

Syndiotactic-Specific Polymerization of Methacrylates by Tertiary Phosphine-Triethylaluminum

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ABSTRACT: Polymerization of MMA with $R_3P-R'_3Al$ in toluene at low temperatures was reinvestigated and was found to give highly syndiotactic PMMA. Among the initiators examined Ph_3P-Et_3Al gave the PMMA with highest syndiotacticity and the polymerization at $-93^\circ C$ yielded PMMA with *rr* content of 95%. PMMAs prepared with Et_3P-Et_3Al and Ph_3P-Et_3Al contained the structural unit comprised of the phosphine components at the chain end as evidenced by ^{31}P and 1H NMR analyses. The results clearly indicate that R_3P takes an important role in the initiation process, though R_3P alone does not polymerize MMA. Methacrylic acid esters of primary and secondary alcohols were also polymerized by these initiators to give highly syndiotactic polymers. Block and random copolymers of MMA with several methacrylates were also obtained. The effect of syndiotacticity on the glass transition temperature (T_g) of PMMA was examined and T_g for 100% syndiotactic PMMA with infinite molecular weight was estimated to be $141^\circ C$.

KEY WORDS Stereospecific Polymerization / Tacticity / Poly(methyl methacrylate) / Polymethacrylate / Trialkylaluminum / Phosphine / Anionic Polymerization / Block Copolymer / Glass Transition Temperature /

Highly syndiotactic poly(methyl methacrylate) (PMMA) has high glass transition temperature (T_g) and is expected to be used as optical materials having high thermostability. PMMAs with syndiotacticity in triad over 90% have been prepared by the polymerizations with Ziegler catalysts,^{1,2} aluminum amide,^{3,4} magnesium amide,⁵ Grignard reagents,⁶⁻⁸ and organocalcium compound.^{9,10} Syndiotactic PMMA with narrow molecular weight distribution (MWD) can be prepared by the living polymerization with bulky alkyl lithium initiators such as 1,1-diphenylhexyllithium in tetrahydrofuran (THF).¹¹⁻¹³ However, the syndiotacticity in triad of the PMMA does usually not exceed around 85%.

Recently, it was found that $t-C_4H_9Li$ gave highly syndiotactic (over 90% in triad) poly-

(methacrylate)s with narrow MWD in toluene at low temperatures in the presence of trialkylaluminums such as triethylaluminum.^{14,15} Polymerization by $t-C_4H_9Li$ alone gave the isotactic polymers with broad MWD and initiator efficiency was low. These results indicate that alkylaluminum dissociates the aggregate of $t-C_4H_9Li$ into monomeric species, leading to high initiator efficiency, and changes of the properties of the propagating species from isotactic-specific to syndiotactic-specific.^{14,15}

In 1960, Murahashi and his coworkers reported that the mixture of triphenylphosphine (Ph_3P) and triethylaluminum (Et_3Al) initiates the polymerization of methyl methacrylate (MMA).¹⁶ Later, Ikeda and his coworkers¹⁷ reported that the Al-C bond of

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Et₃Al is activated in the presence of Lewis base, such as 2,2'-bipyridine and Ph₃P, enough to initiate the polymerization of MMA. In the course of survey for syndiotactic polymerization of methacrylates we realized that most of the initiators containing aluminum compounds initiate syndiotactic-specific polymerization, indicating that aluminum compounds play an important role in syndiotactic-specific polymerization of methacrylates.¹⁸ The idea prompted us to reinvestigate the polymerization of MMA with R₃P-Et₃Al in toluene at low temperatures. The polymerization was found to proceed in a living manner to give highly syndiotactic polymer although the initiator efficiency was less than unity. The preliminary results were reported previously.¹⁹ The present paper describes the detailed study of the polymerization system and its utilization to the preparation of highly syndiotactic block and random copolymers of methacrylates. Tacticity dependence of glass transition temperature of PMMA is also discussed.

EXPERIMENTAL

Methacrylate monomers were purified in usual manner, dried over calcium dihydride (CaH₂) and vacuum-distilled just before use. Et₃Al was obtained commercially and used as a heptane solution. Triethylphosphine (Et₃P) was used as a toluene solution. Commercially obtained Ph₃P and tricyclohexylphosphine were purified by recrystallization from hexane and the purified phosphines were used as toluene solutions. Toluene and heptane were purified in usual manner, dried over metallic sodium and distilled. The purified solvents were mixed with a small amount of *n*-butyllithium to remove a trace amount of water and vacuum distilled just before use. THF was refluxed under nitrogen over CaH₂, distilled into the flask containing LiAlH₄, refluxed over the LiAlH₄, and distilled again into the flask containing LiAlH₄. The THF was vacuum-distilled just before use.

