

Ethylene Polymerization Using $(n\text{-BuCp})_2\text{ZrCl}_2$ Catalyst Activated with a Cross-linked MAO-Supported Cocatalyst

Keun Byoung Yoon*

Optical Interconnection Team, Electronics and Telecommunications Research Institute (ETRI),
161 Gajeong, Yuseong, Daejeon 305-350, Korea

Received January 18, 2004; Revised June 9, 2004

Abstract: A new type of cross-linked methylaluminoxane (MAO)-supported cocatalyst has been prepared by the reaction of a soluble MAO and a cross-linking agent such as an aromatic diamine compound. The cross-linked MAO-supported cocatalyst was used for the polymerization of ethylene in the presence of bis(*n*-butylcyclopentadienyl) zirconium dichloride, $(n\text{-BuCp})_2\text{ZrCl}_2$. The catalyst activity of $(n\text{-BuCp})_2\text{ZrCl}_2$ cocatalyzed with the new supported cocatalyst was higher than that of the commercial silica-supported MAO (SMAO) cocatalyst. The molecular weight and the bulk density of the polyethylene produced by using the new supported cocatalyst were slightly higher than those of polyethylene synthesized using commercial SMAO. The resulting polyethylene particles possess spherical morphologies with very few fine particles.

Keywords: cross-linked MAO supported cocatalyst, ethylene polymerization, spherical morphology.

Introduction

Metallocene catalysts activated by methylaluminoxane (MAO) show extremely high catalyst activity in homogeneous polymerization of ethylene.^{1,2} The usages of homogeneous metallocene/MAO catalysts are difficult in slurry and gas phase processes. The unsuitable morphology results in a high tendency to reactor fouling and separation problems in conventional polyolefin processes. To improve these problems, metallocenes can be immobilized on inert supports. There are many publications describing the immobilization of metallocene onto supports such as Al_2O_3 , MgCl_2 , SiO_2 , MAO-treated SiO_2 , cyclodextrin and synthetic polymers.³⁻⁸ Most of these supported metallocene catalysts exhibited a poor catalyst activity because of a significant steric hindrance around the active site due to the large support surface and deactivation of catalytic sites or inefficient production of active sites during the supporting process.^{9,10}

We here report the preparation of a new supported cocatalysts that a cross-linked MAO onto the spherical silica. The new supported cocatalyst was immobilized on the silica by the fixation of a commercial MAO and simultaneous cross-linking with bifunctional organic compounds, such as aromatic diamine compounds. The polymerization of ethylene has been studied and evaluated as a potential application of

a new supported cocatalyst. We also report the comparison of a new cross-linked MAO supported cocatalysts and a commercial silica supported MAO (SMAO) cocatalyst in combination with bis(*n*-butylcyclopentadienyl)zirconium dichloride($n\text{-BuCp})_2\text{ZrCl}_2$.

Experimental

Materials. Ethylene and nitrogen were purified by the removal of trace of residual moisture and oxygen with columns packed with molecular sieves and oxygen scavengers, respectively. $(n\text{-BuCp})_2\text{ZrCl}_2$ (Strem chem. Co.), MAO (Akzo Nobel), a commercial silica supported MAO cocatalyst (SMAO; Al content = 7.6 wt%; Akzo Nobel), trimethylaluminum (TMA, Aldrich Co., 1.0 mol *n*-hexane solution) and triethylaluminum (TEA, Aldrich Co.; 1.0 mol *n*-hexane solution) were used without further purification. The Silica (SiO_2 , Davidson, Grade #952) was used after dehydration at 600 °C for 10 hrs. Aromatic diamine compounds such as α,α -bis(4-aminophenyl)-1,4-diisopropylbenzene (BADB), 4,4-diaminodiphenylether (ODA), Diaminonaphthalene (NDA), Diaminophenylene (PDA), were used as received from TCI. Toluene and *n*-hexane (JT Baker) were distilled over sodium-benzophenone complex.

Preparation of a New Supported Cocatalysts. All the preparations took place under nitrogen atmosphere using the Schlenk technique. A new supported cocatalyst was produced with the cross-linked MAO and the spherical silica.

