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Copolymerizations of ethylene with 1-decene over various *ansa*-metallocene complexes combined with Al(*i*-Bu)$_3$/[CPh$_3$][B(C$_6$F$_5$)$_4$] cocatalyst

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Summary

Copolymerizations of ethylene with 1-decene were carried out with a series of stereospecific metallocene compounds, *rac*-(EBI)Zr(NMe$_2$)$_2$ [**1**, EBI = ethylene-1,2-bis(1-indenyl)], *rac*-(EBI)Hf(NMe$_2$)$_2$ (**2**), *rac*-Me$_2$Si(1-C$_5$H$_2$-2-Me-4-^{t}Bu)$_2$Zr(NMe$_2$)$_2$ (**3**), ethylidene(cyclopentadienyl)(9-fluorenyl)ZrMe$_2$ [**4**, Et(Flu)(Cp)ZrMe$_2$] and isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe$_2$ [**5**, *i*Pr(Flu)(Cp)ZrMe$_2$], combined with Al(*i*-Bu)$_3$/[CPh$_3$][B(C$_6$F$_5$)$_4$] cocatalyst. All catalyst systems showed very high copolymerization rates and the 1-decene reactivity decreased in the order of **2** > **5** > **1** ~ **4** > **3**. The reactivity product of ethylene and 1-decene ($r_E \times r_D$) was below 1 except **3** catalyst, corresponding to random copolymer structures with an alternating character. The melting point (T$_m$), crystallinity (X$_C$), intrinsic viscosity ([η] and density of the 1-decene/ethylene copolymers decreased markedly with an increase in the 1-decene content, regardless of the type of catalytic system.

Introduction

Metallocene catalysts show better performance than conventional Ziegler-Natta catalysts in the polymerizations of monomers of varying sizes and types, resulting in improved comonomer incorporation and copolymers with more homogenous compositions [1-15]. Metallocene catalysts incorporate ethylene and α-olefins in a random fashion and produce polymers with a narrow polydispersity. Ethylene/1-decene copolymerizations using metallocene compounds have been reported by many authors [9,10]. Previous results showed that the type of catalysts has an important effect on the reactivity of ethylene and 1-decene and the structure and molecular weight of a copolymer.

The usefulness of the *ansa*-metallocene diamide compounds ^{ch}Cp$_2$Zr(NR$_2$)$_2$ (^{ch}CpZr = chiral *ansa*-zirconocene framework) has been demonstrated by utilizing them directly for the highly isospecific polymerization of propylene in the presence of an MAO or a non-coordinative anionic compound as a cocatalyst [16-25]. The efficient synthesis of *ansa*-metallocene via an amine elimination route usually resulted in higher yield with higher *rac*/*meso* ratio than the corresponding dichloride analogue [20-25]. Even though there are some reports [16-19] on the polymerization of α-olefins by using the metallocene amide compounds, there have been no reported results on ethylene/α-olefins copolymerization initiated by the diamide metallocenes. Here, we report the copolymerization behavior of ethylene with 1-decene by using three diamide metallocene compounds that show isospecific feature in α-olefin polymerizations and two syndiospecific metallocenes. For a simplicity of the catalyst system we utilized a non-coordinative anionic compound, $[CPh_3][B(C_6F_5)_4]$, as a cocatalyst.

Experimental

Materials

All materials were handled with Schlenk or glove box techniques under argon atmosphere. Toluene was distilled from sodium prior to use. 1-Decene (Aldrich) was purified by distilling from sodium. Ethylene of polymerization grade (SKC, Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Methylaluminoxane (MAO) (11.6 wt% Al in toluene) was purchased from Akzo Chemicals. $Al(i\text{-}Bu)_3$ (Aldrich) was used without purification. The metallocene compounds, *rac*-$(EBI)Zr(NMe_2)_2$ [**1**, EBI = ethylene-1,2-bis(1-indenyl)] [23], *rac*-$(EBI)Hf(NMe_2)_2$ (**2**) [22], *rac*-$Me_2Si(1\text{-}C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}{}^tBu)_2Zr(NMe_2)_2$ (**3**) [22], ethylidene(cyclopentadienyl)(9-fluorenyl)$ZrMe_2$ [**4**, Et(Flu)(Cp)$ZrMe_2$] [26] and isopropylidene(cyclopentadienyl)(9-fluorenyl)$ZrMe_2$ [**5**, *i*Pr(Flu)(Cp)$ZrMe_2$] [27], and the anionic compound $[CPh_3][B(C_6F_5)_4]$ (**6**) [28] were synthesized according to literature procedures.