Polymerization was carried out in a glass ampoule filled with dried nitrogen. After the prescribed period of time the reaction was terminated with a small amount of methanol. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The precipitate was collected by filtration, washed with hexane and dried under vacuum at room temperature. Block copolymerization was carried out in a three-necked flask equipped with a mechanical stirrer.

For tacticity determination, *t*-butyl ester groups of poly(*t*-butyl methacrylate) (poly(*t*-BMA)) and block copolymer of MMA and *t*-butyl methacrylate (*t*-BMA) were selectively hydrolyzed in a mixture of benzene and methanol (3/2 vol/vol) containing 1.0 v/v% of concentrated hydrochloric acid (12 *N*) under reflux for 2 days. Complete elimination of the *t*-butyl group was confirmed by ¹H NMR spectroscopy. The spectra also indicated that the content of MMA in the block copolymer did not change from the original copolymer and thus the ester groups of MMA were not hydrolyzed during this procedure. Tacticity of the homopolymer was determined from ¹H NMR spectra of PMMA derived from poly(methacrylic acid) by methylation with diazomethane.²⁰ Tacticity of the poly(methacrylic acid) block and PMMA block in the block copolymer could be determined from the corresponding carbonyl carbon NMR signals.²¹

¹H and ¹³C NMR spectra were measured on a JEOL JNM-MH100, JEOL JNM-FX100, JEOL JNM GSX-270, or JEOL JNM GX-500 spectrometer using tetramethylsilane as an internal standard. ³¹P NMR spectra were measured on a JEOL JNM-FX100 spectrometer at 40.3 MHz and the chemical shift was referred to Ph₃P in CDCl₃ (−5.6 ppm).

Number-average molecular weights (\bar{M}_n) were measured on a Hitachi 117 vapor pressure osmometer in toluene at 60.0°C or on a JASCO FLC-A10 GPC chromatograph equipped with Shodex GPC columns A-80M (50 cm × 2) using

THF as an eluent. The chromatogram was calibrated against standard polystyrenes.

RESULTS AND DISCUSSION

Polymerization of MMA

Polymerizations of MMA with Et₃Al and several trialkylphosphines (R₃P) were carried out in toluene for 24 h at low temperatures. The results are summarized in Table I. Under these polymerization conditions, R₃P or Et₃Al alone did not initiate the polymerization of MMA, although Furukawa *et al.* reported that Et₃P reacts with MMA to give low molecular weight product at 20°C.²² All the polymerizations in toluene at –78°C gave syndiotactic PMMAs in 100% yields. Polymerization in THF gave no polymer at –78°C. Et₃Al–triphenylphosphine oxide initiator did not give the polymer. Ph₃P–Et₃Al initiator gave higher molecular weight polymer than Et₃P–Et₃Al, indicating the lower initiator efficiency of Ph₃P–Et₃Al system. Syndiotacticity of the polymer was higher in the polymerizations with

Ph₃P–Et₃Al than in those with Et₃P–Et₃Al, and increased with a decrease in the polymerization temperature as in the other syndiotactic-specific polymerization of methacrylates.^{14,15} The syndiotacticity of the PMMA prepared by Ph₃P–Et₃Al at –93°C was 95% in triad.

The polymerizations with Ph₃P–Et₃Al were carried out at several ratios of Al/P as shown in Table I. With an increase in the ratio of Al/P, molecular weight of the PMMA decreased and initiator efficiency increased, indicating that Et₃Al plays an important role to promote the initiation reaction.

Changes of the yields and molecular weights in the course of the polymerization by Et₃P–Et₃Al in toluene at –78°C are shown in Figures 1 and 2, respectively. Molecular weight of the polymer increased with polymerization time, while the initiator efficiency calculated from the yield and molecular weight increased with time (Figure 2). The results suggest that the initiation reaction is slow and the number of propagating species increases gradually in

Table I. Polymerization of MMA with R₃P–Et₃Al in toluene at –78°C for 24 h^a

R ₃ P	Et ₃ Al	Yield %	\bar{M}_n^b	\bar{M}_w^b	Tacticity/%			Initiator efficiency ^c
	R ₃ P			\bar{M}_n	<i>mm</i>	<i>mr</i>	<i>rr</i>	
Et ₃ P	1	100	4600	2.17	4	15	81	0.87
Et ₃ P ^d	2	100	7800	1.74	4	14	82	1.03
Et ₃ P ^e	1	42	2600	1.78	5	6	89	0.65
Et ₃ P ^f	1	0	—	—	—	—	—	—
Ph ₃ P	1	100	74700	1.57	0	11	89	0.05
Ph ₃ P	2	100	36800	1.44	0	9	91	0.11
Ph ₃ P	4	100	20100	1.75	0	12	88	0.20
Ph ₃ P	10	100	7500	2.48	0	14	86	0.53
Ph ₃ P ^e	1	70	19400	2.03	0	5	95	0.14
<i>c</i> Hex ₃ P ^g	2	100	7800	1.56	0	19	81	0.51
Ph ₃ P=O	2	0	—	—	—	—	—	—

^a MMA, 10 mmol; R₃P, 0.25 mmol; toluene, 40 ml.

