

## Living and Highly Isotactic Polymerization of Methyl Methacrylate by $t\text{-C}_4\text{H}_9\text{MgBr}$ in Toluene

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**ABSTRACT:** Highly isotactic PMMAs with narrow molecular weight distribution ( $\bar{M}_w/\bar{M}_n < 1.2$ ) have been prepared by the polymerization of MMA in toluene at  $-78^\circ\text{C}$  initiated by  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in diethyl ether. The polymerization proceeded in a "living" manner, in which the initiation reaction was fast and quantitative whereas the propagation was slow. The ether solution of  $t\text{-C}_4\text{H}_9\text{MgBr}$  used as the initiator contained almost equal amounts of  $\text{MgBr}_2$  produced by an Wurtz type coupling during the preparation. It has been found from  $^1\text{H}$  NMR analyses that the excess amount of  $\text{MgBr}_2$  contributes to form the initiating species of homogeneous activity and stereospecificity. Polymerizations of MMA by  $n$ -, iso-, and  $s\text{-C}_4\text{H}_9\text{MgBr}$  were also investigated in toluene at  $-78^\circ\text{C}$ . With an increase in the bulkiness of the alkyl group the isotacticity of the polymer increased and the molecular weight distribution became narrower. The addition of  $\text{MgBr}_2$  also increased the isotacticity of the polymer. The results of block copolymerizations of MMA and  $\text{MMA-}d_8$  or ethyl methacrylate are also described.

**KEY WORDS** Methyl Methacrylate /  $t$ -Butylmagnesium Bromide / Isotactic PMMA / Tacticity / Narrow Molecular Weight Distribution / Living Polymerization / Grignard Reagent / Schlenk Equilibrium / Block Copolymerization /  $^1\text{H}$  and  $^{13}\text{C}$  NMR /

Isotactic poly(methyl methacrylate) (PMMA) is usually prepared by an anionic initiator such as alkyl lithium or Grignard reagent in a nonpolar solvent. Such a polymerization system often involves multiple active species and side reactions,<sup>1-11</sup> making the molecular weight distribution (MWD) of the resulting PMMA broad. For example, in the polymerization of alkyl methacrylate by  $n\text{-C}_4\text{H}_9\text{Li}$ <sup>8,10</sup> or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CD}_2\text{Li}$ <sup>12</sup> the initiator reacts with the carbonyl double bond during the initiation process, and this side reaction brings about the formation of propagating species of different tacticities and activities. Moreover, in the polymerization of methacrylate by Grignard reagent, Schlenk equilibrium also makes the reaction complex,<sup>2,6</sup> and these have prevented a clear

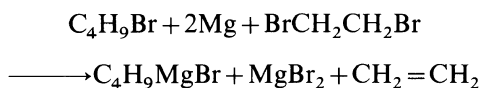
understanding of the reaction mechanism.

In the previous communication,<sup>13</sup> we reported that  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in diethyl ether caused no side reaction in the polymerization of MMA in toluene at  $-78^\circ\text{C}$  and formed highly isotactic PMMA with narrow MWD. That is the first example of the direct preparation of highly isotactic PMMA with narrow MWD, although it was derived from the isotactic poly(triphenylmethyl methacrylate) prepared in THF with an organolithium compound.<sup>14,15</sup> In this work we studied the polymerization of MMA by  $t\text{-C}_4\text{H}_9\text{MgBr}$  under several reaction conditions and clarified the mechanism of formation of highly isotactic PMMA with narrow MWD.

## EXPERIMENTAL

MMA, MMA- $d_8$  and ethyl methacrylate (EMA) were purified by distillation, and then distilled twice over calcium dihydride under high vacuum just before use. Toluene was purified in the usual manner and then distilled under high vacuum after treatment with  $n\text{-C}_4\text{H}_9\text{Li}$ .

$t\text{-C}_4\text{H}_9\text{MgBr}$  was prepared in diethyl ether from  $t$ -butyl bromide and magnesium. The amounts of  $t\text{-C}_4\text{H}_9\text{Mg}$ - group, total magnesium ( $\text{Mg}^{2+}$ ) and total bromide ( $\text{Br}^-$ ) were determined by acid-base titration, chelatometric titration and precipitation titration (Fajans's method), respectively. The procedures were described previously.<sup>13</sup>  $n\text{-C}_4\text{H}_9\text{MgBr}$ ,  $\text{iso-C}_4\text{H}_9\text{MgBr}$  and  $s\text{-C}_4\text{H}_9\text{MgBr}$  were prepared and analyzed similarly.  $\text{iso-C}_4\text{H}_9\text{MgBr}$  and  $s\text{-C}_4\text{H}_9\text{MgBr}$  were also prepared in the presence of 1,2-dibromoethane to obtain a solution of the reagent containing excess amount of  $\text{MgBr}_2$ .



$(t\text{-C}_4\text{H}_9)_2\text{Mg}$  was synthesized by adding a large amount of dioxane to the diethyl ether solution of  $t\text{-C}_4\text{H}_9\text{MgBr}$ . The initiator with various of  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  were prepared by mixing certain amounts of  $t\text{-C}_4\text{H}_9\text{MgBr}$  obtained in diethyl ether and  $(t\text{-C}_4\text{H}_9)_2\text{Mg}$ . A small amount of precipitate was formed during the mixing and the supernatant liquid was used as the initiator solution.

