

Ethylene/ α -Olefin Copolymerization by Nonbridged (Cyclopentadienyl)(aryloxy)Titanium(IV) Dichloride/ $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ Catalyst Systems

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ABSTRACT: A series of nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes of the type, $(\eta^5\text{-Cp}')(\text{OAr})\text{TiCl}_2$ [$\text{OAr} = \text{O-2,4,6-}^i\text{Bu}_3\text{C}_6\text{H}_2$ and $\text{Cp}' = \text{Me}_5\text{C}_5$ (**1**), Me_4PhC_5 (**2**), and $1,2\text{-Ph}_2\text{-4-MeC}_5\text{H}_2$ (**3**)], were prepared and used for the copolymerization of ethylene with α -olefins (e.g., 1-hexene, 1-octene, and 1-octadecene) in presence of Al^iBu_3 and $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (TIBA/B). The effect of the catalyst structure, comonomer, and reaction conditions on the catalytic activity, comonomer incorporation, and molecular weight of the produced copolymers was examined. The substituents on the cyclopentadienyl group of the ligand in **1–3** play an important role in the catalytic activity and comonomer incorporation. The

1/TIBA/B catalyst system exhibits the highest catalytic activity, while the 3/TIBA/B catalyst system yields copolymers with the highest comonomer incorporation under the same conditions. The reactivity ratio product values are smaller than those by ordinary metallocene type, which indicates that the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene by the **1–3**/TIBA/B catalyst systems does not proceed in a random manner. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3085–3092, 2011

Key words: ethylene; α -olefin; copolymerization; titanium(IV); polyolefins

INTRODUCTION

Copolymerization of ethylene with α -olefins has attracted ones attention for decades because ethylene/ α -olefin copolymer is important material in industry with favorable properties and has been applied in many fields in daily life.^{1–7} Evolution of new copolymers nearly depends on designing and synthesis of efficient transition metal catalysts.^{8–14} To date, many catalyst systems have been reported to copolymerize ethylene and α -olefins. Among them, nonbridged half-metallocene group 4 transition-metal complexes exhibit good catalytic activity for ethylene with α -olefins copolymerization in the presence of methylaluminoxane.^{8–15} The complexes that are defined as new generation of highly active catalysts for olefin polymerization are offering new opportunities for the synthesis of olefin copolymers because the synthesis of this type is shorter synthetic

steps with relatively high yield. Nomura et al. reported the nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complex-MAO catalyst system for ethylene polymerization and for ethylene/ α -olefin copolymerization.¹⁵ It was revealed that the effect of the substituents on the cyclopentadienyl group of the ligand was generally a combination of electronic and steric effect on the catalytic activity,^{13,14} coordination of monomers,¹⁶ and molecular weights of the copolymers.^{12,15} Bulky substituents influenced the coordination of monomers, whereas electronic effect of substituents affected the stability of the active sites and influenced the chain growth mechanisms due to differences in Lewis acidity of the metal.^{17,18}

Research on the copolymerization of ethylene and longer chained olefins is becoming one of the most active research fields,^{19–21} because the longer comonomers change the polyethylene properties such as density, melting point, and crystallinity more effectively than smaller units such as propene at the same concentration.^{22–25}

In this work, a series of nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes of the type, $(\eta^5\text{-Cp}')(\text{OAr})\text{TiCl}_2$ [$\text{OAr} = \text{O-2,4,6-}^i\text{Bu}_3\text{C}_6\text{H}_2$ and $\text{Cp}' = \text{Me}_5\text{C}_5$ (**1**), Me_4PhC_5 (**2**), and $1,2\text{-Ph}_2\text{-4-MeC}_5\text{H}_2$ (**3**)] (Chart 1), was prepared and used for the copolymerization of ethylene with longer chained α -olefins (e.g., 1-hexene, 1-octene, and 1-octadecene) in the presence of Al^iBu_3 and $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (TIBA/B). In this study,

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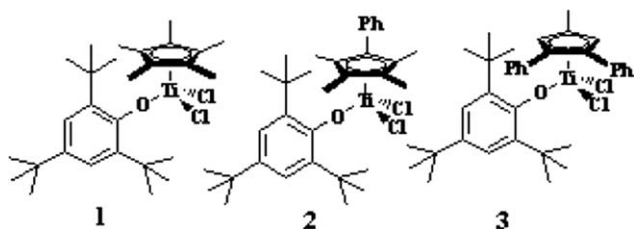


Chart 1 Structure of complexes 1–3.

the objective was to relate differences in the substituents on the cyclopentadienyl group of the ligand in the 1–3 with the polymerization behavior in the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene, three α -olefins of clearly different chain length and potentially different steric requirements for coordination at the active sites.

