

Copolymerizations of Ethylene with 1-Hexene over *ansa*-Metallocene Diamide Complexes

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Received March 14, 2004; Revised April 27, 2004

Abstract: We have performed copolymerizations of ethylene with 1-hexene using various *ansa*-metallocene compounds in the presence of the non-coordinative $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ion pair as a cocatalyst. The metallocenes chosen for this study are isospecific metallocene diamide compounds, *rac*-(EBI)Zr(NMe₂)₂ (**1**, EBI = ethylene-1,2-bis(1-indenyl)), *rac*-(EBI)Hf(NMe₂)₂ (**2**), *rac*-(EBI)Zr(NC₄H₈)₂ (**3**), and *rac*-(CH₃)₂Si(1-C₅H₂-2-CH₃-4-tC₄H₉)₂Zr(NMe₂)₂ (**4**), and syndiospecific metallocene dimethyl compounds, ethylidene(cyclopentadienyl)(9-fluorenyl)ZrMe₂ (**5**, Et(Flu)(Cp)ZrMe₂) and isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe₂ (**6**, *i*Pr(Flu)(Cp)ZrMe₂). The copolymerization rate decreased in the order **4** > **1** ~ **3** > **2** > **5** > **6**. The reactivity of 1-hexene decreased in the order **2** > **6** > **1** ~ **3** ~ **5** > **4**. We characterized the microstructure of the resulting poly(ethylene-*co*-1-hexene) by ¹³C NMR spectroscopy and investigated various other properties of the copolymers in detail.

Keywords: metallocene catalyst, copolymerization, ethylene, 1-hexene, comonomer reactivity.

Introduction

One of the most important advantages of metallocene catalysts is improved comonomer incorporation in a more homogenous way in ethylene/ α -olefin copolymerizations. Several groups have studied ethylene copolymerizations with a variety of α -olefins (C₃-C₁₈) using Group 4 metallocene catalysts cocatalyzed with methylaluminoxane (MAO).¹ In general *ansa*-metallocenes with one or two atoms as bridging groups were more effective for incorporating comonomer than non-bridged metallocenes.¹ Especially the syndiospecific catalyst, say isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe₂ (*i*Pr(Flu)(Cp)ZrMe₂), showed the best tendency for the incorporation of higher α -olefins.

Furthermore, *ansa*-metallocene diamide compounds ^{ch}Cp₂Zr(NR₂)₂ (^{ch}CpZr = chiral *ansa*-zirconocene framework, Cp = cyclopentadienyl) were found to be effective for highly isospecific polymerization of propylene in the presence of MAO.² *In situ* alkylation of ^{ch}CpZr(NR₂)₂ complexes with alkylaluminum followed by ionization by complexes with ammonium salts (e.g., [HNMe₂Ph][B(C₆F₅)₄]) or by alkyl abstraction reagents (e.g., [CPh₃][B(C₆F₅)₄]) has been proved to be an efficient procedure to activate ^{ch}Cp₂Zr(NR₂)₂ for the olefin polymerizations.² The efficient synthetic method of

ansa-metallocene via the amine elimination route usually provided the higher yield with higher *rac*/*meso* ratio (e.g., *rac*-(EBI)Zr(NMe₂)₂ (**1**, EBI = ethylene-1,2-bis(1-indenyl)), *rac*-(EBI)Hf(NMe₂)₂ (**2**), *rac*-(EBI)Zr(NC₄H₈)₂ (**3**) and *rac*-(CH₃)₂Si(1-C₅H₂-2-CH₃-4-tC₄H₉)₂Zr(NMe₂)₂ (**4**))³ than the corresponding dichloride compound.^{4,5}

In the present study, we copolymerized ethylene with 1-hexene using four isospecific diamide *ansa*-metallocene compounds (**1**, **2**, **3** and **4**) and two syndiospecific dimethyl *ansa*-metallocene compounds, ethylidene(cyclopentadienyl)(9-fluorenyl)ZrMe₂ (Et(Flu)(Cp)ZrMe₂, **5**) and *i*Pr(Flu)(Cp)ZrMe₂ (**6**). In order to simplify the catalyst system we have used non-coordinative anionic triphenylcarbenium tetrakis(pentafluoro-phenyl)borate ([CPh₃][B(C₆F₅)₄], **7**) compound as a cocatalyst together with Al(*i*Bu)₃. The results of reactivity ratios and the effect of catalyst type on polymerization rate and polymer properties are presented.