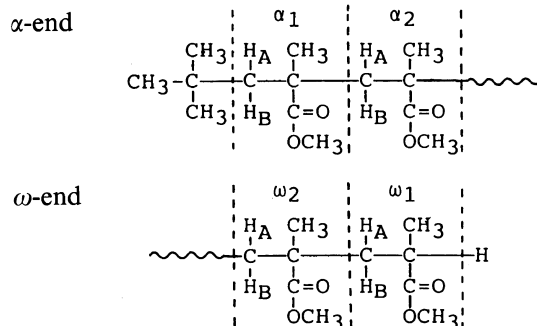
Polymerization was initiated by adding monomer with a hypodermic syringe slowly to an initiator solution in toluene cooled to the polymerization temperature. The reaction vessel was then sealed off. Polymerization was terminated by adding methanol containing HCl (2 *N*) equivalent to the  $\text{Mg}^{2+}$  at the reaction temperature. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric prod-

uct. The precipitate was collected by filtration, washed with hexane and then water several times, and dried under vacuum at 60°C. The polymer thus obtained was dissolved in benzene and the insoluble material was filtered off. The polymer was recovered from the solution by freeze-drying.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-FX100 and a JEOL JNM-GX400 spectrometer, respectively. Triad tacticities of the PMMAs were evaluated from the  $^1\text{H}$  NMR signals of  $\alpha\text{-CH}_3$  protons measured in nitrobenzene- $d_5$  at 110°C. In the previous communication,<sup>13</sup> the tacticities were determined from the spectra measured in chloroform- $d$  at 60°C from which an accurate determination of the fraction of syndiotactic triads was impossible because of the appearance of the signal of the  $t\text{-C}_4\text{H}_9$  group at the initiating end of the polymer chain ( $\alpha$ -end) in the syndiotactic  $\alpha\text{-CH}_3$  proton region. In the spectrum measured in nitrobenzene- $d_5$ , the  $t\text{-C}_4\text{H}_9$  proton signal resonated at 0.82 ppm apart from the syndiotactic  $\alpha\text{-CH}_3$  region where a couple of doublets of weak intensities were appeared (1.045 and 1.063 ppm,  $J=7.2$  Hz). These doublets were assigned to the protons of  $\alpha\text{-CH}_3$  group at the terminating end ( $\omega$ -end) of the polymer chain ( $\omega_1\text{-CH}_3$ ) by 2D NMR spectroscopy.<sup>16</sup> 2D NMR also revealed that the signals of the

$\alpha\text{-CH}_3$ region	Assignment	Chemical shift (ppm)
Syndiotactic (1.01—1.08 ppm)	$\omega_1\text{-CH}_3$ (r)	1.045
	$\omega_1\text{-CH}_3$ (m)	1.063
Heterotactic (1.12—1.19 ppm)	$\alpha_1\text{-CH}_3$ (r)	1.125
	$\omega_2\text{-CH}_3$ (mr)	1.128
	$\alpha_2\text{-CH}_3$ (rm)	1.140
	$\omega_2\text{-CH}_3$ (mm)	1.175
Isotactic (1.23—1.39 ppm)	$\alpha_1\text{-CH}_2$ (r)	1.25
	$\alpha_1\text{-CH}_3$ (m)	1.273
	$\alpha_2\text{-CH}_3$ (mm)	1.282
	$\alpha_1\text{-CH}_2$ (m)	1.28
	$\omega_1\text{-CH}_2$ (m)	1.32

$\alpha\text{-CH}_3$  and  $\text{CH}_2$  groups in the first two and the last two monomeric units at  $\alpha$ - and  $\omega$ -ends overlapped with the resonances of in-chain  $\alpha\text{-CH}_3$  groups as summarized above.<sup>16</sup> The numbering system for the monomeric units at  $\alpha$ - and  $\omega$ -ends is as follows:



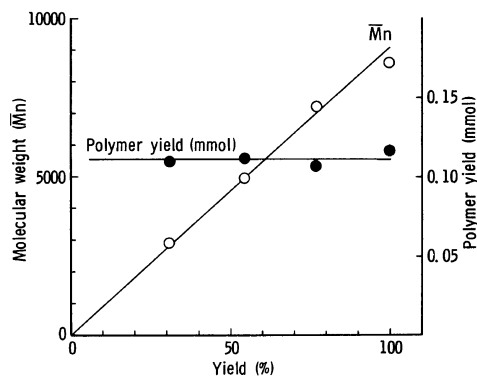
The tacticities of the polymers were calculated according to these peak assignments.<sup>16</sup>

The molecular weights of the polymers were measured on a Hitachi 117 vapor pressure osmometer (VPO) in toluene at  $60^\circ\text{C}$  or on a JASCO FLC-A10 GPC chromatograph with a Shodex GPC column A-80M ( $50\text{ cm} \times 2$ ) and KF-802.5 ( $30\text{ cm} \times 1$ ) with maximum porosity of  $5 \times 10^7$  and  $4 \times 10^4$ , respectively, using tetrahydrofuran as an eluent. The GPC chromatogram was calibrated against standard polystyrene samples. The molecular weights were also determined from the rel-

ative intensities of the  $^1\text{H}$  NMR signals due to the  $t\text{-C}_4\text{H}_9$  and  $\text{OCH}_3$  groups.

