

Homopolymerizations and Random Copolymerizations of Olefins with Amino-Substituted Cyclopentadienylchromium Complexes

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ABSTRACT: 1-(2-*N,N*-Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienyl-chromium dichloride (**1**), (2-*N,N*-dimethylaminoethyl)cyclopentadienylchromium dichloride (**6**), and (2-*N,N*-dimethylaminoethyl)indenylchromium dichloride (**7**) in the presence of modified methylaluminoxane exhibit high catalytic activities for the polymerization of ethylene with random copolymerizations of ethylene with propylene, ethylene with 1-hexene, and propylene with 1-hexene. These initiators conduct polymerizations to give high molecular weight polymers with low polydispersities. However, the stereoregularities are very poor in these reactions. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 2759–2771, 2002

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INTRODUCTION

High-density polyethylenes (PEs) with rather high polydispersities bearing long branches are produced with silica-supported (or modified silica-supported) chromium catalysts, which were discovered in the 1950s by Hogan and Banks at Phillips Petroleum Co.^{1–4} These polymers have great advantages in possessing good processing abilities. Union Carbide Co. discovered the silica-supported chromocene system having excellent catalytic activity.⁵ Despite extensive research, the oxidation state of the active site, exact polymerization mechanism,^{6,7} and the molecular structures of the real catalysts are still unknown because of their heterogeneous structures. We have reported the excellent catalytic activities of

Cr[N(SiMe₃)₂]₃/methylaluminoxane (MAO), Cr[CH(SiMe₃)₂]₂/MAO,⁸ and Cr₂[NtBuSiMe₂]₂-O]₂/MAO⁹ for the polymerization of ethylene, giving polymers with high polydispersities. Heints¹⁰ reported good catalytic activities of (C₅Me₅)Cr-(CH₂SiMe₃)₂/silica for the polymerization of ethylene. More recently, Emrich et al.¹¹ found that half-sandwich-type homogeneous chromium complexes coupled with MAO exhibit excellent activities for the polymerization of ethylene via a chromocycle. Random copolymerization of ethylene with 1-hexene resulted in very low activity with the (*cyclo*-C₄H₈-NC₂H₄C₅Me₄)CrMe₂/MAO initiator.¹² Catalyses of chromium(III) alkyls featuring an amido ligand tethered to a permethylcyclopentadienyl ring¹³ and cyclopentadienylchromium(III) complexes functionalized by quinoline or *N,N*-dimethylaniline¹⁴ are also described for the polymerization of ethylene. Alkylaminophosphanyl-substituted half-sandwich chromium complexes have also indicated good catalytic activities for the polymerization of ethylene.¹⁵ More-detailed

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studies have not been published. We describe the effect of alkyl substitution on Cr–R bonds of half-sandwich chromium complexes, the effect of steric bulkiness of cyclopentadienyl ligands in half-sandwich-type chromium complexes, and the ability of copolymerizations of ethylene with propylene or 1-hexene.

EXPERIMENTAL

General Considerations

All operations were performed under an argon stream with standard Schlenk techniques. Tetrahydrofuran (THF), hexane, and toluene were dried over Na/K alloy and thoroughly degassed by trap-to-trap distillation. Chemically pure (99.9%) ethylene purchased from Koatsu Gas Kogyo and propylene (99.9%) purchased from Sumitomo Seika were used after passing them through phosphorous pentoxide (P_2O_5) powder and KOH pellets. An olefin, 1-hexene, was dried over Na/K alloy. 1H NMR spectra were recorded on a Bruker AMX-400wb spectrometer (400.13 MHz), and chemical shifts were calibrated with benzene (δ 7.20 ppm) in benzene- d_6 (C_6D_6) or chloroform ($CHCl_3$) (7.26 ppm) in chloroform- d ($CDCl_3$). ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (99.45 MHz), and chemical shifts were calibrated with the phenyl signal of *p*-xylene (δ 128 ppm) in 1,2,4-trichlorobenzene at 125 °C or $CDCl_3$ (77.0 ppm) at 30 °C. Number-average (M_n) and weight-average molecular weight (M_w) values of poly(1-hexene) were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 GPC with TSK gel G2000, G3000, G4000, and G5000 columns in chloroform at 40 °C. The flow rate was 1.0 mL min^{-1} . M_n and M_w values of PE, polypropylene, poly(ethylene-*co*-propylene), poly(ethylene-*co*-1-hexene), and poly(propylene-*co*-1-hexene) were determined by GPC on a Waters 150C with a Shodex AT806MS column in *o*-dichlorobenzene at 140 °C. These values were calibrated with standard PP and poly(1-hexene) purchased from the National Institute of Standards and Technology. Electron-impact mass spectra (EIMS) were recorded on a JEOL JMS-SX102A mass spectrometer at 30 eV. Elemental analyses of the complexes were performed on a PerkinElmer 2400 series II CHNS/O analyzer, after packing the organochromium samples in thin tin foils under an argon stream.

Preparation of Chromium Complexes

1-(2-*N,N*-Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienylchromium(III) Dichloride (1)

2-Butenyllithium (0.51 mol) was prepared from the reaction of a mixture of *cis*- and *trans*-2-bromo-2-butene (68.8 g, 0.51 mol) with lithium powder (7.2 g, 1.04 mol) in diethyl ether (500 mL) at 25 °C by stirring the mixture for 4 h at 10 °C. $Me_2N(CH_2)_2COOEt$ (39.7 mL, 0.25 mol) was slowly added to the resulting solution, and the stirring was continued for 12 h. The resulting mixture was poured into aqueous solution (750 mL) saturated with NH_4Cl and extracted with three portions of diethyl ether (50 mL $\times$ 3). The combined extracts were dried over magnesium sulfate ($MgSO_4$) and evaporated to maintain 4-(*N,N*-dimethylaminoethyl)-3,5-dimethylhepta-2,5-dien-4-ol as a yellow oil in 58% yield. The resulting compound (31.6 g, 188 mmol) was slowly added to *p*-TsOH (35.6 g, 188 mmol) dissolved in diethyl ether (150 mL). The mixture was stirred for 5 h at 25 °C and then poured into an aqueous solution saturated with sodium carbonate (Na_2CO_3) and extracted with diethyl ether (25 mL $\times$ 3). Distillation under the reduced pressure afforded $C_5Me_4HCH_2CH_2NMe_2$ in 42% yield (11.6 g). The reaction of this compound (4.0 g, 20.7 mmol) with BuLi (13.7 mL, 20.8 mmol) in diethyl ether gave $LiC_5Me_4CH_2CH_2NMe_2$ in a quantitative yield. The resulting solution was added to the suspension of anhydrous chromium(III) chloride ($CrCl_3$) (3.3 g, 20.6 mmol) in THF (60 mL) at 25 °C, and the stirring was continued overnight. After evaporation of the solution, toluene was added to remove LiCl, and the organic layer was centrifuged and cooled to –25 °C to give $(C_5Me_4CH_2CH_2NMe_2)CrCl_2$ as dark blue needle crystals in 18% yield (1.17 g); mp: 222.5 °C.

