

Polymerization of Higher α -Olefins with a Bis(Phenoxyimine)Ti Complex/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄: Formation of Stereo- and Regioirregular High Molecular Weight Polymers with High Efficiency

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ABSTRACT: The unique catalytic behavior of a bis(phenoxyimine)Ti complex combined with *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ (whose active species is a phenoxyamine Ti complex) is discussed here for use in the polymerization of higher α -olefins (i.e., 1-hexene, 1-octene, 1-decene, and 4-methyl-1-pentene). The catalyst system works as a single-site catalyst and exhibits high activities toward the higher α -olefins that were used in this study. The activities are comparable to or exceed those seen with a common metallocene catalyst, *rac*-[C₂H₄-(1-indenyl)₂]-ZrCl₂. The polymerization rate has a zeroth-order dependence on the concentration of the monomer. To our surprise, the system exhibited higher activities toward higher α -olefins that incorporate more sterically encumbered substituents in close proximity to the olefinic moieties (activity order: 4-methyl-1-pentene > 1-decene > 1-octene > 1-hexene). The resultant polymers have very high molecular weights (M_w 846 000–1 450 000), representing some of the highest reported for poly(higher α -olefins). Microstructural analyses using ¹³C NMR spectroscopy revealed that these high molecular weight polymers possess atactic structures with significant regioirregular units (ca. 50 mol %). Therefore, the catalyst system produced stereo- and regioirregular high molecular weight poly-(higher α -olefin)s (“ultra-random polymers”) with high efficiency.

Introduction

The benefits of molecular catalysts over heterogeneous Ziegler–Natta catalysts for olefin polymerization include the ability to produce narrow molecular weight distribution polymers with controllable regioregularity, stereoregularity, comonomer incorporation, and molecular weight. Consequently, molecular catalysts may display greater control over the properties of the resultant polymers relative to the ill-defined heterogeneous Ziegler–Natta catalysts and, in addition, may help to create polymers with new molecular architectures. The development of group 4 metallocene catalysts and related catalysts, which was initiated in the early 1980s, has enabled the preparation of a variety of polymers with a wide range of macromolecular structures and new or enhanced material properties.¹

Additionally, the recent advent of high-performance non-metallocene catalysts (with no Cp ligands) has offered a great opportunity for producing a variety of polyolefinic materials that are unobtainable by using group 4 metallocene catalysts and related catalysts [e.g., highly branched polyethylenes (PEs), functionalized PEs, high molecular weight monodisperse poly-(1-hexene)s, and polyolefinic block copolymers].^{2–5} These unique polymers are anticipated to possess novel material properties that will open up new applications.

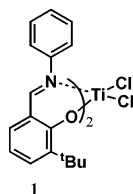
A major focus of our work has involved the development of molecular olefin polymerization catalysts based on transition metal complexes that contain nonsymmetric ligands with electronically flexible properties (ligand-oriented catalyst design research). This approach has led to the discovery of a number of families of transition metal complexes featuring nonsymmetric [O[−], N], [N[−], N], [N, N], [O[−], O], or [O[−], N, N] chelate ligands for olefin polymerization.^{6–10} Among these complexes, bis(phenoxyimine) early transition metal complexes (now known

as FI catalysts) are particularly useful for the preparation of a variety of polyolefinic materials that exhibit unique microstructures.¹¹ For example, upon activation by an appropriate activator, FI catalysts can form vinyl-terminated PEs, Al-terminated PEs, and highly isotactic and syndiotactic polypropylenes (iPPs and sPPs) with extremely high T_m s.^{12,13} Moreover, FI catalysts are capable of producing high molecular weight atactic poly(1-hexene)s containing a high proportion of regioirregular units, well-defined and controlled bi- and trimodal PEs, and a wide array of polyolefinic block copolymers from ethylene, propylene, and higher α -olefins.¹⁴ Many of these FI polymers were unavailable prior to our work.^{6,11} This versatility of FI catalysts vis-à-vis polymer synthesis arises because FI catalysts provide a wide range of catalyst design capability, and in addition, FI catalysts can generate structurally different active species depending on the particular activator that is employed (i.e., MAO:phenoxyimine complex, *i*-Bu₃Al/Ph₃CB(C₆F₅)₄:phenoxyamine complex).¹¹ Recent research performed by Bochmann, Busico, Coates, Pellecchia, Talsi, and others has contributed significantly to the further development of FI catalysts and related complexes, providing useful information about the mechanism for catalysis when using this important class of new-generation olefin polymerization catalysts.^{11,15}

In this article, we present the higher α -olefin polymerization¹⁶ behavior of a bis(phenoxyimine) Ti complex combined with *i*-Bu₃Al/Ph₃CB(C₆F₅)₄, which forms a phenoxyamine Ti complex as a catalytically active species. The catalyst system displays higher activities toward higher α -olefins with sterically bulkier substituents and provides regio- and stereoirregular polymers possessing extremely high molecular weights, with high efficiency. These results are of great significance, since stereo- and regioerrors typically result in reduced catalytic activity and low molecular weight products.

