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Polymerization of Methyl Methacrylate and Its Copolymerization with ϵ-Caprolactone Catalyzed by Isobutylalumoxane Catalyst

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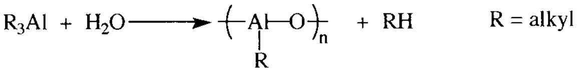
Introduction

In recent years, ring-opening polymerization of lactones has attracted increasing interest because many of the polyesters obtained from these polymerization reactions are potentially biodegradable. For example, [*R*,*S*]-*β*-butyrolactone can be polymerized by alumoxane catalysts into a semicrystalline and biodegradable polyester.[1] Polycaprolactone obtained from the ring-opening polymerization of ϵ-caprolactone (CL) has found uses as materials for controlled release drug delivery systems.[2] CL can be readily polymerized by many different catalysts[3−8] and copolymerized with L-lactide to form a biodegradable block copolymer.[9]

On the other hand, vinyl polymers such as poly(methyl methacrylate), PMMA, are not biodegradable. It would be very desirable to combine the biodegradability of the polyesters and the excellent application properties of polyvinyls. Efforts have been made toward the copolymerization of lactones and vinyl or vinylidene monomers. This type of copolymerization is known as "hybrid copolymerization."[10] In a hybrid copolymerization, the reactive species with different characters and reactivities coexist. Solaro and co-workers[10] attempted the copolymerization of MMA with different lactones using diethylaluminum sulfate (DEAS), triisobutylaluminum (TIBA), and TIBA/H_2O as the catalysts. In their study physical mixtures of homopolymers were obtained, and there was no evidence that any copolymer was formed during the copolymerization. However, as Solaro and co-workers pointed out, the study provided a way of obtaining in situ polymer alloys of PMMA and polyesters, and therefore semibiodegradable polymer blends can be produced. Despite the lack of evidence, they believed that block copolymers of MMA and the lactones might have formed and acted as a compatibilizer for the polymer alloys.

Alumoxanes are the reaction products of a trialkylaluminum with water as shown in the following general reaction equation:



$$R_3Al + H_2O \longrightarrow \left(\underset{R}{\underset{|}{Al}}-O\right)_n + RH \qquad R = \text{alkyl}$$

The specific structures of the alumoxanes are not known, but there is generally no simple formula of the type shown above that can be used to represent the real structure of alumoxanes because the products of the hydrolysis can consist of many different types of oligomeric compounds, which may have linear, cyclic, or even cage structures.[11,12] Alumoxanes are known to activate the transition metal catalysts used for the Ziegler−Natta polymeirzation of olefins, especially for the polymerization of ethylene to the linear polymer and of propylene to the highly isotactic polymer.[13] As mentioned above, alumoxanes can polymerize [*R*,*S*]-*β*-butyrolactone,[1] and it was found that isobutylalumoxane was a good catalyst for the ring-opening polymerizaton of CL.[14] It is natural, therefore, to think of using isobutylalumoxane to copolymerize CL and MMA.

In this paper, we report on our study of the polymerization of MMA and the copolymerization of MMA and CL catalyzed by isobutylalumoxane.

Experimental Section

Chemicals. Isobutylalumoxane was purchased from Akzo Nobel Chemicals as 1 M solution in toluene (Al/O = 1/0.8). Toluene used for the polymer synthesis was refluxed with sodium for at least 48 h and distilled before use. CL and MMA were purchased from Aldrich, dried over CaH_2 for 24 h, and distilled under reduced pressure.

Homopolymerization of MMA. All the glassware used for the polymerization was oven-dried for 24 h and flame-dried under vacuum with argon purge for at least three cycles. A 100 mL Schlenk tube was charged with 3 mL (0.028 mol) of MMA dissolved in 30 mL of toluene, and an appropriate amount of isobutylalumoxane solution was added to the MMA solution at room temperature under argon atmosphere using a syringe. The reaction mixture was heated to the desired temperature while being magnetically stirred. The reaction

Table 1. Reaction Conditions and Polymer Yields of MMA Homopolymerization

rxn ID	IBAO[a] (mol %)	rxn temp (°C)	rxn time (h)	yield[b] (%)
1	1	60	83	<1
2	5	60	83	36
3	5	50	82	53
4	10	60	83	61

[a] Based on monomer amount. [b] Based on weight of monomer.

