Review

Bis(pyrrolide-imine) Ti complexes with MAO: A new family of high performance catalysts for olefin polymerization ☆

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Abstract

This contribution reports on the syntheses, structures and olefin polymerization behavior of Ti complexes having a pair of chelating pyrrolide-imine [N⁻,N] ligands. X-ray analyses as well as ^{1}H NMR studies demonstrate that bis(pyrrolide-imine) Ti complexes (named PI Catalysts) contain approximately octahedrally coordinated metal centers with mutually *trans*-pyrrolide-Ns, *cis*-imine-Ns and *cis*-Cls. DFT studies suggest that PI Catalysts, when activated, provide a metal alkyl in the *cis* position to a vacant coordination site for monomer binding. These theoretical studies also show that the active species derived from PI Catalysts normally possess higher electrophilicity and a sterically more open nature compared with those produced using bis(phenoxy-imine) Ti complexes (Ti–FI Catalysts) which are known as high performance olefin polymerization catalysts. These structural as well as electronic features suggest that PI Catalysts have high potential for the polymerization of olefinic monomers.

Unlike high performance Ti–FI Catalysts, PI Catalysts do not require the presence of steric bulk in close proximity to the anionic donor. PI Catalysts combined with MAO display high ethylene polymerization activities (max. 33,200 kg-polymer/mol-cat/h, 25 °C, atmospheric pressure) comparable to those obtained with early group 4 metallocene catalysts (e.g., Cp_2TiCl_2 16,700 kg-polymer/mol-cat/h) under identical conditions. As expected, PI Catalysts exhibit higher incorporation capability for propylene and 1-hexene relative to FI Catalysts though the incorporation levels are lower than those for Cp_2TiCl_2. To our surprise, PI Catalysts/MAO show remarkably high norbornene (NB) incorporation, superior to that seen with the $[Me_2Si(Me_4Cp)N\text{-}tBu]TiCl_2$ (CGC) catalyst system, and they readily form ethylene–NB copolymers with high NB contents. The highly electrophilic and sterically open nature is probably responsible for the high NB affinity. Additionally, PI Catalysts/MAO possess characteristics of living ethylene polymerization (though under limited conditions) and afford high molecular weight PEs with very narrow molecular weight distributions (M_n 225,000, M_w/M_n 1.15, 10-s polymerization, 25 °C). Moreover, these catalysts can copolymerize ethylene and NB in a highly controlled living manner to afford monodisperse alternating copolymers with very high molecular weights ($M_n > 500,000$, $M_w/M_n < 1.2$) at room temperature. This unique living nature allows the preparation of a number of ethylene- and NB-based block copolymers, including PE-*b*-poly(ethylene-*co*-NB) and poly(ethylene-*co*-NB)$_a$-*b*-poly(ethylene-*co*-NB)$_b$, in which each segment contains a different NB content. These are probably the first examples of the syntheses of block copolymers from ethylene and NB. Consequently, the discovery and application of PI Catalysts has exercised a significant influence on olefin polymerization catalysis and polymer synthesis.
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Keywords: Pyrrolide-imine; Titanium; Olefin polymerization; Norbornene, Living polymerization; Block copolymer


Contents

1. Introduction

A tremendous amount of academic and industrial research during the last two decades has focused on the development of highly active molecular catalysts for the controlled polymerization of olefinic monomers. Molecular catalysts typically possess well-defined, homogeneous active sites, unlike the multi-sited heterogeneous Ziegler–Natta catalysts [1]. Therefore, molecular catalysts offer the advantages of control over chain transfer reactions, comonomer incorporation and polymer stereochemistry, allowing access to a variety of polyolefinic materials with specific microstructures and narrower molecular weight distributions.

Great advances in the design and synthesis of well-defined transition metal complexes for olefin polymerization, in collaboration with the discovery of highly efficient cocatalysts, have played a salient role in activating and accelerating research aimed at developing high-activity molecular catalysts. Group 4 metallocene catalysts and constrained-geometry catalysts (CGCs) have been at the forefront of this development, creating new opportunities for producing a wide array of polymers with distinctive microstructures and enhanced performance qualities [e.g., linear low-density polyethylenes (LLDPEs), elastomers, plastomers, isotactic and syndiotactic polypropylenes (iPPs and sPPs), and syndiotactic polystyrenes (sPSs)] [1]. In recent years, these catalysts have enjoyed success in the commercial production of differentiated polymers such as those listed above.

Due to the demand for greater control over polymer microstructures, as well as the creation of polymers with new compositions and molecular architectures, numerous attempts have been undertaken recently to develop new molecular catalysts other than the existing group 4 metallocene catalysts and CGCs. These research efforts have led to the introduction of quite a few new molecular catalysts based on both early and late transition metals with various ligand frameworks [2]. Upon activation with suitable cocatalysts, these new transition metal complexes can form highly active catalysts that create polymers with unique molecular structures, many of which were previously unobtainable with conventional catalysts (e.g., hyper-branched PEs, ethylene-polar monomer copolymers, high molecular weight monodisperse poly(1-hexene)s and polyolefinic block copolymers) [2].

Since the middle of the 1990s, our interests have centered on the discovery and application of highly active molecular catalysts based on the combination of transition metals and non-symmetric bidentate and tridentate ligands with electronically flexible properties ("ligand-oriented catalyst design research") [3]. In connection with these studies, we discovered a number of families of transition metal complexes featuring monoanionic non-symmetric chelate ligands for olefin polymerization. These complexes, in combination with appropriate cocatalysts [e.g., MAO, $Ph_3CB(C_6F_5)_4$, $MgCl_2$, hetero poly compounds, clay minerals], form high-activity catalysts for the polymerization of ethylene [3a,c,d,4a–4d]. Attractive features of these molecular catalysts include

PI Catalysts   *Ti-FI Catalysts*
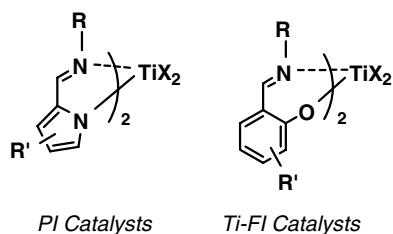
Scheme 1.

the production of very low to ultra-high molecular weight polymers with controlled chain-end structures, highly isotactic and syndiotactic PPs, and the facile incorporation of sterically encumbered monomers such as higher α-olefins and cyclic-olefins. In addition, some of these catalysts possess capability for the living polymerization of ethylene, propylene, ethylene/α-olefins [4e–4i] and ethylene/norbornene (NB) at room temperature or above [5c,5e]. Recent reviews cover much of research on bis(phenoxy-imine) early transition metal complexes (FI Catalysts) [3].

We introduce herein certain catalyst design concepts for acquiring highly active molecular catalysts, and also the discovery and application of pyrrolide-imine ligated Ti complexes (named PI Catalysts) [5–7]. We concentrate on the steric and electronic features of PI Catalysts in comparison with those of bis(phenoxy-imine) Ti complexes (Ti–FI Catalysts) (Scheme 1).

2. Discovery of a highly active bis(pyrrolide-imine) Ti complex

2.1. Catalyst design concept for acquiring high-activity catalysts

The great success of highly active group 4 metallocene catalysts and constrained-geometry catalysts

(CGCs) for olefin polymerization has demonstrated that the discovery of high-activity catalysts for ethylene polymerization has resulted in the development of high performance catalysts that can create polyolefinic materials with new or enhanced performance parameters [1].

