

Stereospecific Polymerization of Methyl α -Phenylacrylate

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ABSTRACT: The polymerization of methyl α -phenylacrylate was carried out in toluene by *n*-BuLi at $-78\sim 30^\circ\text{C}$. The yield of the polymer was highest at -45°C and then decreased with increasing the temperature. No polymer was obtained above 0°C . The polymer obtained at -78°C was rich in isotacticity. By increasing the polymerization temperature the fraction of isotactic triads decreased in association with the increases in the fractions of heterotactic and syndiotactic triads. Above -45°C , the proportion, *I*:*II*:*S* of the polymer obtained was close to 1:2:1, suggesting the random stereoregulation in the propagating step. The *random polymer* was also obtained by *n*-BuLi in polar solvent such as THF at low temperature as well as by AIBN. The addition of a small amount of methanol to the polymerization system by *n*-BuLi in toluene increased the yield, isotacticity, and molecular weight of the polymer, and the maximum values were obtained at $\text{CH}_3\text{OH}/n\text{-BuLi}=0.83$. The polymerization by $(i\text{-}o\text{-Bu})_2\text{AlNPh}_2$ in toluene at -78°C gave a syndiotactic polymer in low yield. The reactivity of methyl α -phenylacrylate in anionic polymerization is briefly discussed in comparison with those of some other methyl α -alkylacrylates.

KEY WORDS Stereospecific Polymerization / Poly(methyl α -phenylacrylate) / *n*-Butyllithium / Diisobutylaluminum Diphenylamide / Random Polymer / ^{13}C NMR Spectrum / DSC Analysis /

Stereospecific polymerizations of methyl and other alkyl methacrylates have been reported by many authors. However, little attention has been paid to stereoregulation in the polymerization of α -alkylacrylate other than methacrylate.^{1,2} There have been only a few investigations on the polymerization of methyl α -phenylacrylate (MPhA).^{1,3} Tsuruta and Chikanishi¹ prepared poly(methyl α -phenylacrylate) (PMPHA) by using anionic catalysts such as *n*-BuLi, CaZnEt_4 , and SrZnEt_4 . They found that the fraction of the polymer insoluble in methyl ethyl ketone had some crystallinity compared with the soluble fraction, although the tacticity of polymer was not investigated in detail.

In a previous paper we reported on the polymerizations of methyl α -ethyl- and α -*n*-propylacrylate by *n*-BuLi, where the dependence of the polymer tacticities on the polymerization temperature was found to be greatly different from that in the polymerization of methyl methacrylate (MMA).

In this work the polymerization of MPhA was carried out by *n*-BuLi and other initiators in various solvents, and unusual dependence of the stereoregularity of the polymer was found on the polymerization conditions.

EXPERIMENTAL

Materials

MPhA was obtained by the reaction of formaldehyde and dimethyl oxalyl phenylacetate, which was prepared from methyl phenylacetate, dimethyl oxalate, and sodium methoxide, according to the procedure of Ames and Davey.⁴ The crude product was fractionally distilled under reduced nitrogen pressure: bp $59.5\text{--}60.5$ (2 mm); n_D^{25} 1.5380. The NMR spectrum (5.0-% CCl_4 solution) showed peaks at 3.72 ppm (singlet, 3.00H) assigned to the methoxyl methyl protons, 5.78 ppm and 6.25 ppm (two doublets, 1.90H) assigned to the methylene protons and about 7.25 ppm (multiplet, 5.10H) assigned to the phenyl protons. The monomer was stirred and

redistilled over calcium hydride under high vacuum just before use.

Toluene and toluene- d_6 were purified and dried in the usual manner⁵ and were distilled over calcium hydride. Before use they were mixed with a small amount of *n*-BuLi in toluene and redistilled under high vacuum.

Tetrahydrofuran(THF) was refluxed and distilled over calcium hydride, and was redistilled over lithium aluminum hydride under high vacuum. 2-Methyltetrahydrofuran, 1,2-dimethoxyethane and diethyl ether were similarly purified as above.

Pyridine and methanol were purified as usual⁵ and redistilled under high vacuum after being dried by molecular-sieves type 4A at 0°C.

Nitrobenzene- d_5 was obtained commercially and used without further purification.

n-BuLi was prepared in *n*-heptane, toluene or toluene- d_6 according to Ziegler's method from *n*-butyl chloride and metallic lithium under argon atmosphere.⁶ The concentration was measured by means of the double titration method.⁷

Phenylsodium was prepared in *n*-heptane from metallic sodium and chlorobenzene under nitrogen atmosphere at room temperature.⁸

Diisobutylaluminum diphenylamide, (*iso*-Bu)₂AlNPh₂ was prepared by the reaction of triisobutyl aluminum and diphenylamine in toluene at 90°C and used as a toluene solution.^{9,10}

Phenylmagnesium bromide(PhMgBr) was prepared from phenyl bromide and magnesium in diethyl ether and the ether was replaced with toluene by distillation.

Ethylaluminum dichloride and sodium dispersion were commercially obtained and used as a toluene solution and a dispersion in *n*-hexane, respectively.