^b Determined by GPC.

^c Calculated from the amounts of R₃P used and of polymer molecule formed which was determined from the yield and \bar{M}_n value.

^d Et₃P, 0.125 mmol.

^e Polymerization at –93°C.

^f Polymerization in tetrahydrofuran.

^g Tricyclohexylphosphine.

the course of polymerization. The increase of the molecular weight of the polymer despite of the increasing amount of the propagating species during the polymerization strongly indicates that the polymerization has the living character.

PMMA's prepared with $\text{Et}_3\text{P-Et}_3\text{Al}$ and $\text{Ph}_3\text{P-Et}_3\text{Al}$ showed ^{31}P NMR signals at 15.3 and 12.7 ppm, respectively, which may be due to the phosphine fragments introduced at the

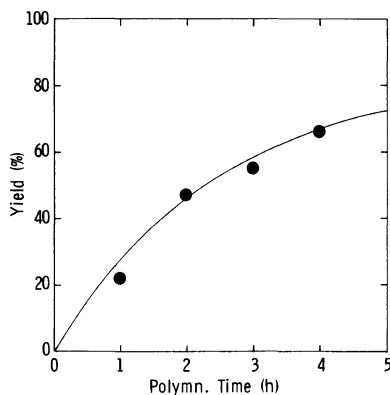


Figure 1. Time-conversion plots for the polymerization of MMA in toluene at -78°C with $\text{Et}_3\text{P-Et}_3\text{Al}$. (MMA, 20 mmol; Et_3P , 0.20 mmol; toluene, 20 ml.)

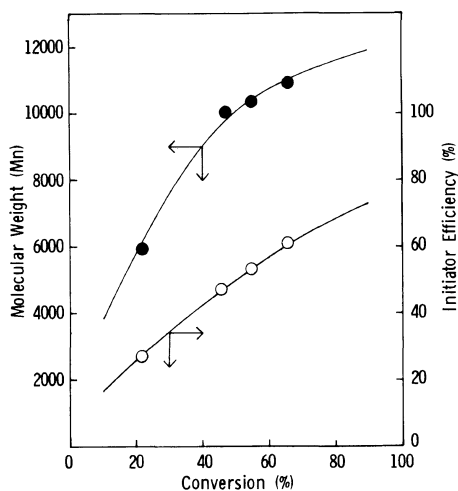


Figure 2. Time dependence of M_n and initiator efficiency in the polymerization of MMA with $\text{Et}_3\text{P-Et}_3\text{Al}$ in toluene at -78°C . (MMA, 20 mmol; Et_3P , 0.20 mmol; toluene, 20 ml.)

end of the polymer molecules. In order to obtain further information on this point, totally deuterated MMA (MMA-d_8) was polymerized with the undeuterated $\text{Et}_3\text{P-Et}_3\text{Al}$ initiator. The resulting poly(MMA-d_8) showed ^1H NMR

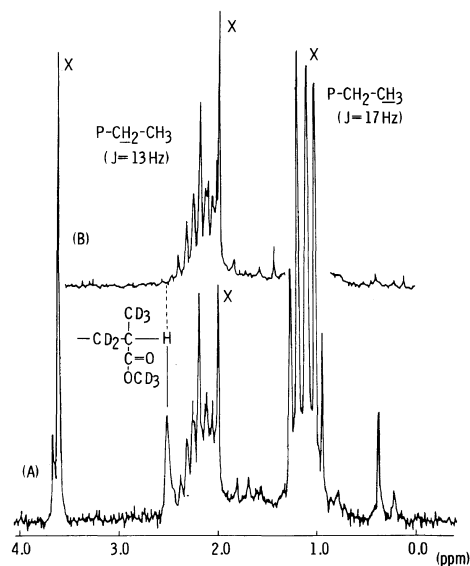


Figure 3. 100 MHz ^1H NMR spectra of poly(MMA-d_8) prepared with $\text{Et}_3\text{P-Et}_3\text{Al}$ (1/2) in toluene at -78°C (nitrobenzene- d_5 at 110°C). The polymerization was terminated with CH_3OH (A) or CD_3OD (B) (MMA-d_8 , 5 mmol; Et_3P , 0.125 mmol; toluene, 5 ml.). X represents the signals due to the remaining protons in the monomer units.

