

Polymerization of Ethylene by Zirconocene–B(C₆F₅)₃ Catalysts with Aluminum Compounds

SHENGSHENG LIU, GUANGQIAN YU, BAOTONG HUANG

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, People's Republic of China

Received 30 January 1997; accepted 25 March 1997

ABSTRACT: Ethylene polymerization by zirconocene–B(C₆F₅)₃ catalysts with various aluminum compounds has been investigated. It is found that the catalytic activity depended on zirconocenes used, and especially on the type of aluminum compounds. For Et(H₄Ind)₂ZrCl₂ (H₄Ind : tetrahydroindenyl), the activity decreases in the following order: Me₃Al > *i*-Bu₃Al > Et₃Al ≧ Et₂AlCl. While for Cp₂ZrCl₂ (Cp : cyclopentadienyl), it varies as follows: *i*-Bu₃Al > Me₃Al ≧ Et₃Al. Furthermore, the activity is significantly affected by the addition mode of the catalytic components, which may imply that the formation of active centers is associated with an existing concentration of catalytic components. Results of thermal behavior of polyethylene (PE) studied by differential scanning calorimetry (DSC) show that crystallinity of the polymer prepared with Et₃Al is higher than that with Me₃Al or *i*-Bu₃Al. It is also found that the number-average molecular weight (\bar{M}) of the polymers prepared with Me₃Al or *i*-Bu₃Al is much higher than that with Et₃Al. ¹H-NMR studies substantiate that *i*-Bu₃Al is a more efficient alkylation agent of Cp₂ZrCl₂ in comparison with Me₃Al. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1715–1720, 1997

Key words: ethylene; polymerization; zirconocene; aluminium compound; ¹H-NMR

INTRODUCTION

The homogeneous Ziegler–Natta catalyst Cp₂TiCl₂–R₂AlCl, first described by Breslow and Newburg,^{1,2} has low activity for ethylene polymerization because of bimolecular deactivation due to reductive metathesis. Kaminsky and Sinn obtained an extremely active catalyst by substituting Zr for Ti and using methylaluminumoxane (MAO) as cocatalyst.³ Furthermore, Kaminsky et al.⁴ found that *rac*-Et(Ind)₂ZrCl₂–MAO[Et(Ind)₂ = ethylene–bis(indenyl)] can catalyze stereospecific polymerization of α -olefin in soluble systems. Metallocene catalysts that provide

access to, besides isotactic,^{5,6} isotactic–stereoblock,⁷ syndiotactic,⁸ and isotactic–atactic, block⁹ polypropylenes have been developed. Unfortunately, these catalysts require a large amount of MAO to realize the maximum catalytic activity, which, on some extent, may impair its value in commercial applications. In view of this, much effort has been made not only to lower the amount of MAO in polymerization but also to find a new cocatalyst in place of MAO.

One way of lowering the amount of MAO is to immobilize the zirconocene on a support, such as SiO₂, Al₂O₃, or other supports of high surface area.^{10–16} In several cases, it is claimed that additional MAO is not needed during polymerization if it is initially deposited on the surface during preparation of the supported catalyst. Since many polyolefin manufacturing plants are based on fluidized bed technology, the supported metallocene

Correspondence to: S. Liu

Contract grant sponsor: National Natural Science Foundation of China (NNSFC).

Journal of Applied Polymer Science, Vol. 66, 1715–1720 (1997)

© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/091715-06

Table I Ethylene Polymerization with Et(H₄Ind)₂ZrCl₂-B(C₆F₅)₃-R₃Al

No.	R ₃ Al (mmol)	Activity (10 ⁶ g mol Zr)	Crystallinity (%)	T _m (°C)	\bar{M}	
1	Me ₃ Al	0.20	1.20	58.8	138.8	1.59 × 10 ⁵
2	Me ₃ Al	0.45	1.61	—	—	—
3	Me ₃ Al	0.60	1.82	—	—	—
4	Me ₃ Al	1.00	1.48	—	—	—
5	Et ₃ Al	0.40	0.62	—	—	—
6	Et ₃ Al	0.80	0.50	74.5	135.2	0.35 × 10 ⁵
7	<i>i</i> -Bu ₃ Al	0.40	1.25	57.3	136.7	2.15 × 10 ⁵
8	<i>i</i> -Bu ₃ Al	0.60	1.01	—	—	1.48 × 10 ⁵
9	<i>i</i> -Bu ₃ Al	1.00	0.85	—	—	—
10	EtAlCl ₂	1.00	trace	—	—	—
11	MAO	3.00	3.18	—	134.4	1.08 × 10 ⁵

Conditions: Et(H₄Ind)₂ZrCl₂, 2 μmol; B(C₆F₅)₃, 3 μmol; toluene, 100 mL; ethylene pressure, 0.4 atm; 50°C, 30 min. Order of addition of catalysts: R₃Al; Et(H₄Ind)₂ZrCl₂; B(C₆F₅)₃.

catalysts would add new dimensions to their usefulness.

On the other hand, satisfactory results have been obtained by using new activators in the place of MAO, such as [C₆H₅(CH₃)₂NH⁺][⁻B(C₆F₅)₄], [(C₆H₅)₃C⁺][⁻B(C₆F₅)₄], and B(C₆F₅)₃.¹⁷⁻¹⁹ A significant advantage is that only a stoichiometric amount of the cocatalyst is required to achieve the maximum catalytic activity of the system.

This article reports the results of ethylene polymerization by zirconocene-B(C₆F₅)₃ catalyst with different aluminum compounds, such as Me₃Al, Et₃Al, *i*-Bu₃Al, etc. The properties of polyethylene (PE) prepared with the above catalytic systems have been characterized. The interaction between Cp₂ZrCl₂, B(C₆F₅)₃, and R₃Al was studied by ¹H-NMR spectroscopy.

EXPERIMENTAL

Materials

Ethylene, polymerization-grade from Liaoyang Chemical Corporation, was used without further treatment. Toluene as the solvent was dried with 4A molecular sieves, then distilled in the presence of Na-K alloy. Cp₂ZrCl₂, Et(H₄Ind)₂ZrCl₂, and B(C₆F₅)₃ were of commercial origin (Boulder Scientific Company, Mead). Me₃Al, Et₃Al, *i*-Bu₃Al, and Et₂AlCl (Fluka AG, Buchs) were used as received.

Polymerization

Polymerization of ethylene was carried out with stirring in a 250 mL glass reactor under an atmosphere of argon. After evacuating the reactor for 1 h, it was filled with purified argon to atmospheric pressure, and toluene was injected into the reactor; and the monomer, aluminum compound, zirconocene, and B(C₆F₅)₃ were added separately in that order. After a specified polymerization time, an ethanol solution of hydrochloric acid was injected into the reactor to quench the polymerization. The polymer was washed several times with ethanol and dried under vacuum at 50°C for two days.

Characterization

Differential scanning calorimetry (DSC) measurements were made with a Perkin-Elmer DSC-7 system. Each sample was heated from 40 to 100°C at a heating rate of 10°C min and kept at this temperature for 5 min. It was then cooled to 40°C at a rate of 10°C min and reheated at the same rate. The values of melting point (T_m) were obtained in the second scan. Crystallinity of the polymers was calculated from the equation

$$\chi (\%) = (\Delta H_m / \Delta H_m^\circ) \times 100$$

where ΔH_m is the heat of fusion of the samples, as determined from the DSC curves of the second heating process, and ΔH_m° is the heat of fusion of perfectly crystalline polyethylene, 286 J g.²⁰