Nitrogen and argon were purified by passing them through a column packed with the molecular sieves 4A cooled at -78°C.

Polymerization

A glass ampoule equipped with a three-way stopcock was evacuated and dried by blowing with a gas burner flame, and was filled with dry nitrogen. Then the solvent and the monomer were introduced into the ampoule with a

hypodermic syringe. To the monomer solution cooled at a given temperature, the catalyst solution was added by a syringe to initiate the polymerization and the ampoule was immediately sealed off.

After the desired reaction time polymerization was stopped by adding a small amount of methanol and the polymer obtained was precipitated by pouring the reaction mixture into a large amount of methanol. After standing it overnight, the polymer was collected by filtration, washed thoroughly with methanol and dried *in vacuo* at about 50°C.

In the polymerization carried out with the addition of a small amount of methanol, a given amount of methanol in toluene was introduced into the solution of *n*-BuLi with stirring at -78°C and allowed to react for 10 min. Then the polymerization was initiated by the slow addition of the monomer solution in toluene.

Measurements

The NMR spectrum of polymer was taken with a JEOL 100-MHz spectrometer (JNM-4H-100) on the solution in nitrobenzene- d_5 at 150°C using hexamethyldisilane as an internal standard. The reaction of methanol and *n*-BuLi was studied in toluene- d_6 using a 60-MHz NMR spectrometer (JNM-C60HL). The chemical shift in toluene- d_6 was referred to the signal of C₆D₆CD₂H contained in the solvent.

The ¹³C NMR spectrum was taken at 22.5°C on a JEOL C60HL spectrometer with a 15.09-MHz RF unit using the neat liquid in an 8 mmϕ sample tube. The ¹³C-¹H decoupling technique was employed. Chemical shifts were referred to the carbon disulfide used as an external standard, showing the high field shift as a positive value. The precisions were within ±0.1 ppm.

The solution viscosity of the polymer was determined in toluene at 30.0±0.02°C using a Ubbelohde-type viscometer.

Differential scanning calorimetric analyses of the polymers were carried out on a Rigaku Denki calorimeter, Model 8001 SL/C, at a heating rate of 10°C/min using the aluminum sample pans with lids. Aluminum oxide was used as a reference.

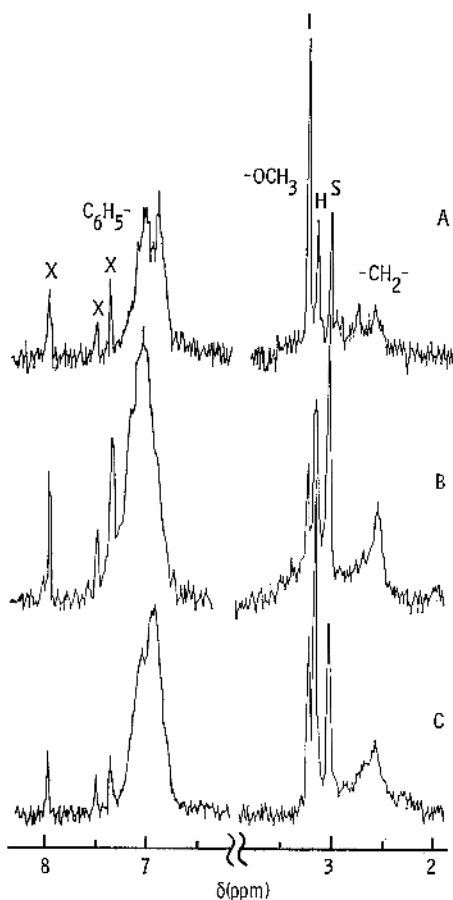


Figure 1. NMR spectra of PMPPhAs in nitrobenzene- d_6 at 150°C: A, prepared by n -BuLi in toluene at -78°C . B, prepared by $(\text{iso-Bu})_2\text{AlNPh}_2$ in toluene at -78°C . C, Prepared by n -BuLi in 1,2-dimethoxyethane at -40°C . The peaks labelled X are due to the phenyl protons of nitrobenzene.

RESULTS

NMR Spectrum and Tacticity of PMPPhA

In Figure 1 are shown the spectra of three samples of PMPPhA. Polymer A was obtained in toluene by n -BuLi at -78°C , polymer B in toluene by $(\text{iso-Bu})_2\text{AlNPh}_2$ at -78°C and polymer C in 1,2-dimethoxyethane by n -BuLi at -40°C . All the spectra consisted of three groups of signals corresponding to phenyl, methoxyl methyl, and β -methylene protons with increasing magnetic field, although the last two

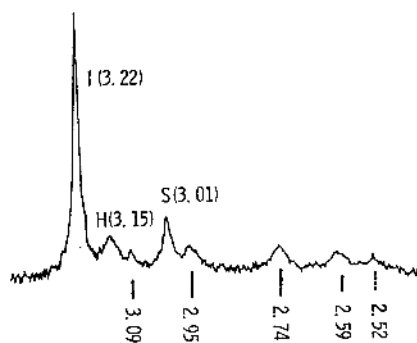


Figure 2. NMR spectrum of isotactic PMPPhA obtained in toluene by n -BuLi at -78°C with a small amount of methanol ($\text{CH}_3\text{OH}/n\text{-BuLi}=0.83$) (Slow sweep of methoxyl methyl and methylene resonances): —, meso methylene resonance; ----, racemic methylene resonance.