Copolymerization procedure

Copolymerization was carried out in a 250 ml glass reactor at 70 °C and $P_{C2H4} = 1.3$ atm with 80 mL toluene as solvent. A magnetic stirring bar was utilized for agitation. Firstly toluene and prescribed amounts of 1-decene, $Al(i\text{-}Bu)_3$ 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 was stabilized at 70 °C, compound **6** dissolving in toluene was introduced into the reactor by a syringe and then the copolymerization started. The polymerization was quenched by introducing 150 ml methanol containing a HCl (5 *v/v*%) into the reactor after 20 min of copolymerization run.

Copolymer characterization

The ^1H NMR and ^{13}C NMR spectra of polymers were recorded on a Varian Unity Plus 300 spectrometer at 120 °C. Samples for the 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*). Thermal data were obtained by Dupont differential scanning calorimeter (DSC, Model-900) instrument system at a 10 °C/min. The intrinsic viscosity was measured in decalin at 135 ± 0.1 ℃ using an Ubbelohde viscometer. Density of copolymers was measured by using density gradient column according to the standard test method, ASTM D1505-79.

Results and Discussion

Both activity and comonomer incorporating ability are important factors in the ethylene/α-olefin copolymerizations. In order to check the effect of comonomer on the polymerization activity, a series of copolymerization was carried out for 20 min by changing $[D]/[E]$ molar ratio (D and E denote 1-decene and ethylene, respectively). A 5.0 μmol/L of diamide catalysts (**1**, **2**, **3**) was used for polymerizations and a minimum amount of $Al(i\text{-}Bu)_3$ ($[Al]/[cat] = 30$) for both alkylating the catalysts and scavenging the impurities existed in the reaction system [16-19], together with **6** ($[6]/[cat] = 1$) as a cocatalyst system. Somewhat larger amounts (30.0 μmol/L) of **4** and **5** catalysts were used combined with $Al(i\text{-}Bu)_3$/**6** ($[Al]/[cat] = 10$, $[6]/[cat] = 1$) cocatalyst system. Figure 1 shows the dependence of the average rate of polymerization on $[D]/[E]$ ratio in the feed. Addition of 1-decene results in an enhancement of the polymerization rate for all the catalytic systems. The activity increase in the ethylene/α-olefin copolymerizations was also reported by many authors [8.13.29]. One possible explanation of this phenomenon is due to the growing number of active center. This is possible because the active centers were not all active in the homopolymerization. Another explanation is that the rate constant of the insertion step is increased by the addition of α-olefin [8]. Recent detailed works on the effect of α-olefin addition on the rate change showed that the rate enhancement seemed to depend on the heterogeneity of the polymerization [29,30]: no rate enhancement occurred when the polymer was soluble in the reaction medium. Homopolymerization of ethylene with *ansa*-metallocene compounds of this study showed a pronounced change in the viscosity of solvent during the early stage of the polymerization. In this stage the formation of fibrous polymer was sticking on the magnetic stirrer bar and polymer precipitated as particulate or as agglomerate. These solid polymers should prevent ethylene monomer from diffusing to the active sites. However, the incorporation of 1-decene into polymer changes linear polyethylene chain to branched chain, enhancing the solubility of the polymer in toluene. In this way the diffusion limitation is certainly relieved to some extent. The relief of diffusion limitation is one of the most important factors for the rate enhancement.

Comparing the *ansa*-metallocenes of this study, one can find the activity of the C_2-symmetric catalysts is higher than that of C_s-symmetric catalysts. For steric reasons, the space volume between the cyclopentadienyl ligands available for Me_2Si-bridged catalyst (**3**) is larger than for bisindenyl system (**1**, **2**) [31]. In this sense Me_2Si-bridged catalyst shows higher activity than ethylene-bridged catalysts. The zirconocenes are more efficient than hafnocene analogues have been also described for dichloride metallocenes [32-36]. It may be attributed to differences in concentration of active centers induced by different carbon-metal bond strengths.

