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Isospecific Polymerization of Methyl Methacrylate Initiated by Chiral Zirconocenedimethyl/$Ph_3CB(C_6F_5)_4$ in the Presence of Lewis Acid

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ABSTRACT: Polymerization of methyl methacrylate (MMA) was conducted with the catalyst systems of *rac*-$Et(Ind)_2Zr(CH_3)_2$/$Ph_3CB(C_6F_5)_4$, *rac*-$Et(IndH_4)_2Zr(CH_3)_2$/$Ph_3CB(C_6F_5)_4$, and *rac*-$Me_2Si(Ind)_2Zr(CH_3)_2$/$Ph_3CB(C_6F_5)_4$. These catalysts only were found to be inactive. However, the addition of suitable Lewis acids like alkylzinc and alkylaluminum compounds gave highly isotactic PMMA. The isotactic pentad [mmmm] in PMMA as well as the propagation rate constant (k_p) depended significantly upon the zirconocene compounds. Both the microstructure ([mmmm]) and propagation rate constant (k_p) increased in the following order: $Me_2Si(Ind)_2 < Et(IndH_4)_2 < Et(Ind)_2$. The microstructure of PMMA was also affected slightly by alkylzinc compounds: $(CH_2)_2CH{=}CH_2 > CH_2CH_3 > (CH_2)_3CH_3$. When the polymerization was initiated by the *rac*-$Et(Ind)_2Zr(CH_3)_2$/$Ph_3CB(C_6F_5)_4$/$Zn(C_2H_4CH{=}CH_2)_2$ catalyst system at 0 °C in toluene, the molecular weight of PMMA increased in proportion to the conversion of MMA. The increase of temperature from 0 to 80 °C caused a decrease in isotactic pentad content by approximately 10%. The isotactic polymerization of MMA was revealed to proceed by an enantiomorphic site-controlled mechanism.

Introduction

It has been recently reported that syndiotactic PMMA with monodispersed high molecular weights can be obtained with some lanthanocene catalysts.[1] Isotactic living polymerization of MMA is also known to proceed by the chain-end-controlled mechanism[2] in the presence of t-C_4H_9MgBr at very low temperature.[3]

On the other hand, an equimolar mixture of a chiral *ansa*-zirconocene [e.g., *rac*-$Et(Ind)_2Zr(CH_3)_2$] and a suitable Lewis acid [e.g., $Ph_3CB(C_6F_5)_4$] has been proved to produce a coordinatively unsaturated cationic zirconocene species, which can promote highly isospecific polymerization of propylene in high yield[4] by an enantiomorphic site-controlled mechanism.[5]

More recently, we applied such a zirconocene catalyst in the stereospecific polymerization of MMA and have found that no polymer can be obtained from the equimolar mixture of zirconocene and Lewis acid; however, highly isotactic PMMA can be obtained with the equimolar mixture [*rac*-$Et(Ind)_2Zr(CH_3)_2$/$Ph_3CB(C_6F_5)_4$ (or $B(C_6F_5)_4$)] in the presence of $Zn(C_2H_5)_2$ by the enantiomorphic site-controlled mechanism.[6] The use of an achiral metallocene like $Cp_2Zr(CH_3)_2$ gave syndio-rich PMMA by the chain-end-controlled mechanism. We have investigated the role of $Zn(C_2H_5)_2$ in the $Cp_2Zr(CH_3)_2$/$Ph_3CB(C_6F_5)_4$ system and found that $Zn(C_2H_5)_2$ mainly takes part in the initiation reaction.[7] In this study, we have investigated the effects of ligand structure, Lewis acid, and polymerization conditions on the isospecific polymerizations.

Experimental Section

Methyl methacrylate (MMA) and toluene were dried over calcium hydride and distilled before use. *rac*-$Et(Ind)_2Zr(CH_3)_2$, *rac*-$Et(IndH_4)_2Zr(CH_3)_2$, and *rac*-$Me_2Si(Ind)_2Zr(CH_3)_2$ were synthesized from the corresponding zirconocene chloride[4,8,9] and methyllithium according to the similar procedure reported previously.[4] $Zn(C_2H_4CH{=}CH_2)_2$ and $Zn(C_4H_9)_2$ were synthesized from the corresponding Grignard reagents and $ZnCl_2$. $Zn(C_2H_5)_2$, $Al(i\text{-}C_4H_9)_3$, and $Ph_3CB(C_6F_5)_4$ were donated from Tohso Akzo Co., Ltd. Other chemicals of research grade were commercially obtained and used without further purification.

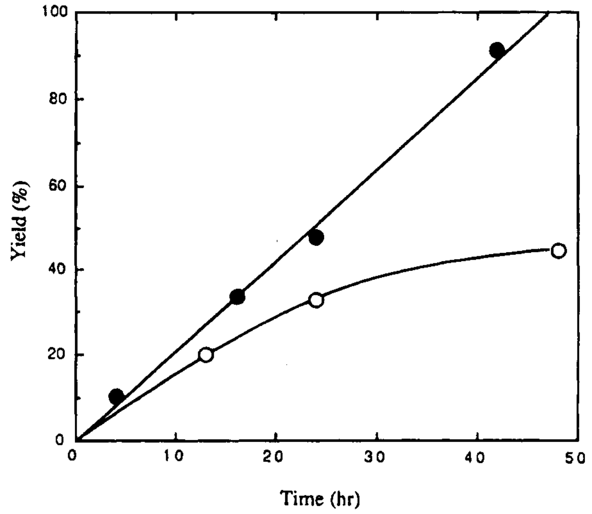

Figure 1. Comparison of $Zn(C_2H_5)_2$ (○) and $Zn(C_2H_4CH{=}CH_2)_2$ (●) with respect to the relation of polymer yield and polymerization time. Polymerization conditions: [$Et(Ind)_2Zr(CH_3)_2$] = [$Ph_3CB(C_6F_5)_4$] = 0.25 mM, [Zn] = 98 mM, $[MMA]_0$ = 467 mM at 0 °C in toluene.

