

Copolymerization of Ethylene and 1-Hexene Using (*n*-BuCp)₂ZrCl₂ Catalyst Activated by the Cross-linked MAO Supported Cocatalyst

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Introduction

Metallocene/methylaluminoxane (MAO) catalytic systems have grown in importance since their discovery in the 1980s.^{1,2} Many studies concerning the effect of metallocene structures both on catalyst copolymerization reactivity and on copolymer properties have been carried out.³⁻⁶ Copolymers of ethylene with α -olefins such as 1-butene, 1-hexene and 1-octene are very important commercial products classified as linear low density polyethylene (LLDPE). There have been many efforts towards finding more efficient catalysts to produce copolymers having desired physical properties.⁷⁻⁹ Ziegler-Natta catalysts produce copolymers with wide molecular weight distribution (MWD) and short chain branching distribution (SCBD) because of multiple active sites. In contrast, homogeneous metallocenes are single-site catalysts and produce very uniform copolymers with a narrow MWD and SCBD.^{10,11}

It is very useful to understand the origin of MWD and SCBD of copolymers made with different catalysts, especially how to manipulate catalyst structure to modify polymer microstructure, since these distributions determine the polymer applications. The MWD of polymers can easily be determined by gel permeation chromatography (GPC). However, the analysis of SCBD of copolymers is more elaborate. The most common technique for this purpose is to use temperature rising elution fractionation (TREF).^{12,13} TREF is now a common technique in the polyolefin industry to analyze the SCBD of copolymers.

The subject of this work is to study the copolymerizations of ethylene and 1-hexene using (*n*-BuCp)₂ZrCl₂ activated with the cross-linked methylaluminoxane (MAO) supported cocatalyst. The effects of 1-hexene concentrations in the feed on catalyst activity, copolymer composition, and polymer properties were investigated. Comparison of the catalyst properties with (*n*-BuCp)₂ZrCl₂ was carried out with the different cocatalyst system of the cross-linked MAO supported cocatalyst, the known MAO supported cocatalyst (SMAO) system, and soluble MAO. In addition, the microstructure, molecular weight distribution and morphology of the resulting copolymers were explored.

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. Bis(*n*-butylcyclopentadienyl) zirconium dichloride ((*n*-BuCp)₂ZrCl₂, Strem Chem. Co.), methylaluminoxane (MAO, Akzo Nobel), a commercial silica supported MAO cocatalyst (SMAO, Al content = 7.6 wt%, Akzo Nobel) and triethylaluminum (TEA, Aldrich Co., 1.0 mol *n*-hexane solution) were used without further purification. The Silica (SiO₂, Davidson, Grade #952) was used after dehydration at 600 °C for 10 hrs. Aromatic diamine compound such as α, α' -bis(4-aminophenyl)-1,4-diisopropylbenzene (BADB) was used as received from TCI. Toluene and *n*-hexane (JT Baker) were distilled over sodium-metal. 1-Hexene (Aldrich) was purified by distillation over calcium hydride.

Preparation of the Cross-linked MAO Supported Cocatalysts. In the previous work,¹⁴ the preparation of the cross-linked MAO supported cocatalyst (CMAO) was described. The CMAO was prepared by the reaction of a soluble MAO and the cross-linking agent such as aromatic diamine compound (BADB).

Copolymerization and Analytical Procedures. The copolymerization was carried out in a 2 L autoclave reactor equipped with a mass flow meter and a temperature control unit, which consists of a cooling coil and electric heater. The reactor was filled with *n*-hexane (1 L), oxygen scavenger (1.0 mmol of triethylaluminum (TEA)) and the required amounts of 1-hexene and then the catalyst system was charged into the reactor. The catalyst system was prepared as follows; to a suspension of cocatalyst in 30 mL of *n*-hexane, the homogeneous (*n*-BuCp)₂ZrCl₂ solution was added and stored for 10 min. After the injection of the catalyst system, the reactor was heated to the polymerization temperature. The copolymerization was initiated by the introduction of ethylene. The monomer pressure was kept constant during polymerization by the continuous addition of ethylene (115 psig).

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The monomer flow rate was monitored continuously through a mass flow meter and the polymerization was carried out for 20 min.

The average molecular weights and the molecular weight distributions (M_w/M_n) of the resulting copolymers were determined by a gel permeation chromatography (GPC, Polymer Lab.-2000, UK) at 135 °C with 1,2,4-trichlorobenzene as a solvent. The molecular weight was calculated from a universal calibration curve of the standard polystyrene and a linear low-density polyethylene. ¹³C-NMR spectra of copolymers were recorded at 135 °C and 98.7 MHz (Bruker 400) in 1,2,4-trichlorobenzene/benzene-*d*₆. The melting temperature and heat of fusion of copolymers were characterized by means of DSC (Perkin-Elmer 7). The morphology of copolymers were observed with SEM (Hitachi).

