Copolymerization of Ethylene/α-Olefins over (2-MeInd)₂ZrCl₂/MAO and (2-BzInd)₂ZrCl₂/MAO Systems

JIN-SAN YOON,¹ DONG-HO LEE,¹ EUN-SOO PARK,¹ IK-MO LEE,² DUCK-KYUNG PARK,² SUNG-OUK JUNG²

¹ Department of Polymer Science and Engineering, and ²Department of Chemistry, Inha University, 402-751 Inchon, Korea

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ABSTRACT: Ethylene homopolymerization and ethylene/ α -olefin copolymerization were carried out using unbridged and 2-alkyl substituted bis(indenyl)zirconium dichloride complexes such as (2-MeInd)₂ZrCl₂ and (2-BzInd)₂ZrCl₂. Various concentrations of 1-hexene, 1-dodecene, and 1-octadecene were used in order to find the effect of chain length of α -olefins on the copolymerization behavior. In ethylene homopolymerization, catalytic activity increased at higher polymerization temperature, and (2-MeInd)₂ZrCl₂ showed higher activity than (2-BzInd)₂ZrCl₂. The increase of catalytic activity with addition of comonomer (the synergistic effect) was not observed except in the case of ethylene/1-hexene copolymerization at 40°C. The monomer reactivity ratios of ethylene increased with the decrease of polymerization temperature, while those of α -olefin showed the reverse trend. The two catalysts showed similar copolymerization reactivity ratios. $(2-MeInd)_2ZrCl_2$ produced the copolymer with higher M_w than $(2-BzInd)_2ZrCl_2$. The melting temperature and the crystallinity decreased drastically with the increase of the α -olefin content but T_m as a function of weight fraction of the α -olefins showed similar decreasing behavior. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 928-937, 2000

Key words: ethylene; α -olefin; copolymerization; metallocene catalysts

INTRODUCTION

Homogeneous Ziegler-Natta catalysts, initiated by Cp_2TiCl_2/R_2AlCl^1 have been used mainly to investigate the mechanism of olefin polymerization due to the lower activity toward olefin polymerization. However, Sinn et al.² discovered that Cp_2ZrCl_2 with a large amount of methylaluminoxane (MAO) instead of alkyl aluminum showed higher activity toward ethylene polymerization and much attention to the metallocene catalysts has been attracted since then.³⁻⁶

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Olefin polymerization behaviors depend principally on the structures of the metallocene catalysts^{7–9}; generally, syndiospecific (C_S symmetric) metallocenes are known to be more effective to the ethylene/ α -olefin copolymerization than isospecific (C₂ symmetric) or unbridged ones.¹⁰ Unbridged metallocene catalysts with Cp ligands showed lower activity for ethylene polymerization than those with indenyl (Ind) ones.⁴ Alkyl substitution into indenyl ligands enhanced the catalyst activity for ethylene polymerization^{12,13} and the catalyst activity was dependent on the steric bulkiness and electronic nature (electron donating or withdrawing ability) of the substituents.¹⁴⁻¹⁶ Recently, we have found that (2-MeInd)₂ZrCl₂, a unbridged metallocene catalyst, was very active for propylene polymerization as well as for ethylene polymerization.¹⁷ Curiously

Correspondence to: J.-S. Yoon (jsyoon@inha.ac.kr). Contract grant sponsor: KOSEF (Interdisciplinary re-

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enough the rate of propylene polymerization by this type of catalysts increased, while that of ethylene polymerization decreased, as the polymerization temperature was lowered.

In this paper we report the polymerization behavior of ethylene homopolymerization and ethylene/ α -olefin copolymerization with bis(2-methyl indenyl)zirconium dichloride ((2-MeInd)₂ZrCl₂)) and bis(2-benzyl indenyl)zirconium dichloride ((2-BzInd)₂ZrCl₂).