Polymerization of MMA was carried out under a dry nitrogen atmosphere in a 100-mL round-bottomed flask equipped with a magnetic stirrer. Described amounts of toluene, MMA, and a toluene solution of $Zn(C_2H_5)_2$ were injected into the flask, and the mixture was stirred for 1 h at 0 °C. To the mixture was then added a toluene solution of $Ph_3CB(C_6F_5)_4$ (5.0 mM, 1.0 mL), and polymerization was started by adding a toluene solution of $Et(Ind)_2Zr(CH_3)_2$ (5.0 mM, 1.0 mL). The polymerization was quenched by acidic methanol at 0 °C. The polymer produced was precipitated into methanol, followed by drying in vacuo at 40 °C for 8 h. Polymerizations at higher temperatures were carried out by setting the reactor into the temperature-controlled oil bath immediately after injecting a zirconocene compound at room temperature.

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Table 1. Results of Isospecific Polymerization of MMA[a]

				polymer structure (%)[c]				
run no.	catalyst	ZnR_2	yield[b] (%)	mm	mr	rr	M_n[d] (×10⁴)	M_w/M_n
43-1	Et(Ind)$_2$	CH$_2$CH$_3$	33	96.5	2.5	1.0	39.3	1.43
34-3	Et(Ind)$_2$	(CH$_2$)$_3$CH$_3$	82	94.5	3.5	2.0	60.0	1.30
39-2	Et(Ind)$_2$	(CH$_2$)$_2$CH=CH$_2$	48	98.0	1.3	0.7	59.9	1.30
40-1	Et(IndH$_4$)$_2$	CH$_2$CH$_3$	79	94.4	3.7	1.9	32.0	1.32
40-2	Et(IndH$_4$)$_2$	(CH$_2$)$_3$CH$_3$	68	95.1	3.7	1.2	40.5	1.30
40-3	Et(IndH$_4$)$_2$	(CH$_2$)$_2$CH=CH$_2$	64	95.5	3.3	1.2	33.9	1.25
31-2	Me$_2$Si(Ind)$_2$	CH$_2$CH$_3$	25	86.8	5.8	7.4	11.4	1.71
34-2	Me$_2$Si(Ind)$_2$	(CH$_2$)$_3$CH$_3$	38	84.6	7.5	7.9	37.1	1.41
28-3	Me$_2$Si(Ind)$_2$	(CH$_2$)$_2$CH=CH$_2$	34	91.4	5.3	2.3	34.5	1.34

[a] Polymerization conditions: [Zr] = [Ph$_3$CB(C$_6$F$_5$)$_4$] = 0.25 mM, [ZnR$_2$] = 98 mM, [MMA]$_0$ = 467 mM, 0 °C in toluene for 24 h. [b] Yield = weight of polymer obtained/weight of monomer introduced. [c] Measured by ^{1}H NMR. [d] Measured by GPC, calibrated by PMMA standards.

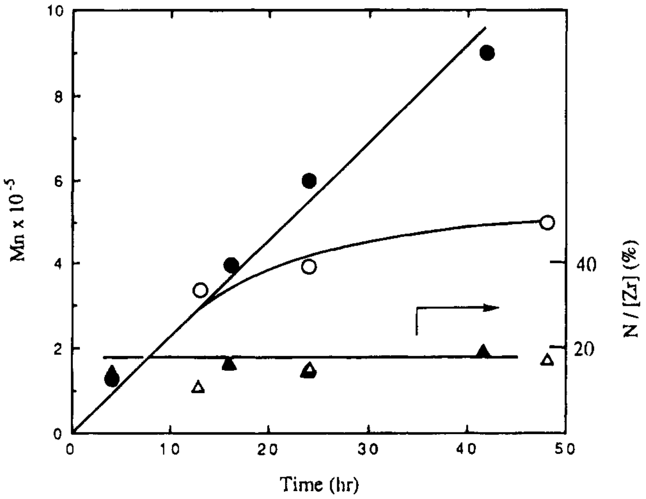


Figure 2. Relation of the molecular weight (M_n) and the polymer chain number (N/[Zr]) to polymerization time in the presence of Zn(C$_2$H$_5$)$_2$ (○, △) or Zn(C$_2$H$_4$CH=CH$_2$)$_2$ (●, ▲). Polymerization conditions: see Figure 1.

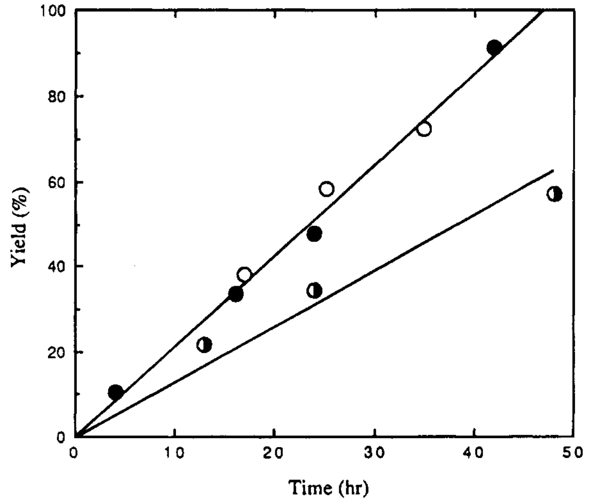


Figure 3. Plots of the polymer yield against the polymerization time (●, Et(Ind)$_2$Zr(CH$_3$)$_2$; ○, Et(IndH$_4$)$_2$Zr(CH$_3$)$_2$; ◑, Me$_2$Si(Ind)$_2$Zr(CH$_3$)$_2$). Polymerization conditions: [Zr] = [Ph$_3$CB(C$_6$F$_5$)$_4$] = 0.25 mM, [Zn(C$_2$H$_4$CH=CH$_2$)$_2$] = 98 mM, [MMA]$_0$ = 467 mM, in toluene, at 0 °C.

