

NOTES

Polymerization of α -Trifluoromethylvinyl Acetate

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(Received August 4, 1989)

KEY WORDS α -Trifluoromethylvinyl Acetate / Anionic Polymerization /
Ziegler Catalyst /

Fluoro- and fluoroalkyl-substituents exert a high electron-withdrawing inductive effect which reduces the electron density of vinyl groups so that reactivity towards carbanions may increase. Fluorine-containing vinyl monomers, therefore, may readily undergo anionic polymerization. The e -values of Alfrey-Price's Q, e -scheme are the most important scale to assess the effects of substituents on the reactivity of vinyl monomers. It has previously been reported that the e -values of fluoroalkyl acrylates and methacrylates are so large that these monomers are readily polymerized with anionic polymerization initiators of relatively low basicity.¹⁻³

The present paper deals with the anionic polymerization of α -trifluoromethylvinyl acetate ($\text{CH}_2=\text{C}(\text{CF}_3)\text{OCOCH}_3$) (TFMVA) with several anionic initiators and Ziegler-type catalysts. Radical copolymerization of TFMVA (M_1) with vinyl acetate (M_2) gives the monomer reactivity ratios of $r_1=0.25$, $r_2=0.20$, and $Q=0.069$, $e=1.51$ ⁴ though the homopolymer of TFMVA is not obtained under radical polymerization conditions. It is, therefore, obvious that the reactivity of TFMVA is scarcely demonstrated. TFMVA may be polymerized under anionic polymerization conditions if the

strong electron-withdrawing inductive effect of trifluoromethyl group overcomes the difficulties resulting from non-conjugation of the monomer.

In this article the anionic polymerization reactivity of TFMVA is estimated as polymer yields based on a survey of several different initiators from a table of the relationship between the reactivity of vinyl monomers and that of anionic initiators.⁵ Polymerization with Ziegler-type catalysts is also investigated since TFMVA is a non-conjugated monomer.

EXPERIMENTAL

Reagents

TFMVA (from Central Glass Co.) was purified by refluxing over calcium hydride and then distilling under purified nitrogen atmosphere: bp 88.0°C. Toluene, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were purified in the usual way and distilled over calcium hydride under nitrogen. Commercial *n*-butyllithium (hexane solution) and *n*-butylmagnesium bromide (diethyl ether solution) were used after determining concentrations by alkalimetry. The disodium salt of α -methylstyrene living oligomer, $\text{Na}^+(\alpha\text{-MeSt})_n^-\text{Na}^+$, was synthesized from sodium metal and α -methylstyrene under nitrogen. LiZnC_4H_9 -

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$(C_2H_5)_2$ and $LiAlC_4H_9(C_2H_5)_3$ were synthesized from an equimolar reaction of *n*-butyllithium with diethylzinc or triethylaluminum, respectively, under nitrogen. Potassium *tert*-butoxide was purified by sublimation under reduced pressure and stored under nitrogen. Organozinc⁶⁻⁸ and organoaluminum compounds⁹ were synthesized according to the literature. Diethylzinc and triethylaluminum were distilled under reduced pressure and stored under nitrogen. Titanium tetrachloride was refluxed over copper turnings and distilled under nitrogen. Titanium trichloride, vanadium trichloride, and vanadyl acetylacetonate were dried under reduced pressure. A Ziegler-type catalyst was prepared by adding an organometallic compound to an inorganic metal salt with an appropriate molar ratio in the corresponding solvent and aging for 1 h at room temperature.

Procedures

A glass ampoule was charged with the

monomer (10 mmol), initiator (0.2 mmol) and solvent (12 ml) under nitrogen. The ampoule was sealed and kept at constant temperature. After an appropriate time polymerization was terminated with hydrochloric acid/methanol and the reaction mixture was poured into methanol. The precipitate was filtered off and dried under reduced pressure. 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 to get rid of the initiator residue and the polymer was obtained by removing benzene by lyophilization.