The microstructure and the incorporation of comonomer into the polymeric chain were measured by using ^{13}C NMR spectroscopy [37,38]. The monomer reactivity ratios were estimated from ^{13}C NMR spectra using the following equations [1]:

$$r_E = 2[EE]/[ED]\cdot X; \quad r_D = 2[DD]\cdot X/[ED] \qquad (1)$$

where $[EE]$, $[ED]$ and $[DD]$ denote *diad* sequences distributions in the copolymers and X is the amount concentration ratio of $[E]/[D]$ in the feed. Table 1 shows the relative amount of *triads* sequence, incorporation amount of $[D]$ and reactivity ratio with varying $[D]$ mol% in the feed obtained for all catalyst systems.

Table 1 also gives a direct comparison of the degree of 1-decene incorporated in the

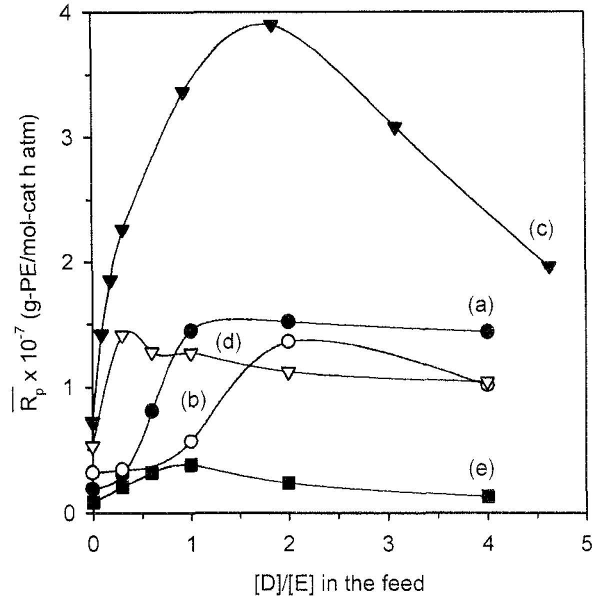

Figure 1. Effect of 1-decene concentration on polymerization rate: (a) **1**/Al(i-Bu)$_3$/**6**, (b) **2**/Al(i-Bu)$_3$/**6**, (c) **3**/Al(i-Bu)$_3$/**6**, (d) **4**/Al(i-Bu)$_3$/**6**, and (e) **5**/Al(i-Bu)$_3$/**6** catalyst systems. For **1** , **2** and **3** catalysts, [Al(i-Bu)$_3$]/[cat]/[**6**] = 30/1/1 ([cat] = 5.4 μM), and for **4** and **5** catalysts, [Al(i-Bu)$_3$]/[cat]/[**6**] = 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).

copolymer. It is surprising to note that the hafnocene catalyst (**2**) presents the highest 1-decene incorporation. Previously, a lot of reports showed that iPr(Cp)(Flu)ZrCl$_2$ was the so-called most effective in inserting α-olefins into an ethylene copolymer or a propylene copolymer backbone [14,39,40]. On the basis of the comonomer content in copolymers summarized in Table 1, one can summarize that the incorporation amount of 1-decene into the copolymer decreases in the following order: **2** > **5** > **1** ~ **4** > **3**. The values of the product $r_E \times r_D$ are below 1.0 except **3** catalyst, demonstrating the copolymers correspond to random copolymer structures with somewhat alternating character. The $r_E \times r_D$ values of **3** catalyst are more than 1.0, which proposes a tendency to have long ethylene and some block sequences of DD.

Table 2 summarizes the properties of copolymers. All the values of melting point (T_m), crystallinity (X_C), intrinsic viscosity ([η]) and density of the copolymers decreased markedly with an increase of the 1-decene amount, regardless of the type of catalytic system. The copolymers of the highest comonomer contents obtained by **2** and **5** catalysts showed amorphous behavior. The copolymers showed a broad range of melting temperature. The copolymers synthesized by **2**, **4** and **5** catalysts showed the duplicate peaks or the peaks with shoulder. The intrinsic viscosity of copolymers decreased generally by the increase of the comonomer concentration in the feed, most probably due to the chain transfer to the comonomer. The copolymers obtained with hafnocene catalyst (**2**) were characterized by much higher molecular weight than those obtained by other catalysts. This is one of the advantages of hafnocene catalysts over zirconocenes catalysts. The **5** catalyst produced copolymer with viscosity average molecular weight only 15,600 g/mol, but the hafnocene system produced copolymer