EXPERIMENTAL

Materials

 $(2-\text{MeInd})_2\text{ZrCl}_2$ and $(2-\text{BzInd})_2\text{ZrCl}_2$ were prepared and recrystallized by following the procedures described in the literature.¹⁷ MAO (Akzo Chemical Co., MMAO-type 4, 6.4 wt % solution in toluene) was used without further purification. Toluene was refluxed for over 8 h in the presence of sodium and benzophenone and used after the second distillation. Purity of ethylene gas was more than 99.5%, and trace of impurities was removed by passing the gas successively through CaCl₂ and CaSO₄. 1-Hexene, 1-dodecene, and 1-octadecene were purchased from Aldrich Co. (Milwaukee, WI) and purified by vacuum distillation.

Polymerization

Ethylene Homopolymerization

All polymerization reactions were carried out in a 500-mL glass reactor with a magnetic stirrer. One hundred milliliters of toluene was used as a reaction medium and the reaction temperature was maintained at 40, 20, 0, and -20° C, respectively. Ethylene gas was introduced first at 1 atm and MAO and the catalyst $(5.9 \times 10^{-5} M)$ were added consecutively. The ratio of concentration of cocatalyst to that of catalyst ([Al]/[Zr]) was maintained at 2000. The reaction time was 30 min, and the reaction was terminated by adding a mixed solution of methanol and HCl. The products were washed with plenty of methanol three times and dried in a vacuum oven (30°C) until constant weight was attained.

Ethylene/α-olefin Copolymerization

The same reactor described above was used. Ethylene gas was first introduced at 1 atm and α -olefins (1-hexene, 1-dodecene, and 1-octadecene) were added to be 0.05 M, 0.10 M, 0.20 M, and 0.25 M, respectively. The reaction temperature was also maintained at 40, 20, 0 and -20° C, respectively. The copolymerization was initiated by addition of MAO and catalysts ($5.9 \times 10^{-5} M$). Al/Zr mole ratio was also maintained at 2000 and the reaction was carried out for 30 min. Drying and washing of the products were accomplished following the same procedure as in the ethylene polymerization.

Characterization of Polymers

¹³C-NMR spectra of the products were recorded at 130°C on a Fourier transform (FT)-nuclear magnetic resonance (NMR) spectrometer (AC-250; Bruker, Billerica, MA) operating at 62.896 MHz. NMR samples were prepared by dissolving 20–50 mg of the polymers in 0.3 mL of 1,2,4-trichlorobenzene (10 wt % of 1,2-dichlorobenzene-d₄ mixed solvent). Molecular weight and molecular weight distribution of the polymers were obtained by gel permeation chromatography (Model 150C plus; Waters Co., Milford, MA) at 135°C. The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) (DSC 7; Perkin Elmer, Norwalk, CT). Thermal history of the products due to the different reaction temperatures was removed by scanning to 160°C with the heating rate of 10°C/min first and cooling at the rate of 5°C/min to room temperature. Then the crystallized samples were reheated at 10°C/ min to 160°C and the second scan DSC thermogram was obtained.

RESULTS AND DISCUSSION

Catalyst Activity

Table I and II show the results of copolymerization of ethylene/1-hexene and ethylene/1-dodecene with $(2-\text{MeInd})_2\text{ZrCl}_2$, respectively. Table III represents the results of copolymerization of ethylene/1-dodecene with $(2-\text{BzInd})_2\text{ZrCl}_2$. Activity of the catalysts increased with elevating polymerization temperature and $(2-\text{MeInd})_2\text{ZrCl}_2$ was more active than $(2-\text{BzInd})_2\text{ZrCl}_2$. The activity difference of those two catalysts became more pronounced at a higher polymerization temperature. This can be rationalized by the fact that methyl substituent is an electron-donating group, and benzyl is sterically bulky one, with less electron-