The molecular weight and molecular weight distribution were measured by GPC (Shimadzu 9A) at room temperature using chloroform as solvent and calibrated with standard PMMA samples. The ^{1}H and ^{13}C NMR spectra were measured in chloroform-*d* at 50 °C with a JEOL EX-400 NMR spectrometer. Broad-band decoupling was used to remove the ^{13}C–^{1}H coupling. The center peak of chloroform-*d* (77.0 ppm) and the peak of undeuterated chloroform (7.25 ppm) were used as internal references for ^{13}C NMR and ^{1}H NMR, respectively.

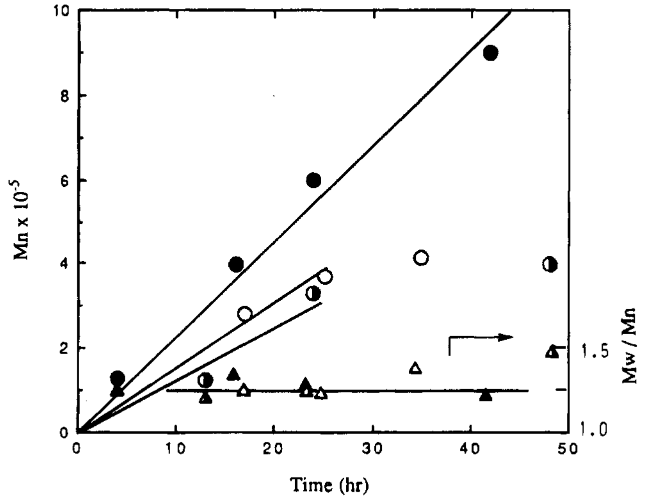


Figure 4. Relationship between M_n and the polymerization time (●, ▲, Et(Ind)$_2$Zr(CH$_3$)$_2$; ○, △, Et(IndH$_4$)$_2$Zr(CH$_3$)$_2$; ◑, ▲, Me$_2$Si(Ind)$_2$Zr(CH$_3$)$_2$). Polymerization conditions: see Figure 3.

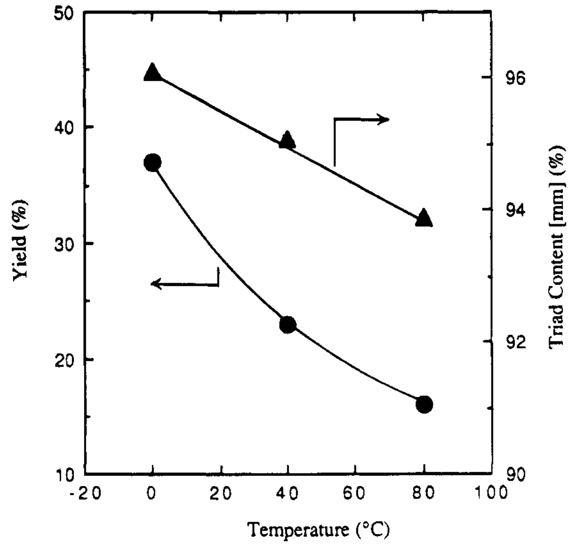


Figure 5. Relation of the polymer yield and isotactic triad (mm) content (measured by ^{1}H NMR) to polymerization temperatures. [Et(Ind)$_2$Zr(CH$_3$)$_2$] = [Ph$_3$CB(C$_6$F$_5$)$_4$] = 0.23 mM, [Zn(C$_2$H$_5$)$_2$] = 214 mM, [MMA]$_0$ = 850 mM in toluene.

Results and Discussion

Polymerization of MMA was carried out in toluene at 0 °C for 24 h with some chiral zirconocenedimethyl combined with Ph$_3$CB(C$_6$F$_5$)$_4$ in the presence of several dialkylzinc compounds. Ph$_3$CB(C$_6$F$_5$)$_4$ is reported to be one of the best activators in the propene polymerization by a zirconocenedimethyl catalyst system.[4] The polymer

Table 2. Effect of $Zn(C_2H_5)_2$ Concentration[a]

run no.	$[Zn(C_2H_5)_2]$ (mM)	yield[b] (%)	M_n[c] ($\times 10^4$)	M_w/M_n	$N/[Zr]$[d] (%)
31-1	49	24	15.0	1.70	29
31-2	98	25	11.4	1.71	41
31-3	300	11	5.0	2.05	41
31-3	500	8	4.3	2.15	34

[a] Polymerization conditions: $[Me_2Si(Ind)_2Zr(CH_3)_2]$ = $[Ph_3CB(C_6F_5)_4]$ = 0.25 mM, $[MMA]_0$ = 467 mM at 0 °C in toluene for 24 h. [b] Yield = weight of polymer obtained/weight of monomer introduced. [c] Measured by GPC, calibrated by PMMA standards. [d] N means polymer chain number.

yield together with some analytical results of the polymerization is summarized in Table 1. The polymer yield was found to be dependent upon the ligand of the zirconocene compounds and the dialkylzinc compounds as well. It may be roughly said, however, that the polymer yield decreased approximately in the following order: $Et(IndH_4)_2 > Et(Ind)_2 > Me_2Si(Ind)_2$.

On the other hand, both the isotacticity and molecular weight of PMMA decreased as follows: $Et(Ind)_2 > Et(IndH_4)_2 > Me_2Si(Ind)_2$. All the catalyst systems gave PMMA with narrow polydispersity.