ELEM. ANAL. Calcd. for $CrC_{13}H_{22}NCl_2$: C, 49.53%; H, 7.03%; N, 4.51%; Cl, 22.49%; Cr, 16.49%. Found: C, 49.56%; H, 7.08%; N, 4.52%; Cl, 22.39%; Cr, 16.45% (oxidation method). EIMS for ^{52}Cr (relative intensity): m/z = 314 (M^+ , 35), 278 ($M^+ - Cl$, 58), 243 ($M^+ - Cl_2$, 5), 192 ($M^+ - CrCl_2$, 76), 134 (18), 58 (100).

1-(2-*N,N*-Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienyldimethylchromium(III) (2)

To the THF solution of **1** (0.30 g, 0.95 mmol), was slowly added 1.1 M of MeLi/diethyl ether solution

(3.3 mL, 3.8 mmol) at -78°C . The resulting mixture was stirred overnight, and then the solvent was removed by flash distillation. The residue was extracted with hexane (100 mL), the and resulting LiCl was removed by centrifugation. The solution was concentrated and stored at -25°C to give **2** as red-purple crystals (0.22 g, 0.81 mmol) in 85% yield; mp: 198.5°C .

ELEM. ANAL. Calcd. for $\text{CrC}_{15}\text{H}_{28}\text{N}$: C, 65.65%; H, 10.30%; N, 5.11%; Cr, 18.94%. Found: C, 65.69%; H, 10.33%; N, 5.20%; Cr, 18.78 (oxidation method). EIMS for ^{52}Cr (relative intensity): m/z = 274 (M^+ , 20), 259 ($\text{M}^+ - \text{Me}$, 33), 244 ($\text{M}^+ - \text{Me}_2$, 2), 225 ($\text{M}^+ - \text{CrMe}_2$, 56), 58 (100).

1-(2-*N,N*-Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienyldi-*t*-butylchromium(III) (3)

To the THF solution of **1** (0.30 g, 0.95 mmol), was slowly added 1.64 M of *t*BuLi/pentane solution (2.3 mL, 3.8 mmol) at -78°C . The resulting mixture was stirred overnight, and the solution was evaporated to dryness. The residue was extracted with hexane (100 mL), and LiCl was removed by centrifugation. The solution was concentrated and stored at -25°C to give **3** as black crystals (0.10 g, 0.33 mmol) in 35% yield; mp: 156.8°C .

ELEM. ANAL. Calcd. for $\text{CrC}_{21}\text{H}_{40}\text{N}$: C, 70.33%; H, 11.27%; N, 3.91%; Cr, 14.50%. Found: C, 70.38%; H, 11.30%; N, 3.96%; Cr, 14.36% (oxidation method). EIMS for ^{52}Cr (relative intensity): m/z = 359 (M^+ , 8), 302 ($\text{M}^+ - t\text{Bu}$, 16), 244 ($\text{M}^+ - t\text{Bu}_2$, 2), 225 ($\text{M}^+ - \text{Cr}t\text{Bu}_2$, 66), 58 (100).

(2-*N,N*-Dimethylaminoethyl)cyclopentadienylchromium Dichloride (III) (6) and (2-*N,N*-Dimethylaminoethyl)cyclopentadienyldimethylchromium (III) (4)

A lump of sodium (2.76 g, 120 mmol) and 90 mL of THF were placed in a 200-mL round-bottom flask and cooled to 0°C . Freshly distilled cyclopentadiene (11 mL, 122 mmol) was added dropwise via syringe to the mixture. The resulting mixture was allowed to stir at 25°C until the sodium was completely consumed. The resulting solution was added to a suspension of 2-(*N,N*-dimethylamino)ethyl chloride hydrochloride (8.6 g, 60 mmol) in THF (60 mL) at 0°C . The resulting mixture was refluxed for 4 h. The solution was quenched with 20 mL of water, and the organic layer was dried over MgSO_4 . The solution was evaporated to dryness, and the residue was distilled with Kugelrohr

to give 5.8 g (43.2 mmol) of $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{NMe}_2$ as a yellow oil in 72% yield.

^1H NMR (CDCl_3 , 400 MHz): δ 6.0–6.5 (m, Cp, 3H), 2.9–3.0 (m, CH_2 , 2H), 2.4–2.7 (m, CH_2 , 4H), 2.3 (s, Me, 6H).

Resulting $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{NMe}_2$ (1.0 g, 7.3 mmol) and 30 mL of THF were placed in a round-bottom flask and cooled to 0°C . BuLi/hexane solution (1.6 M, 4.7 mL, 7.3 mmol) was added via syringe. After stirring the mixture for 4 h at 25°C , the resulting solution was added to the suspension of anhydrous CrCl_3 (1.1 g, 7.3 mmol) in THF (30 mL). Stirring was continued overnight, and then 100 mL of THF were added. To the supernatant liquid was added 50 mL of hexane. The resulting mixture was centrifuged to separate LiCl. After concentration of the solution, the resulting solution was stored at -25°C to induce the crystals of **6** as blue crystals (0.31 g, 1.17 mmol) in 16% yield; mp: 227.2°C .

ELEM. ANAL. Calcd. for $\text{CrC}_9\text{H}_{14}\text{NCl}_2$: C, 41.73%; H, 5.41%; N, 5.41%; Cl, 27.37%; Cr, 20.07. Found: C, 41.67%; H, 5.39%; N, 5.43%; Cl, 27.45%; Cr, 20.04% (oxidation method). EIMS for ^{52}Cr (relative intensity): m/z = 259 (M^+ , 15), 223 ($\text{M}^+ - \text{Cl}$, 16), 188 ($\text{M}^+ - \text{Cl}_2$, 8), 136 ($\text{M}^+ - \text{CrCl}_2$, 46), 58 (100).

To the THF solution of **6** (0.24 g, 0.95 mmol), was slowly added 1.14 M MeLi/diethyl ether solution (3.3 mL, 3.8 mmol) at -78°C . The resulting mixture was stirred overnight, and the solution was evaporated to dryness. The residue was extracted with hexane (100 mL), and LiCl was removed by centrifugation. The supernatant liquid was concentrated and stored at -25°C to give **4** as purple crystals (0.19 g, 0.9 mmol) in 90% yield; mp: 189.7°C .

