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Anionic polymerization of fluorine-containing vinyl monomers

8. Pentafluorophenylmethyl methacrylate*

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Summary

The anionic polymerization of pentafluorophenylmethyl methacrylate (PFPMA) were examined with several anionic initiators. The initiators of relatively low activity such as t-C_4H_9OK, organozinc compounds and $Al(C_2H_5)_3$ produced poly(PFPMA) in fairly high yields though no polymer was obtained by the initiations of n-C_4H_9Li and C_2H_5MgBr within 7 days. The anionic polymerization reactivity of PFPMA was found to be strongly affected by the pentafluorophenyl group though the e-value of PFPMA is similar to those of methyl methacrylate and benzyl methacrylate.

Introduction

It is expected that fluoro- or fluoroalkyl-substituents possess a high electron-withdrawing effect which reduces the electron density of the vinyl groups so that the reactivity towards carbanions may be increased. The high e-values of fluoroalkyl acrylates and methacrylates(1), and methyl 2-trifluoromethylacrylate(2) has been reported. The anionic polymerizations of fluoroalkyl acrylates and methacrylates have revealed that the polymers of these compounds are produced with the initiators of relatively low reactivity such as organoaluminum compounds, and detailed study on initiation and propagation reactions has been reported(3). The anionic polymerization of ethyl 2-trifluoromethylacrylate has also exhibited that the polymer is yielded with t-C_4H_9OLi, t-C_4H_9OK and organoaluminum compounds(4,5), and the anionic polymerization reactivity decreases with increase of trifluoromethyl-substitution at ester alkyl group(6). The reactivity of fluorinated acrylates and methacrylates is, therefore, strongly influenced by the strong electron withdrawing fluoroalkyl groups.

To get preliminary information on the effect of pentafluorophenyl group to the anionic polymerization reactivity of methacrylates, the present paper is concerned with the polymerization of pentafluorophenylmethyl methacrylate(PFPMA). It has previously been reported that the e-value of PFPMA is 0.48, and the effect of pentafluorophenyl group on the reactivity of vinyl group is similar to the nonfluorinated phenyl group in radical copolymerization (7). By referring to the table of the relationship between the reactivity of vinyl monomers and of anionic initiators proposed by

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Tsuruta(8), several different initiators were surveyed.

Experimental

Materials

Pentafluorophenylmethyl methacrylate(PFPMA) was synthesized from pentafluorophenylmethanol (form Japan Catalytic Chemical Ind.) and methacryloyl chloride in the presence of triethylamine(7). PFPMA was further purified by refluxing over calcium hydride and distillation before use. Toluene and tetrahydrofuran(THF) were purified by the usual methods. Commercial n-C_4H_9Li(hexane solution) was used after determination of the concentration by double titration method(9), and C_2H_5MgBr(ether solution) by alkalimetry. t-C_4H_9OK was purified by sublimation under reduced pressure. $LiZnC_4H_9(C_2H_5)_2$ and $LiAlC_4H_9(C_2H_5)_3$ were synthesized from the equimolar reactions of n-C_4H_9Li with $Zn(C_2H_5)_2$ or $Al(C_2H_5)_3$, respectively. $BaZn(C_2H_5)_4$ was synthesized from barium metal and $Zn(C_2H_5)_2$(10). Commercial $Zn(C_2H_5)_2$ and $Al(C_2H_5)_3$ were distilled under reduced pressure. Other organozinc(11,12) and organoaluminum compounds(13) were synthesized according to the literatures. All the materials were stored under purified nitrogen atmosphere.

Polymerization

PFPMA(6.16 mmol,1 ml),initiator (0.25 mmol) and solvent (10 ml) were added to a polymerization ampule under nitrogen atmosphere. The ampule was sealed and kept at constant temperature. After an appropriate time the polymer was isolated by reprecipitation from methanol and dried to constant weight.

Measurements

NMR spectra were recorded in deuterated chloroform($CDCl_3$) on a JEOL JNM-GSX 270 instrument. Gel permeation chromatogram was measured with a TOYO SODA HLC-802A equipped with TSK gel G4000HXL-G3000HXL-G2000HXL column series using THF as eluent.