signal groups overlapped each other to some extent. The resonance due to the methoxyl protons split into three peaks at 3.01, 3.15, and 3.22 ppm. In polymer A the intensity of the peak at 3.22 ppm was the strongest of the three. The polymer prepared in toluene by n -BuLi with a small amount of methanol ($\text{CH}_3\text{OH}/n\text{-BuLi}=0.83$) at -78°C gave a spectrum in which the peak at 3.22 ppm was very intense as shown in Figure 2. The β -methylene resonances consisted of a typical AB quartet at 2.59, 2.74, 2.95, and 3.09 ppm and a small singlet at 2.52 ppm. The quartet is considered to be attributed to meso-methylene protons and the small singlet to racemic ones.¹¹ These results indicate that the peak at 3.22 ppm can be assigned to the methoxyl methyl protons in isotactic configuration. On the other hand, in the spectrum of polymer B the peak at 3.01 ppm was the most intense methoxyl methyl resonance and the absorption due to the racemic methylene protons at 2.52 ppm was strongest among the methylene resonances. The catalyst $(\text{iso-Bu})_2\text{AlNPh}_2$ was reported to give syndiotactic polymers in the polymerizations of methyl, ethyl, n -butyl, and diphenylmethyl methacrylates and of methyl α -ethylacrylate in toluene at low temperature.^{2,9,10,12} Therefore, the peak at 3.01 ppm can be assigned to the methoxyl methyl protons in syndiotactic triads and, accordingly, the peak at 3.15 ppm to those in heterotactic triads. The spectrum

of polymer C shows the polymer being rich in heterotactic configuration. The fractions of tactic triads in the polymers obtained were determined by the intensity measurements of three methoxyl peaks as above.

The resonances of phenyl protons were slightly

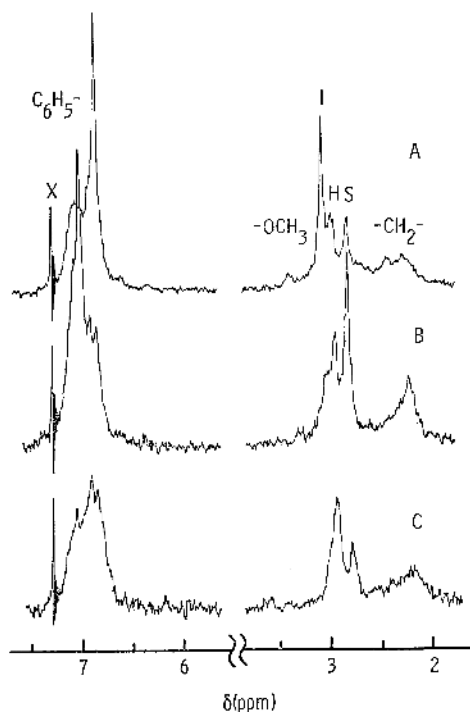


Figure 3. NMP spectra of PMPHAs in chloroform- d_1 at 60°C. The symbols, A, B, and C denote the same meanings as those in Figure 1. The peak labelled X is due to the proton of chloroform contained in the solvent.

different among the spectra of these three polymers in their fine splittings. When the spectra were measured in chloroform- d_1 , the resolutions of these resonances were so enhanced that the differences became clearer (Figure 3). On the contrary, the resolutions of methoxyl proton signals were poorer in the spectra taken in chloroform- d_1 and the resonances of isotactic and heterotactic triads were not resolved into each peak in the spectrum of polymer C. The separation of the three methoxyl proton resonances was also not sufficient either in benzene or toluene.

Polymerizations by *n*-BuLi in Toluene at Various Temperatures

The polymerization was carried out in toluene by *n*-BuLi at $-78 \sim 30^\circ\text{C}$. The results are shown in Table I. The yield of the polymer was highest at -45°C . It decreased with an increase in the temperature, and no polymer was obtained above 0°C . The solution viscosity of the polymer decreased with increasing the polymerization temperature.

The polymer obtained at -78°C was rich in isotacticity. By increasing the polymerization temperature the fraction of isotactic triads (*I*) decreased in association with the increases in the fractions of heterotactic (*H*) and syndiotactic triads (*S*). The proportion *I*:*H*:*S* of the polymer obtained above -45°C was close to 1:2:1, suggesting that the stereoregulation in the propagation step was random.

Even if the polymerization was initiated at 0°C , if the reaction mixture was then brought to -78°C , the yield, the solution viscosity, and

Table I. Polymerization of MPhA in toluene by *n*-BuLi at various temperatures^a

No.	Polymerization		Yield, %	Tacticity, %			$4I/S/H^2$	<i>I</i> / <i>S</i>	η_{sp}/c , dl/g
	Temp, °C	Time, hr		<i>I</i>	<i>H</i>	<i>S</i>			
1	-78	24	31.6	56.2	25.1	18.7	6.67	3.00	0.128
3	-45	24	40.0	29.2	47.0	23.8	1.26	1.23	0.092
21	-30	120	13.8	21.6	52.3	26.1	0.83	0.83	0.050
17	-20	118	1.3	19.1	49.8	31.1	0.96	0.61	—
4	0	195	0	—	—	—	—	—	—
5	30	195	0	—	—	—	—	—	—
16 ^b	0 → -78 ^b	24	40.9	59.0	20.6	20.4	11.3	2.89	0.111

^a Monomer, 13.6 mmol; toluene, 7 ml; *n*-BuLi, 0.65 mmol.