*e-mail: kbyoon@etri.re.kr

1598-5032/08/336-06©2004 Polymer Society of Korea

The cross-linked MAO was prepared with a soluble MAO and an aromatic diamine compound as a cross-linking agent in toluene. The expectative structure of the new supported cocatalyst is shown in Scheme I.

Cocatalyst-A was prepared as a following procedure. 1.0 M MAO solution and 0.025 M PDA in toluene were mixed and reacted for 2 hrs at 50 °C. This resulting solution was added to two grams of silica in 100 mL toluene at 50 °C for 6 hrs. Then the mixture was filtered, the obtained solid was washed ten times with toluene. The solid cocatalyst was dried under reduced pressure until free-flowing conditions were reached. Cocatalyst-B, -C and -D was prepared with NDA, ODA and BADB as a cross-linking agent, respectively. The aluminium content of a new supported cocatalyst was analyzed by an inductively coupled plasma emission spectrophotometer (ICP, Jobin Yvon 38 plus).

Polymerization and Analytical Procedures. The ethylene polymerization was carried out in a 2 L autoclave reactor equipped with a mass flow meter and a temperature control unit, which consists a cooling coil and electric heater. The polymerization medium (1 L of *n*-hexane) and oxygen scavenger (1.0 mmol of triethylaluminium (TEA)) were added to the reactor at room temperature under nitrogen purging, followed by the addition of a catalyst system. The catalyst system was prepared as follows; to a suspension of cocatalyst in 30 mL of *n*-hexane, the homogeneous $(n\text{-BuCp})_2\text{ZrCl}_2$ solution was added and stored at 10 min. The catalyst system was injected into the reactor. After the injection of the catalyst system, the reactor was heated to the polymerization temperature. The polymerization started by the pressurizing of the reactor with ethylene (total pressure = 115 psig). The

monomer flow rate was monitored continuously through a mass flow meter and the polymerization was carried out for 1 hr. The polymerization was terminated by the addition of an excess amount of methanol after the gaseous monomer was vented.

The average molecular weights and the molecular weight distributions (M_w/M_n) of the resulting polyethylene were determined by a gel permeation chromatography (GPC, PL2000, UK) at 135 °C with 1,2,4-trichlorobenzene as the solvent. The molecular weight was calculated from a universal calibration curve of the standard polystyrene and a linear low-density polyethylene. The morphology of the polymer particles was observed with a scanning electron microscopy (SEM, Hitachi S-2460N). The bulk density of the polymer particles was measured according to ASTM Standard D 1895. The particle size distribution of the polyethylene was estimated with a Malvern Particle Sizer (M6.10).

Results and Discussion

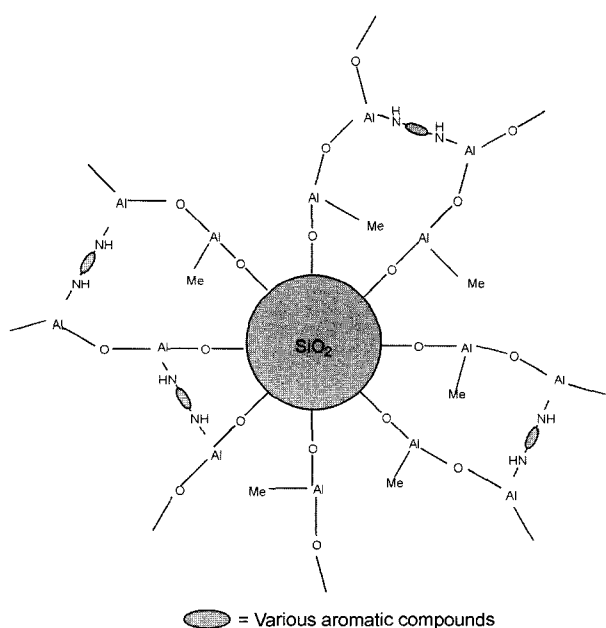
Polymerization Behaviors of $(n\text{-BuCp})_2\text{ZrCl}_2$ with a New Supported Cocatalysts. An important parameter for the polymerization with a metallocene catalyst is the ratio of aluminoxane to transition metal. The metallocene complexes required an excess amount of methylaluminoxane (MAO) for an acceptable activity in homogeneous polymerization. The major advantage of the supported metallocene catalyst and the supported cocatalyst is low MAO/Metallocene ratio and a spherical morphology of the obtained polymer.