EXPERIMENTAL

Materials

All experiments involving air-sensitive compounds were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene was distilled from sodium/benzophenone ketyl under nitrogen prior to use. 1-Hexene, 1-octene, and 1-octadecene were dried over calcium hydride for several days and filtered under nitrogen prior to use. Al^iBu_3 was purchased from Aldrich. $\text{Cp}'\text{TiCl}_3$ ^{26–28} and $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ ^{29–31} were prepared according to methods reported in the literature. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO.

The preparation of $(\eta^5\text{-Me}_5\text{C}_5)(\text{O-2,4,6-}^t\text{Bu}_3\text{C}_6\text{H}_2)\text{-TiCl}_2$ (1)

Into a sealed Schlenk tube containing $(\eta^5\text{-Me}_5\text{C}_5)\text{-TiCl}_3$ (1.16 g, 4.0 mmol), $\text{LiO-2,4,6-}^t\text{Bu}_3\text{C}_6\text{H}_2$ (1.0 equiv.) was added in one portion, then 15 mL toluene was added at room temperature. The reaction mixture was stirred at 60°C for 8 h. The mixture was then filtered through Celite pad, and the filter cake was washed with hexane (2 × 15 mL). The combined filtrate and the wash were taken to dryness under reduced pressure to give a red-dark solid. By washing with hexane, the deep red solid material of complex 1 can be gained. Yield: 90%. Elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{44}\text{OTiCl}_2$: C, 65.25, H, 8.60. Found: C, 65.21, H, 8.55. ¹H-NMR (CDCl_3 , 300 MHz; 298 K): δ 7.418 (s, 2H, Phenoxy), 2.083 (s, 15H $\text{Cp}'\text{-Me}$), 1.363 (s, 18H, Phenoxy), 1.309 (s, 9H, Phenoxy). ¹³C-NMR (CDCl_3 , 75.4 MHz; 298 K): δ 164.73

(1C, Phenoxy), 143.59 (1C, Phenoxy), 138.80 (2C, Phenoxy), 133.65 (5C, Cp'), 121.87 (1C, Phenoxy), 121.50 (1C, Phenoxy), 36.23 (1C, ^tBu), 34.55 (3C, ^tBu), 32.07 (3C, ^tBu), 31.70 (3C, ^tBu), 31.50 (1C, ^tBu), 30.40 (1C, ^tBu), 13.66 (5C, Me).

The preparation of $(\eta^5\text{-Me}_4\text{PhC}_5)(\text{O-2,4,6-}^t\text{Bu}_3\text{C}_6\text{H}_2)\text{-TiCl}_2$ (2)

It was synthesized following a similar procedure of complex 1. Yield: 92%. Elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{46}\text{OTiCl}_2$: C, 68.63, H, 8.03. Found: C, 68.59, H, 8.01. ¹H-NMR (CDCl_3 , 300 MHz; 298 K): δ 7.10–7.15 (m, 5H, Ph), 7.08 (s, 2H, Phenoxy), 2.31 (s, 6H, Me), 2.22 (s, 6H, Me), 1.36 (s, 9H, ^tBu), 1.25 (s, 18H, ^tBu). ¹³C-NMR (CDCl_3 , 75.4 MHz; 298 K): δ 165.92 (1C, Phenoxy), 144.18 (1C, Phenoxy), 139.87 (2C, Phenoxy), 135.96 (1C, Ph), 133.62 (2C, Ph), 133.23 (2C, Ph), 130.34 (1C, Ph), 128.56 (2C, Phenoxy), 128.09 (1C, Cp'), 127.62 (2C, Cp'), 121.96 (2C, Cp'), 36.36 (1C, ^tBu), 34.91 (6C, ^tBu), 32.09 (2C, ^tBu), 31.81 (3C, ^tBu), 15.39 (2C, Me), 14.30 ppm (2C, Me).

