SHORT COMMUNICATIONS

**Anionic Polymerization of Fluorine-Containing Vinyl Monomers
VII. *o*- and *p*-Trifluoromethylstyrenes**

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In previous papers,¹⁻⁷ it was pointed out that the e values of fluoroalkyl acrylates and methacrylates are so large that these monomers readily undergo anionic polymerization. Fluoroalkyl substituents exert a highly electron-withdrawing effect which reduces the electron density of the vinyl groups so that reactivity towards carbanions is increased.

Though the same effect should appear in the polymerization of fluorine-containing styrene derivatives, only a few studies on the polymerization of these monomers with anionic initiators have been reported.⁸ Therefore, detailed polymerization conditions such as anionic initiators and solvents are scarcely known. According to the table of the relationship between the reactivity of vinyl monomers and of anionic initiators proposed by Tsuruta,⁹ monomers with high e values produce polymers with anionic initiators of relatively low basicity.

To obtain preliminary information on the general trend of the anionic polymerization of trifluoromethyl-substituted styrenes, the present paper is concerned with the investigation of combinations of monomers and initiators which produce polymers of *o*-trifluoromethylstyrene and *p*-trifluoromethylstyrene by surveying the typical anionic polymeriza-

tion initiators and solvents.

EXPERIMENTAL

Reagents

o-Trifluoromethylstyrene (**1**) was synthesized from CH_3MgI and *o*-trifluoromethylbenzaldehyde (from Central Glass Co.) in anhydrous ether, followed by dehydration with phosphorous pentoxide in anhydrous benzene.¹⁰ *p*-Trifluoromethylstyrene (**2**) was synthesized by the same method. Both monomers were refluxed over CaH_2 , distilled under reduced pressure and stored under nitrogen. Toluene and tetrahydrofuran (THF) were refluxed over CaH_2 and then distilled under nitrogen. 1,2-Dimethoxyethane (DME) was refluxed with CaH_2 and distilled under nitrogen. The distillate was further purified by refluxing with $\text{Al}(\text{C}_2\text{H}_5)_3$ and distillation under nitrogen. Commercial $n\text{-C}_4\text{H}_9\text{Li}$ and Grignard reagents were used after determination of the concentrations of the active species by alkalimetry. Potassium *tert*-butoxide was purified by sublimation *in vacuo* and stored under nitrogen. $\text{LiZnC}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ and $\text{LiAlC}_4\text{H}_9(\text{C}_2\text{H}_5)_3$ were synthesized from $n\text{-C}_4\text{H}_9\text{Li}$ and $\text{Zn}(\text{C}_2\text{H}_5)_2$ or $\text{Al}(\text{C}_2\text{H}_5)_3$, respectively, under nitrogen. The disodium

salt of living α -methylstyrene oligomer was synthesized from sodium metal and α -methylstyrene under nitrogen. Sodium naphthalene was synthesized from sodium metal and naphthalene under nitrogen. Organozinc compounds were synthesized from $\text{Zn}(\text{C}_2\text{H}_5)_2$ and methanol according to the literature.^{11,12} Commercial $\text{Zn}(\text{C}_2\text{H}_5)_2$ and $\text{Al}(\text{C}_2\text{H}_5)_3$ were distilled under reduced pressure and stored under nitrogen atmosphere.

Procedures

A glass ampule was charged with monomer (6.7 mmol), initiator (0.13 mmol) and solvent (6.0 ml) using a syringe under nitrogen atmosphere. The polymer was isolated by precipitation with methanol and dried to constant weight.

^1H NMR spectrum was registered with a HITACHI model R-600 FT-NMR spectrometer. GPC was measured with a TOYO SODA HLC-802A equipped with a TSK gel G4000HXL-G3000HXL-G2000HXL column series using THF as the eluent.

RESULTS AND DISCUSSION

The results of the polymerization of **1** with several anionic initiators are summarized in Table I. Active initiators for the styrene po-

lymerization such as $n\text{-C}_4\text{H}_9\text{Li}$, α -methylsty-

Table I. Anionic polymerization of *o*-trifluoromethylstyrene^a

Initiator	Solvent	Temp	Time	Yield
		°C	day	%
$n\text{-C}_4\text{H}_9\text{Li}$	Toluene	-72	5	0
		0	5	0
		60	5	13.1
	THF	60	5	6.3
	DME	80	7	27.0
$\text{Na}^+ (\alpha\text{-Mest})_n^- \text{Na}^+$	DME	80	7	32.9
Na-Naphthalene	DME	80	7	28.7
$\text{LiZnC}_4\text{H}_9 (\text{C}_2\text{H}_5)_2$	Toluene	60	4	15.5
		60	16	43.7
	THF	60	4	6.5
	DME	80	7	39.2
	Toluene	0	5	0
$n\text{-C}_4\text{H}_9\text{MgBr}$	THF	60	4	9.8
	DME	80	7	52.8
	Toluene	0	5	0
$\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$	DME	80	7	28.8
$\text{tert-C}_4\text{H}_9\text{OK}$	Toluene	0	5	0
$\text{Zn} (\text{C}_2\text{H}_5)_2$	Toluene	0	5	0
		60	4	5.8
		60	16	26.9
	THF	60	4	4.7
	DME	80	7	21.0
	Toluene	60	5	5.9
	THF	60	4	5.2
$\text{Al} (\text{C}_2\text{H}_5)_3$	DME	80	7	33.8

^a Monomer, 6.7 mmol; initiator, 0.13 mmol; solvent, 6 ml.