## RESULTS AND DISCUSSION

Polymerization of MMA was carried out with  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$  at various ratios of monomer to initiator. The results are shown in Table I. The number average molecular weights ( $\bar{M}_n$ ) of the polymer measured by GPC, VPO, and by end-group assay using  $^1\text{H}$  NMR spectroscopy



**Figure 1.** Relationship between number average molecular weight ( $\bar{M}_n$ ) and polymer yield in the polymerization of MMA by  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$ ; the polymerizations were conducted for different polymerization times. MMA, 10 mmol;  $t\text{-C}_4\text{H}_9\text{MgBr}$ , 0.11 mmol; toluene, 5 ml.

**Table I.** Polymerization of MMA by  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$ <sup>a</sup>

No.	$t\text{-C}_4\text{H}_9\text{MgBr}$ mmol	Time h	Yield %	Tacticity/%			$\bar{M}_n$				
				I	H	S	VPO	GPC	$^1\text{H}$ NMR	Calcd	$\bar{M}_w^b$ $\bar{M}_n$
1	0.20	24	73	96.3	3.6	0.1	3660	3510	3560	3700	1.14
2	0.40 <sup>c</sup>	72	100	96.5	3.2	0.3	4930	5650	4940	5060	1.10
3	0.11	120	100	96.8	2.9	0.3	10100	10400	9520	9160	1.10
4	0.10 <sup>c</sup>	145	99	96.7	3.0	0.3	21200	21200	20800	19900	1.08
5	0.20 <sup>d</sup>	24	100	96.0	3.1	0.9	6100	5600	—	5060	1.43
6	0.40 <sup>e</sup>	24	100	1.4	19.2	79.4	16500	14500	—	2560	3.10

<sup>a</sup> MMA 10.0 mmol, toluene 5 ml.

<sup>b</sup> Determined by GPC.

<sup>c</sup> MMA 20.0 mmol, toluene 10 ml.

<sup>d</sup> Polymerization at  $-40^\circ\text{C}$ .

<sup>e</sup>  $(t\text{-C}_4\text{H}_9)_2\text{Mg}$  was used as an initiator.

**Table II.** Polymerization of MMA by  $t\text{-C}_4\text{H}_9\text{MgBr}/(t\text{-C}_4\text{H}_9)_2\text{Mg}$  in toluene at  $-78^\circ\text{C}$  for 24h<sup>a</sup>

[Mg <sup>2+</sup> ] [ $t\text{-C}_4\text{H}_9\text{Mg}$ ]	Yield %	Tacticity/%			$\bar{M}_n$		$\bar{M}_w^b$
		I	H	S	Obsd <sup>b</sup>	Calcd	$\bar{M}_n$
0.53	100	2	16	82	14400	3060	2.85
0.87	96	32	22	46	4910	2940	54.0
0.95	97	88	6	6	3760	2970	16.6
1.06	100	96	4	0	3190	3060	1.83
1.50	98	96	4	0	3260	3000	1.15
2.24	69	96	4	0	2230	2130	1.10

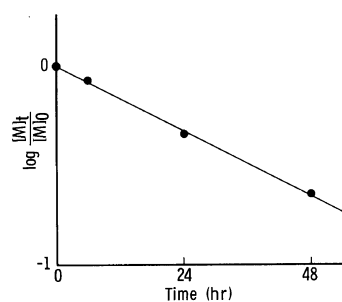
<sup>a</sup> MMA 10 mmol, [MMA]/[ $t\text{-C}_4\text{H}_9\text{Mg}$ ] = 30 mol/mol, toluene 5 ml.

<sup>b</sup> Determined by GPC.

agreed well with each other, and also with the values calculated from the amount of the monomer consumed and the initiator used. Thus the  $\bar{M}_n$  of the polymer can be easily controlled by changing the ratio of initial amounts of MMA and initiator. In all the cases, the polymer was highly isotactic and of low polydispersity. The  $\bar{M}_w/\bar{M}_n$  ratios were about 1.1. The rate of polymerization was small at  $-78^\circ\text{C}$ , and was enhanced at  $-40^\circ\text{C}$  although the MWD became a little broader.

The polymerizations were carried out in toluene at  $-78^\circ\text{C}$  for different polymerization times. The results are shown in Figure 1. The  $\bar{M}_n$  increased proportionally to the polymer yield. The amounts in mmol of polymer molecules were independent of the yield and just corresponded to the amount of  $t\text{-C}_4\text{H}_9\text{MgBr}$  used. These results indicate that the polymerization has the "living" character.

