

Higher α -Olefin Polymerization Behavior of a Bis(Phenoxy-Imine)Titanium Complex/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ Catalyst System

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Catalytic behavior of a bis(phenoxy-imine)Ti complex/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system for higher α -olefin polymerization was investigated. The catalyst system exhibited higher activities towards α -olefins having larger molecular sizes and formed ultra-high molecular weight poly(higher α -olefin)s.

The search for olefin polymerization catalysts that have the ability to incorporate large monomers (e.g., higher α -olefins, styrene, norbornene and their derivatives) with high productivity has been intense. This is because such catalysts may provide access to polyolefinic materials with new or enhanced performance parameters. The development of single-site catalysts, represented by group 4 metallocenes,¹ half-sandwich Ti amide complexes,² and recently-emerging post-metallocenes,³ has allowed for the preparation of a variety of high performance polymers involving or consisting of large monomers, such as linear low-density polyethylenes, high molecular weight poly(1-hexene)s, ethylene-styrene interpolymers (ESI), syndiotactic polystyrenes (sPS), and cyclic olefin copolymers (COC), all of which are difficult or impossible to prepare using conventional heterogeneous catalysts. Therefore, single-site catalysts have revolutionized polyolefin chemistry.

Despite the enormous advancement made with single-site catalysts, one limitation remains: the polymerization rate for α -olefins, generally, decreases with the increase in molecular size of reacting monomers due to steric hindrance, which is normally accompanied by reduced molecular weight of the resulting polymer. These facts restrict the preparation of sterically-bulky-monomer-based polymers having high molecular weights. Accordingly, the development of catalysts capable of incorporating monomers independent of their steric bulk and, at the same time, producing high molecular weight polymers, is badly required.

Previously, on the basis of a ligand-oriented catalyst design

concept,⁴ we have developed a new family of bis(phenoxy-imine) group 4 metal complexes, named FI Catalysts.⁵ These catalysts display unique performance for olefin polymerization. Recently, we found that Ti-FI Catalysts polymerized 1-hexene to produce high molecular weight atactic poly(1-hexene) including frequent regioerrors.^{5c} Further research led us to the discovery of highly unusual polymerization behavior of Ti-FI Catalysts. In this communication, we describe unprecedented catalytic behavior of a Ti-FI Catalyst for the polymerization of higher α -olefins.

The complex, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]titanium(IV)dichloride (**1**), was investigated for its potential as a higher α -olefin polymerization catalyst. Thus, polymerizations of 1-hexene,⁶ 1-octene, and 1-decene with the complex **1** using methylalumoxane (MAO) or *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ as a cocatalyst were carried out at 25 °C.

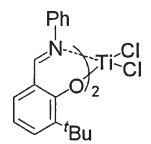


Figure 1. Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]titanium(IV)-dichloride **1**.

Upon activation with MAO, the complex **1** displayed virtually no reactivity towards these higher α -olefins, producing neither polymeric nor oligomeric materials. Taking into account the fact that the complex **1** with MAO converted ethylene to high molecular weight polyethylene with high activity^{5a,b} the poor results obtained with the higher α -olefins probably stem from steric hindrance: the catalytically active species possesses insufficient room for the polymerization of higher α -olefins.⁷

In sharp contrast, the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system was an active catalyst for higher α -olefin polymerization and furnished amorphous, sticky polymers under the same conditions. The relevant results are collected in Table 1, which also includes the results with *rac*-[C₂H₄-(1-in-

Table 1. Polymerization results with *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ cocatalyst

Run	Complex	Monomer	Yield /g	TOF /min ⁻¹ ·[monomer/mol·L ⁻¹]	<i>M</i> _w ^a /10 ⁴	<i>M</i> _w / <i>M</i> _n ^a
1	1	1-hexene	2.173	80.7	72	1.68
2	1	1-octene	3.340	119	95	1.74
3	1	1-decene	4.327	146	82	1.75
4	1	4-MP-1 ^b	5.567	209	140	1.81
5	2	1-hexene	8.924	331	5.9	1.68
6	2	1-octene	5.896	206	4.3	1.88
7	2	1-decene	4.136	140	4.2	1.77
8	2	4-MP-1 ^b	2.200	82.6	3.8	1.75

Conditions: 25 °C, 20 min, heptane 60 mL, monomer 40 mL, **1**/*i*-Bu₃Al = 0.005/0.15 mmol/mmol (pretreated, 10 min.), Ph₃CB(C₆F₅)₄ 0.006 mmol, *i*-Bu₃Al 0.05 mmol (total 0.20 mmol). ^aDetermined by GPC using polystyrene calibration ^b4-methyl-1-pentene.

