Highly Isotactic and Living Polymerization of Ethyl Methacrylate with t-C$_4$H$_9$MgBr in Toluene and the Preparation of Block and Random Copolymers with High Stereoregularity

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ABSTRACT: The polymerization of ethyl methacrylate (EMA) with t-C$_4$H$_9$MgBr in toluene at low temperature gave a highly isotactic polymer as in the case of living and highly isotactic polymerization of methyl methacrylate (MMA) with t-C$_4$H$_9$MgBr. Although the molecular weight distribution (MWD) of the poly(EMA) was bimodal, both species giving higher and lower molecular weight fractions contributed to the formation of highly isotactic block copolymers with bimodal MWD, indicating the living nature of both species. The polymerization of EMA with the living anion of isotactic PMMA formed with t-C$_4$H$_9$MgBr gave a highly isotactic block copolymer with unimodal MWD. This suggests that the multiplicity of active species observed in the polymerization of EMA with t-C$_4$H$_9$MgBr was caused by the initiation of EMA with t-C$_4$H$_9$MgBr. Conventional copolymerization of EMA and MMA afforded a highly isotactic copolymer with bimodal MWD, confirming the above consideration. ^{13}C NMR spectrum of the copolymer indicated the comonomer sequence to be random. Glass transition temperatures of the isotactic and syndiotactic copolymers of EMA and MMA could be changed from 8 to 120°C by changing composition and tacticity.
    KEY WORDS   Isotactic Living Polymerization / Anionic Polymerization / Multiplicity of Active Species / Copolymer / Glass Transition Temperature / Methyl Methacrylate / Ethyl Methacrylate / ^{13}C NMR /

Many papers have been published on the stereospecific polymerization of methacrylates with various anionic initiators. Isotactic polymethacrylates are usually prepared in non-polar solvents by anionic initiators such as alkyllithium or Grignard reagent.[1,2] However, most of the polymerization reactions cannot be fully controlled owing to side reactions and multiplicity of active species, making the molecular weight distribution (MWD) of the resulting polymer broad. Recently, we found that polymerization of methyl methacrylate (MMA) with t-C$_4$H$_9$MgBr prepared in diethyl ether gave highly isotactic poly(methyl methacrylate) (PMMA) with narrow MWD in a living manner in toluene at −78°C.[3,4] Stereoregularity in the anionic polymerization of methacrylates usually depends on the structure of the ester groups. For example, in the polymerization of ethyl methacrylate (EMA) with n-C$_4$H$_9$Li in toluene at −78°C, there are at least two types of active species which give isotactic and syndiotactic-rich polymers,[5] while the polymerization of MMA under the same conditions gives isotactic-rich polymer only.

In this article, anionic polymerization of EMA by t-C$_4$H$_9$MgBr in toluene was studied in detail, especially in regard to the stereo-

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regularity of the polymer and living character of the polymerization. The copolymerization of MMA and EMA as well as the polymerization of EMA with the PMMA living anion or the polymerization of MMA with the poly-(EMA) living anion were also studied to prepare copolymers and block copolymers with high stereoregularity. The effects of tacticity and comonomer composition on glass transition temperature of the copolymers were also examined using highly stereoregular copolymers.

EXPERIMENTALS

Monomers were purified by fractional distillation, dried over calcium dihydride and vacuum-distilled just before use.

t-C_4H_9MgBr was prepared from t-C_4H_9Br and Mg in diethyl ether.[4] $(t$-$C_4H_9)_2Mg$ was prepared by adding a large amount of 1,4-dioxane to the t-C_4H_9MgBr solution. The polymerization was carried out in a glass ampoule filled with dry nitrogen. Block copolymerization was performed in a reaction vessel equipped with a mechanical stirrer. The polymerization reactions were terminated with methanol containing a small amount of HCl at the polymerization temperature. After the solvent and unreacted monomer were removed under high vacuum, the residue was dissolved in benzene. Insoluble materials were removed by centrifugation and the polymeric material was recovered by freeze-drying. When the formation of high molecular weight product ($M_n \geq 2 \times 10^4$) was expected, the polymer was recovered by precipitation from the reaction mixture with hexane, followed by filtration and drying in vacuo.

^1H and ^{13}C NMR spectra were measured on a JNM-GX500 or JNM-FX100 NMR spectrometer. In the ^1H NMR spectra of poly(EMA) and copolymer of EMA with MMA measured in $CDCl_3$ at 55°C and at 100 MHz, the methyl proton signals of ester group in EMA unit overlapped with α-methyl proton signals for the isotactic sequence. However, triad tacticity could be determined by the peak eliminated FT NMR method.[6] The chemical shift difference between the α-CH_3 proton signals for MMA and EMA units in the copolymers was so small that the average tacticity was obtained by this method. Molecular weights were determined on a Hitachi 117 vapor pressure osmometer in toluene at 60°C or a JASCO FLC-A10 GPC chromatograph equipped with Shodex GPC columns KF803 and A-80M using tetrahydrofuran as an eluent. GPC chromatogram was calibrated against standard polystyrene samples.