Table 2. Molecular Weights of the PMMA Samples

	peak I[a]			peak II			total		
rxn no.	$M_w \times 10^{-6}$	$M_n \times 10^{-6}$	PDI	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	PDI	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	PDI
1	3.1	1.2	2.6	33	25	1.3	1590	42	37.5
2	1.5	0.9	1.7	41	27	1.5	431	50	8.7
3							3840	1170	3.3
4	2.7	1.1	2.4	35	22	1.6	750	32	23.8

[a] Weight, M_w, and number, M_n, average molecular weights and PDI, polydispersity index, as determined by GPC analysis of chloroform solutions relative to polystyrene standards.

Table 3. Glass Transition Temperature and Tacticity of Polymer Sample 3

T_g (°C, by DSC)	131.5
syndiotactic diad (%, by ^1H NMR)	86.0
syndiotactic diad (%, by ^{13}C NMR)	93.0
triad tacticity (%, by ^{13}C NMR)	mm = 5.5 rr = 91.5 mr = 3.0

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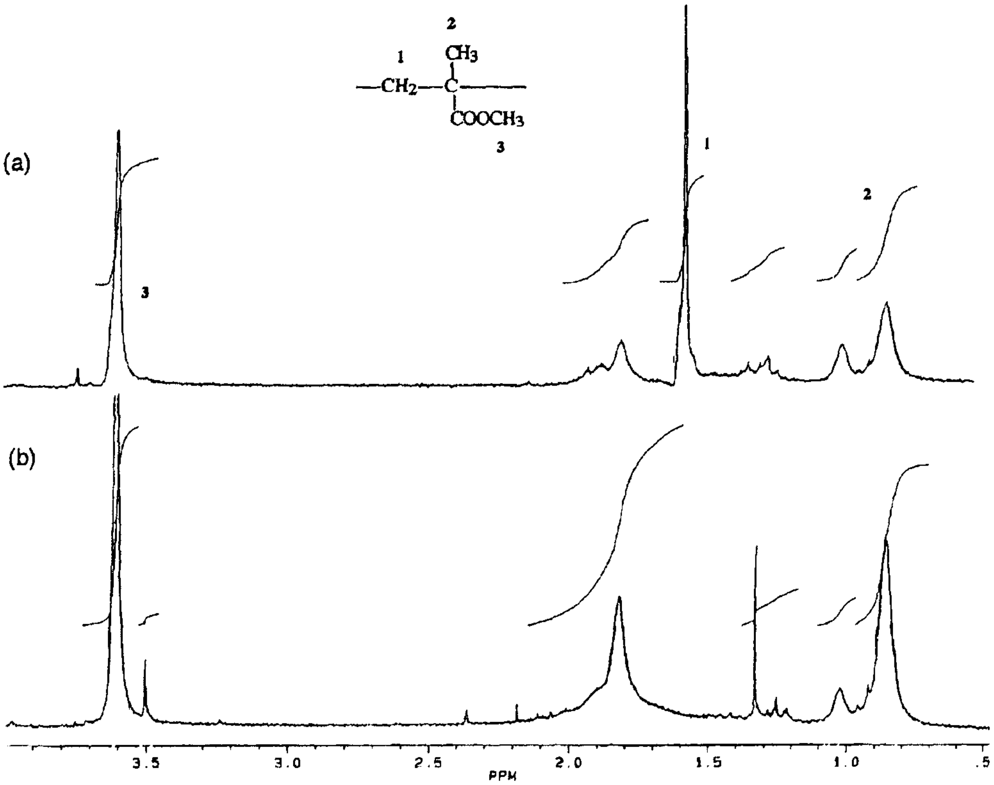

Figure 1. ^{1}H NMR spectra of PMMA obtained (a) at room temperature without any catalyst and (b) with IBAO catalyst (sample 3 in Table 1).

Table 4. MMA/CL Copolymerization

rxn ID[a]	MMA/CL (molar ratio)	yield[b] (%)
A	20/80	30.3
B	50/50	37.4
C	80/20	22.2

[a] Reaction conditions: toluene = 30 mL, IBAO = 5 mol %, reaction temperature = 50 °C, and total reaction time = 93 h. [b] Based on weight of monomer.

