

Stereospecific Polymerization of Methyl Methacrylate Initiated by Dimethylzirconocene/ $B(C_6F_5)_3$ (or $Ph_3CB(C_6F_5)_4/Zn(C_2H_5)_2$)

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Stereospecific polymerization of methyl methacrylate (MMA) has been intensively investigated in anionic polymerizations initiated by lithium alkyls or Grignard reagents. Both isotactic and syndiotactic poly(methyl methacrylate) (PMMA) can be produced, but only at very low temperatures.¹ Recently, much attention was focused on lanthanocene hydride and alkyl compounds, which polymerize olefins² without any cocatalyst in high yields and also produce syndiotactic PMMA³ with very narrow molecular mass distributions at ambient temperatures. Cationic metallocene compounds of the Group 4 elements, which have similar electronic structures, have attracted more attention due to high activity and high stereospecificity in olefin polymerization.⁴ It has been recently reported that a cationic zirconocene compound, $Cp_2Zr(CH_3)(THF)^+BPh_4^-$, promotes syndiospecific polymerization of MMA in the presence of neutral zirconocene ($Cp_2Zr(CH_3)_2$),^{5a} and a substoichiometric mixture (ca. 1:3) of $[nBu_3NH][BPh_4]$ and *rac*- or (*S*)-(+)- $Et(H_4Ind)_2Zr(CH_3)_2$ gives isotactic PMMA in polar solvent like CH_2Cl_2 .^{5b}

More recently, we have found that the catalyst composed of a dimethylzirconocene compound and a stoichiometric amount of Lewis acid like $B(C_6F_5)_3$

promotes the polymerization of MMA in the presence of $Zn(C_2H_5)_2$ at ambient temperature in toluene. A chiral racemic zirconocene compound, *rac*- $Et[Ind]_2Zr(CH_3)_2$, gave highly isotactic PMMA, while an achiral zirconocene, $Cp_2Zr(CH_3)_2$, gave syndio-rich atactic PMMA. This paper reports the preliminary results of these polymerizations.

Results and Discussion. Addition of $B(C_6F_5)_3$ (**1**) or $Ph_3CB(C_6F_5)_4$ (**2**) and equimolar $Cp_2Zr(CH_3)_2$ (**3**) into a toluene solution of MMA could not initiate polymerization of MMA. Under these conditions metallocene cationic complexes (e.g., $Cp_2Zr(CH_3)^+B(C_6F_5)_4^-$) are formed in high yield. When MMA was at first mixed with $Zn(C_2H_5)_2$ in a toluene solvent and aged for 1 h before subsequent addition of compounds **1** and **3** (see the Experimental Part), however, polymerizations were initiated to give PMMAs with high molecular weight and narrow molecular mass distributions in good yields. Some complexes were formed between MMA and $Zn(C_2H_5)_2$, which were indicated by a downfield shift of carbonyl of MMA from 167.7 to 167.9 ppm and an upfield shift of methylene protons of $Zn(C_2H_5)_2$ from 7.2 to 7.0 ppm observed in the ¹³C NMR spectrum after aging. It was confirmed from a ¹³C NMR spectrum that no polymerization occurred until final addition of zirconocene. In this condition, however, almost no polymer could be obtained when CH_2Cl_2 was used as the solvent, which was reported as a good solvent for the polymerization of MMA with the $Cp_2Zr(CH_3)(THF)^+BPh_4^-/Cp_2Zr(CH_3)_2$ catalyst.⁵ The results of polymerizations conducted in toluene are summarized in Table 1. The ¹³C NMR spectrum of a typical polymer is displayed in Figure 1, whereas the pentad distributions are shown in Table 2, both of which indicate that PMMA produced with $Cp_2Zr(CH_3)_2$ is a syndio-rich atactic polymer. The microtacticity distributions of the polymer were found to obey Bernoullian statistics (Table 2), suggesting that

