[Review Paper]

Fl Catalysts: Unique Olefin Polymerization Catalysis for Formation of Value-added Olefin-based Materials

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This review describes the olefin polymerization behavior of bis(phenoxy-imine) and bis(phenoxy-ketimine) early transition metal complexes (a.k.a. Fl catalysts). Fl catalysts display unique catalytic properties due to the coordination of a pair of non-symmetric, electron-withdrawing and reactive [O-, N] chelating ligands (Fl ligands). Moreover, Fl ligand structures can be readily tailored from the electronic and steric point of view. Thus, Fl catalysts in combination with appropriate activators are capable of producing a wide variety of unique olefin-based materials (Fl polymers). Specific examples of Fl polymers include selective vinyl-terminated polyethylenes, ultra-high molecular weight linear polyethylenes, well-defined and controlled multimodal polyethylenes, ethylene/polar monomer copolymers, highly syndiotactic and isotactic polypropylenes with exceptionally high $T_m$s, ethylene- and propylene-based end-functionalized polymers, a wide array of polyolefinic block copolymers from ethylene, propylene and higher $\alpha$-olefins, and ultra-fine non-coherent polyethylene particles. These Fl polymers display new or enhanced material properties, and to this end, several Fl polymers are now entering the industrial phase.

Keywords
Fl catalyst, Olefin polymerization, Polyolefin, Olefin-based material, Block copolymer, Supported catalyst

1. Introduction

Catalysts have made, and will continue to make, a huge contribution to human development1. Almost all processes in the chemical industry rely on a wide variety of catalysts for the manufacture of chemicals and materials. The polyolefin industry is no exception to this rule in that the discovery of a binary mixture of a titanium halide species and an organo-aluminum compound (such as TiCl4 and AlEt2Cl) by Ziegler and Natta in the 1950s launched the production of high-density polyethylenes (PEs) and isotactic polypropylenes (iPPs), a catalytic revolution for which Ziegler and Natta won the Nobel Prize in Chemistry in 19632.

Following this significant beginning, the next step that helped the polyolefin industry to evolve was the development of highly active MgCl2-supported TiCl4 catalysts in the late 1960s. These catalysts simplified the production process, cut production costs, increased productivity, improved material properties, and produced higher quality, more reasonably priced high-density PEs, linear low-density PEs, highly isotactic PPs (iPPs) and polyolefinic elastomers. The drawback with these MgCl2-supported catalysts, however, is that their heterogeneous and multi-site nature make it difficult to precisely control the polyolefin structure at the molecular level (and thus optimize material properties).

Now while the MgCl2-supported catalysts are still the pillars of the polyolefin industry, polyolefins arising from single-site group 4 metalloocene catalysts (molecular catalysts) are becoming much more industrially relevant. The main reason for this is that as a result of rational catalyst design, these single-site metalloocene catalysts can control the macromolecular structures of the resultant polymers allowing for the formation of new or differentiated polyolefins possessing superior material properties3~5.

Because of the success of single-site group 4 metalloocene catalysts in the commercial production of high-performance polymers, a search for even newer single-site catalysts that can provide even higher catalyst efficiency and even greater control over polymer architectures was recently begun. By focusing on the design and synthesis of new transition metal complexes, new, diverse, and highly active single-site catalysts based on both early and late transition metals have been created to help propel olefin polymerization into the future6~19. These complexes, when activated, exhibit very high catalytic activity, and the most novel of them exhibit unique polymerization catalysis to form hyperbranched PEs, monodisperse poly($\alpha$-olefin),

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ethylene/methyl acrylate copolymers, and α-olefin-based block copolymers.

In our own work\(^{20}\)~\(^{28}\), we have developed bis(phenoxy-imine) and bis(phenoxy-ketimine) early transition metal complexes (now known as FI catalysts) for the controlled (co)polymerization of olefinic monomers. FI catalysts combined with appropriate activators display unique and versatile polymerization catalysis, represented by precise control over chain transfers, MAO (methylaluminoxane)- and borate-free polymerization catalysis, and high functional group tolerance. As a result of unique catalysis, FI catalysts have created a wide variety of unique olefin-based materials, many of which were previously unavailable with other catalysts\(^{29}\)~\(^{32}\).

Therefore, the discovery and development of FI catalysts has had a significant impact on the growth of olefin polymerization catalysis, and has revealed a number of new polymerization reactions that have brought forth new polymer architectures, and in addition, new insights into the factors that control activity and selectivity within olefin polymerization catalysis have been revealed. It must also be added that current research conducted by Arriola, Bochmann, Busico, Cavallo, Coates, Gibson, Marks, Mühlaupt, Pellecchia, Repo, Scott, Talsi, and others has made a significant contribution toward the further development of FI and related catalysts and resultant polymer formation\(^{33}\)~\(^{52}\).