Results and Discussion

Figure 1 shows the kinetic profiles obtained for the copolymerization of ethylene and 1-hexene with different catalyst systems. It was noticeable that homogeneous MAO with (*n*-

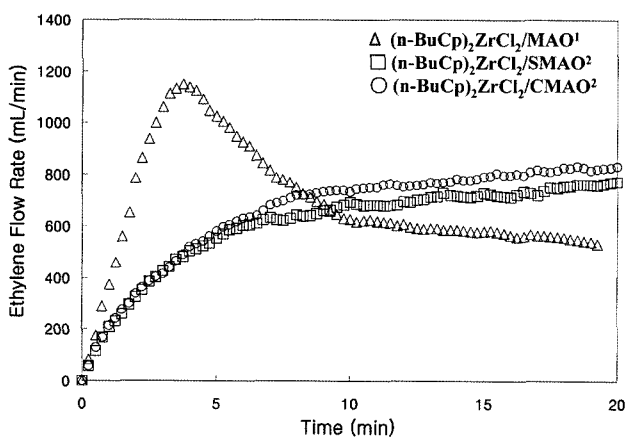


Figure 1. Kinetic profiles of ethylene/1-hexene copolymerization with different catalyst systems.

¹Polymerization condition: [Al]/[Zr]=100, TEA=1 mmol, 80 °C, 20 min, $P_{\text{ethylene}}=115$ psig, [Zr]=2.0 $\mu\text{mol/L}$.

²Polymerization condition: [Al]/[Zr]=40, TEA=1 mmol, 80 °C, 20 min, $P_{\text{ethylene}}=115$ psig, [Zr]=12.5 $\mu\text{mol/L}$.

BuCp)₂ZrCl₂ displays higher catalytic activity than the corresponding supported catalyst systems at the early stage of the polymerization. However, the supported catalyst system was exhibited slow but steady rate rising as the reaction went on.

The kinetic profile of homogeneous catalyst system shows that the maximum polymerization rate was reached in less than 4 min followed by the drastic rate descending, indicating that all the catalytic sites were formed at the early stage of polymerization. On the other hand, the kinetic profile of the supported system exhibits clearly that the catalytic sites were formed not so quickly as those of a homogeneous catalyst system. The constant polymerization rate was observed at supported catalytic systems.

The catalyst activity of various catalyst systems and the properties of the produced polymers such as molecular weight, molecular weight distribution, density and 1-hexene contents of the produced copolymers were examined and the results are shown in Table I.

The catalyst activities of (*n*-BuCp)₂ZrCl₂/CMAO was slightly higher than those of (*n*-BuCp)₂ZrCl₂/SMAO.¹⁴ The important feature of the cross-linked MAO supported cocatalysts with (*n*-BuCp)₂ZrCl₂ is that good catalyst activities for the copolymerization were represented even at the very low [Al]/[Zr] ratio ([Al]/[Zr]=40) comparing with the homogeneous cocatalyst. The copolymer could not obtained with homogeneous catalytic system at the same polymerization conditions ([Al]/[Zr]=40).

Molecular weights of the formed copolymers from the supported catalyst systems were slightly greater than those of the copolymers from the homogeneous metallocene catalyst. In terms of the amount of the incorporated comonomer into the polymer chain the polymers from the immobilized catalyst displayed lower values than those obtained from the homogeneous counterpart. It is believed that homogeneous catalyst prefers to incorporate 1-hexene comonomer into the polyethylene chain to the supported catalyst systems. It can be evidenced by the fact that the copolymers from the homogeneous catalyst exhibited lower density due to the higher 1-hexene incorporation than those from the heterogeneous catalysts.^{15,16} This could be interpreted by the fixed structural

Table I. Copolymerization of Ethylene and 1-Hexene with Different Catalyst Systems

Catalyst	Activity	M_w (kg/mol)	M_w/M_n	Density	1-Hexene Content in mol%
(<i>n</i> -BuCp) ₂ ZrCl ₂ /MAO ^c	21000	150	2.6	0.9214	1.6
(<i>n</i> -BuCp) ₂ ZrCl ₂ /MAO ^d	trace	-	-	-	-
(<i>n</i> -BuCp) ₂ ZrCl ₂ /CMAO ^d	20160	178	2.3	0.9237	1.3
(<i>n</i> -BuCp) ₂ ZrCl ₂ /SMAO ^d	16320	166	2.5	0.9250	1.0

^aAll copolymers were prepared at $M_H/(M_H+M_E) = 0.3$.