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Scheme 1. Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]titanium(IV) Dichloride (**1**)



Results and Discussion

1-Hexene Polymerization Using Complex **1 with MAO or *i*-Bu₃Al/Ph₃CB(C₆F₅)₄.** The bis(phenoximine) Ti complex (complex **1**, Scheme 1) used in this study is bis[*N*-(3-*tert*-butylsalicylidene)anilinato]titanium(IV) dichloride, which was prepared and purified according to published procedures.^{7f} As reported, complex **1** forms structurally different catalytically active species as a result of using methylaluminoxane (MAO) and *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ as an activator. Namely, complex **1** with MAO generates a phenoximine complex (as expected), whereas with *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ it forms a phenoxamine complex as the catalytically active species.^{7f,12c} It has been suggested that a phenoxamine ligand for the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system is produced from the reduction of a phenoximine ligand by *i*-Bu₃Al (and its contaminant *i*-Bu₂AlH) with concurrent formation of isobutene (Scheme 2).

A reduction process such as this has also been observed for bis(phenoximine)Zr or Hf complexes,^{7c,g,12c} a relevant imine-phenoxo Ti complex [1-(N=CH-Ph)-2-O-3,5-di-*t*-Bu-C₆H₃]₂-TiCl₂,^{10d} and other group 4 transition metal complexes that contain phenoximine ligands.¹⁵ⁱ This suggests that the reduction of the imine moiety of a phenoximine group 4 metal complex by *i*-Bu₃Al (and its contaminant *i*-Bu₂AlH) is not unusual, though little has been reported about such a reduction of free imine functionality.

Since phenoximine and phenoxamine ligands possess considerably different electronic and steric characteristics, we were interested in the catalytic behavior of complex **1** with MAO and *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ for the polymerization of sterically encumbered higher α -olefins, which may yield further insights into how the ligand affects the polymerization catalysis of phenoxy-based catalysts.

Complex **1** was investigated for its potential as a catalyst for 1-hexene polymerization using MAO or *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ as an activator at 25 °C in an *n*-heptane solvent. Complex **1** in combination with MAO displayed practically no reactivity toward 1-hexene, generating neither polymeric nor oligomeric materials. We noted that the complex **1**/MAO system exhibits very high activity for ethylene polymerization and much lower activity for propylene polymerization, by a factor of 1/1000.^{7a,f,12e} Therefore, the inactivity toward 1-hexene probably stems from the fact that a cationic phenoximine complex originating from complex **1** with MAO possesses insufficient space for 1-hexene polymerization.

Table 1. Results of 1-Hexene Polymerization with Complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ at Various Temperatures^a

entries	temp (°C)	yield (g)	TOF ^b (min ⁻¹)	conv ^c (%)	<i>M</i> _w ^d (×10 ³)	<i>M</i> _w / <i>M</i> _n ^d
1	0	0.235	56	0.9	652	1.61
2	10	0.547	130	2	778	1.49
3	25	0.930	221	3	719	1.73
4	40	1.010	240	4	659	1.68
5	60	1.310	311	5	551	1.90

^a Conditions: *n*-heptane 50 mL, 1-hexene 40 mL (0.320 mol), pretreated solution of complex **1** (5 μ mol)/*i*-Bu₃Al (0.15 mmol), Ph₃CB(C₆F₅)₄ (0.006 mmol), *i*-Bu₃Al (0.05 mmol), polymerization time 10 min. ^b Turnover frequency. ^c Calculated by (polymer yield (g)/total monomer (g)) × 100. ^d Determined by GPC using polystyrene calibration.

Table 2. Polymerization Results with Complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ at Various 1-Hexene Concentrations^a

entries	[1-hexene] (mol/L)	yield (g)	TOF ^b (min ⁻¹)	conv ^c (%)	<i>M</i> _w ^d (×10 ³)	<i>M</i> _w / <i>M</i> _n ^d
1	0.5	0.274	651	7	600	1.69
2	0.75	0.288	684	5	666	1.76
3	1.5	0.248	589	2	711	1.89
4	3.0	0.225	542	1	735	1.70

^a Conditions: solvent *n*-heptane, 1-hexene (total volume 90 mL), 25 °C, 5 min, pretreated solution of complex **1** (1 μ mol)/*i*-Bu₃Al (0.03 mmol), Ph₃CB(C₆F₅)₄ (2 μ mol), *i*-Bu₃Al (0.17 mmol). ^b Turnover frequency. ^c Calculated by (polymer yield/total monomer) × 100. ^d Determined by GPC using polystyrene calibration.