Glass transition temperatures were measured on a Rigaku DSC-8230 differential scanning calorimeter at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Polymerization of EMA with t-C_4H_9MgBr in Toluene

t-C_4H_9MgBr prepared in diethyl ether gives living and highly isotactic PMMA with narrow MWD in toluene at low temperature.[3,4] We found that the initiator solution contains an excess amount of $MgBr_2$, which affects the Schlenk equilibrium of the Grignard reagent:

$$2RMgX \rightleftharpoons R_2Mg + MgBr_2$$
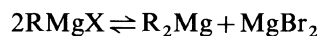
Since RMgX gives an isotactic PMMA and R_2Mg a syndiotactic one,[7,8] the ratio of Mg/t-C_4H_9– is an important factor for the formation of highly isotactic PMMA.[4]

Table I shows the results of the polymerization of EMA with t-C_4H_9MgBr of various Mg/t-C_4H_9– ratios in toluene at −78°C. The initiators with various Mg/t-C_4H_9– ratios were prepared by mixing certain amounts of t-C_4H_9MgBr (Mg/t-C_4H_9–=2.21) and $(t$-$C_4H_9)_2Mg$. The initiator with a Mg/t-C_4H_9– ratio of 0.69, which should contain a large fraction of $(t$-$C_4H_9)_2Mg$, gave syndiotactic-rich polymer and the initiators with Mg/t-C_4H_9– ratios of 1.17, 1.84, and 2.21

Table I. Polymerization of EMA in toluene at $-78°C$ for 48 h with t-C_4H_9MgBr
of various Mg/t-C_4H_9- ratios[a]

Mg/t-C_4H_9-	t-C_4H_9Mg-	Yield[d]	$M_n/10^{3c}$	$\bar{M}_w$	$\bar{M}_n/10^3$		Tacticity/%[e]		
mol/mol	mmol	%		$\bar{M}_n$	High[d]	Low[d]	mm	mr	rr
0.69	0.18	99.3	56.2	7.39	—	—	12	20	68
1.17	0.20	88.8	14.8	4.66	118	7..2	97	3	0
1.84	0.19	95.6	15.7	3.45	118	9.6	97	3	0
2.21	0.20	87.9	13.0	2.99	80	8.5	97	3	0

[a] EMA 20 mmol, toluene 10 ml.
[b] Hexane insoluble part.
[c] Determined by GPC.
[d] Molecular weights at peak maxima of higher and lower molecular weight peaks in GPC curve.
[e] Determined from ^1H NMR spectra by peak elimination method.[6]

gave highly isotactic poly(EMA)s. MWDs of the isotactic polymers were bimodal but difference between molecular weights of the higher and lower molecular weight fractions increased with decreasing Mg/ t-C_4H_9- ratio and, as a result, the M_w/M_n increased. Thus, the dependency of the stereospecificity on the Mg/t-C_4H_9- ratio of the initiator in the polymerization of EMA is very similar to that in the polymerization of MMA,[4] but the isotactic-specific active species in the polymerization of EMA is not a single type in regard to reactivity.

Temperature dependence of polymerization was examined at $0 \sim -78°C$ at a ratio of initial concentration of monomer to that of initiator, $[M]_0/[I]_0$ of 50. GPC chromatograms of the polymers formed are shown in Figure 1. Polymers formed at $0 \sim -30°C$ showed unimodal MWD but M_w/M_n increased with decreasing temperature (1.25—1.86). In this temperature range, the yields decreased with increasing temperature, indicating the occurrence of termination reactions at higher temperature. Polymers formed at and below $-40°C$ showed bimodal or trimodal MWD. All the polymers were highly isotactic ($mm \geq$ 95%), except for the polymer formed at 0°C ($mm:mr:rr = 92:6:2$). These results suggest that at lower temperatures the highly isotactic-specific active species having different re-
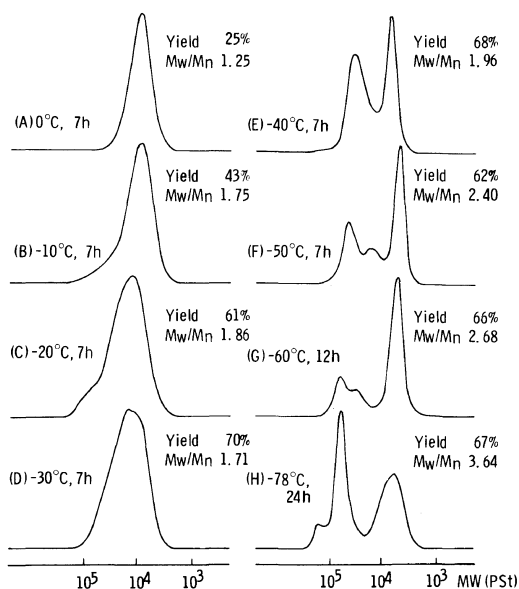
Figure 1. GPC curves of poly(EMA)s prepared with t-C_4H_9MgBr in toluene at various temperatures. EMA 10 mmol, t-C_4H_9MgBr ($[Mg^{2+}]/[t$-$C_4H_9-] = 1.30$) 0.2 mmol, toluene 5 ml.

activities propagate independently to give polymers which show distinctive GPC peaks.

