Ethylene Copolymerization with 1-Octene Using a 2-Methylbenz[*e*]indenyl-Based *ansa*-Monocyclopentadienylamido Complex and Methylaluminoxanes Catalyst

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ABSTRACT: A new effective constrained geometry catalyst precursor for the ethylene/1-octene copolymerization, namely 2-methylbenz[*e*]indenylamido complex $[\eta^5:\eta^1\text{-(2-MeBenzInd)SiMe}_2\text{N}^t\text{Bu]TiCl}_2$ (**4**), was synthesized. Activated with methylaluminoxane (MAO), the complex **4** showed (a) an improved copolymerization activity and stability, (b) an enhanced comonomer incorporation in the copolymer, and (c) most importantly, an increased copolymer molecular weight, when compared with the previously employed catalysts. The polymerization conditions were found to have a significant effect on the catalyst activity, 1-octene incorporation, molecular weight, and even copolymer microstructure. For the copolymerization parameters, the values $r_E \approx 2.20$ for ethylene and $r_O \approx 0.55$ for 1-octene with $r_E \cdot r_O \approx 1.21$ were obtained, reflecting a pronounced tendency for the random distribution of the comonomers in the copolymer chain. The ^{13}C NMR analysis revealed that the E−O copolymer generated by the MAO-activated complex **4** has a regioirregular arrangement of the 1-octene repeat units as a result of some tail-to-tail incorporation of the 1-octene comonomer.

Introduction

The ethylene−α-olefin copolymers are of great practical importance. Most of the conventional Ziegler−Natta catalysts are, however, less effective in initiating the copolymerization of ethylene with α-olefins, and the copolymers formed, if any, are inhomogeneous with regard to comonomer incorporation and molecular-weight distribution.[1] The properties and performance of an olefin copolymer are determined by the comonomer content, molecular weight, and molecular-weight distribution and, most importantly, by the comonomer distribution within and between single polymer chains. The development of single site metallocene catalysts for olefin polymerization has opened new opportunities for the synthesis of copolymers with controlled comonomer incorporation, uniform structure, and properties.[2]

Constrained geometry catalysts of *ansa*-monocyclopentadienylamido group 4 metal complexes, developed by Bercaw and by researchers at Dow and Exxon,[3,4b,c] are currently of great scientific and technological interest as a new generation of metallocene catalysts[4] useful in the copolymerization of ethylene with higher α-olefins. In addition to their relatively high catalytic activity, these catalysts produce high-molecular-weight copolymers with varying levels of comonomer incorporation. The copolymer molecular weight is independent of comonomer incorporation but dependent on the metallocene structure. Most remarkable is the recent development of uniform ethylene/1-octene copolymers which were obtained with the constrained geometry catalysts of $[\eta^5:\eta^1\text{-(Me}_4\text{C}_5\text{)SiMe}_2\text{N}^t\text{Bu]TiCl}_2$[3] and $[\eta^5:\eta^1\text{-(Ind)SiMe}_2\text{N}^t\text{Bu]TiCl}_2$.[5] These ethylene/1-octene materials exibit excellent mechanical properties and melt processability.

For practical applications of metallocene-based ethylene/1-octene copolymerization catalysts, the ability to further improve the catalytic activity and stability, and to control the comonomer incorporation, the molecular weight as well as the branching frequency within the polymer backbone are important issues in the design of the catalyst. To this end, we synthesize a new 2-methylbenz[*e*]indenyl-based constrained geometry catalyst and investigate its catalytic behavior in the copolymerization of ethylene and 1-octene and the microstructure of the resulting ethylene/1-octene copolymer.

Experimental Section

Materials. All operations or reactions were performed under an inert nitrogen atmosphere using the Schlenk or drybox techniques. Toluene, diethyl ether, tetrahydrofuran (THF), hexane, and pentane were refluxed over sodium benzophenone ketyl, from which they were freshly distilled prior to use. Methylene chloride and 1-octene were purified by distillation over CaH_2 and stored in a storage tube containing activated 4A molecular sieves under high-purity nitrogen. Polymerization-grade ethylene was further purified before being fed to the reactor, by passing it through a DC-IB gas purification equipment containing a supported MnO oxygen-removal column and an activated 4A molecular sieve column. Methylaluminoxane (MAO)[1b] was prepared as described in the literature; the residual TMA (trimethylaluminum) content in MAO was about 28 mol %. 2-Methylbenz[*e*]indene (**1**) was synthesized according to literature[6] and characterized by elemental analysis, NMR, and mass spectroscopy. $[\eta^5:\eta^1\text{-(C}_5\text{H}_5\text{)SiMe}_2\text{N}^t\text{Bu]TiCl}_2$[3,4], $[\eta^5:\eta^1\text{-(Me}_4\text{C}_5\text{)SiMe}_2\text{N}^t\text{Bu]TiCl}_2$[3,4] and $[\eta^5:\eta^1\text{-(Ind)SiMe}_2\text{N}^t\text{Bu]-TiCl}_2$[4h,5] compounds were prepared as described in the literature. All other reagents were purchased from Aldrich and were used without further purification. ^{1}H NMR spectra were performed with a JEOL FX-200 spectrometer. Elemental analyses were carried out with a PE-2400 spectrometer.