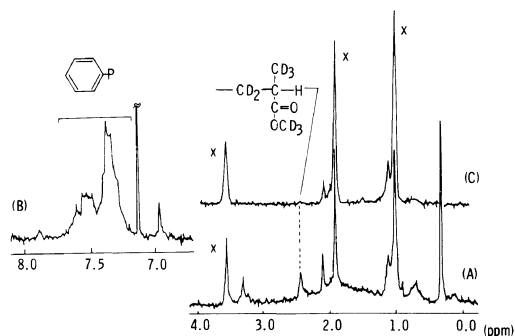
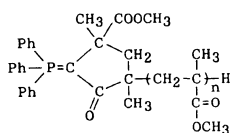


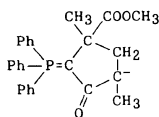
Figure 4. 100 MHz ^1H NMR spectra of poly(MMA-d_8) prepared with $\text{Ph}_3\text{P-Et}_3\text{Al}$ (1/2) in toluene at -78°C . ((A) and (C), nitrobenzene- d_5 at 110°C ; (B), nitromethane- d_3 at 100°C .) The polymerizations were terminated with CH_3OH (A) and (B) or CD_3OD (C) (MMA-d_8 , 5 mmol; Ph_3P , 0.25 mmol; toluene, 5 ml.). X represent the signals due to the remaining protons in the monomer units.

signals at 1.05 and 2.10 ppm due to the methyl and methylene protons of ethyl groups with J_{P-H} couplings ($J_{P-CH_2} = 13$ Hz, $J_{P-C-CH_3} = 17$ Hz) and J_{H-H} coupling ($J_{H-H} = 7.4$ Hz) (Figure 3A). The polymer formed with Ph₃P-Et₃Al showed phenyl signals at 7.2–7.7 ppm but no signals due to the protons of ethyl group which would be introduced from Et₃Al into the polymer chain (Figure 4). The singlet signals at 2.45 ppm was assigned to the methine protons at the right ends of the polymer chains and disappeared when the polymerization was terminated with methanol-*d*₄ (Figures 3B and 4C). The intensity measurements indicated that the polymer obtained with Et₃P-Et₃Al contained 2.85 ethyl (0.95 Et₃P-) and 0.95 methine protons per polymer molecule, and those obtained with Ph₃P-Et₃Al 2.90 phenyl (0.97 Ph₃P-) groups and 1.03 methine protons per polymer molecules. These results clearly indicate that the Et₃P and Ph₃P participate in the initiation process of these polymerizations and the propagation reaction proceeds in a living manner.

Dimer, trimer and tetramer of the following structures ([1] $n=0, 1$ and 2) have been isolated from the products of the oligomerization of MMA with Ph₃P-Et₃Al in toluene at -78°C .²³



[1]



[2]

The dimer showed ³¹P NMR signals at 11.7 and 12.1 ppm due to the *cis* and *trans* isomers, respectively. These chemical shift values are close to that of the polymer obtained with Ph₃P-Et₃Al, indicating that the polymerization was initiated with the dimer anion of the structure [2] and the polymer obtained had the phosphorane structure at the left end of the chain as shown above. The dimer anion is considered to form through the addition of

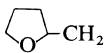
Ph₃P onto C=C double bond of MMA activated by coordination of Et₃Al to the carbonyl group, although the true mechanism of formation is not clear at present. Elimination of two hydrogen atoms from two MMA units is necessary for formation of the dimer anion of structure [2], and this may occur by the aid of Et₃Al to form Et₂Al⁺ which acts as a counter cation of the dimer anion. Activation of methacrylate by aluminum compound was demonstrated recently by Kanetaka *et al.*, who showed that enamines can initiate polymerization of methacrylate activated with methylaluminum bis(2,6-di-*t*-butylphenoxide).²⁴

As mentioned above the initiator efficiencies are less than unity and tacticity of the polymer depends on the structure of phosphine. The unreacted phosphine in the polymerization mixture may coordinate with Et₂Al⁺ and affect the stereospecificity of the propagating species.