Polymerization of ethylene was carried out with $(n\text{-BuCp})_2\text{ZrCl}_2$ and various supported cocatalysts for evaluation of a new supported cocatalyst. The results are summarized in Table I.

The cross-linked MAO supported cocatalysts and $(n\text{-BuCp})_2\text{ZrCl}_2$ catalyst systems showed good catalyst activities for the ethylene polymerization (4,000~11,000 kg-PE/mol-Zr · h) at very low [Al]/[Zr] ratio ([Al]/[Zr]=20). As long as we understand, this is the first example to demonstrate that the cross-linked MAO supported cocatalyst has exhibited a good performance.

The Cocatalyst-D showed higher catalyst activity than others. The catalyst activity of the catalyst systems using a cross-linked MAO cocatalyst increased in the following order BADB > NDA > PDA > ODA, which indicated the cocatalyst containing a bulky structural diamine led to higher activity than a rigid diamine.

The molecular weight (M_w), the molecular weight distribution (M_w/M_n) and the bulk density of polyethylene products are also tabulated in Table I. The molecular weight of polyethylene produced with the cross-linked MAO supported cocatalyst was slightly higher than that of a commercial SMAO. However, the molecular weight of polyethylene produced with the cross-linked MAO supported cocatalyst



Scheme I. The Expectative Structure of a New Supported Cocatalyst.

were independent of the structure of diamine compounds, all the obtained polyethylene have the weight-average molar mass (M_w) of 410,000 ($\pm 15,000$).

The molecular weight distribution of the obtained polyethylene with the cross-linked MAO supported cocatalyst was very narrow ($M_w/M_n = 2.0 \sim 2.1$). This result indicates that these catalyst systems have a single site character.

The bulk density of polyethylene is a function of the polymerization rate. The bulk density slightly increased with increasing the polymerization activity. In case of Cocatalyst-D, the bulk density of obtained polyethylene was much higher than that of MAO/SiO₂.

The aluminium content of the cross-linked MAO supported cocatalysts (about 7~8 wt%) were twice as much as that of the directly MAO supported cocatalyst (MAO/SiO₂; about 3.2 wt%), because the cross-linked MAO supported cocatalysts are build up of core network due to the cross-linking between MAO and aromatic diamine compounds.

The effect of MAO and BADB ratio on the catalyst activity and characteristics of polyethylene were investigated and the results were summarized in Table II.

The core network of the cocatalyst has positive influence on the overall catalyst performance. The aluminium contents and catalyst activity increased with increasing [Al]/[NH₂] ratio, however the molecular weight of obtained polyethylene slightly decreased. The difference in the catalyst activity can be explained by the different nature of the surface of the cocatalyst.¹¹ The ratio of [Al]/[NH₂] determines the

chemical properties of the cross-linked system as well as the mechanical stability of the catalyst system during the polymerization.¹² Especially, the bulk density sharply decreased with increasing [Al]/[NH₂] ratio.

The enhancement of the catalyst activity was due to the diminishment of a free trimethylaluminium (TMA) in catalyst system. The degree of cross-linking increased to an extent and the amount of a free TMA decreased during the reaction of BADB and a soluble MAO. For evaluation of these results, polymerization of ethylene carried out in homogeneous catalyst systems. The results are shown in Table III.