In the presence of $Zn(C_2H_5)_2$ or $Zn(C_2H_4CH{=}CH_2)_2$, polymerization of MMA was then carried out with a *rac*-$Et(Ind)_2Zr(CH_3)_2/Ph_3CB(C_6F_5)_4$ catalyst system at 0 °C in toluene by changing the polymerization time. Plots of the polymer yields (Y) against the polymerization time are shown in Figure 1. In Figure 2, the molecular weight of the polymer (M_n) and the number of produced polymer chains (N) are plotted against the polymerization time. When polymerization was conducted in the presence of $Zn(C_2H_4CH{=}CH_2)_2$, both Y and M_n increased in proportion to the polymerization time, indicating that living polymerization proceeds with zero-order kinetics with respect to the monomer concentration. The initiating efficiency ($N/[Zr]$) of the catalyst system was estimated to be approximate 18%. When $Zn(C_2H_5)_2$ was used, both Y and M_n displayed a tendency to increase to a constant value along with the polymerization time, keeping molecular mass distribution unchanged (M_w/M_n = 1.42−1.44), whereas the number of

Table 3. Pentad Structure of PMMA[a]

run no.	catalyst	ZnR_2	temp (°C)	pentad fraction (%)[b] mmmm	mmmr	rmmr	mmrm	rmrm	mmrr	rmrr	mrrm	rrrm	rrrr	selectivity β	triad test[c] 2[rr]/[mr]
43-1	$Et(Ind)_2$	C_2H_5	0	94.0	2.3	0	0	0	2.5	0	1.2	0	0	0.987	0.96
29-1	$Et(Ind)_2$	C_2H_5	80	84.1	6.9	0	0	0	6.1	0	2.9	0	0	0.965	0.95
39-2	$Et(Ind)_2$	$C_2H_4CH{=}CH_2$	0	96.6	1.4	0	0	0	1.3	0	0.7	0	0	0.993	1.0
40-1	$Et(IndH_4)_2$	C_2H_5	0	90.3	4.2	0	0	0	3.7	0	1.8	0	0	0.980	0.98
40-3	$Et(IndH_4)_2$	$C_2H_4CH{=}CH_2$	0	91.9	3.1	0	0	0	3.3	0	1.7	0	0	0.983	0.95
28-1	$Me_2Si(Ind)_2$	C_2H_5	0	71.5	7.7		0.6		9.5		3.5	2.5	4.7	0.953[d]	2.1
28-3	$Me_2Si(Ind)_2$	$C_2H_4CH{=}CH_2$	0	86.3	5.7	0	0	0	5.5	0	2.5	0	0	0.969	0.91

[a] Polymerization conditions: refer to Table 1. [b] Observed in ^{13}C NMR spectra of carbonyl resonances. β is the selectivity of one prochiral face on the enantiomorphic site. [c] 2[rr]/[mr] = 1 for an enantiomorphic site-controlled mechanism. [d] Calculated according to a two-site model with parameters ω = 0.902 and Pr = 0.840.