In this contribution, we would like to describe the discovery and application of FI catalysts, this being mainly based on our own work, but we would also like to include some as yet unpublished results, and we plan to focus on the key features of FI catalysts, and by doing so, aim to reveal how these key features have led to unique olefin polymerization catalysis and distinctive polymer formation.

2. Discovery of FI Catalysts

In contrast to conventional concepts regarding the development of olefin polymerization catalysts that emphasize metals, we have carried out research based on a "ligand oriented catalyst design concept," a concept that is founded on the belief that the flexible electronic nature of a ligand is a key requirement for achieving high activity\(^{20}\). This is because DFT (Density Functional Theory) calculations performed on a model metallocene catalyst \(\text{H}_2\text{SiCp}_2\text{ZrMe}^+\) for ethylene polymerization (Fig. 1) suggested that ethylene polymerization is a process that involves intense electron exchange between a ligand and a metal\(^{27}\).

The research based on the ligand oriented catalyst design concept has resulted in the discovery of a number of highly active catalysts for the polymerization of ethylene, which include: phenoxy-imine ligated early transition metal complexes (FI catalysts), pyrroliide-imine ligated group 4 transition metal complexes (PI catalysts), indolide-imine ligated Ti complexes (II catalysts), imine-phenoxy ligated group 4 transition metal complexes (IF catalysts), phenoxy-ether ligated Ti complexes (FE catalysts), imine-phenoxy ligated group 4 transition metal complexes (IF catalysts), phenoxy-ether ligated Ti complexes (FE catalysts), imine-phenoxy ligated group 4 transition metal complexes (IF catalysts), and tris(pyrazolyl)borate ligated Ta complexes (PB catalysts) (Fig. 2)\(^{20}\)~\(^{32}\).

The successful discovery of a series of high-activity catalysts based on the ligand oriented catalyst design concept is proof that this concept works as a basis for developing new highly active olefin polymerization catalysts.

Of the high-activity catalysts that were discovered on the basis of the ligand oriented catalyst design concept, FI catalysts in particular display high ethylene polymerization activity which normally surpasses that of group 4 metallocene catalysts\(^{33}\). The highest activity displayed by FI catalyst 1 (Table 1) reached an astonishing catalyst turnover frequency (TOF) value of 64,900/
s/atm at 25°C (reacting 64,900 ethylene molecules per second at room temperature under atmospheric pressure conditions). This TOF is a new record not only for olefin polymerization, but for any catalytic reaction using an artificial catalyst. Structures of the FI catalysts that are discussed in this review are summarized in Table 1.

3. Key Features of FI Catalysts

FI catalysts have the following structural and electronic features resulting in unique polymerization catalysis and distinctive polymer formation.

3.1. Structural Features

A general synthetic route for FI catalysts is shown in Fig. 3. FI catalysts are readily prepared by the complexation of FI ligands and early transition metal compounds. In general, FI ligands can be obtained in practically quantitative yields by the Schiff-base condensation of ortho-hydroxy aromatic aldehydes or ketones and primary amines. These phenol derivatives and amines are easily synthesized, and thus have a rich inventory of commercially available compounds. Therefore, FI catalysts have a wide range of catalyst design possibilities, which is the most important feature of FI catalysts. As a result of this feature, FI catalysts have enormous and diverse ligand structures with a wide variety of substituents, including O, S, N, P and halogen-based functional groups. This enormous structural diversity of FI catalysts has given rise to unprecedented olefin polymerization catalysis and unique polymer formation. For example, Zr-FI catalysts possessing electron-donating groups in the R³ positions or bridged FI ligands at the R¹ positions normally display a thermally robust nature and polymerize ethylene with high efficiency at high temperatures (e.g., 2, 143 kg-PE/mmol-cat./h, 150°C, 3.0 MPa ethylene pressure). Additionally, Ti-FI catalysts possessing fluorine atom(s) ortho to the imine-N (e.g., 3 and 4) can induce highly controlled living ethylene and highly syndiospecific living propylene polymerizations.