Bearing this in mind, the purpose of our research has been the discovery of highly active molecular catalysts for the polymerization of ethylene and their application to value-added polymers that are inaccessible with conventional catalysts. In general, a molecular catalyst for olefin polymerization is composed of a central metal, ligand(s), a growing polymer chain, a coordinated olefin and a cocatalyst (Fig. 1). As depicted in Fig. 2, DFT studies [8] using a metallocene catalyst as a model suggest that ethylene polymerization is a process that involves intense electron exchange between a ligand and a metal, probably to reduce the energy increase during the course of the polymerization [9]. Because all transition metals (even Mn and Fe) inherently possess ethylene insertion ability, we have reasoned that the combination of a transition metal and electronically flexible ligand(s) can afford a highly active ethylene polymerization catalyst. In short, we have postulated that ligands play the predominant role in polymerization
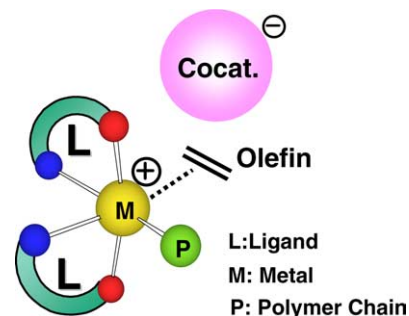

Fig. 1. A schematic structure of a molecular catalyst for olefin polymerization.
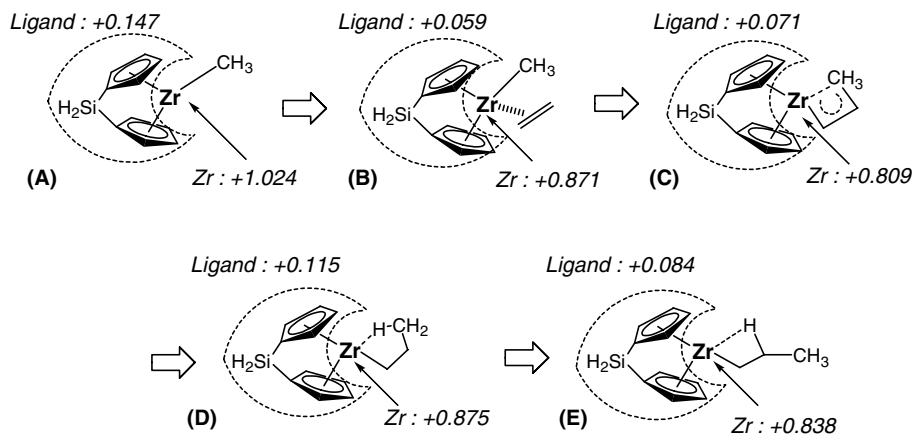

Fig. 2. Electron exchange between the Zr-center and a Cp-based ligand (model: SiH$_2$ (Cp$_2$)Zr$^+$R) for ethylene polymerization; (A) methyl cationic species, (B) ethylene coordinated adduct, (C) transition state, (D) γ-agostic n-propyl cationic species, (E) β-agostic n-propyl cationic species.

catalysis among typical catalyst components and that the electronically flexible properties of ligands are a requirement for achieving high activity ("ligand-oriented catalyst design concept") as long as a cationic species derived from a precatalyst complex possesses enough space for ethylene polymerization. We have given the name *fundamentally active ligands* (FALs) to electronically flexible ligands that can receive electrons from the coordinating ethylene through a metal and release electrons whenever required to facilitate the ethylene insertion process. Fundamentally active ligands typically possess well-balanced electron-donating and-withdrawing properties (evidenced by a small energy gap between HOMO and LUMO), which are anticipated to expedite ethylene polymerization processes.

In addition, we have deliberately focused on non-symmetric ligands that have an electronically flexible nature, since there had been less investigation into transition metal complexes bearing non-symmetric ligands as olefin polymerization catalysts when we initiated this research [2]. Therefore, transition metal complexes with fundamentally active ligands that are non-symmetric in nature were considered to be viable catalysts for ethylene polymerization.

2.2. Search for highly active molecular catalysts for ethylene polymerization

Four examples of the fundamentally active ligands that were created with the aid of DFT calculations are listed in Fig. 3, which includes imine-pyridine, phenoxy-imine, pyrrolide-imine and indolide-imine chelate ligands. These ligands possess a smaller energy gap between HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) than a Cp ligand ($C_5H_5^-$) and thus presumably display electronically more flexible properties than the Cp ligand.

We believe that these fundamentally active ligands combined with transition metals might be expected to yield high-activity ethylene polymerization catalysts as long as any cationic species derived from the resulting complex has an appropriate electron deficiency (10- to 16-electron species) as well as a pair of *cis*-located sites, which are needed for polymerization.

A large number of transition metal complexes whose cationic complexes are 10- to 16-electron species (including those with the fundamentally active ligands described above) were investigated to determine their potential as ethylene polymerization catalysts with MAO activation at 25 °C under atmospheric pressure. As a result, we discovered a number of new families of highly active catalysts for the polymerization of ethylene, which contain, for example, phenoxy-imine [3,4], pyrrolide-imine [5–7], indolide-imine [10], phenoxy-pyridine [11], imine-phenoxy [12], phenoxy-ether [13],
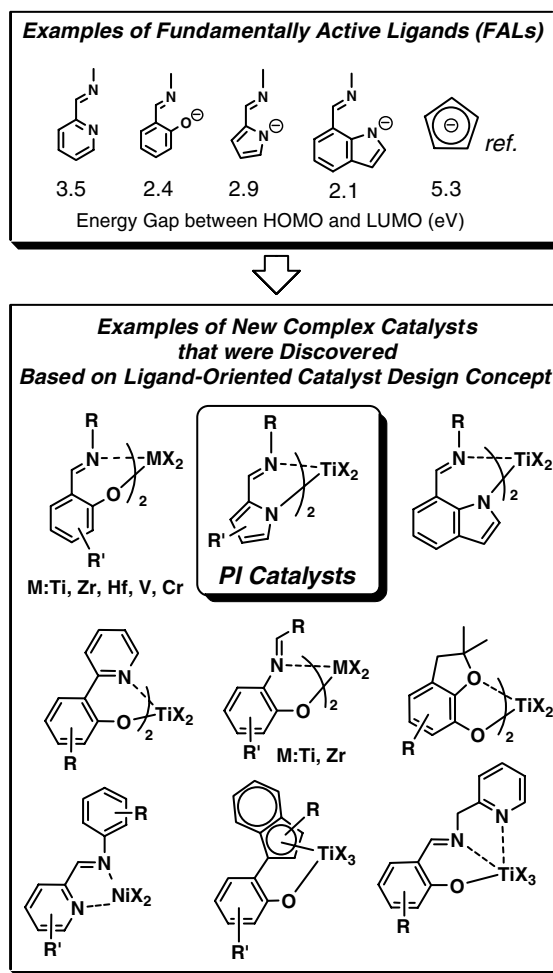
Fig. 3. Examples of fundamentally active ligands (FALs) and new complex catalysts that were discovered based on the ligand-oriented catalyst design concept.

imine-pyridine [14], phenoxy-cyclopentadienyl [15] and phenoxy-imine-pyridine chelate ligands [16]. Among the new transition metal complexes that were discovered through ligand-oriented catalyst design research, bis(phenoxy-imine) early transition metal complexes (known as FI Catalysts) and bis(pyrrolide-imine) Ti complexes in particular show high ethylene polymerization activities.

2.3. Discovery of a highly active bis(pyrrolide-imine) Ti complex (a PI Catalyst)

We noted that an FI Catalyst requires steric bulk *ortho* to the phenoxy-O in order to exhibit high ethylene polymerization activity [3]. The steric bulk is thought to afford steric protection toward the anionic phenoxy-O donors from coordination with Lewis acidic compounds and the inducement of effective ion separation between the cationic active species and an anionic cocatalyst, resulting in enhanced catalytic activity. Thus, bis(pyrrolide-imine) Ti complexes **1**–**3** with a series of substituents

(H, Me and SiMe$_3$) adjacent to the anionic pyrrolide-N donors were prepared and examined as ethylene polymerization catalysts. The polymerization results may provide information on the potential of bis(pyrrolide-imine) Ti complexes for ethylene polymerization, and additional information about the effect of the substituent adjacent to the pyrrolide-N on catalytic performance.

Bis(pyrrolide-imine) Ti complexes **2** and **3**, which possess the Me and SiMe$_3$ groups, proved poor catalysts for ethylene polymerization under the conditions employed (activity < 100 kg-PE/mol-cat/h) (Scheme 2). Instead, bis(pyrrolide-imine) Ti complex **1** with an H atom adjacent to the pyrrolide-N formed PE with an M_w of 67,000 and a high activity of 6000 kg-PE/mol-cat/h. These facts show that, for bis(pyrrolide-imine) Ti complexes **2** and **3**, the Me and SiMe$_3$ groups in close proximity to the pyrrolide-Ns evidently provide unfavorable steric hindrance to ethylene polymerization. This is in sharp contrast to FI Catalysts, which require steric congestion near the polymerization center in order to display high activity. The activity obtained with **1** (6000 kg-PE/mol-cat/h) is extremely high for a Ti complex with no Cp ligand(s) [2c]. In fact, the activity exceeds that displayed by Ti–FI Catalyst **4**: [2-(Ph-NCH)-3-tBu-C$_6$H$_3$O]$_2$TiCl$_2$ under analogous conditions (3480 kg-PE/mol-cat/h) [5d]. The molecular weight distribution (M_w/M_n) of the PE formed with **1** is 2.21, indicative of single-site catalysis. The high activity, together with the single-site behavior that was observed, would indicate the high potential of bis(pyrrolide-imine) Ti complexes for olefin polymerization. Considering that a pyrrolide-N is a weaker donor than a phenoxy-O, a bis(pyrrolide-imine) Ti complex probably generates a catalytically active cationic species with higher electrophilicity than a Ti–FI Catalyst, which may lead to unique polymerization catalysis.