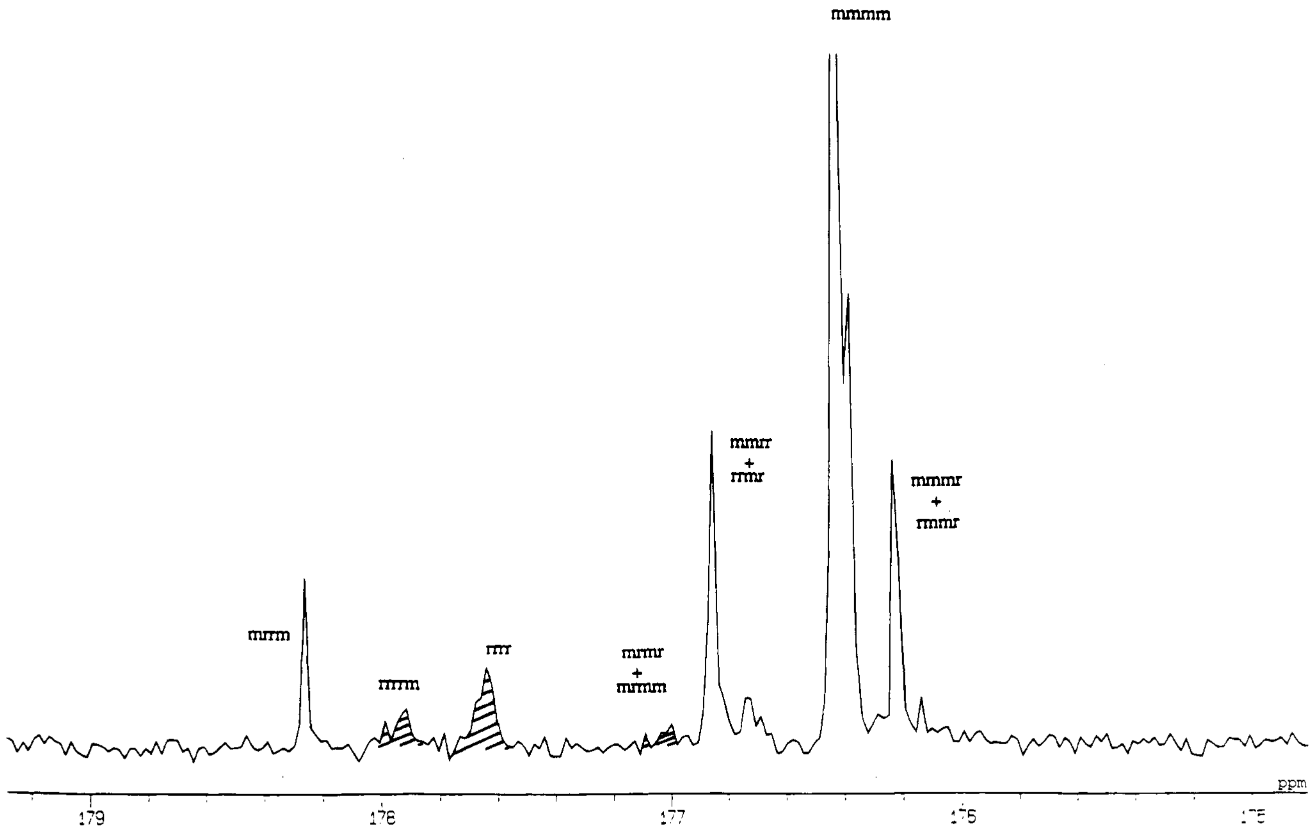


Figure 6. 100-MHz ^{13}C NMR spectrum of carbonyl resonances of iso-PMMA obtained from $Me_2Si(Ind)_2Zr(CH_3)_2/Ph_3CB(C_6F_5)_4$ at the following conditions: $[Me_2Si(Ind)_2Zr(CH_3)_2]$ = $[Ph_3CB(C_6F_5)_4]$ = 0.25 mM, $[Zn(C_2H_5)_2]$ = 98 mM, $[MMA]_0$ = 467 mM in toluene at 0 °C for 24 h.

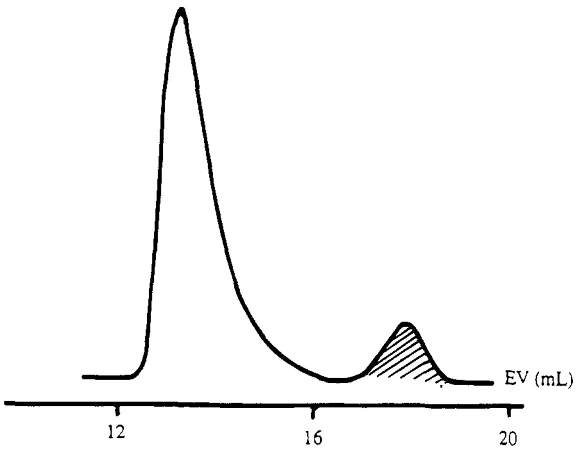


Figure 7. GPC profiles of PMMA produced in the presence of Al(i-C_4H_9)$_3$. Synthesis conditions: [Et(Ind)$_2$Zr(CH_3)$_2$] = [$Ph_3CB(C_6F_5)_4$] = 0.25 mM, [Al(i-C_4H_9)$_3$] = 197 mM, [MMA]$_0$ = 467 mM in toluene at 0 °C for 24 h.

polymer chains calculated from Y and M_n did not change so much. Therefore, the decline of the molecular weight along with the polymerization time is mainly attributed to the termination reactions. However, it should be noticed here that the slopes of M_n–time plots within the initial 20 h in Figure 2 coincide with each other, which suggests the change of alkylzinc compounds does not affect the propagation rate.

Zn($C_2H_4CH{=}CH_2$)$_2$ was then used in the polymerization of MMA. Various zirconocene compounds were used as catalysts combined with an equimolar amount of $Ph_3CB(C_6F_5)_4$. The results obtained are illustrated in Figures 3 and 4. The polymer yields increased approximately in proportion to the polymerization time for the three zirconocene compounds (Figure 3). The molecular weight of the polymer produced with the *rac*-Et(Ind)$_2$Zr(CH_3)$_2$ increased linearly with the polymerization time, keeping the molecular weight distribution unchanged as described above, while those produced with the other zirconocene catalysts showed a tendency to reach constant values with the molecular weight distribution broadened (Figure 4). Therefore, it seems that transfer reactions occurred in the latter polymerization systems. From the initial slopes of the M_n–time plots in Figure 4, however, we can roughly estimate the propagation rate constant (k_p), which depends upon the zirconocene catalysts. The values obtained were 2.3 × 10^2, 1.5 × 10^2, and 1.3 × 10^2 (h^{-1}) for Et(Ind)$_2$, Et(IndH_4)$_2$, and Me_2Si(Ind)$_2$, respectively.

The effects of the polymerization temperature and the concentration of alkylzinc compounds on the polymer yield were also investigated in some detail. The polymer yield decreased monotonously with an increase in the polymerization temperature from 0 to 40 and 80 °C (Figure 5). It was found that no more living polymerization of MMA proceeds at 40 and 80 °C even by using the *rac*-Et(Ind)$_2$Zr(CH_3)$_2$–Zn($C_2H_4CH{=}CH_2$)$_2$ catalyst system. The typical results of MMA polymerization obtained with different concentrations of alkylzinc compounds are shown in Table 2. The maximum polymer yield was obtained with approximately 50 mM alkylzinc compounds. The use of an excess amount of alkylzinc compounds caused a decrease in the polymer yield as well as the molecular weight of PMMA produced.

To check whether the isotactic polymers are produced by the enantiomorphic site-controlled mechanism or the chain-end-controlled mechanism, typical polymers were analyzed by ^{13}C NMR, the results of which are summarized in Table 3.