Since an FI catalyst contains two bidentate non-symmetric phenoxy-imine ligands, it can potentially display five isomers from A to E (Fig. 4) arising from the coordination modes of ligands in an octahedral configuration. X-ray analysis has established that, in the solid state, an FI catalyst normally exists as the isomer A, meaning, it has a trans-O, cis-N, and cis-Cl arrangement, and thus C₂ symmetry. The C₂-symmetric nature implies that the catalyst may be an isospecific catalyst for propylene polymerization, but actually not. When FI catalysts possess extremely bulky groups on the imine-Ns (N-C₆H₄-2,6-R₂, R: Me, i-Pr), they can adopt a cis-O, trans-N and cis-X (X = O-i-Pr) arrangement. Any further increase in the steric bulk of the R¹ substituent (N-C₆H₄-2,6-Ph₂ or N-CHPh₂) forces one of the N-Ti bonds to become dissociated, resulting in a five-coordinated complex.

In solution, however, FI catalysts generally exist as a mixture of isomer A, which is normally predominant (trans-O, cis-N, and cis-Cl arrangement: C₂ symmetry), and isomer B (cis-O, cis-N, and cis-Cl arrangement: C₁ symmetry). These isomers are often fluxional and can mutually transform each other on a nuclear magnetic resonance (NMR) time scale. Some of the unique polymerization characteristics of FI
Table 1  Structures of FI Catalysts 1-38

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Table 1  Structures of FI Catalysts 1-38

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catalysts stem from this structurally dynamic nature.

Interestingly, Zr-FI catalyst 5, which has two cumyl groups that are located ortho and para to the phenoxy-O, predominantly exists as isomer B. Upon activation with MAO, 5 generates well-defined PEs with temperature-dependent unimodal, bimodal and trimodal molecular weight distributions61). As with neutral FI catalysts, the cationic species derived from FI catalysts can potentially exhibit five isomers depending on the ligand coordination modes; three of the five isomers have cis-located polymerization sites. The presence of these isomers probably is the reason for this multimodal behavior. Moreover, for the C2 symmetric FI catalysts, fluxional isomerization between two enantiomers (Λ/Δ racemization) was proposed by theoretical calculations for a syndioslective propylene polymerization with Ti-FI catalysts65), as has been suggested by low temperature VT-NMR experiments for a cationic monobenzyl Hf-FI catalyst49) and other relevant complexes66). Therefore, the fluxionality of FI catalysts is an important feature in understanding their unique polymerization characteristics.

For ‘ordinary’ C2 symmetric FI catalysts (with a trans-O, cis-N and cis-X configuration), the two imine-Ns are located on a plane defined by a central metal (M) and two cis-located X ligands, and thus the R1 substituents on the imine-Ns are on a plane at the backside of the X-M-X moiety, whereas the R2 substituents ortho to the phenoxy-Os are situated above and below the X-M-X moiety (Fig. 5)22). Since two X-bound sites are transformed into olefin polymerization sites after activation, these R1 and R2 substituents are located in a strategic position capable of influencing polymerization behavior of FI catalysts.

The localized structure of an FI catalyst can be modified by the selection of the activation method. Namely, the phenoxy-imine ligand is converted to a phenoxy-amine ligand by the reduction with i-Bu3Al (and its contaminant i-Bu2AlH) with the coproduction of isobutene, resulting in the generation of a bis(phenoxy-amine) complex having a sterically-encumbered i-Bu2Al group attached to the amine-donor (Fig. 6)53),67).

Therefore, an FI catalyst combined with i-Bu3Al/Ph3C(C6F5)4 forms a bis(phenoxy-amine) complex, as a catalytically active species, which possesses a sterically crowded environment near the polymerization center. The bis(phenoxy-amine) complex derived from the FI catalyst and i-Bu3Al/Ph3C(C6F5)4 can produce ultrahigh molecular weight polymers due to the discouragement of chain transfer by the sterically-encumbered i-Bu2Al group attached to the amine-donor30),31). For example, Zr-FI catalyst 6/i-Bu3Al/Ph3C(C6F5)4 affords an amorphous ethylene/propylene copolymer having an exception-ally high molecular weight (Mw) of 10,200,000 (Mw/Mn 2.52, propylene content 20 mol%) (70°C, 0.9 MPa ethylene/propylene total pressure). This molecular weight represents the highest molecular weight known for linear, synthetic copolymers to date68).