(*tert*-Butylamino)dimethyl(2-methylbenz[*e*]indenyl)silane (2).[7] To a stirred solution of 2-methylbenz[*e*]indene (**1**) (18.02 g, 100 mmol) in 100 mL of diethyl ether, a 2.5 M solution of butyllithium in hexane (40 mL, 100 mmol) was added within

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60 min at 0 °C. After the mixture was stirred at 0 °C for 1 h and at room temperature for 4 h, the resulting solution was transferred to an addition funnel under a nitrogen atmosphere and then added dropwise at 0 °C within 2 h to a solution of dichlorodimethylsilane (250 mL, 2.06 mol) in diethyl ether (250 mL). The resulting suspension was stirred for 1 h at 0 °C followed by 1 h at room temperature, and the solvent and excess dichlorodimethylsilane were removed under vacuum. After lithium chloride was precipitated with methylene chloride and filtered, followed by the removal of the solvent, 21.82 g (80%) of a slightly yellow solid was obtained. ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.34~8.20 (m, 6H, arom H), 7.18 (dd, 1H, H−C_5(2)), 3.58 (s, 1H, H−C_5(1)), 0.41 (s, 6H, $SiCH_3$). MS(EI): *m/z* 263 (M^+). Anal. Calcd for $C_{16}H_{17}SiCl$: C, 73.15; H, 6.47. Found: C, 73.40; H, 6.51.

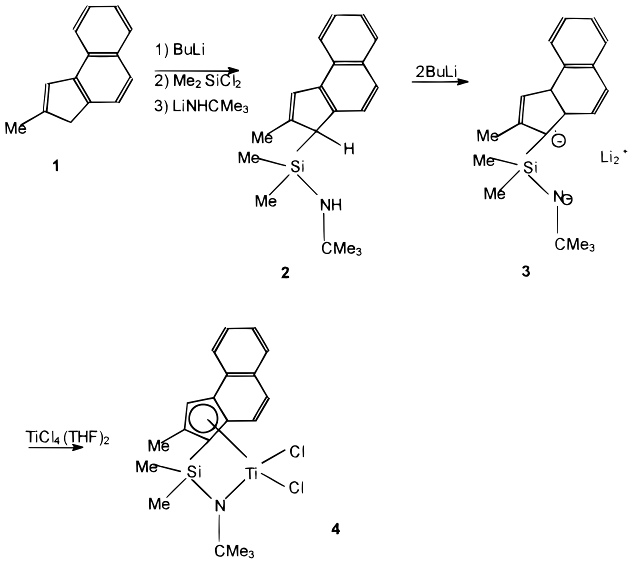
To a solution of this crude (chlorodimethyl)(2-methylbenz[*e*]indenyl)silane (21.82 g, 80 mmol) in diethyl ether (150 mL), a solid lithium *tert*-butylamide (6.33 g, 80 mmol) was added at 0 °C over a period of 1 h. Stirring overnight at room temperature generated a light yellow suspension. Following the removal of all volatiles under vacuum, lithium chloride was precipitated with methylene chloride and filtered off. After the removal of the solvent and distillation under vacuum, the product was extracted with 150 mL of pentane, which was then removed, leaving 17.45 g (70.5% yield) of **2** as a colorless viscous oil. ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.30~8.20 (m, 6H, arom H), 6.95~7.15 (dd, 1H, H−C_5(3)), 3.56 (s, 1H, H−C_5(1)), 2.38 (d, 3H, CH_3), 1.27 (s, 9H, $NCCH_3$), 0.71 (br s, 1H, NH), −0.03, 0.02 (s, 3H, $SiCH_3$). MS(EI): *m/z* 309 (M^+). Anal. Calcd for $C_{20}H_{27}NSi$: C, 77.66; H, 8.73; N, 4.53. Found: C, 77.45; H, 8.70; N, 4.58.

{*tert*-Butyl[dimethyl(2-methylbenz[*e*]indenyl)silyl]amido}dilithium (3). A solution of 17.45 g (56.4 mmol) of (*tert*-butylamino)dimethyl(2-methylbenz[*e*]indenyl)silane (**2**) in 250 mL of diethyl ether was cooled to −78 °C. Under a nitrogen atmosphere, 45.2 mL (112.8 mmol) of 2.5 M *n*-butyllithium in hexane was added with a syringe. After the solution was stirred for 2 h at −78 °C, it was gradually warmed to room temperature and subsequently stirred overnight. The yellow precipitate formed was collected by filtration. This product was washed with pentane and then dried under vacuum to produce 17.75 g (98.0% yield) of **3** as a yellow powder. The yield was almost quantitative.