ELEM. ANAL. Calcd. for $\text{CrC}_{15}\text{H}_{28}\text{N}$: C, 60.60%; H, 9.18%; N, 6.43%; Cr, 23.85%. Found: C, 60.23%; H, 10.33%; N, 6.40%; Cr, 23.04% (oxidation method). EIMS for ^{52}Cr (relative intensity): m/z = 218 (M^+ , 9), 203 ($\text{M}^+ - \text{Me}$, 23), 188 ($\text{M}^+ - \text{Me}_2$, 2), 136 ($\text{M}^+ - \text{CrMe}_2$, 56), 58 (100).

(2-*N,N*-Dimethylaminoethyl)cyclopentadienyldibenzylchromium (III) (5)

To the THF solution of **6** (0.52 g, 2.0 mmol), was slowly added 2.0 M of benzylmagnesium chloride/THF solution (5.0 mL) at -78°C . The resulting mixture was stirred overnight, and the solution was evaporated to dryness. The residue was extracted with toluene (100 mL), and MgCl_2 was removed by centrifugation. The solution was con-

centrated and stored at $-25\text{ }^{\circ}\text{C}$ to give **5** as dark purple crystals (0.24 g, 0.64 mmol) in 32% yield; mp: $154.6\text{ }^{\circ}\text{C}$.

ELEM. ANAL. Calcd. for $\text{CrC}_{23}\text{H}_{28}\text{N}$: C, 74.60%; H, 7.58%; N, 3.78%; Cr, 14.04. Found: C, 74.55%; H, 7.40%; N, 3.75%; Cr, 14.30% (oxidation method). EIMS for ^{52}Cr (relative intensity): $m/z = 370$ (M^+ , 5), 279 ($\text{M}^+ - \text{CH}_2\text{Ph}$, 23), 188 [$\text{M}^+ - (\text{CH}_2\text{Ph})_2$, 4], 136 ($\text{M}^+ - \text{CrMe}_2$, 65), 58 (100).

(2-*N,N*-Dimethylaminoethyl)indenylchromium Dichloride(III) (7)

Indene (7.4 mL, 63 mmol) and 45 mL of THF were placed in a 200-mL round-bottom flask. The mixture was cooled to $0\text{ }^{\circ}\text{C}$, and 1.6 M of BuLi/hexane solution (39.5 mL, 63 mmol) were added via syringe. The reaction mixture was allowed to warm to $25\text{ }^{\circ}\text{C}$ and stirred there for 2 h. The resulting solution was added to a suspension of 2-(*N,N*-dimethylamino)ethyl chloride hydrochloride (4.5 g, 31.5 mmol) in THF (30 mL) at $0\text{ }^{\circ}\text{C}$. The resulting mixture was refluxed for 4 h. The solution was hydrolyzed with 20 mL of H_2O , and the organic layer was concentrated. The residue was distilled under reduced pressure with Kugelrohr to give (indenyl) $\text{CH}_2\text{CH}_2\text{NMe}_2$ as a yellow oil (2.0 g, 10.7 mmol) in 34% yield.

^1H NMR (CDCl_3 , 400 MHz) δ 7.2–7.5 (m, indenyl, 4H), 6.3 (s, indenyl, 1H), 3.4 (s, indenyl, 2H), 2.6–2.7 (m, CH_2 , 4H), 2.4 (s, Me, 6H).

(Indenyl) $\text{CH}_2\text{CH}_2\text{NMe}_2$ (1.0 g, 5.3 mmol) and 15 mL of THF were placed in a 100-mL round-bottom flask. After cooling the mixture to $0\text{ }^{\circ}\text{C}$, 1.6 M of BuLi/hexane (3.4 mL, 5.5 mmol) were added via syringe. The resulting solution was added to the suspension of anhydrous CrCl_3 (0.85 g, 5.3 mmol) in 15 mL of THF at $25\text{--}30\text{ }^{\circ}\text{C}$. The mixture was stirred overnight. After the centrifugation to separate LiCl, the solution was evaporated to dryness. Hexane was added to the residue, and the suspension was centrifuged again. Concentration of the solution followed by cooling to $-25\text{ }^{\circ}\text{C}$ gave **7** as green crystals (0.21 g, 0.69 mmol) in 13% yield; mp: $210.3\text{ }^{\circ}\text{C}$.

ELEM. ANAL. Calcd. for $\text{CrC}_{13}\text{H}_{16}\text{NCl}_2$: C, 50.52%; H, 5.18%; N, 4.53%; Cl, 22.94%; Cr, 16.82. Found: C, 50.35%; H, 5.09%; N, 4.35%; Cl, 22.96%; Cr, 17.25% (oxidation method). EIMS for ^{52}Cr (relative intensity): $m/z = 309$ (M^+ , 10), 274 ($\text{M}^+ - \text{Cl}$, 23), 238 ($\text{M}^+ - \text{Cl}_2$, 2), 186 ($\text{M}^+ - \text{CrCl}_2$, 53).

Polymerization of Ethylene and Propylene with Chromium Complex

To a solution of a chromium complex (0.01 mmol) in 30 mL of toluene was added modified methyla-

luminoxane (MMAO) (100 equiv) or $\text{Ph}_3\text{C}[(\text{C}_6\text{F}_5)_4]$ (1.1 equiv) at ambient temperature in a 50-mL Schlenk tube. After cooling the system to $-78\text{ }^{\circ}\text{C}$, the system was evacuated, and ethylene or propylene was introduced from the gas cylinder. Then the temperature was quickly raised to $25\text{ }^{\circ}\text{C}$ with vigorous stirring to start the polymerization. After standing for 10 min or 1 h, the polymerization mixture was poured into excess methanol to quench the polymerization reaction. Resulting white polymer was dried *in vacuo*.

Random Copolymerization of Ethylene with Propylene

Ethylene and propylene were introduced into the evacuated Schlenk-type reaction tube filled with 30 mL of toluene (cooled to $-78\text{ }^{\circ}\text{C}$) in a flow rate of 28:42 (volume) (1:1 molar ratio), and the mixture was raised to $25\text{ }^{\circ}\text{C}$ with vigorous stirring. Then a chromium complex (0.01 mmol) with MMAO (100 equiv) dissolved in 3 mL of toluene were added to start the polymerization reaction, and the reaction vessel was stored for 10–30 min at that temperature. After a fixed time (typically 1 h), the reaction mixture was poured into excess methanol to precipitate the resulting polymer samples.

Random Copolymerization of Propylene with 1-Hexene

Propylene was introduced into a 5-mL Schlenk-type reaction tube filled with 30 mL of toluene at $-78\text{ }^{\circ}\text{C}$ after evacuating the system and introducing an argon gas, and the tube was allowed to warm to $25\text{ }^{\circ}\text{C}$. Then a fixed amount of 1-hexene and a chromium complex/MMAO (0.01/1 mmol) were added to initiate the polymerization. After a fixed time, the solution was poured into excess methanol to precipitate the copolymer.