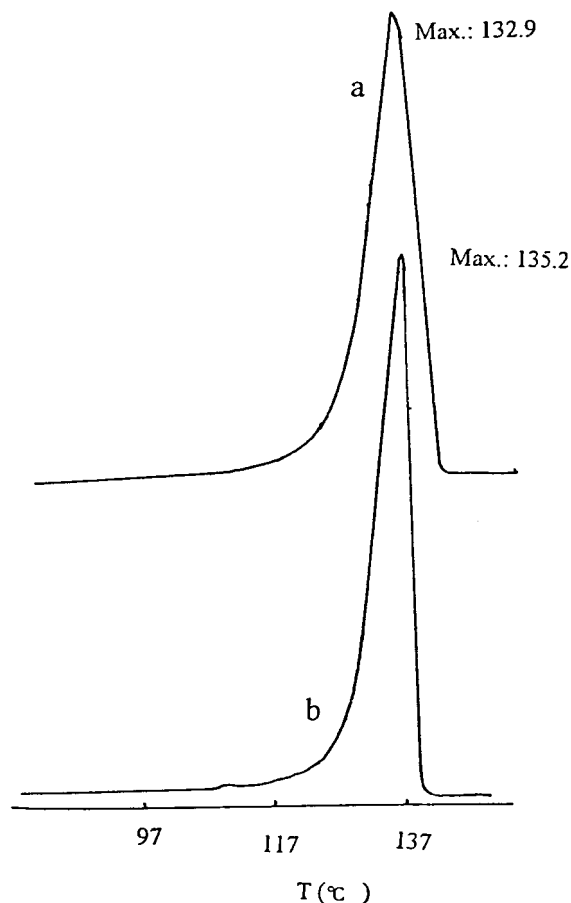


Figure 1 DSC curves of PE prepared with the $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3\text{-Et}_3\text{Al}$ catalyst: (a) the first heating process; (b) the second heating process.

The number-average molecular weight (\bar{M}) of the polymers were determined from the following equation²¹:

$$[\eta] = 2.30 \times 10^{-4} \bar{M}^{0.82}$$

where $[\eta]$ denotes the intrinsic viscosity of the polymer solution obtained with an Ubbelohde viscometer in decalin at 135°C according to the usual procedure.

¹H-NMR analyses of the reactions between Cp_2ZrCl_2 and $\text{B}(\text{C}_6\text{F}_5)_3\text{-R}_3\text{Al}$ were performed at room temperature with a Varian NMR-400 spectrometer operating in Fourier transform mode. The benzene- d_6 (99%, Aldrich) used as solvent was dried over calcium hydride for several days, followed by distillation. The chemical shift of benzene protons as internal standard is $\delta = 7.27$ ppm. About 6 mg (20 μmol) of Cp_2ZrCl_2 were dissolved

in 0.5 mL of benzene- d_6 , then aluminum compounds and $\text{B}(\text{C}_6\text{F}_5)_3$ were introduced to the nuclear magnetic resonance (NMR) tube.

RESULTS AND DISCUSSION

Polymerization with $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3\text{-R}_3\text{Al}$ System

According to the generally accepted point of view, zirconocenium species can be produced by the reaction of dimethyl zirconocene derivative with $\text{B}(\text{C}_6\text{F}_5)_3$. For dichlorozirconocene, it needs to be alkylated first, followed by extraction of the anionic ligand to produce the active species.

Despite several papers on zirconocene- $\text{B}(\text{C}_6\text{F}_5)_3$ catalyst in ethylene or propylene polymerization,²²⁻²⁴ the effect of aluminum compounds on these polymerizations seems to be scarce. In the present work, different aluminum compounds are employed to alkylate dichlorozirconocene. The results of ethylene polymerization with $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3\text{-R}_3\text{Al}$ were summarized in Table I.