The preparation of $(\eta^5\text{-1,2-Ph}_2\text{-4-MeC}_5\text{H}_2)(\text{O-2,4,6-}^t\text{Bu}_3\text{C}_6\text{H}_2)\text{-TiCl}_2$ (3)

It was synthesized following a similar procedure of complex 1. Yield: 72%. Elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{44}\text{OTiCl}_2$: C, 70.71, H, 7.25. Found: C, 70.67, H, 7.23. ¹H-NMR (CDCl_3 , 300 MHz; 298 K): δ 7.45–7.48 (q, 4H, Ph), 7.28–7.29 (d, 4H, Ph), 7.26–7.27 (d, 2H, Ph), 7.18 (s, 2H, Phenoxy), 6.42 (s, 2H, $\text{Cp}'\text{H}$), 1.94 (s, 3H, Me), 1.42 (s, 18H, ^tBu), 1.32 (s, 9H, ^tBu). ¹³C-NMR (CDCl_3 , 75.4 MHz; 298 K): δ 165.84 (1C, Phenoxy), 145.09 (2C, Ph), 140.24 (1C, Phenoxy), 135.49 (2C, Phenoxy), 133.85 (4C, Ph), 132.73 (4C, Ph), 130.01 (2C, Ph), 128.67 (2C, Phenoxy), 128.20 (2C, Cp'), 123.09 (2C, Cp'), 122.01 (1C, Cp'), 36.38 (1C, ^tBu), 34.96 (2C, ^tBu), 32.15 (6C, ^tBu), 31.74 (3C, ^tBu), 14.70 (1C, Me) ppm.

Copolymerization of ethylene with α -olefin

A dry 250 mL steel autoclave with a magnetic stirrer was charged with a solution of appropriate amounts of α -olefin in toluene (80 mL), thermostated at the desired temperature, and saturated with ethylene (1 atm). The polymerization reaction was started by injection of a mixture of catalyst and Al^iBu_3 in toluene (10 mL) and a solution of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ in toluene (10 mL) at the same time, and the vessel was repressurized to needed pressure with ethylene immediately. After the desired period of time, the reactor was vented. The copolymer was precipitated from methanol/HCl, filtered, washed three times with methanol, and then dried *in vacuo* to a constant weight.

Characterization

The ^{13}C -NMR data of the copolymers were obtained on a Varian Unity 400-MHz spectrometer at 125°C with $o\text{-C}_6\text{D}_4\text{Cl}_2$ as the solvent and tetramethylsilane as the internal standard. The differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC 204 differential scanning calorimeter. Each sample was heated from 20 to 160°C at a heating rate of 10°C/min and reheated at the same rate. Only the second the heating curve was analyzed. The molecular weights and polydispersity indices of the polymer samples were determined at 150°C with a PL-GPC 220 high-temperature chromatograph equipped. 1,2,4-Trichlorobenzene was used as the solvent. The calibration was made with polystyrene standard.

RESULTS AND DISCUSSION

Copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene

The effect of Al/Ti mol ratio, reactor temperature, and ethylene pressure in the ethylene/1-hexene copolymerization by the 1/TIBA/B catalyst system was summarized in Table I. The 1-hexene content in the copolymer increases with the increase of temperature due to the increase in the molar ratios of 1-hexene and ethylene initial concentrations, which could be attributed to that the ethylene concentration decreased with the temperature increase. It is observed that the catalytic activity increases with the increase of Al/Ti mol ratio until reaching the maximum values and then decreases (14.9×10^3 , $17.9 \times$

10^3 , 19.8×10^3 , and 14.7×10^3 $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$ at Al/Ti = 160, 180, 200, and 220, respectively). Further increase in the Al/Ti mol ratio results in a decrease in the catalytic activity. It is possible that excessive Al^iBu_3 would consume so much $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ that the catalyst could not be efficiently activated.³² In addition, it is also observed that the catalytic activity increases at higher ethylene pressure, but 1-hexene content in the resultant copolymer decreases at higher ethylene pressure.

Copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene catalyzed by the 1–3/TIBA/B catalyst systems was studied in detail under various comonomer concentrations in the feed and the results were summarized in Tables II–IV. The abilities of the 1–3/TIBA/B catalyst systems to catalyze ethylene/1-hexene, ethylene/1-octene and ethylene/1-octadecene copolymerization were investigated under ethylene pressure 4 atm. The data of Tables II–IV indicate that the effect of the substituents on the cyclopentadienyl group of the ligand in 1–3 on the catalytic activity and comonomer incorporation is obvious. With five electron-donating methyl groups on the cyclopentadienyl group, the 1/TIBA/B catalyst system displays the highest catalytic activity of 19.8×10^3 $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$ (Run 2, Table II). Under same conditions, when one methyl group is replaced by electron-withdrawing phenyl, the 2/TIBA/B catalyst system exhibits a moderate catalytic activity of 15.9×10^3 $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$ (Run 6, Table II). With a change in one methyl group and two phenyl, the 3/TIBA/B catalyst system presents the lowest catalytic activity of 12.1×10^3 $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$ (Run 10, Table II). The same trend has been observed with

TABLE I
Copolymerization Results of Ethylene with 1-Hexene by the 1/TIBA/B Catalyst System^a