Conversely, on activation with *i*-Bu₃Al/Ph₃CB(C₆F₅)₄, complex **1** furnished an amorphous, sticky polymer with high efficiency (TOF 257 min⁻¹) under the same polymerization conditions as were used for the MAO activation (Table 3, entry 1). GPC analysis revealed that the poly(1-hexene) that was produced possesses a very high *M*_w of 846 000, which represents one of the highest reported molecular weights for poly(1-hexene)s. The narrow molecular weight distribution (*M*_w/*M*_n) of 1.65 is consistent with the operation of a single-site catalyst. As reported in our previous paper, the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system is long-lived and has a catalytic lifetime of at least 60 min for the polymerization of 1-hexene at 25 °C.^{14a} The high activity, single-site behavior and long life of the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system indicate the very high potential of this catalyst system for the polymerization of 1-hexene.

When the polymerization was conducted in a toluene solvent instead of in *n*-heptane, the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system did not exhibit any polymerization activity toward 1-hexene. This observation can probably be attributed to the suppression of 1-hexene coordination to the Ti center due to coordination competition between toluene and the 1-hexene, leading to the prevention of polymerization in the toluene solvent. Similar deleterious effects of the toluene solvent on ethylene and propylene polymerization with the same catalyst system were also observed.^{7f,17} McConville et al. reported a similar observation for 1-hexene polymerization with diamide-ligated Ti complexes.^{3f,g}

Scheme 2. Plausible Pathway for the Formation of an Active Species Derived from Complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄

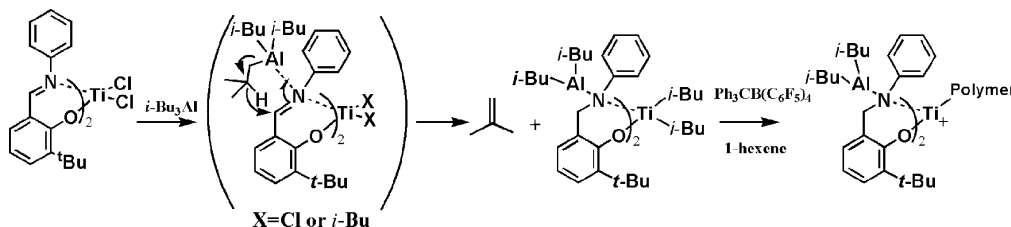


Table 3. Higher α -Olefin Polymerization Results with Complex **1** and *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ 2/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄^a

entries	complexes	monomer	yield (g)	TOF ^b (min ⁻¹)	conv ^c (%)	M_w^d ($\times 10^3$)	M_w/M_n^d
1	1	1-hexene	2.166	257	12	846	1.65
2	1	1-octene	3.230	288	14	906	1.68
3	1	1-decene	4.327	308	15	850	1.75
4	1	4-methyl-1-pentene	5.004	595	28	1450	1.71
5	2	1-hexene	5.334	634	30	60	1.85
6	2	1-octene	3.870	345	16	49	1.59
7	2	1-decene	4.136	295	14	42	1.77
8	2	4-methyl-1-pentene	1.110	132	6	35	1.68

^a Conditions: monomer (0.211 mol), *n*-heptane (total volume 90 mL), 25 °C, 20 min, pretreated solution of complex **1** or **2** (5 μ mol)/*i*-Bu₃Al (0.15 mmol), Ph₃CB(C₆F₅)₄ (0.006 mmol), *i*-Bu₃Al (0.05 mmol). ^b Turnover frequency. ^c Calculated by (polymer yield (g)/total monomer (g)) $\times$ 100. ^d Determined by GPC using polystyrene calibration.

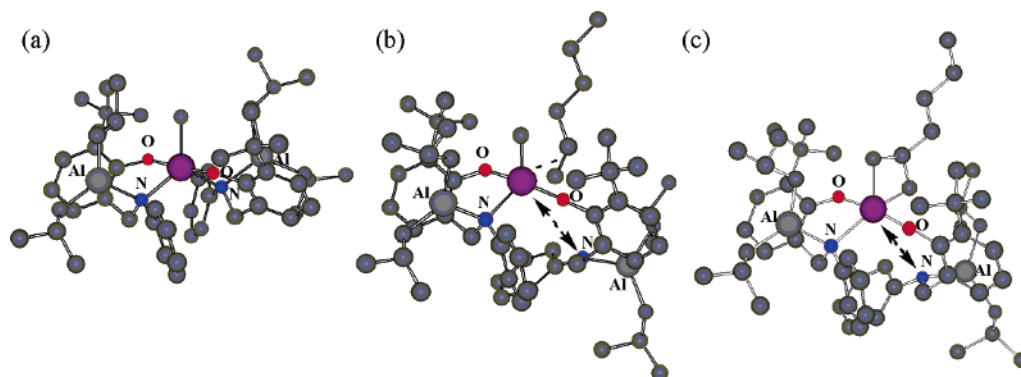


Figure 1. Calculated structures of cationic phenoxyamine complexes in the absence of 1-hexene (a), in the presence of 1-hexene (1-hexene-coordinated state) (b), and for transition state (c) (polymer chain model: methyl group).