Polymerization of Various Methacrylates

Polymerization of various methacrylates other than MMA with Et₃P-Et₃Al and Ph₃P-Et₃Al were carried out in toluene at -78°C for 24 h. The results are shown in Table II. All the methacrylates except for *t*-butyl methacrylate (*t*-BMA) gave highly syndiotactic polymers in high yields. MWD's of the polymers were fairly narrow as compared with that of PMMA prepared under the same conditions, and became narrower as the ester group became bulkier. Initiator efficiency in the polymerization with Ph₃P-Et₃Al was lower than that with Et₃P-Et₃Al as in the case of the polymerization of MMA. *t*-BMA gave heterotactic polymer with Et₃P-Et₃Al in lower yield and no polymer with Ph₃P-Et₃Al. The bulky ester group prevents syndiotactic propagation, which inevitably results in the formation of heterotactic polymer, since the system is syndiotactic-specific and isotactic propagation is also prevented.²⁴ Bulkiness of *t*-butyl group weakens the coordination of Et₃Al to carbonyl group of *t*-BMA and the monomer is less activated. This is the reason why *t*-BMA can

Table II. Polymerization of various methacrylates other than MMA with R₃P–Et₃Al(1/2) in toluene at –78°C for 24 h^a

Ester group	R ₃ P	Yield	\bar{M}_n^b	\bar{M}_w^b	Tacticity/%		
		%		\bar{M}_n	<i>mm</i>	<i>mr</i>	<i>rr</i>
C ₂ H ₅	Et ₃ P	100	6700	1.64	1	11	88
	Ph ₃ P	100	126000	1.40	0	8	92
iso-C ₃ H ₇	Et ₃ P	100	36100	1.25	1	14	85
	Ph ₃ P	100	195000	1.29	0	11	89
<i>t</i> -C ₄ H ₉	Et ₃ P	60	89500	1.16	6	57	37
	Ph ₃ P	0	—	—	—	—	—
CH ₂ =CH–CH ₂	Et ₃ P	100	13400	1.51	0	12	88
	Ph ₃ P	100	55000	1.43	0	10	90
C ₆ H ₅ –CH ₂	Et ₃ P	100	25000	1.33	0	11	89
	Ph ₃ P	100	66500	1.64	0	10	90
CH ₃ OCH ₂ CH ₂	Et ₃ P	100	12800	1.28	3	10	87
	Ph ₃ P	100	54400	1.21	1	8	91
 -CH ₂	Et ₃ P	100	126000	1.29	0	12	88
	Ph ₃ P	0	—	—	—	—	—

^a Monomer, 10 mmol; R₃P, 0.25 mmol; toluene, 10 ml.^b Determined by GPC.**Table III.** Copolymerization of MMA with alkyl methacrylate with Ph₃P–Et₃Al(1/2) in toluene at –78°C for 24 h^a

Comonomer	MMA	Yield	\bar{M}_n^b	\bar{M}_w^b	Tacticity/%		
	mol%	%		\bar{M}_n	<i>mm</i>	<i>mr</i>	<i>rr</i>
EMA	46	100	87000	1.29	0	10	90
iso-PMA	50	100	143000	1.35	0	18	82
<i>t</i> -BMA	50	100	305000	1.20	{ 0 ^c 8 ^d	{ 18 ^c 48 ^d	{ 82 ^c 44 ^d
Allyl MA	50	100	44600	1.67	0	11	89

^a [Total monomer]₀/[Ph₃P]₀ = 40; monomer, 10 mmol; toluene, 10 ml.^b Determined by GPC.^c MMA unit centered triad determined by ¹³C NMR.^d Methacrylic acid unit centered triad determined by ¹³C NMR after selective hydrolysis of *t*-BMA units.

not be polymerized with less basic Ph₃P. As described in the following section, *t*-BMA can be copolymerized with MMA by Ph₃P–Et₃Al. Inability of *t*-BMA to homopolymerize with Ph₃P–Et₃Al should be ascribed to non-occurrence of initiation reaction.

The Et₃P–Et₃Al and Ph₃P–Et₃Al initiators gave no polymers in THF (*cf.* Table I). Polymerizations of methacrylates having ester groups with ether oxygen were examined and

the results are included in Table II. 2-Methoxyethyl methacrylate gave highly syndiotactic polymers in quantitative yields with both initiators. 2-Tetrahydrofurfuryl methacrylate gave highly syndiotactic polymer in 100% yield with Et₃P–Et₃Al but no polymer with Ph₃P–Et₃Al. Glycidyl methacrylate was not polymerized with both initiators. Et₃Al strongly coordinates with more basic oxygen of tetrahydrofurfuryl or glycidyl group and this

results in the decrease in the extent of activation of C=C double bond of the monomers with Et₃Al.