Attempt To Perform the Random or Block Copolymerizations of Ethylene with Methyl Methacrylate

Random copolymerizations of ethylene with methyl methacrylate (MMA) were examined as follows. Ethylene was bubbled into 30 mL of toluene held in a 50-mL Schlenk tube at a rate of 120 mL/min, and then 2 mL of MMA were added. A toluene solution (3 mL) of **7**/MMAO (**7** 0.01 mmol, MMAO 1 mmol) was added to the mixture of ethylene and MMA, and stirring of the mixture

Table 1. Polymerizations of Ethylene with Alkyl-Substituted Complexes $[(C_5Me_4)CH_2CH_2NMe_2]CrR_2$

Initiator	Cocatalyst	Solvent	Activity/ 10^4	$M_n/10^4$	M_w/M_n
1	MMAO	Toluene	36.1	8.8	6.9
1	MMAO	Hexane	3.3	4.5	10.5
1	MAO	Toluene	26.8	5.5	7.5
2	MMAO	Toluene	59.8	9.7	3.5
2	MMAO	Hexane	62.5	8.8	3.8
2	MMAO	Toluene	60.2	9.5	3.4
2	MAO	Toluene	38.5	7.8	3.7
2	$Ph_3C[B(C_6F_5)_4]$	Toluene	0.0	—	—
3	MMAO	Toluene	38.3	4.5	6.7
4	MMAO	Toluene	35.8	7.6	7.2
5	MMAO	Toluene	32.9	6.5	8.9

Initiator 0.01 mmol, solvent 30 mL, $[Al]/[Cr] = 100$ mol/mol, $[B]/[Cr] = 1.1$ mol/mol, ethylene 1 atm, temperature 25 °C, polymerization period 10 min, and activity g-PE/mol of Cr · h.

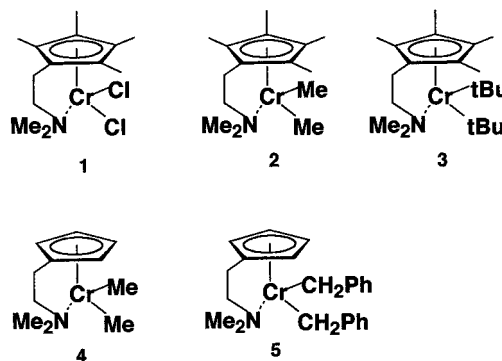
was continued for 1 h at 25 °C. After pouring the solution into excess methanol (MeOH), precipitated polymer was dried *in vacuo*. Block copolymerization was carried out as follows. Ethylene was bubbled into 30 mL of toluene held in a 50-mL Schlenk tube at a rate of 120 mL/min, and a toluene solution (3 mL) of **7**/MMAO (**7** 0.01 mmol, MMAO 1 mmol) was added. After stirring the mixture for 30 min, 2 mL of MMA were added, and the copolymerization was carried out for 30 min. The resulting polymer solution was poured into excess MeOH to precipitate the copolymer.

RESULTS AND DISCUSSION

Polymerizations with Alkyl-Substituted Chromium Complexes $(C_5Me_4CH_2CH_2NMe_2)CrR_2$ and $(C_5H_4CH_2CH_2NMe_2)CrR_2$

Ethylene polymerization with the homogeneous $(C_5Me_4CH_2CH_2NMe_2)CrCl_2$ **1**/MMAO system showed high activity (46×10^4 g-PE/mol of Cr · h). Substitution of the Cl group with an alkyl group would raise the activity because of the enhanced electron donation to the Cr atom and the better solubility of the resulting complexes. In fact, complex **1** is almost insoluble in hexane and hence showed low activity, whereas the methyl analogue **2** is soluble in hexane, and good activity was observed. Results of the polymerization are summarized in Table 1. As expected, the **2**/MMAO system (1:100 molar ratio, MMAO; $(AlMeO)_n/(Al-iBuO)_m = 3/1$ mol/mol) in toluene showed higher activity than the **1**/MMAO system. The use of MMAO as a cocatalyst is more effective than the

use of conventional MAO regarding the activity, molecular weight, and polydispersity. The addition of an excess amount of MMAO in the ratio of $[Al]/[Cr] = 1000$ mol/mol gave nearly the same result with that of $[Al]/[Cr] = 100$ mol/mol. The combination of $Ph_3C[B(C_6F_5)_4]$ with **2** revealed almost no activity toward the polymerization of ethylene presumably because of the lack of the complexation ability toward the Cr complex (see Scheme 1). The substitution with the *t*-Bu group brings about the remarkable lowering of the activity because of the enhanced thermal instability of the resulting **3**. Similarity of the activity between **1**/MMAO and **2**/MMAO indicates that species **1** revealed the activity after converting **1** to **2**. As a whole, the previous conversion to the $-CrR_2$ species does not merit so much because the resulting complex becomes air and moisture sensitive. The activities for less-crowded complexes, **4** and **5**, were comparable to that of **1**. Therefore, we



Scheme 1

Table 2. Effect of Steric Bulkiness of Cp' Ligand on the Polymerization of Ethylene

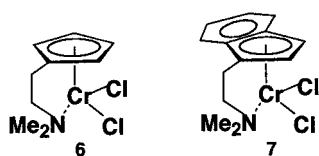
Initiator	Temperature (°C)	Activity/10 ⁴	$M_n/10^4$	M_w/M_n
1	25	36.1	8.8	6.9
1	50	32.5	5.6	3.8
6	0	57.3	11.6	8.2
6	25	29.3	5.3	6.6
6	50	26.8	1.8	3.5
7	0	43.0	25.5	6.7
7	25	38.3	21.6	2.5
7	50	29.7	19.8	2.1

Initiator 0.01 mmol, toluene 30 mL, ethylene 1 atm, [Al]/[Cr] = 100 mol/mol, polymerization period 10 min, and activity g-PE/mol of Cr · h.

can conclude that alkyl substitution does not affect so much the activity of the complexes.

Effect of Steric Bulkiness of the Cp' Ring on the Polymerization of Ethylene

To examine the steric effect of Cp' ligand on the polymerization activity, we prepared **6** and **7** and examined their activities toward the polymerization of ethylene (Table 2, Scheme 2). As a result, the **7**/MMAO system reveals nearly the same activity with the **1**/MMAO system, whereas the resulting molecular weights are higher ($M_n > 20 \times 10^4$) and the polydispersity are remarkably lower at 25 °C. The activity, molecular weight, and polydispersity for the **6**/MMAO system are nearly the same as those obtained with the **1**/MMAO system. The ¹³C NMR spectrum of the PE obtained with the **7**/MMAO system indicates the presence of a methyl branch of only 1–2 mol % against the linear main chain when the polymerization was carried out at 50 °C, whereas the methyl branch significantly reduces by the reaction at 0 °C. The molecular weights of the polymers decreased by raising the polymerization temperature from 0 to 50 °C because of the frequent β-hydride elimination. Molecular weight distributions also decreased with rising temperature, presumably because of the rapid propagation that causes nearly the same lengths of the polymer chain.