Considering that an amine nitrogen with an alkylaluminum group is a weaker donor than an imine nitrogen, and thus provides a weaker N–Ti interaction, the great difference in catalytic behavior between the phenoxyimine complex (MAO activation) and the phenoxyamine complex (*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ activation) is presumably associated with the fact that the phenoxyamine complex potentially provides a larger space for polymerization and possesses higher electrophilicity at the Ti center than the phenoxyimine complex. Since we have not yet succeeded in the isolation and characterization of a catalytically active phenoxyamine complex, DFT calculations¹⁸ were performed on a cationic phenoxyamine Ti complex with a *i*-Bu₂Al group on the amine donor in order to gain more insight into the structure of the active species (Figure 1). As a result, the cationic complex was shown to assume a distorted trigonal-bipyramidal geometry with a trans-O disposition (Ti–N distance 2.19, 2.21 Å; Ti–O distance 1.88, 1.89 Å).¹⁹ Interestingly, the calculations also suggest that a (1-hexene)-coordinated cationic complex assumes a square-pyramidal geometry, in which one of the amine donors on the phenoxyamine ligands is detached from the central metal (Ti–N distance 4.37 Å, Figure 1b), resulting in the loss of C₂ symmetry. In addition, one of the amine donors also becomes detached during a transition state leading to 1-hexene insertion (Ti–N distance 3.75 Å, Figure 1c). This detachment is probably due to steric repulsion between a coordinated 1-hexene and the *i*-Bu₂Al group on the amine donor, suggesting that 1-hexene is a better donor than an Al-attached amine nitrogen for the Ti center. The formal lower electron count [the cationic phenoxyamine complex is a 12-electron species (excluding the 2-electron donation from 1-hexene) during the course of the polymerization, as compared with the 14-electrons for the cationic phenoxyimine complex] is likely to lead to a highly electrophilic catalyst fragment, which is consistent with inactivity in a toluene solvent. Additionally, the detachment of one of the amine donors may result in a catalyst that displays a low degree of polymerization stereocontrol. In

fact, complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ was revealed to form atactic poly(1-hexene)s, which will be discussed later.

1-Hexene Polymerization Behavior of the Complex **1 Catalyst System.** The results of 1-hexene polymerization with the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system at five different polymerization temperatures (0, 10, 25, 40, and 60 °C) are collected in Table 1.

It can be seen from Table 1 that increasing the polymerization temperature afforded a corresponding increase in catalytic activity. Thus, the catalyst system furnished an activity of 56 min⁻¹ at 0 °C (entry 1), and its activity increased to a very high value of 311 min⁻¹ at 60 °C (entry 5). The poly(1-hexene)s that were produced possess narrow molecular weight distributions (M_w/M_n 1.49–1.90), suggesting that the polymers are formed from a single polymerization site, with practically fixed rates of chain propagation and termination for each temperature. The molecular weights are very high (M_w 551 000–778 000) over the temperature range 0–60 °C, and therefore the polymerization temperature has no significant effect on the molecular weights over these temperatures. It is particularly noteworthy that the system forms high molecular weight poly(1-hexene)s at increased temperatures, since an increase in the polymerization temperature normally enhances the rate of chain termination relative to that of chain propagation, resulting in low molecular weight products.

A series of experiments performed at four different 1-hexene concentrations (0.5–3.0 mol/L) were undertaken to obtain further insight into polymerization catalysis using the complex **1** catalyst system.

Table 2 displays the polymerization results. To our surprise, changes in the 1-hexene concentration have little influence on the polymerization behavior of the catalyst system. Thus, the polymerization rate and the product molecular weight have practically a zeroth-order dependence on the 1-hexene concentration. While a zeroth-order dependence on monomer concentration is observed with Ni-based olefin polymerization cata-