Run	Al/Ti ^b	T ^c (°C)	Ethylene ^d (atm)	Activity ^e (10^3)	1-Hexene content ^f (mol %)	M_w ^g (10^3)	PDI ^g
1	200	30	4	6.7	9.9	143	2.16
2	200	45	4	13.6	13.3	124	2.18
3	200	60	4	19.8	17.8	103	2.19
4	200	70	4	19.6	18.9	88	2.21
5	160	60	4	14.9	n.d. ^h	101	2.17
6	180	60	4	17.9	n.d. ^h	98	2.20
7	220	60	4	14.7	n.d. ^h	83	2.22
8	200	60	3	16.3	19.6	92	2.24
9	200	60	5	23.1	15.7	112	2.18
10	200	60	6	27.2	13.4	123	2.16

^a Reaction conditions: catalyst 1 0.3 μmol , concentration of the 1-hexene 0.5 mol/L, toluene + 1-hexene total 100 mL, molar ratio of B/Ti 1.5, polymerization time 10 min.

^b Molar ratio of Al/Ti.

^c Polymerization temperature.

^d Ethylene pressure.

^e Activity in $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$.

^f Determined by ^{13}C -NMR.

^g Determined by GPC.

^h n.d., not determined.

TABLE II
Copolymerization Results of Ethylene with 1-Hexene by the 1-3/TIBA/B Catalyst Systems^a

Run	Cat. (μmol)	1-Hexene ^b (mol/L)	Activity ^c (10^3)	1-Hexene ^d content (mol %)	M_w^e (10^3)	PDI ^e
1	1(0.3)	0.3	13.6	12.0	133	2.15
2	1(0.3)	0.5	19.8	17.8	103	2.19
3	1(0.5)	0.7	14.9	22.5	77	2.24
4	1(0.5)	0.9	10.3	26.4	56	2.29
5	2(0.4)	0.3	10.0	10.5	122	2.13
6	2(0.4)	0.5	15.9	15.7	95	2.16
7	2(0.6)	0.7	12.0	20.1	70	2.19
8	2(0.6)	0.9	8.2	23.8	49	2.24
9	3(0.4)	0.3	5.7	14.5	98	2.16
10	3(0.4)	0.5	12.1	21.4	68	2.22
11	3(0.7)	0.7	8.2	26.0	45	2.25
12	3(0.7)	0.9	4.7	30.8	20	2.32

^a Reaction conditions: ethylene pressure 4 atm, toluene + 1-hexene total 100 mL, molar ratio of Al/Ti 200, molar ratio of B/Ti 1.5, polymerization temperature 60°C, polymerization time 10 min.

^b 1-Hexene concentration in the feed.

^c Activity in $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$.

^d Determined by ^{13}C -NMR.

^e Determined by GPC.

these catalyst systems as for the ethylene/1-octene and 1-octadecene copolymerization (e.g., Runs 2, 6, 10 in Tables III and IV). The order of catalyst activity toward ethylene/ α -olefins copolymerization is $3 < 2 < 1$ under same conditions. These results might be mainly ascribed to the electronic effect of the substituents on the cyclopentadienyl group because it has been well known that the catalytic activity of metallocene catalysts could be increased by electron-

donating groups on the ligand and decreased by electron-withdrawing groups. Furthermore, the data of Tables II–IV indicate that the steric effect of the substituents on the cyclopentadienyl group of the ligand in 1–3 affect the ability of the catalysts to control comonomer incorporation. For instance, changing one methyl substituent in 1 (1-hexene content (mol %) = 17.8, Run 2 in Table II) to one phenyl substituent in 2 results in a decrease in comonomer

TABLE III
Copolymerization Results of Ethylene with 1-Octene by the 1-3/TIBA/B Catalyst Systems^a

Run	Cat. (μmol)	1-Octene ^b (mol/L)	Activity ^c (10^3)	1-Octene ^d content (mol %)	M_w^e (10^3)	PDI ^e
1	1(0.3)	0.3	14.9	10.6	145	2.04
2	1(0.3)	0.5	21.5	15.9	122	2.08
3	1(0.5)	0.7	17.3	20.4	101	2.13
4	1(0.5)	0.9	13.9	24.2	83	2.18
5	2(0.5)	0.3	11.0	9.9	132	2.02
6	2(0.5)	0.5	16.6	12.5	118	2.05
7	2(0.7)	0.7	13.4	16.3	97	2.08
8	2(0.7)	0.9	9.1	19.7	79	2.13
9	3(0.5)	0.3	6.5	11.7	109	2.05
10	3(0.5)	0.5	12.6	18.2	76	2.11
11	3(0.9)	0.7	9.0	21.4	59	2.14
12	3(0.9)	0.9	5.8	26.3	24	2.21

^a Reaction conditions: ethylene pressure 4 atm, toluene + 1-octene total 100 mL, molar ratio of Al/Ti 200, molar ratio of B/Ti 1.5, polymerization temperature 60°C, polymerization time 10 min.