**Scheme 2**

Effect of Steric Bulkiness of the Cp' Ring on the Polymerization of Propylene

These initiators are capable of initiating the polymerization of propylene, although their activities are lower than that for the polymerization of ethylene (Table 3). The **7**/MMAO system especially produced high molecular weight polypropylene, although the activities are lower than those of complexes **1** and **6**. A very narrow molecular weight distribution was observed in the case of the **6**/MMAO system at 25 °C. In this case, the size of the cyclopentadienyl (C₅H₄) ring suits well for starting the propylene polymerization. Although we can see an increase of activity by raising the polymerization temperature for ethylene polymerization, raising the temperature resulted in a significant decrease of activity for the propylene polymerization, presumably because of the large steric hindrance between the coordinating propylene molecule and the metal sphere. ¹³C NMR analysis of polypropylene obtained with **7**/MMAO revealed the presence of a mmmm:mmmr:rmrr:mmrm + rmrr:rrrm:rrrr:mmrr:mmrm sequence of the 6.7:7.2:7.3:7.7:20.7:8.8:2.2:19.0:20.4 ratio according to the literature,¹⁶ indicating the formation of an atactic polymer (see Fig. 1).

Effect of Steric Bulkiness of the Cp' Ring on the Polymerization of 1-Hexene

Polymerization of 1-hexene was carried out with the **1**, **6**, and **7**/MMAO systems. The results are listed in Table 4. This kind of polymerization results in a polymerization in high yield, but the molecular weights are relatively low because of the strong steric repulsion between the metal and

Table 3. Polymerization of Propylene with Complexes **1**, **6**, and **7**/MMAO Systems

Initiator	Temperature (°C)	Activity/ 10^4	$M_n/10^4$	M_w/M_n
1	0	2.1	2.4	1.7
1	25	5.4	4.4	1.6
6	0	1.1	2.0	1.4
6	25	5.0	5.7	1.1
7	0	0.8	4.2	3.7
7	25	7.2	11.3	1.6

Initiator 0.01 mmol, toluene 30 mL, propylene 1 atm, $[Al]/[Cr] = 100$ mol/mol, polymerization period 1 h, and activity g -polypropylene/mol of Cr $\cdot$ h.

alkyl group of 1-hexene. Frequent β elimination should occur. ^{13}C NMR analysis of the polymer obtained with **7**/MMAO indicates the formation of the following sequence, that is, mmmm:mmmr + rmmr + mmrr:mmrm + rmrr:mmmr + rrrr:mmrrr:mmrm of the 13.6:26.1:19.6:4.2:26.5:10.0 ratio according to the literature.¹⁷ This result suggests the formation of an atactic polymer. The production of the mmmm sequence (13.6%) exceeds 7% of mmmm for polypropylene because of the steric bulkiness of 1-hexene (Fig. 2). Thus, complexes **1**, **6**, and **7** have good catalytic activities for polymerizations of ethylene, propylene, and 1-hexene under mild conditions because of

the wide coordination space around the metal sphere. One of the characteristics of this polymerization lies in the relatively low polydispersity.

Random Copolymerizations of Ethylene with Propylene

Ethylene/propylene thermoplastic elastomers (EP rubber) are a typical functional polyolefin. Because homopolyethylene and homopropylene are usually crystalline polymers, which lacks elastic properties, we prepare ethylene/propylene random copolymers with complexes **1**, **6**, and **7** in the presence of excess MMAO. The results are

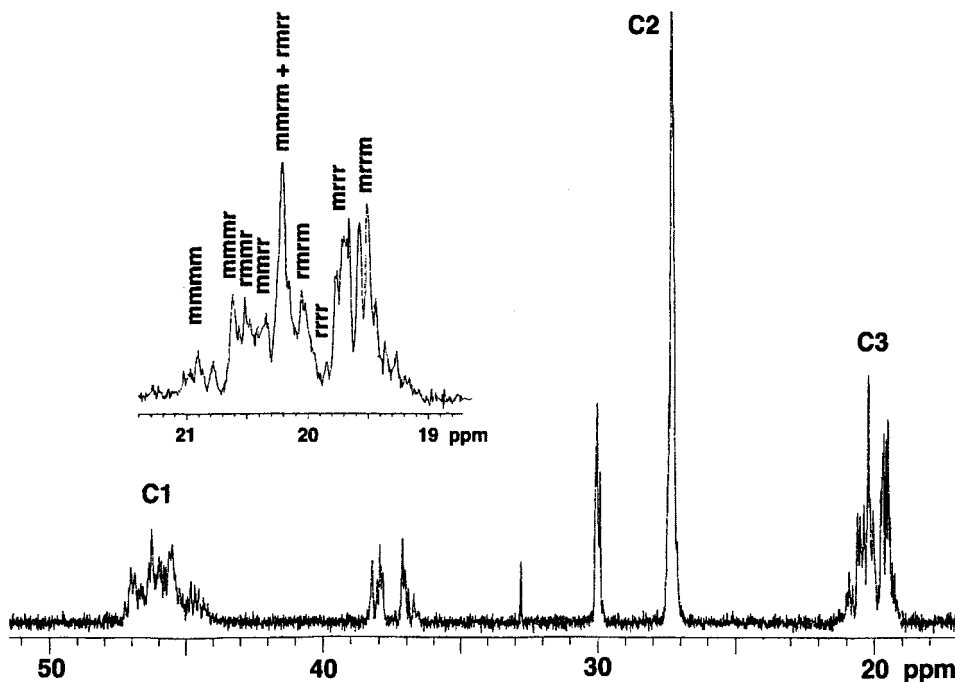


Figure 1. ^{13}C NMR spectrum of polypropylene obtained by **7**/MMAO (100 MHz in 1,2,4-trichlorobenzene/ p -xylene- d_{10} at 125 °C).

Table 4. Polymerization of 1-Hexene with Complexes **1**, **6**, and **7**/MMAO Systems

Initiator	Yield (%) ^a	$M_n/10^4$	M_w/M_n
1	77	0.8	1.6
6	48	1.1	1.5
7	89	1.4	1.4

Initiator 0.03 mmol, toluene 10 mL, propylene 1 atm, $[Al]/[Cr] = 100$ mol/mol, polymerization period 12 h, polymerization temperature 25°C, and activity g-PE/mol of Cr · h.