3. 2.  Electronic Features

FI catalysts are heteroatom [O, N] coordinated early transition metal complexes, which makes FI catalysts different from group 4 metalloene catalysts that possess cyclopentadienyl (Cp) carbanion-based ligands. Because of the coordination of heteroatom-based [O, N] ligands that are more electron withdrawing than Cp carbanion-based ligands, the catalytically active species originating from FI catalysts possess a highly electro-
philic nature relative to the active species derived from group 4 metallocene catalysts (Table 2). High electrophilicity is normally advantageous for exhibiting high catalyst efficiency for olefin polymerization \(^{69,70}\). Additionally, such character is advantageous for the incorporation of olefins with a high nucleophilic nature such as bridged-cyclic-olefins (e.g., norbornene) \(^{23,27,70}\).

Additionally, \([O^-, N]\) ligation renders the metal-ligand bonding properties of FI catalysts more ionic and polarized compared to the bonding properties of group 4 metallocene catalysts. Indeed, NMR studies on FI catalysts \(^7\) and \(^8\) in combination with Ph\(_3\)CB(C\(_6\)F\(_5\))\(_4\) or B(C\(_6\)F\(_5\))\(_3\), together with the behavior of the resulting ion pairs that were precipitated out as an oil from a toluene solution, suggest that the resulting ion pairs possess a highly ionic character compared to those derived from group 4 metallocene catalysts \(^{71}\).

Due to this ionic and polarized nature, FI catalysts are more strongly adsorbed on the surfaces of inorganic compounds (e.g., MgCl\(_2\), hetero-poly compounds, clays) than group 4 metallocene catalysts are, and moreover, they undergo chemical interactions to the degree that an inorganic compound can function as an activator. Indeed, FI catalysts can form highly active supported catalysts in combination with MgCl\(_2\)/R\(_n\)Al(OR)\(_n\), hetero-poly compounds/R\(_3\)Al, and clays/R\(_3\)Al, establishing MAO- and borate-free supported olefin polymerization catalysts \(^{30}-^{32}\). \(^1\) They allow for a wide variety of catalyst design possibilities because of the coordination of a pair of non-symmetric, electron-withdrawing and reactive \([O^-, N]\) ligands that are readily synthesized. Due to these features, FI catalysts exhibit unique and versatile catalytic properties that cannot be replicated by conventional olefin polymerization catalysts \(^{30}-^{32}\).

4. Preparation of Unique Olefin-based Materials with FI Catalysts

As described above, FI catalysts have the following key features because of the coordination of a pair of non-symmetric, electron-withdrawing and reactive \([O^-, N]\) ligands that are readily synthesized. Due to these features, FI catalysts exhibit unique and versatile catalytic properties that cannot be replicated by conventional olefin polymerization catalysts \(^{30}-^{32}\).

- They allow for a wide variety of catalyst design possibilities because of ligand accessibility and amenability to modification (enormous structural diversity) \(^{30}\),
- They can exist as mixtures of isomers that are capable of mutually transforming (multimodal behavior) \(^{61,64}\),
- Syndiospecific propylene polymerization despite \(C_2\) symmetric nature \(^{79}\),
- They allow the ligand structure to change from phenoxy-imine to phenoxy-amine (formation of ultra-high molecular weight polymers) \(^{59,80}\) and isotactic polymers \(^{79}\),
- They generate highly electrophilic active species that are highly ionic and polarized (high incorporation capability for strained cyclic-
olefin\(^{81}\), versatility vis-à-vis activator selection resulting in MAO- and borate-free supported catalysts\(^{72}\)), and (5) they display high functional group tolerance (ethylene/polar monomer copolymerization\(^{78}\)). Examples of value-added olefin-based materials that have been created by FI catalyst technology are introduced below.

### 4.1. Al- and Vinyl-terminated PEs

The R\(^1\) substituents (on the imine-Ns), which are on a plane at the backside of the polymerization sites, exercise enormous influence on chain transfer reactions, resulting in the achievement of selective synthesis of both Al- and vinyl-terminated PEs.

We have shown that Zr-FI catalyst 9 having a 2-i-propylphenyl group at the R\(^1\) position in combination with MAO or MAO plus trimethylaluminum quantitatively generates Al-terminated PEs (Al-PEs) possessing low-to-very-high molecular weights and narrow-to-broad molecular weight distributions with high productivity (Table 3)\(^{82}\). The i-Pr group mitigates β-H transfer, which leads to the exclusive chain transfer to alkylaluminum, and selectively forms Al-PEs.