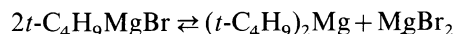
The polymerization reaction was followed in toluene- $d_8$  at  $-78^\circ\text{C}$  by measuring the intensities of vinylidene methylene proton signals of MMA. The signal of  $t\text{-C}_4\text{H}_9\text{MgBr}$  at 1.58 ppm disappeared on the addition of MMA, indicating a fast initiation reaction. The propagation was very slow compared to the initiation reaction, and the rate of the polymerization fitted first order plots (Figure 2). The rate constant for the propagation reaction was found to be  $4.3 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$ . Thus, fast initiation and slow propagation



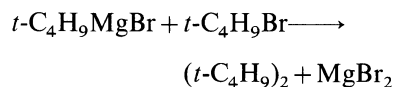
**Figure 2.** First order plots of the polymerization of MMA by  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$ . MMA, 10 mmol;  $t\text{-C}_4\text{H}_9\text{MgBr}$ , 0.11 mmol; toluene, 5 ml.

as well as the living character are responsible for the formation of PMMA with narrow MWD.

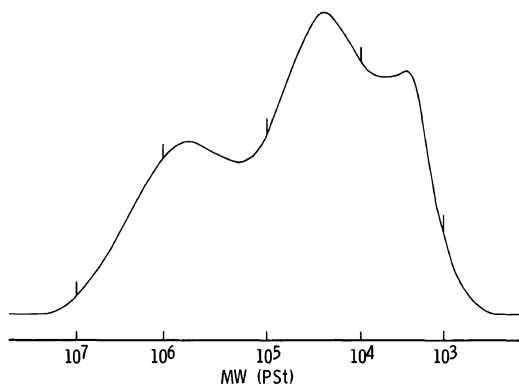
Grignard reagent is considered to exist in the well-known Schlenk equilibrium.



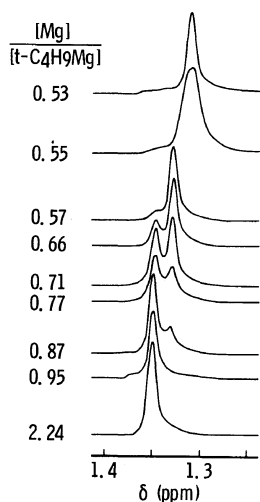
$t\text{-C}_4\text{H}_9\text{MgBr}$  used in this study was prepared in diethyl ether and was found to contain  $\text{Mg}^{2+}$  2.2 times as much as  $t\text{-C}_4\text{H}_9\text{Mg}$ -group. The  $\text{MgBr}_2$  should be formed through the reaction of  $t\text{-C}_4\text{H}_9\text{MgBr}$  and  $t\text{-C}_4\text{H}_9\text{Br}$  during preparation of the Grignard reagent.



This suggests that the Schlenk equilibrium is in favor of the side of " $t\text{-C}_4\text{H}_9\text{MgBr}$ ." In order to study the reaction between Schlenk



**Figure 3.** GPC curves of PMMA prepared by  $t\text{-C}_4\text{H}_9\text{MgBr}/(t\text{-C}_4\text{H}_9)_2\text{Mg}$  ( $[\text{Mg}^{2+}]/[t\text{-C}_4\text{H}_9\text{Mg}] = 0.87$ ) in toluene at  $-78^\circ\text{C}$  for 24 h. MMA, 10 mmol;  $[\text{MMA}]/[t\text{-C}_4\text{H}_9\text{Mg}] = 30$  mol/mol; toluene, 5 ml. PMMA:  $\bar{M}_n = 4910$ ,  $\bar{M}_w/\bar{M}_n = 54.0$ , tacticity ( $I, H, S$ ) = (32, 22, 46).



**Figure 4.**  $^1\text{H}$  NMR spectra of  $t\text{-C}_4\text{H}_9\text{MgBr}/(t\text{-C}_4\text{H}_9)_2\text{Mg}$  with various ratios of  $[\text{Mg}^{2+}]/[t\text{-C}_4\text{H}_9\text{Mg}]$  in toluene- $d_8$  at  $-40^\circ\text{C}$ .  $[t\text{-C}_4\text{H}_9\text{Mg}] = 0.055$  M; ether/toluene- $d_8 = 1/5$  v/v.

equilibrium and the results of polymerization, initiators with various ratios of  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  were prepared by mixing certain amounts of  $t\text{-C}_4\text{H}_9\text{MgBr}$  obtained in diethyl ether and  $(t\text{-C}_4\text{H}_9)_2\text{Mg}$ , and used for the polymerization of MMA in toluene at  $-78^\circ\text{C}$ . The results are shown in Table II. When the ratios of  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  were larger than 1.5, highly isotactic PMMAs with

narrow MWD were formed and the  $\bar{M}_n$ 's agreed well with the calculated values. The polymers obtained by the initiator with  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  of 0.87–0.95 had trimodal MWD, suggesting the coexistence of at least three propagating species with different stereoregularities (Figure 3).