We have, therefore, named the newly discovered pyrrolide-imine ligated Ti complexes "PI Catalysts" after the Japanese pronunciation of the ligand "Pirorido-Imin haiishi", which, by coincidence, is the same as the abbreviation of the ligand name in English, unlike FI Catalysts.
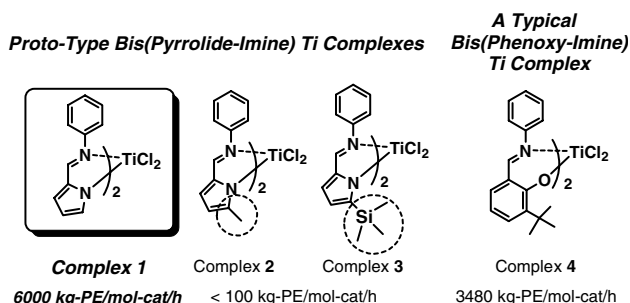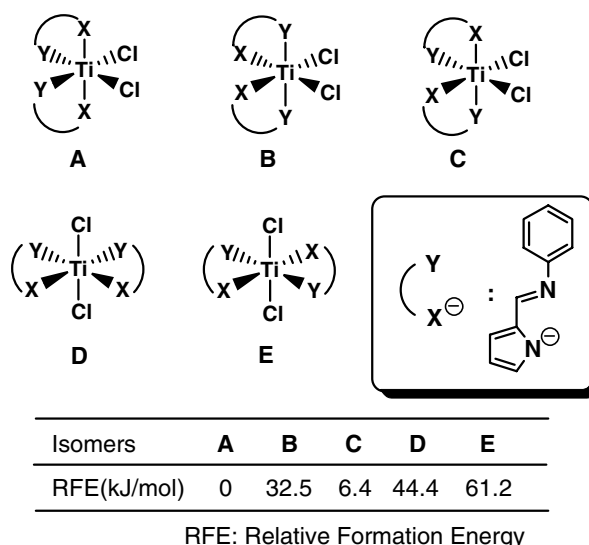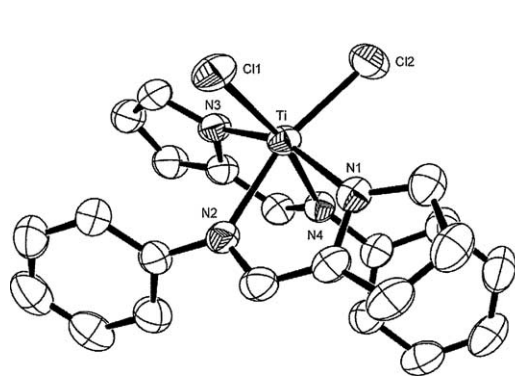
3. Structural and electronic features of PI Catalysts

Since a PI Catalyst contains a pair of non-symmetric bidentate ligands, it potentially displays five isomers (A–E) arising from the coordination modes of the two ligands in an octahedral geometry (Scheme 3). In general, the ^{1}H NMR spectrum of a PI Catalyst exhibits a single sharp resonance for the methine proton (−HN=C−) of the pyrrolide-imine ligand, consistent with an octahedral coordination structure. DFT studies suggest that PI Catalyst **1** assumes isomer A, with a *trans*-pyrrolide-Ns, *cis*-imine-Ns and *cis*-Cls disposition, which is consistent with the predicted structure on the basis of simple valence shell electrons repulsion concepts. In fact, X-ray crystallographic analysis has established that, in the solid state, PI Catalyst **1** possesses an approximately octahedrally coordinated Ti center and C_2 symmetry, with a *trans*-pyrrolide-Ns, *cis*-imine-Ns and *cis*-Cls arrangement (Fig. 4) [5b]. Additionally, X-ray analysis of PI Catalysts **5** and **7** (both highly active catalysts for ethylene polymerization, see entries 2, 4 in Table 1) also indicates that they possess the same configurations as **1**.

DFT calculations were performed on a methyl cationic complex (an initial active species generated from PI Catalyst **1** with MAO) in the presence of ethylene, to obtain information about the structure of the catalytically active species (Fig. 5). The calculations reveal that an ethylene-coordinated cationic species assumes an octahedral geometry with a *trans*-pyrrolide-Ns, *cis*-imine-Ns and *cis*-Me/coordinated ethylene disposition, which fulfils the pivotal requirement for a high efficiency catalyst; i.e., a growing polymer chain and a coordinated-ethylene group in the *cis*-position. An inspection of the calculated structure indicates that the phenyl group on the imine-N is located in close proximity to

Proto-Type Bis(Pyrrolide-Imine) Ti Complexes | A Typical Bis(Phenoxy-Imine) Ti Complex

Complex 1 — 6000 kg-PE/mol-cat/h
Complex 2 — < 100 kg-PE/mol-cat/h
Complex 3
Complex 4 — 3480 kg-PE/mol-cat/h

Scheme 2.

Isomers	A	B	C	D	E
RFE(kJ/mol)	0	32.5	6.4	44.4	61.2

RFE: Relative Formation Energy

Scheme 3.

Distances (Å)		Angles (°)	
Ti–Cl(1)	2.2506(7)	Cl(1)–Ti–Cl(2)	97.82(3)
Ti–Cl(2)	2.2598(6)	Cl(1)–Ti–N(1)	101.77(5)
Ti–N(1)	2.043(2)	Cl(1)–Ti–N(2)	90.95(4)
Ti–N(2)	2.215(2)	Cl(1)–Ti–N(3)	91.68(5)
Ti–N(3)	2.033(2)	Cl(1)–Ti–N(4)	165.45(4)
Ti–N(4)	2.185(2)	Cl(2)–Ti–N(1)	91.31(5)
		Cl(2)–Ti–N(2)	165.47(4)
		Cl(2)–Ti–N(3)	104.10(5)
		Cl(2)–Ti–N(4)	93.03(4)
		N(1)–Ti–N(2)	75.50(6)
		N(1)–Ti–N(3)	158.04(6)
		N(1)–Ti–N(4)	87.60(6)
		N(2)–Ti–N(3)	87.12(6)
		N(2)–Ti–N(4)	80.54(5)
		N(3)–Ti–N(4)	76.22(6)

Fig. 4. Molecular structure of PI Catalyst **1** and selected bond distances and angles. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

Table 1
Ethylene polymerization results with PI Catalysts **1**, **5–9**, Ti–FI Catalysts **4**, Cp_2TiCl_2 and Cp_2ZrCl_2

Entry	Complex	Activity (kg-PE/mol-cat/h)	M_w ($/10^3$)[a]
1	**1** (PI)	6000	75
2	**5** (PI)	360	412
3	**6** (PI)	780	441
4	**7** (PI)	14,100	2601
5	**8** (PI)	20,400	2720
6	**9** (PI)	33,200	3167
7	**4** (Ti–FI)	3480	368
8	Cp_2TiCl_2	16,700	1253
9	Cp_2ZrCl_2	20,000	1000

Conditions: 25 °C, 5 min, atmospheric pressure, ethylene gas feed (100 L/h).
Complex 1 µmol, MAO 1.25 mmol as Al, toluene 250 ml.
[a] Calculated from intrinsic viscosity.

Fig. 5. Calculated structure of ethylene-coordinated cationic species derived from PI Catalyst **1**.

the active site, suggesting that the substituent on the imine-N is the strategic substituent vis-à-vis catalyst design. Additionally, the calculations suggest that the cationic complex has approximate C_2 symmetry if one ignores the non-equivalence of the methyl group and the coordinated ethylene, implicating that PI Catalysts may be iso-specific catalysts for α-olefin polymerization when the active species are not fluxional on the time scale of chain propagation.

As discussed, PI Catalysts **2** and **3**, with the Me and $SiMe_3$ groups adjacent to the pyrrolide-Ns, display very low productivity in the polymerization of ethylene unlike PI Catalyst **1**. The calculated structure of a methyl cationic complex originating from **3** is displayed in Fig. 6(A). The $SiMe_3$ group seems to provide steric con-
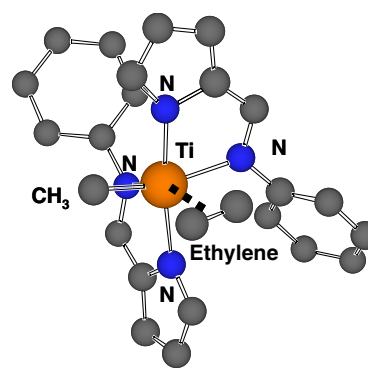
gestion near the polymerization center, which diminishes the rate of chain propagation. This is probably because it obstructs ethylene from gaining access to the active site and subsequent insertion into the Ti–carbon bond.