^a Polymer yield based on feeded amount of monomer.

listed in Table 5. The feeding ratio of ethylene to propylene is 1:1 as determined by the gas flow-meter. Complexes **1** and **6** produced the copolymer containing PE and polypropylene units in nearly the same ratio at 30 °C, whereas the ratio changed to 90/10–95/5 when the reaction temperature was lowered to 0 °C because the monomer reactive ratio of ethylene is higher than that of propylene. In the case of indenyl complex **7**, the ratio of ethylene to propylene is higher as compared with the **1** and **6** systems even at 30 °C, presumably because of the steric bulkiness of the indenyl ligand. Thus, higher molecular weight with relatively low polydispersity was realized with complex **7**. The results of polymerizations

with **1** and **6** agreed well with the fact that the activity for ethylene homopolymerization increased, and that for homopolypropylene decreased by lowering the reaction temperature to 0 °C.

Structural analysis of random copolymers was carried out on the basis of ^{13}C NMR according to the literature.¹⁸ Samples were prepared as 10% (w/w) solutions of polymer in 1,2,4-trichlorobenzene (Fig. 3). The nomenclature used to assign peaks to types of carbon follows Carman and Wilkes.¹⁹ A methylene carbon is identified as S with two Greek letters indicating its distance in both directions from the nearest tertiary carbons. The letter δ indicates that a methylene is in the δ or further position relative to tertiary carbons. Similarly, a methane carbon is identified as T with two Greek letters showing the positions of the nearest tertiary carbons. A methyl carbon is given the letter P with two Greek letters that are the same as those for the attached tertiary carbon. An example of the nomenclature for methylene carbon is as follows

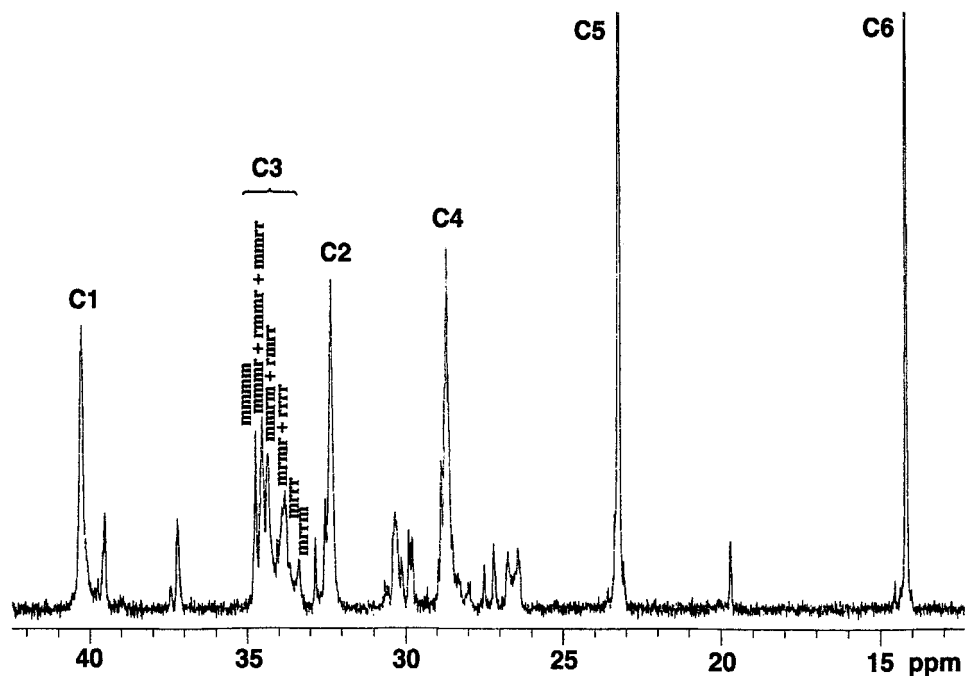
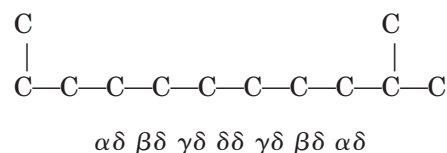


Figure 2. ^{13}C NMR spectrum of poly(1-hexene) obtained by **7**/MMAO (100 MHz in $CDCl_3$ at 25 °C).

Table 5. Random Copolymerization of Ethylene with Propylene

Initiator	Temperature (°C)	Activity/ 10^4	Resulting E/P ^a	Ratio $M_n/10^4$	M_w/M_n
1	0	25.2	90/10	4.9	5.4
1	25	20.2	48/52	1.1	2.3
6	0	10.5	95/5	4.3	6.7
6	25	17.7	50/50	3.6	1.7
7	0	12.6	96/4	27.1	1.8
7	25	37.3	94/6	22.3	2.0

^a Ethylene/propylene ratio (mol/mol), initiator 0.01 mmol, toluene 30 mL, ethylene/propylene feeding ratio = 1/1 mol/mol, $[Al]/[Cr] = 100$ mol/mol, polymerization period 1 h, and activity g -PEP/mol of $Cr \cdot h$.

Figure 3 portrays the ^{13}C NMR spectrum in which peaks attributable to $S\alpha\beta$ and $S\beta\gamma$, ascribed to chemical inversion, cannot be found. Therefore, it is possible to determine the dyad distribution from the methylene data by the equations $PP = S\alpha\alpha$, $EP = S\alpha\gamma + S\alpha\delta$, and $EE = 1/2(S\beta\delta + S\delta\delta) + 1/4S\gamma\delta$. Furthermore, the triad distribution can be calculated from both the methane and methylene data by the following relationships: $PPP = T\beta\beta$, $PPE = T\beta\delta$, $EPE = T\delta\delta$, $PEP = S\beta\beta = 1/2S\alpha\gamma$, $EEP = S\alpha\delta = S\beta\delta$, and $EEE = 1/2S\delta\delta + 1/4S\gamma\delta$. The monomer composition can be calculated from both the dyad and triad distributions by the following equations: $P = PP + 1/2PE$, $E = EE + 1/2PE$, $P = PPP + PPE$

+ PEP, and $E = EEE + EEP + EPE$. The calculated results of the dyad and triad distributions of the EP samples obtained with **1**, **6**, and **7**/MMAO at 25 °C are tabulated in Table 6. When the idealized random copolymerization proceeds, the PP/PE/EE ratio should be 0.25/0.5/0.25, whereas the PPP/PPE/EPE/PEP/EEP/EEE ratio should be 0.125/0.25/0.125/0.125/0.25/0.125. The results of copolymerization initiated by **1**, **6**, and **7**/MMAO are nearly consistent with these data. Although the EP copolymer could be obtained with conventional Ziegler–Natta,²⁰ homogeneous $V(acac)_3/AlEt_2Cl$,²¹ and Kaminsky-type metallocene systems,^{22–24} the Ziegler–Natta system initiates the block-type copolymerization, and the vanadium