Reaction Temp. (°C) ^a	1-Hexene Feed [<i>M</i>]	$\begin{array}{c} \text{Activity} \\ (\times 10^5)^{\mathrm{b}} \end{array}$	Yields (g)	H in Copolymer (mol %) ^c	$\begin{array}{c} T_m \\ (^{\circ}\mathrm{C})^\mathrm{d} \end{array}$	ΔH_m (J/g)	$egin{array}{c} X_c \ (\%) \end{array}$	$M_w \ (imes 10^5)$	M_w/M_n
40	0	8.01	2 62	0	122.1	186 1	68.0	7.06	3.07
40	0.05	8.34	2.05	64	104.1	70.4	96 1	5.88	2.18
	0.05	0.04	2.40	10.4	104.1	10.4 07 0	20.1	2.05	2.10
	0.10	9.30	2.70	12.3		21.2	10.1	3.00	3.00
	0.20	11.88	3.50	20.8				2.17	2.72
	0.25	13.15	3.88	23.8	_	_	_	2.25	2.89
20	0	8.47	2.50	0	133.9	152.2	56.4	11.54	2.79
	0.05	7.16	2.11	5.1	106.8	72.2	26.8	10.92	3.21
	0.10	7.50	2.21	9.7	98.9	54.8	20.3	3.08	3.00
	0.20	8.63	2.55	15.7				3.30	2.83
	0.25	7.96	2.35	19.0	—	—	—	3.52	2.78
0	0	7.55	2.23	0	133.8	141.5	52.4	23.22	2.84
-	0.05	7.96	2.35	2.9	115.8	101.7	37.7	24.53	2.76
	0.10	7.61	2.25	61		70.8	26.2	24.03	2.71
	0.20	8 4 9	2.50	11.0		41.3	15.3	22.81	2.66
	0.25	8.20	2.42	14.2	_			19.75	2.34
-20	0	5.99	1.77	0	133.1	133.7	49.5	25.65	2.61
	0.05	6.51	1.92	1.8	113.8	104.5	38.7	25.78	2.29
	0.10	5.82	1.72	3.5	107.9	86.6	32.1	23.23	2.54
	0.20	6.20	1.83	6.6	99.1	66.7	24.7	25.66	2.71
	0.25	5.84	1.72	8.7	96.3	60.0	22.2	23.01	2.63

Table I Effect of Comonomer Addition on Catalytic Activity and Polymer Properties for Ethylene/1-Hexene Copolymer over (2-MeInd)₂ZrCl₂

^a Reaction conditions: $[Zr] = 5.9 \times 10^{-5} M$, [Al]/[Zr] = 2000.

^b Activity = g polymer/mol-Zr hour atm. ^c Determined by ¹³C-NMR spectra.

^d Determined by DSC.

donating nature. The catalytic activity of (2-MeInd)₂ZrCl₂ for ethylene/1-hexene copolymerization was higher than that for both ethylene/1dodecene and ethylene/1-octadecene copolymerizations (Table IV). Fink and coworkers^{18,19} also found that the catalytic activity decreased with the increase of chain length of α -olefin in ethylene/ α -olefin copolymerization in the presence of Me₂Si(Ind)₂ZrCl₂ and i-Pr(Cp)(Flu)ZrCl₂.

The synergistic effect, where the catalytic activity increases with α -olefin concentration,²⁰⁻²⁴ was observed in the copolymerization of ethylene/ 1-hexene by (2-MeInd)₂ZrCl₂ at 40°C. Meanwhile, in the reactions below 20°C the catalytic activity did not depend significantly on the content of 1-hexene. In ethylene/1-dodecene copolymerization with either (2-MeInd)₂ZrCl₂ or (2-BzInd)₂ZrCl₂, the synergistic effect was absent and the catalytic activity decreased as the content of 1-dodecene increased. The same tendency was also observed in the reactions done by Bukatov et al.,²² who

adopted the stereorigid complexes such as Me₂Si(Ind)₂ZrCl₂ and i-Pr(Cp)(Flu)ZrCl₂ as catalysts. They observed the synergistic effect in the copolymerization of ethylene/1-hexene but not in the copolymerization of ethylene/1-dodecene nor in that of ethylene/1-octadecene. They explained the synergistic effect by the fact that the presence of comonomer units in the polymer lowered the crystallinity of the polymer, making the polymer more swellable in the reaction medium. The swelling of the polymer allowed the monomer molecules to access to the active center more easily. Increase in the number of active centers or increase in the insertion rate of monomer was considered as another origin for the synergistic effect.²¹