Alternatively, Zr-FI catalysts incorporating cycloalkyl groups at the R\(^1\) positions, combined with MAO, provide vinyl-terminated PEs, with high efficiency\(^{83}\). For example, FI catalysts 10-14 with MAO at 25°C transform ethylene into vinyl-terminated low molecular weight PEs (\(M_w 2000-14,000\)), vinyl selectivity 90-96%) while maintaining higher catalytic activities than Cp:ZrCl\(_2\)/MAO (28 kg-PE/mmole-cat./h) under the same conditions (Table 4). Product analyses have revealed that the vinyl-terminated PEs have linear structures with practically no branching. Ethylene pressure studies along with X-ray analyses and DFT calculations have demonstrated that β-H transfer to the incoming monomer is the predominant chain transfer process, which accounts for the production of the vinyl-terminated PEs. The above Al-PEs and vinyl-terminated PEs can be converted to a variety of functionalized PEs\(^{84}\). For instance, with hydrogen peroxide oxidation using Na\(_2\)WO\(_4\) as a catalyst, a vinyl-terminated PE (\(M_w 2000, M_n/M_w 1.7\), vinyl group 95%, \(T_m 122°C\)) is readily converted to the corresponding epoxy-terminated PE (\(T_m 121°C\)) in practically quantitative yield\(^{85}\). In addition, a diol-terminated PE (\(T_m 121°C\)) is obtained by the in-situ hydrolysis of the above epoxy-terminated PE using aqueous 2-propanol. Conversely, the Alder-Ene reaction of vinyl-terminated PE (\(M_w 1800, M_n/M_w 2.2\), vinyl group 94%, \(T_m 122°C\)) with maleic anhydride in the presence of nitrobenzene or 2,6-di-i-butyl-4-methylphenol yields the corresponding succinic anhydride-terminated PE (\(T_m 121°C\))\(^{86}\). The succinic anhydride-terminated PE exhibits higher melt viscosity and higher thermal stability than the parent vinyl-terminated PE due to the presence of the chain-end succinic anhydride group. Interestingly, the Na salt of this succinic anhydride-terminated PE forms nano-sized particles (diameter 10-30 nm) and worm-like fibers (fibril diameter 20-30 nm, length 60-270 nm) as self-assemblies in water (Fig. 7).

### 4.2. Well-defined Multimodal PEs

As discussed, an FI catalyst potentially exhibits five isomers stemming from the coordination modes of ligands in an octahedral geometry, indicating that an FI catalyst has the ability to produce well-defined multimodal polymers that may display an excellent combina-

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**Table 3** Ethylene Polymerization Data for FI Catalyst 9 with MAO or MAO Plus Me\(_3\)Al

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<td>0</td>
<td>500</td>
<td>58</td>
<td>716000</td>
<td>2.6</td>
<td>0/100</td>
</tr>
<tr>
<td>4</td>
<td>0.250</td>
<td>0.5</td>
<td>7500</td>
<td>34</td>
<td>12000</td>
<td>2.0</td>
<td>0/100</td>
</tr>
<tr>
<td>5</td>
<td>0.250</td>
<td>0.20</td>
<td>900</td>
<td>41</td>
<td>201000</td>
<td>5.9</td>
<td>0/100</td>
</tr>
</tbody>
</table>

Conditions: toluene, 25°C, 5 min (30 min\(^{80}\)), ethylene 0.1 MPa, FI catalyst 9 0.5 mmol.  
\(a\) kg-polymer/mmol-cat./h. \(b\) Determined by GPC. \(c\) Chain-end group: vinyl/methyl (molar ratio).

**Table 4** Ethylene Polymerization Data for FI Catalysts 10-14 with MAO

<table>
<thead>
<tr>
<th>Entry</th>
<th>FI catalyst</th>
<th>Activity(^{a})</th>
<th>(M_w) (^{b})</th>
<th>(M_n/M_w) (^{b})</th>
<th>Vinyl end(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>50.4</td>
<td>4400</td>
<td>2.0</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>31.6</td>
<td>2000</td>
<td>1.7</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>22.0</td>
<td>2000</td>
<td>1.7</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>67.2</td>
<td>3600</td>
<td>2.1</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>87.7</td>
<td>14000</td>
<td>1.7</td>
<td>90</td>
</tr>
</tbody>
</table>

Conditions: toluene, 25°C, 5 min, ethylene 0.1 MPa, FI catalyst 0.5 mmol, MAO 0.625 mmol as Al.  
\(a\) kg-polymer/mmole-cat./h. \(b\) Determined by GPC. \(c\) Degree of vinyl unsaturation at one of the two polymer chain ends, determined by \(^1\)H NMR.
tion of material properties and processability. For example, Zr-FI catalysts 15 and 16, having a methyl or methoxy group at the R3 position (R1ʹ phenyl, R2ʹ t-Bu) exhibit bimodal behavior at 75°C to produce well-defined bimodal PEs, though Zr-FI catalyst 17 bearing a C6F5 group at the R1 position (R2ʹ t-Bu, R3ʹ methoxy) displays unimodal behavior.