^b M_E and M_H stand for the concentration of ethylene and 1-hexene in *n*-hexane, respectively.

^cPolymerization condition: [Al]/[Zr]=100, TEA=1 mmol, 80 °C, 20 min, $P_{\text{ethylene}}=115$ psig, [Zr]=2.0 $\mu\text{mol/L}$.

^dPolymerization condition: [Al]/[Zr]=40, TEA=1 mmol, 80 °C, 20 min, $P_{\text{ethylene}}=115$ psig, [Zr]=12.5 $\mu\text{mol/L}$, Activity: kg-Copolymer/mol-Zr·h.

characteristics of silica surface¹⁷ which blocked one side of the metallocene faces to induce to the steric limitation, thereby reducing the comonomer accessibility to the active site.

It was found out that MWD of copolymers made with different catalyst systems did not show a significant difference. That might indicate the formation of the uniform catalyst site regardless of the catalyst type.

Ziegler-Natta and heterogeneous metallocene catalysts are capable of replicating their morphology into the morphology of polymer particles.^{14,18} In order to observe copolymer morphology, micrographs of copolymers were obtained by SEM and are shown in Figure 2.

These copolymer particles adapt a spherical morphology and duplicated the spherical shape of the original silica. The particles were essentially spherical but the exterior surface of the particles was microglobules. The microglobules usually form globular aggregates which can be interconnected by fibers originated as a result of the expansion of polymer

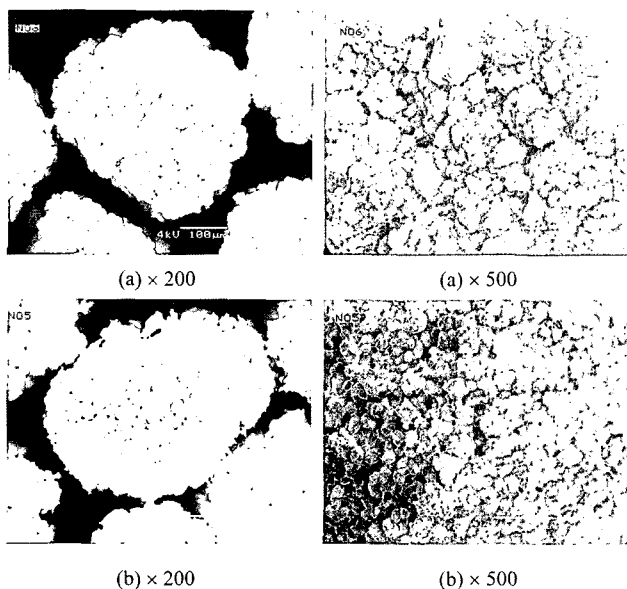


Figure 2. SEM images of copolymers obtained with (a) $(n\text{-BuCp})_2\text{ZrCl}_2/\text{CMAO}$ and (b) $(n\text{-BuCp})_2\text{ZrCl}_2/\text{SMAO}$ catalyst system. All copolymers were prepared at $M_H/(M_H + M_E) = 0.3$ (see Table I).

Table II. Dyad-Triad Sequence Distribution^a of Ethylene/1-Hexene Copolymer Prepared with Different Catalyst Systems

Catalyst	H	EE	EH	HH	EEE	HEE	HEH	EHE	HHE	HHH
$(n\text{-BuCp})_2\text{ZrCl}_2/\text{MAO}^b$	1.6	95.3	3.1	0.0	92.5	6.1	0.0	1.4	0.0	0.0
$(n\text{-BuCp})_2\text{ZrCl}_2/\text{CMAO}^c$	1.3	96.1	2.6	0.0	93.2	5.7	0.0	1.1	0.0	0.0
$(n\text{-BuCp})_2\text{ZrCl}_2/\text{SMAO}^c$	1.0	96.8	2.2	0.0	93.9	5.3	0.0	0.8	0.0	0.0

All copolymers were prepared at $M_H/(M_H + M_E) = 0.3$.

^aTriad sequences were calculated by the Randall method.²¹

^bPolymerization condition: $[\text{Al}]/[\text{Zr}] = 100$, TEA = 1 mmol, 80 °C, 20 min, $P_{\text{ethylene}} = 115$ psig, $[\text{Zr}] = 2.0$ $\mu\text{mol/L}$.