Monomer Reactivity Ratios for Copolymerization

The monomer reactivity ratios for ethylene/ α -olefin copolymerization of $(2-MeInd)_2ZrCl_2$ and $(2-MeInd)_2ZrCl_2$

Reaction Temp. (°C) ^a	1-Hexene Feed [<i>M</i>]	$\begin{array}{c} \text{Activity} \\ (\times 10^5)^{\text{b}} \end{array}$	Yields (g)	D in Copolymer (mol %) ^c	$\mathop{T_m}\limits_{(^\circ\mathrm{C})^\mathrm{d}}$	ΔH_m (J/g)	$egin{array}{c} X_c \ (\%) \end{array}$	M_w (×10 ⁵)	M_w/M_n
40	0	8.91	2.63	0	133.1	186.1	68.9	7.06	3.07
	0.05	6.52	1.92	2.4	114.4	87.6	32.4	9.53	2.47
	0.10	6.47	1.91	3.5	109.5	67.1	24.9	8.57	2.38
	0.20	6.53	1.93	5.5	_	28.3	10.5	3.72	2.28
	0.25	6.29	1.86	5.8	_	23.8	8.8	4.23	2.35
20	0	8.47	2.50	0	133.9	152.2	56.4	11.54	2.79
	0.05	6.35	1.87	2.9	110.4	76.9	28.5	20.44	2.71
	0.10	6.40	1.89	4.2	104.4	54.0	20.0	18.76	2.72
	0.20	6.72	1.98	4.7	97.4	42.8	15.9	18.71	2.67
	0.25	6.30	1.86	5.1	_	38.9	14.4	21.22	2.58
0	0	7.55	2.23	0	133.8	141.5	52.4	23.22	2.79
	0.05	5.76	1.70	2.0	117.8	95.3	35.3	46.71	2.31
	0.10	5.91	1.74	2.5	112.8	84.8	31.4	48.23	2.32
	0.20	5.18	1.53	3.0	105.4	76.3	28.3	24.45	2.28
	0.25	4.93	1.45	3.8	100.2	61.7	22.9	21.97	2.49
-20	0	5.93	1.75	0	133.1	133.7	49.5	25.65	2.61
	0.05	5.18	1.53	1.8	119.6	99.5	36.9	23.41	1.93
	0.10	4.73	1.40	2.0	114.6	95.8	35.5	15.86	1.93
	0.20	4.30	1.27	2.9	107.8	76.8	28.5	12.33	1.78
	0.25	4.25	1.25	3.3	103.9	70.9	26.3	12.55	1.78

Table II Effect of Comonomer Addition on Catalytic Activity and Polymer Properties for Ethylene/1-Dodecene Copolymer over (2-MeInd)₂ZrCl₂

^a Reaction conditions: $[Zr] = 5.9 \times 10^{-5} M$, [Al]/[Zr] = 2000.

^b Activity = g polymer/mol-Zr hour atm. ^c Determined by ¹³C-NMR spectra.

^d Determined by DSC.

BzInd)₂ZrCl₂ were measured from the mole fraction of the α -olefin in the reaction medium and the content of the α -olefin units in the copolymer. Ethylene concentration in the toluene at the reaction temperature was estimated by using the following equation quoted by Kissin.²⁵

$$C_M = K_M \exp(Q/RT) P_M$$

where C_M , K_M , and Q represent the concentration, Henry's constant, and heat of solution for ethylene, respectively. The concentration of ethylene in toluene was determined to be 0.12 M(40°C), 0.16 M (20°C), 0.23 M (0°C), and 0.34 M $(-20^{\circ}C)$, respectively. The composition of the copolymers was determined according to Randall's paper²⁶ from the ¹³C-NMR spectra of the copolymers. The monomer reactivity ratios were calculated by the following equations from the diad sequence distributions of the ¹³C-NMR spectra.⁸

$$r_E = 2[EE]/[EC]X$$
 $r_C = 2[CC]X/[EC]$ (2)

where [EE], [EC], and [CC] represent the diad sequence distributions in the copolymers and *X* is the ratio of the mole fraction of ethylene (E) to that of comonomer (C) in the feed.

