

SHORT COMMUNICATIONS

## Preparation of Highly Isotactic Poly(methyl methacrylate) of Low Polydispersity

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Several recent publications have been presented on the syntheses of syndiotactic poly(methyl methacrylate)s (PMMA) of low polydispersity by alkylolithium in a polar solvent<sup>1-4</sup> and a group transfer reaction.<sup>5</sup> For these syntheses except for group transfer polymerization, alkylolithium having a bulky alkyl group was usually used as an initiator to avoid side reactions. However, to our knowledge, there has been no investigation on the preparation of highly isotactic PMMA with narrow molecular weight distribution. Isotactic PMMA is usually prepared by an anionic initiator in a nonpolar solvent. Such a polymerization system may involve multiple active species and side reactions,<sup>6-16</sup> causing the molecular weight distribution to be broad. In the polymerization of MMA by  $C_2H_5MgBr$  or  $C_4H_9MgCl$ , the initiator reacted with both the carbonyl double bond of the monomer and vinyl double bond during the initiation process, and the resulting alkyl isopropenyl ketone was incorporated into the polymer chain, as evident by the totally deuterated monomer technique.<sup>16</sup> In this work, we found that  $t$ - $C_4H_9MgBr$  prepared in diethyl ether caused no side reaction and formed pure PMMA of narrow molecular weight distribution.

MMA and MMA- $d_8$  were purified by distil-

lation, and distilled twice over calcium dihydride under high vacuum just before use.  $t$ - $C_4H_9MgBr$  was prepared in diethyl ether from  $t$ -butyl bromide and magnesium. A solution of 12.3 g (90 mmol) of  $t$ -butyl bromide in 27 ml anhydrous diethyl ether was dropped slowly on the 3.3 g (135 mmol) of magnesium turnings covered with 54 ml of diethyl ether over a period of 1 h. Stirring was continued for one additional hour under reflux. The reaction mixture was allowed to stand overnight to precipitate the unreacted magnesium. The supernatant solution was separated from the precipitate with a hypodermic syringe and used as an initiator solution. The yield of  $t$ -alkylmagnesium bromide from the bromide and magnesium is generally low and depends on the form of magnesium and rate of addition of the halide solution.<sup>17,18</sup> The concentration of the  $t$ - $C_4H_9Mg$ -group in the  $t$ - $C_4H_9MgBr$  solution used in this work was determined as 0.289 *N* (28.9% yield from  $t$ - $C_4H_9Br$  used) by hydrolysis with excess 0.1 *N* HCl and back-titration with 0.1 *N* NaOH using phenolphthalein as the indicator. However, the solution was found to contain 0.812 *M* of  $Mg^{2+}$  by chelatometric titration with EDTA using Eriochrome Black T as the indicator. The concentrations of  $t$ - $C_4H_9MgBr$  shown in the

text are those of the *t*-C<sub>4</sub>H<sub>9</sub>Mg-group.

Polymerization was initiated by adding the monomer with a hypodermic syringe slowly to the initiator solution in toluene cooled to the polymerization temperature. The reaction vessel was then sealed off. The polymerization was terminated by adding methanol containing HCl (2 *N*) equivalent to the Mg<sup>2+</sup> at the reaction temperature. 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 several times and dried under vacuum. 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.

<sup>1</sup>H NMR spectra were recorded on a JEOL JNM-FX100 (FT) spectrometer. The molecular weights of the polymers were measured on a Hitachi 117 vapor pressure osmometer in toluene at 60°C or on a JASCO FLC-A10 GPC chromatograph with a Shodex GPC column A-80M (50 cm × 2) and KF-802.5 (30 cm × 1) with maximum porosity of 5 × 10<sup>7</sup> and 4 × 10<sup>4</sup>, respectively, using tetrahydrofuran as the solvent. The GPC chromatogram

was calibrated against standard polystyrene samples.

Table I shows the results of polymerization of MMA in toluene at -78°C for several polymerization times at the initial ratio of the monomer to initiator of 50/1. The polymerization proceeded slowly and was completed by 48 h. The number average molecular weight of the polymer increased with time and agreed well with the expected value. In all cases, the polymers were highly isotactic and of low polydispersity. The results clearly indicate that all the polymer chains are living during the polymerization and that there exists only one type of propagating species. The rate of polymerization was greatly enhanced at -40°C, although the molecular weight distribution became slightly broad. The molecular weight of the polymer could be controlled by changing the ratio of initial concentrations of the monomer and initiator as shown in Table I.

In order to obtain further information on the polymerization with *t*-C<sub>4</sub>H<sub>9</sub>MgBr, MMA-*d*<sub>8</sub> was polymerized in toluene at -78°C at the initial ratio of monomer to initiator of 50/1. The polymer obtained showed two singlets in the <sup>1</sup>H NMR spectrum at 0.81 and 2.46 ppm

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

<i>t</i> -C <sub>4</sub> H <sub>9</sub> MgBr	Time	Yield	Tacticity/% <sup>b</sup>			<i>M</i> <sub>n</sub> <sup>c</sup>		<i>M</i> <sub>w</sub> <sup>c</sup>
			I	H	S	Obsd	Calcd	
mmol	h	%						<i>M</i> <sub>n</sub>
0.40	24	100	97.1	2.9	~0	2290	2560	1.27
0.20	24	73	97.2	2.8	~0	3510	3700	1.14
0.20	48	100	97.4	2.6	~0	5010	5060	1.18
0.10	120	100	98.4	1.6	~0	9320	10060	1.19
0.10 <sup>d</sup>	145	99	99.2	0.8	~0	20400	19900	1.12
0.20 <sup>e</sup>	24	100	97.1	2.9	~0	5600	5060	1.43
0.50 <sup>f</sup>	24	100	95	5	~0	1620	2060	1.85

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

<sup>b</sup> Determined from the  $\alpha$ -methyl proton signals. Signals due to syndiotactic triads were very weak, however, an accurate determination of the intensity was not possible owing to overlapping with the signal of *t*-butyl group incorporated at the beginning of the polymer chain.