Experimental

Materials. All reactions were performed under a purified argon atmosphere using standard glove box and Schlenk techniques. Ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. 1-Hexene was purified by distillation over calcium hydride. Triisobutylaluminum (Al(*i*Bu)₃, Aldrich Chem. Co.) and compound **7** (Tosoh Akzo Co. Ltd.) were

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used without further purification. Toluene was refluxed over sodium/benzophenone and stored over molecular sieves (4A). The metallocene compounds **1-6** were synthesized according to literature procedures.^{3c,6,7}

Copolymerization. All the copolymerizations were carried out in a 250 mL glass reactor at 70 °C and $P_{C_2H_4} = 1.3$ atm with 80 mL toluene as solvent. A magnetic stirring bar was utilized for agitation. Toluene and required amounts of 1-hexene, Al(*i*-Bu)₃ and catalyst were introduced into the reactor sequentially in a glove box. The argon was then pumped off and the reactor was filled with ethylene monomer. After the temperature increased up to 70 °C, compound **7** dissolved in toluene was delivered into the reactor using a syringe. Copolymerization was then performed for 20 min, followed by quenching with 150 mL methanol containing HCl (5 v/v-%).

Ethylene monomer concentration (C_M) in toluene was calculated by application of Henry equation, $C_M = K_H^0 \exp(E/RT)P_M$, where P_M is the monomer pressure (atm) over the solution, K_H^0 is the Henry constant at temperature T (mol L⁻¹), and E is a molar heat of solution, an empirical parameter (cal mol⁻¹) describing dependence of K_H^0 on temperature. Previous report¹⁰ showed that $E = 2.57$ kcal mol⁻¹ and $K_H^0 = 1.74 \times 10^{-3}$ mol L⁻¹ atm⁻¹.

Characterization. Thermal analysis of copolymer was carried out by using Dupont differential scanning calorimeter (DSC, Model-900) at 10 °C/min heating rate under nitrogen atmosphere. The crystallinity was calculated from the heat of fusion, $(\Delta H_f/\Delta H_f^0) \times 100$, where ΔH_f was the heat of fusion of the sample as determined from the DSC curve, and ΔH_f^0 is the heat of fusion of folded-chain polyethylene (269.9 J · g⁻¹).⁸ The density of polymer was estimated by using a density gradient column according to ASTM D 1505-79.

¹³C NMR spectra of copolymers were recorded and measured at 120 °C on a Varian Unity Plus 300 spectrometer operating at 75.5 MHz. Samples for ¹³C NMR spectra were prepared by dissolving 50 mg of polymer in 0.5 mL of benzene-*d*₆/1,2,4-trichlorobenzene-*d*₃ (1/5 v/v). The composition of copolymers was analyzed according to the standard test method for the determination of LLDPE composition,^{9,10} and the reactivity parameters were calculated using diad sequence distributions according to the literature.^{1a,10} Copolymers were fractionated by boiling ethyl ether and n-hexane sequentially by using a Soxhlet apparatus for 6 hrs. The intrinsic viscosity was measured in tetrahydronaphthalene at 135 ± 0.1 °C by using an modified Ubbelohde viscometer.