The polymerization of EMA with t-C_4H_9MgBr ($[EMA]_0/[t$-$C_4H_9MgBr]_0 = 50$) was carried out at -78 and $-60°C$ for various polymerization times. Figure 2 shows the first order plots of monomer consumption for the polymerizations. The linear relations obtained indicate that the propagation rate obeys first

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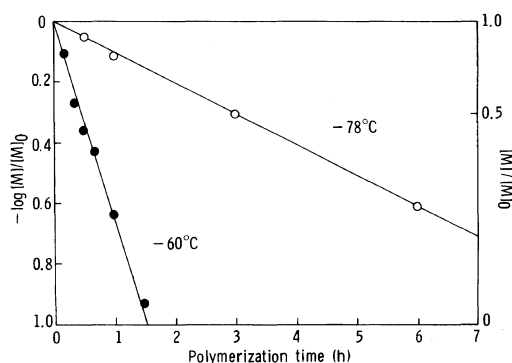
Figure 2. First order plots of monomer consumption for the polymerization of EMA with t-C_4H_9MgBr in toluene at -60 and $-78°C$. EMA 10 mmol, t-C_4H_9MgBr ($[Mg^{2+}]/[t$-C_4H_9-$] = 1.30$) 0.2 mmol, toluene 5 ml.

order kinetics, though the MWD was not unimodal and thus the active species was not single. The apparent rate constants for propagation at -78 and $-60°C$ were found to be 2.2×10^{-3} and 13.4×10^{-3} l mol^{-1} s^{-1}, respectively. The rate constant for propagation at $-78°C$ is five times as large as that for the polymerization of MMA with t-C_4H_9MgBr at the same temperature (4.3×10^{-4} l mol^{-1} s^{-1}).[4] The larger propagation rate for the polymerization of EMA could be ascribed partly to the existence of the active species which gives a higher molecular weight fraction as described below.

Figure 3 illustrates the GPC chromatograms of the polymers prepared at $-60°C$ for various polymerization times. The chromatogram of the polymer formed in the polymerization for 10 min consisted of two sharp peaks (Figure 3A). As the polymerization proceeded, the peak maxima for both fractions shifted to the higher molecular weight side, and the higher molecular weight peak further split into two peaks. The M_n's and yields of the lower and higher molecular weight fractions were estimated by the deconvolution of the chromatograms. Plots of M_n's against the yield of each fraction gave linear relations as shown in Figure 4. Though the total number of molecule estimated was slightly less than the amount of
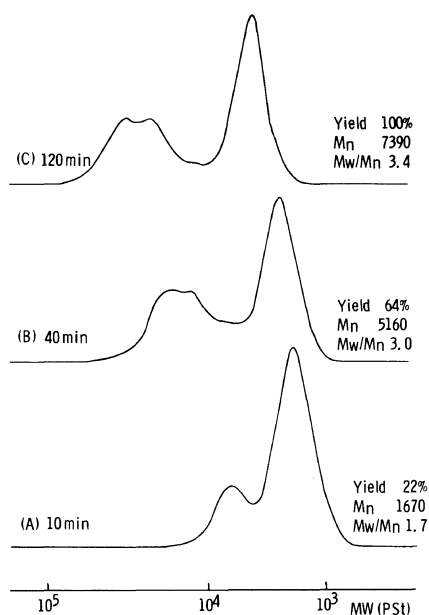
Figure 3. GPC curves of poly(EMA)'s prepared with t-C_4H_9MgBr in toluene at $-60°C$ for various times. EMA 10 mmol, t-C_4H_9MgBr ($[Mg^{2+}]/[t$-C_4H_9-$] = 1.30$) 0.2 mmol, toluene 5 ml.

initiator used, probably because the M_n's were determined by GPC, the number of polymer molecules in each fraction was almost constant during the polymerization. The number for the higher molecular weight fraction formed for 10 min was smaller than others probably due to incomplete separation in the GPC chromatogram. These results suggest that in the polymerization of EMA with t-C_4H_9MgBr in toluene at $-60°C$ there exist at least two types of propagating species which are living and highly isotactic–specific but have different activities.