It can be seen from Table I that aluminum compounds are so important that they can cause up to a more than a three-fold difference in polymerization activity under otherwise identical conditions. Activities of the aluminum compounds decrease in the following order: $\text{Me}_3\text{Al} > i\text{-Bu}_3\text{Al} > \text{Et}_3\text{Al} \gg \text{EtAlCl}_2$. The much lower activity achieved by Et_2AlCl may be attributed to the fact that Et_2AlCl cannot effectively alkylate dichloro-

Table II Ethylene Polymerization with $\text{Cp}_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3\text{-R}_3\text{Al}$ System

No.	R_3Al	(mmol)	Activity (10^6 g mol Zr)
12	Me_3Al	1.0	0.05
13	Me_3Al	2.0	0.03
14	Et_3Al	0.6	trace
15	Et_3Al	2.0	trace
16	$i\text{-Bu}_3\text{Al}$	0.2	trace
17	$i\text{-Bu}_3\text{Al}$	0.4	0.52
18	$i\text{-Bu}_3\text{Al}$	0.6	0.82
19	$i\text{-Bu}_3\text{Al}$	0.8	1.35
20	$i\text{-Bu}_3\text{Al}$	1.0	1.10
21	$i\text{-Bu}_3\text{Al}$	1.5	0.68
22	$i\text{-Bu}_3\text{Al}$	2.0	0.30

Conditions: Cp_2ZrCl_2 2 μmol ; others as in Table I.

Table III Effect of Mode of Catalyst Addition on Ethylene Polymerization

No.	<i>i</i> -Bu ₃ Al (mmol)			Activity (10 ⁶ g mol Zr)
	To Reactor	From Ampoule	Total	
23	0.2	0.1	0.3	1.10
24	0.2	0.2	0.4	2.65
25	0.2	0.3	0.5	1.55
26	0.2	0.4	0.6	1.15
27	1.3	0.2	1.5	trace
28	1.5	0.2	1.7	trace

Conditions: Cp₂ZrCl₂, 2 μmol; others as in Table I.

zirconocene due to its relatively low content of alkyl groups in Et₂AlCl.

The effect of concentration of aluminum compounds on activity is evident. For Me₃Al, polymerization activity increased with increments of Me₃Al from 0.2 to 0.6 mmol; however, it decreased slightly, with a further increase in concentration. The same results were obtained when using *i*-Bu₃Al as the cocatalyst in place of Me₃Al.

It is well known that the melting point (T_m) of PE is lowered after reheating to erase the thermal history.²⁵ For the polymer prepared with Et₃Al in this work, however, the T_m value from the second heating process is higher than that from the first one (Fig. 1), the reason for which is not explicit.

Comparing the data in Table I, one can see that:

- (1) The polymers obtained with Me₃Al or *i*-Bu₃Al have much higher number-average molecular weight ($\bar{M} = 1.48\text{--}2.15 \times 10^5$) than that with Et₃Al ($\bar{M} = 0.35 \times 10^5$), which may imply that the polymer chain transfer to Et₃Al is easier than to Me₃Al or *i*-Bu₃Al.
- (2) Using MAO in place of B(C₆F₅)₃/*i*-Bu₃Al (or Me₃Al), the polymer has a lower \bar{M} .
- (3) Crystallinity of polymers obtained with Et₃Al is higher than that with *i*-Bu₃Al or Me₃Al.

Polymerization with Cp₂ZrCl₂-B(C₆F₅)₃-R₃Al System

Results of ethylene polymerization with Cp₂ZrCl₂/B(C₆F₅)₃/R₃Al system are tabulated in Table II.

The effect of aluminum compounds on polymerization is evident (Table II). For *i*-Bu₃Al, the activity increased monotonously with [*i*-Bu₃Al] un-

til it reached 0.8 mmol (1.35×10^6 g mol Zr) and then decreased rapidly on further increase in *i*-Bu₃Al until it reached only 0.30×10^6 g mol Zr at [*i*-Bu₃Al] of 2.0 mmol. It is deduced that the surplus *i*-Bu₃Al may lead to the formation of species like [Cp₂ZrR⁺][⁻Cl₂AlR₂], preventing further reaction between the alkylated zirconocene and B(C₆F₅)₃. As we know, the species [Cp₂ZrR⁺][⁻ClB(C₆F₅)₃]²³ is highly active, whereas the species as [Cp₂ZrR⁺][⁻Cl₂AlR₂] are much less active, which probably explains the lowering in activity when *i*-Bu₃Al exceeds a certain amount.