Results and Discussion

Effect of 1-Hexene Concentration on the Copolymerization Activity and 1-Hexene Reactivity. Both activity and incorporating ability are most important factors for the α -olefin/ethylene copolymerization. A series of copolymeriza-

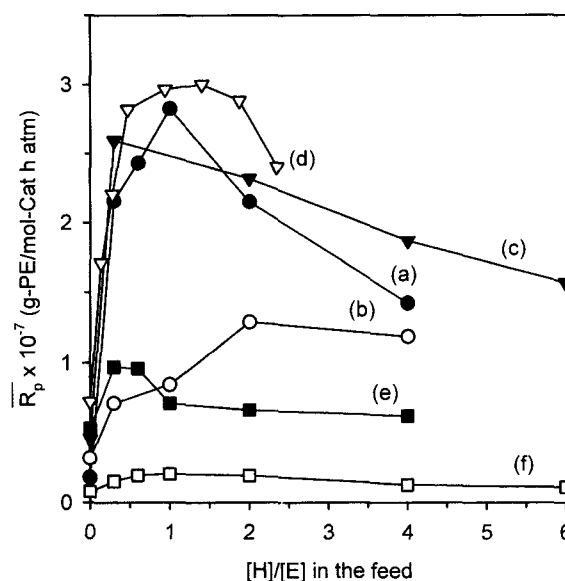


Figure 1. Effect of 1-hexene concentration on polymerization rate: (a) 1/Al(*i*-Bu)₃/7, (b) 2/Al(*i*-Bu)₃/7, (c) 3/Al(*i*-Bu)₃/7, (d) 4/Al(*i*-Bu)₃/7, (e) 5/Al(*i*-Bu)₃/7, and (f) 6/Al(*i*-Bu)₃/7 catalyst systems. For 1, 2, 3 and 4 catalysts, [Al(*i*-Bu)₃]/[cat]/[7] = 30/1/1 ([cat] = 5.4 μM), and for 5 and 6 catalysts, [Al(*i*-Bu)₃]/[cat]/[7] = 10/1/1 ([cat] = 30.0 μM). All runs were carried out at 70 °C with ethylene pressure of 1.3 atm in toluene solvent (80 mL) for 20 min.

tions of ethylene and 1-hexene were carried out for 20 min at 70 °C by using 6 different catalysts in a wide range of [H]/[E] ratio (H and E denote 1-hexene and ethylene, respectively). A 5.0 μmol/L of diamide catalysts (**1**, **2**, **3**, **4**) was used for polymerizations and a minimum amount of Al(*i*-Bu)₃ ([Al]/[cat] = 30), which was used both to alkylate the catalysts and to scavenge the impurities existed in the reaction system,² together with **7** ([7]/[cat] = 1) as a cocatalyst system. Somewhat larger amount (30.0 μmol/L) of **5** and **6** was used as catalysts in the presence of Al(*i*-Bu)₃/6 ([Al]/[cat] = 10, [6]/[cat] = 1) cocatalyst system. Figure 1 shows the polymerization rate (as R_p) versus [H]/[E] ratio profile. The rates of homopolymerizations of ethylene in the absence of comonomer were characterized by a sharp decline of rate after reaching maximum rate within a few minute caused by dramatic change of media viscosity and polymer precipitation.¹¹ When 1-hexene is introduced to the reactor, the polymerization rates are enhanced very much for all catalyst systems. The rate enhancement effect of 1-hexene is evident at [H]/[E] < 1. At higher [H]/[E] ratios, however, the R_p values start to decline except **2** catalyst. Similar dependence of copolymerization rate on [H]/[E] ratio in feed were reported for *rac*-(EBI)ZrCl₂/MAO^{1c} and Me₂Si[Ind]₂ZrCl₂/MAO¹² catalyst systems. Different results were also reported by Quijada with *rac*-(EBI)ZrCl₂/MAO^{1b} and Fink with *i*Pr(Flu)(Cp)ZrMe₂/MAO^{12,1m} which showed continuously increased polymerization rate with the increase of [H]/[E]

ratio in feed. The different result should come from different polymerization conditions such as catalyst concentration, aluminum to catalyst molar ratio as well as polymerization temperature. From the direct comparison of the catalysts of the present catalytic systems, one can find the activity of the C_2 -symmetric catalysts is much higher than that of C_s -symmetric catalysts. The space volume between the cyclopentadienyl ligands available for silyl-bridged catalyst (**4**) is larger than in bisindenyl systems (**1**, **2**, **3**),¹³ resulting in silyl-bridged catalyst shows higher activity than ethyl-bridged catalysts. The zirconocene (**1**) is more efficient than hafnocene analogue