^b 1-Octene concentration in the feed.

^c Activity in $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$.

^d Determined by ^{13}C -NMR.

^e Determined by GPC.

TABLE IV
Copolymerization Results of Ethylene with 1-Octadecene by the 1-3/TIBA/B Catalyst Systems^a

Run	Cat. (μmol)	1-Octadecene ^b (mol/L)	Activity ^c (10^3)	1-Octadecene ^d content (mol %)	M_w ^e (10^3)	PDI ^e	T_m ^f ($^{\circ}\text{C}$)
1	1(0.8)	0.3	18.0	3.2	184	2.16	106.5
2	1(0.8)	0.5	24.8	5.1	163	2.19	85.4
3	1(0.8)	0.7	32.8	7.0	140	2.25	66.5
4	1(0.8)	0.9	27.6	8.7	122	2.32	–
5	2(1.2)	0.3	13.7	2.2	169	2.14	116.6
6	2(1.2)	0.5	21.1	3.5	154	2.18	103.3
7	2(1.2)	0.7	27.5	4.8	136	2.20	90.2
8	2(1.2)	0.9	23.4	6.1	117	2.27	77.4
9	3(1.2)	0.3	8.5	3.7	130	2.17	101.8
10	3(1.2)	0.5	16.3	6.2	108	2.24	75.7
11	3(1.2)	0.7	20.4	8.2	84	2.26	–
12	3(1.2)	0.9	18.7	10.0	63	2.35	–

^a Reaction conditions: ethylene pressure 4 atm, toluene + 1-octadecene total 100 mL, molar ratio of Al/Ti 200, molar ratio of B/Ti 1.5, polymerization temperature 60 $^{\circ}\text{C}$, polymerization time 10 min.

^b 1-Octadecene concentration in the feed.

^c Activity in $\text{kg}_{\text{pol}}/\text{mol}_{\text{Ti}}\cdot\text{h}$.

^d Determined by ^{13}C -NMR.

^e Determined by GPC.

^f Determined by DSC.

incorporation (1-hexene content (mol %) = 15.7, Run 6 in Table II). One methyl group and two phenyl-substituted **3** shows the highest ability of comonomer incorporation [1-hexene content (mol %) = 21.4, Run 10 in Table II]. Similarly, this trend can also be shown from the ethylene/1-octene and 1-octadecene copolymerization (Runs 2, 6, 10 in Tables III and IV). This result suggests that the steric effect of the substituents on the cyclopentadienyl group plays an important role in determining the comonomer incorporation because the bulky substituents influenced the coordination of comonomers. Such the effect of substituent group was also observed in the ethylene/1-hexene copolymerization by the nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes in the presence of methylaluminoxane (MAO).¹²

The influence of the comonomer feed concentration for the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene by the 1-3/TIBA/B catalyst systems was also examined, as shown in Tables II–IV. The comonomer contents increase with the increase of the comonomer feed concentration. The incorporation ability for comonomer of smaller size is higher than that for the long chain comonomer under similar conditions (1-hexene > 1-octene > 1-octadecene), which could be attributed to that the coordination ability of the bulkier comonomer is lower than that of the comonomer of smaller size.³³ The comonomer incorporation ability of our catalyst systems seems to be similar to that of the $[\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)(\text{N}^t\text{Bu})]\text{TiCl}_2/\text{MAO}$ catalyst system under the

similar conditions.³⁴ However, the molecular weight of the copolymers produced by our catalyst systems is much higher compared to the one of the copolymers from the latter catalyst system due probably to that the electronic effect of the substituents on the cyclopentadienyl group plays a significant role in the M_w of the resultant copolymer. The catalytic activity by the 1-3/TIBA/B catalyst systems increase with the increase of the comonomer feed concentration until reaching the maximum values and then decrease. The decrease in the catalytic activity may be explained as follows. With the increase of comonomer contents, steric hindrance around the active site increases so that it makes the insertion of ethylene to an active metal-carbon bond difficult. A similar “comonomer effect” on the catalytic activity was also observed previously in the ethylene/ α -olefin copolymerization.^{35–38}

Characterizations of the copolymers

The copolymers obtained were characterized by means of ^{13}C -NMR, GPC, and DSC.