The catalyst activity increased with addition of BADB in an MAO solution. This result suggests that a free TMA affects the catalyst activity. Michiels *et al.* observed that the

Table III. Polymerization of Ethylene Using Homogeneous Catalyst System

(<i>n</i> -BuCp) ₂ ZrCl ₂ ($\mu\text{mol/L}$)	Cocatalyst	Activity	M_w (kg/mol)	M_w/M_n
2	Soluble MAO	11,200	180	1.9
2	MAO+BADB solution	14,200	230	1.9
2	Dried MAO	12,500	205	2.0

Polymerization condition: [Al]/[Zr] = 100, [Al]/[NH₂] = 40.
TEAL = 1 mmol, 80 °C, 1 hr, $P_{\text{ethylene}} = 115$ psig.
Activity: kg-PE/mol-Zr · h.

Table I. Polymerization of Ethylene Using (*n*-BuCp)₂ZrCl₂ Activated with Various Cross-linked MAO Supported Cocatalysts

Cocatalyst	Al content (wt%)	Activity	M_w (kg/mol)	M_w/M_n	Bulk Density (g/cc)
Cocatalyst-A	7.0	6,400	395	2.1	0.28
Cocatalyst-B	7.5	7,800	405	2.0	0.30
Cocatalyst-C	7.8	4,060	395	2.1	0.29
Cocatalyst-D	8.2	10,970	420	2.1	0.32
SMAO	7.6	7,500	380	1.9	0.30
MAO/SiO ₂	3.2	300	295	2.2	0.22

Cocatalyst preparation condition: [Al]/[NH₂] = 40.

Polymerization condition: [Al]/[Zr] = 20, TEAL = 1 mmol, 80 °C, 1 hr, $P_{\text{ethylene}} = 115$ psig, [Zr] = 2.0 $\mu\text{mol/L}$.

Activity: kg-PE/mol-Zr · h.

Table II. Effect of [Al]/[NH₂] Ratio on Ethylene Polymerization Using Supported Cocatalyst

[Al]/[NH ₂]	Al content (wt%)	Activity	M_w (kg/mol)	M_w/M_n	Bulk Density (g/cc)
20	5.6	4,300	425	2.0	0.33
30	7.5	8,600	430	2.1	0.31
40	8.2	10,970	420	2.1	0.32
60	9.8	12,600	390	2.7	0.28
80	13.5	15,800	380	3.5	0.22

Polymerization condition: [Al]/[Zr] = 20, TEAL = 1 mmol, 80 °C, 1 hr, $P_{\text{ethylene}} = 115$ psig, [Zr] = 2.0 $\mu\text{mol/L}$.

Activity: kg-PE/mol-Zr · h.

catalyst activity for ethylene polymerization increases at low TMA concentrations of an MAO solution. The catalyst activity decreased at higher TMA/MAO ratio.¹³

To improve above results, we examined the $^1\text{H-NMR}$ study of an MAO solution and *in situ* reaction of BADB and an MAO solution¹⁴ and the spectra are shown in Figure 1.

In spectrum of an MAO solution, a broad resonance peaks at $\delta = -0.7 \sim -0.2$ ppm observed to the methyl protons of the oligomeric MAO $[-\text{O}-\text{Al}(\text{CH}_3)-]$ and a sharp singlet at $\delta = -0.4$ ppm also observed, which is the methyl protons of a free TMA.¹⁵ In spectrum of *in situ* reaction of BADB and an MAO solution, the intensity of methyl peak ($\delta = -0.4$ ppm) of a free TMA decreased. The intensity ratio of the methyl protons of TMA ($I_{\delta = -0.4 \text{ ppm}}/I_{\delta = -0.7 \sim -0.2 \text{ ppm}}$) was 1/34 in an MAO solution. However, the value of the $I_{\delta = -0.4 \text{ ppm}}/I_{\delta = -0.7 \sim -0.2 \text{ ppm}}$ dramatically decreased to 1/62 in an MAO and BADB reaction solution. An increment of the catalyst activity in our catalyst system due to the formation of a stable core network and the diminishment of a free TMA during the reaction of diamine compounds and a soluble MAO.

The molecular weight of polyethylene also increased with addition of BADB in MAO solution. Concerning the influence of the free TMA on a molecular weight, it is generally recognized that remained alkylaluminum at the homogeneous catalyst system results in a higher rate for the β -elimination to give rise to the formation of a low molecular weight of polyethylene.