Table V shows the reactivity ratios for ethylene/ α -olefin copolymerization by (2-MeInd)₂ZrCl₂ and (2-BzInd)₂ZrCl₂. The monomer reactivity ratios were also determined by the Fineman-Ross method.27

$$X - (X/Y) = r_E(X^2/Y) - r_C$$
(3)

where *Y* represents the molar concentration ratio of ethylene (E) to comonomer (C) in the copolymer.

It was expected here that r_E of ethylene/1-hexene copolymerization over (2-MeInd)₂ZrCl₂ in Ta-

Reaction Temp. (°C) ^a	1-Hexene Feed [<i>M</i>]	$\begin{array}{c} \text{Activity} \\ (\times 10^5)^{\text{b}} \end{array}$	Yields (g)	D in Copolymer (mol %) ^c	$\mathop{T_m}\limits_{(^\circ\mathrm{C})^\mathrm{d}}$	ΔH_m (J/g)	X_c (%)	$M_w \ (imes 10^5)$	M_w/M_n
40	0	8.56	2.52	0	132.0	151.9	56.3	4.97	3.33
	0.05	5.97	1.76	2.3	114.9	90.2	33.4	3.54	3.86
	0.10	5.52	1.63	4.3	94.8	52.8	19.6	2.63	3.24
	0.20	5.21	1.54	5.9	_	22.5	8.3	0.71	2.75
	0.25	5.48	1.62	6.7	—	—	—	0.74	3.08
20	0	7.63	2.25	0	132.7	150.9	55.9	7.31	2.74
	0.05	5.70	1.68	2.4	113.4	89.2	33.0	5.32	3.72
	0.10	5.22	1.54	3.5	106.8	66.3	24.6	4.46	3.33
	0.20	5.14	1.52	5.5		29.3	10.9	2.75	3.17
	0.25	4.69	1.38	6.1	—	17.4	6.4	3.10	2.91
0	0	6.45	1.90	0	133.2	148.1	54.9	7.60	2.53
	0.05	5.24	1.55	1.9	117.4	97.7	36.2	7.45	2.42
	0.10	4.98	1.47	2.3	113.3	91.4	33.9	6.89	2.37
	0.20	4.55	1.34	3.4	97.6	70.6	26.1	5.07	2.19
	0.25	4.45	1.31	3.8	92.3	60.2	22.3	5.08	2.27
-20	0	6.21	1.83	0	133.6	143.8	53.3	7.90	2.31
	0.05	3.50	1.03	1.7	121.6	108.1	40.0	11.41	2.63
	0.10	3.90	1.15	2.5	115.7	82.8	30.7	9.35	2.48
	0.20	3.45	1.02	2.8	104.3	79.2	29.3	6.06	2.20
	0.25	3.61	1.07	3.6	99.9	64.4	23.9	7.17	2.29

Table III Effect of Comonomer Addition on Catalytic Activity and Polymer Properties for Ethylene/1-Dodecene Copolymer over (2-BzInd)₂ZrCl₂

^a Reaction conditions: $[Zr] = 5.9 \times 10^{-5} M$, [Al]/[Zr] = 2000.