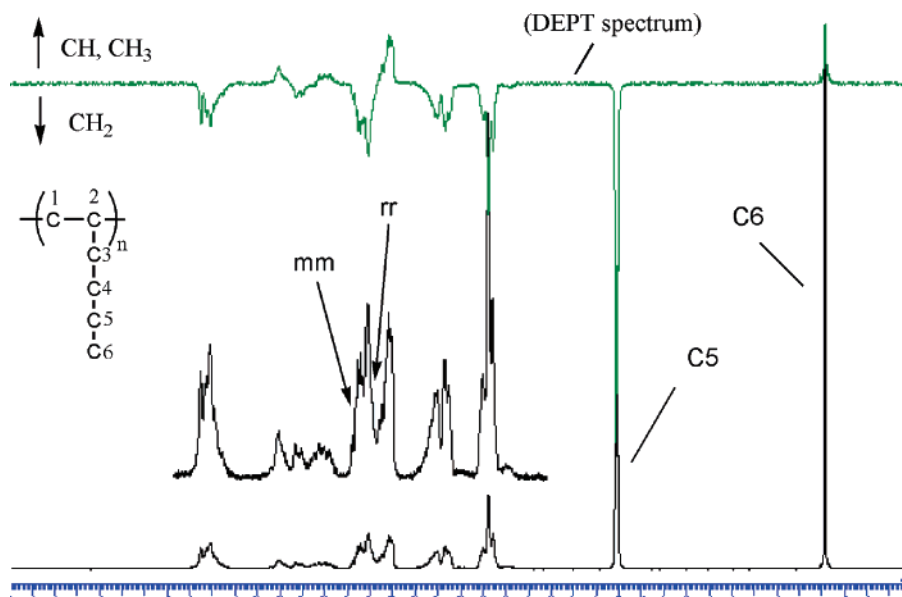


Figure 2. ^{13}C NMR spectrum for the poly(1-hexene) formed with complex **1** (Table 3, entry 1).

lysts,²⁰ this is a rare example for a group 4 metal-based catalyst. In fact, for the *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ **2**/MAO catalyst system, the rate of propagation has been reported to be first order with respect to 1-hexene concentration.^{16p} Although the reason for the zeroth-order dependence is unclear at the current time, one possible explanation is that, under the conditions examined, the cationic complex virtually exists as a (1-hexene)-coordinated form, presumably due to the highly electrophilic as well as sterically open nature of the cationic active species.²¹ The elucidation of the zeroth-order dependence will be the subject of future investigation at our laboratory, which will provide further information about the nature of the catalyst system.²²

Higher α -Olefin Polymerization Behavior of Complex **1/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄.** In view of the intriguing results obtained for the 1-hexene polymerization trials, the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ system was evaluated as a catalyst for the polymerization of 1-octene, 1-decene, and 4-methyl-1-pentene. These α -olefins possess sterically bulkier substituents than 1-hexene. Polymerizations were performed with the same monomer concentration conditions (2.11 mol/L) at 25 °C in an *n*-heptane solvent. For comparison, the polymerization results of *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (**2**) as well as the 1-hexene polymerization results with complexes **1** and **2** are also included in Table 3.

The monomer conversions obtained under the conditions that were studied fell in the ranges between 12 and 28% (complex **1**) and 6–30% (complex **2**). The activities displayed by the complex **1** catalyst system lie in the range of 257–595 min^{−1}, which are comparable or superior to those seen with **2**. A striking feature observed for the complex **1** catalyst system is that an increase in the molecular size of the reacting olefin resulted in enhanced catalytic activity (activity order: 4-methyl-1-pentene > 1-decene > 1-octene > 1-hexene). This is remarkable because an olefin polymerization catalyst normally shows lower reactivity toward sterically larger olefins due to steric hindrance, as observed for *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (**2**), whose activity decreased with increasing molecular size of the reacting olefin. One explanation for this unusual behavior is that a sterically bulkier side chain derived from the last-inserted α -olefin of the growing polymer chain opens the phenoxyamine ligands wider, thereby facilitating the coordina-

tion of the α -olefin to the metal and its insertion into the metal–carbon bond. This postulate may provide a strategy for the design of catalysts with a high incorporation ability for sterically large monomers. Notably, the complex **1** catalyst system displayed far higher activity than *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (**2**) with respect to 4-methyl-1-pentene polymerization (entries 4 and 8). The high reactivities exhibited by the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system toward 1-octene, 1-decene, and 4-methyl-1-pentene suggest the structurally open nature of the active species and, at the same time, the high potential of the complex **1** catalyst system for the polymerization of sterically bulky monomers.

The resultant poly(higher α -olefin)s possess very high molecular weights (*M_w*s) ranging from 846 000 to 1 450 000; these values are an order of magnitude larger than those seen with *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (*M_w* 35 000–60 000). As far as we are aware, the molecular weights of the poly(1-octene) and the poly(1-decene), in addition to that of the poly(1-hexene), represent some of the highest values reported to date for molecular olefin polymerization catalysts. Moreover, the molecular weight of the poly(4-methyl-1-pentene) (*M_w* 1 450 000) is probably the highest among poly(4-methyl-1-pentene)s ever synthesized. The molecular weight distributions (*M_w*/*M_n*) of the polymers lie in the range 1.65–1.75, indicating that all of the high molecular weight poly (higher α -olefin)s are produced by a chemically homogeneous catalyst.