Table II. Anionic polymerization of *p*-trifluoromethylstyrene^a

Initiator	Solvent	Temp	Time	Yield
		°C	day	%
<i>n</i> -C ₄ H ₉ Li	Toluene	60	7	4.0
	THF	60	5	60.0
	DME	80	7	19.4
Na ⁺ (α-MeSt) _n ²⁻ Na ⁺	DME	80	7	30.7
Na-Naphthalene	DME	80	7	53.0
LiZnC ₄ H ₉ (C ₂ H ₅) ₂	Toluene	60	7	33.4
	THF	60	5	5.8
	DME	80	7	54.1
LiAlC ₄ H ₉ (C ₂ H ₅) ₃	Toluene	60	7	5.0
	THF	60	7	12.0
	DME	80	7	44.6
<i>n</i> -C ₄ H ₉ MgBr	Toluene	60	7	3.6
	THF	60	5	14.5
	DME	80	7	18.9
C ₆ H ₅ CH ₂ MgCl	Toluene	60	7	0.2
	THF	60	5	13.8
	DME	80	7	29.5
<i>tert</i> -C ₄ H ₉ OK	Toluene	60	7	3.0
	THF	60	7	0.2
	DME	80	7	1.5
Zn (C ₂ H ₅) ₂	Toluene	60	7	0
	THF	60	5	3.5
	DME	80	7	18.3
Zn (C ₂ H ₅) ₂ /CH ₃ OH (1 : 1)	DME	80	7	5.1
	DME	80	7	47.2
	DME	80	7	33.8
Al (C ₂ H ₅) ₃	Toluene	60	7	0.1
	THF	60	5	0.3
	DME	80	7	4.2

^a Monomer, 6.7 mmol; initiator, 0.13 mmol; solvent, 6 ml.

rene oligomer dianion and sodium naphthalene give low polymer yields in toluene and THF. However, these initiators give appreciable yields in DME solutions. LiZnC₄H₉-(C₂H₅)₂, one of the 'ate' complexes which show high activity to the polymerization of fluoroalkyl acrylates and methacrylates,⁵ yields the solid polymer of **1** in toluene and DME. The polymer yields increase with prolonged polymerization time as shown in the polymerization system of LiZnC₄H₉(C₂H₅)₂ in toluene. Grignard reagents such as *n*-C₄H₉MgBr and C₆H₅CH₂MgCl which are not able to initiate the anionic polymeriza-

tion of styrene yield poly(**1**) in DME. Zn-(C₂H₅)₂ and Al(C₂H₅)₃ which are active initiators of 2,2,2-trifluoro-1-trifluoromethyl-ethyl methacrylate,^{4,7} and unable to initiate the polymerization of styrene produce polymers of **1** with appreciable yields in DME. Zn(C₂H₅)₂ also gives a higher yield with increasing polymerization time similar to the LiZnC₄H₉(C₂H₅)₂ system.

As shown in Table II, **2** shows, as a whole, similar polymerization activity to **1** except for a few cases such as *n*-C₄H₉Li in THF and Al(C₂H₅)₃ initiation.

GPC of poly(**1**) and poly(**2**) are shown in

Figure 1. Typical gel permeation chromatograms of poly(1) (A) and poly(2) (B) produced with $\text{LiZnCl}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ in 1,2-dimethoxyethane at 80°C in 7 days.

Figure 1. Both polymers possess a unimodal molecular weight distribution with an average molecular weight of 2.3×10^5 for poly(1) and 6.2×10^4 for poly(2) as calculated from the standard polystyrene calibration curve. The ^1H NMR spectra of the same polymers are shown in Figure 2. Absorptions assignable to phenyl protons, methine protons and methylene protons of poly(1) (A) are observed at $\delta = 7.2$, 2.8, and 1.5 ppm, respectively, with an intensity ratio of 4:1:2. On the other hand, the absorption of phenyl protons of poly(2) (B) is split into two peaks, probably because the electronic effect of the *p*- CF_3 group towards *ortho*-protons and *meta*-protons is different. Absorptions of methine protons and methylene protons in the main chain overlap at $\delta = 1.6$ ppm.

The simple addition polymerization of the vinyl group takes place predominantly without any remarkable side reactions in the systems of **1** and **2** polymerizations since the molecular weight distributions are unimodal and no peaks assignable to vinyl protons ($\delta = 6.0$ – 7.0 ppm) or other additional signals are observable in ^1H NMR.

As a tentative conclusion, trifluoromethylstyrenes are polymerized by the initiators of

Figure 2. ^1H NMR of poly(1) (A) and poly(2) (B). (The same samples as in Figure 1 were used.)

lower basicity which are not able to produce the polymers of styrene.

Detailed studies on polymerization mechanisms such as initiation, propagation and termination reactions, and of the effect of

ortho-, *meta*-, and *para*-trifluoromethyl groups on the polymerization reactions are now under way.

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