Table 5. GPC and DSC Analysis of the Copolymerization Products

sample	M_w[a] ($\times 10^{-3}$)	M_n[a] ($\times 10^{-3}$)	PDI[a]	T_m[b] (°C)	ΔH_m[b] (J/g)
A	16.6	11.0	1.5	61.4	86.8
B	28.2	15.3	1.8	62.9	119.0
C	89.8	26.6	3.4	59.5	32.4

[a] Weight, M_w, and number, M_n, average molecular weights and PDI, polydispersity index, as determined by GPC analysis of chloroform solutions relative to polystyrene standards. [b] Melting temperature, T_m, and heat of fusion, determined from DSC thermograms; data from the second heating scan was used.

temperature was kept for 83 h. The polymerization product was precipitated in 300 mL of methanol containing 3.5 mL of concentrated hydrochloric acid. The polymer obtained was filtered, washed with three portions of 35 mL of methanol, and dried under vacuum at room temperature for 24 h.

MMA was also polymerized at room temperature for 1 week without any catalyst. The PMMA sample so obtained was referred to as "PMMA obtained without catalyst at room temperature".

Copolymerization of MMA and CL. MMA and CL of appropriate molar ratios were added to the Schlenk tubes. The catalyst amount used was 5 mol % based on total monomer moles. The reaction temperature was 50 °C, and the reaction time was 93 h.

Polymer Characterization. Molecular weights were determined by GPC analysis. Polystyrene samples with low polydispersities were used as the standards to generate calibration curves. Thermal analysis was carried out with a Du Pont DSC-2000. The polymer samples were heated at a rate of 20 °C/min to determine the glass transition temperatures (T_g), melting temperatures (T_m), and the heats of fusion (ΔH_m). The thermogram of the second heating cycle was used for the determination of T_g.

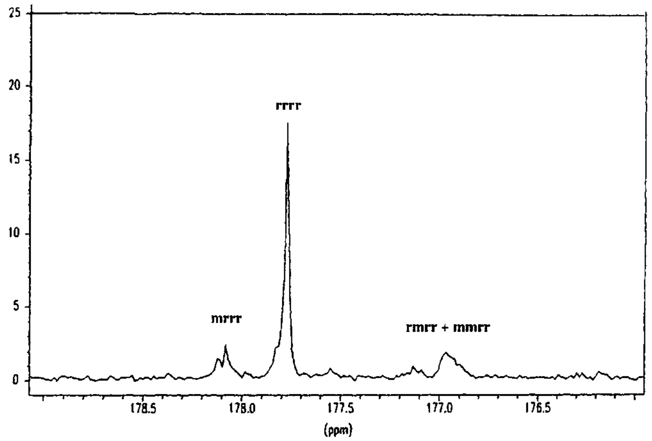

Figure 2. Expanded carbonyl region of the ^{13}C NMR spectrum of PMMA sample obtained with IBAO catalyst (sample 3 in Table 3).

^{1}H NMR spectra were recorded at 200 MHz on a Bruker 200 AC spectrometer; $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as the internal reference. ^{13}C NMR spectra were recorded on a Brucker 300 MSL spectrometer at 75.4 MHz; $CDCl_3$ was used as the solvent and the internal reference at 77.00 ppm.

Results and Discussion

Homopolymerization of MMA. Homopolymerization of MMA was carried out at 60 and 50 °C using isobutylalumoxane (IBAO) as the catalyst. Table 1