(**2**) have also been described for dichloride metallocenes,¹⁴ which may be attributed to differences in concentration of active centers and different carbon-metal bond strengths. In summary, the copolymerization rate decreases in the order of **4** > **1** ~ **3** > **2** > **5** > **6**.

In order to investigate the microstructure of the resulting copolymers we have conducted ¹³C NMR spectroscopy analyses.¹⁰ The monomer reactivity ratios were estimated from the following equations:^{1a}

$$r_E = 2[EE]/[EH] \cdot X; \quad r_H = 2[HH] \cdot X/[EH]$$

Table I. Monomer Sequence Distributions of Poly(ethylene-co-1-hexene) Determined by ¹³C NMR Spectra. Detailed Polymerization Conditions are in Figure 1. r_E and r_D are Reactivity Ratios of Ethylene and 1-decene, Respectively

Cat	Run No.	[H] _{in feed} mol-%	[HHH]	[EHH] [HHE]	[HEH]	[EHE]	[EEH] [HEE]	[EEE]	[HH]	[HE]	[EE]	[H] _{in polym} mol-%	r_E	r_H	$r_E \times r_H$
1	11	23.1	-	-	-	1.05	3.02	99.93	-	2.56	97.44	1.28	22.9	-	-
	12	37.5	-	-	-	3.04	4.71	92.25	-	5.40	94.60	2.70	21.0	-	-
	13	50.0	-	-	-	5.66	4.97	89.37	-	8.15	91.85	4.08	22.5	-	-
	14	66.7	-	1.22	2.02	10.29	11.19	75.28	0.61	18.52	80.87	9.87	17.5	0.033	0.58
	15	80.0	-	3.92	4.10	12.37	16.32	63.29	1.96	26.59	71.45	15.26	21.5	0.037	0.80
2	21	23.1	-	-	2.35	2.65	4.54	90.46	-	7.27	92.73	3.64	7.7	-	-
	22	50.0	-	0.84	6.23	10.45	8.18	74.30	0.42	21.19	78.39	11.02	7.4	0.040	0.30
	23	66.7	-	2.42	8.24	16.77	12.48	60.09	1.21	32.66	66.13	14.30	8.1	0.037	0.30
	24	80.0	2.82	3.24	14.54	23.50	20.60	35.22	4.44	50.00	45.56	29.44	7.3	0.044	0.32
3	31	23.1	-	-	-	1.42	2.80	95.78	-	2.82	97.18	1.41	20.7	-	-
	32	66.7	-	0.70	1.66	8.41	8.02	81.21	0.35	14.44	85.21	7.57	23.6	0.024	0.57
	33	80.0	-	2.36	5.35	12.96	12.20	67.13	1.18	25.59	73.23	13.98	22.9	0.023	0.52
	34	85.7	1.10	5.80	10.98	32.97	17.68	31.47	4.00	55.69	40.31	31.85	21.6	0.024	0.52
4	41	12.3	-	-	-	0.22	0.64	99.14	-	0.54	99.46	0.27	51.2	-	-
	42	21.9	-	-	-	0.50	1.17	98.33	-	1.09	98.91	0.55	50.8	-	-
	43	31.9	-	-	-	0.78	2.04	97.18	-	1.80	98.20	0.90	51.2	-	-
	44	48.4	-	-	-	1.26	4.74	94.20	-	3.43	96.57	1.72	52.8	-	-
	45	58.4	-	0.38	-	1.59	6.98	91.05	0.19	5.27	94.54	2.83	50.4	0.050	2.52
	46	65.2	-	0.26	-	1.92	9.36	88.08	0.32	6.92	92.76	3.78	50.2	0.049	2.46
5	51	23.1	-	-	-	1.71	2.06	96.23	-	2.74	97.26	1.37	21.3	-	-
	52	37.5	-	-	-	2.19	6.74	91.07	-	5.56	94.44	2.78	20.4	-	-
	53	50.0	-	-	-	4.03	9.34	86.63	-	8.70	91.30	4.35	21.0	-	-
	54	66.7	-	-	0.63	7.80	14.02	77.55	-	15.44	84.56	7.72	21.9	-	-
	55	80.0	-	3.64	3.35	14.90	31.74	44.37	1.82	37.94	60.24	20.79	20.7	0.024	0.69
6	61	23.1	-	-	-	1.77	7.00	91.23	-	5.27	94.73	2.64	10.8	-	-
	62	37.5	-	-	-	4.70	11.10	84.20	-	10.25	89.75	5.13	10.5	-	-
	63	50.0	-	0.56	1.84	6.88	13.94	76.78	0.28	15.96	83.76	8.26	10.5	0.035	0.37
	64	66.7	-	1.86	3.92	15.79	17.12	61.31	0.93	29.20	68.97	15.53	9.57	0.032	0.31
	65	80.0	-	5.84	10.35	20.99	20.04	42.78	2.92	44.28	52.80	25.06	9.54	0.033	0.31