The microstructure of the copolymers was analyzed with ^{13}C -NMR spectroscopy. Typical ^{13}C -NMR spectra of poly(ethylene-*co*-1-hexene), poly(ethylene-*co*-1-octene), and poly(ethylene-*co*-1-octadecene) samples are presented in Figures 1–3, respectively. The carbon assignments were established according to the rules of Linderman and Adams.³⁹ The percentage of comonomer incorporation in the copolymer

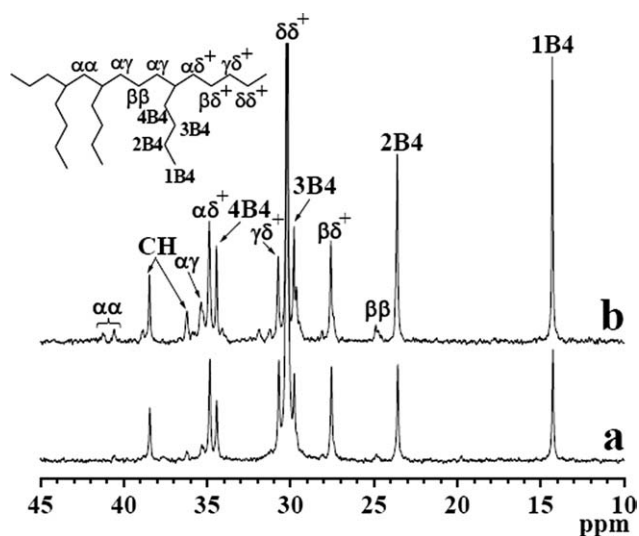


Figure 1 ^{13}C -NMR spectra of ethylene/1-hexene copolymers with different percentages of 1-hexene incorporated: (a) 14.5 mol % (Run 9 in Table II); (b) 30.8 mol % (Run 12 in Table II).

chain was studied by ^{13}C -NMR spectroscopy. The representative ^{13}C -NMR spectra of the ethylene/1-hexene copolymers obtained with different percentages of 1-hexene incorporation are shown in Figure 1, where the peaks corresponding to carbon from the 1-hexene side chain, CH, alternative sequence (24.2–25.2 ppm, $\beta\beta$), and block type sequence (40.2–41.7 ppm, $\alpha\alpha$) increase as the degree of incorporation

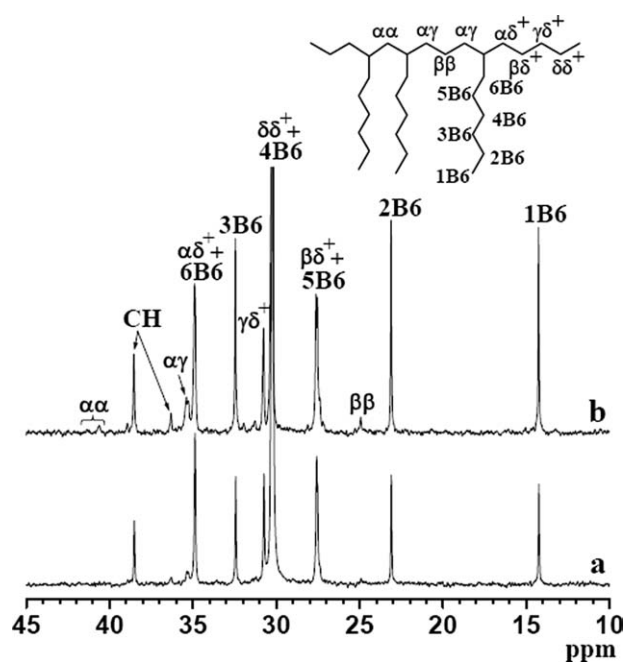


Figure 2 ^{13}C -NMR spectra of ethylene/1-octene copolymers with different percentages of 1-octene incorporated: (a) 11.7 mol % (Run 9 in Table III); (b) 26.3 mol % (Run 12 in Table III).