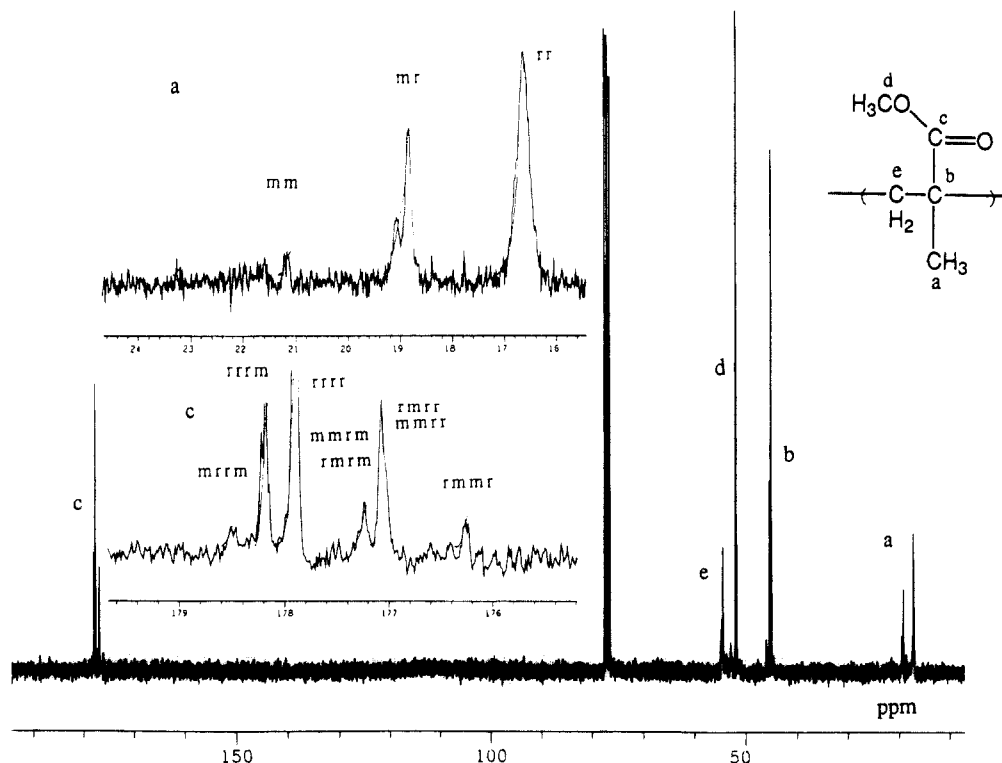


Figure 1. ¹³C NMR spectrum of atactic poly(MMA) obtained in run no. 7 (Table 1).

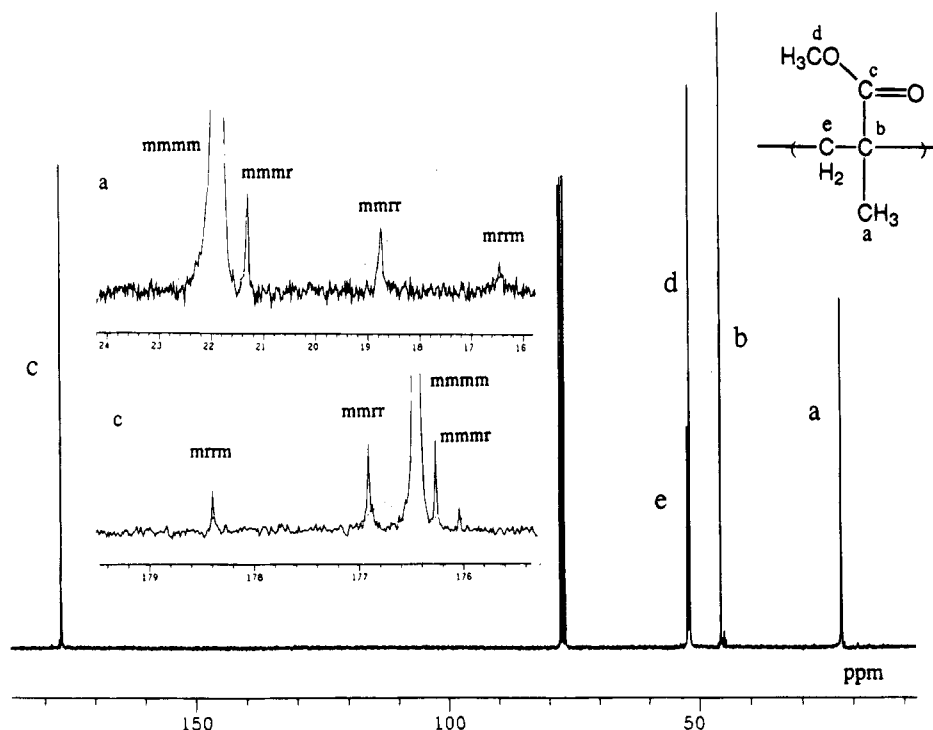


Figure 2. ^{13}C NMR spectrum of isotactic poly(MMA) obtained in run no. 2 (Table 1).

the syndiospecific polymerization proceeds via a chain end-controlled mechanism. Similar results have been reported with the lanthanocene³ and $\text{Cp}_2\text{ZrCH}_3(\text{THF})^+\text{BPh}_4^-/\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ catalysts.