{η^1:η^5-[(*tert*-Butylamido)dimethylsilyl](2-methylbenz[*e*]indenyl)}titanium dichloride (4).[8] To a solution of {*tert*-butyl[dimethyl(2-methylbenz[*e*]indenyl)silyl]amido}dilithium (**3**) (17.75 g, 55.4 mmol) in 200 mL of toluene, $TiCl_4(THF)_2$ (18.70 g, 56.0 mmol) was added at −78 °C as a toluene solution (150 mL) with a syringe within 1 h. After the mixture was slowly warmed to reach room temperature, the red suspension was stirred 24 h and then filtered. The removal of toluene from the supernatant in a vacuum provided a sticky dark red solid. A red/orange microcrystalline solid of [η^5:η^1-(2-MeBenzInd)$SiMe_2N^tBu$]$TiCl_2$ (**4**) (5.19 g, 22%) was collected by sublimation at 120 °C and 10^{-4} Torr. ^{1}H NMR ($CDCl_3$ at 25 °C): δ 8.07~8.25 (m, 1H, arom H), 7.58~7.90 (m, 5H, arom H), 7.25 (t, 1H, H−C_5(3)), 2.85 (s, 3H, CH_3), 1.29(s, 9H, $NCCH_3$), 0.90(s, 3H, $SiCH_3$), 0.56(s, 3H, $SiCH_3$). MS(EI): *m/z* 426 (M^+). Anal. Calcd for $C_{20}H_{25}Cl_2NSiTi$: C, 56.38; H, 5.87; N, 3.29. Found: C, 56.50; H, 5.85; N, 3.45.

Copolymerization Procedure. The copolymerization of ethylene with 1-octene was carried out in a 500-mL glass reactor equipped with a magnetic stirrer. Selected amounts of solvent (e.g., toluene) and 1-octene were added to the reactor with a syringe under a nitrogen atmosphere followed by the addition of an appropriate amount of MAO. The reactor was placed in a bath at the desired polymerization temperature. The inert gas was removed, and then the reactor was saturated with ethylene for about 30 min. The copolymerization started when a titanium catalyst solution in toluene was injected into the reactor with a syringe. To keep its concentration in solution constant, ethylene was continuously supplied to the reactor via a pressure regulator under a pressure dependent on the polymerization temperature and reaction medium. Its flow was measured with a mass flow controller, and the vapor pressure of the solvent was taken into account when the ethylene concentration was calculated. The concentration of ethylene in the copolymerization system was determined by gas chromatography (GC). The copolymerization process was quenched with 5% HCl in methanol. The precipitated polymer was washed with methanol, subsequently collected by filtration, and dried in a vacuum oven at 70 °C to constant weight. The copolymerization products were then fractionated with toluene at room temperature and at its boiling point for 20 h each, and the fractions were dried in a vacuum oven at 80 °C to constant weight.

Scheme 1



Polymer Analyses. ^{13}C NMR spectra of the copolymers were recorded at 130 °C using a JEOL FX-200 spectrometer with a 45° pulse angle, 8-μs pulse width, 10-s pulse repetition, 8000-Hz spectral width, and at least 16 000 data scans. The solution in *o*-dichlorobenzene containing up to 30 wt % polymer was introduced in a 10-mm NMR tube. The 1-octene content in the copolymers was estimated from ^{13}C NMR spectra as indicated in the literature.[9] The molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the copolymer were determined at 135 °C by gel-permeation chromatography (GPC) (Waters 150C GPC) using *o*-dichlorobenzene as the solvent and standard polystyrene as the reference. The glass-transition temperature, melting temperature, and crystallinity of the copolymer were determined by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 instrument at a heating rate of 10 °C/min. Any thermal history in the polymers was eliminated by first heating the specimen to 180 °C, cooling at 20 °C/min to −150 °C, and then recording the second DSC scan.

Results and Discussion

Preparation of *ansa*-Monocyclopentadienylamido Complex 4. The ligand was prepared according to a published procedure.[6] The constrained geometry complex **4**, [η^5:η^1-(2-MeBenzInd)$SiMe_2N^tBu$]$TiCl_2$, was synthesized following the pathway presented in Scheme 1. A detailed description of the synthetic method was given in the Experimental Section. We found that the reaction of the dilithio salt with $TiCl_4(THF)_2$ in toluene constitutes a feasible metathesis route toward the preparation of 2-methylbenz[*e*]indenylamido complex **4** with a yield of 22%. The product, obtained as a red/orange, slightly air-sensitive microcrystalline solid, by sublimation at 120 °C and 10^{-4} Torr, was characterized by elemental analysis, NMR, and mass spectroscopy.