Table 1 Monomer sequence distributions of poly(ethylene-*co*-1-decene) determined by ^{13}C NMR spectra [a)]

Cat	Run No.	$[D]_{feed}$ (mol-%)	DDD	EDD DDE	DED	EDE	EED DEE	EEE	$[D]_{polym}$ (mol-%)	r_E [b)]	r_D [b)]	$r_E \times r_D$
1	11	23.1	-	-	-	0.78	2.72	96.50	0.78	27.5		
	12	37.5	-	-	0.91	1.52	3.24	94.33	2.03	28.4		
	13	50.0	-	-	1.69	2.55	4.84	90.92	2.55	28.0		
	14	66.7	-	-	2.22	5.56	8.84	83.38	6.10	28.8		
	15	80.0	-	1.40	3.43	9.83	15.85	69.49	11.64	28.3	0.016	0.45
2	21	23.1	-	-	-	4.14	8.32	87.54	4.15	6.6	-	-
	22	50.0	-	-	2.71	13.71	12.52	71.06	13.71	6.8	-	-
	23	66.7	-	1.72	4.86	22.40	15.08	55.94	18.69	7.1	0.024	0.17
	24	80.0	-	4.92	10.48	31.69	13.34	39.57	28.11	7.2	0.024	0.17
3	31	8.5	-	-	-	-	0.54	99.46	0.14	68.6	-	-
	32	15.6	-	-	-	0.23	0.62	99.15	0.27	68.1	-	-
	33	23.6	-	-	-	0.35	1.02	98.63	0.43	71.2	-	-
	34	48.1	-	-	-	1.09	3.02	95.89	1.30	69.4	-	-
	35	65.0	-	0.42	0.42	2.59	3.94	92.63	2.81	69.7	0.044	2.98
	36	75.5	-	1.16	1.49	4.78	6.84	85.73	4.52	69.7	0.049	3.41
	37	82.2	-	2.22	2.28	7.32	8.64	79.54	6.80	71.1	0.042	2.99
4	41	23.1	-	-	-	0.90	1.82	97.28	0.91	32.6	-	-
	42	37.5	-	-	-	1.65	3.75	94.60	1.76	32.3	-	-
	43	50.0	-	-	0.45	2.78	5.02	91.75	2.87	32.8	-	-
	44	66.7	-	-	1.66	5.38	7.78	85.18	5.47	32.7	-	-
	45	80.0	-	1.21	2.61	10.71	10.84	74.63	10.28	33.1	0.016	0.53
5	51	23.1	-	-	-	3.47	3.58	92.93	2.64	10.8	-	-
	52	37.5	-	-	0.66	6.68	4.76	87.90	4.86	11.2	-	-
	53	50.0	-	-	0.94	12.30	5.34	81.42	7.96	10.6	-	-
	54	66.7	-	1.12	2.45	16.76	13.86	65.81	13.91	10.9	0.021	0.23
	55	80.0	0.58	2.84	9.27	20.81	21.33	45.17	23.08	10.6	0.024	0.25

[a)] Detailed polymerization conditions are in Fig. 1.

[b)] r_E , r_D: Reactivity ratios of ethylene and 1-decene, respectively.

with 398,800 g/mol at the same polymerization conditions.

The density of copolymers decreased sharply by the incorporation of 1-decene unit in the polymer backbone for all the catalytic systems. For example, the density changes in a wide range from 0.965 g/cm^3, which corresponds to high density polyethylene, to 0.828 g/cm^3, which corresponds to ultra-low density polyethylene, for **2**/Al(*i*-Bu)$_3$/**6** catalytic system. Table 2 also summarizes the fractionation results of some copolymers. The copolymers were fractionated by ethyl ether and *n*-hexane sequentially, using a Soxhlet apparatus for 6 h. All the copolymers of [*D*] = 23.1 mol-% in the feed were insoluble in ethyl ether. With the increase of 1-decene content in copolymer, ether soluble fraction increased and *n*-hexane insoluble fraction decreased. The copolymers containing a large amount of 1-decene (see run no. 24 and 55) were almost completely soluble in *n*-hexane.

