reported that the *e* value of MTFMA is 2.50 by the mercury method developed by Giese.³ Iwatsuki *et al.*⁴ recently reported the MTFMA produced the polymer with radical initiators such as AIBN and BPO by bulk polymerization method though the polymer yields are less than 20%. They have also reported that the *e* value of MTFMA is 2.9 calculated from the copolymerization parameters with methyl

methacrylate, *p*-chlorostyrene and styrene.

This paper deals with further development of anionic polymerization of ETFMA initiated with organoaluminum compounds and 'ate' complexes possessing aluminum or zinc atoms as poly(ETFMA) was obtained by the initiation of triethylaluminum and organozinc compounds reported preliminarily in the previous paper.¹ It has been reported that these initiators are active for anionic polymerizations of fluorine-containing vinyl monomers such as 2,2,2-trifluoroethyl methacrylate (TFEM) and 2,2,2-trifluoro-1-trifluoromethylethyl methacrylate (HxFIM)^{5,6} which are hardly polymerized with typical anionic initiators such as *n*-butyllithium and organo-magnesium compounds.⁷

EXPERIMENTAL

Most of experiments were carried out under purified nitrogen atmosphere to preclude oxygen and atmospheric moisture.

ETFMA (from Central Glass Co.) was refluxed over calcium hydride and then distilled; bp 103—105. $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ and $\text{LiAlC}_4\text{H}_9(\text{C}_2\text{H}_5)_3$ were synthesized from equi-

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molar reactions of *n*-butyllithium with diethylzinc or triethylaluminum, respectively. Diethyl(acetylacetonato)aluminum (Et_2Alacac) and diethyl(ethyl cyanoacetato)aluminum (Et_2AlECA) were synthesized from equimolar reactions of triethylaluminum (Et_3Al) with acetylacetone or ethyl cyanoacetate, respectively.⁸ Commercial diethylzinc and Et_3Al were distilled under reduced pressure. Toluene and tetrahydrofuran (THF) were purified by the usual methods. Polymerization procedures and the measurements were described before.^{1,7}

RESULTS AND DISCUSSION

As has been reported before,¹ ETFMA is polymerized anionically with the initiators of intermediate reactivities such as lithium *t*-butoxide, potassium *t*-butoxide, Et_3Al and ethylzinc alkoxide complexes.

Table I shows the results of the further investigation of ETFMA polymerization with Et_3Al and diethylaluminum active methylene chelate compounds which are well-known initiators of anionic polymerization of vinyl ketones.⁸ Et_2AlECA is found to be of the highest reactivity for polymerization of ETFMA. In THF a solid polymer is produced quantitatively with Et_2AlECA at 80°C and the polymer yield decreases with lowering the polymerization temperatures. Et_2AlECA also produces the polymer with sufficient yields in

Table I. Anionic polymerization of ETFMA with organoaluminum compounds^a

Initiator	Solvent	Temp	Yield
		°C	%
Et_3Al	Toluene	40	45.2
		20	17.5
		0	20.1
		−20	22.4
Et_2AlECA	Toluene	80	54.7
		40	44.1
		0	60.7
		−20	19.6
		−78	36.4
		80	100
	THF	40	59.3
		0	11.2
		−20	21.8
		−78	8.6
Et_2Alacac	Toluene	40	0.4
		0	74.8
		−20	0
	THF	40	2.5
		0	1.6
		−20	10.9

^a Polymerization time, 7 days.

Table II. Anionic polymerization of ETFMA with ate complexes^a

Initiator	Solvent	Temp	Yield
		°C	%
$\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$	Toluene	80	11.7
		0	1.0
		−78	3.9
	THF	80	80.6
		0	14.3
		−20	10.7
$\text{LiAlC}_4\text{H}_9(\text{C}_2\text{H}_5)_3$	Toluene	−78	17.0
		80	25.9
		40	31.4
		0	15.5
		−20	10.7
		−78	5.5
	THF	80	28.8
		40	22.1
		0	13.2
		−20	5.8
		−78	9.4

^a Polymerization time, 7 days.

Figure 1. GPC of poly(ETFMA) produced with Et_3Al in toluene at 40°C.

toluene media. Et_2Alacac shows less reactive compared to Et_2AlECA .

The molecular weight distribution of the polymer produced with Et_3Al in toluene at 40°C is found to be bimodal and shows small oligomer peaks (Figure 1), though the distribution of the polymer yielded with $t\text{-C}_4\text{H}_9\text{OK}$ is very wide, from 1 million to several hundred.

The results of the anionic polymerization of ETFMA with ate complexes are summarized in Table II. $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ which is an active initiator for polymerization of TFEM and HxFIM, shows higher reactivity for polymerization of ETFMA in THF. Higher temperature is preferable as far as the polymer yields are concerned. $\text{LiAlC}_4\text{H}_9(\text{C}_2\text{H}_5)_3$ initiations produce appreciable yields of poly(ETFMA) both in toluene and in THF at higher polymerization temperature though

this initiator is totally less reactive than $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ in the anionic polymerization of ETFMA.

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