Results and discussion

The results of the polymerization of PFPMA with several anionic initiators are summarized in Table 1. Active initiators for methyl methacrylate polymerization such as n-C_4H_9Li and C_2H_5MgBr exhibit very low polymer yields in toluene and THF. Ate complexes possessing lithium cation which show high activity to the polymerization of fluoroalkyl methacrylates(14) give the polymers of PFPMA in fairly high yields. t-C_4H_9OK, which is soluble in several organic solvents, produces the poly(PFPMA) in high yield with prolonged polymerization time. Appreciably high yields are obtained with organozinc compounds which have mainly been studied as ring-opening polymerization initiators of methyloxirane. These organozinc initiators have also given the polymers of ethyl 2-trifluoromethylacrylate(4), o- and p-trifluoromethylstyrenes(15). The polymer yields are found to increase with increasing polymerization time and 84% yield of poly(PFPMA) is obtained after 10 days in the system initiated with $[C_2H_5ZnMP]_2[Zn(MP)_2]_2$ in THF at 40°C, as shown in Table 1. On the other hand organoaluminum compounds, by some of which it is possible to produce fluoroalkyl acrylate and methacrylate polymers(3), show low anionic polymerization activity.

Table 1: Anionic polymerization of pentafluorophenylmethyl methacrylate(PFPMA)

Initiator	Solvent	Temp. (°C)	Time (day)	Yield (%)
n-C_4H_9Li	Toluene	40	2	9.8
	THF	40	1	0
C_2H_5MgBr	Toluene	40	1	0
$BaZn(C_2H_5)_4$	THF	40	2	8.8
$LiZnC_4H_9(C_2H_5)_2$	THF	40	2	30.2
$LiAlC_4H_9(C_2H_5)_3$	THF	40	2	23.1
t-C_4H_9OK	THF	-20	2	0
		-20	10	0.2
		0	2	0
		0	10	4.0
		40	2	8.5
		40	10	54.2
$Zn(C_2H_5)_2$	THF	-20	2	3.1
		0	2	3.2
		40	2	19.6
$[(C_2H_5ZnOCH_3)_6 \cdot Zn(OCH_3)_2]$	THF	40	2	17.9
$[C_2H_5ZnMP]_2[Zn(MP)_2]_2$ a)	THF	40	1	31.0
			2	33.6
			4	35.7
			7	50.4
			10	84.0
$Al(C_2H_5)_3$	THF	40	2	9.7
$(C_2H_5)_2AlDMM$ b)	Toluene	40	2	0.9
	THF	40	2	1.4
$(C_2H_5)_2Alacac$ c)	Toluene	40	2	0
	THF	40	2	6.8
$(C_2H_5)_2AlECA$ d)	Toluene	40	2	0
	THF	40	2	0.2

a) $MP=CH_3OCH_2CH(CH_3)O-$

b) Diethyl(dimethyl malonato) aluminum

c) Diethyl(acetylacetonato) aluminum

d) Dirthyl(ethyl cyanoacetato) aluminum

The anionic polymerization reactivity of PFPMA is, therefore, as high as that of vinyl ketones in terms of the reactivity towards initiators(8) since PFPMA is polymerized with organozinc compounds. This means that pentafluorophenyl group has influence on the reactivity of vinyl group of