Use of Et₃Al and Me₃Al in place of *i*-Bu₃Al gives rise to reduction in activity. The activities of various aluminum compounds used as cocatalyst decrease in the following order: *i*-Bu₃Al > Me₃Al > Et₃Al.

Change in mode of addition of catalytic components was performed as follows. Only part of the *i*-Bu₃Al (0.2 mmol) was first added to the reactor, and the rest of the *i*-Bu₃Al and the whole of Cp₂ZrCl₂ and B(C₆F₅)₃ were introduced to a 40 mL ampoule containing 20 mL toluene, which were then injected into the polymerization reactor. It is found that, as shown in Table III, the polymerization behavior is dramatically altered.

For experiments 23–26, the activities are relatively higher at total amounts of *i*-Bu₃Al, as shown in Table II. When the total amount of *i*-Bu₃Al reaches 0.4 mmol, the activity is 2.65×10^6 g mol Zr, a five-fold increase as compared to No. 13 in Table II.

Keeping the catalytic components in the ampoules unchanged, extremely low activities were obtained with further increment of *i*-Bu₃Al in the polymerization reactor (Nos. 27, 28). It is inferred that the highly active species of [Cp₂ZrR⁺][⁻ClB(C₆F₅)₃] produced in the ampoule is de-

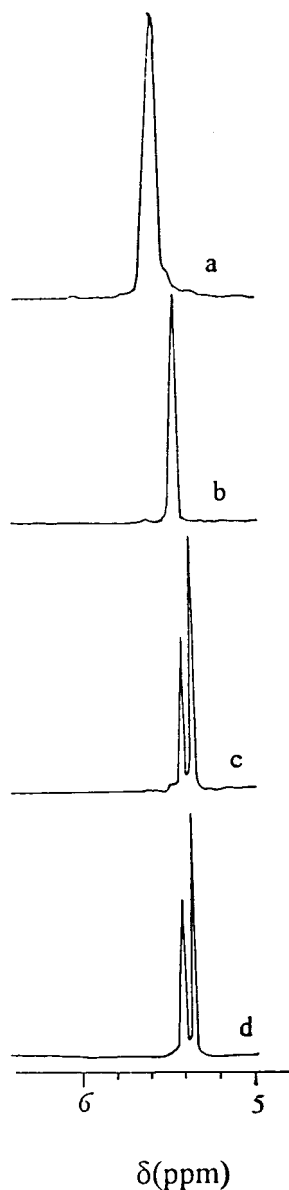
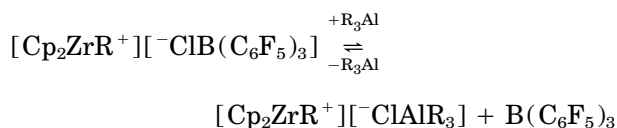


Figure 2 $^1\text{H-NMR}$ spectra of the catalytic components ($\text{B}(\text{C}_6\text{F}_5)_3$ is abbreviated as B): (a) $\text{Cp}_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3$ ($\text{B-Zr} = 1$); (b) $\text{Cp}_2\text{ZrCl}_2\text{-}i\text{-Bu}_3\text{Al}$ ($\text{Al-Zr} = 1$); (c) (b)- $\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{B-Zr} = 1$); (d) $\text{Cp}_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3\text{-}i\text{-Bu}_3\text{Al}$ ($\text{Al-Zr} = 5$; $\text{B-Zr} = 1$).

stroyed by the excess $i\text{-Bu}_3\text{Al}$ in the reactor, and the formation of active centers results at a required concentration of the catalytic components. The reversible reaction between different active species may be represented as



Compared with the usual addition procedure, a change in the mode of addition of the catalysts with limited amount of total $i\text{-Bu}_3\text{Al}$ leads to much higher activity, which is significant for commercial utilization.