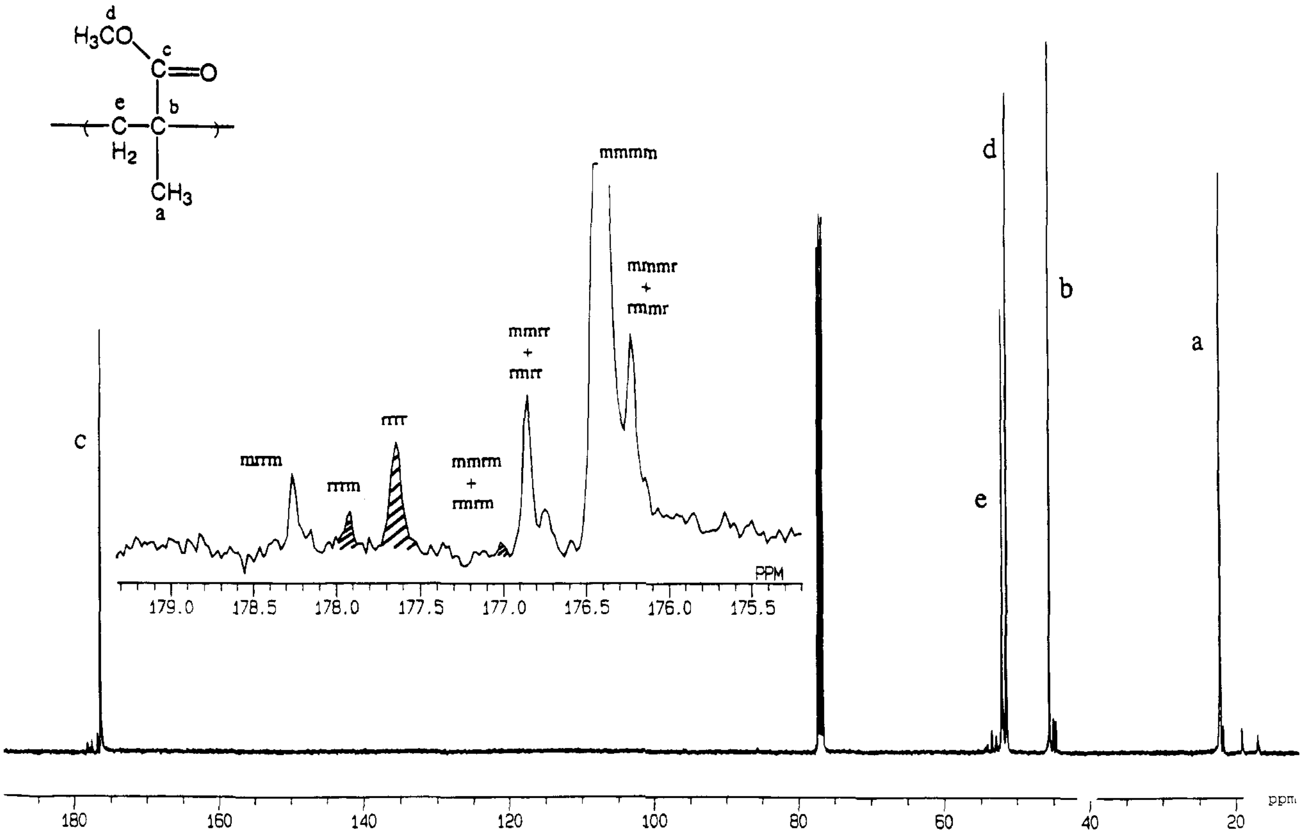


Figure 8. 100-MHz ^{13}C NMR spectrum of iso-PMMA initiated by *rac*-Et(Ind)$_2$Zr(CH_3)$_2$/$Ph_3CB(C_6F_5)_4$ in the presence of Al(i-C_4H_9)$_3$. Polymerization conditions are shown in Figure 7.

Table 4. Results of MMA Polymerization with Triisobutylaluminum[a]

				wt fraction[c]				
run no.	catalyst	[Al] (mM)	yield[b] (%)	high (%)	low (%)	M_n[d] ($\times 10^5$)	M_w/M_n[d]	N/[Zr][e] (%)
27-3	$Et(Ind)_2$	197	82	81	19	5.08	1.25	24
40-4	$Et(IndH_4)_2$	98	49	94	6	2.09	1.31	41
30-2	$Me_2Si(Ind)_2$	98	49	88	12	1.73	1.53	47
30-3	$Me_2Si(Ind)_2$	197	43	91	9	1.68	1.35	43
30-4	$Me_2Si(Ind)_2$	394	2	90	10	0.91	1.51	4

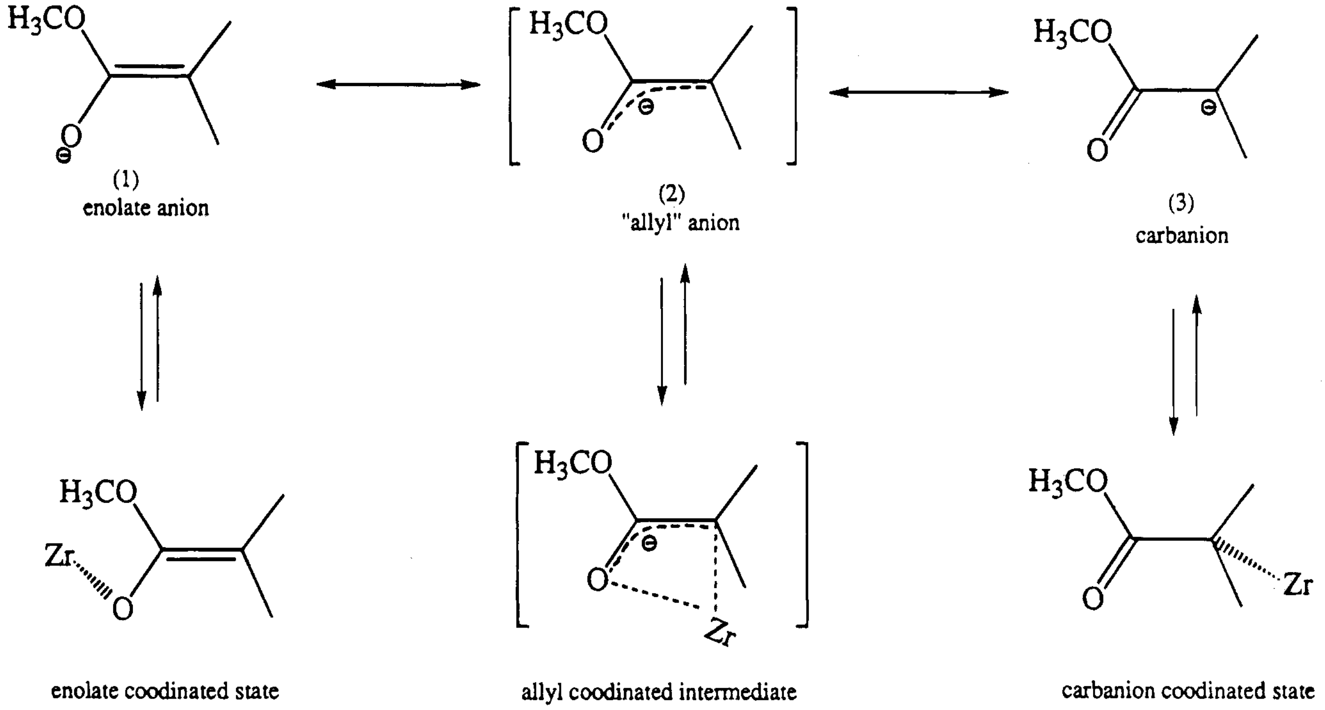
[a] Polymerization conditions: [Zr] = $[Ph_3CB(C_6F_5)_4]$ = 0.25 mM, $[MMA]_0$ = 467 mM, polymerization at 0 °C for 24 h. [b] Yield = weight of polymer obtained/weight of monomer introduced. [c] Weight fraction of two GPC profiles. [d] Measured by GPC, calibrated with PMMA standards. [e] Polymer chain number N = yield (g) × weight fraction (H)/M_n.