Conclusions

Copolymerizations of ethylene with 1-decene over five different *ansa*-metallocene compounds, three isospecific and two syndiospecific, showed that all catalyst systems showed very high copolymerization rates and the 1-decene reactivity decreases in the order of **2** > **5** > **1** ~ **4** > **3**. All copolymers had basically random structures according to $r_E \times r_D$ values; however, copolymers obtained by **1**, **2**, **4** and **5** catalysts had some

Table 2 Characterization and fractionation of poly(ethylene-*co*-1-decene)

Cat	Run No.	$[D]_{feed}$ (mol-%)	$\bar{R}_p$ [a] x 10^{-6}	$[D]_{polym}$ (mol-%)	T_m (°C)	X_C [b] (%)	$[\eta]$ [c]	Density (g/cm^3)	E [d]	C_6 [d]	R [d]
1	10	0	1.91	0	136.0	54.0	1.835	0.9658			
	11	23.1	3.07	0.78	122.5	45.0	0.990	0.9381	0	0	100
	12	37.5	8.10	2.03	118.7	32.4	0.929	0.9273			
	13	50.0	14.5	2.55	110.9	31.8	0.920	0.9209			
	14	66.7	15.2	6.10	98.6	24.0	0.845	0.9083			
	15	80.0	14.4	11.64	75.0	3.7	0.712	0.8912	36.4	63.6	0
2	20	0	3.20	0	131.6	56.6	5.163	0.9650			
	21	23.1	3.44	4.15	93.6, 120.8	18.8	2.151	0.9168	0	33.0	67.0
	22	50.0	5.68	13.71	62.9, 110.5	2.0	1.840	0.8850			
	23	66.7	13.6	18.69	n.d.	n.d.	1.223	0.8431			
	24	80.0	10.2	28.11	n.d.	n.d.	0.938	0.8276	100	0	0
3	30	0	7.23	0	134.1	70.2	1.582	0.9655			
	31	8.5	14.2	0.14	128.0	58.8	1.019	0.9503			
	32	15.6	18.6	0.27	124.7	47.3	0.842	0.9430			
	33	23.6	22.6	0.43	122.0	45.9	0.729	0.9394	0	1.0	99.0
	34	48.1	33.6	1.30	117.7	35.3	0.694	0.9364			
	35	65.0	39.0	2.81	113.5	30.9	0.624	0.9254			
	36	75.5	30.8	4.52	99.8	1.6	0.587	0.9125			
	37	82.2	19.6	6.80	94.6	4.7	0.556	0.9050	16.6	57.0	26.4
4	40	0	5.31	0	135.3	58.4	0.788	0.9632	0	0.3	99.7
	41	23.1	14.19	0.91	128.8	55.8	0.653	0.9412	0	1.0	99.0
	42	37.5	13.69	1.76	127.7	43.4	0.649	0.9372			
	43	50.0	12.72	2.87	126.8	34.6	0.656	0.9227			
	44	66.7	11.21	5.47	116.6, 123.0	24.3	0.581	0.9107			
	45	80.0	10.42	10.28	110.2, 119.9	5.5	0.509	0.8950	23.8	44.8	31.4
5	50	0	0.8	0	133.5	52.3	0.534	0.9669	0	1.4	98.6
	51	23.1	2.05	2.14	123.1	43.1	0.720	0.9284	0	1.9	98.1
	52	37.5	3.21	4.86	109.7	24.7	0.646	0.9157			
	53	50.0	3.80	7.96	108.8	19.6	0.660	0.8992	12.6	34.8	52.6
	54	66.7	2.38	13.91	51.0, 79.9	4.0	0.554	0.8893			
	55	80.0	1.27	23.08	n.d.	n.d.	0.319	0.8825	98.2	1.8	0

[a] Average rate of polymerization in g-PE mol-Zr^{-1}h^{-1}atm^{-1}.

[b] Crystallinity calculated on the basis of folded chain polyethylene crystal [15].

[c] Intrinsic viscosity measured by viscometry.

[d] Fractions of copolymer soluble in each boiling solvent (E: ethyl ether; C_6: n-hexane) and the residue (R) fraction.

alternating feature ($r_E \times r_D < 1.0$) and those by **3** some blocky character ($r_E \times r_D > 1.0$). The T_m, X_C, $[\eta]$ and density of copolymers decreased markedly with an increase in the 1-decene incorporation, regardless of the type of catalytic system. The hafnocene amide catalyst (**2**) had some advantages because it showed the highest 1-decene incorporation capability and high copolymerization rate, and yielded copolymers with high molecular weight and wide range of density.

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