On the other hand, the ^{13}C NMR spectrum of PMMA produced with *rac*- $\text{Et}[\text{Ind}]_2\text{Zr}(\text{CH}_3)_2$ is shown in Figure 2, which is an isospecific catalyst in, e.g., the polymerization of propylene. From the spectrum, together with the analytical results listed in Table 2, it is clear that the polymer is highly isotactic, with a high molecular weight and a broader molecular mass distribution. The intensity ratios of [mmmr]:[mmrr]:[mrrm] pentads were found to be approximately 2:2:1. Therefore, isotactic polymerization proceeds via an enantiomorphic site-controlled mechanism, which is completely different from the chain end-controlled mechanism in isotactic polymerization of MMA with Grignard reagents in toluene.¹ The remarkable feature of this catalyst system is that the isotactic selectivity was very high (the selectivity of one prochiral face on the enantiomorphic site: $\beta = 0.99$) even at a temperature as high as 40 °C, which indicates that the isotactic propagation site is very stable in the presence of $\text{Zn}(\text{C}_2\text{H}_5)_2$. Furthermore, the glass transition temperature (T_g) of the isotactic PMMA measured by DSC was about 55.0 ± 2.5 °C, which

is very close to the theoretical value calculated previously.⁶

We also attempted to employ $(\text{iPr})\text{FluCpZr}(\text{CH}_3)_2$ to polymerize MMA, which is a syndiospecific catalyst in the polymerization of propylene. But no polymer was obtained under the conditions shown in Table 1.

While the dependence of stereoselectivity on zirconocene was described above, the effect of zinc compounds was also investigated by using the $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{B}(\text{C}_6\text{F}_5)_3$ system. Use of $\text{Zn}(\text{CH}_3)_2$ or $\text{Zn}[(\text{CH}_2)_2\text{CH}=\text{CH}_2]_2$ only resulted in a trace amount of PMMA, of which the structure was similar to that obtained by $\text{Zn}(\text{C}_2\text{H}_5)_2$. Besides $\text{Zn}(\text{C}_2\text{H}_5)_2$, stronger Lewis acids like $\text{B}(\text{C}_2\text{H}_5)_3$ and $\text{Al}(\text{C}_2\text{H}_5)_3$ were used as well; however, the polymerization could not be induced. Further study is in progress to investigate the role of $\text{Zn}(\text{C}_2\text{H}_5)_2$ as well as the mechanism of polymerization, the results of which will be reported elsewhere.

Experimental Part. MMA monomer and toluene were dried over calcium hydride and distilled before use. $\text{B}(\text{C}_6\text{F}_5)_3$,⁷ $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$,⁸ *rac*- $\text{Et}[\text{Ind}]_2\text{Zr}(\text{CH}_3)_2$,⁹ $(\text{iPr})\text{FluCpZr}(\text{CH}_3)_2$,¹⁰ $\text{Zn}(\text{CH}_3)_2$ ¹¹ were synthesized according to the literature. $\text{Zn}[(\text{CH}_2)_2\text{CH}=\text{CH}_2]_2$ was synthesized from a stoichiometric mixture of the Grignard reagent

Table 1. Polymerization Results of MMA^a

run no.	catalyst	$[\text{Zn}(\text{C}_2\text{H}_5)_2]$ (mM)	temp (°C)	yield ^b (%)	M_n^c ($\times 10^4$)	M_w/M_n	T_g (°C)
1	$\text{Et}(\text{Ind})_2\text{Zr}(\text{CH}_3)_2/1$ or 2	0	0	0			
2	$\text{Et}(\text{Ind})_2\text{Zr}(\text{CH}_3)_2/1$	214	0	38	23.2	1.78	52.8
3	$\text{Et}(\text{Ind})_2\text{Zr}(\text{CH}_3)_2/2$	214	0	37	29.0	1.62	57.6
4	$\text{Et}(\text{Ind})_2\text{Zr}(\text{CH}_3)_2/1$	214	40	23	15.2	1.70	54.5
5	$\text{Cp}_2\text{Zr}(\text{CH}_3)_2/1$ or 2	0	0	0			
6	$\text{Cp}_2\text{Zr}(\text{CH}_3)_2/1$	8.18	0	26	103	1.25	128
7	$\text{Cp}_2\text{Zr}(\text{CH}_3)_2/1$	214	0	64	48.2	1.38	128
8	$\text{Cp}_2\text{Zr}(\text{CH}_3)_2/1$	214	40	8	12.6	1.85	122
9	$(\text{iPr})\text{FluCpZr}(\text{CH}_3)_2/1$ or 2	214	0 or 40	0			