Several other routes were also explored to synthesize the complex **4**. The reaction of 2-methylbenz[*e*]indenyl

Table 1. Copolymerization of Ethylene and 1-Octene Using Different Constrained Geometry Catalysts[a]

C_p	10^{-7} A[b]	1-octene content in copolymer,[c] mol %	10^{-4} M_w,[d] g/mol	M_w/M_n[d]
C_5H_5	0.76	29.0	7.8	2.0
Me_4C_5	2.95	40.8	22.5	1.8
indenyl	0.93	32.2	10.4	1.9
2-methylbenzindenyl	3.08	42.5	32.7	1.8

[a] Polymerization conditions: $P_E = 2.2$ bar, [ethylene] = 0.22 mol/L, [1-octene] = 0.85 mol/L, [Ti] = 100 μmol/L, MAO/Ti = 1000 (mol/mol), solvent toluene, total volume (1-octene + toluene) = 100 mL, polymerization time = 10 min, $T_p = 80$ °C. [b] A = activity in g of bulk polymer/[mol of Ti·mol of total monomers (ethylene + octene)·h]. [c] Determined by ^{13}C NMR. [d] Measured by GPC using polystyrene standards.

dimagnesio dichloride salt with $TiCl_3(THF)_3$ followed by oxidation with $PbCl_2$ was unsuccessful, as was its reaction with $TiCl_4(THF)_2$ or the reaction of the dilithio salt with $TiCl_4$.

Ethylene/1-Octene Copolymerization Using the Complex 4. The synthesized *ansa*-monocyclopentadienylamido complex **4** was activated with MAO and used to copolymerize ethylene and 1-octene. To ensure an almost constant comonomer concentration, the copolymerization was terminated after 10 min by adding an acidic methanol solution. The results are compared in Table 1 with those we obtained using the previously employed catalysts. Table 1 shows that, compared with C_5H_5- and indenyl-based systems, the 2-methylbenzindenyl-based complex **4** provides an enhanced copolymerization activity (more than 2−3 times), an excellent incorporation of 1-octene into the polyethylene main chain, and an increased molecular weight. The activity of **4** is, however, comparable to that of a Me_4C_5-based catalyst. The 1-octene content of the copolymer prepared with the complex **4** is much higher than those obtained with the previously employed catalysts. Most remarkable is the unusually high molecular weight of the copolymer obtained with **4**; the polymer molecular weight is over 30% higher than that involving Me_4C_5, and much higher than those based on the unsubstituted cyclopentadienyl and indenyl. From these findings one can conclude that the catalyst activity, polymer molecular weight, and comonomer incorporation are very sensitive to the nature of the substituent on the Cp ring. The findings suggest that the presence of the electron-donating alkyl or aryl substituents in the complex **4** may facilitate the replacement of the negatively charged chlorine by MAO via the weakening of the positive charge on Ti. This also weakens the interaction between Ti and MAO, thus allowing for a more rapid insertion of the comonomers in the growing polymer chain. In addition, the bulky substituents might favor conformations of the chain which make the interaction of the active titanium site with β-H stronger and thus the chain termination more difficult.

Compared to the bis-Cp metallocenes,[10] catalyst **4** provides a higher activity and polymer molecular weight and better comonomer incorporation. This may be attributed to the more stable, and highly open and reactive, active site formed upon activation with the cocatalyst.

Table 2 summarizes results regarding the ethylene copolymerization with 1-octene catalyzed by methylaluminoxane-activated **4,** for various copolymerization conditions. To obtain information regarding the catalytically active sites, the copolymerization products were fractionated with toluene at room temperature and with boiling toluene, for 20 h each, followed by GPC and NMR analysis of the resulting fractions. As demonstrated by control fractionation, ^{13}C NMR spectra and GPC analysis of the corresponding fractions, the toluene-soluble fractions were ethylene/1-octene copolymers. As shown in Table 2, all the copolymerization products were almost 100% soluble in toluene. It was also found that the 1-octene content in both the room-temperature toluene and boiling toluene-soluble fractions was identical. This indicates that the copolymerization samples are homogeneous with respect to the 1-octene incorporation. Moreover, the toluene-soluble fractions had very-narrow-molecular-weight-distribution. These results suggest that the complex **4**, activated by MAO, is a single-site active catalyst. Similar single-site mechanisms have also been noted with other constrained geometry catalysts employed for the ethylene/1-octene copolymerization[3] or for the ethylene/styrene copolymerization.[11] In contrast, the conventional Ziegler−Natta catalysts, which contain several kinds of active sites, provide various fractions with different comonomer contents, comonomer distribution in a copolymer, and/or polymer molecular weights.

Ethylene and 1-octene were copolymerized in toluene at 40, 80, 100, and 160 °C (runs 1−4, Table 2) to investigate the temperature dependence of the activity. The results indicate a large increase in activity with increasing temperature. In addition, the molecular weight (M_w) increases as the temperature decreases. At 40 °C, the M_w of the copolymer is 4.29×10^5 while at 80 °C it becomes 3.2×10^5. This occurs because the β-H elimination requires a significant activation energy and the lowering of the temperature decreases its rate. Thus, the molecular weight of the copolymer increases. One can notice that the complex **4** leads to a high M_w (1.12×10^5) without a decrease in the copolymerization activity even at temperatures as high as 160 °C. This indicates that the catalyst is extremely stable. The stability of complex **4** is higher than that of the Me_4C_5-based catalyst, since the latter provides a copolymer molecular weight of 6.0×10^4 at 160 °C but with an appreciable decrease in the catalyst activity.