The Effect of the Cocatalyst Amount and the Polymerization Temperature on the Catalyst Activity. Metallocene/MAO catalyst systems require an excess amount of MAO for an acceptable activity under the homogeneous polymerization condition. The major advantage of the supported metallocene catalyst is a low $[\text{MAO}]/[\text{Metallocene}]$ ratio and the prevention of reactor fouling. The ratio of aluminoxane to transition metal has a significant impact on the catalyst performance for many supported catalyst systems.^{16,17} The effect of $[\text{Al}]/[\text{Zr}]$ ration on polymerization of ethylene

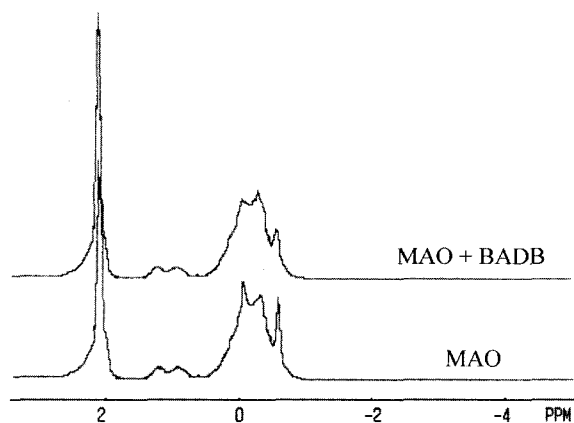


Figure 1. $^1\text{H-NMR}$ spectra of a reaction mixture of MAO and BADB and a soluble MAO.

was investigated and the results are shown in Figure 2.

In Figure 2, the catalyst activity increased with increasing $[\text{Al}]/[\text{Zr}]$ ratio. The Cocatalyst-D was more active than others in the whole experimental regions. In our investigations, the catalyst activity decreased in the following order Cocatalyst-D > SMAO > Cocatalyst-B > Cocatalyst-A > Cocatalyst C. The cross-linked MAO supported cocatalysts and $(n\text{-BuCp})_2\text{ZrCl}_2$ catalyst system showed good catalyst activities (above 8,000 kg-PE/mol-Zr · h) under the low $[\text{Al}]/[\text{Zr}]$ condition ($[\text{Al}]/[\text{Zr}] = 40$).

The effect of polymerization temperature on catalyst activity of $(n\text{-BuCp})_2\text{ZrCl}_2/\text{Cocatalyst-D}$ and $(n\text{-BuCp})_2\text{ZrCl}_2/\text{SMAO}$ catalyst systems were studied and the results are shown in Figure 3.

The catalyst activity increased with increasing temperature up to 100 °C in both catalyst systems. According to Chien,

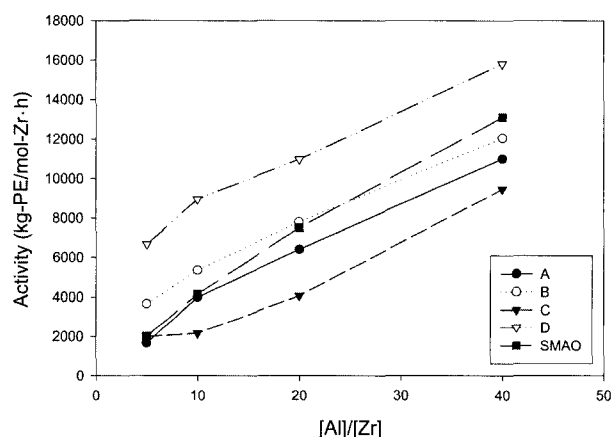


Figure 2. Effect of $[\text{Al}]/[\text{Zr}]$ ratio on ethylene polymerization using various supported cocatalysts. Polymerization condition: $[\text{Zr}] = 2.0 \mu\text{mol/L}$, 80 °C, 1 hr, $P_{\text{ethylene}} = 115$ psig.