The M_n's of the higher molecular weight fractions were one order larger than those of the lower molecular weight fractions both in the polymerizations at -78 and $-60°C$. Thus, one can assume that the rate constants for the propagation of the active species giving the higher molecular weight fractions (k_H) are 10 times as large as those of the species giving lower molecular weight fractions (k_L). On the
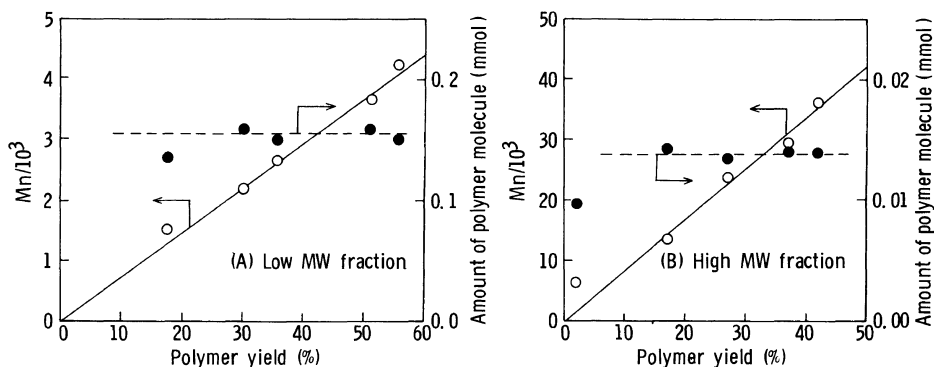
Figure 4. Changes of M_n and number of polymer molecules for higher (A) and lower (B) molecular weight fractions of poly(EMA) prepared with t-C$_4$H$_9$MgBr in toluene at $-60°$C. EMA 10 mmol, t-C$_4$H$_9$MgBr ([Mg^{2+}]/[t-C$_4$H$_9^-$] = 1.30) 0.2 mmol, toluene 5 ml.

other hand, the ratio of the numbers of polymer molecules (mol l^{-1}) in the higher (N_H) and lower molecular weight fractions (N_L) was 1 : 27 at $-78°$C and 1 : 11 at $-60°$C. Then, the average rate of polymerization R_P is written as follows using the average rate constant k:

$$R_P = k(N_L + N_H)[M] = (k_L N_L + k_H N_H)[M]$$

By using the ratio of $k_H/k_L \simeq 10$, k_L can be written as follows:

$$k_L = k(1 + N_H/N_L)/(1 + 10 \cdot N_H/N_L)$$

where N_H/N_L is 1/11 at $-60°$C and 1/27 at $-78°$C.

Then, k_L and k_H were estimated as follows;

$$k_L = 7.7 \times 10^{-3} \ (-60°C) \quad \text{and}$$
$$1.66 \times 10^{-3} \ (-78°C),$$

$$k_H = 77 \times 10^{-3} \ (-60°C) \quad \text{and}$$
$$16.6 \times 10^{-3} \ (-78°C).$$

k_L at $-78°$C is still higher than the rate constant for the polymerization of MMA under the same conditions $(4.3 \times 10^{-4} \ l \ mol^{-1} s^{-1})$.[4] Thus, the higher apparent rate constant for the polymerization of EMA than that for the polymerization of MMA is ascribable not only to the formation of highly active species in small amounts but also to the enhanced reactivity of the predominant species. Thus, the

structure of the monomer affects the rate constant for polymerization with t-C$_4$H$_9$MgBr. Although the difference in structure of the highly isotactic–specific active species giving higher and lower molecular weight fractions is not clear at present, there is the possibily that the highly active and highly isotactic–specific active species are produced.

Copolymerization of EMA with MMA

The polymrization of MMA with the living anion of poly(EMA) formed with t-C$_4$H$_9$MgBr was carried out in toluene at $-60°$C under several conditions as shown in Table II to examine the living nature of the anion. Figure 5 shows GPC curves of the isotactic block copolymers of EMA and MMA (A, C, and E) and those of the poly(EMA) formed in the control experiments (B, D, and F). The control poly(EMA) showed bimodal MWD and the $\bar{M}_w/\bar{M}_n$ values (1.43—3.01) increased as the [M]$_0$/[I]$_0$ ratio increased. Both the higher and lower molecular weight peaks in the chromatograms of the parent poly(EMA) shifted to the higher molecular weight side on block copolymerization. The $\bar{M}_n$'s and weight fractions of higher and lower molecular weight fractions were roughly estimated from the GPC curves by deconvoluting the chromatograms. The number of polymer molecules in each

Table II. M_n and numbers of polymer molecules (N) in the higher and lower molecular weight fractions of poly(EMA) and poly(EMA)-*block*-PMMA prepared with $t\text{-}C_4H_9MgBr$ in toleune at $-60°C$

| $[EMA]_0/[MMA]_0/[t\text{-}C_4H_9MgBr]_0$[a]	Yield	High MW fraction			Low MW fraction		
		$\bar{M}_n/10^{3}$ [b]	N[c]		$\bar{M}_n/10^{3}$ [b]	N[c]	
mol/mol/mol	%		mmol	%		mmol	%
20 / 0 / 1	100	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]
20 / 50 / 1	100	32.5	0.049	(5)	6.13	0.93	(95)
30 / 0 / 1	100	16.9	0.040	(4)	3.17	0.86	(96)
30 / 50 / 1	100	43.6	0.052	(5)	6.29	0.97	(95)
50 / 0 / 1	100	30.2	0.062	(6)	4.24	0.90	(94)
50 / 50 / 1	100	58.3	0.043	(5)	9.13	0.90	(95)