The calculated structures of the catalytically active cationic species stemming from PI Catalyst **1** and Ti–FI Catalyst **4** are displayed in Figs. 6(B) and (C). A comparison of their molecular structures indicates that PI Catalyst **1** provides more space for olefin polymerization than Ti–FI Catalyst **4**, due to the absence of a sterically encumbered substituent adjacent to the pyrrolide-N. Additionally, DFT studies show that the active species derived from PI Catalyst **1** possesses higher electrophilicity at the Ti center compared with that of Ti–FI Catalyst **4** (Mulliken charge of the Ti in atomic unit, **1**: 2.131: **4**: 2.005). Considering that the active species derived from a typical metallocene (Cp_2TiCl_2) has a Mulliken charge (Ti) of 1.308, PI Catalyst **1** exhibits particularly high electrophilicity. Further DFT studies have confirmed the generality of these structural and electronic features of the active species originating from PI Catalysts. Therefore, a PI Catalyst generates a catalytically active species that has a sterically more open nature and higher electrophilicity than a Ti–FI Catalyst. These features of a PI Catalyst may give rise to differen-
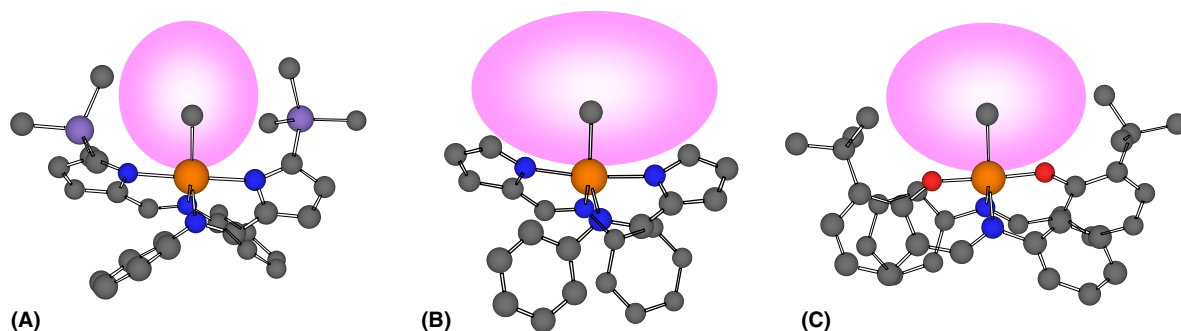
Fig. 6. Calculated structures of cationic active species generated from PI Catalyst **3** (A), PI Catalyst **1** (B) and Ti–FI Catalyst **4** (C).

tiated catalytic properties compared with a Ti–FI Catalyst.

4. Synthesis of PI Catalysts

A general synthetic route to PI Catalysts is depicted in Scheme 4. The pyrrolide-imine ligands are easily prepared by the acid-catalyzed Schiff-base condensation of pyrrole-2-carboxaldehyde or its derivatives and a wide range of primary amines. The condensation is straightforward and normally proceeds with high yields. Complex formation is readily achieved by the treatment of the lithium salt of the pyrrolide-imine ligand with $TiCl_4$. This route utilizes materials that are easily prepared, relatively stable and display high reactivity. Moreover, this route does not involve any troublesome steps that can lead to a low yield. The overall yields when starting from pyrrole-2-carboxaldehyde are usually good (e.g., PI Catalyst **1**, 51%).

As discussed on the basis of both DFT and X-ray studies, the substituent on the imine-N is located near the polymerization center, and thus it should have a considerable effects on the catalytic properties of a PI Catalyst. Fortunately, strategic substituents can be easily introduced by the use of primary amines, for which there is a rich inventory of commercially available compounds. Therefore, PI Catalysts can be synthesized with ease and, in addition, they possess a wide range of catalyst design possibilities.
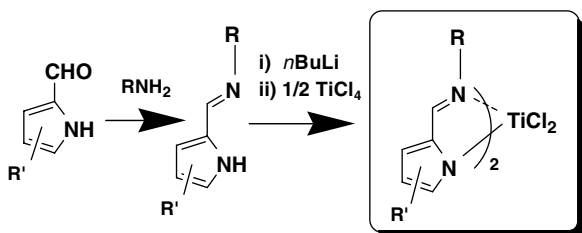
5. Olefin polymerization behavior of PI Catalysts

5.1. Ethylene polymerization with PI Catalysts

Since the substituent on the imine-N is situated near the active site, PI Catalysts **1**, **5**–**9** were evaluated, with MAO activation, for the polymerization of ethylene to obtain information on the effect of this substituent on ethylene polymerization behavior [5a,5b]. The polymerization results are presented in Table 1, which also includes the results for Ti–FI Catalyst **4**, Cp_2TiCl_2 and Cp_2ZrCl_2 as a reference.

PI Catalysts **1**, **5**–**9** are active ethylene polymerization catalysts under the conditions examined, and form highly linear PEs (branching less than 1 per 1000 carbon atoms; IR analyses). The basic trend observed is that an increase in the steric bulk of the substituent results in enhanced catalytic activity. A reasonable hypothesis is that the sterically more-encumbered substituent on the imine-N induces more effective ion-separation between the cationic active species and an anionic cocatalyst. In addition, it gives better steric protection to the imine-N from Lewis acidic compounds present in a polymerization medium, leading to increased catalytic activity. It should be noted that PI Catalyst **9**, which includes a cyclooctyl group on the imine-N, gives an activity of 33,200 kg-PE/mol-cat/h, which compares favorably with Cp_2TiCl_2 or Cp_2ZrCl_2 combined with MAO. In fact, the activity (33,200 kg-PE/mol-cat/h) obtained with **9** represents one of the highest values reported to date for molecular Ti catalysts under atmospheric pressure conditions.

Additionally, the data summarized in Table 1 demonstrate that sterically more-encumbered substituents on the imine-Ns generally afford higher molecular weight PEs. The steric congestion provided by the substituent, which probably reduces the rate of chain transfer more significantly than that of chain propagation, is responsible for the enhancement of the product molecular weight.

Interestingly, on activation with $iBu_3Al/$ $Ph_3CB(C_6F_5)_4$, PI Catalysts generate strikingly high

Scheme 4.

molecular weight PEs, unlike the situation with MAO activation. For example, PI Catalyst 1 with iBu_3Al/ $Ph_3CB(C_6F_5)_4$ under atmospheric pressure produces a PE with exceptionally high molecular weight ($M_v > 4,000,000$) displaying a high activity of 1900 kg-PE/mol-cat/h. This molecular weight ($M_v > 4,000,000$) is one of the highest for PEs prepared with molecular catalysts. Similarly, PI Catalysts 5–7 can convert ethylene to ultra-high molecular weight PEs ($M_v > 4,000,000$) with high efficiency (1500–2000 kg-PE/mol-cat/h). These ultra-high molecular weight PEs possess great potential for use in materials that require high strength (e.g., artificial bones, artificial legs, bullet-proof vests). We attribute the formation of the ultra-high molecular weight PEs to a bis(pyrrolide-amine) Ti complex with a iBu_2Al group attached to the amine-donor that is produced as a result of the reduction of the imine functionality by iBu_3 Al with the concurrent formation of isobutene. Similar observations (i.e., imine reduction with i Bu_3Al to generate amine-functionality) were made for bis(phenoxy-imine) Ti complexes (Ti–FI Catalysts) [17].

5.2. Ethylene/propylene, 1-hexene or norbornene copolymerization with PI Catalysts

Given the established high catalytic performance of PI Catalysts for the polymerization of ethylene, we examined their catalytic behavior for ethylene/propylene, ethylene/1-hexene and ethylene/norbornene (NB) copolymerizations [5d]. A comparison of the copolymerization results with those of FI Catalysts will give some insight into how the highly electrophilic and sterically open nature of PI Catalysts affects the incorporation ability for these comonomers.

Table 2 summarizes the ethylene/propylene copolymerization results with PI Catalysts 1, 7, Ti–FI Catalyst 4 and with Cp_2TiCl_2 as a reference; MAO was used as the cocatalyst. All the catalyst systems produce ethylene–propylene copolymers, which range from semi-crystalline to amorphous materials. Although Cp_2TiCl_2 displays the highest propylene incorporation (41.6 mol%, 580 kg-polymer/mol-cat/h), PI Catalysts 1 and 7 have higher affinity for propylene and form copolymers with much higher propylene contents (1: 30.5 mol%, 310 kg-polymer/mol-cat/h, 7: 23.4 mol%, 1310 kg-polymer/mol-cat/h) compared with Ti–FI Catalyst 4 (4.5 mol%). The sterically more open nature of the active species from PI Catalysts 1 and 7 relative to that from Ti–FI Catalyst 4 probably accounts for the high propylene incorporation.