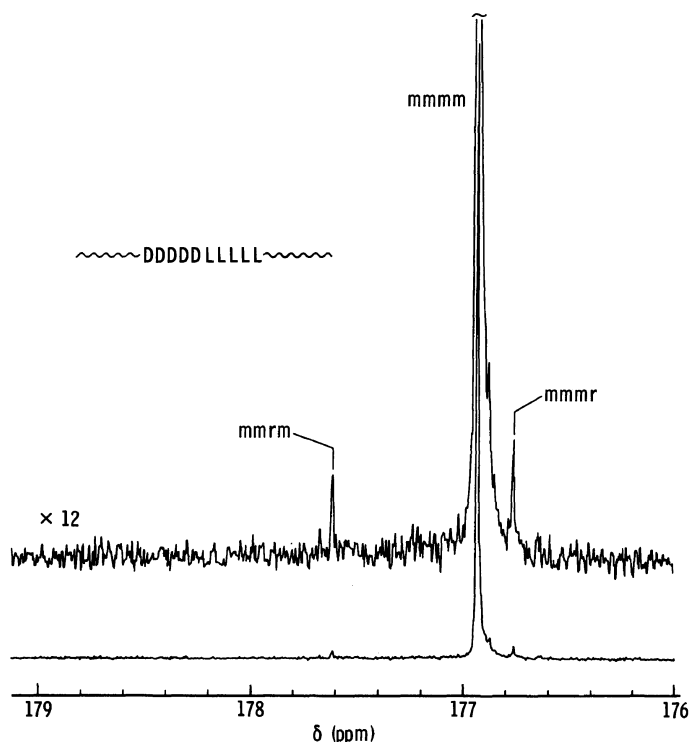
$^1\text{H}$  NMR studies on the mixtures of  $t\text{-C}_4\text{H}_9\text{MgBr}$  and  $(t\text{-C}_4\text{H}_9)_2\text{Mg}$  of various  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  ratios were attempted at  $-78^\circ\text{C}$  but without success owing to poor resolution of the spectra at this temperature. The measurements at  $-40^\circ\text{C}$  in toluene were successful and the spectra are presented in Figure 4. The  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in diethyl ether ( $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg} = 2.24$ ) showed a singlet at 1.35 ppm, and  $(t\text{-C}_4\text{H}_9)_2\text{Mg}$  ( $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg} = 0.53$ ) at 1.31 ppm. The mixtures, the  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  ratio of which was between 0.57 and 0.87, exhibited two singlets at 1.33 and 1.35 ppm. With a decrease of the ratio of  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$  from 0.87 to 0.57 the intensity of the peak at 1.35 ppm decreased accompanied with an increase in the intensity at 1.33 ppm. The mixture with  $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg} = 0.55$  showed the resonance similar to that of  $(t\text{-C}_4\text{H}_9)_2\text{Mg}$ .

From the results described in Table II and Figure 4, it is believed that " $t\text{-C}_4\text{H}_9\text{MgBr}$ " and " $(t\text{-C}_4\text{H}_9)_2\text{Mg}$ " give a highly isotactic and a syndiotactic PMMA, respectively, and that the species which shows the  $^1\text{H}$  NMR signal at 1.33 ppm gives a syndiotactic-rich polymer.

Figure 5 shows  $^{13}\text{C}$  NMR signals of carbonyl carbons in the PMMA prepared by  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$  (No. 4 in Table I). Two weak signals of equal intensities due to mmm and mmmr pentads are observed besides a strong signal due to an mmmm pentad, but no other pentad signals. Therefore, the steric defect in the polymer chain can be depicted as follows:



This means that one racemo enchainment



**Figure 5**  $^{13}\text{C}$  NMR signal of the carbonyl carbon in the PMMA prepared by  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$ . Nitrobenzene- $d_5$ ,  $110^\circ\text{C}$ , 100 MHz.

causes the inversion of isotactic propagating species, and that the stereoregulation in this polymerization is chain-end controlled. This polymer had  $\overline{\text{DP}}$  of about 200 and 3.0% of the heterotactic triads. So there exist about three switching points of monomer placements in a polymer chain. 2D NMR analysis<sup>16</sup> revealed that the configurational dyad sequence at the  $\omega$ -end was not regular, showing the reaction between the propagating anion and the terminating reagent, methanol, was not stereospecific. Hence, it is noteworthy that structural analyses of the low molecular weight products should be conducted taking into account the steric irregularity at the chain end.

Block copolymers of MMA and MMA- $d_8$  or ethyl methacrylate (EMA) were prepared by  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene at  $-78^\circ\text{C}$  (Table III). The compositions and molecular

weights of the copolymers agreed well with the calculated values, respectively, indicating the formation of block copolymers. The block copolymers of MMA and MMA- $d_8$  had narrow MWD, and this type of block copolymerization has provided valuable samples for detailed analysis of polymer structure by 2D NMR spectroscopy.<sup>16</sup> The PMMA-block-PEMA obtained was highly isotactic, but the MWD was rather broad.