Interestingly, Zr-FI catalyst 5 incorporating two cumyl groups at the R2 and R3 positions, in conjunction with MAO, forms uni-, bi- and tri-modal PEs in a controlled manner, simply by varying the polymerization temperatures (Fig. 8)51). 1H, 13C as well as 15N NMR studies have demonstrated that 5 exists as a mixture of isomers (the predominant isomer: B, Fig. 4). Moreover, the multimodal PEs made with 5/MAO possess virtually linear structures, and polymerization time and Al(MAO)/Zr molar ratio have little influence on catalytic activities and multimodal behavior. Altogether, we have concluded that the multimodal behavior stems from isomers of the catalytically active species. These are the first examples of well-defined bi- and tri-modal PEs derived from structural isomers that originate from different modes of the ligand coordination. These results, therefore, provide a unique strategy to produce well-defined multimodal polyolefins by a single homogeneous catalyst in a single stage polymerization process.

4.3. Ultra-high Molecular Weight Linear PEs

The R2 substituent is located at a strategic position capable of controlling comonomer incorporation. Additionally, the R2 substituent exercises a great influence on catalytic activity, and hence the R2 substituent plays a key dual role for polymerization catalysis due to the steric congestion, near the polymerization center, provided by the R2 substituent. A striking feature is that a sterically encumbered R2 substituent induces extremely high selectivity for ethylene relative to α-olefins (e.g., Zr-FI catalyst 18, R2 = cumyl; approximately 300 times more reactive to ethylene compared with propylene), which is unachievable with conventional catalysts. This hitherto-unknown polymerization catalysis has led to the creation of unique polymers such as ultra-high molecular weight linear PEs and multi-block copolymers comprised of PEs and ethylene/α-olefin amorphous copolymers.

An application of the high selectivity for ethylene compared to α-olefins (and vinyl-terminated macro-monomers) is their ability to produce ultra-high molecular weight linear PEs. Zr-FI catalysts having a sterically encumbered R2 substituent combined with SiO2-supported MAO or MgCl2/R’Al(OR)3 yield ultra-high molecular weight PEs having neither short nor long chain branches along the polymer backbone, unlike the ultra-high molecular weight PEs produced with conventional catalysts. For example, FI catalyst 19 with SiO2-supported MAO gives ultra-high molecular weight linear PEs (80°C, 0.8 MPa ethylene pressure; productivity 560 kg-PE/mmol-Zr, Mv 4,400,000).

Similarly, FI catalyst 20 coupled with isolated MgCl2/Et2Al(OR)3-a [OR: 2-ethyl-1-hexoxy group] also provides ultra-high molecular weight linear PEs (80°C, 0.8 MPa ethylene pressure; productivity 360 kg-PE/mmol-Zr, M, 3,000,000). These ultra-high molecular weight PEs displayed morphologies consisting of well-defined spherical particles (e.g., bulk density of the PE formed with 20/MgCl2/Et2Al(OR)3-a; 0.50 g/ml)22). These good morphology ultra-high molecular weight linear PEs are ideal high strength materials, and thus
4.4 Ultra-fine Non-coherent PE Particles

As described, MgCl2/R1′nAl(OR)3-n activates and simultaneously immobilizes FI catalysts to form supported FI catalysts capable of producing good morphology polymers. We have demonstrated that the combination of an FI catalyst with an isolated ultra-fine particle MgCl2/R1′nAl(OR)3-n support has brought forth an extraordinary opportunity for the preparation of ultra-fine, non-coherent PE particles that are unprecedented polyethylenic materials72).

With these supported catalysts, we have succeeded in the creation of ultra-fine spherical particle PEs of 3 to 30 μm in diameter. To our delight, the particle sizes are controllable to the micron, and the particle size distributions are normally narrow, with this new supporting catalyst technology. For example, FI catalyst 20 supported on isolated MgCl2/Bu_nAl(OR)3-n having a particle size of 1.5 μm in diameter furnishes high molecular weight PEs (Mw, 3,100,000) composed of non-coherent, spherical particles of 10 μm in diameter (Fig. 9(A)). In addition, ultra-fine non-coherent PE particles of 5 and 3 μm were also synthesized using this technology (Figs. 9(B), (C)). Moreover, with a technology that allows for the production of ultra-fine non-coherent particle PEs in our possession, we have successfully prepared hollow particle PEs (Fig. 9(D)) as a result of the removal of MgCl2 support by treatment with chelating agents such as acetyl acetonate. We believe these ultra-fine non-coherent particle PEs have high potential as materials for sintered sheets and filters, light diffusion films, cosmetics, high-performance modifiers, and so forth.