Ethylene/1-hexene copolymerization was also investigated (Table 3). The same trend of comonomer reactivity as seen in ethylene/propylene copolymerization was observed; namely, Cp_2TiCl_2 exhibits the highest incorporation capability for 1-hexene (5.1 mol%, 2030 kg-polymer/mol-cat/h), followed by PI Catalyst 1 (1.9 mol%, 3690 kg-polymer/mol-cat/h), PI Catalyst 7 (1.7 mol%, 4580 kg-polymer/mol-cat/h) and Ti–FI Catalyst 4 (0.4 mol%, 2110 kg-polymer/mol-cat/h). The

Table 2
Ethylene/propylene copolymerization results with PI Catalysts 1, 7, Ti–FI Catalyst 4 and Cp_2TiCl_2

Entry	Complex	Activity(kg-polymer/mol-cat/h)	M_w $(/10^3)$[a]	M_w/M_n[a]	Propylene content (mol%)[b]
1	1 (PI)	310	20	1.94	30.5
2	7 (PI)	1310	1339	2.61	23.4
3	4 (Ti–FI)	480	228	2.00	4.5
4	Cp_2TiCl_2	580	242	2.22	41.6

Conditions: 25 °C, 30 min, atmospheric pressure, ethylene/propylene mix gas feed (50/150 L/h). Complex 1 μmol, MAO 1.25 mmol as Al, toluene 250 ml.
[a] Determined by GPC using ethylene-propylene copolymer calibration.
[b] Determined by IR.

Table 3
Ethylene/1-hexene copolymerization results with PI Catalysts 1, 7, Ti–FI Catalyst 4 and Cp_2TiCl_2

Entry	Complex	Activity(kg-polymer/mol-cat/h)	M_w $(/10^3)$[a]	1-Hexene content (mol%)[b]
1	1 (PI)	3690	70	1.9
2	7 (PI)	4580	747	1.7
3	4 (Ti–FI)	2110	220	0.4
4	Cp_2TiCl_2	2030	143	5.1

Conditions: 25 °C, 5 min, atmospheric pressure, ethylene gas feed (100 L/h). Complex 1 μmol, MAO 1.25 mmol as Al, charged 1-hexene 10 ml, toluene 250 ml.
[a] Calculated from intrinsic viscosity.
[b] Determined by IR.

copolymers produced with these catalysts have relatively low levels of 1-hexene incorporation, probably due to the inherent steric bulk of 1-hexene.

Considering that the catalytically active species stemming from Cp_2TiCl_2 possesses the lowest electrophilicity (Mulliken charge of the Ti in atomic unit, 1.308) and the most available room for polymerization, and that the catalytically active species from PI Catalysts **1** and **7** have higher electrophilicity and sterically more open natures than that from Ti–FI Catalyst **4**, steric factors play a more important role than electronic factors in the incorporation of propylene or 1-hexene with the catalyst systems that were employed (Mulliken charge of the Ti in atomic unit, **1**; 2.131, **7**; 2.060, **4**; 2.005).

We also examined the ethylene/NB copolymerization behavior of the same catalyst systems (Table 4). The data demonstrate that PI Catalysts **1** and **7** display the highest NB incorporation (**1**: 32.0 mol%, 1476 kg-polymer/mol-cat/h, **7**: 26.5 mol%, 4272 kg-polymer/mol-cat/h), followed by Ti–FI Catalyst **4** (4.3 mol%, 216 kg-polymer/mol-cat/h) and Cp_2TiCl_2 (1.2 mol%, 18,156 kg-polymer/mol-cat/h). These results are in stark contrast to those for the ethylene/propylene and ethylene/1-hexene copolymerizations with the same catalysts. It should be pointed out that PI Catalysts **1** and **7** exhibit higher NB incorporation than $Me_2Si(Me_4Cp)$ $(N\text{-}tBu)TiCl_2$ (CGC), which is well-known to possess very high incorporation ability for sterically hindered olefinic monomers [1d]. The results obtained with PI Catalysts are of great significance because of the importance of ethylene–NB copolymers (cyclic-olefin copolymers, COCs) in various fields due to their remarkable material properties (e.g., high thermal stability, high transparency, high refractive indices) [18]. Taking into account the fact that NB is a sterically encumbered olefinic monomer and, in addition, possesses higher nucleophilicity (HOMO – 7.25 eV, DFT calculation) than propylene (HOMO – 7.66 eV) and 1-hexene (HOMO – 7.60 eV), the excellent NB incorporation is probably due to the highly electrophilic and sterically

open nature of the active species originating from PI Catalysts. The ethylene/NB copolymerization results suggest that electronic factors in particular play a crucial role in the incorporation of NB, unlike that of propylene or 1-hexene for the catalyst systems employed. Remarkably, the copolymers formed with PI Catalysts **1** and **7** (entries 6 and 7 in Table 4) exhibited high NB contents with narrow molecular weight distributions (1.08 and 1.11, respectively) and were free of olefinic end groups, indicating that PI Catalysts with MAO may exhibit characteristics for the living copolymerization of ethylene and NB under the given conditions.

6. Catalytic properties of PI Catalysts for ethylene and/or NB (co-)polymerizations

6.1. Living copolymerization of ethylene and norbornene with PI Catalysts

A plot of M_n and M_w/M_n values vs. polymerization time, for the copolymerization of ethylene and NB with PI Catalyst **7** at 25 °C, is shown in Fig. 7(A). The M_n value increased linearly with polymerization time, and the narrow M_w/M_n value was retained for each run (M_w/M_n 1.07–1.16), showing that PI Catalyst **7**/MAO is indeed living. The GPC peaks of the copolymers formed from **7** shifted to the higher molecular weight region with increasing polymerization time, while the unimodal shape was maintained and no shoulder peak and/or low molecular weight tail was detected during the course of the polymerization [Fig. 7(B)]. These results indicate that PI Catalyst **7**/MAO mediates the highly controlled living copolymerization of ethylene and NB at room temperature and affords high molecular weight monodisperse ethylene–NB copolymers. The highest M_n value of the copolymer made with **7**/MAO (M_n 521,000, M_w/M_n 1.16) represents one of the highest reported values to date for monodisperse ethylene–NB copolymers.

Table 4
Ethylene/NB copolymerization results with PI Catalysts **1**, **7**, Ti–FI Catalyst **4**, Cp_2TiCl_2 and $[Me_2Si(Me_4Cp)N\text{-}tBu]TiCl_2$

Entry	Complex	Charged NB (g)	Activity (kg-polymer/mol-cat/h)	M_n $(/10^3)$[a]	M_w/M_n[a]	NB content (mol%)[b]
1	**1** (PI)	1	1476	139	1.29	32.0
2	**7** (PI)	1	4272	652	1.28	26.5
3	**4** (Ti–FI)	1	216	52	1.14	4.3
4	Cp_2TiCl_2	1	18,156	594	3.69	1.2
5	$[Me_2Si(Me_4Cp)N\text{-}tBu]TiCl_2$	1	0	–	–	–
6	**1** (PI)	10	540	72	1.08	47.4
7	**7** (PI)	10	2742	285	1.11	45.0
8	$[Me_2Si(Me_4Cp)N\text{-}tBu]TiCl_2$	10	15,360	858	4.66	31.2

Conditions: 25 °C, 5 min, atmospheric pressure, ethylene gas feed (50 L/h).
Complex 1 μmol, cocatalyst: (entries 1–7) MAO 1.25 mmol as Al, (entry 8) iBu_3Al 1.25 mmol, $Ph_3CB(C_6F_5)_4$ 6 μmol, toluene 250 ml.
 [a] Determined by GPC using polystyrene calibration.
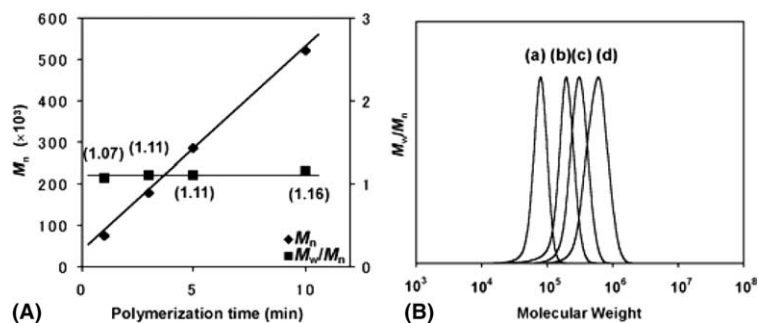 [b] Determined by ^{13}C NMR.