Microstructures of the Poly(higher α -olefin)s That Were Produced. The microstructure of a sample of poly(1-hexene) that was generated using the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system was investigated using ^{13}C NMR spectroscopy. The assignments were based on the results of distortionless enhancement by polarization transfer (DEPT) NMR experiments, on the relative peak intensities, and on a comparison of the observed chemical shifts with the calculated data as well as data from the literature.^{16l,m,p,23}

Figure 2 demonstrates the ^{13}C NMR spectrum of poly(1-hexene) formed with the complex **1** catalyst system (Table 3, entry 1).

The spectrum involves peaks attributable to isotactic triads (*mm*: 34.7–34.9 ppm) and syndiotactic triads (*rr*: 33.9–34.0 ppm) that are very weak relative to the other peaks. These results indicate the atactic nature of the polymer. This very low degree

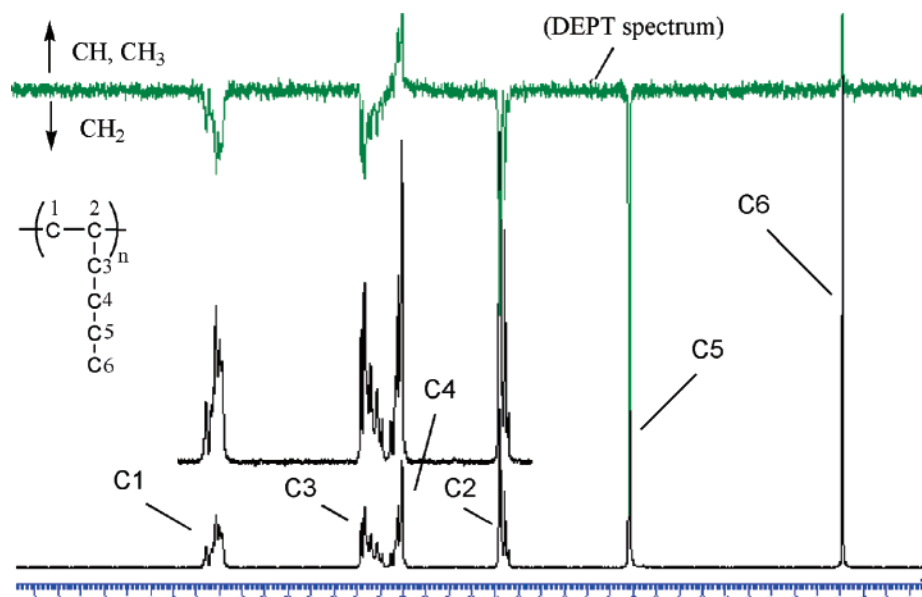


Figure 3. ^{13}C NMR spectrum for the poly(1-hexene) formed with $[\text{ArN}(\text{CH}_2)_3\text{NAr}]\text{TiCl}_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$)/ $i\text{-Bu}_3\text{Al}/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$.

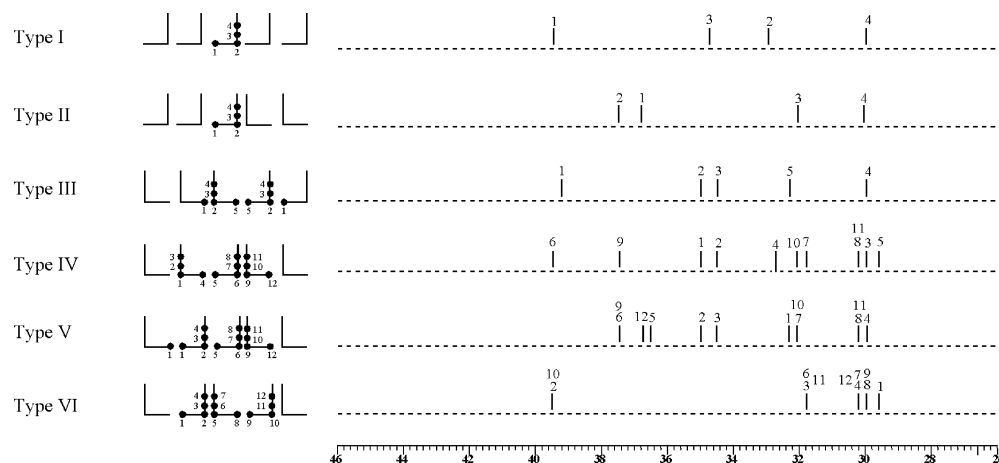


Figure 4. Possible linkage types I–VI and calculated ^{13}C NMR chemical shifts for poly(1-hexene).

of polymerization stereocontrol further confirms the structurally open nature of the catalytic site. The formation of a high molecular weight (M_w 846 000) atactic polymer is highly significant because aspecific catalysts normally produce low molecular weight polymers. The sharp peaks at 13.9 and 23.2 ppm are assigned to the methyl carbon (C6) and its neighboring methylene carbon (C5) in the side chain, respectively. For comparison, the spectrum of the atactic and regioregular poly(1-hexene) produced with $[\text{ArN}(\text{CH}_2)_3\text{NAr}]\text{TiCl}_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$)/ $i\text{-Bu}_3\text{Al}/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, as developed by McConville et al., is displayed in Figure 3.^{3f,g,24}