^b Polymerization was carried out at 0°C for 1 hr and then at -78°C for 24 hr.

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Table II. Polymerization of MPhA by *n*-BuLi in various solvents for 24 hr at -78°C ^a

No.	Solvent	Yield, %	Tacticity, %			$4IS/H^2$	η_{sp}/c dl/g,
			<i>I</i>	<i>H</i>	<i>S</i>		
1	Toluene	31.6	56.2	25.1	18.7	6.62	0.128
6	THF	56.8	25.9	49.7	24.4	1.02	0.043
7 ^b	Toluene-THF	62.6	24.1	50.6	25.3	0.95	0.040
19	2-Me-THF ^c	42.9	24.4	51.6	24.0	0.88	0.063
15 ^{a, f}	$\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$	43.9	20.4	52.8	26.8	0.78	0.268
16 ^e	$(\text{CH}_3\text{CH}_2)_2\text{O}$	25.5	29.1	47.7	23.2	1.18	0.048
9 ^{e, f}	Pyridine	5.2	20.9	51.3	27.8	0.89	-

^a Monomer, 13.6 mmol; solvent, 7 ml; *n*-BuLi, 0.65 mmol.

^b Toluene, 3.5 ml; THF, 3.5 ml.

^c 2-Methyltetrahydrofuran.

^d *n*-BuLi, 1.36 mmol.

^e Polymn. time, 219 hr.

^f Polymn. temp, -40°C .

the tacticity of the polymer were closely similar to those in the polymerization carried out at -78°C thoroughly from the beginning (Table I). This indicates that the ceiling temperature of this monomer lies between 0 and -20°C .

Polymerization by *n*-BuLi in Various Solvents

The results of the polymerization by *n*-BuLi in various solvents are summarized in Table II. The polymerization in THF at -78°C gave the polymer in good yield, although the molecular weight was fairly low. The tacticity of the polymer was close to random, since the value $4IS/H^2$ was equal to unity and the proportion $I:H:S \approx 1:2:1$. The polymerization carried out in other ethers or in a mixture of toluene and THF gave nearly the same results. The polymerization in pyridine gave a polymer in low yield.

Effect of Methanol on the Polymerization by *n*-BuLi at -78°C

The effect of a small amount of methanol on the polymerization was investigated. The results are illustrated in Figure 4. The yield and the solution viscosity of the polymer first increased with increasing the ratio of methanol to *n*-BuLi. They reached maxima at the ratio of 0.83 and then decreased rapidly. Similar change was observed in the fraction of isotactic triads. The polymer obtained at $\text{CH}_3\text{OH}/n\text{-BuLi} = 0.83$ had highest isotacticity (68.4% in triads).

The reaction of methanol and *n*-BuLi was

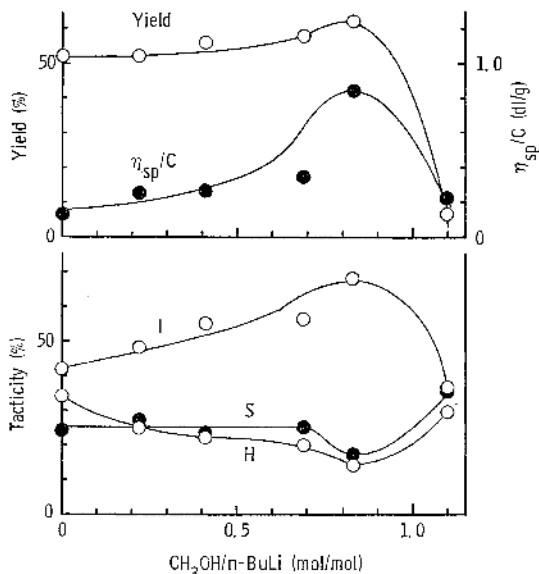


Figure 4. Effect of methanol on the polymerization of MPhA in toluene by *n*-BuLi at -78°C for 24 hr: monomer, 13.6 mmol; *n*-BuLi, 0.65 mmol; total volume, 10 ml.

investigated by NMR spectroscopy in the absence of the monomer. A solution of methanol in toluene- d_8 was mixed with an *n*-BuLi solution in an NMR sample tube at -78°C . The concentration of *n*-BuLi was raised to about three times that in the polymerization reaction, and the spectrum of the reaction mixture was measured after 30 min at -78°C .