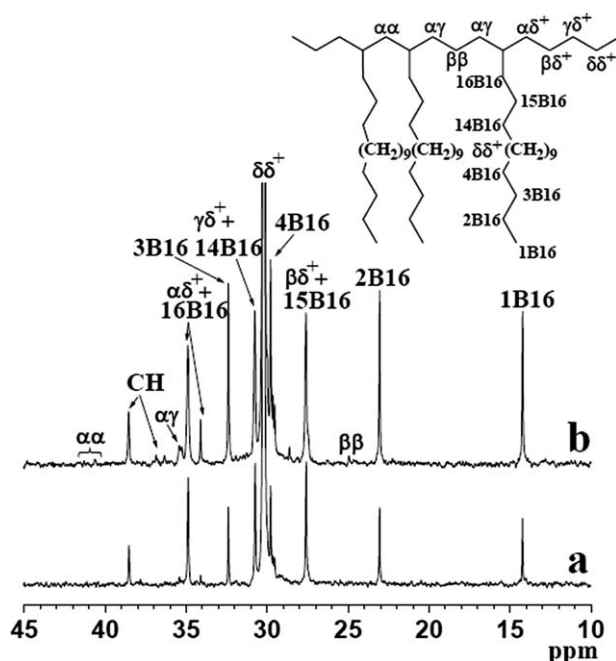


Figure 3 ^{13}C -NMR spectra of ethylene/1-octadecene copolymers with different percentages of 1-octadecene incorporated: (a) 3.7 mol % (Run 9 in Table IV); (b) 10.0 mol % (Run 12 in Table IV).

increases. The similar changes can be seen in the representative ^{13}C -NMR spectra of the poly(ethylene-*co*-1-octene)s and poly(ethylene-*co*-1-octadecene)s obtained with different percentages of comonomer incorporation, as shown in Figures 2 and 3, respectively.

The ethylene and comonomer reactivity ratios (r_E , r_H , r_O , and r_{OD} are the reactivity ratios of ethylene, 1-hexene, 1-octene, and 1-octadecene, respectively) for the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene by the 3/TIBA/B catalyst system were calculated from Fineman-Ross plots,⁴⁰ as shown in Figures 4–6. The values of r_E and r_H are 4.69 and 0.085, respectively, in the ethylene/1-hexene copolymerization. The values of r_E and r_O are 6.11 and 0.069, respectively, in the ethylene/1-octene copolymerization. While the values of r_E and r_{OD} are 21.96 and 0.022, respectively, in the ethylene/1-octadecene copolymerization. The ratio of r_H/r_E , r_O/r_E , and r_{OD}/r_E are 0.018, 0.011, and 0.0010, respectively, which can be used to compare the relative comonomer incorporation ability.^{41,42} The reactivity ratio product value is an indicator for the distribution of the monomers within a polymer chain. The reactivity ratio product ($r_E \cdot r_H$, $r_E \cdot r_O$, and $r_E \cdot r_{OD}$ are 0.40, 0.42, and 0.48, respectively) values are smaller than those by ordinary metallocene type, which indicated that the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene by the 3/TIBA/B catalyst system did not proceed in a random manner.⁴³ The reactivity ratio product values were also

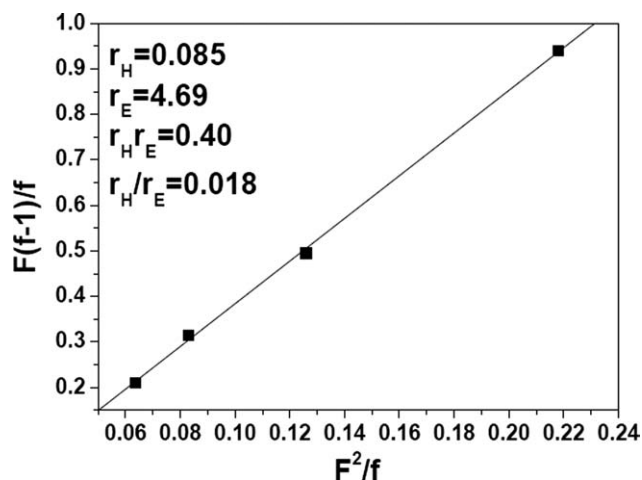


Figure 4 Fineman-Ross plot for ethylene/1-hexene copolymerization with the 3/TIBA/B catalyst system.

small in the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene by both the 1/TIBA/B catalyst system ($r_E \cdot r_H$, $r_E \cdot r_O$, and $r_E \cdot r_{OD}$ are 0.41, 0.44, and 0.45, respectively) and the 2/TIBA/B catalyst system ($r_E \cdot r_H$, $r_E \cdot r_O$, and $r_E \cdot r_{OD}$ are 0.42, 0.45, and 0.49, respectively). In most cases of ethylene/ α -olefin copolymerization, especially by ordinary metallocene type, the reaction proceeds in a random manner, but nonbridged half-titanocenes containing an aryloxo,⁶ amide^{44,45} ligand does not. Therefore, this is one of the unique characteristics seen in the copolymerization using half-titanocene containing anionic ancillary donor ligand. One possible explanation for small reactivity ratio product values by the 1-3/TIBA/B catalyst system might be due to the result of internal rotation of aryloxo group which would form high percentage of favored conformation in equilibrium among the catalytically-active species as described by Nomura et al.¹²