The spectrum corresponding to poly(1-hexene) produced using the complex **1** catalyst system (Figure 2) exhibits complex additional peaks in the regions around 30.3–31.9 and 35.4–38.5 ppm when compared with the spectrum obtained using the McConville Ti catalyst (Figure 3). These peaks probably originate from enchainment regioerrors. DEPT experiments suggest that the peaks in the regions around 35.4–36.7 and 37.6–38.5 ppm are derived from methine carbons and that the peaks in the regions around 30.3–31.9 and 36.8–37.4 ppm originate from methylene carbons, respectively. The ^{13}C NMR chemical shifts calculated according to the Lindeman–Adams empirical rules²⁵ for possible six linkage types I–VI with several different sequences involving chemical inversion units are summarized in Figure 4.²⁶

Considering the peak intensities together with the calculated chemical shifts and the DEPT results, the peaks in the region around 35.4–36.7 ppm can be assigned to the methine (C2) carbons on the polymer backbone for linkage types III and V (Figure 5). Additionally, the peaks in the regions around 36.8–37.4 and 37.6–38.5 ppm are attributed to the methylene (C1) and methine (C2) carbons on the polymer backbone of linkage type V, respectively.

The peaks in the region of 30.3–31.9 ppm are attributable to the methylene carbons (C1, C3) of linkage types III and V. Likewise, the other peaks in the regions around 28.3–29.2, 32.9–33.7, 33.7–34.9, and 40.2–41.8 ppm can be assigned on the basis of similar considerations (Figure 5). The differences between the calculated and observed values probably originate from the influence of stereoirregularity.

The relative peak intensities indicate that the poly(1-hexene) does not contain linkage types II, IV, and VI and that the ratio of linkage types I, III, and V is 45/22/33. Consequently, the high molecular weight poly(1-hexene) has an atactic structure with ca. 50 mol % of regiorregular units.²⁷ Considering that a 2,1-regioerror can have a detrimental effect on polymer molecular weights and normally encourages chain termination (which usually leads to low molecular weights), the production of high molecular weight poly(1-hexene) including frequent regioerrors is of great significance. We noted that the content

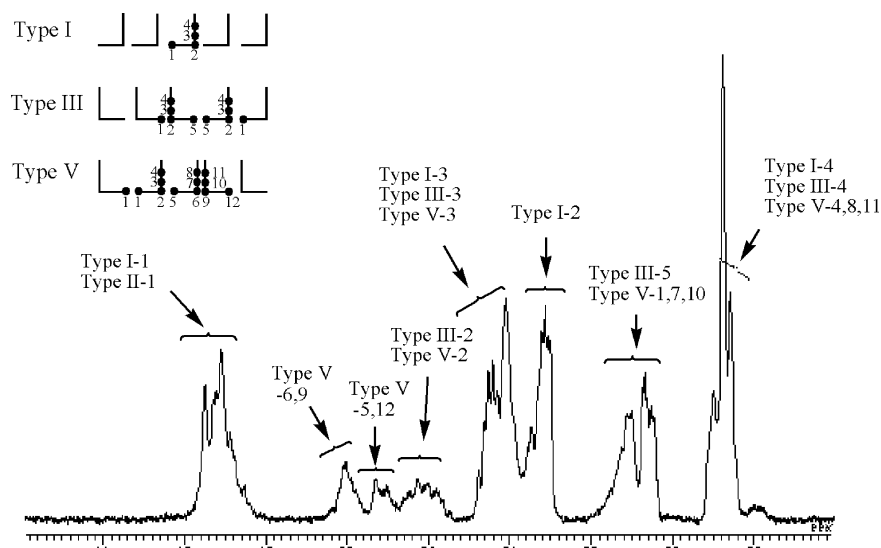


Figure 5. Assignments for the poly(1-hexene) formed with complex 1.

of regioerrors (ca. 50 mol %) is much higher than that for polypropylene (regioirregular units 9 mol %) produced using the same catalyst system.^{12c} The increased 2,1-insertion for 1-hexene polymerization is presumably derived from the enhanced steric congestion provided by the poly(1-hexene) chain attached to the Ti center relative to the polypropylene chain. The steric congestion places the butyl substituent of the reacting 1-hexene in the opposite direction to the polymer chain, resulting in a preference for 2,1-insertion.

Likewise, the microstructures of the poly(1-octene) and poly(1-decene) formed using the complex 1 catalyst system were analyzed by means of ¹³C NMR and were found to be similar to that of the poly(1-hexene) (see Supporting Information). Namely, the poly(1-octene) and poly(1-decene) possess atactic structures with 56 mol % [poly(1-octene): linkage type I 44 mol %, III 24 mol %, V 32 mol %] and 58 mol % [poly(1-decene): linkage type I 42 mol %, III 25 mol %, V 33 mol %] of regioirregular units, respectively.