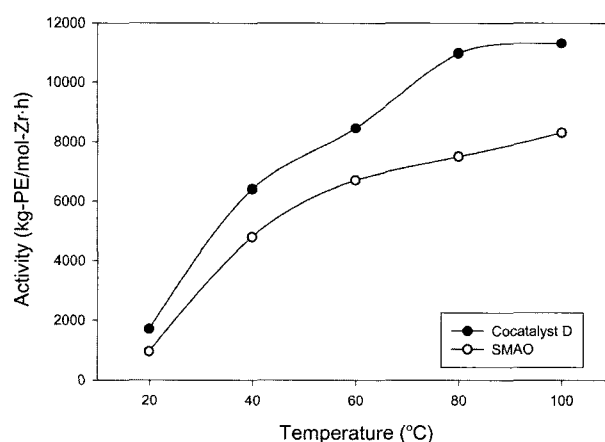


Figure 3. Effect of polymerization temperature on ethylene polymerization using Cocatalyst-D and SMAO (Polymerization condition: $[\text{Al}]/[\text{Zr}] = 20$, $[\text{Zr}] = 2.0 \mu\text{mol/L}$, 1 hr, $P_{\text{ethylene}} = 115$ psig).

the catalyst activity decreased at high polymerization temperature under homogeneous polymerization condition, because of the dissociation of the π -olefin complex.¹⁸ In our case, we do not have experimental evidence to show whether a deactivation process of the active species is taking place with increasing polymerization temperature. It was proposed that an active site of our catalyst system was stable at high temperature.

Morphology of Polyethylene. The supported catalyst is able to replicate its particle size distribution into the morphology of the polyethylene particles, as it is known from the conventional Ziegler-Natta catalysts.^{19,20} The morphology of the produced polyethylene should be controlled by the morphology of the catalyst particles. The particle size distribution and the morphology of polyethylene were observed with a particle size analyzer and SEM, and the results are shown in Figures 4 and 5, respectively.

The supported cocatalysts build up a core with an average thickness of 10–20 μm around the starting silica particles, in Figure 4. Furthermore, the relative uniformity of the cross-linked MAO supported cocatalyst become apparent. These polyethylene particles have very few fine particles. Their medium size is about 500 μm and the particle size analysis indicates that only 1.5% of the particles have smaller than 200 μm of diameter.

A scanning electron microscopy (SEM) was used to examine the morphology of the polyethylene particles. The images in Figure 5 illustrate the typical exterior of the spherical polyethylene particles. These polyethylene particles adapt a spherical morphology and duplicate the spherical shape of the original SiO_2 support. The particles were essentially spherical but the exterior surface of the particles was rough. The irregular exterior appearance of these particles suggests that the particles are an agglomeration of smaller particles.

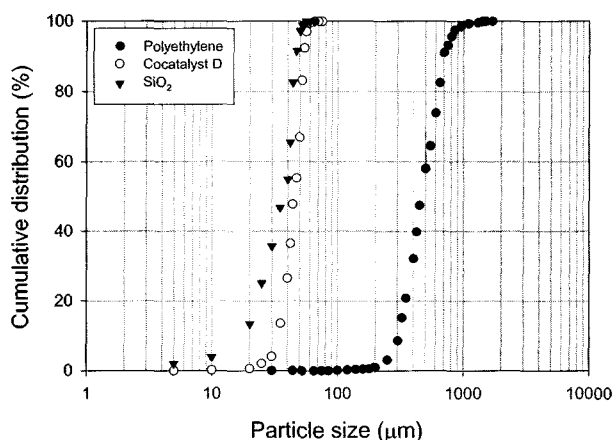
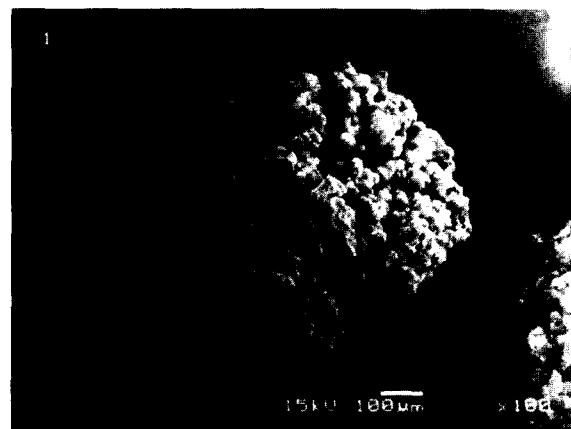


Figure 4. Morphology control of the polyethylene particle for the cross-linked MAO supported cocatalysts.