Fig. 7. (A) Plots of M_n and M_w/M_n vs. polymerization time with PI Catalyst **7**/MAO. (B) GPC profile of the ethylene–NB copolymer produced with PI Catalyst **7**/MAO: (a) 1 min, M_n 74,000, M_w/M_n 1.07; (b) 3 min, M_n 179,000, M_w/M_n 1.11; (c) 5 min, M_n 285,000, M_w/M_n 1.11; (d) 10 min, M_n 521,000, M_w/M_n 1.16.

Likewise, PI Catalysts **1**, **8**, and **9** copolymerize ethylene and NB in a highly controlled living manner and form high molecular weight copolymers with very narrow molecular weight distributions (M_n 61,000–600,000, M_w/M_n 1.07–1.23, NB contents 44.0–48.6 mol%). Considering that there are only a few examples of catalysts that promote the (quasi) living copolymerization of ethylene and NB [19], the discovery of PI Catalyst systems that carry out highly controlled living ethylene/NB copolymerization is highly significant [5c,5e].

^{13}C NMR studies of the living copolymers reveal that PI Catalysts/MAO have a very high propensity to produce alternating copolymers [e.g., the copolymer formed with **7**/ MAO, M_n 285,000, M_w/M_n 1.11, NB 45.0 mol%, –NB–ethylene–*NB*–ethylene–NB– 95.4%, –ethylene–*NB*–(ethylene)$_n$–, 3.7%, (entry 7 in Table 4)], which possess stereoirregular structures, despite the C_2-symmetric nature of the catalysts. The sterically open nature of the active sites of PI Catalysts may be associated with the low degree of polymerization stereocontrol. However, it cannot be ruled out that a fluxional isomerization between the diastereomeric Λ and Δ configurations is responsible for the atactic nature of the PI Catalyst systems [3c,3e].

The ^{13}C NMR studies also demonstrate that copolymerization is initiated by NB insertion into the Ti–Me bond of the initial active species and that the active species mostly exists as a NB-last-inserted species. These facts further confirm the high incorporation capability of PI Catalysts/MAO for NB (Fig. 8).

6.2. Ethylene and/or NB (co-)polymerization with PI Catalyst 7/MAO

To obtain insight into the highly controlled living copolymerization, we conducted homopolymerization of ethylene and NB using **7** /MAO. For ethylene homopolymerization (25 °C, 5 min, atmospheric pressure), the catalyst system produced PE with an M_w/M_n of 2.10, indicative of a non-living nature under the conditions examined. To our surprise, **7**/MAO formed a very narrow molecular weight distribution PE that had a high molecular weight (M_n 225,000, M_w/M_n 1.15) after 10-s polymerization, although the M_w M_n was somewhat broadened after 30-s polymerization (M_n 429,000, M_w/M_n 1.38). These facts show that PI Catalyst **7**/MAO possesses characteristics of living ethylene polymerization and that chain growth can occur without significant chain transfer or termination for a short polymerization time. While the ability of **7**/MAO for promoting living ethylene polymerization is lower than that of fluorinated Ti–FI Catalysts, the ability is higher than non-fluorinated Ti–FI Catalysts, judging from the molecular weight and molecular weight distributions that were attained [2d–4f,4h,4i,20].

Conversely, PI Catalyst **7**/MAO showed virtually no reactivity toward NB homopolymerization. Interestingly, though the treatment of **7**/MAO with NB in toluene for 20 min generated neither polymeric nor oligomeric materials, the subsequent addition of ethylene to the resultant mixture formed a high molecular
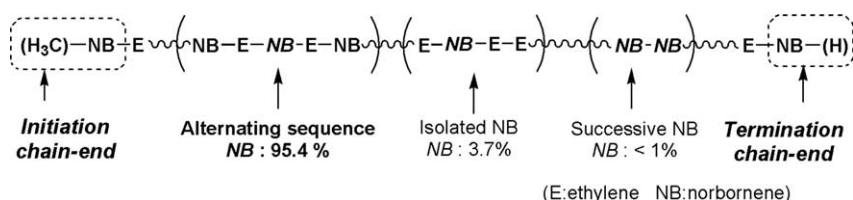

Fig. 8. Structure of the living ethylene–NB copolymer arising from PI Catalyst **7**/MAO (entry 7 in Table 4).

weight copolymer with a narrow molecular weight distribution (M_n 338,000, M_w/M_n 1.29). This fact suggests the high stability of a catalytically active species generated from **7**/MAO under the conditions where no insertion of monomers occurs for 20 min. The coordination of NB to the active species is presumably responsible for these observations, whereby catalyst decay is suppressed as a consequence of steric protection of the active site and the reduced electrophilicity of the Ti center.

To gain further information about the living copolymerization, we investigated the effect of the NB/ethylene molar ratio on the copolymerization. These studies revealed that the NB/ethylene ratio in the polymerization medium has a great influence on the molecular weight distribution; i.e., the catalyst system produces very narrow molecular weight distribution copolymers at NB/ethylene molar ratios of larger than ca. 1 (Fig. 9). In addition, the data demonstrate that an NB content of greater than ca. 30 mol% is required in order to yield copolymers with a narrow molecular weight distribution. These results indicate that the presence of a certain amount of NB in the polymerization medium and/or in the polymer chain is a requirement for living copolymerization, indicative of the crucial role of NB in achieving highly controlled living copolymerization.

6.3. Origin of highly controlled living copolymerization

A plausible polymerization mechanism for ethylene/NB copolymerization with a PI Catalyst/MAO system
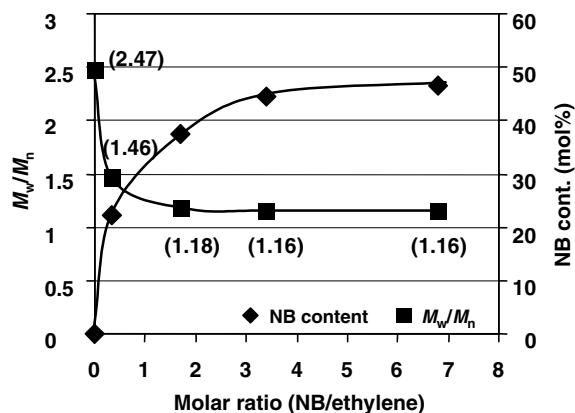

Fig. 9. Plots of M_w/M_n and NB content vs NB/ethylene molar ratio with PI Catalyst **7**/MAO.

is depicted in Scheme 5. As mentioned previously, chain-end analysis indicates the initial generation of the Ti–NB–CH₃ species (**1**). Taking into account the fact that the catalyst system prefers the formation of an alternating copolymer, after the production of (**1**), propagation predominantly occurs by the sequential insertion of ethylene followed by NB according to the sequence (A)–(B)–(C)–(D).

An NB-last-inserted species (**2**) is thought to exhibit considerable stability toward chain-transfer reactions due to the difficulty in β-H transfers, whereas an ethylene-last-inserted species (**4**) probably undergoes relatively fast chain transfer [21]. Indeed, ethylene/NB
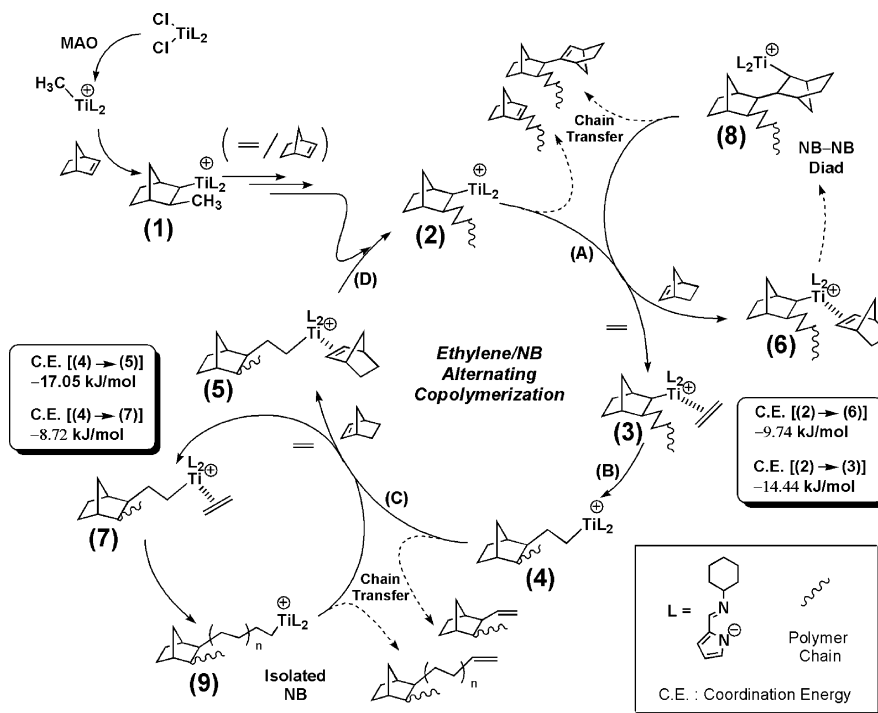
Plausible Mechanism for Living Ethylene/NB Copolymerization Promoted by PI Catalyst / MAO

Scheme 5.

copolymerization conducted at 90 °C for 1 min furnished a broadened molecular weight distribution copolymer (M_n 13,800, M_w/M_n 1.86) that has a vinyl end-group derived from a β-H transfer from the last-inserted ethylene unit. Thus, the achievement of highly controlled living copolymerization is as a result of the stabilization of an ethylene-last-inserted species (**4**) toward chain transfers and its smooth transformation to a chain-transfer-wise stable NB-last-inserted species (**2**).