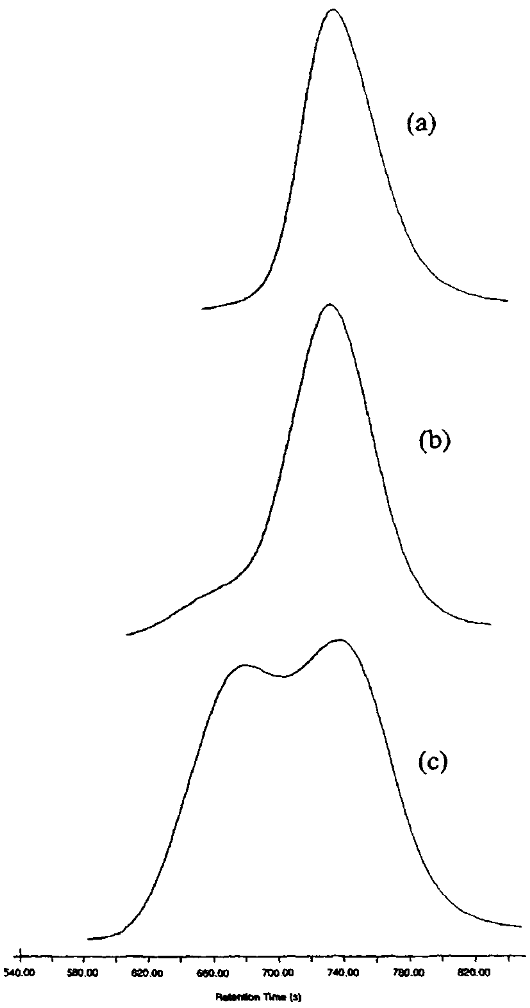

Figure 3. GPC graphs of MMA/CL copolymerization products in Table 4.

shows the polymerization conditions and the corresponding yields. It can be seen that increasing the IBAO amount increased the polymer yield. It is interesting to see that when the reaction temperature was lowered from 60 to 50 °C, the polymer yield increased from 34% to 53% (entries 2 and 3). This is presumably because at the higher temperature the alumoxane-catalyzed polymerization competed with the thermal polymerization of MMA, and at a lower temperature thermal polymerization was suppressed. This assumption is supported by the GPC results, as shown in Table 2.

As can be seen in Table 2, all PMMA samples except no. 3 showed bimodle GPC graphs, indicating multiple reactive species in the reaction system. The polymerization can go presumably by thermal and coordination mechanisms. The higher molecular weight peaks (peak I in Table 2) can be assumed to result from the thermal polymerization, whereas the lower molecular weight peaks (peak II in Table 2) were due to the coordination polymerization catalyzed by IBAO. When the reaction temperature was lowered from 60 to 50 °C, peak I disappeared, and the molecular weight distribution was relatively narrower (see entry 3 in Table 2). This result could be due to the absence of thermal polymerization at 50 °C.

Differential scanning colorimetry (DSC) thermograms showed that all PMMA samples obtained had glass transition temperatures (T_g) of approximately 131 °C. The unusually high T_g must be due to the high syndiotacticity (discussed below) of the polymers since free-radically prepared PMMA usually possesses a T_g of 105 °C and a syndiotactic diad of 75%.[15]

To obtain NMR information on the polymers, a PMMA sample was obtained by polymerizing MMA at room temperature without any catalyst for a week, and this sample was considered thermally polymerized PMMA. A ^{1}H NMR spectrum was acquired for this PMMA and compared with that of sample 3 in Tables 1 and 2, which was polymerized by IBAO catalyst, and both NMR spectra are shown in Figure 1. The 0.85 ppm peak was assigned to the syndiotactic diad and 1.03 ppm to the isotactic diad. The integration gave the syndiotactic diad percentage of each sample. For the PMMA obtained at room temperature without any catalyst, its syndiotactic diad percentage was found to be 75% (Figure 1a), and PMMA sample 3 had a syndiotactic diad of 86% (Figure 1b). Similar results were also obtained by ^{13}C NMR analysis. Figure 2 shows the expanded carbonyl region of the ^{13}C NMR spectrum of sample 3. The peaks were assigned to different pentads,