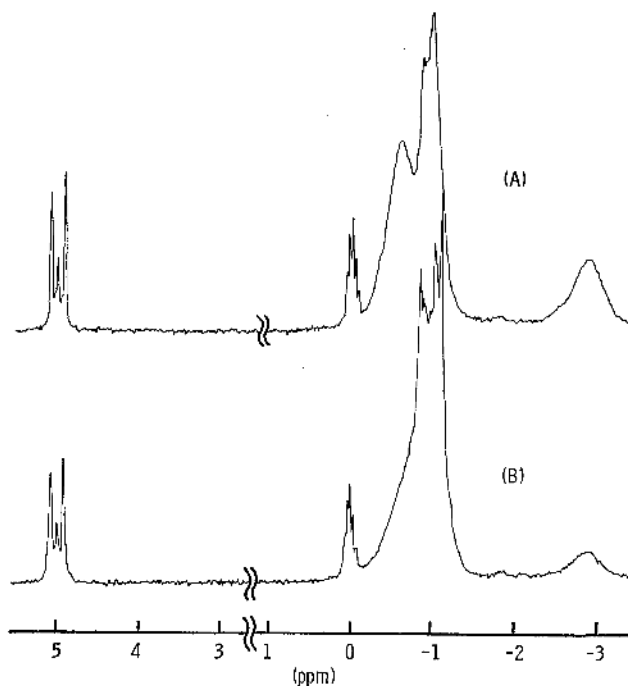


Figure 5. NMR spectra of (A) *n*-BuLi and (B) the reaction mixture of methanol and *n*-BuLi ($\text{CH}_3\text{OH}/n\text{-BuLi}=0.5$) in toluene- d_8 at -78°C .

In Figure 5 are shown the spectra of *n*-BuLi solution in toluene- d_8 and of the reaction mixture of methanol and *n*-BuLi ($\text{CH}_3\text{OH}/n\text{-BuLi}=0.5$). The spectrum of *n*-BuLi in toluene- d_8 consists of three signal groups at -2.88 , -1.03 , and -0.61 ppm, which correspond to the protons of methylene group adjacent to lithium atom, the methyl protons and the protons of other two methylene groups, respectively. In the spectrum of the reaction mixture the relative intensity of methylene resonance at -2.88 ppm decreased and a new singlet appeared at -1.13 ppm overlapping with the methyl resonance of *n*-BuLi. This singlet peak must be due to the methyl protons of lithium methoxide produced.

The amount of *n*-BuLi remaining in the reaction mixture was determined by the measurement of relative intensity of the methylene resonance at -2.88 ppm to the resonance at about 5.0 ppm due to the phenyl protons of toluene contained in the solvent toluene- d_8 . The results are shown in Table III. The amount of residual *n*-BuLi decreased with an increase in the ratio of methanol to *n*-BuLi. However, even

Table III. Reaction of methanol and *n*-BuLi in toluene- d_8 ^a

$\text{CH}_3\text{OH}/n\text{-BuLi}$, mol/mol	Unreacted <i>n</i> -BuLi, %
0.25	77.0
0.50	58.5
1.00	32.0
1.50	0.0

^a Initial amount of *n*-BuLi, 0.185 mmol; the volume of the reaction mixture, 0.5 ml.

in the equimolar reaction mixture 31% of *n*-BuLi remained unreacted under the reaction conditions described above. The amount of *n*-BuLi became zero at $\text{CH}_3\text{OH}/n\text{-BuLi}=1.5$.

Polymerization by Various Catalysts

The polymerization was carried out in toluene by various catalysts. The results are summarized in Table IV. Phenylsodium and sodium dispersion gave no polymer at 0°C . The syndiotacticity of the polymer prepared by $(i\text{-}so\text{-Bu})_2\text{AlNPh}_2$ was 48% in triads. The polymerization by PhMgBr as well as EtAlCl_2 gave a polymer rich in

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 Table IV. Polymerization of MPhA in toluene by various catalysts^a

No.	Catalyst	Polymerization		Yield, %	Tacticity, %			4IS/H ²
		Temp, °C	Time, hr		I	H	S	
1	<i>n</i> -BuLi	-78	24	31.6	56.2	25.1	18.7	6.62
12	PhNa	0	146	0	—	—	—	—
13	Na sand	0	146	0	—	—	—	—
11	(<i>iso</i> -Bu) ₂ AlNPh ₂	-78	120	4.8	20.4	32.0	47.6	3.80
18	PhMgBr	30	96	1.0	32.7	41.7	25.6	1.93
20	EtAlCl ₂ ^b	-78	73	1.1	32.0	36.3	31.7	3.09
10 ^c	AIBN	60	529	0.3	21	50	29	0.98

^a Monomer, 13.6 mmol; catalyst, 0.65 mmol; toluene 7 ml.

^b 0.58 mmol.

^c Bulk polymerization; AIBN, 0.13 mmol.

heterotactic triads in low yield. It is noteworthy that the polymerization of this acrylate monomer was initiated by EtAlCl₂, which is considered as a cationic initiator, although the mechanism of the initiation was not certain. The radical polymerization by AIBN gave a polymer having nearly random tacticity in very low yield.