(a)



(b)

Figure 5. SEM images of PE particles produced by (a) cocatalyst-A and (b) cocatalyst-D.

Conclusions

The cross-linked methylaluminoxane (MAO) supported cocatalyst was used for polymerization of ethylene in the presence of bis(*n*-butylcyclopentadienyl) zirconium dichloride, $(n\text{-BuCp})_2\text{ZrCl}_2$. A new supported cocatalyst was prepared by the reaction of the soluble MAO and the cross-linking agent, such as an aromatic diamine compound. The cross-linked MAO supported cocatalyst and $(n\text{-BuCp})_2\text{ZrCl}_2$ catalyst system showed a good activity for the ethylene polymerization at very low $[\text{Al}]/[\text{Zr}]$ ratio. The catalyst activity of the new supported cocatalyst was higher than that of the commercial silica-supported MAO cocatalyst (SMAO). The molecular weight and the bulk density of polyethylene produced with the new supported cocatalyst were higher than those of polyethylene with a commercial SMAO. The resulting polyethylene particles show a spherical morphology with very few fine particles.

References

- (1) W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, 1413 (1998).
- (2) H. H. Britzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, **34**, 1143 (1995).
- (3) D. H. Lee, H. B. Lee, S. K. Noh, J. H. Kim, K. B. Yoon, H. J. Kim, and S. S. Woo, *Korea Polym. J.*, **5**, 234 (1997).
- (4) K. Soga and M. Kaminaka, *Makromol. Chem.*, **194**, 1745 (1993).
- (5) K. Soga, T. Uozumi, M. Saito, and T. Shiono, *Macromol. Chem. Phys.*, **195**, 1503 (1994).
- (6) J. C. W. Chien and D. He, *J. Polym. Sci., Polym. Chem.*, **29**, 1603 (1991).
- (7) D. H. Lee and K. B. Yoon, *Macromol. Rapid Commun.*, **15**, 841 (1994).
- (8) M. Kioka and N. Kashiwa, *U.S. Patent* 5,362,824.
- (9) K. J. Chu, B. P. Joao, and A. Penlidis, *J. Polym. Sci., Polym. Chem.*, **38**, 462 (2000).
- (10) E. Ernst, J. Reubner, and W. Neibl, "Proceeding of *MetCon96*".
- (11) R. Schmidt, H. G. Alt, and J. Ebenhoch, *J. Appl. Polym. Sci.*, **80**, 613 (2001).
- (12) J. Reußner, P. Denifl, and W. Neißl, "Proceeding of *SPO97*", p.87 (1997).
- (13) W. Michiels and Munoz-Escalona, *Macromol. Symp.*, **97**, 171 (1995).
- (14) E. W. Hansen, R. Blom, and P. O. Kvernberg, *Macromol. Chem. Phys.*, **202**, 2880 (2001).
- (15) L. Reconi, S. Bossi, and L. Abis, *Macromolecules*, **23**, 4489 (1990).
- (16) L. Noristi, P. C. Barbè, and G. Baruzzi, *Macromol. Chem.*, **192**, 1115 (1991).
- (17) P. Galli, P. C. Barbè, and L. Noristi, *Die Angew. Makromol. Chem.*, **120**, 73 (1994).
- (18) W.-M. Tsai and J. C. W. Chien, *J. Polym. Sci., Polym. Chem.*, **32**, 149 (1994).
- (19) W. Kaminsky, A. Bark, and R. Steiger, *J. Molecular Catalysis*, **74**, 109 (1992).
- (20) T. Yamasaki, *Catalysis Today*, **23**, 425 (1995).