Table IV shows the results of polymerizations in toluene at  $-78^\circ\text{C}$  with  $n$ -, iso-,  $s$ - and  $t$ -butylmagnesium bromides.  $n\text{-C}_4\text{H}_9\text{MgBr}$  gave syndiotactic PMMAs in low yields, and the tacticities depended on the initiator concentration probably due to the coexistence of isotactic and syndiotactic active species. The  $\overline{M}_n$ 's of the polymers were much larger than the expected values and the MWDs were very broad. As the alkyl group became bul-

**Table III.** Block copolymerizations of MMA, MMA-*d*<sub>8</sub>, and EMA initiated by *t*-C<sub>4</sub>H<sub>9</sub>MgBr in toluene at -78°C<sup>a</sup>

M <sub>1</sub>	mmol	M <sub>2</sub>	mmol	Block copolymer							
				Yield	[m <sub>2</sub> ]	Tacticity/% <sup>b</sup>			$\bar{M}_n$		$\bar{M}_w^c$
						%	[m <sub>1</sub> ]	I	H	S	
MMA	1.0	MMA	19.0	100	19.0	97	3	0	9950	10100	1.15
MMA	1.0	MMA- <i>d</i> <sub>8</sub>	19.0	100	19.0	—	—	—	11800	10800	1.21
MMA- <i>d</i> <sub>8</sub>	1.0	MMA	19.0	100	19.0	97	3	0	10500	10100	1.13
MMA	5.0 <sup>d</sup>	—	—	100	—	97	3	0	1200	1060	1.38
MMA	5.0 <sup>d</sup>	EMA <sup>e</sup>	10.0	100	2.0	95 <sup>f</sup>	5 <sup>f</sup>	0 <sup>f</sup>	3120 <sup>g</sup>	3340	1.51

<sup>a</sup> *t*-C<sub>4</sub>H<sub>9</sub>MgBr 0.20 mmol, toluene 10 ml. M<sub>1</sub> was polymerized for 24 h and then M<sub>2</sub> was added to be polymerized further for 144 h.

<sup>b</sup> Determined from <sup>1</sup>H NMR spectra.

<sup>c</sup> Determined by GPC.

<sup>d</sup> *t*-C<sub>4</sub>H<sub>9</sub>MgBr 0.50 mmol.

<sup>e</sup> M<sub>2</sub> was polymerized for 48 h.

<sup>f</sup> Determined from a <sup>13</sup>C NMR spectrum.

<sup>g</sup> Determined by VPO.

**Table IV.** Polymerization of MMA by C<sub>4</sub>H<sub>9</sub>MgBr in toluene at -78°C<sup>a</sup>

C <sub>4</sub> H <sub>9</sub> -	C <sub>4</sub> H <sub>9</sub> MgBr		Yield	Tacticity/%			$\bar{M}_n$		$\bar{M}_w^b$
	[Mg <sup>2+</sup> ]	%		I	H	S	Obsd <sup>b</sup>	Calcd	
	[C <sub>4</sub> H <sub>9</sub> Mg]								$\bar{M}_n$
<i>n</i> -C <sub>4</sub> H <sub>9</sub> <sup>c</sup>	1.0	8.1	11.0	15.3	73.7	12000	1680	13.4	
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1.0	14.1	20.5	15.2	64.3	7420	760	11.2	
iso-C <sub>4</sub> H <sub>9</sub>	1.1	33.1	92.5	5.4	2.1	5540	2270	2.29	
iso-C <sub>4</sub> H <sub>9</sub>	2.5 <sup>d</sup>	21.7	95.5	4.5	0.0	4410	1140	2.12	
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	1.2	100	95.5	4.5	0.0	4930	5060	1.29	
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	2.4 <sup>d</sup>	94.5	96.8	3.2	0.0	4680	4790	1.21	
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	2.2	100	97.4	2.6	0.0	5010	5060	1.18	

<sup>a</sup> MMA 20 mmol, C<sub>4</sub>H<sub>9</sub>MgBr 0.40 mmol, toluene 10 ml, time 72 h.

<sup>b</sup> Determined by GPC.

<sup>c</sup> C<sub>4</sub>H<sub>9</sub>MgBr 0.10 mmol.

<sup>d</sup> The Grignard reagent was prepared in the presence of 1,2-dibromoethane (C<sub>4</sub>H<sub>9</sub>Br + Mg + BrCH<sub>2</sub>CH<sub>2</sub>Br → C<sub>4</sub>H<sub>9</sub>MgBr + MgBr<sub>2</sub> + CH<sub>2</sub>=CH<sub>2</sub>). The solutions of the reagents were found to contain excess MgBr<sub>2</sub> by acid-base, chelatometric and precipitation (Fajans's method) titrations as indicated above.

kier, the isotacticity of the polymer increased greatly and the MWD became narrower. In the polymerization by *s*-C<sub>4</sub>H<sub>9</sub>MgBr and *t*-C<sub>4</sub>H<sub>9</sub>MgBr the initiator efficiencies were almost 100%, and the MWDs were narrow. *t*-C<sub>4</sub>H<sub>9</sub>MgBr gave the PMMA with the highest isotacticity and the narrowest MWD.