Copolymerization of MMA with Other Methacrylates

Copolymerization of MMA with ethyl

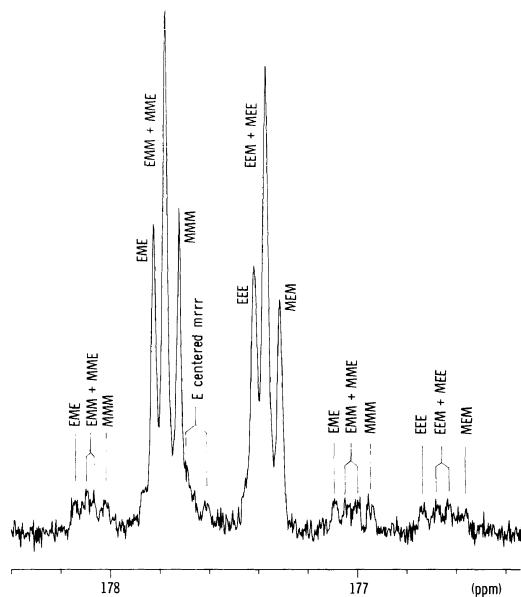


Figure 5. 125 MHz ¹³C NMR spectrum of carbonyl carbons in poly(MMA-*co*-EMA) prepared with Ph₃P–Et₃Al (1/2) in toluene at –78°C (CDCl₃ at 55°C). M and E denote the MMA and EMA units, respectively.

(EMA), isopropyl, *t*-butyl and allyl methacrylates were carried out with Ph₃P–Et₃Al in toluene at –78°C for 24 h at the initial monomer ratio of unity (Table III). Copolymers with fairly narrow MWD's were obtained in 100% yield, although the cosyndiotacticity decreased with increasing bulkiness of the ester group. It should be noted that *t*-BMA, which can not be polymerized with Ph₃P–Et₃Al, gave a copolymer with MMA quantitatively. Cotacticity of the copolymer was much less regular than those of the other copolymers.

Figure 5 shows carbonyl region of ¹³C NMR spectrum of the poly(MMA-*co*-EMA) (MMA : EMA = 1 : 1). The signals of MMA and EMA units are sensitive to the configurational pentad sequences and each configuration-sensitive signal also showed further splittings due to the triad monomer sequences.¹⁶ The signal assignment was made by the comparison of the spectra of the copolymers with different comonomer compositions and the two homopolymers, and was indicated in the Figure. Peak intensities for the MMA and EMA centered triads in *rrrr* configurational pentad, MMM : MME : EME and MEM : MEE : EEE (M, MMA unit; E, EMA unit), are nearly 1 : 2 : 1, indicating the random distribution of monomeric units.

Table IV. Block copolymerization of MMA and EMA by Et₃P–Et₃Al(1/2) in toluene at –78°C^a

M ₁	M ₂	Yield %	\bar{M}_b^b	\bar{M}_w^c	MMA content mol%	Tacticity ^d /%					
						PMMA block			Poly(EMA) block		
						<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>
MMA ^c	—	100	8030	2.34	100	3	15	82	—	—	—
MMA	EMA	100	11100	1.38	49.6	0	14	86	0	12	88
EMA ^c	—	100	10800	1.64	100	—	—	—	1	11	88
EMA	MMA	100	16500	1.40	51.3	0	12	88	0	10	90

^a M₁ = M₂ = 50 mmol; Et₃P, 1.25 mmol; toluene, 100 ml; time, 24 h + 24 h.

^b Determined by VPO.

^c Determined by GPC.

^d Tacticities of copolymer and homopolymer were determined from ¹³C and ¹H NMR spectra, respectively.

^e Monomer, 10 mmol; Et₃P, 0.25 mmol; toluene, 10 ml; time, 24 h.

Block Copolymerization of MMA and EMA or t-BMA

As described above, the propagating species in the polymerizations of MMA with $\text{Et}_3\text{P-Et}_3\text{Al}$ and $\text{Ph}_3\text{P-Et}_3\text{Al}$ have living character although the initiation reaction is not fast. Thus, the preparation of PMMA-*block*-PEMA

was tried by adding EMA to the polymerization mixture of MMA with $\text{Et}_3\text{P-Et}_3\text{Al}$ after all the monomer was consumed (Table IV). The polymer obtained had higher molecular weight than the PMMA obtained from the control experiment, and showed carbonyl carbon NMR spectrum very similar to the superimposed spectrum of those for highly syndiotactic PMMA and PEMA (Figure 6). The peak assignments shown in the figure were made by the comparison with the those for the homopolymers. Only the difference is that the weak signals due to MME and EEM triads exist in the spectrum of the polymer from the block copolymerization. These results are the clear indication that the block copolymer of PMMA-*block*-PEMA is formed. As described previously, in the polymerization with $\text{Et}_3\text{P-Et}_3\text{Al}$ or $\text{Ph}_3\text{P-Et}_3\text{Al}$ initiation reaction is slow and occurs in the course of the polymerization as well. The fact that the M_n of the block copolymer is lower than the calculated value is due to the formation of PEMA homopolymer during the block copolymerization. Similarly, a syndiotactic block copolymer of PEMA and PMMA was prepared and characterized as shown in Table IV. Triad tacticities of PMMA and PEMA blocks were estimated from the carbonyl carbon NMR signals based on the assignments shown in