Therefore, the high molecular weight poly(higher α -olefin)s synthesized using the complex 1 catalyst system possess atactic structures with significant regioirregular units (ca. 50 mol %). It is worth noting that the complex 1 catalyst system forms highly regioirregular, high molecular weight poly(higher α -olefin)s with high efficiency because 2,1-insertions typically lower both catalytic activity and product molecular weight through competing chain release processes.²⁸ These are probably the first examples of high molecular weight poly(higher α -olefin)s with atactic structures containing a significant amount of regioirregular units. We have given the name "ultra-random polymers" to these stereo- and regioirregular high molecular weight poly(higher α -olefin)s. Because of their high molecular weights and their sticky and transparent nature, these ultra-random polymers may serve as adhesives and/or additives. Research into the properties of ultra-random polymers is already underway as well as more detailed catalysis studies.

Conclusion

The higher α -olefin polymerization behavior of a bis-(phenoxyimine) Ti complex with the *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ and MAO catalyst systems has been discussed. Although the MAO activation system (a phenoxyimine complex) is a poor catalyst, the *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ activation system (a phenoxyamine complex) produces very high molecular weight poly(higher α -olefin)s, displaying high activity with a zeroth-order depen-

dence on the monomer concentration. DFT calculations suggest that one of the amine donors is detached during the course of the polymerization. The polymerization activity increases as the molecular size of the reacting monomer increases. The very high molecular weight poly(higher α -olefin)s possess atactic structures with ca. 50 mol % of regioirregular units. The formation of stereo- and regioirregular high molecular weight poly(higher α -olefin)s (ultra-random polymers) with high efficiency is highly significant. The catalyst system introduced herein demonstrates the unique catalytic properties of a phenoxyamine ligated Ti complex and may provide a strategy for the design of catalysts with high incorporation capability for sterically encumbered monomers.

Experimental Part

General Procedures and Materials. All manipulations of air- and/or water-sensitive materials were performed under a dry nitrogen atmosphere using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Anhydrous solvents (dichloromethane (CH₂Cl₂) and toluene) were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. *n*-Heptane (Wako Pure Chemical Industries, Ltd.) was dried over Al₂O₃. *i*-Bu₃Al (Tosoh Fine Chem. Corp.) and Ph₃CB(C₆F₅)₄ (Asahi Glass Co.) were used as received. MAO was purchased from Tosoh Fine Chem. Corp. 1-Hexene, 1-octene (Mitsubishi Chem. Co.), 1-decene (Wako Pure Chemical Industries, Ltd.), and 4-methyl-1-pentene (Mitsui Chemicals) were dried over Al₂O₃. *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ was synthesized by following a published method.²⁹ All of the other chemicals were obtained commercially and were used as supplied.

General Polymerization Procedure. Polymerizations were carried out using a 200 mL glass reactor equipped with a mechanical stirrer, a temperature probe, and a condenser. A solution of a prescribed amount of higher α -olefin in *n*-heptane (90 mL) and a solution of a prescribed amount of 0.25 M *i*-Bu₃Al solution in *n*-heptane were added to the nitrogen-purged reactor. The resulting mixture was kept at 25 °C. A mixture of a prescribed amount of complex 1 or 2 and 30 equiv of *i*-Bu₃Al in *n*-heptane (8.0 mL) was prepared in a Schlenk tube and stirred for 10 min at room temperature. The resulting *n*-heptane solution and a prescribed amount of Ph₃CB(C₆F₅)₄ solution in CH₂Cl₂ were added to the reactor in that order to initiate polymerization. After a prescribed time, the polymerization was terminated by adding MeOH (2 mL). The resulting solution was washed with acidic water (50 mL containing 2 mL of concentrated HCl) and then with water (50 mL $\times$ 2). The organic layer was concentrated in vacuo at 40 °C and dried overnight in a vacuum oven at 130 °C.

The molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the poly(1-hexene), poly(1-octene), poly(1-decene), and poly(4-methyl-1-pentene) were determined using a Waters 150-C gel permeation chromatograph equipped with Waters-Styragel columns 10^5 and 10^6 Å at 40 °C, using polystyrene calibration. CHCl_3 was used as a solvent at a flow rate of 1.5 mL/min. ^{13}C NMR spectra for the polymers were recorded on either a JEOL-LA 500 or a JEOL EX270 spectrometer at 125 or 67.5 MHz at 120 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ solvent, with a peak for 13.86 ppm derived from methyl carbon in the side chain as an internal standard.

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Supporting Information Available: DFT calculation results for cationic phenoxyamine complexes; ^{13}C NMR spectra of the poly(1-octene) and poly(1-decene) together with calculated chemical shifts for linkage types I–VI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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