4.5 Ethylene/Norbornene Copolymers

Ethylene/bridged-cyclic-olefin copolymers represented by ethylene/norbornene (NB) copolymers possess high thermal stability and useful optical properties that are imparted by the cyclic-olefin component. NB has a higher HOMO energy level (−7.25 eV, DFT calculations) than ethylene (−8.15 eV) and propylene (−7.66 eV)81), thus showing a more nucleophilic nature than the nature possessed by these common olefinic monomers. As discussed, the catalytically active species stemming from FI catalysts have a more electrophilic nature than the nature stemming from group 4 metallocene catalysts. These facts suggest the high potential of FI catalysts for ethylene/NB copolymerization.

As anticipated, Ti_FI catalysts can achieve strikingly high NB incorporation relative to high-performance group 4 metallocene catalysts for ethylene/NB copolymerization81). Table 5 displays the copolymerization results, which also includes the results obtained for Me2Si(Me4Cp)(Nt-Bu)TiCl2 (CGC), rac-[Et(Ind)2]ZrCl2 and [Me2C(Flu)(Cp)]ZrCl2 for comparison. While Ti_FI catalyst 21 (R2 = i-Bu) combined with MAO was a poor catalyst for this copolymerization, Ti_FI catalysts 22 and 23 (bearing the phenyl group at the R2 position) with MAO activation formed copolymers of very high Tgs and NB contents (22: Tgs 120°C, NB content 45.7 mol%, 23: Tgs 126°C, NB content 46.1 mol%) with high efficiency under the given conditions.

These results indicate that the phenyl group at the R2
position induces far higher NB incorporation than the \( t \text{-Bu} \) group. Although this appears contradictory to the X-ray structures (Fig. 10), DFT calculations suggest that the phenyl group provides a sterically more open active site than the \( t \text{-Bu} \) group because of its rotation to evade the steric hindrance.

Significantly, the copolymers made with Ti-FI catalysts 22 and 23 possess higher \( T_g \)s and NB contents than those formed with CGC, \( \text{rac-}[\text{Et(Ind)}_2]\text{ZrCl}_2 \) and \( [\text{Me}_2\text{C(Flu)(Cp)}]\text{ZrCl}_2 \), which are well-known for achieving the high incorporation of NB. In fact, Ti-FI catalysts 22 and 23 are some of the best catalysts for ethylene/NB copolymerization in terms of NB incorporation and catalyst efficiency. Considering that these Ti-FI catalysts generate a sterically more encumbered active site than the above metallocene catalysts, these results stand as further evidence that the highly electrophilic nature of the catalyst is of central importance for achieving efficient NB co-enchainment.

\[ ^{13}\text{C NMR microstructural analysis demonstrated that Ti-FI catalysts 22 and 23 have a very high propensity to form an alternating copolymer (22: NB content 48.4 mol\%, \( \text{NB-E-NB-E-NB} \), 96.1%; \( \text{E-NB-E-NB} \), 3.9%; 23: NB content 48.9 mol\%, \( \text{NB-E-NB-E-NB} \), 96.0%; \( \text{E-NB-E-NB} \), 4.0%). Interestingly, 22/MAO mediates living ethylene/NB copolymerization under the conditions that we examined, as demonstrated by the linear relationship of molecular weight and polymer yield (Fig. 11). The living nature probably stems from the fact that the catalytically active species originating from Ti-FI catalyst 22 has a highly electrophilic nature and thus possesses a high affinity for NB, as well as displaying some characteristics of living ethylene polymerization.\]

4. 6. Ethylene/Polar Monomer Copolymers

As introduced, FI catalysts have higher functional group tolerance due to the coordination of phenoxy-imine [O, N] ligands than group 4 metallocene catalysts, though both are group 4 metal-based catalysts, a fact revealed by DFT calculations.\(^{78}\)