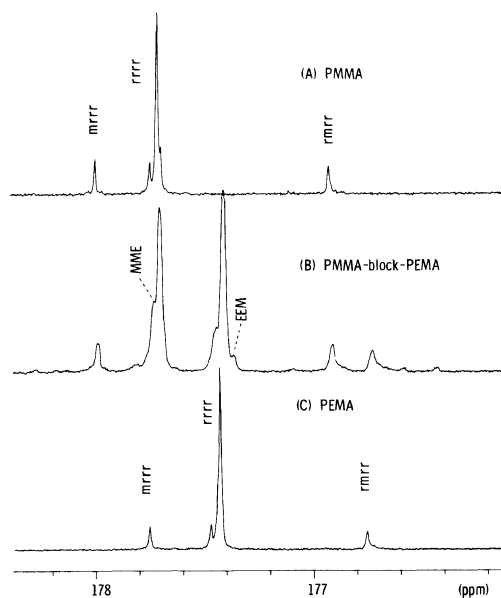


Figure 6. 125 MHz ^{13}C NMR spectrum of carbonyl carbons in PMMA (A), PMMA-*block*-poly(EMA) (B), and poly(EMA) (C) prepared with $\text{Et}_3\text{P-Et}_3\text{Al}$ (1/2) in toluene at -78°C (CDCl_3 at 55°C). M and E denote the MMA and EMA units, respectively.

Table V. Block copolymerization of MMA and *t*-BMA with $\text{Ph}_3\text{P-Et}_3\text{Al}$ (1/2) in toluene at -78°C ^a

M_1	M_2	M_1 Ph ₃ P	Time h	Yield %	\bar{M}_n^b	\bar{M}_w^b \bar{M}_n	N^c 10^{-3} mmol	Tacticity/% ^d					
								PMMA block			Poly(<i>t</i> -BMA) block		
								<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>
MMA	—	40	48	100	118500	1.73	8.4	0	10	90	—	—	—
MMA	<i>t</i> -BMA	40	96	100	295800	2.66	8.1	0	12	88	2	39	59
MMA	—	20	48	100	35260	2.05	28.4	0	10	90	—	—	—
MMA	<i>t</i> -BMA	20	96	100	91050	2.43	26.4	0	12	88	2	45	53

^a Toluene, 20 ml; M_1 , 10 mmol; M_2 , 9.9 mmol.

^b Determined by GPC.

^c Number of polymer molecules.

^d Determined by ^{13}C NMR of hydrolyzed polymers.

Figure 6B.

As reported briefly,²⁵ pure block copolymer of MMA and *t*-BMA could be prepared with Ph₃P–Et₃Al inspite of the presence of the unreacted initiator due to the low initiator efficiency. Block copolymerization was carried out with Ph₃P–Et₃Al in toluene at –78°C by adding *t*-BMA to the reaction mixture of MMA after all the MMA was consumed (Table

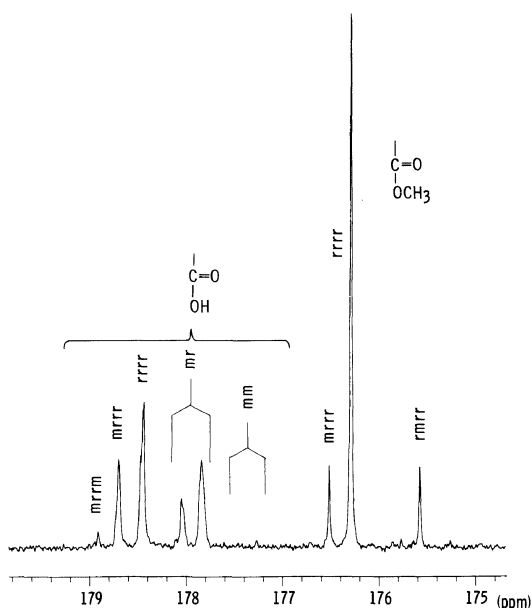


Figure 7. 67.9 MHz ¹³C NMR spectrum of carbonyl carbons in PMMA-*block*-poly(methacrylic acid) derived from PMMA-*block*-poly(*t*-butyl methacrylate) prepared with Ph₃P–Et₃Al (1/2) in toluene at –78°C (DMSO-*d*₆ at 110°C).