Table 2 shows that the catalyst activity, the 1-octene incorporation, and the molecular weight of the copolymer depend on the concentrations of the monomers (runs 2 and 9−13). Both the catalyst activity and copolymer molecular weight decrease substantially when the amount of the less reactive, more sterically hindered 1-octene is increased. The 1-octene incorporation is, however, proportional to the 1-octene content in the feed. With 1-octene concentrations varying between 0 and 1.70 mol/L, the 1-octene incorporation varied between 0 and 53.5 mol % (0 and 82 wt %). The 1-octene content in the copolymer reached 58.5 mol % when the much higher concentration of 4.25 mol/L of 1-octene was used in the feed. On the other hand, compared to 1-octene homopolymerization (runs 5−8), one can notice a significant increase in the copolymerization productivity and copolymer molecular weight upon addition of ethylene. This increase cannot be accounted for only by the faster rate of ethylene insertion relative to 1-octene. It mostly results from the so-called “comonomer effect”, which was observed in both heterogeneous and homogeneous Ziegler−Natta catalysts for ethylene copolymerization with olefins.[12] Indeed, the rate of 1-octene polymerization in the presence

Table 2. Ethylene Copolymerization with 1-Octene Using [η^5: η^1-(2-MeBenzInd)SiMe$_2$N^{t}Bu]TiCl$_2$/MAO Catalyst[a]

run	T_p, °C	Al/Ti, mol/mol	[octene], mol/L	[ethylene], mol/L	yield, g	10^{-7} A[b]	fractions in toluene, wt %[c]	1-octene content in copolymer, mol %[d]	T_g,[e] °C	T_m,[e] °C	crystallinity,[f] %	10^{-4} M_w,[g] g/mol	M_w/M_n[g]
1	40	1000	0.85	0.22	1.8	1.0	99.8					42.9	1.7
2	80	1000	0.85	0.22	5.5	3.1	100.0	42.5	−65.2	nd[h]	nil	32.7	1.8
3	100	1000	0.85	0.22	7.1	4.0	99.8	42.7		nd	nil		
4	160	1000	0.85	0.22	7.0	4.0		47.2				11.2	1.7
5	80	1000	4.25	0	3.0	0.4		100.0	−65.0			8.4	1.9
6	80	1000	4.25	0.01	7.3	1.0	99.7	58.5	−72.0	nd	nil	16.8	1.8
7	80	1000	1.70	0	1.2	0.4		100.0				8.0	1.7
8	80	1000	1.70	0.02	4.0	1.4						18.5	1.9
9	80	1000	1.70	0.22	5.0	1.6	100.0	53.5	−70.0	nd	nil		
10	80	1000	0.45	0.22	4.3	3.9	99.9	22.1	−57.0	nd	nil	35.5	1.8
11	80	1000	0.26	0.22	3.5	4.4	99.8	12.3	−46.5	58	14		
12	80	1000	0.16	0.22	3.1	4.9		5.5	−30.2	101	32	38.6	1.9
13	80	1000	0	0.22	1.8	4.9	0.3	0	−80.5	138	76	54.3	1.8
14	80	500	0.85	0.22	2.7	1.5		42.5	−65.2	nd	nil	21.9	1.7
15	80	2000	0.85	0.22	6.2	3.5	100.0	43.0				35.7	1.9
16	80	3000	0.85	0.22	7.5	4.2	99.9	42.8	−65.4	nd	nil	39.8	1.8

[a] Polymerization conditions: $P_E = 2.2{\sim}3.2$ bar, depending on polymerization temperature, [Ti] = 100 μmol/L, solvent toluene, total volume (1-octene + toluene) = 100 mL, polymerization time = 10 min. [b] A = activity in g of bulk polymer/[mol of Ti · mol of total monomers (ethylene + octene)·h]. [c] The 1-octene content in the copolymer in both ambient temperature toluene-soluble fractions and boiling toluene-soluble fractions is identical. [d] Determined by ^{13}C NMR. [e] Determined by DSC, heating rate of 10 K/min. [f] Determined by DSC. [g] Measured by GPC using polystyrene standards. [h] Not detectable.