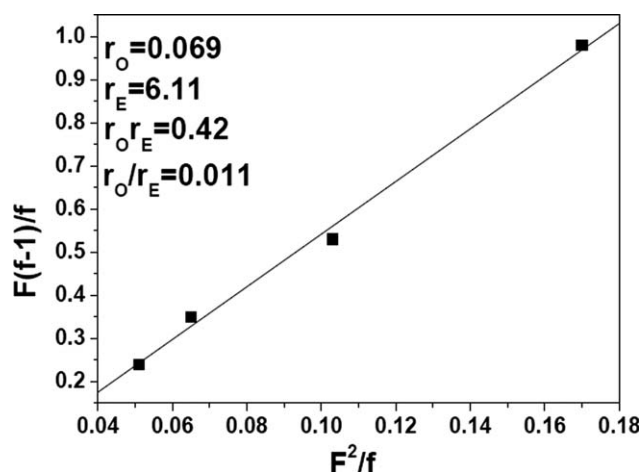


Figure 5 Fineman-Ross plot for ethylene/1-octene copolymerization with the 3/TIBA/B catalyst system.

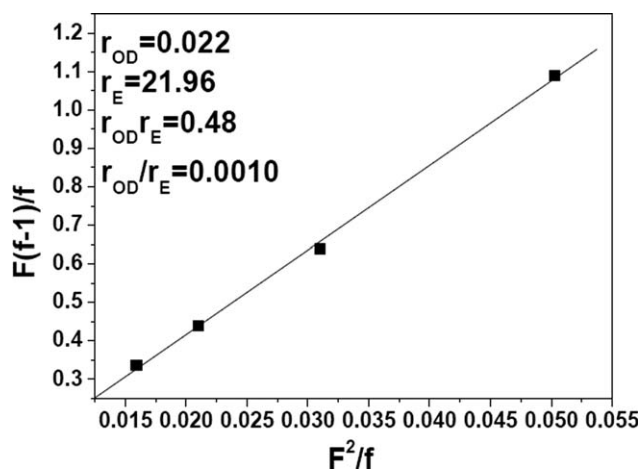


Figure 6 Fineman-Ross plot for ethylene/1-octadecene copolymerization with the 3/TIBA/B catalyst system.

The GPC analyses revealed that the poly(ethylene-*co*-1-hexene)s, poly(ethylene-*co*-1-octene)s, and poly(ethylene-*co*-1-octadecene)s produced by the 1-3/TIBA/B catalyst systems possess high moderate molecular weights with narrow molecular weight distributions and the results were summarized in Tables II-IV. The molecular weight of the poly(ethylene-*co*-1-hexene)s by the 1/TIBA/B catalyst system decreases with the increase of reactor temperature, while increases at higher ethylene pressure, as shown in Table I. The molecular weight of the copolymers obtained shows high sensitivity to the comonomer concentration in the feed. The molecular weight of the poly(ethylene-*co*-1-hexene)s, poly(ethylene-*co*-1-octene)s, and poly(ethylene-*co*-1-octadecene)s decreases with the increase of comonomer content (Tables II-IV), which may be attributed to the β -hydride elimination.

The melting temperature of the poly(ethylene-*co*-1-octadecene)s produced by the 1-3/TIBA/B catalyst systems decreases with the increase of the comonomer feed concentration and the comonomer content (Table IV). There is no melting point for resultant poly(ethylene-*co*-1-hexene)s and poly(ethylene-*co*-1-octene)s with a high comonomer incorporation, which indicates indirectly that the tropism of the comonomer in the polymer chain is out-of-order.

CONCLUSIONS

Nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) dichlorides 1-3, activated with TIBA/B, are efficient catalysts for the copolymerization of ethylene with 1-hexene, 1-octene, and 1-octadecene. The catalytic activity, comonomer incorporation, and molecular weight of the copolymers produced can be controlled by the variation of catalyst structure, comonomer, and reaction parameters such as the reaction

temperature, ethylene pressure, and comonomer feed concentration. The catalytic activity increase as well as ability of comonomer incorporation in the order: $3 < 2 < 1$ and $2 < 1 < 3$ under same conditions. With the 1-3/TIBA/B catalyst systems, tendency of comonomer incorporation is 1-hexene > 1-octene > 1-octadecene. In addition, the reactivity ratio product ($r_E \cdot r_H$, $r_E \cdot r_O$, and $r_E \cdot r_{OD}$) values are smaller than those by ordinary metallocene type, which indicated that the copolymerization by the 1-3/TIBA/B catalyst systems did not proceed in a random manner.

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