where $[EE]$, $[EH]$ and $[HH]$ denote *diad* sequences distributions in the copolymers and X is the amount concentration ratio of $[E]/[H]$ in the feed. Table I gives a direct comparison of 6 different catalysts to incorporate 1-hexene unit in the copolymer backbone. It is surprising to note that the hafnocene system (**2**/Al(*i*-Bu)₃/7) presents the highest 1-hexene incorporation, even higher than **6** catalyst, which has been known to show the best comonomer reactivity in *ansa*-metallocene systems.^{1a,n,10} Table I also summarizes the relative amount of triads sequence, incorporation percentages of $[H]$ and reactivity ratio with varying $[H]$ in feed. The result shows that most of the 1-hexene units were isolated in the copolymer between polyethylene blocks. As the concentration of 1-hexene in the copolymer increased, 1-hexene unit became closer and even HHH sequence appeared in the spectra of copolymer with higher incorporated 1-hexene. On the basis of the comonomer content in copolymers summarized in Table I it can be concluded that the incorporation of 1-hexene into the copolymer decreases in the following order: **2** > **6** > **1** ~ **3** ~ **5** > **4**. The values of the product $r_E \times r_H$ are below 1 except **4**/Al(*i*-Bu)₃/7 catalyst, showing all copolymers have predominantly random structures with some alternating unit. For **4**/Al(*i*-Bu)₃/7 catalyst the values of $r_E \times r_H$ are larger than 1, demonstrating its tendency to have long ethylene.

In order to address the performance of a catalyst for ethylene/ α -olefin copolymerization, both copolymerization rate and comonomer reactivity should be considered. Usually, comonomer reactivity causes lower copolymerization rate (e.g. **6**). Considering the two factors, one can conclude that diamide hafnocene **2**/Al(*i*-Bu)₃/7 catalyst shows the best performance. If one consider the properties of the resulting copolymers, the advantage of **2** catalyst becomes more evident (*vide infra*).