[a] $t\text{-}C_4H_9MgBr$ ($[Mg^{2+}]/[t\text{-}C_4H_9-]=1.30$) 1.0 mmol, $[EMA+MMA]/\text{toluene}=1.43\ \text{mol}\ l^{-1}$.
[b] Estimated from GPC curve.
[c] Number of polymer molecules in mmol and in percentage determined from M_n and amount of each fraction estimated by deconvoluting the GPC chromatogram.
[d] Peak separation in the GPC curve was not enough to estimate these values (see Figure 5F).
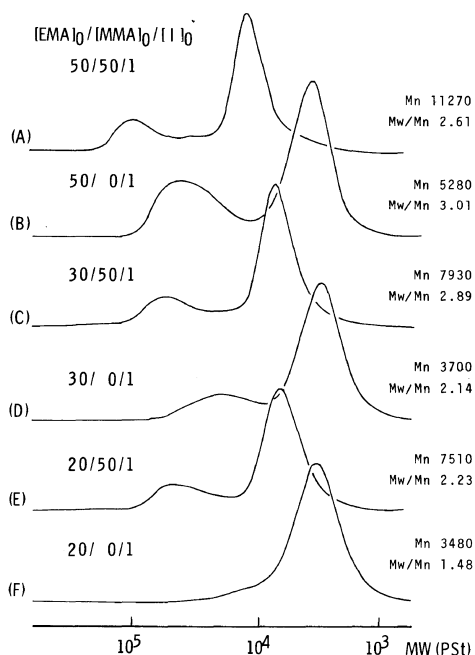
Figure 5. GPC curves of poly(EMA)-*block*-PMMA's (A), (C), and (E) and poly(EMA)'s (B), (D), and (F) prepared with $t\text{-}C_4H_9MgBr$ in toluene at $-60°C$ (*cf.* Table II).

copolymerization. Thus the living character of both higher and lower molecular weight poly(EMA) propagating species at $-60°C$ is indicated. The constant ratios of the numbers of polymer molecules in the higer and lower molecular weight fractions suggest that the number of active species giving the higher molecular weight fraction is governed mainly by the initiator itself and not by impurities contained in the monomer.

We recently developed an on-line GPC/ NMR instrument in which a 500 MHz NMR spectrometer is linked to a GPC chromatograph as a detector[9-12] and used it for analysis of the molecular weight dependence of copolymer composition in block and random copolymers of MMA and butyl methacryate.[11] GPC/NMR analysis of the block copolymer of EMA and MMA (Figure 5A) indicated that both the higher and lower molecular weight fractions contained comparable amounts of MMA and EMA units.[14] If the poly(EMA) anions giving the higher and lower molecular weight fractions add MMA at a similar rate, the content of the MMA unit in the higher molecular weight fraction should be much lower than that in the lower molecular weight

fraction determined from these data (Table II) was almost constant regardless of the $[M]_0/[I]_0$ ratio, and hardly changed on block

Table III. Preparation of isotactic PMMA-*block*-poly(EMA) with *t*-C_4H_9MgBr
in toluene at $-60°C^a$

MMA	EMA	$[M]_0/[I]_0$	Yield	$\bar{M}_n$		$\bar{M}_w{}^c$	MMA/EMA^d in polymer	Tacticity/%^{e}		
mol	mol	mol/mol	%	Obsd^b	Calcd	$\bar{M}_n$		*mm*	*mr*	*rr*
0.70	0.70	100^f	97	12500	10800	1.29	59/59	97	2	1
0.50	0.90	280	88	26900	26900	2.11	97/151	95	3	2
0.30	0.91	300	99	27200	30900	1.76	64/182	95	3	2
1.18	0.25	285	100	29700	29200	1.42	35/50/200^g	97	2	1
0.80	0.40	90^f	100	8200	9400	1.17	25/28/25^g	95	3	2

^{a} $[MMA+EMA]_0$/toluene$= 2.0$ $(mol\,l^{-1})$, $[Mg^{2+}]/[t\text{-}C_4H_9\text{-}] = 1.70$.
^{b} Determined by VPO.
^{c} Determined by GPC.
^{d} Number of monomeric units per chain determined by chemical composition and M_n data for the copolymer.
^{e} Determined from ^1H NMR spectra by peak elimination method.[6]
^{f} $[Mg^{2+}]/[t\text{-}C_4H_9\text{-}] = 2.21$.
^{g} Triblock copolymer; PMMA-*block*-poly(EMA)-*block*-PMMA.

fraction. Therefore, the results mean that the poly(EMA) anions giving the higher molecular weight fraction add much more MMA molecules than those giving the lower molecular weight one. The difference in the reactivity of the poly(EMA) anions is retained even when the anions turn into MMA anions during the propagation process of MMA. The details of the analysis of various copolymers of MMA and EMA by the GPC/NMR method will be published in the near future.