 Reaction of MPhA and *n*-BuLi at 25°C

The reaction of MPhA and *n*-BuLi was briefly investigated at 25°C by NMR spectroscopy. A mixture of MPhA and *n*-BuLi (3:1 mol/mol) was allowed to react at 25°C for 48 hr in toluene-*d*₈ in an NMR sample tube and the reaction mixture was subjected to an NMR

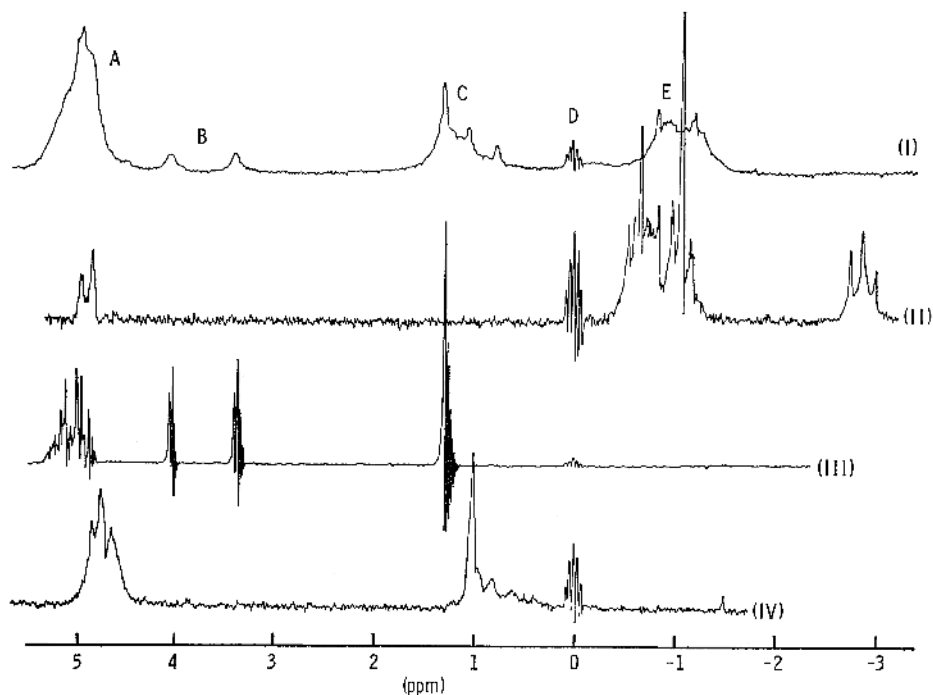
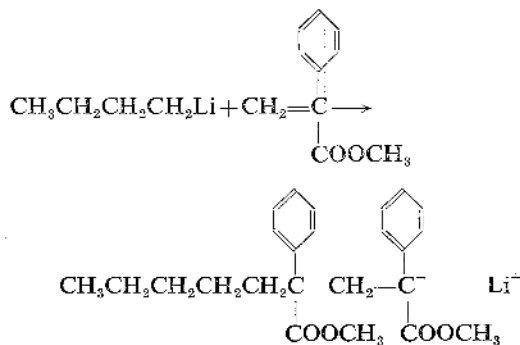


Figure 6. NMR spectra of toluene-*d*₈ solution of (I) the reaction mixture of MPhA and *n*-BuLi (3/1 mol/mol), (II) *n*-BuLi and (III) MPhA at 25°C, and (IV) that of isotactic PMPhA at 100°C.

measurement at 25°C. The spectrum is given in Figure 6, together with the spectra of *n*-BuLi(II), MPhA(III) and PMPPhA rich in isotacticity(IV), each of which was dissolved in toluene-*d*₈.

In the spectrum of the reaction mixture(I) there are five groups of rather broad signals as follows: A, at about 5.0; B, 4.1 and 3.4; C, 1.8~0.1; D, 0.0; E, -0.1~-1.8 ppm. The resonance at -2.88 ppm in spectrum II disappeared in spectrum I. As stated previously it corresponds to the methylene protons adjacent to the lithium in *n*-BuLi. The signals A correspond to the protons of phenyl groups in the MPhA, the reaction product and a small amount of toluene contained in toluene-*d*₈, and the signals D are responsible for the methyl protons of the last. The signals B are due to the vinyl protons of MPhA. While the intensities of the signals, A and D, must be constant during the reaction, the reaction resulted in the decrease in the signals B to 34% of the original, indicating that the main product at 25°C was the dimer anion.



The protons of pentyl group in the anion may resonate at the position of signals E, and those of another methylene and two methoxyl methyl groups at the position of the signal group C. The resonance of the methoxyl methyl protons in the unreacted MPhA appeared at 1.32 ppm. The relative intensities of B, C, and E, 1.0:5.6:5.5, were in good agreement with the calculated ratio for an equimolar mixture of MPhA and the dimer anion 1.0:5.5:5.5. The prolonged reaction caused broadening of the signals, but gave almost no effect on the relative intensities of the signals. The broadening of the signals may indicate that the dimer anion aggregates through

the lithium with the elapse of time. The splittings of the signals of the methoxyl methyl protons in the dimer anion may be caused by the presence of stereoisomers.

It has been reported that lithium methoxide was formed during the polymerization of methyl methacrylate (MMA) in toluene by *n*-BuLi.¹³ However, the formation of methoxide seemed not to occur in the reaction of *n*-BuLi and MPhA, since the intensity of the absorption at -1.13 characteristic of methyl protons in lithium methoxide did not increase during the reaction.