DFT studies show that an NB-coordinated ethylene-last-inserted species (**5**) is more stable than the corresponding ethylene-coordinated species (**7**) by 8.33 kJ/mol, indicative of the prevailing coordination of NB to the Ti center of the ethylene-last-inserted species. The coordination of highly nucleophilic and sterically encumbered NB to the ethylene-last-inserted active species probably stabilizes the active species toward chain transfer and catalyst decay. This is because the coordination reduces the electrophilicity of the active site and, in addition, provides steric congestion in close proximity to the active site. The facile insertion of NB to the ethylene-last-inserted species is indicated by the fact that a growing polymer chain is detected exclusively as an NB-last-inserted state when the living copolymerization was quenched. The highly electrophilic and sterically open nature of the active site is probably responsible for the high NB affinity and the facile NB insertion.

Because the living copolymers contain some isolated NB units that are present in the consecutive ethylene units, the reaction pathway (**4**)–(**7**)–(**9**) is also involved in the living copolymerization. As discussed, the PI Catalyst systems can show the characteristics of living ethylene polymerization albeit under limited conditions. These characteristics would allow the successive enchainment of ethylene without significant chain transfer with the ethylene–NB copolymer exhibiting living character.

rac-Et(Ind)$_2$ZrCl$_2$ and Me$_2$Si(Me$_4$Cp)(*N-t*Bu)TiCl$_2$ catalyst systems have been reported to promote the (quasi) living copolymerization of ethylene and NB and to yield copolymers with narrow molecular weight distributions (e.g., M_n 133,000, M_w/M_n 1.16) in the presence of a large excess of NB to ethylene in a polymerization medium [19c,19d]. Considering that the active species derived from these Cp-based catalysts possess much lower electrophilicity than those from PI Catalysts, the (quasi) living copolymerizations achieved by *rac*-Et(Ind)$_2$ZrCl$_2$ and Me$_2$Si(Me$_4$Cp)(*N-t*Bu)TiCl$_2$ catalyst systems are probably due to the enhancement of NB coordination to an ethylene-last-inserted species and the acceleration of NB insertion to the active species with the aid of a high NB concentration with, simultaneously, a large excess of NB to ethylene in the reaction medium.

We have concluded that the highly controlled living copolymerization of PI Catalysts/MAO stems from the fact that the active species of PI Catalysts possess high affinity and high incorporation ability for NB as well as the characteristics of living ethylene polymerization, though under limited conditions. The high affinity and high incorporation capability for NB probably results from the highly electrophilic and sterically open nature of the active species. The results described herein provide a new strategy for the development of high performance catalysts for the living copolymerization of ethylene and cyclic-olefins with high nucleophilicity.

7. Synthesis of ethylene- and NB-based block copolymers

One of the most attractive features of a living olefin polymerization catalyst lies in its capability to create well-defined block copolymers, that possess potential uses in a broad spectrum of applications, including compatibilizers, elastomers and composite materials. As described, PI Catalysts/MAO can effectively polymerize ethylene and ethylene/NB in a living fashion, allowing the creation of block copolymers with various architectures from ethylene and NB. We have therefore demonstrated the utility of the PI Catalysts through the syntheses of ethylene- and NB-based block copolymers consisting of crystalline and amorphous segments or two different kinds of amorphous segments (Fig. 10) [5e].

A PE-*b*-poly(ethylene-*co*-NB)$_1$ was synthesized using a sequential addition polymerization procedure. The
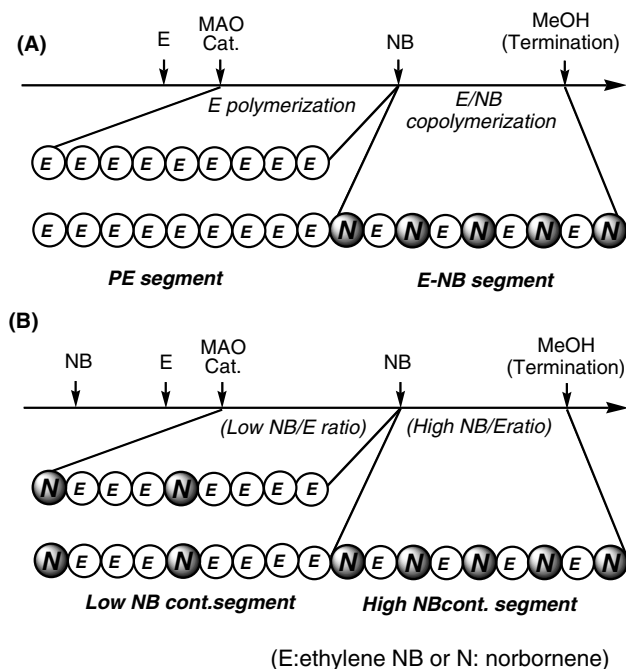

Fig. 10. Synthesis of ethylene- and NB-based block copolymers.

addition of **7**/MAO to a solution of ethylene resulted in the rapid formation of a living PE after 10 s (M_n 119,000, M_w/M_n 1.34). The subsequent addition of NB to this living chain end in the presence of ethylene afforded a PE-*b*-poly(ethylene-*co*-NB)$_1$ (M_n 414,000, M_w/M_n 1.56, NB content 31.5 mol%). A shift of the GPC elution curves for the first PE segment and the final PE-*b*-poly(ethylene-*co*-NB)$_1$ toward the high-molecular-weight region demonstrates the formation of the desired block copolymer (Fig. 11). TEM analyses further confirmed the creation of the block copolymer, and simultaneously, show its high potential as a new material composed of crystalline PE and amorphous poly(ethylene-*co*-NB) segments that are chemically linked (Fig. 12).

Likewise, four kinds of poly(ethylene-*co*-NB)$_a$-*b*-poly(ethylene-*co*-NB)$_b$s in which each segment contains a different NB content were prepared using solutions of ethylene/NB (Table 5). The poly(ethylene-*co*-NB)$_2$-*b*-poly(ethylene-*co*-NB)$_3$ (M_n 745,000, M_w/M_n 1.23, NB content 34.3 mol%) and poly(ethylene-*co*-NB)$_4$-*b*-
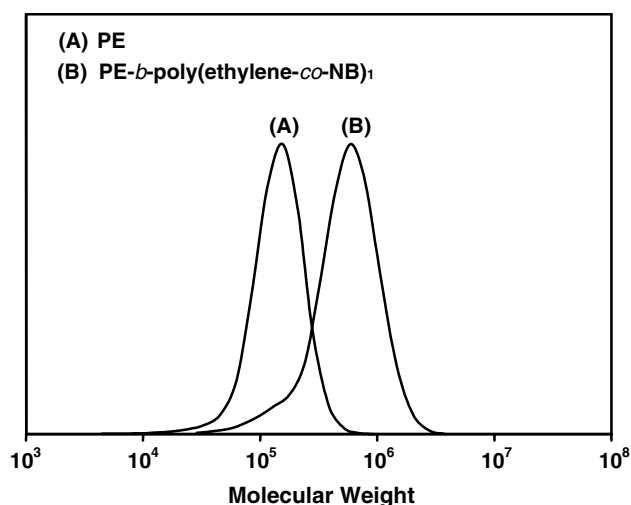

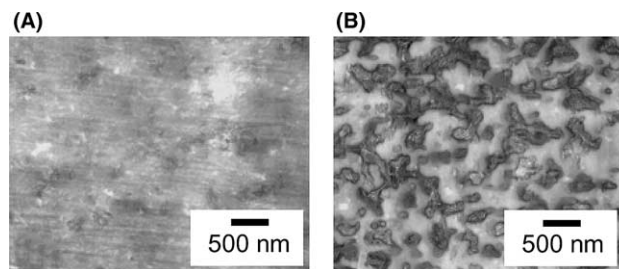**(A)**   **(B)**

500 nm   500 nm

Fig. 12. TEM micrographs of (A) PE-*b*-poly(ethylene-*co*-NB)$_1$; (B) PE and poly(ethylene-*co*-NB) blend polymer (blend conditions: toluene, reflux temperature, 1 h).

poly(ethylene-*co*-NB)$_5$ (M_n 783,000, M_w/M_n 1.32, NB content 30.1 mol%) have two T_gs derived from their first and second segments. Conversely, poly(ethylene-*co*-NB)$_6$-*b*-poly(ethylene-*co*-NB)$_7$ (M_n 507,000, M_w/M_n 1.65, NB content 28.7 mol%) displays both T_m (46 °C, stemming from the first crystalline segment) and T_g (123 °C, originating from the amorphous second segment). Similarly, poly(ethylene-*co*-NB)$_8$-*b*-poly(ethylene-*co*-NB)$_9$ (M_n 424,000, M_w/M_n 1.66, NB content 27.4 mol%) also exhibits T_m (88 °C) and T_g (116 °C). As disclosed in our patents, these are probably the first examples of the syntheses of block copolymers from ethylene and NB [7b].