Polymerization of EMA with the living PMMA formed with *t*-C_4H_9MgBr in toluene at $-60°C$ gave isotactic PMMA-*block*-isotactic poly(EMA) whose MWD were unimodal but rather broad (Table III). The block copolymer with shorter poly(EMA) block had relatively narrow MWD. Figure 6 shows GPC chromatograms of PMMA-*block*-poly(EMA) with the $\overline{DP}$ of each block of 59 and PMMA obtained in the control experiment. The GPC curve of the block copolymer did not show any peak in the range of the elution time where the control PMMA showed its peak, indicating that all the PMMA living anions and EMA to form the block copolymer. The MWD of this block copolymer is fairly narrow in contrast to the case of poly(EMA)-*block*-PMMA
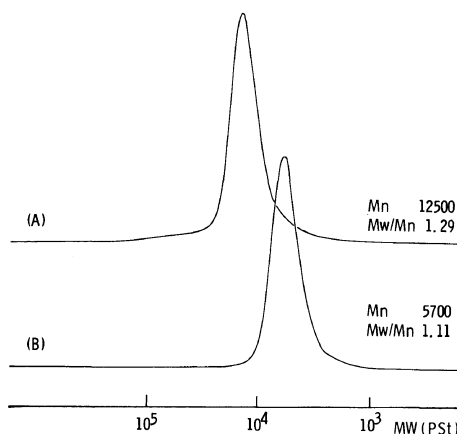
Figure 6. GPC curves of PMMA-*block*-poly(EMA) (A) and poly(EMA) (B) prepared with *t*-C_4H_9MgBr in toluene at $-60°C$. (A): MMA 0.70 mol, EMA 0.70 mol, *t*-C_4H_9MgBr ($[Mg^{2+}]/[t\text{-}C_4H_9\text{-}] = 1.74$) 14.0 mmol, toluene 700 ml. (B): MMA 10 mmol, *t*-C_4H_9MgBr ($[Mg^{2+}]/[t\text{-}C_4H_9\text{-}] = 1.74$) 0.2 mmol, toluene 5 ml.

(Figure 5A) with similar molecular weight and composition. As the poly(EMA) block length became longer, MWD of the block copolymer became broader (Table III). However, the polymerization of EMA with PMMA anion did not involve remarkable multimodal MWD differently from the homopolymerization of EMA and the polymerization of MMA with

Table IV. Preparation of isotactic poly(MMA-co-EMA) with t-C_4H_9MgBr
in toluene at $-60°C^a$

MMA	EMA	$[M]_0/[I]_0$	Yield	$\bar{M}_n$		$\bar{M}_w^c$	MMA/EMA^d	Tacticity/%^{e}		
mol	mol	mol/mol	%	Obsd^b	Calcd	$\bar{M}_n$	in polymer	mm	mr	rr
42	11	290	93	35500	27800	3.57	78/22	96	3	1
460	460	300	93	31800	29900	1.78	51/49	96	3	1
10	10	103^f	100	11300	11200	1.53	51/49	96	3	1
10	29	240	96	25700	25500	2.42	26/74	97	2	1

^{a} $[MMA+EMA]_0$/toluene$=2.0$ (moll^{-1}), $[Mg^{2+}]/[t\text{-}C_4H_9\text{-}]=2.21$.
^{b} Determined by VPO.
^{c} Determined by GPC.
^{d} Determined from ^1H NMR spectra.
^{e} Determined from ^1H NMR spectra by peak elimination method.[6]
^{f} $[Mg^{2+}]/[t\text{-}C_4H_9\text{-}]=1.74$.

poly(EMA) anion. Thus, the multiple active species observed in the homopolymerization of EMA with t-C_4H_9MgBr in toluene at low temperatures may mostly occur in the initiation process.

In a similar manner, isotactic triblock copolymers, PMMA-block-poly(EMA)-block-PMMA, with fairly narrow MWD were also obtained as shown in Table III. All the M_n values determined by VPO are close to the expected values, indicating the quantitative initiation by t-C_4H_9MgBr in these polymerizations.