Table 5. Pentad Structure of PMMA Obtained with Triisobutylaluminum[a]

		pentad fraction (%)[b]										parameters[c]		
run no.	catalyst	mmmm	mmmr	rmmr	mmrm	rmrm	mmrr	rmrr	mrrm	rrrm	rrrr	β	ω	Pr
27-3	$Et(Ind)_2$	87.0	1.7		0.1		3.7		0.9	1.5	5.1			
		(86.93)	(1.55)	(0.14)	(0.05)	(0.27)	(1.77)	(1.65)	(0.89)	(1.65)	(5.10)	0.991	0.908	0.862
40-4	$Et(IndH_4)_2$	84.1	4.0		0.2		5.1		1.9	1.0	3.8			
		(83.99)	(3.84)	(0.10)	(0.09)	(0.20)	(3.94)	(1.04)	(1.97)	(1.03)	(3.80)	0.978	0.940	0.888
30-3	$Me_2Si(Ind)_2$	78.2	3.8		0.1		5.6		1.3	2.7	8.3			
		(77.32)	(3.63)	(0.18)	(0.12)	(0.34)	(3.87)	(2.18)	(1.93)	(2.17)	(8.26)	0.977	0.867	0.887

[a] Polymerization conditions: refer to Table 4. [b] Observed in ^{13}C NMR of carbonyl resonances of PMMA. The value in parentheses is calculated from a two-site model. [c] β is the selectivity of one prochiral face on the enantiomorphic site; ω is weight fraction of polymer derived from the isotactic site; Pr is the probability of syndiotactic propagation in the syndiospecific site.