Table 3. Effect of Polymerization Medium on Ethylene Copolymerization with 1-Octene Using the 4/MAO Catalyst[a]

run	polymerization medium	dielectric constant, ϵ	yield, g	10^{-7} A[b]	1-octene content in copolymer, mol %[c]	10^{-4} M_w[d], g/mol	M_w/M_n[d]
17	*o*-dichlorobenzene	9.93	8.9	5.0	43.1	34.1	1.9
18[e]	*o*-dichlorobenzene	9.93	8.0	4.5	43.2	14.5	2.0
19[f]	*o*-dichlorobenzene	9.93	7.1	4.0	45.3	10.5	1.8
20	*m*-dichlorobenzene	5.04	6.6	3.7	42.4	31.2	1.8
21	chlorobenzene	5.62	6.8	3.8	42.7	30.0	1.9
22	toluene	2.38	5.5	3.1	42.5	30.2	1.8

[a] Polymerization conditions: $P_E = 2.2{\sim}3.2$ bar, depending on polymerization medium and temperature, [ethylene] = 0.22 mol/L, [1-octene] = 0.85 mol/L, [Ti] = 100 μmol/L, MAO/Ti = 1000 mol/mol, total volume (1-octene + solvent) = 100 mL, polymerization time = 10 min, T_p = 80 °C. [b] A = activity in g of bulk polymer/[mol of Ti · mol of total monomers (ethylene + octene)·h]. [c] Determined by ^{13}C NMR. [d] Measured by GPC using polystyrene standards. [e] T_p = 140 °C. [f] T_p = 160 °C.

of ethylene is much higher than in its absence. This enhancement is likely a consequence of the higher number of active centers in the presence of ethylene.

The effect of MAO concentration on the copolymerization can be determined from runs 2 and 14−16 of Table 2. Increasing the Al/Ti mole ratio enhances both the catalyst activity and the copolymer molecular weight. This might be due to the stablization of the active site against deactivation and chain termination. Similar effects have been observed with other metallocene catalysts employed for olefin polymerization.[2]

The copolymerization parameters were calculated using the Fineman and Ross equation: $(1 - F)/f = r_2(F/f) - r_1$. Because this equation is valid at monomer conversions less than 10%, only data obtained at short polymerization time or low feed concentrations have been employed. These data are not listed in Table 2. The calculations provided the values $r_E = 2.26$ for ethylene and $r_O = 0.53$ for 1-octene ($r_E \cdot r_O = 1.20$). This indicates an almost random distribution of comonomer units in the copolymer chain, as also evidenced by the ^{13}C NMR spectra and the corresponding sequence assignment in the copolymers (vide infra). As expected, generally, a higher 1-octene content is associated with a lower-glass-transition temperature of the ethylene/1-octene copolymer (Table 2). Depending upon the 1-octene content in copolymers, the DSC results indicate that the present E−O copolymers are either semicrystalline or amorphous. Compared to polyethylene, we found that a 5.5 mol % 1-octene incorporation significantly decreases the melting temperature from 138 to 101 °C and the copolymer crystallinity from 76 to 32%. When the 1-octene content was increased to 12.3 mol %, the T_m and crystallinity became as low as 58 °C and 14%, respectively. The increased content and random distribution of 1-octene most probably facilitate the decreased crystallinity. In addition, a decay of crystallinity is probably due to the regioirregular arrangement of the 1-octene units in the copolymer caused by the tail-to-tail incorporation of a small amount of 1-octene (vide infra). This kind of incorporation is characteristic of complex **4** but does not occur in the previously employed catalysts. The higher the tail-to-tail incorporation of 1-octene, the lower the crystallinity of the copolymer. As shown in Table 2, when the 1-octene content was increased above 22 mol %, the copolymer became amorphous, without a detectable melting point and crystallinity. The copolymer with a 1-octene content higher than 20 mol % is an elastomer, which can be used as a component in polymer composites or alloys.[13]

The polymerization medium has a strong effect on the catalytic behavior of metallocenes.[1b,14] Therefore, the effect of the reaction medium on the catalytic activity of the complex **4** in the ethylene copolymerization with 1-octene was investigated by replacing toluene (dielectric constant $\epsilon = 2.38$) with o-dichlorobenzene ($\epsilon = 9.93$), m-dichlorobenzene ($\epsilon = 5.04$), or chlorobenzene ($\epsilon = 5.62$) (Table 3). The trends regarding the effect of temperature on M_w and activities in *o*-dichlorobenzene (runs 17−19, Table 3) are similar to those in toluene

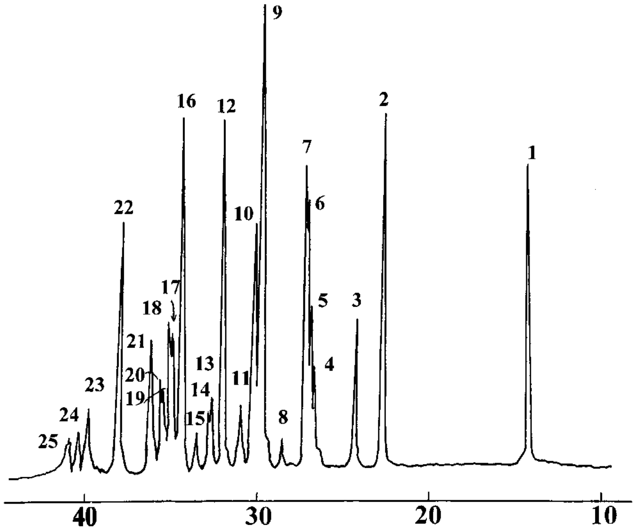


Figure 1. ^{13}C NMR spectrum of poly(ethylene-*co*-1-octene) obtained using the complex **4**/MAO Catalyst (run 2 in Table 2).