Properties of Copolymers. Table II summarizes the properties of resulting copolymers obtained by using 6 different catalytic systems. All the values of melting point (T_m), crystallinity (X_C), intrinsic viscosity ($[\eta]$) and density of the poly(ethylene-*co*-1-hexene) decrease markedly with an increase of the 1-hexene content incorporated in the copolymer backbone. The copolymers containing high comonomer contents obtained with **2**, **3** and **6** catalysts show clearly amorphous behavior. All the copolymers show melting peaks over a broad temperature range. The copolymers synthesized by **2** and **6** catalysts show duplicate peaks or peaks with shoulder due to a polymerization at different active centers or to a consequence of chain heterogeneity.¹⁵ The less branched molecules, formed by more stable crystals and containing thicker lamellae, will crystallize at higher temperatures and the most branched populations at the lowest temperature. According to some recent reports¹⁶ concerning the crystallization of homogeneous ethylene copolymers, these polymers show a broad range of structures from highly crystalline, lamellar morphologies to a granular mor-

phology of low crystallinity copolymers, thus show a broad range of melting temperature. In the density range from 0.910 to 0.890 g/cm³ these copolymers are claimed to present a mixed morphology of small lamellae and bundled crystals. At densities below 0.890 g/cm³ no lamellae or spherulites are existed any more and only fringed micelles or bundled crystals are present.¹⁶

The decrease of intrinsic viscosity arises from the reduction of molecular weight with increase of the feed ratio of comonomer. A popular explanation for this molecular weight decrease could be the chain transfer to the comonomer. The copolymer obtained with diamide hafnocene catalyst presented much higher molecular weight than those obtained by other catalysts. This is one of the most important advantages of hafnocene catalyst over zirconocenes catalysts. The **6** catalyst produces the polyethylene with average-viscosity molecular weight only 15,600 g/mol, but the hafnocene catalyst with 398,800 g/mol average-viscosity molecular weight at the same polymerization conditions.

Table II shows the density of copolymer determined by density gradient column. The density decreases sharply with the low incorporation of 1-hexene unit for all catalyst systems. At the high 1-hexene incorporation amount the density declines moderately. The density of copolymers produced by **2**/Al(*i*-Bu)₃/7 catalyst system changes over a wide range from 0.965 g/cm³ (high density polyethylene) to 0.845 g/cm³ (ultra-low density polyethylene). Table II also summarizes the fractionation result of representative copolymers. The copolymers are fractionated by ethyl ether and *n*-hexane sequentially, using a Soxhlet apparatus for 6 hrs. All copolymers prepared in the presence of $[H]_{in\ feed} = 23.1$ mol-% are insoluble in ethyl ether. With the increase of 1-hexene content in copolymer, ether soluble fraction increase and *n*-hexane insoluble fraction decreases. Comparing run no. 24 to 65 as well as run no. 21 to 61, one can conclude that the anti-solvent ability of copolymers produced by **2** catalyst is better than that produced by **6** catalyst.

Conclusions

Copolymerizations of ethylene with 1-hexene were carried out by a series of metallocene compounds in the presence of Al(*i*-Bu)₃/[CPh₃][B(C₆F₅)₄] as a cocatalyst system. The copolymerization rate decreases in the order of **4** > **1** ~ **3** > **2** > **5** > **6**, while 1-hexene reactivity decreases in the order of **2** > **6** > **1** ~ **3** ~ **5** > **4**. The $r_E \times r_H$ values are below 1 for **1**, **2**, **3**, **5** and **6** catalysts, indicating the resulting copolymers have predominantly random structure with some alternating character. The $r_E \times r_H$ values for **4**/Al(*i*-Bu)₃/7 catalyst are larger than 1, proposing a tendency to have long ethylene block.