$^1\text{H-NMR}$ Analyses of the Catalysts

The reaction between Cp_2ZrCl_2 , $\text{B}(\text{C}_6\text{F}_5)_3$, and R_3Al in benzene- d_6 at room temperature was monitored by means of $^1\text{H-NMR}$ spectroscopy. Dissolution of solid $\text{B}(\text{C}_6\text{F}_5)_3$ ($20 \mu\text{mol}$) in a solution of Cp_2ZrCl_2 ($20 \mu\text{mol}$) gave no new signals, except that at $\delta = 5.86$ ppm, assigned to be due to cyclopentadienyl of Cp_2ZrCl_2 [Fig. 2(a)]. It is inferred that no interaction between Cp_2ZrCl_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ occurred. For $\text{Cp}_2\text{ZrCl}_2\text{-}i\text{-Bu}_3\text{Al}$ ($\text{Al-Zr} = 1$), a signal appeared at $\delta = 5.724$ ppm, assigned to be due to cyclopentadienyl of $\text{Cp}_2\text{Zr}(i\text{-Bu})\text{Cl}$ [Fig. 2(b)]. The alkylation reaction between Cp_2ZrCl_2 and $i\text{-Bu}_3\text{Al}$ is almost complete in

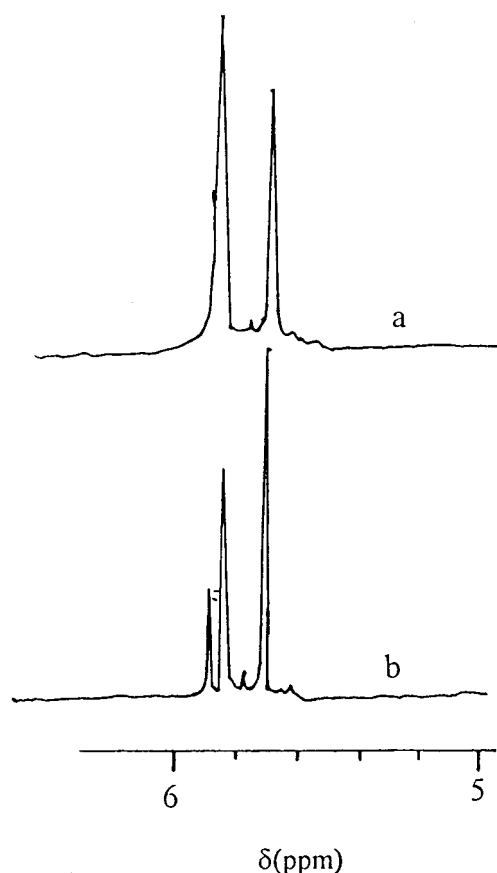


Figure 3 $^1\text{H-NMR}$ spectra of the $\text{Cp}_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3\text{-Me}_3\text{Al}$ system ($\text{B-Zr} = 1$): (a) $\text{Al-Zr} = 5$; (b) $\text{Al-Zr} = 20$.

the case of Al–Zr = 1. Addition of $B(C_6F_5)_3$ (B–Zr = 1) to the solution of $Cp_2ZrCl_2-i-Bu_3Al$ led to the appearance of two signals at $\delta = 5.641$ and 5.585 ppm, respectively [Fig. 2(c)], substantiating the reaction between $B(C_6F_5)_3$ and $Cp_2Zr(i-Bu)Cl$. The spectrum of $Cp_2ZrCl_2-B(C_6F_5)_3-i-Bu_3Al$ [Fig. 2(d)] on direct addition of the three components to the NMR tube (Al–Zr = 5) is almost the same as in Fig. 1(c).