DSC Analysis of the Polymer

The differential scanning calorimetric thermograms of PMPPhAs are shown in Figure 7. Isotactic and heterotactic PMPPhAs had a glass transition temperature* (*T*_g) at 124 and 118°C, and began to decompose at about 241 and 265°C, respectively. The *T*_g of some isotactic poly(α -alkylacrylates) and polymethacrylates obtained from DSC thermograms are listed in Table V. The bulkier the α -alkyl substituent

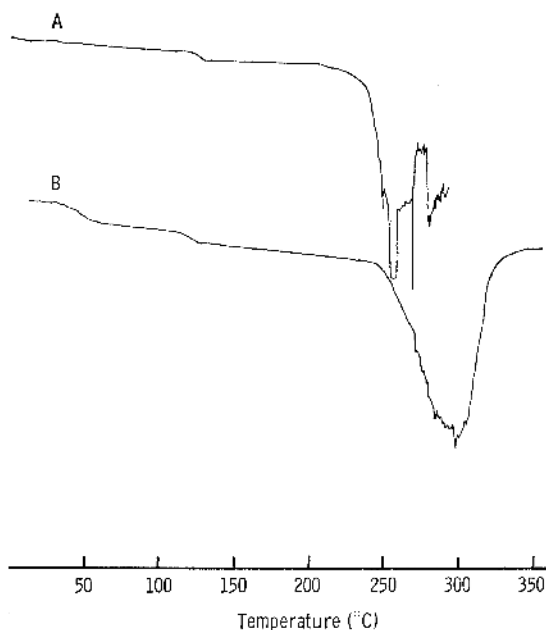


Figure 7. DSC thermograms of (A) isotactic and (B) heterotactic PMPPhAs.

* Kraus¹⁴ reported that the *T*_g of PMPPhA was 110°C by dilatometric measurements, although the tacticity of the polymer was not described.

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Table V. Glass transition temperatures of isotactic polyacrylates by DSC analysis

(A)	$\begin{array}{c} R_1 \\ \\ -CH_2-C- \\ \\ COOCH_3 \end{array}$				
R_1	CH_3^a	C_2H_5	$n-C_3H_7$	C_6H_5	
$T_g, ^\circ C$	45	55	65	124	
(B)	$\begin{array}{c} CH_3 \\ \\ -CH_2-C- \\ \\ COOR_2 \end{array}$				
R_2	CH_3^a	$CH_2C_6H_5$	$CH(C_6H_5)_2$	$C(C_6H_5)_3$	
$T_g, ^\circ C$	45	48	103	148	

^a W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *J. Polym. Sci.*, **46**, 317 (1960).

or the ester group, the higher the T_g of the polymer.

DISCUSSION

Stereoregulation in the Polymerization

In previous works^{2,15} we investigated the temperature dependences of the polymer tacticities in the polymerizations of MMA, and methyl α -ethylacrylate and methyl α -*n*-propylacrylate by *n*-BuLi in toluene. In Table VI the tacticities of these polyacrylates prepared at $-78^\circ C$ are shown together with that of PMPHA. The isotacticity decreases in the order of PMMA, poly(methyl α -ethylacrylate), poly(methyl α -*n*-propylacrylate) and PMPHA, suggesting that the bulky α -substituent makes unfavorable an isotactic propagation in the stereoregulation.

Table VI. Tacticity of poly(methyl α -substituted acrylate) prepared by *n*-BuLi in toluene at $-78^\circ C$

α -Substituent	Tacticity, %		
	<i>I</i>	<i>H</i>	<i>S</i>
CH_3	73.2	17.2	9.6
C_2H_5	69.5	10.8	19.5
$n-C_3H_7$	62.5	35.7	1.8
C_6H_5	56.2	25.1	18.7

The isotacticities of poly(methyl α -ethylacrylate) and poly(methyl α -*n*-propylacrylate) obtained in toluene by *n*-BuLi were strongly increased with an increase in the polymerization temperature, compared with an only slight increase in the isotacticity of PMMA. On the contrary, in the case of PMPHA the isotacticity was greatly decreased with increasing polymerization temperature. The values of $4IS/H^2$ and $I/S^{16,17}$ also decreased with an increase in the polymerization temperature and became about unity above $-45^\circ C$ (Table I), indicating that the probability of isotactic placement of monomer units became equal to that of syndiotactic one during the chain propagation.¹¹ The *random polymer* was also obtained by *n*-BuLi in polar solvent such as THF at low temperatures as well as by radical initiation.

In the polymerization of MPhA by *n*-BuLi the bulky phenyl group in α -position may loosen the interaction between the anionic chain end and the lithium counterion, and the chain end may be close to a free propagating species at higher temperature even in a nonpolar solvent as well as in a polar solvent.

The formation of the *random polymer* under these conditions indicates that the steric requirements of the phenyl and carbomethoxy groups at the α -position of the monomer are nearly equal in the stereoregulating step and their effects contribute equally to the controlling mechanism for the addition mode of an incoming monomer. The steric effect, of course, must involve a true "size" effect and an electrostatic one. In these cases the growing end of the polymer may behave similarly to a free propagating species regardless of the solvent and the catalyst used.