^cPolymerization condition: $[\text{Al}]/[\text{Zr}] = 40$, TEA = 1 mmol, 80 °C, 20 min, $P_{\text{ethylene}} = 115$ psig, $[\text{Zr}] = 12.5$ $\mu\text{mol/L}$.

particle.¹⁹

The microstructures of copolymers were investigated with ¹³C-NMR. Dyad-triad sequence distribution of ethylene/1-hexene copolymers prepared with different catalyst systems were analyzed on the basis of Randall method as shown in Table II. It was observed that there was neither HHE nor HHH copolymer triad sequence on ¹³C-NMR spectra. This indicates clearly the absence of 1-hexene blocky sequences on polymer backbone.

The number of short chain branch (CH_3 per 1000 carbon) was calculated by ¹³C-NMR. The value was 5 in copolymers produced with the supported catalyst systems and the value was 6 in copolymers produced with the homogeneous catalyst system. Both supported and homogeneous catalytic systems produced random copolymers.

Figure 3 represents the comparison of temperature rising elution fractionation (TREF) profiles among the copolymers produced with the different catalyst systems. The homogeneous and supported catalyst systems showed narrow distribution profile. The highly crystalline fraction was not detected in all profiles. TREF profile of copolymer obtained with homogeneous catalyst system was observed at low temperature, because of high contents of 1-hexene as well as low MW. According to the MWD and TREF profile results, homogeneous and supported metallocene catalyst systems

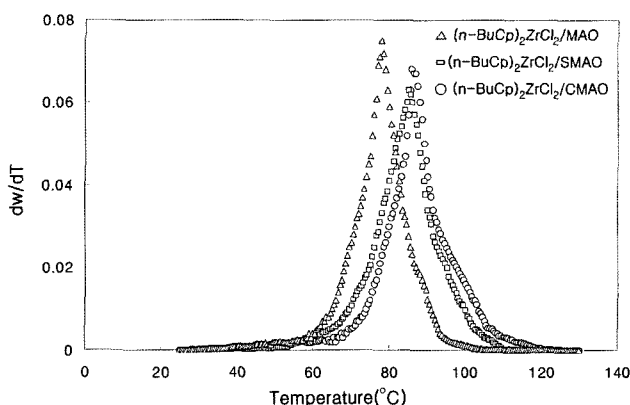


Figure 3. Temperature rising elution fractionation (TREF) profiles of the copolymers produced with the different catalyst systems. All copolymers were prepared at $M_H/(M_H + M_E) = 0.3$ (see Table I).

are single-site catalysts and produce very uniform copolymers with narrow MWD and short chain branch distribution (SCBD).

It is reported that the catalytic activity was strongly influenced by the increasing of 1-hexene concentration within the range of study. Galland *et al.*²⁰ studied the copolymerization of ethylene and 1-hexene with the catalyst $(n\text{-BuCp})_2\text{ZrCl}_2$ in both homogeneous and silica-supported systems. They observed that the catalyst activity of the copolymerization system was higher than that of ethylene homopolymerization.

Table III and Figure 4 show that the influence of 1-hexene concentration in the feed on catalyst activity and properties of the resulting copolymers produced with $(n\text{-BuCp})_2\text{ZrCl}_2/\text{CMAO}$ and $(n\text{-BuCp})_2\text{ZrCl}_2/\text{MAO}$ catalyst systems. We observed the same activity enhancement with the copolymerization. As shown in Table III, it is clearly demonstrated

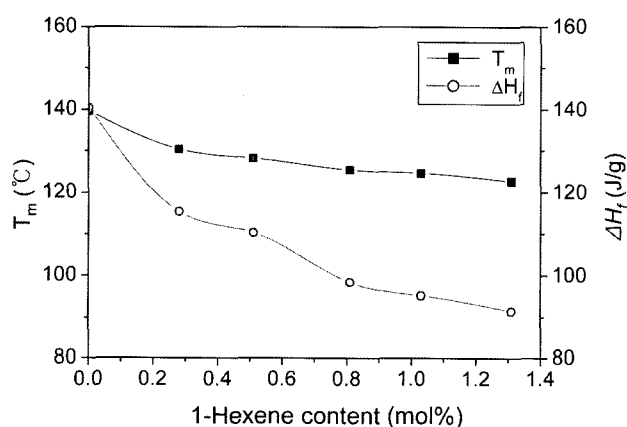


Figure 4. Melting temperature and heat of fusion of copolymers obtained with $(n\text{-BuCp})_2\text{ZrCl}_2/\text{CMAO}$ catalyst system.

that the addition of 1-hexene resulted in the increase of catalytic activity from 12,720 kg-polymer/mol-Zr-hr of homopolymerization to 20,160 kg-polymer/mol-Zr-hr of copolymerization. The molecular weight of the copolymer decreased as the comonomer concentration in the feed increased. In the copolymerization, β -hydride elimination, as well as monomer and comonomer transfer reactions, may take place. The results indicate that an olefin comonomer was involved in polymer chain transfer reactions, which was also confirmed by Quijada *et al.*²² However, the MWD of copolymers could not affect on the comonomer concentration.