(runs 1−4, Table 2). However, the activity and its decrease with increasing reaction temperature are higher in *o*-dichlorobenzene. This indicates that a higher dielectric constant (ϵ) increases the activity but decreases more rapidly the stability of the active species with increasing reaction temperature. The activity increases because higher dielectric media substantially reduce the kinetic barrier to the separation of charged species in the ion pair formed between complex **4** and MAO, thus promoting the copolymerization activity.[14] However, the polymerization medium has no obvious effect on the 1-octene incorporation and the molecular weight of the copolymer.

Microstructure of Ethylene/1-Octene (E−O) Copolymers. Solvent extraction was carried out, followed by NMR analysis of the resulting fractions, to investigate the microstructure of the E−O copolymers. The nomenclature suggested by Kimura[9] will be employed. It was found that the spectra of the E−O copolymers of various 1-octene contents exhibited the same resonances, but with different relative abundances of the signals. The signal at 29.95 ppm, which can be partially assigned to the $S_{\delta\delta}$ carbon in the ethylene sequence of polyethylene, decreased moderately in relative abundance with increasing 1-octene incorporation, confirming the tendency of the ethylene monomer to form long sequences. On the other hand, the resonances at 26.95, 33.86, 35.70, and 41.37 ppm, which are near to those assigned to the $CH_2(5)$, CH, $CH_2(6)$, and $\alpha\alpha$ carbon in the 1-octene sequence (OOO) of poly(1-octene), were tremendously reduced in relative abundance after ethylene incorporation, indicating the trend of 1-octene toward forming isolated or very short sequences in the ethylene/1-octene copolymer. On the basis of the ^{13}C NMR spectrum of the 1-octene homopolymer, we assigned these resonances to the corresponding carbon in the sequences OOO and OOOO in E−O copolymers. The ^{13}C NMR spectrum of sample 2 (run 2 in Table 2) is presented in Figure 1 as an example. The chemical shift assignments are listed in Table 4. They were obtained by comparing the observed ones to those calculated with the empirical method of Grant and Paul.[15]

As revealed by Table 4, the E−O copolymers contain EOE, OOE, EOO, OEE, OEO, OOO, OEEO, EOOE, and other such sequences. However, the ^{13}C NMR spectrum of the E−O copolymer obtained via the complex **4** differs from those of the copolymers prepared via the Ziegler−Natta catalysts.[9,16] Compared to ^{13}C NMR spectra of the copolymers prepared by Kimura[9] and Randall,[16] the resolution of the spectrum of the present copolymer (Figure 1) is very high in the region 35.00−35.70 ppm, and consequently, the resonances at 35.00, 35.20, 35.45, and 35.70 ppm can be easily assigned to the sequences EOEO, OOEE, EOO + OOEO, and OOO. In addition, some of the resonances of the present E−O copolymer

Table 4. ^{13}C NMR Chemical Shift Assignments for Ethylene−1-Octene Copolymer Obtained with 4/MAO Catalyst[a]

peak no.	carbon assignment	sequence assignment	chemical shift calculated	chemical shift observed
1	CH_3	EOE + OOE + EOO + OOO	14.07	14.15
2	$CH_2(2)$	EOE + OOE + EOO + OOO	22.68	22.72
3	$\beta\beta$	OEO	25.11	24.85
4	$CH_2(5)$	OOO	27.56	26.95
5	$CH_2(5)$	EOO + OOE	27.56	27.27
6	$CH_2(5)$	EOE	27.56	27.40
7	$\beta\delta$	OEE + EEO	27.56	27.65
8	$\beta\gamma$	OEE$\underline{\mathbf{O}}$	28.05	28.15
9	$\delta\delta + CH_2(4)$	EEE + EOE + EOO + OOE + OOO	30.01	29.95
10	$\gamma\delta$	OEEE + EEEO	30.44	30.49
11	$\gamma\gamma$	OEEO	30.87	30.98
12	$CH_2(3)$	EOE + OOE + EOO + OOO	31.78	32.10
13	$\alpha\beta$	OOE$\mathbf{O}$ + $\mathbf{O}$EOO	32.44	32.65
14	$\alpha\beta$	EOE$\underline{\mathbf{O}}$ + $\underline{\mathbf{O}}$EOE	32.89	32.95
15	CH	OOO	33.22	33.86
16	$\alpha\delta + CH_2(6)$	EOEE + EEOE + EOE	34.89	34.85
17	$\alpha\gamma$	EOEO	35.22	35.00
18	$\alpha\delta + CH_2(6)$	OOEE + EEOO + EOO + OOE	35.52	35.20
19	$\alpha\gamma$	OOEO	35.75	35.45
20	$CH_2(6)$	OOO	35.75	35.70
21	CH	OOE + EOO	35.85	35.98
22	CH	EOE	38.00	38.18
23	$\alpha\alpha$	EOOE	39.77	39.81
24	$\alpha\alpha$	OOOE + EOOO	40.20	41.02
25	$\alpha\alpha$	OOO	40.63	41.37