Measurements

The ¹H NMR spectrum was recorded on a JEOL JNM-GSX270 instrument using deuterated chloroform as the solvent and tetramethylsilane as the internal standard. Gel permeation chromatogram obtained using a TOSOH HLC-802A equipped with TSK gel

Table I. Anionic polymerization of TFMVA with typical anionic initiators

Run No.	Initiator	Solvent	Temp.	Time	Yield
			°C	day	%
1	<i>n</i> -C ₄ H ₉ Li	Toluene	-20	7	0
2	Na ⁺ (α -MeSt) _n ²⁻ Na ⁺	Toluene	-20	10	5.1
3			40	10	13.4
4			80	10	4.8
5		DME	40	10	2.1
6	LiZnC ₄ H ₉ (C ₂ H ₅) ₂	Toluene	-20	7	0
7	LiAlC ₄ H ₉ (C ₂ H ₅) ₃	Toluene	60	7	0
8	<i>n</i> -C ₄ H ₉ MgBr	Toluene	40	10	0
9		DME	40	10	0
10	<i>tert</i> -C ₄ H ₉ OK	Toluene	-20	7	0
11	Zn(C ₂ H ₅) ₂	Toluene	-20	7	0
12	C ₂ H ₅ Zn(CH ₃ COCHCOCH ₃)	Toluene	40	7	0
13	C ₂ H ₅ ZnOCH ₃	Toluene	40	7	0.2
14	Zn(OCH ₃) ₂	Toluene	40	7	0
15	[Zn(OCH ₃) ₂ (C ₂ H ₅ ZnOCH ₃) ₆]	Toluene	40	7	0
16	[C ₂ H ₅ ZnMP] ₂ [Zn(MP) ₂] ₂ ^a	Toluene	40	7	2.5
17	Zn(C ₂ H ₅) ₂ -H ₂ O (1:1)	Toluene	40	7	0
18	Zn(C ₂ H ₅) ₂ -H ₂ O (1:0.5)	Toluene	-20	7	4.6
19	Al(C ₂ H ₅) ₃	Toluene	40	7	0
20	(C ₂ H ₅) ₂ Al(CH ₃ COCHCOCH ₃)	Toluene	40	7	0

^a MP = CH₃OCH₂CH(CH₃)O-

G4000HXL-G3000HXL-G2000HXL column series, with THF as the eluent.

RESULTS AND DISCUSSION

The results of the anionic polymerization of TFMVA with typical anionic polymerization initiators are summarized in Table I. *n*-C₄H₉-Li, which is an active initiator for methyl acrylate and methyl methacrylate polymerizations gives no polymer, probably because the addition reaction of initiating carbanions to the carbonyl double bond (carbonyl addition) takes place in preference to the addition on the vinyl group (conjugated addition).¹⁰ α -Methylstyrene living oligomer dianion, which possesses delocalized carbanions and shows high reactivity in the anionic polymerization of 2,2,2-trifluoroethyl methacrylate and 2,2,2-trifluoro-1-trifluoromethylethyl methacrylate,¹¹ produces oily materials in fair yields. Absorp-

tion assignable to phenyl protons was observed in ¹H NMR, and the molecular weight of the product measured by GPC eluogram was about 1×10^3 as calculated from standard polystyrene calibration. The products obtained, therefore, were found to be oligomers of TFMVA attached to α -methylstyrene oligomers.

The 'ate' complexes, well-known compounds reacting preferentially with the vinyl group rather than with the carbonyl group¹² and producing the polymers of fluorinated acrylate derivatives,^{13,14} give no poly(TFMVA).

tert-C₄H₉OK, which is soluble in several organic solvents and yields polymers of ethyl and fluoroalkyl α -trifluoromethylacrylates,^{15,16} shows also no activity. Organozinc and organoaluminum compounds exhibit almost no activity although these initiators have produced *o*- and *p*-trifluoromethylstyrene polymers.¹⁷