^a Polymerization conditions: $[\text{Zr}] = 0.227$ mM; **1**, $\text{B}(\text{C}_6\text{F}_5)_3$; **2**, $\text{Ph}_3\text{C}(\text{C}_6\text{F}_5)_4$; $[\text{1}] = [\text{2}] = 0.227$ mM, $[\text{MMA}] = 0.85$ M, toluene = 13.3 mL for 24 h. ^b Yield = weight of polymer obtained/weight of monomer used. ^c Measured by GPC calibrated with standard polystyrene samples.

Table 2. Observed and Calculated Steric Pentad Distributions of PMMA^a

run no.	catalyst	temp (°C)	pentad fraction (%) ^b						triad test ^c		
			mmmm	mmmr	rmrr	mmrm	rmrr	rrrm	rrrr	4[rr]/[mm]/[mr] ²	2[rr]/[mr] ²
1	Cp ₂ Zr(CH ₃) ₂	0	0.0 (0.1)	0.0 (0.6)	2.1 (1.7)	4.3 (3.9)	21.4 (21.8)	18.8 (18.5)	51.8 (51.8)	0.92	(5.6)
2	Cp ₂ Zr(CH ₃) ₂	40	0.0 (0.1)	0.0 (1.1)	3.6 (2.4)	7.2 (5.9)	21.6 (25.0)	20.8 (20.2)	42.8 (42.8)	1.2	(4.7)
3	Et(Ind) ₂ Zr(CH ₃) ₂	0	94.0 (94.2)	2.3 (2.3)	0.0 (0.0)	0.0 (0.0)	2.5 (2.3)	0.0 (0.0)	0.0 (0.0)	(72)	0.96
4	Et(Ind) ₂ Zr(CH ₃) ₂	40	94.0 (94.2)	2.4 (2.3)	0.0 (0.0)	0.0 (0.0)	2.4 (2.3)	0.0 (0.0)	0.0 (0.0)	(78)	1.0

^a Polymerization conditions: see Table 1. ^b Calculated from carbonyl absorption in ¹³C NMR spectra. Values in parentheses were calculated from the Bernoullian equations with $P = 0.85$ (0 °C), and 0.81 (40 °C) for atactic PMMA and from site-controlled equations with $\beta = 0.99$ for isotactic PMMA. (β is the selectivity of one prochiral face on the enantiomeric site). ^c $4[\text{rr}]/[\text{rr}]/[\text{mr}]^2 = 1$ for a chain end-controlled mechanism; $2[\text{rr}]/[\text{mr}] = 1$ for a site-controlled mechanism.

and ZnCl₂. Zn(C₂H₅)₂ and Ph₃CB(C₆F₅)₄ were donated by Tosoh Akzo Co. Ltd. The other chemicals were research grade and were purchased from commercial sources and used without further purification.

Polymerization of MMA was carried out under a dry nitrogen atmosphere in a 100-mL round-bottomed flask equipped with a magnetic stirrer. A typical polymerization process is as follows: toluene (13.3 mL), MMA (2.0 mL), and a 1.0 M heptane solution of Zn(C₂H₅)₂ (4.7 mL) were injected into the flask, and the mixture was stirred for 1 h at 0 °C. After the addition of a 5.0 mM toluene solution of B(C₆F₅)₃ (1.0 mL), a 5.0 mM toluene solution of Cp₂Zr(CH₃)₂ (1.0 mL) was immediately injected to start the polymerization. The polymerization was quenched at 0 °C with methanol mixed with hydrochloric acid. The polymer produced was precipitated into methanol, followed by drying in vacuo at 60 °C for 8 h.

The molecular weight and molecular mass distribution were measured by GPC (Shimadzu 9A) at room temperature using chloroform as the solvent and calibrated with standard polystyrene samples. The glass transition temperature (T_g) was measured with a Seiko DSC-220C calorimeter at a heating rate of 10 °C/min. The ¹³C NMR spectra were measured in chloroform-*d* at room temperature with a JEOL GX-270 NMR spectrometer. Broad-band decoupling was used to remove the ¹³C-¹H coupling. The center peak of chloroform-*d* was used as the internal reference (77.0 ppm).

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