[a] Methine carbons in the main chain are denoted CH; the branch carbons are denoted $CH_2(n)$ and the number (n) in parentheses indicates the position relative to the methyl group in the branch chain; the inverted 1-octene repeat unit in copolymer is denoted $\underline{\mathbf{O}}$.

can be attributed to the sequences OEE**O** (28.15 ppm), OOE**O** (32.65 ppm), and EOE**O** (32.95 ppm), which indicate the presence of inverted 1-octene repeat units caused by the tail-to-tail incorporation of 1-octene. It is found that the extent of tail-to-tail incorporation of 1-octene is proportional to its content in the copolymers, suggesting a regioirregular arrangement of 1-octene units. The regioirregular arrangement of 1-octene units results in a significant decrease in crystallinity, and even in the disappearance of the crystalline peaks at high contents of 1-octene (more than 20 mol %) as already noted.

The copolymerization parameters (r), calculated from the triad distribution in the NMR spectrum,[9,16,17] provided the values $r_E = 2.20$ for ethylene and $r_O = 0.55$ for 1-octene with $r_E \cdot r_O = 1.21$. They are almost identical to those calculated above by the Fineman−Ross method. These results clearly indicate that the complex **4** generates a random ethylene/1-octene copolymer.

According to ^{1}H NMR, only vinyl-type end groups, corresponding to the NMR resonance at 2.20 ppm, are present in the copolymer. This indicates that a termination via the β-hydride elimination occurred. A similar behavior was observed when the catalyst [(Me$_4$C$_5$)-SiMe$_2$N^{t}Bu]TiCl$_2$/MAO was used for the copolymerization of ethylene and 1-octene.[4a,4g] In contrast, only vinylidene end groups, corresponding to the NMR signal at 4.65 ppm, were detected with the bis-Cp metallocenes,[10] indicating that the mechanisms of chain termination are different in the two cases. It should be noted that when the catalyst based on complex **4** was used, a reinsertion of vinyl groups to formed chains occurred. This could be detected by monitoring the disappearance of the vinyl-type end group in the NMR spectrum, particularly at high polymerization temperatures.

Conclusion

A new constrained geometry titanium complex based on the 2-methylbenz[*e*]indenyl ligand [η^5:η^1-(2-MeBenzInd)SiMe$_2$N^{t}Bu]TiCl$_2$ (**4**) was synthesized as a catalyst precursor for the copolymerization of ethylene and 1-octene. When activated with methylaluminoxane (MAO), the complex **4** provided an improved copolymerization activity and stability, a good incorporation of 1-octene into the polyethylene main chain, and a significant increase of the molecular weight of poly(ethylene-*co*-1-octene), when compared with the previously employed catalysts. The present catalyst gave rise to a secondary insertion of 1-octene (as a tail-to-tail microstructure) in ethylene/1-octene copolymers.

The copolymerization behavior, catalyst activity, 1-octene incorporation in copolymers, and polymer molecular weight are dependent on the comonomer feeds, polymerization temperature, polymerization medium, and Al/Ti mole ratio. Both the molecular-weight distribution and the homogeneity with respect to 1-octene incorporation support the conclusion that the complex **4** is a single-site catalyst. The value of copolymerization parameters, calculated either by the Fineman−Ross equation or on the basis of the triad distribution in the NMR spectra ($r_E = 2.20$ and $r_O = 0.55$, $r_E \cdot r_O = 1.21$), indicates the formation of random copolymers. The copolymers containing more than 20 mol % 1-octene are amorphous, without detectable melting temperature and crystallinity, and can be employed as elastomers and blend toughening agents.

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(7) Lithium 2-methylbenz[*e*]indenide reacts with dichlorodimethylsilane in ether to give a mixture of chlorodimethyl(2-methylbenz[*e*]indenyl)silane and di(2-methylbenz[*e*]indenyl)-dimethylsilane which is difficult to separate. One way to reduce the amount of di(2-methylbenz[*e*]indenyl)dimethylsilane is to add an excess of dichlorodimethylsilane and to control the reaction temperature and the dropwise addition rate of lithium 2-methylbenz[*e*]indenide.

(8) The reaction of [(2-MeBenzInd)SiMe$_2$N(t-Bu)]Li$_2$ with TiCl$_4$-(THF)$_2$ often provides the complex (**4**) with much lower yields. High dilution and moderate mixing of a toluene solution of TiCl$_4$(THF)$_2$ and [(2-MeBenzInd)SiMe$_2$N(t-Bu)]Li$_2$ can slightly increase the yield.

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