The powerful strategy of block copolymer formation based on the unique catalysis of PI Catalysts is being further applied to the syntheses of ethylene, α-olefin and cyclic-olefin copolymers with new architectures.

8. Group 4 transition metal complexes other than Ti possessing pyrrolide-imine ligand(s)

Aside from the bis(pyrrolide-imine) Ti complexes (PI Catalysts), we successfully prepared their Zr and Hf counterparts (Zr– and Hf–PI Catalysts), which proved to be highly active catalysts for the polymerization of ethylene [6]. For example, Zr-PI Catalyst **10**, which bears a 1-adamantyl group on the imine-N,

(A) PE

(B) PE-*b*-poly(ethylene-*co*-NB)$_1$

Fig. 11. GPC profile of the PE-*b*-poly (ethylene-*co*-NB)$_1$ formed with PI Catalyst **7**/MAO: (A) prepolymer, M_n 119,000, M_w/M_n 1.34; (B) diblock copolymer, M_n 414,000, M_w/M_n 1.56.

Table 5
Synthesis of various block copolymers using PI Catalyst **7**/MAO

Entry	Prepolymer						Diblock copolymer					
	First block	M_n (/10^3)[a]	M_w/M_n[a]	NB content (mol%)[b]	T_g (°C)[c]	T_m (°C)[c]	Second block	M_n (/10^3)[a]	M_w/M_n[a]	NB content (mol%)[b]	T_g (°C)[c]	T_m (°C)[c]
1	PE	119	1.34			134	(E-*co*-NB)$_1$	414	1.56	31.5	[d]	[d]
2	(E-*co*-NB)$_2$	329	1.11	26.2	52		(E-*co*-NB)$_3$	745	1.23	34.3	50,119	
3	(E-*co*-NB)$_4$	406	1.28	19.5	20		(E-*co*-NB)$_5$	783	1.32	30.1	17,123	
4	(E-*co*-NB)$_6$	267	1.39	12.6		46	(E-*co*-NB)$_7$	507	1.65	28.7	123	46
5	(E-*co*-NB)$_8$	223	1.38	7.5		88	(E-*co*-NB)$_9$	424	1.66	27.4	116	88

[a] Detremined by GPC using polystyrene standard.
[b] Measured by ^{13}C NMR.
[c] Measured by DSC.
[d] Indistinguishable due to the overlap of T_g and T_m; E: ethylene.

Zr-PI Catalyst **10** (M = Zr)
Hf-PI Catalyst **11** (M = Hf)
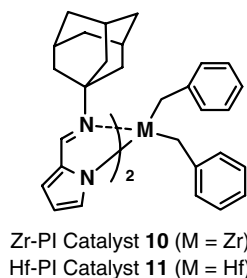
Scheme 6.

demonstrates a high activity of 22,900 kg-PE/mol-cat/h in association with MAO. In addition, the Hf congener **11** polymerizes ethylene with an activity of 2100 kg-PE/mol-cat/h under the same conditions. These results show that, in addition to Ti–PI Catalysts, Zr- and Hf-PI Catalysts are also useful catalysts for ethylene polymerization, which in turn indicates the high potential of pyrrolide-imine ligands for olefin polymerization (Scheme 6).

Bochmann et al. and Mashima et al. have worked on group 4 metal PI Catalysts or related catalysts, some of which exhibit very high activities for the polymerization of ethylene [22a–22c]. Recently, Ziegler and co-workers have reported calculation results regarding ethylene polymerization with PI Catalysts [22d]. It is anticipated that future research on PI Catalysts and other relevant catalysts will result in the discovery of additional high performance molecular catalysts for olefin polymerization, which will provide opportunities to synthesize unique olefin-based materials with distinctive microstructures and related properties.

9. Conclusion

Ligand-oriented catalyst design research has resulted in the discovery of PI Catalysts, which are based on non-symmetric, electronically flexible pyrrolide-imine chelate ligands combined with Ti metals. DFT studies suggest that the catalytically active cationic species originating from PI Catalysts possess a highly electrophilic and sterically open nature when compared to FI Catalysts. Upon activation with MAO, PI Catalysts display high ethylene polymerization activities without any bulky alkyl substituents adjacent to the anionic pyrrolide-N donors, in marked contrast to FI Catalysts, which normally require sterically encumbered substituents in close proximity to the anionic phenoxy-O donors. The highest activity demonstrated by a PI Catalyst exceeds that of Cp_2TiCl_2 or Cp_2ZrCl_2 with MAO. PI Catalysts/MAO exhibit some unique catalytic features, including very high incorporation capability for NB, and the characteristics of living ethylene and living ethylene/NB (co)polymerizations. The highly electrophilic

as well as the sterically open nature of the active species accounts for these key features. In particular, the highly electrophilic nature of the Ti center, which leads to a strong electronic interaction between the Ti center and an olefinic monomer, contributes significantly to the achievement of these unique catalytic features. The unique properties enable the synthesis of a variety of polyolefinic materials, including high molecular weight monodisperse PEs, ethylene- NB copolymers and a number of ethylene- and NB-based block copolymers, many of which were either difficult or impossible to prepare from conventional Ziegler–Natta catalysis. Therefore, PI Catalysts have been widening the scope of those polyolefinic materials that are accessible using transition metal-based molecular catalysis.

We have currently revealed that an electronic attractive interaction between a fluorinated phenoxy-imine ligand and a growing polymer chain can have significant beneficial effects on the catalytic properties of FI Catalysts [3b,3c,4e–4i,23]. The unique catalysis of PI Catalysts described herein, coupled with the above effects regarding FI Catalysts, provide a clear demonstration that an electronic attractive interaction can have a tremendous influence on catalytic behavior (i.e., highly controlled living ethylene and propylene polymerizations, highly controlled living ethylene/NB copolymerization) (Fig. 13), which may lead to hitherto-unknown polymerization catalysis. It is now clear that the advent of the new high performance molecular catalysts represented by FI Catalysts and PI Catalysts for olefin polymerization has initiated a revolution in the fields of polymerization catalysis and polymer synthesis.
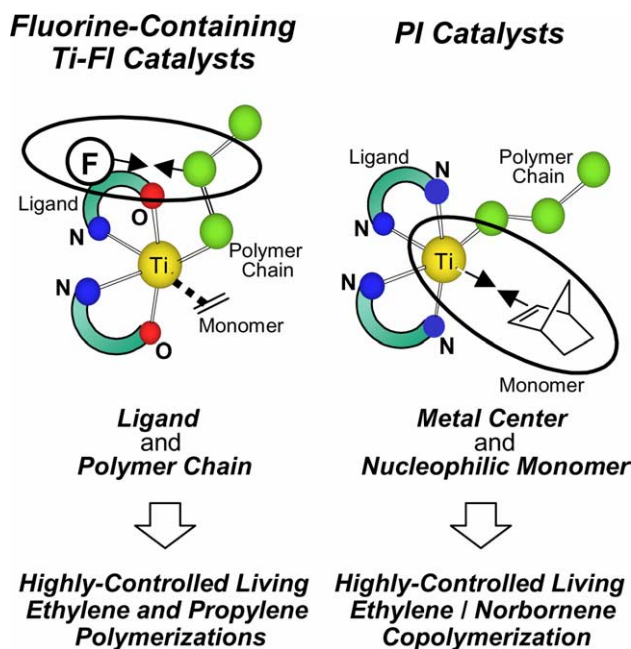

Fig. 13. "Electronic attractive interaction" for unique olefin polymerization catalysis.

Acknowledgements

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