Conventional copolymerization of EMA and MMA with t-C_4H_9MgBr in toluene at $-60°C$ gave highly isotactic copolymer, but its MWD was not unimodal (Figure 7). The chromatogram of the copolymer consisted of a strong narrow peak and a broad higher molecular weight peak of weak intensity. As EMA content in the initial monomer mixture increased, the amount of higher molecular weight fraction increased. These results also suggest that active species with which EMA participates in the initiation process tend to produce multiple active species. GPC/NMR analysis revealed that the compositions of the higher and lower molecular weight fractions were almost identical.[14] The copolymerization was also carried out under several conditions
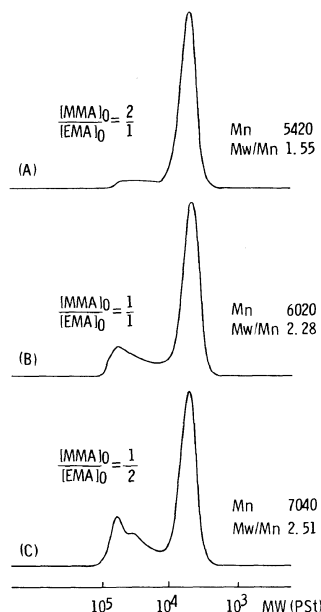

Figure 7. GPC curves of poly(MMA-co-EMA)'s prepared with t-C_4H_9MgBr in toluene at $-60°C$ for 24 h at several feed ratios. MMA$+$EMA 10 mmol, t-C_4H_9MgBr ($[Mg^{2+}]/[t\text{-}C_4H_9\text{-}]=1.30$) 0.2 mmol, toluene 5 ml.

to obtain higher molecular weight copolymers as shown in Table IV. The results include a large scale preparation. The Mn values determined by VPO were close to the expected ones, indicating high initiator efficiency in the copolymerization.

^{13}C NMR chemical shifts of carbonyl
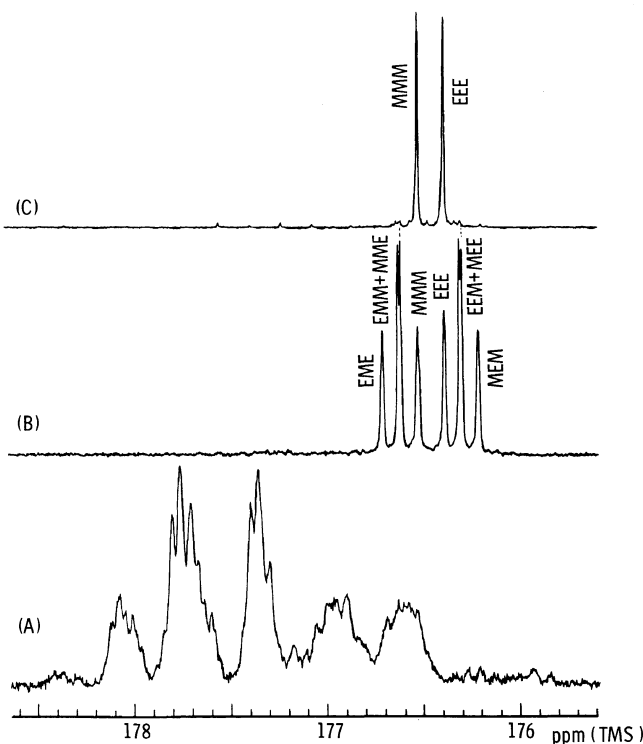
Figure 8. 125 MHz ^{13}C NMR spectra of carbonyl carbons in poly(MMA-*co*-EMA) prepared with AIBN at 60°C (A), that prepared with *t*-C$_4$H$_9$MgBr in toluene at −60°C (B) and PMMA-*block*-poly(EMA) prepared with *t*-C$_4$H$_9$MgBr in toluene at −60°C (C). M and E denote MMA and EMA units, respectively. The spectra were measured in CDCl$_3$ at 55°C.

carbons of polymethacrylates are known to be sensitive to stereochemical sequences. Pentad to heptad assignments were made for radically prepared PMMA.[13,14] The carbonyl carbon signals for the copolymer of methacrylate are sensitive both to pentad stereochemical sequences and to triad comonomer sequences. Thus, it should be hard to make assignment of the signals in regard to both tactic and comonomer sequences, especially in the case of the copolymer with low stereoregularity.

Figure 8A shows the 125 MHz ^{13}C NMR spectrum of carbonyl carbons in a radically prepared copolymer of MMA and EMA with 1:1 composition. The spectrum was much complicated due to the existence of different configurational sequences as well as different compositional sequences. The high stereo-

regularity of block and random copolymers prepared with *t*-C$_4$H$_9$MgBr made the spectrum simple and permitted us to distinguish the peak splittings due to tacticity and monomer sequence distribution. Figure 8B shows the ^{13}C NMR spectrum of highly isotactic random copolymer obtained by the polymerization of an equimolar mixture of MMA and EMA with *t*-C$_4$H$_9$MgBr in toluene at −60°C. The signals of MMA- and EMA-centered sequences in the *mmmm* configurational pentad showed splittings due to the triad monomer sequences. The peak assignments indicated in the figure were made by comparing the spectra of the isotactic copolymers with different compositions with those of both isotactic homopolymers. Small slittings observed in the peaks assigned to (MME+EMM) and (MEE+EEM) (M,

MMA unit, E, EMA unit) might be due to the effects of longer sequences or different conformations, although the reason is not clear at present. The relative peak intensities of MMA : MME + EMM : EME and EEE : EEM + MEE : MEM were 1 : 2 : 1, indicating that the distributions of both MMA- and EMA-centered triads of comonomer sequences are almost random.