V). As described in the previous sections, *t*-BMA is polymerized by Ph₃P–Et₃Al but copolymerized with MMA by the same initiator. Even though appreciable amount of Ph₃P and Et₃Al remain unreacted, they could not initiate the polymerization of the second monomer, *t*-BMA, in the block copolymerization and the *t*-BMA reacts only with PMMA anions to form block copolymer. The amounts in mmol of the block copolymers were calculated from the *M_n*'s and the compositions and found to be very close to those of the PMMAs obtained in the control experiments (Table V). This is the strong indication that only the block copolymers were formed. The poly(*t*-BMA) block of the copolymer can be easily and selectively hydrolyzed to poly(methacrylic acid) block as described in the Experimental section. Thus the triad tacticities of PMMA and poly(*t*-BMA) blocks were determined from the carbonyl carbon NMR signals of the hydrolyzed copolymer, PMMA-*block*-poly(methacrylic acid). As seen in Figure 7, PMMA block is highly syndiotactic and poly(methacrylic acid) block is less stereoregular (Table V). The syndiotacticity of the poly(*t*-BMA) block is, however, higher than that of poly(*t*-BMA) prepared with Et₃P–Et₃Al (Table II). The result strongly indicates that R₃P should exist near the propagating species to affect their stereospecificities.

Table VI. *T_{g∞}* and *K* values for highly syndiotactic PMMAs^a

Initiator	Solvent	Temp	Racemo dyad/%	Number of samples	Range of <i>M_n</i>	<i>T_{g∞}</i>	<i>K</i> × 10 ⁻⁵
		°C				°C	°C
<i>m</i> -VBzMgCl ^b	THF	–98	95.8–98.2	9	4300–44900	135	1.32
Ph ₃ P–Et ₃ Al	Toluene	–93					
DPhMPLi ^c	THF	–78	89.8–91.6	6	5600–599000	128	0.99
AIBN	Bulk	60	78	4	8700–87200	123	0.76

^a PMMAs of different *M_n*'s were prepared by varying the ratio of monomer to initiator.

^b *m*-Vinylbenzylmagnesium chloride.

^c 1,1-Diphenyl-3-methylpentyllithium.

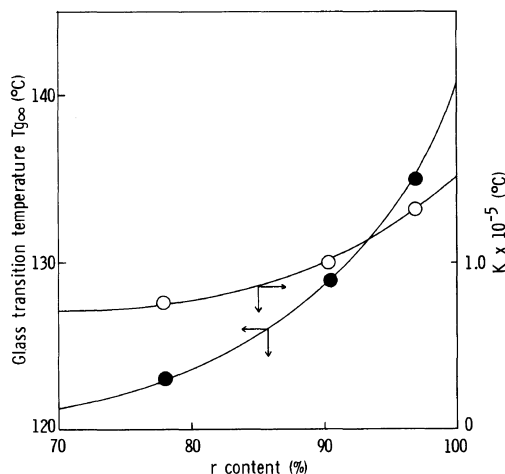


Figure 8. Tacticity dependence of glass transition temperature of PMMA with infinite molecular weight, $T_{g\infty}$, and K value in eq 1.

Tacticity Dependence of Glass Transition Temperature (T_g) for PMMA

T_g of PMMA is known to increase with an increase in the syndiotacticity and molecular weight. The T_g of PMMA with infinite molecular weight ($T_{g\infty}$) can be calculated by the following equation:

$$T_{g\infty} = T_{g\text{obsd}} + K/\bar{M}_n \quad (1)$$

K , constant; \bar{M}_n , number average molecular weight.²⁷ K values and $T_{g\infty}$'s for the PMMAs of different syndiotacticities prepared with several initiators and classified into three series, were determined using this equation, (Table VI), and are plotted against the fractions of the r dyads (Figure 8). From the Figure the expected T_g value for the completely syndiotactic PMMA ($r=100\%$) with infinite M_n was estimated to be 141°C . Thompson²⁷ estimated the $t_{g\infty}$ for completely syndiotactic PMMA to be 160°C by using the PMMAs with different \bar{M}_n 's which were prepared by γ -ray irradiation of several PMMA samples with different tacticities. The difference between these two estimations may be due to the fact that Thompson neglected the change in tacticity during the γ -irradiation. Allen *et al.*²⁸ reported

a linear correlation between T_g and fraction of meso dyad (m): $T_g(K) = 406.6 - 76.6m$, T_g for 100% syndiotactic PMMA to be 133.4°C . However, Figure 8 indicates the deviation of linearity at higher r content. The present results are derived from the T_g data for highly syndiotactic PMMA and should give more reliable data for $T_{g\infty}$ of 100% syndiotactic PMMA. It should also be noted that K value depends on tacticity as shown in Figure 8. Therefore, the prediction of T_g by eq 1 should be made after careful determination of K value.

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