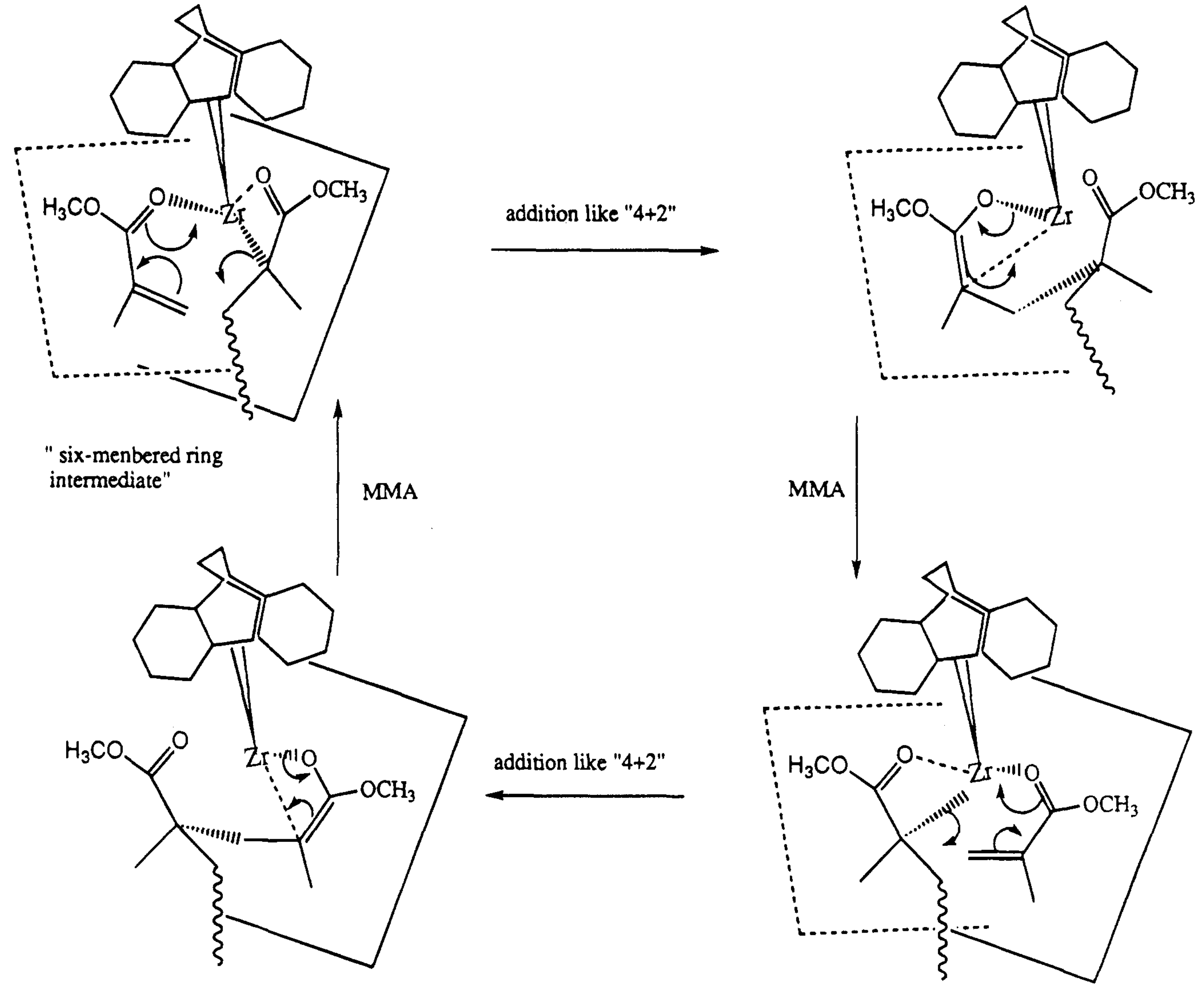
Scheme 1



The defects in the pentad structures of these polymers (except for the polymer obtained with the *rac*-$Me_2Si(Ind)_2Zr(CH_3)_2$–$Zn(C_2H_5)_2$ catalyst system) obeyed the statistics derived from the enantiomorphic site model, i.e., [mmmr]:[mmrr]:[mrrm] = 2:2:1, where the probabilities of insertion from one of the two prochiral faces in the enantiomorphic site (β) were calculated to be approximately 0.99, 0.98, and 0.97 for the *rac*-$Et(Ind)_2Zr(CH_3)_2$, *rac*-$Et(IndH_4)_2Zr(CH_3)_2$, and *rac*-$Me_2Si(Ind)_2Zr(CH_3)_2$ catalysts. The polymer obtained with the *rac*-$Me_2Si(Ind)_2Zr(CH_3)_2$–$Zn(C_2H_5)_2$ catalyst system, however, displayed the resonances attributed to syndiotactic structure (Figure 6). Therefore, the polymer was analyzed by a two-site model:[10] an isospecific site by enantiomorphic site control and a syndiospecific site by chain end control. The parameters were estimated to be β = 0.95, Pr (probability of syndiotactic propagation in the syndiospecific site) = 0.84, and ω (weight fraction of PMMA produced by the isospecific site) = 0.90.

Trialkylaluminum is known to function as an activator of MMA in anionic polymerizations.[11] From such a viewpoint, polymerization of MMA was carried out using triisobutylaluminum in place of alkylzinc compounds. The GPC profiles and the ^{13}C NMR spectrum of a typical polymer are given in Figures 7 and 8, which suggest that the product is a mixture composed of two kinds of PMMA. The weight fraction of the lower molecular weight part in GPC is equal to the weight fraction of the syndiotactic sequences in ^{13}C NMR, which indicates that one component is isotactic PMMA with a high molecular weight and the other is syndio-rich PMMA

Scheme 2



with a very low molecular weight. The results of polymerization with different catalysts and the pentad structures of the polymers are summarized in Tables 4 and 5.

The steric defects of the isotactic sequence shown in Table 5 approximately fit the following statistics equation:[5] [mmmr]:[mmrr]:[mrrm] = 2:2:1, indicating that isotactic polymerization proceeds by the enantiomorphic site-controlled mechanism. The β values obtained by the two-site model described above were found to be very high (Table 5) and in good agreement with the results from alkylzinc compounds. The syndio-rich PMMA with a very low molecular weight might be formed with some aluminum-related active species, the detail of which is, however, not clear at present.

Finally, a plausible mechanism of the isotactic polymerization of MMA with the aid of alkylzinc and alkylaluminum compounds is considered. The alkylzinc and alkylaluminum compounds are considered as activators of MMA in the initiation and are not involved in the propagation reaction.[7] The stereoselectivity of catalysts is not so sensitive to the polymerization temperature (Table 3), which completely differs from the observation in the group transfer polymerization (GTP) proceeding with a normal enolate species. Considering the similarities between zirconocene cation and lanthanocene together with the results reported by Yasuda et al.[1] and Collins et al.,[12] we suppose that the propagating species in the present system is the zirconium enolate cation.

Considering the existence of the resonance between the enolate anion (**1**) and the carbon anion (**3**) (Scheme 1), an "allyl" intermediate (**2**) can be assumed, in which the π electrons fluent along the conjugation atoms. This allyl anion coordinates to the zirconocene to form an allyl type coordinated intermediate, which may take a plane structure (Scheme 2). Due to the bulkiness of zirconocene ligands as well as the allyl character, the plane may be forbidden to turnover; i.e., the configuration can be frozen. Whereas, the monomer may coordinate to the zirconocene in a plane avoiding the steric bulkiness of the ligands. Through a possible 4 + 2 cycle addition of the two conjugation double bonds of MMA to the π bond between Zr^{4+} and the allyl anion, new C−C and Zr−O σ-bonds may be formed. According to the equilibrium shown in Scheme 1, a new allyl intermediate can be reproduced in the same configuration with the former due to the C_2 symmetry of the zirconocene compounds.

Conclusion

Highly isotactic PMMA was synthesized with the *ansa*-zirconocenedimethyl/$Ph_3CB(C_6F_5)_4$ catalysts combined with suitable Lewis acids. The isotactic polymerization was found to proceed by an enantiomorphic site-controlled mechanism. Living polymerization of MMA took place when the polymerization was conducted at 0 °C in toluene by the *rac*-Et(Ind)$_2$Zr(CH$_3$)$_2$/Ph$_3$CB(C$_6$F$_5$)$_4$/Zn(C$_2$H$_4$CH=CH$_2$)$_2$ catalyst system. Raising the polymerization temperature from 0 to 80 °C caused a decrease in the polymer yield and molecular weight while keeping the catalyst isospecificity almost unchanged. The use of triisobutylaluminum as a Lewis acid also gave highly isotactic PMMA with a small amount of syndio-rich PMMA as the byproduct.

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