Figure 8C illustrates the spectrum of PMMA-*block*-poly(EMA) prepared from the isotactic PMMA living anion at −60°C. The biblock copolymer, in which the DP's of both sequences are 59, showed two strong signals at 176.51 and 176.37 ppm with weak signals of equal intensity at 176.60 and 176.28 ppm. The first two strong signals were assigned to carbonyl carbons of the MMM and EEE triads in isotactic configuration (*mmmm*), respectively, by referring to the spectra of isotactic PMMA and poly(EMA). The latter weak signals were assigned to MME and MEE triads in the *mmmm* configuration by comparing the spectrum with that of the random copolymer. These triads should exist at the switching point of MMA and EMA sequences;

$$\cdots M\ M\ M\ \overline{M\ M\ E}\ E\ E\ E\cdots .$$

In another respect, the existence of these triads indicates that the PMMA and poly(EMA) blocks are linked together, and thus the signals permit us to distinguish the block copolymer from blend of isotactic PMMA and isotactic poly(EMA). Some other small peaks ascribable to chain end units were also observed in the spectrum. The details will be published elsewhere.

Glass Transition Temperature of Stereoregular Copolymer

Glass transition temperature (T_g) of copolymer generally varies with its composition. It is also known that T_g of polymethacrylate strongly depends on its tacticity; isotactic
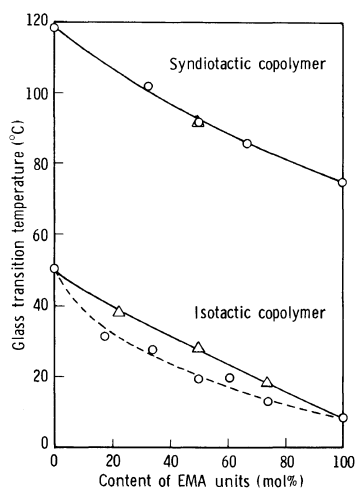

Figure 9. Glass transition temperature of isotactic and syndiotactic block and random copolymers of EMA and MMA with various compositions. ○, block copolymer; △, random copolymer.

PMMA has lower T_g than syndiotactic PMMA. Therefore, control of the stereo-regularity of the copolymer may provide another means for the control of T_g of the copolymer. Figure 9 shows T_g's of isotactic and syndiotactic block and random copolymers of MMA and EMA. The syndiotactic copolymers were prepared with t-C_4H_9Li-(n-$C_4H_9)_3Al$ as reported previously.[15] Isotactic random copolymers of MMA and EMA prepared with t-C_4H_9MgBr (*cf.* Table IV) lay between 8 and 49°C ($\bar{M}_n = 1.13$—3.55×10^4) and decreased with increase in the content of EMA units in the copolymer. The isotactic block copolymers of MMA and EMA ($\bar{M}_n = 0.82$—2.97×10^4) showed single T_g's which also decreased as EMA content increased and were slightly lower than those of the random copolymers with similar compositions. The random copolymer with a 1 : 1 composition ($\bar{M}_n = 31800$) had T_g of 29°C, while the block copolymer with the same composition ($\bar{M}_n = 12500$) showed T_g of 19°C. A 1 : 1 mixture of isotactic PMMA ($\bar{M}_n = 16400$, $T_g = 49°C$) and isotactic poly(EMA) ($\bar{M}_n = 13000$, $T_g = 8°C$) showed two T_g's of

44°C and 4°C. The single T_g of the block copolymer seems to indicate that the copolymer does not show microphase separation, probably because of too short chain length of either block to form the microphase.[16] The block copolymer of polystyrene and poly(α-methylstyrene) is known to have single T_g[17] and exhibit one-phase behavior.[18] However, Gaur and Wunderlich found that the block copolymers of higher molecular weights (400000—1060000) have two glass transitions, even thought the transitions occur in a wider temperature range than those of the corresponding homoplymers.[19] Thus, investigation on the effects of block length on glass transition of the isotactic block copolymer of PMMA and poly(EMA) is needed and the preparation of the copolymer with various molecular weights in now under way for this purpose.

T_g's of the syndiotactic random and block copolymers prepared with t-C$_4$H$_9$Li–(n-C$_4$H$_9$)$_3$Al[15] increased from 75 to 120°C with increasing MMA content. Therefore, T_g's of the copolymer could be controlled in the temperature range of 8 to 120°C by changing the tacticity and copolymer composition. The isotactic copolymers whose T_g's are around room temperature showed shape-memory ability; the copolymer sample stretched 3 times as much as the original sample in length at 60°C and shrank back immediately to the original length when warmed at 60°C.

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