^b Activity = g polymer/mol-Zr hour atm. ^c Determined by ¹³C-NMR spectra. ^d Determined by DSC.

ble V was overestimated, because the comonomer conversion in the ethylene/1-hexene copolymerization was high, so that the reaction medium became richer in ethylene than in the comonomer

as the comonomer conversion increased. Ethylene/1-hexene copolymerization was carried out again, and the comonomer conversion was kept to be 6–15%. However r_E and r_C values thus ob-

Table IV Effect of Comonomer Addition on Catalytic Activity and Polymer Properties for Ethylene/I-Octadecene Copolymer over (2-MeInd)₂ZrCl₂

Reaction Temp. (°C) ^a	1-Hexene Feed [<i>M</i>]	$\begin{array}{c} \text{Activity} \\ (\times 10^5)^{\text{b}} \end{array}$	Yields (g)	O in Copolymer (mol %) ^c	$\begin{array}{c} T_m \\ (^{\circ}\mathrm{C})^\mathrm{d} \end{array}$	ΔH_m (J/g)	X_c (%)	$M_w \ (imes 10^5)$	M_w/M_n
0	0	7.55	2.23	0	133.8	141.5	52.4	23.22	2.84
	0.05	7.26	2.14	0.9	116.5	84.3	31.2	24.16	3.02
	0.10	6.93	2.04	1.8	109.7	48.3	17.9	24.61	2.76
	0.20	6.70	1.98	2.1		32.7	12.1	23.33	2.57
	0.25	6.61	1.95	2.3	_	23.3	8.6	20.18	2.58

^a Reaction conditions: $[Zr] = 5.9 \times 10^{-5} M$, [Al]/[Zr] = 2000.

^b Activity = g polymer/mol-Zr hour atm. ^c Determined by ¹³C-NMR spectra.

^d Determined by DSC.

			F	Finemen-Ross			¹³ C-NMR		
Catalyst	Reaction Temp. (°C)	Comonomer	r_E	r_C	$r_E \cdot r_C$	r_E	r_{C}	$r_E \cdot r_C$	
2-Me	40	1-Hexene	2.95	0.20	0.59	$3.24 (4.10)^{a}$	$0.16 \\ (0.15)^{\mathrm{a}}$	0.52	
2-Me		1-Dodecene	13.4			13.9			
2-Bz		1-Dodecene	12.4	_	_	12.2			
2-Me	20	1-Hexene	4.14	0.15	0.62	$4.53 (4.64)^{a}$	$0.15 \\ (0.13)^{\mathrm{a}}$	0.68	
2-Me		1-Dodecene	14.7	_	_	14.4			
2-Bz		1-Dodecene	13.1	_	_	13.7			
2-Me	0	1-Hexene	7.29	0.12	0.87	7.40 (6.45) ^a	$0.11 \\ (0.12)^{a}$	0.81	
2-Me		1-Dodecene 1-	21.6	—	—	22.1		—	
2-Me		Octadecene	37.1		_	36.5			
2-Bz		1-Dodecene	21.2	_	_	21.7			
2-Me	-20	1-Hexene	12.9	0.07	0.91	12.7 (12.4) ^a	$0.07 \\ (0.10)^{\mathrm{a}}$	0.89	
2-Me		1-Dodecene	24.7	_		25.1		_	
2-Bz		1-Dodecene	23.8	—	—	23.6	—	—	

Table V Values of Reactivity Ratios for Ethylene/α-Olefin Copolymerization

^a Result of copolymerization terminated at a conversion between 6% and 15%.

tained in Table V were most identical to the above results. r_E values of ethylene/1-dodecene and ethylene/1-octadecene either over $(2-MeInd)_2ZrCl_2$ or $(2-BzInd)_2ZrCl_2$ were obtained controlling the comonomer conversion to be 5–20%.



Figure 1 Fineman-Ross plot for ethylene/1-hexene copolymerization. Polymerization temperature: 20°C, (2-MeInd)₂ZrCl₂.