Anionic polymerization of TFMVA is then

Table II. Polymerization of TFMVA with Ziegler type catalysts

Run No.	Initiator	Solvent	Temp.	Time	Yield
			°C	day	%
21	TiCl ₃ -Al(C ₂ H ₅) ₃ (1:3) ^a	Toluene	40	7	8.6
22			80	7	18.4
23		THF	40	7	12.3
24			80	7	30.2
25		DME	40	7	12.4
26			80	7	26.8
27	TiCl ₃ -Al(C ₂ H ₅) ₃ (1:1)	Toluene	80	7	0
28			80	7	19.5
29		DME	80	7	2.9
30			40	7	7.3
31	TiCl ₄ -Al(C ₂ H ₅) ₃ (1:3)	DME	80	7	5.5
32			80	7	6.6
33	TiCl ₄ -Zn(C ₂ H ₅) ₂ (1:1)	DME	80	7	5.1
34			80	7	6.2
35	VCl ₃ -Al(C ₂ H ₅) ₃ (1:1)	Toluene	80	7	4.6
36			80	7	11.0
37	VCl ₃ -Al(C ₂ H ₅) ₃ (1:3)	DME	80	7	26.7
38			80	7	3.2
39	VO(acac)-Al(C ₂ H ₅) ₃ (1:1)	Toluene	80	7	10.0
40			80	7	6.3
41	(1:3)	Toluene	80	7	12.0
42			80	7	16.0

^a TiCl₃ (0.2 mmol) and Al(C₂H₅)₃ (0.6 mmol) were used as catalysts.

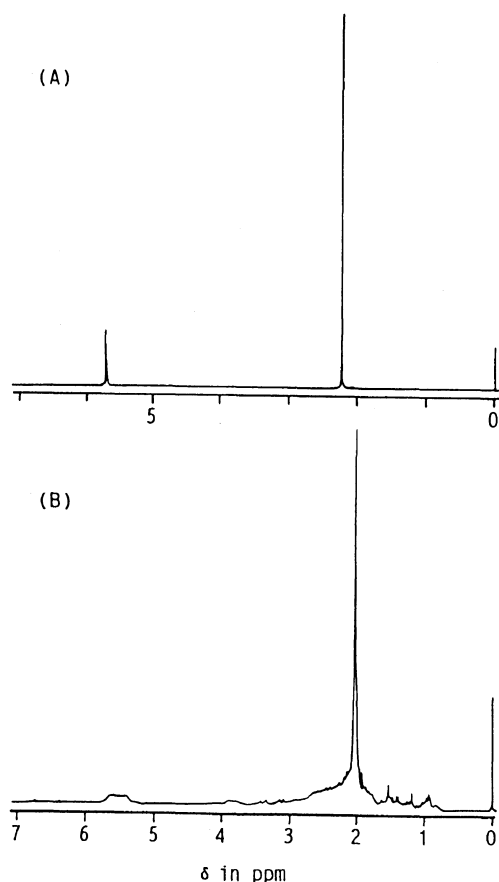


Figure 1. ^1H NMR spectra of TFMVA monomer (A) and the product (Run No. 23).

concluded to be very difficult, probably because the inductive effect of trifluoromethyl group scarcely overcomes the difficulties arising from non-conjugation of the monomer.

As mentioned before, polymerization with Ziegler-type catalysts was examined since TFMVA cannot be polymerized under anionic polymerization conditions. The results are shown in Table II. The yields of products are found much higher than those in Table I. Especially $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$ (1:3) systems are found to form products in yields as high as 30% in ethereal solvents. Other catalysts possessing vanadium ions also exhibit fairly high activity.

Figure 1 shows the ^1H NMR spectra of

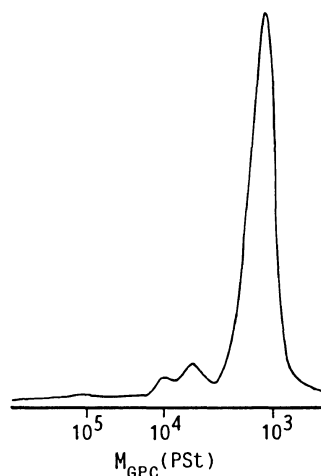


Figure 2. GPC eluogram of the product (Run No. 23).

TFMVA monomer and the product (Run No. 23). Absorptions at 2.0 ppm and 1.5–2.8 ppm are assignable to methyl and methylene protons, respectively, of the poly(TFMVA) in Figure 1(B). The large part of the product is, therefore, concluded to be derived from the addition polymerization of the vinyl group. However, other structures than that coming from vinyl polymerization might exist in the product since a small peak around 5.5 ppm may be assigned to vinyl protons. The molecular weight distribution of the same sample is also complex as shown in Figure 2. Small amounts of high molecular weight polymers are included in the product though the molecular weight of the largest peak is 1×10^3 .

It may be concluded that Ziegler-type catalysts examined here give oligomers of TFMVA which contain small amounts of high polymers, though the monomer is basically impossible to yield polymers under anionic polymerization conditions.

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