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

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

<sup>e</sup> Polymerization at -40°C.

<sup>f</sup> De-etherated *t*-C<sub>4</sub>H<sub>9</sub>MgBr was used.

## Highly Isotactic PMMA of Low Polydispersity

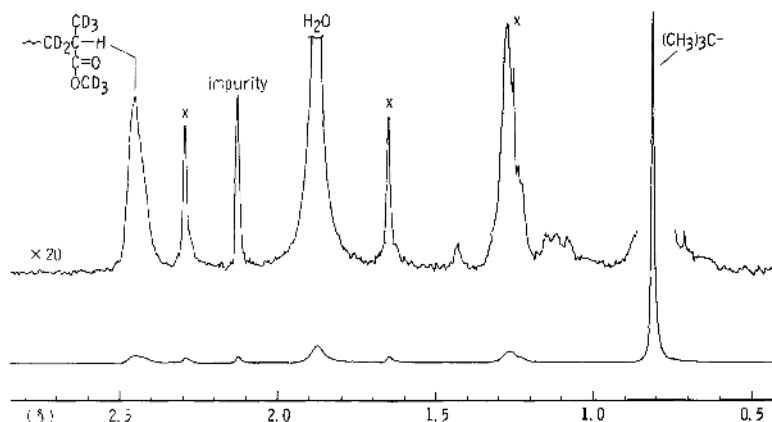


Figure 1.  $^1\text{H}$  NMR spectrum of P(MMA- $d_8$ ) prepared in toluene at  $-78^\circ\text{C}$  with  $t\text{-C}_4\text{H}_9\text{MgBr}$  (nitrobenzene- $d_5$ ,  $110^\circ\text{C}$ , 100 MHz). X: signal due to the remaining proton(s) in the monomeric units.

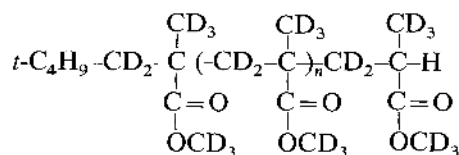
Table II. Number of initiator fragments and terminal methine protons per P(MMA- $d_8$ ) molecule prepared with  $t\text{-C}_4\text{H}_9\text{MgBr}$  in toluene

$t\text{-C}_4\text{H}_9\text{MgBr}$ mmol	Temp $^\circ\text{C}$	Time h	Yield %	$M_n^b$	$t\text{-C}_4\text{H}_9\text{CD}_2\text{-C}$ $\begin{array}{c}   \\ \text{CD}_3 \\   \\ \text{C}=\text{O} \\   \\ \text{OCD}_3 \end{array}$	$\text{-CD}_2\text{-C-H}$ $\begin{array}{c}   \\ \text{CD}_3 \\   \\ \text{C}=\text{O} \\   \\ \text{OCD}_3 \end{array}$
0.50	-78	24	100	1370	1.0	0.96
0.10	-78	72	85	5100	1.0	0.97
0.10	-40	2	63	3300	1.0	0.87

<sup>a</sup> MMA- $d_8$  5.0 mmol, toluene 5 ml.

<sup>b</sup> Determined by vapor pressure osmometer.

which were assigned to the  $t\text{-C}_4\text{H}_9$ -group at the beginning of the chain and the methine proton attached to the MMA- $d_8$  unit at the chain end,<sup>19</sup> respectively (Figure 1). The  $t\text{-C}_4\text{H}_9$ -group was introduced into the polymer chain through the initiation reaction and the methine proton by termination with methanol. Measurements of absolute intensity<sup>13</sup> of these signals and molecular weight of the polymer indicated the polymer to contain one  $t\text{-C}_4\text{H}_9$ -group at the beginning of the chain and one terminal methine proton at the chain end (Table II).



From the results mentioned above, it is clear that there occurs no side reaction in the polymerization in toluene at  $-78^\circ\text{C}$  with  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in diethyl ether. This must be one important reason why highly isotactic PMMAs of low polydispersity are obtained. Highly isotactic PMMA was also obtained in the polymerization in toluene with  $t\text{-C}_4\text{H}_9\text{MgBr}$  prepared in tetrahydrofuran and

de-etherated but the molecular weight distribution was very broad, indicating the existence of multiple active species.<sup>7,10</sup> When the *t*-C<sub>4</sub>H<sub>9</sub>MgBr prepared in diethyl ether was de-etherated and used as an initiator, highly isotactic PMMA of fairly narrow molecular weight distribution was obtained (Table I). A detailed study of the structure of *t*-butylmagnesium halide is now under way in connection with the polymerization mechanism.

The poly(MMA-*d*<sub>8</sub>) molecule prepared in toluene at -40°C with *t*-C<sub>4</sub>H<sub>9</sub>MgBr contained one *t*-C<sub>4</sub>H<sub>9</sub>-group at the beginning of the chain but its terminal methine proton was less than unity (0.87) (Table II). This may indicate that there occurred side reactions such as spontaneous termination reaction through the formation of cyclic ketone unit at the chain end, causing a rather broad distribution of molecular weight (Table I).

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