The T_m , X_C , $[\eta]$ and density of the poly(ethylene-*co*-1-hexene) decreased markedly with an increase of the 1-hexene content incorporated in the copolymer regardless of the

Table II. Characterization and Fractionation of Poly(ethylene-co-1-hexene)^a

Cat	Run No.	[H] _{in feed} mol-%	R_p^b $\times 10^{-6}$	T_m (°C)	X_C^c (%)	$[\eta]^d$	density (g/cm ³)	E^e	C_6^e	R^e
1	10	0	1.80	136.0	54.0	1.835	0.9648			
	11	23.1	21.57	119.2	38.0	1.379	0.9342	0	2.4	97.6
	12	37.5	24.33	107.2	29.6	1.096	0.9224			
	13	50.0	28.24	106.9	27.9	0.983	0.9212			
	14	66.7	21.51	78.2	3.0	0.732	0.9004			
	15	80.0	14.25	70.6	2.1	0.678	0.8913	69.3	30.7	0
2	20	0	3.20	131.6	56.6	5.163	0.9650			
	21	23.1	7.13	103.0	22.0	3.441	0.9481	0	7.0	93.0
	22	50.0	8.45	82.8	7.6	2.566	0.9038	20.1	27.0	52.9
	23	66.7	12.89	73.9	3.4	1.851	0.8879	36.0	31.2	32.8
	24	80.0	11.85	n.d	n.d	1.168	0.8450	77.2	22.8	0
3	30	0	4.59	134.0	71.8	1.461	0.9442			
	31	23.1	25.94	129.7	35.9	1.220	0.9344	0	10.4	89.6
	32	66.7	23.20	107.8	14.4	0.938	0.8939			
	33	80.0	18.69	83.1	1.5	0.616	0.8834			
	34	85.7	15.68	n.d	n.d	0.490	0.8813	70.1	29.9	0
4	40	0	7.23	134.1	70.2	1.582	0.9655			
	41	12.3	17.11	124.3	64.3	0.929	0.9474			
	42	21.9	22.05	119.4	56.4	0.833	0.9430	0	0	100
	43	31.9	28.20	117.7	51.6	0.729	0.9382			
	44	48.4	29.65	116.3	46.5	0.732	0.9308			
	45	58.4	30.02	112.5	42.9	0.696	0.9207			
	46	65.2	28.84	109.2	36.9	0.634	0.9232	0	11.6	88.4
	47	70.1	24.05	99.0	9.2	0.420	0.9122			
5	50	0	5.31	135.5	58.39	0.788	0.9632			
	51	23.1	9.70	131.7	52.20	0.710	0.9497	0	1.2	98.8
	52	37.5	9.59	129.1	42.27	0.707	0.9400			
	53	50.0	7.12	124.1	54.24	0.659	0.9386			
	54	66.7	6.64	120.6	27.03	0.603	0.9198			
	55	80.0	6.20	99.3, 117.8	7.24	0.596	0.8916	48.3	38.5	13.2
6	60	0	0.81	133.5	52.3	0.534	0.9669			
	61	23.1	1.52	118.8	34.4	0.569	0.9363	0	12.3	87.7
	62	37.5	1.95	114.4	31.6	0.644	0.9155			
	63	50.0	2.05	106.5	8.2	0.639	0.9086			
	64	66.7	1.93	n.d	n.d	0.442	0.8882			
	65	80.0	1.26	n.d	n.d	0.274	0.8625	100	0	0

^aDetailed polymerization conditions are in Figure 1. ^bAverage rate of polymerization in g-PE mol-Zr⁻¹h⁻¹atm⁻¹.

^cCrystallinity calculated on the basis of folded chain polyethylene crystal.¹⁰ ^dIntrinsic viscosity measured by viscometry,

^eFractions of copolymer soluble in each boiling solvent (E: ethyl ether; C₆: *n*-hexane) and the residue (R) fraction.

type of catalytic system. The copolymers produced by hafnocene **2** catalyst are characterized by much higher molecular weight than those by other catalytic systems and have a wide range of density from 0.965 to 0.845 g/cm³. The hafnocene amide catalyst has a lot of advantages over other catalyst systems investigated in this study, in that it shows the highest comonomer incorporation ability and high copolymerization rate, and that it produces copolymers with high molecular weights and a wide range of density.

Acknowledgements. This work was supported by Pusan National University Grant and the Brain Korea 21 Project. .

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