Figure 1 shows the typical Fineman-Ross plot for the ethylene/1-hexene copolymerization results exhibiting, a reasonally good linear relationship between LHS of Eq. (2) and X^2/Y . r_E and r_C were determined from the slope and the intersection, respectively. r_E increased with chain length of the α -olefin and lower temperature resulted in the larger value of r_E . The catalytic activity of (2-MeInd)₂ZrCl₂ toward ethylene homopolymerization increased, while the activity toward propylene or 1-hexene homopolymerization decreased as the polymerization temperature went up.²⁸ Since the interchange rate between racemic and meso rotamers of the metallocene catalyst is expected to slow down with the decrease of the reaction temperature, α -olefins such as propylene and 1-hexene, which were polymerized mainly by the racemic isomer, have more time to coordinate into the metal center and to insert into the M-C bond, and thus the polymerization rate should increase with decrease in the reaction temperature. Meanwhile, the rate of transition between racemic and meso rotamers does not affect the polymerization behavior of ethylene because the polymerization can be done by both rotamers. Therefore, homopolymerization rate of ethylene decreased and that of α -olefin increased with decreasing reaction temperature. Waymouth

Catalyst Con	nonomer	Reaction Temp. (°C)	r_E	r_C	Determination Method	Reference
Et(Ind) ₂ ZrCl ₂ Prope	ne (90/10)	40	7.69	0.09	¹³ C-NMR	31
Me ₂ Si(Ind) ₂ ZrCl ₂ Prope	ne (75/25)		4.23	0.12		
Ind ₂ ZrBz ₂ Prope	ne (75/25)		25.42			
Ind ₂ ZrCl ₂ Prope	ne (85/15)		13.75	0.18		
Cp ₂ ZrCl ₂ Prope	ne (85/15)		16.53			
(n-butCp) ₂ ZrCl ₂ Prope	ne (50/50)		25.89	0.03		
(90/10))		19.61			
Rac-Et(Ind) ₂ ZrCl ₂ Buten	ie	30	19.4	0.05	¹³ C-NMR	32
$Rac-Et(Ind)_2HfCl_2$ Buten	ie		5.4	0.17		
Cp ₂ ZrCl ₂ Prope	ne	40	16.9	0.03	¹³ C-NMR	8
Hexer	ne		23.8			
Et(IndH ₄) ₂ ZrCl ₂ Prope	ne		11.6	0.08		
Hexer	ne		12.1	0.03		
IPr(Cp)(Flu)ZrCl ₂ Prope	ne		7.0	0.07		
Hexer	ne		5.7	0.05		
(n-butCp) ₂ ZrCl ₂ Prope	ne	40	2.7	_	¹³ C-NMR	11
Hexer	ne		9	(0.7)		
Ind ₂ ZrCl ₂ Prope	ne		20	_		
Hexer	ne		19	_		
(CH ₃) ₂ SiCp ₂ ZrCl ₂ Hexer	ne	60	44.75	0	¹³ C-NMR	33
			32.67	0.027	Fineman-Ross	
Octen	e		43.35	0	¹³ C-NMR	
			42.28	0.035	Fineman-Ross	
Cp ₂ ZrCl ₂ Hexer	ne		74.60	0	¹³ C-NMR	
			62.31	0.003	Fineman-Ross	
Octen	e		99.43	0	¹³ C-NMR	
			61.56	0.030	Fineman-Ross	
$C_2H_4(Ind)_2ZrCl_2$ Hexer	ne		36.00	0	¹³ C-NMR	
			31.00	0.013	Fineman-Ross	
Octen	e		_	_	¹³ C-NMR	
			_	_	Fineman-Ross	
Ind ₂ ZrCl ₂ Hexer	ne		86.70	0	¹³ C-NMR	
			88.00	0.005	Fineman-Ross	
Octen	e		_		¹³ C-NMR	
			—	—	Fineman-Ross	

Table VI Reactivity Ratios for Ethylene/α-Olefin Copolymerization

and coworkers 29,30 also reported that the rate of homopolymerization of propylene over (2-PhInd)_2ZrCl_2/MAO increased with decreasing temperature.