Table III shows the density of copolymers determined by density gradient column. The density was decreased sharply with the incorporation of 1-hexene units. The density of copolymers can be ranged from 0.9511 g/cm³ (high density polyethylene) to 0.9237 g/cm³ (linear low-density polyethylene) depending upon the contents of incorporated 1-hexene.

The thermal properties of copolymers obtained with $(n\text{-BuCp})_2\text{ZrCl}_2/\text{CMAO}$ were characterized by using DSC and the results are shown in Figure 3. The heat of fusion (ΔH_f) and the melting temperature were measured on samples that had been previously melted and recrystallized with the use of a Perkin Elmer DSC-7 calorimeter at a heating rate of 5 °C/min. From the ΔH_f the percentage of crystallinity was calculated: $X_c = \Delta H_f (100/270)$.²³ The melting temperature of copolymers slightly decreased with increasing 1-hexene contents (from 140 to 123 °C). In contrast to the melting temperature difference the crystallinity difference of copolymers was changed significantly by the increment of 1-hexene contents (from 51 to 34%). This result suggests that the presence of a small amount of the branch exerts a considerable influence on the crystallinity of the copolymers rather

Table III. Properties of Copolymers Produced with $(n\text{-BuCp})_2\text{ZrCl}_2/\text{CMAO}$ and $(n\text{-BuCp})_2\text{ZrCl}_2/\text{MAO}$ Catalyst System at Different Ethylene/1-Hexene Feed Ratio

Catalyst	$M_H/(M_H + M_E)$	Activity	M_w (kg/mol)	M_w/M_n	Density	1-Hexene content in mol%
$(n\text{-BuCp})_2\text{ZrCl}_2$ /CMAO ^a	0	12,720	298	2.3	0.9511	-
	0.06	12,000	220	2.4	0.9340	0.3
	0.12	12,480	212	2.3	0.9313	0.5
	0.18	12,960	196	2.3	0.9287	0.8
	0.24	16,800	183	2.2	0.9256	1.0
	0.30	20,160	178	2.3	0.9237	1.3
$(n\text{-BuCp})_2\text{ZrCl}_2$ /MAO ^b	0	14,500	234	2.2	0.9485	-
	0.12	15,200	189	2.3	0.9301	0.9
	0.24	19,500	165	2.3	0.9240	1.2
	0.30	21,000	150	2.6	0.9214	1.6

^aPolymerization condition: $[\text{Al}]/[\text{Zr}] = 40$, TEA = 1 mmol, 80 °C, 20 min, $P_{\text{ethylene}} = 115$ psig, $[\text{Zr}] = 12.5$ $\mu\text{mol/L}$.

^bPolymerization condition: $[\text{Al}]/[\text{Zr}] = 100$, TEA = 1 mmol, 80 °C, 20 min, $P_{\text{ethylene}} = 115$ psig, $[\text{Zr}] = 2.0$ $\mu\text{mol/L}$. Activity: kg-Polymer/mol-Zr · h.

than melting temperature itself.¹⁷

In conclusion, we obtained the linear low density polyethylene (LLDPE) type copolymers by using (*n*-BuCp)₂ZrCl₂ catalyst with the new supported cocatalyst, such as cross-linked MAO supported cocatalyst. The catalyst activity and comonomer contents of copolymers by using the (*n*-BuCp)₂ZrCl₂ with the new supported cocatalyst were slightly higher than those of copolymers with the commercially employing supported cocatalyst. The spherical morphology of copolymers obtained with new catalytic system and duplicated the morphology of original silica. The density, melting temperature and crystallinity decreased with an increase of comonomer concentration in the feed. (*n*-BuCp)₂ZrCl₂ catalyst with the new supported cocatalyst produced copolymers of ethylene and 1-hexene with narrow molecular weight distribution. The sequence analysis by ¹³C NMR spectra exhibited randomly distributed short chain branches on copolymer.

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