In the polymerization of MMA by alkyl-lithium it was found that the attack of anions on the carbonyl group produced lithium methoxide, which affected the stereoregulation in the propagating step.^{8,18} However, in the reaction of MPhA and *n*-BuLi at $25^\circ C$, about 30 – $40^\circ C$ higher than the ceiling temperature of this monomer, *n*-BuLi used was completely consumed in the formation of the dimer anion and no formation of the methoxide was observed. On the other hand, the addition of methanol to the polymerization system in toluene

gave the highest yield, isotacticity, and molecular weight of the polymer at $\text{CH}_3\text{OH}/n\text{-BuLi} = 0.83$, where lithium methoxide might affect the propagating species.

$(i\text{-iso-Bu})_2\text{AlNPh}_2^{9,10}$ and PhMgBr^{19} are known to form syndiotactic and isotactic polymers, respectively, in the polymerization of MMA in toluene. However, the polymers of MPhA prepared by these catalysts could not have distinct stereoregularities, but seemed rather heterotactic. It is considered that if the stereoregulation by these catalysts is controlled by a coordinated anionic mechanism,^{20,21} in the polymerization of MPhA the bulky phenyl group on the α -position makes the coordination of the monomer unfavorable, resulting in the low reactivity of this monomer and in the low stereoregularity of the polymer. Similar results have been reported on the polymerization of methacrylic esters having large ester groups.¹²

Reactivity of MPhA

Chikanishi and Tsuruta reported that the anionic polymerization of α -substituted acrylic ester produced a high polymer in fairly good yield at low temperature, if the substituent is n -alkyl or phenyl, but the monomer having a secondary alkyl group as substituent did not give any polymer insoluble in methanol.¹ They explained the fairly high reactivity of MPhA in terms of the polar character of the phenyl groups.²²

In order to get further information on the reactivity of acrylic ester in anionic polymerization the β -carbon resonance of the vinyl double bond was measured on some monomers. The results are listed in Table VII. The β -carbon of MPhA resonated at a lower field than that of MMA, indicating the lower π -electron density on the β -carbon.^{23,24} This

suggests that the electron-withdrawing effect of the phenyl group in MPhA overcomes its steric effect and enhances the reactivity of this acrylate monomer in anionic polymerization. On the other hand, the π -electron density of β -carbon increases in the order of α -methylacrylate, α -ethylacrylate, and α -isopropylacrylate, suggesting that the reactivities of the last two acrylates are reduced not only by the steric hindrance but by the electron-repelling power of the alkyl group.

Glass Transition Temperature of PMPPhA

PMPPhA represents a structural link between PMMA and polystyrene. Therefore it is of interest to note the physical properties of PMPPhA in comparison with those of PMMA and polystyrene. The T_g of isotactic PMPPhA was considerably higher than not only those of isotactic poly(methyl α -alkylacrylate)s but also that of isotactic polystyrene (100°C),²⁵ as expected by the bulkiness and the low flexibility of the phenyl group directly attached to the backbone of polyacrylate. The same sort of behaviour of the phenyl group can be observed in the series of polymers such as methyl methacrylate, benzyl methacrylate, diphenylmethyl methacrylate, and trityl methacrylate (Table V), although the phenyl groups are distant from the polymer backbone.

Solvent Effect on NMR Spectrum of PMPPhA

The separation between the three methoxy resonances in the NMR spectrum corresponding to tactic triads was clearer in nitrobenzene- d_5 than in chloroform- d_1 , and the reverse trend was observed in the resonances of the α -phenyl protons. Similar differences²⁶ were reported between the spectra of PMMA measured in benzene and in chloroform, and were considered to be attributed to the ring current of the benzene molecule and the slight difference in the orientation of the solvent with respect to the three tactic forms of the polymer.

In the chloroform- d_1 solution of PMPPhA the solvent molecule may preferentially orient to the phenyl ring of the polymer by a hydrogen-bond-like interaction between the deuteron in the chloroform and the π -electrons in the aromatic ring. The interaction may occur in different ways with three tactic forms of the

Table VII. ^{13}C chemical shift of β -carbon of vinyl group in methyl α -substituted acrylates

Substituent	Chemical shift, ppm
CH_3	68.6
C_2H_5	70.5
$i\text{-C}_3\text{H}_7$	72.0
C_6H_5	66.7

polymer. On the other hand, in the solution in nitrobenzene- d_6 the solvent molecule may orient in the vicinity of the methoxyl group in such a way that the aromatic ring of the solvent lies as far as possible from the π -electron systems of the phenyl ring and the carbonyl oxygen in the polymer. This orientation is probably facilitated by the dipole—dipole interaction between the polar molecule of nitrobenzene and the methoxyl group to result in the clear separation of the three methoxyl signals. No enhancement in resolution of the methoxyl resonance observed in toluene or benzene may be caused by the lack of this dipole—dipole interaction. Similar solvent effect of the nitrobenzene was observed for the polymers of methyl α -ethylacrylate and α -*n*-propylacrylate.²⁷

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