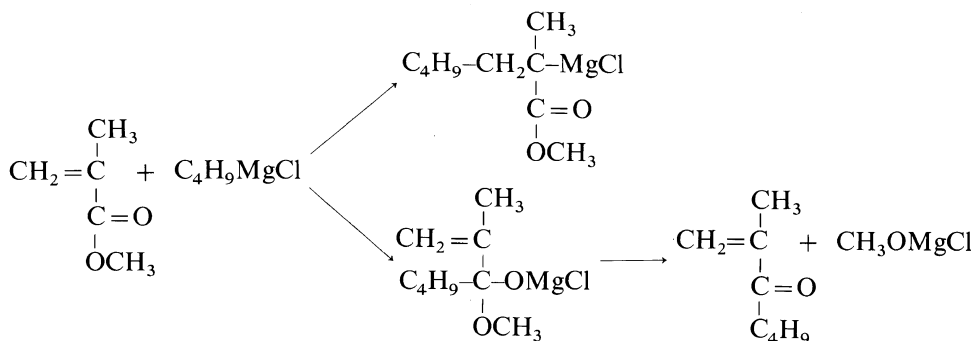
Mg<sup>2+</sup>/C<sub>4</sub>H<sub>9</sub>Mg values for butylmagnesium bromides other than *n*-C<sub>4</sub>H<sub>9</sub>MgBr exceeded unity, and the values became larger as the butyl group became bulkier. The effect of MgBr<sub>2</sub> was confirmed by the fact that the isotacticities of the polymers prepared with iso-C<sub>4</sub>H<sub>9</sub>MgBr and *s*-C<sub>4</sub>H<sub>9</sub>MgBr increased

and the MWDs were narrowed upon the addition of excess  $\text{MgBr}_2$  (Table IV). It should be noted that the rate of polymerization was reduced upon the addition of  $\text{MgBr}_2$ .

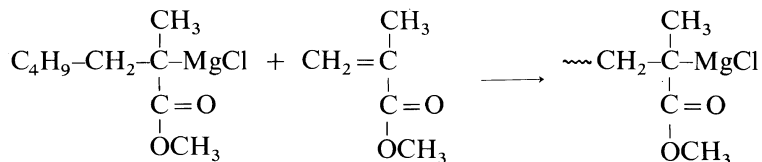
## DISCUSSION

In the polymerization of MMA with Grig-

nard reagent or alkyllithium, the initiator reacts with both vinylidene and carbonyl double bond of MMA at the initial stage of polymerization.<sup>8,10,17,18</sup> In the polymerization with  $n\text{-C}_4\text{H}_9\text{MgCl}$ <sup>17</sup> the initiating species and butyl isopropenyl ketone form simultaneously at the early stage of polymerization.

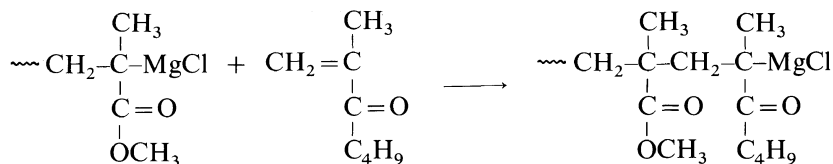


The initiating species add MMA to form propagating species.



However, the ketone is more reactive than MMA as evidenced from the higher  $Q$  and  $e$  values<sup>18</sup> than those of MMA. As a result, a part of the propagating species are attacked

by the ketone. The resulting species ending with BIPK unit are less reactive than those ending with the MMA unit and remain unreacted during the polymerization.



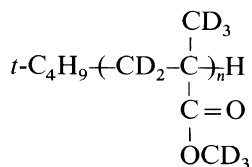
Thus, participation of the ketone in the polymerization should make MWD broad.  $\text{CH}_3\text{OMgCl}$  formed simultaneously with the ketone would coordinate with the propagating chain end to produce the species of different activities and stereoregularities. This also contributes to the multiple active species and stereoblock or stereoblend polymer formation.

As a result of the carbonyl attack by  $n\text{-C}_4\text{H}_9\text{MgCl}$ , the efficiency of the initiator is less than unity if it is calculated assuming each polymer and oligomer molecule to contain one initiator fragment at the  $\alpha$ -end of the chain.

As described in the previous paper,<sup>13</sup> the polymer of  $\text{MMA-}d_8$  prepared with  $t\text{-C}_4\text{H}_9\text{MgBr}$  at  $-78^\circ\text{C}$  showed two  $^1\text{H}$  NMR signals



at 0.81 and 2.46 ppm which were assigned to *t*-C<sub>4</sub>H<sub>9</sub> group at the  $\alpha$ -end of the chain and the methine proton attached to the MMA unit (MMA-H) at the  $\omega$ -end of the chain, respectively. Measurements of the absolute intensities of these signals and  $\bar{M}_n$  on the polymer indicated the polymer to contain one *t*-C<sub>4</sub>H<sub>9</sub>-group at the  $\alpha$ -end and one MMA-H at the  $\omega$ -end. No sign of side reaction was detected in the spectrum. Thus the polymer should be the pure MMA polymer as shown below:



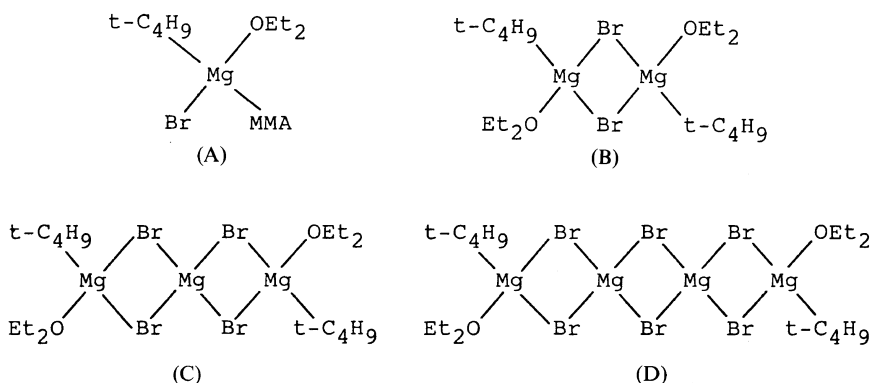
The agreement of the  $\bar{M}_n$ s determined by NMR with those by VPO (Table I) is other evidence that the polymer has the structure represented above.