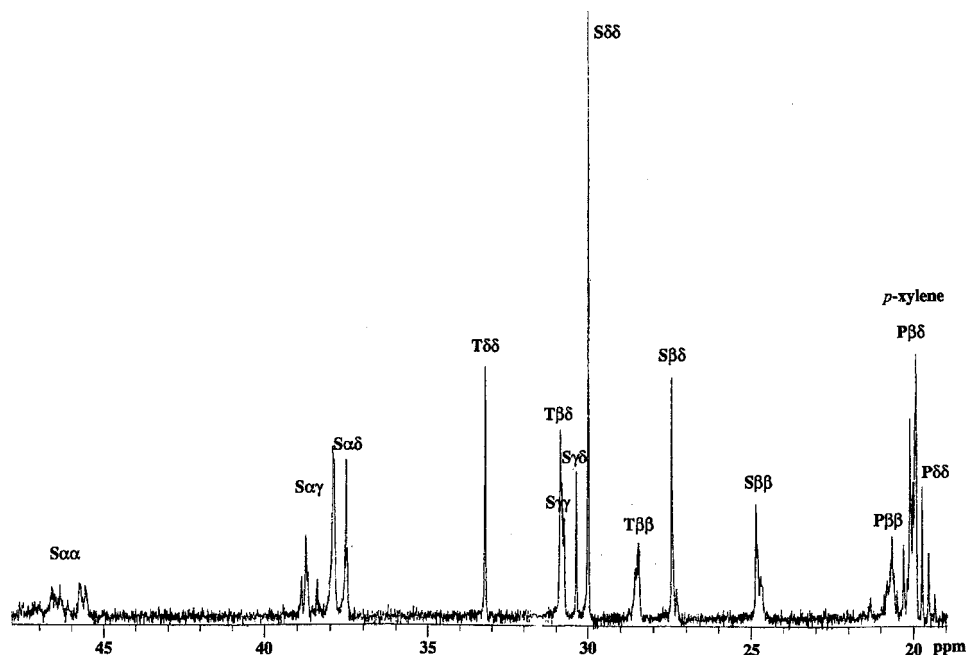


Figure 3. ^{13}C NMR spectrum of ethylene/propylene copolymer obtained by **7**/MMAO (100 MHz in 1,2,4-trichlorobenzene/ p -xylene- d_{10} at 125 °C).

Table 6. Dyad and Triad Distribution of EP Copolymers Obtained with **1**, **6**, and **7**/MMAO

Initiator	PP	PE	EE	PPP	PPE	EPE	PEP	EEP	EEE
1	0.32	0.42	0.26	0.14	0.24	0.15	0.15	0.15	0.17
6	0.27	0.46	0.27	0.09	0.24	0.15	0.14	0.24	0.14
7	0.18	0.50	0.32	0.08	0.17	0.20	0.12	0.25	0.18

system creates the random copolymerization to give a high content of the polypropylene unit. Control of the polypropylene unit is impossible in the cases of the vanadium systems. Metallocene catalyst also gives rise to the formation of random copolymers but requires expensive MAO or MMAO in the [Al]/[Zr] ratio of 1000/10,000 mol/mol. Therefore, we can conclude that these half-sandwich-type Cr systems possess the following merits: (1) high activity is attained with the smaller amount of MMAO, [Al]/[Cr] = 100 mol/mol; (2) the desired random copolymerization proceeds at will to give high molecular weight polymers with low polydispersities; and (3) high activity and low polydispersity were also attained for polymerizations of ethylene.

Random Copolymerization of Ethylene with 1-Hexene

The **1**, **6**, and **7**/MMAO systems also produced the random copolymer by the reaction of ethylene with 1-hexene, although the relative activities are lower than that for ethylene/propylene copolymerization (Table 7). In every case, the content of the ethylene unit is higher than that of the 1-hexene unit, although only 0.12 g (5 mmol) of ethylene is dissolved in 30 mL of toluene as evidenced by gravimetric analysis. The resulting ratio cannot be controlled by the addition of a different amount of 1-hexene. Although complex **1** pro-

duced low molecular weight polymers, complex **7** gave rise to the formation of high molecular weight polymers with relatively low polydispersities. Polymer structures were analyzed on the basis of ^{13}C NMR with reference to Hsieh's and Randall's report.²⁵ A typical example is displayed in Figure 4 that was obtained with **7**/MMAO using 5 mL of 1-hexene. Peaks 1–24 were divided into eight groups, A–H (A 1–3, B 4, C 5–11, D 12–17, E 18–19, F 20–22, G 23, H 24), and the peak area was expressed as TA–TH. Then the following relation was observed regarding the triad assignment: $\text{EHE} = T_{\text{B}}$, $\text{EHH} = 2(T_{\text{G}} - T_{\text{B}} - T_{\text{A}})$, $\text{HHHm} = 2T_{\text{A}} + T_{\text{B}} - T_{\text{G}}$, $\text{HEH} = T_{\text{F}}$, $\text{HEE} = 2(T_{\text{G}} - T_{\text{A}} - T_{\text{F}})$, and $\text{EEE} = 1/2(T_{\text{A}} + T_{\text{D}} + T_{\text{F}} - 2T_{\text{G}})$. Furthermore, we can draw the following relation: $\text{HH} = \text{HHH} + 1/2\text{HHE}$, $\text{HE} = 2\text{EHE} + \text{EHH}$, $\text{H} = \text{HH} + 1/2\text{HE}$, and $\text{E} = \text{EE} + 1/2\text{HE}$. Results of the analysis are given in Table 8. Although the resulting polymer exhibits a high content of ethylene block EEE, we can see a relatively high content of the EHE and EEH sequences. The small amount of the HHH and HHE sequences indicates the HH sequence is absent for the resulting copolymers.

Random Copolymerization of Propylene with 1-Hexene

Random copolymerizations of propylene with 1-hexene were carried out with **1**, **6**, and **7**/MMAO

Table 7. Random Copolymerization of Ethylene with 1-Hexene

Initiator	1-Hexene (mL)	Activity/ 10^4	Resulting E/H ^a	Ratio $M_n/10^4$	M_w/M_n
1	2.5	4.5	85/15	0.5	2.8
1	5.0	5.1	79/21	0.5	2.8
6	2.5	3.2	96/4	9.3	2.7
6	5.0	4.3	86/14	10.1	1.9
7	2.5	6.6	82/18	11.5	2.9
7	5.0	7.3	82/18	15.7	2.0

^a Ethylene 1-hexene ratio (mol/mol), initiator 0.01 mmol, toluene 30 mL, [Al]/[Cr] = 100 mol/mol, polymerization period 1 h, and activity g-PEH/mol of Cr · h.