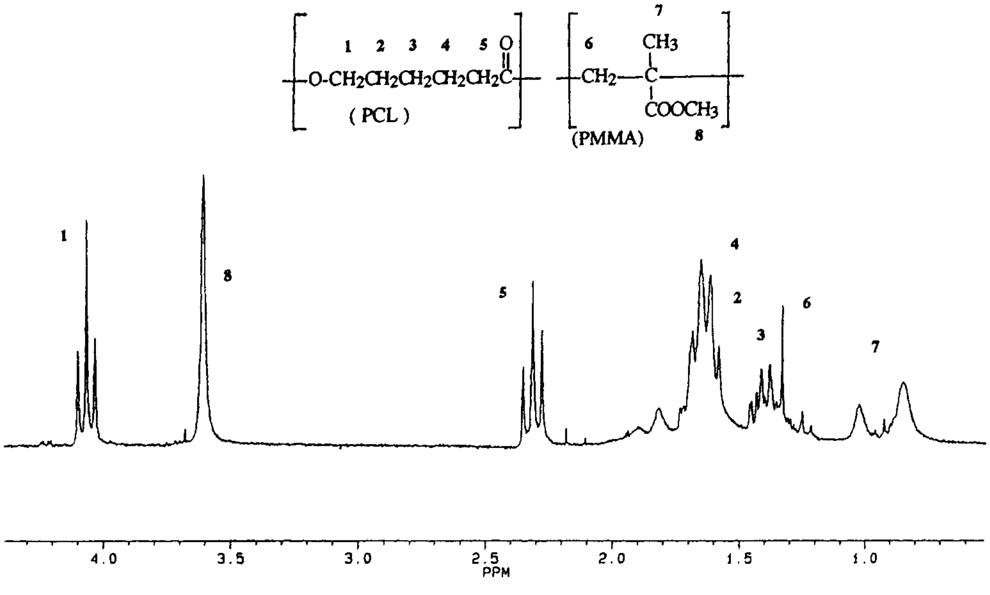

Figure 4. ^{1}H NMR spectrum of copolymerization sample C in Table 4.

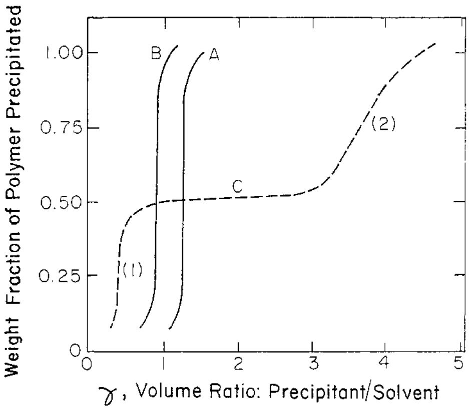

Figure 5. Fractional precipitation of a PMMA−PCL blend, C, and of copolymers A and B (Table 4, entries A and B).

as shown in the figure. The syndiotactic diad percentage was calculated by integration of these pentad peaks. For sample 3, the result was 93%. The NMR and DSC results are summarized in Table 3.

Copolymerization of MMA and CL by IBAO. Table 4 gives the molar ratios of MMA and CL in the copolymerization and the corresponding polymer yields. At low MMA/CL ratios (entries A and B), the polymers obtained had only one peak on their GPC graphs (A and B, Figure 3), and their polydispersities were quite low (see Table 5). The single GPC peak and low molecular weight distribution of samples A and B suggest that polymer A and B are copolymers, not blends of PMMA and PCL. However, at higher MMA/CL ratio (entry C in Table 4) a bimodle GPC graph was obtained (Figure 3C). This may indicate that, at 50 °C with CL as the comonomer, the thermal polymerization of MMA could not be suppressed, as was the case of MMA homopolymerization at 50 °C by IBAO in the absence of CL (see the discussion part concerning MMA homopolymerization).

Table 5 summarizes the results of GPC and DSC analysis.

Figure 4 shows the ^{1}H NMR spectrum of copolymerization product C (see Table 4). The proton signals that belong to PMMA and PCL units are assigned unambiguously as shown in Figure 4.

Fractional Precipitation. Fractional precipitation experiments provide definite evidence for the formation of block or graft copolymers.[16] Figure 5 shows the fractional precipitation curves for two P(MMA-*g*-CL) samples (A and B in Table 4). In Table 4, the weight percentage of the precipitated polymer was plotted versus γ, the ratio of the precipitant volume (petroleum ether) to solvent volume (THF). Precipitation results of a 50:50 physical mixture of PMMA ($\gamma = 0.4$) and PCL ($\gamma = 3.5$) are also included in the figure. It can be seen that precipitation curves of block or graft copolymers are located between the curves of PMMA and PCL components of the blend. Because sample A has a higher CL unit content than does sample B, the precipitation curve of sample A ($\gamma = 1.1-1.2$) is closer to the PCL curve than sample B, which has a γ value of 0.5−0.7. Furthermore, sample A was precipitated with a higher amount of the precipitant from THF solution as was expected.

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