It is expected from the results in Table IV that the bulky alkyl group prevents the Grignard reagent from being involved in the side reaction and makes the polymerization living to produce the PMMA with narrow MWD. Salonen and his coworker<sup>19</sup> studied the reactions of ethyl  $\alpha$ -(2-furyl)acrylate with various alkylmagnesium halides. CH<sub>3</sub>MgI reacted with the acrylate completely in 1,2-manner. The extent of 1,2-addition decreased with an increase in the bulkiness of alkyl group and

*t*-C<sub>4</sub>H<sub>9</sub>MgCl reacted only in a 1,4-manner. The results are consistent with those of our polymerizations.

As mentioned in the previous section, Grignard reagent usually exists as an equilibrium mixture,  $2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$ . In the solution of *t*-C<sub>4</sub>H<sub>9</sub>MgBr prepared in diethyl ether the equilibrium shifts on the side of "*t*-C<sub>4</sub>H<sub>9</sub>MgBr" owing to the existence of excess MgBr<sub>2</sub>. The results shown in Tables II, IV and Figure 4 clearly indicate that "*t*-C<sub>4</sub>H<sub>9</sub>MgBr" gives highly isotactic PMMA and "*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Mg" syndiotactic polymer. Matsuzaki suggested that in the polymerization of MMA by phenylmagnesium bromide, active species for isotactic polymer were "*C*<sub>6</sub>H<sub>5</sub>MgBr" and those for syndiotactic-rich polymer were "*C*<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Mg".<sup>6</sup> Isotactic polymerization has never been observed with dialkylmagnesium initiators with the single exception of dibenzylmagnesium prepared from dibenzylmercury.<sup>20</sup>

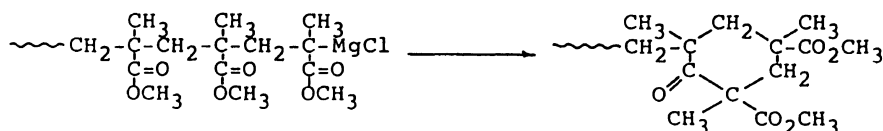
The structure of the initiating species in our isospecific polymerization with *t*-C<sub>4</sub>H<sub>9</sub>MgBr is not clear at present, but the following structures, (A), (B), (C), and (D), may be proposed. In this polymerization, the efficiency of the initiator is almost 100%, isotacticity of the polymer is extremely high and MWD is narrow. This suggests that the initiating site should be homogeneous in reactivity and stereospecificity.



Allen and Williams<sup>21</sup> proposed the structure similar to (A) as the initiating species in the polymerization of MMA in toluene with de-etherated  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in THF, on the basis that the isotactic initiating sites should be chiral. However, in our polymerization the stereoregulation is chain-end controlled (*cf.* Figure 5) and the initiating sites are not necessarily chiral. The solubility of ether-solvated  $\text{MgBr}_2$  in toluene may be low as indicated by Allen and Mair.<sup>5</sup> Moreover, the viscosity of the polymerization mixture decreased remarkably when a small amount of methanol was added to quench the living end. Then, the structures (C) and (D) may possibly be considered as the initiating

species, particularly (D), in which two  $t\text{-C}_4\text{H}_9\text{-Mg-}$  groups are located apart from each other enough to act independently as the initiating sites of the same reactivity and stereoregularity. The association of the propagating anions may serve to prevent the side reactions such as the terminating reaction through the formation of the cyclic ketone unit at the  $\omega$ -end. If this is the case, the meaning of Schlenk equilibrium should be somewhat changed. A detailed investigation on this problem is now under way.

In the polymerization at  $-40^\circ\text{C}$ , some of the propagating species form cyclic ketone unit at the  $\omega$ -ends, which makes the MWD a little broad (*cf.* Table I, No. 6).



The cyclization reaction is much enhanced at  $0^\circ\text{C}$  and about 90% of the propagating species formed the cyclic ketone unit when the species prepared in toluene at  $-78^\circ\text{C}$  was kept at  $0^\circ\text{C}$  for 24 h.<sup>22</sup> Thus, the polymerization at  $-78^\circ\text{C}$  is required to prepare the PMMA with narrow MWD.

In conclusion,  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in diethyl ether exists as " $t\text{-C}_4\text{H}_9\text{MgBr}$ " itself, and causes no side reaction in the polymerization of MMA in toluene at  $-78^\circ\text{C}$  to produce highly isotactic PMMA with narrow MWD. The reaction is completely living, and the amounts of the propagating species are the same as that of the initiator used and constant during the polymerization at  $-78^\circ\text{C}$ .

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