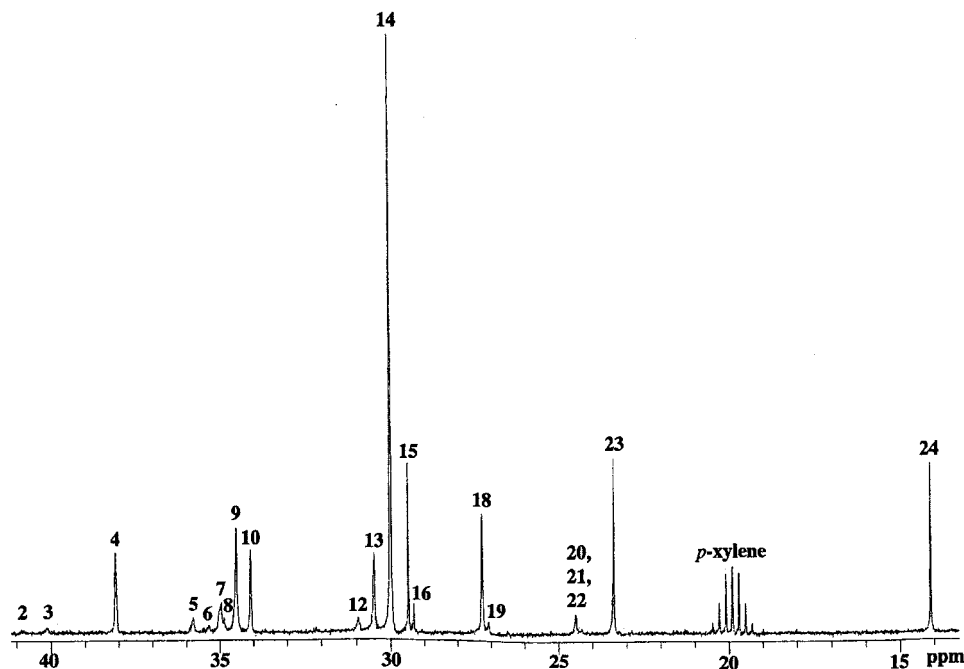


Figure 4. ^{13}C NMR spectrum of ethylene/1-hexene copolymer obtained by **7**/MMAO (100 MHz in 1,2,4-trichlorobenzene/*p*-xylene- d_{10} at 125 °C).

as initiators. In these experiments, we used both a low concentration of 1-hexene (0.7 mL, 5.6 mmol) and a high concentration of 1-hexene (5.0 mL, 39.2 mmol). The result is shown in Table 9. In a reaction vessel, 0.26 g (6.0 mmol) of propylene is dissolved (saturated) as evidenced by gravimetric analysis. Therefore, nearly the same moles of propylene and 1-hexene are dissolved in the case of 0.7 mL of 1-hexene. The content of the 1-hexene unit in the resulting polymer varies (8–48%) with the feeding amount of 1-hexene. The activity and resulting molecular weight were sufficiently high, and the polydispersity became very small when we used the **7**/MMAO system as an initiator. The polymer structure was analyzed according to Soga's report, but we failed to assign each peak in a more-precise way.²⁶ Dyad distribution of the resulting copolymer is given in Table 10. Thus, desired random copolymerization proceeded when

we used complexes **6** and **7**, presumably because of less electron deficiency on the metal. We measured the ^{13}C NMR spectrum of the resulting polymer obtained with **7**/MMAO but failed to make a more-precise assignment.

Attempted Block and Random Copolymerizations of Ethylene with MMA

Block or random copolymerizations of olefins with polar monomers remain an ultimate goal in the polyolefin chemistry because these processes promise to endow the hydrophilic materials with remarkably high adhesive, dyeing, and moisture-absorption properties. Block copolymerizations of ethylene with polar monomers such as MMA, alkyl acrylate, and ϵ -caprolactone with rare-earth-metal complexes;^{27–29} block copolymerization of norbornene with MMA using ROMP tech-

Table 8. Dyad and Triad Distribution of Ethylene/1-Hexene Copolymers

Initiator	HH	HE	EE	HHH	HHE	EHE	HEH	EEH	EEE
1	0.03	0.36	0.61	0.00	0.07	0.14	0.03	0.29	0.47
6	0.00	0.27	0.73	0.00	0.00	0.14	0.01	0.23	0.62
7	0.05	0.25	0.70	0.02	0.05	0.10	0.04	0.21	0.58

Table 9. Random Copolymerization of Propylene with 1-Hexene

Initiator	1-Hexene (mL)	Activity/ 10^4	Resulting P/H	Ratio ^a $M_n/10^4$	M_w/M_n
1	0.7	7.8	85/15	2.7	1.8
1	5.0	9.8	64/36	1.1	2.0
6	0.7	8.3	92/8	6.5	1.2
6	5.0	14.3	52/48	5.2	1.5
7	0.7	5.6	82/18	18.5	1.5
7	5.0	15.3	53/27	14.7	1.7

^a Propylene/hexane ratio (mol/mol), initiator 0.01 mmol, toluene 30 mL, [Al]/[Cr] = 100 mol/mol, propylene 1 atm, polymerization period 30 min, activity *g*-copolymer/mol of Cr · h, and polymerization temperature 25 °C.

niques,³⁰ block copolymerizations of ethylene with substituted norbornene derivatives using Ni-salicylaldehyde complex,³¹ and block copolymerization of ethylene with polar olefins initiated by Kaminsky-type catalysts^{32,33} may be the sole examples of this type of sequential addition polymerization. Johnson and coworkers^{34,35} reported the random copolymerizations of olefins with alkyl acrylate, but the resulting acrylate unit is located primarily at the terminal end of branches. In this sense, the resulting polymers are not the real random copolymers.

Therefore, we have attempted to perform the block or random copolymerization of ethylene and MMA with a chromium complex. Block copolymerization was carried out by the addition of ethylene to the complex **7**/MMAO system followed by the addition of 2 mL of MMA. The resulting polymer is composed of two GPC peaks (peak area: 7:1 ratio), one of which (smaller part) is poly(methyl methacrylate) (PMMA) that can be readily washed away with THF or CHCl_3 . The remained larger peak is composed of only homopolyethylene as evidenced by ^1H NMR, indicating that block copolymerization does not proceed with the **7**/MMAO system. Random copolymerization of ethylene with MMA again gives rise to the formation of homopolyethylene with a low yield of PMMA in a 3:1 ratio as evidenced by the solubility tests. Therefore, chromium complex/MMAO

systems do not produce block and random copolymers.

CONCLUSION

Activities for homopolymerizations of ethylene, propylene, and 1-hexene with the activities for copolymerizations of ethylene with propylene, ethylene with 1-hexene, and propylene with 1-hexene were examined with a variety of half-sandwich-type chromium complexes. Among them, the **7**/MMAO system exhibits high activities for copolymerization of ethylene with propylene or 1-hexene in addition to the homopolymerization of ethylene and propylene.

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Table 10. Dyad for Propylene/1-Hexene Copolymers

Initiator	HH	PH	PP	H	P
1	0.14	0.44	0.42	0.36	0.64
6	0.26	0.45	0.29	0.48	0.52
7	0.27	0.45	0.28	0.50	0.50

Polymerization temperature 25 °C.

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