However, contrary to expectations, r_E increased and r_C decreased with decreasing temperature in the copolymerization of ethylene/1-hexene, ethylene/1-dodecene, and ethylene/1-octadecene over (2-MeInd)₂ZrCl₂, as shown in Table V. Those results imply that the coordination and the insertion steps of α -olefin at the active centers of the catalyst are largely dependent on the nature of adjacent polymer chain end. The average reactivity ratios calculated from ¹³C-NMR spectra were quite similar to those determined from the Fineman-Ross plot, and the values for both (2-MeInd)₂ZrCl₂ and (2-BzInd)₂ZrCl₂ were almost identical. Table VI summarizes the reactivity ratios of ethylene/ α -olefin copolymerization reported previously. r_E spans from 5.7 in the copolymerization of ethylene/1-hexene at 40°C with i-Pr(Cp)(Flu)ZrCl₂ to 86.7 at 60°C with (Ind)₂ZrCl₂. In contrast, values of r_E for ethylene/1-hexene copolymerization over (2-MeInd)₂ZrCl₂ were about 3 and about 13, respectively, which represented that (2-MeInd)₂ZrCl₂ was superior to the other catalysts in the ethylene/ α -olefin copolymerizations.

Characteristics

Tables I, II, III, and IV show the molecular weight and the melting point of ethylene/1-hexene, ethylene/1-dodecene, and ethylene/1-octadecene copolymers. M_w (the weight average molecular weight) decreased with increasing polymerization temperature and with increasing content of the α -olefin. The molecular weight decrease was ascribed to the fact that the chain transfer to α -olefin could take place more easily than the chain transfer to ethylene. However, molecular weight did not seem to be affected by chain length of the α -olefin as long as the molar content of the α -olefin was equivalent. Molecular weight of the copolymers prepared with (2-MeInd)₂ZrCl₂ was higher than that of the copolymers made with $(2-BzInd)_2ZrCl_2$. But the extent of decrease in T_m of poly(ethylene-co-1-dodecene) prepared by either of the two catalysts was similar. Figures 2 and 3 show respectively the dependence of T_m and crystallinity of the copolymer on the mole fraction of the comonomers. ${\cal T}_m$ and the crystallinity of the copolymer having equivalent molar content of α -olefin decreased more rapidly in case when longer comonomer was used. However, plot of ${\cal T}_m$ against the weight fraction of the α -olefin showed almost similar correlations, independently of the type of the comonomers, the type of the catalysts, reaction temperature, and molecular weight of the copolymers (Fig. 4).



Figure 2 Plot of T_m versus comonomer content in the copolymer.



Figure 3 Plot of DSC crystallinity versus comonomer content in the copolymer.

CONCLUSIONS

Ethylene and α -olefin copolymerizations were carried out with unbridged metallocene catalysts such as $(2-MeInd)_2ZrCl_2$ and $(2-BzInd)_2ZrCl_2$. The catalytic activity of $(2-MeInd)_2 ZrCl_2$ was higher than that of (2-BzInd)₂ZrCl₂ and the difference in the activity of the two catalysts became more significant as the reaction temperature increased. The synergistic effect, the increasing effect of α -olefin on the catalytic activity, was observed in the reaction of ethylene/1-hexene at 40°C, but such phenomena disappeared when the reaction temperature was lower or when comonomers longer than 1-hexene were used. r_E values decreased with increasing temperature but r_{C} showed the reverse trend in the copolymerization in spite of the fact that rate of ethylene homopolymerization increased while that of 1-hexene homopolymerization decreased as the reaction temperature rose. (2-MeInd)₂ZrCl₂ produced the copolymer of higher M_w than $(2-BzInd)_2ZrCl_2$. Nevertheless, the reactivity ratios of the copolymerizations with both catalysts were similar. The melting point of the copolymers prepared with higher α -olefin decreased faster with increasing mole fraction of the α -olefin. In contrast the plot of T_m as a function of the comonomer weight fraction showed negligible dependence on the catalyst type, comonomer, reaction temperature, and molecular weight of the copolymers.



Figure 4 Plot of T_m versus weight fraction of comonomer.

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