The spectrum of $Cp_2ZrCl_2-B(C_6F_5)_3-Me_3Al$ system is shown in Figure 3. If one divides the signals into two parts, that from the alkylated complex and that from the nonalkylated complex, the alkylation reaction is calculated by integration to be approximately 34% complete at an Al–Zr ratio of 5 [Fig. 3(a)]. At a higher Al–Zr ratio of 20, the signals assigned to cyclopentadienyl of Cp_2ZrCl_2 become complicated, and the conversion is approximately 60%. The conclusion reached is that $i-Bu_3Al$ is a more effective alkylating agent of Cp_2ZrCl_2 than Me_3Al . Since the ternary system $Cp_2ZrCl_2-B(C_6F_5)_3-R_3Al$ is more complex than the binary system Cp_2ZrCl_2-MAO or $Cp_2ZrR_2-B(C_6F_5)_3$, further study is in progress and will be reported later.

REFERENCES

1. D. S. Breslow and N. R. Newburg, *J. Am. Chem. Soc.*, **79**, 5073 (1957).
2. D. S. Breslow and N. R. Newburg, *J. Am. Chem. Soc.*, **81**, (1959).
3. H. Sinn, W. Kaminsky, H.-J. Vollmer, and R. Woldt, *Angew. Chem. Int. Ed. Engl.*, **19**, 390 (1980).
4. W. Kaminsky, K. Kulper, H. H. Brintzinger, and F. R. W. P. Wild, *Angew. Chem. Int. Ed. Engl.*, **24**, 507 (1985).
5. J. A. Ewen, L. Haspeslagh, J. L. Atwood, and H. Zhang, *J. Am. Chem. Soc.*, **109**, 6544 (1987).
6. J. A. Ewen, in *Catalytic Polymerization of Olefin*, T. Keii and K. Soga, Eds., Elsevier, New York, 1986, p. 271.
7. J. A. Ewen, *J. Am. Chem. Soc.*, **106**, 6355 (1984).
8. J. A. Ewen, R. L. Jones, A. Razavi, and J. D. Ferrara, *J. Am. Chem. Soc.*, **110**, 6255 (1988).
9. D. T. Mallin, M. D. Rausch, Y. Lin, S. Dong, and J. C. W. Chien, *J. Am. Chem. Soc.*, **112**, 2030 (1990).
10. J. C. W. Chien and D. He, *J. Polym. Sci., Polym. Chem.*, **29**, 1603 (1991).
11. S. Collins, W. M. Kelly, and D. A. Holden, *Macromolecules*, **25**, 1780 (1992).
12. W. Kaminsky and F. Renner, *Makromol. Chem., Rapid Commun.*, **14**, 239 (1993).
13. K. Soga and M. Kaminaka, *Makromol. Chem., Rapid Commun.*, **13**, 221 (1992).
14. K. Soga and M. Kaminaka, *Makromol. Chem. Phys.*, **195**, 1369 (1994).
15. H. C. Welborn, Eur. Pat. 0-334-887 (1989).
16. M. Kloka and N. Kashiwa, Eur. Pat. 0-285-443 (1988).
17. G. G. Hlatky, H. W. Turner, and R. R. Eckman, *J. Am. Chem. Soc.*, **111**, 2728 (1989).
18. J. C. W. Chien, W.-M. Tsai, and M. R. Rausch, *J. Am. Chem. Soc.*, **113**, 8570 (1991).
19. X. Yang, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, **113**, 3623 (1991).
20. A. P. Gray, *Thermochim. Acta* **1**, 563 (1970).
21. D. G. Boucher, I. W. Parsons, and R. N. Haward, *Makromol. Chem.*, **175**, 3641 (1974).
22. J. C. W. Chien and B. P. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, **26**, 3089 (1988).
23. J. C. W. Chien, W. Song, and M. D. Rausch, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 2387 (1994).
24. W.-M. Tsai and J. C. W. Chien, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 149 (1994).
25. P. J. Lemstra, *Polym. Commun.*, **32**, 343 (1990).