denyl)₂]ZrCl₂ (**2**), a typical metallocene catalyst, as comparison. The complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system exhibited activities that range from 81 to 146/min⁻¹·[monomer/mol·L⁻¹] towards the higher α-olefins, comparable to those obtained with *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (**2**) under identical conditions. The basic trend observed for the catalyst system concerning catalytic activity is that increase in molecular size of the reacting olefin resulted in enhanced catalytic activity (activity order; 1-decene, 1-octene, and 1-hexene). The trend is remarkable because, generally, an olefin polymerization catalyst shows lower reactivity towards larger olefins, as observed for *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (**2**) whose activity decreased with the increase in the molecular size of the reacting olefin. The results suggest that an active species originating from the catalyst system possesses a structurally open nature regarding the cationic metal coordination sphere and, as a result, the coordination of the higher α-olefin is not the rate-determining step of the polymerization process.

Remarkably, the poly(higher α-olefin)s arising from the catalyst system have very high molecular weights in the range of 720000–950000, the values being an order of magnitude larger than those seen by *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂ (*M_w* 42000–59000). It is of significance to note that the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system exhibits a very high incorporation ability for higher α-olefins to produce poly(higher α-olefin)s having high molecular weights and high activity. The molecular weight distribution (*M_w*/*M_n*) values of the polymers formed from the catalyst system lie in the range of 1.68–1.75, indicating that the polymers are produced by a single-site catalyst.

Previously, based on the protonolysis results of a mixture of the complex **1** and *i*-Bu₃Al, an active species generated from the system is assumed to be a phenoxy-amine complex.^{5b} ¹H NMR studies of mixtures of the complex **1** and *i*-Bu₃Al at 25 °C revealed that the phenoxy-imine ligand was reduced by *i*-Bu₃Al to a phenoxy-amine ligand with the coproduction of isobutene. Addition of Ph₃CB(C₆F₅)₄ and 1-hexene to the resulting mixture in the NMR tube produced poly(1-hexene). These results, as well as the single-site catalysis displayed by the system, suggest that a bis(phenoxy-amine)Ti complex with Al attached to nitrogens is the catalytically active species which is derived from the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ system.

Considering that an amine-nitrogen is a weak donor relative to an imine-nitrogen, the great difference in catalytic behavior as a result of using MAO and *i*-Bu₃Al/Ph₃CB(C₆F₅)₄ as cocatalysts is probably associated with the fact that the phenoxy-amine complex provides larger space for the polymerization of olefins than the phenoxy-imine complex. The highly unusual observation regarding the catalytic activity of the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system (the opposite activity order observed for *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂) can be explained as follows: a sterically bulkier side chain derived from the last inserted higher α-olefin of the growing polymer chain opens the phenoxy-amine ligands wider, which facilitates the higher α-olefin's coordination to the metal and its insertion into the metal-carbon bond. This postulate may provide a new strategy for the design of catalysts with high incorporation ability for sterically bulky monomers.

The high reactivity of the system towards large olefins was more pronounced in the polymerization of 4-methyl-1-pentene (Table 1, entry 4). Thus, the catalyst system provided glassy

poly(4-methyl-1-pentene) having an exceptionally high molecular weight (*M_w* 1400000) with a narrow, unimodal molecular weight distribution (*M_w*/*M_n* 1.81) as well as very high activity (209/min⁻¹·[monomer/mol·L⁻¹]). These results are in stark contrast to those seen by *rac*-[C₂H₄-(1-indenyl)₂]ZrCl₂. To our knowledge, the molecular weight, *M_w* 1400000, is the highest encountered for homogeneous olefin polymerization catalysts for the polymerization of 4-methyl-1-pentene. These results suggested that the complex **1**/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ system has high potential for the polymerization of sterically bulky monomers.

In summary, unique catalytic behavior of a bis(phenoxy-imine)Ti complex (an FI Catalyst)/*i*-Bu₃Al/Ph₃CB(C₆F₅)₄ catalyst system for the polymerization of higher α-olefins has been discussed. The catalyst system displays higher activities towards higher α-olefins with sterically bulkier substituents and produces poly(higher α-olefin)s with extremely high molecular weights. We will report further on this unique catalyst system in due course.

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- 7 Propylene polymerization results with complex **1** under atmospheric pressure at 25 °C. MAO: 0.86 g/mmol-cat-h, *M_w* 4300, *M_w*/*M_n* 1.13, *i*-Bu₃Al/Ph₃CB(C₆F₅)₄: 48 g/mmol-cat-h, *M_w* 8286000, *M_w*/*M_n* 4.15.