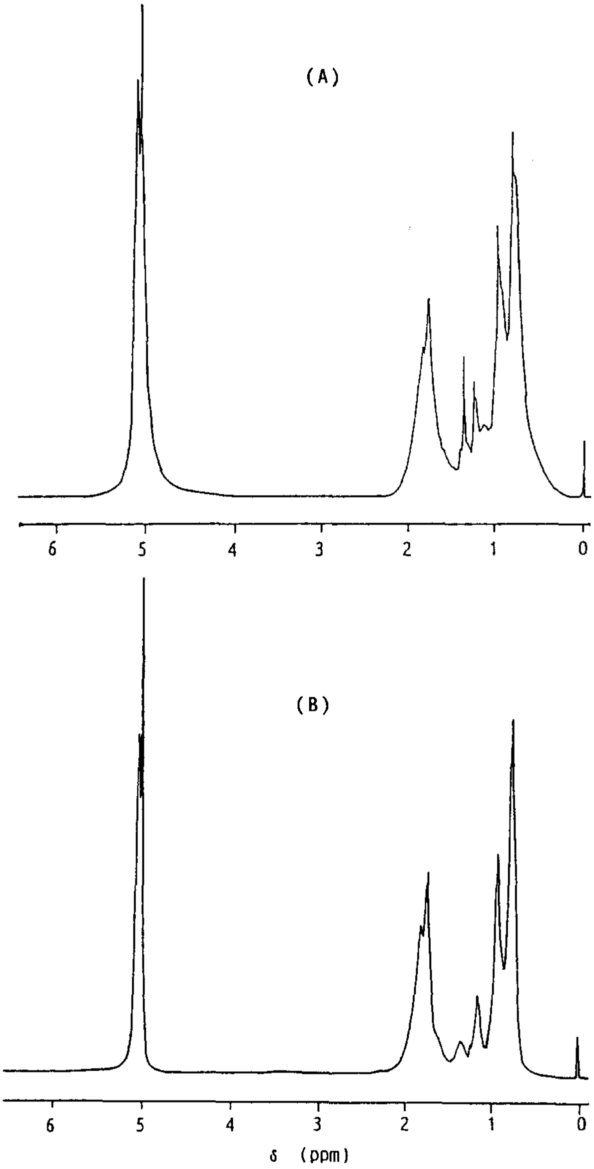

Figure 1. ^1H NMR spectra of poly(PFPMA) prepared with radical polymerization (A) and $[C_2H_5ZnMP]_2[Zn(MP)_2]_2$ for 10 days (B)

PFPMA though the e-value of PFPMA derived from radical copolymerization parameters with styrene is similar to those of methyl methacrylate and benzyl methacrylate(16). Poly(FPFMA) produced with organozinc compound was soluble in benzene, toluene, THF, 1,4-dioxane, diethyl ether, acetone, chloroform, ethyl acetate, dimethyl sulfoxide and N,N-dimethylformamide, and insoluble in n-bexane, cyclohexane and methanol.

Figure 1 shows the ^1H NMR spectra of poly(PFPMA) obtained with radical polymerization(A) and $[C_2H_5ZnMP]_2[Zn(MP)_2]_2$ for 10 days(B). Absorptions assignable to methyl protons, methylene protons of the polymer main chain, and methyleyne protons of the ester groups are observed at δ=0.6-1.2, 1.8, and 5.0ppm, respectively, with an intensity ratio of 3:2:2. The absorption assignable to the 2-methyl protons in Figure 1(B) is different from that in Figure 1(A). F.A. Bovey, U. Johnsen, and A. Nishioka have independently reported the iso-, hetero- and syndio-tacticity of poly(methyl methacrylate) is correlated with the ^1H NMR absorptions of 2-methyl protons(17). The tacticity of the poly(PFPMA) prepared with organozinc initiator might, therefore, be different from that of the radical polymerization. As shown in Figure 2, the molecular weight distribution of poly(PFPMA) is unimodal and the molecular weight of the peak based on the standard polystyrene calibration is $8.4X10^4$.

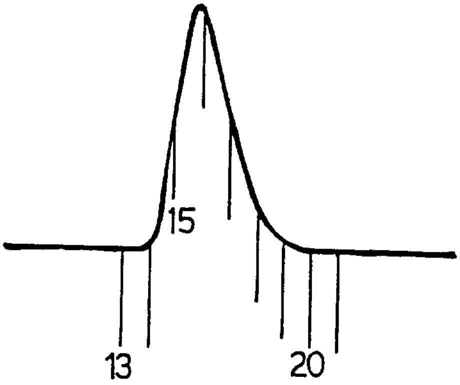

Figure 2. GPC eluogram of poly(PFPMA) prepared with $[C_2H_5ZnMP]_2[Zn(MP)_2]_2$ for 10 days

In conclusion the anionic polymerization of PFPMA may take place via anionic addition polymerization without remarkable side reactions with the initiators of relatively low activity such as $t-C_4H_9OK$ and $[C_2H_5ZnMP]_2[Zn(MP)_2]_2$. The tacticity of the poly(PFPMA) prepared with organozinc initiator might be different from that of radical polymerization.

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