Table 6 displays ethylene/5-hexen-1-yl acetate (HA) copolymerization results. Under the conditions examined, \( \text{Cp}_2\text{TiCl}_2 \) and CGC showed no reactivity probably because of the deactivation caused by the coordination of the carbonyl moiety of HA. Conversely, FI catalysts 21, 22 and 24 produced high molecular weight copolymers of narrow molecular weight distributions with very high activity.\(^{78}\). \(^{13}\text{C NMR}, \) together with GPC-IR analysis, showed a narrow HA distribution and the randomly distributed nature of HA. A comparison of the data in Table 6 indicates that the phenyl group induces higher HA incorporation and catalytic activity, further confirming the beneficial effect of the phenyl group at the R\(^2\) position. Significantly, FI catalysts 22 and 24 mediated this copolymerization even in the presence of an excess amount of HA to MAO. The HA content reached 3.2 mol\% (\( M_w 23,000, M_w/M_n 1.6 \)). Moreover, these catalysts promote ethylene/norbornen-2-yl acetate copolymerization to afford the corresponding copolymers (e.g., 22: ethylene/norbornen-2-yl acetate content 1.2 mol\%, \( M_w 119,000, M_w/M_n 2.8 \)).

The above results may open the door to polar monomer copolymerization with early transition metal catalysts, which is a long-standing challenge in the field of polymerization catalysis.

4. 7. Highly Syndiotactic and Isotactic PPs

As described, an FI catalyst generally assumes a C\(_2\)-symmetric trans-O, cis-N and cis-Cl configuration as the predominant isomer. Additionally, DFT calculations suggest that a catalytically active species derived
from an FI catalyst favors a C_2-symmetric configuration with a trans-O, cis-N and cis-polymer chain/coordinat-
ed olefin disposition. Hence, FI catalysts were target-
ed as catalysts capable of forming iPPs via a site-
control mechanism.

Zr- and Hf-FI catalysts 25 and 26, combined with
MAO, display high reactivity toward propylene and
provide propylene oligomers (aPPs), Zr_ and Hf_FI catalysts
with the same
responsible for the observed stereocontrol,
and
responding Ti_FI cata-

ization). For example, Zr- and Hf_FI catalysts
R2 position, and

est with high molecular weig-

ated olefin disposition. Hence, FI catalysts were target-
ted as catalysts capable of forming iPPs
the resultant polymer is syndiotactic (rr 79%), and
that a chain-end control mechanism with a 2,1-insertion is

ible for the observed stereocontrol, regardless of the
C_2 symmetric catalyst (37,58,80). To our sur-
prise, microstructural analysis by 13C NMR shows that
the resultant polymer is syndiotactic (rr 79%), and
that a chain-end control mechanism with a 2,1-insertion is

m of the isospecific polymerizations is phenoxy-

amine ligated complexes. Elaborate catalyst design
work focusing on the substituents at the R1 and R2 posi-
tions has resulted in the discovery of FI catalysts
afford highly isotactic PPs that are compa-

Table 6 Ethylene/5-Hexen-1-yl Acetate Copolymerization Data for FI Catalysts 21, 22, 24 and Typical Metalloocene Catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Comonomer [mmol]</th>
<th>Yield [g]</th>
<th>Activity [m]</th>
<th>Comonomer content [mol%]</th>
<th>Mw [g/mmol]</th>
<th>Mw/Mn</th>
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<tr>
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<td>1.00</td>
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<td>86</td>
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<td>497000</td>
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<td>0.81</td>
<td>269000</td>
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</tr>
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<td>0.90</td>
<td>273000</td>
<td>2.2</td>
</tr>
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</tr>
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<td>2.00</td>
<td>0.235</td>
<td>71</td>
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<td>69000</td>
<td>1.7</td>
</tr>
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<td>5.25</td>
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<td>2.45</td>
<td>20000</td>
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</tr>
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<td>24</td>
<td>5.25</td>
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<td>15</td>
<td>3.20</td>
<td>23000</td>
<td>1.6</td>
</tr>
<tr>
<td>8</td>
<td>Cp2TiCl_2</td>
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<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>CGC</td>
<td>1.00</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Conditions: toluene, 25°C, 10 min.
a) Charged 5-hexen-1-yl-acetate, ethylene 0.1 MPa, complex 20 μmol as Al. b) kg-polymer/mmol-cat/h.
c) Determined by 1H NMR. d) Determined by GPC.

Further research has led to the discovery of Ti-FI cata-
lyst 28, which possesses a trimethylsilyl group at the
R^2 position, and which produces a highly syndiotactic
PP (rr 91%, 1°C polymerization) with a very high T_m of
140°C, on activation with MAO (88). Surprisingly,
the corresponding fluorinated Ti-FI catalyst 4 with MAO at
0°C affords enhanced tacticity PP (rr 94%) with an
extremely high T_m of 156°C, representing one of the highest T_m for sPPs ever synthesized (39,84). A detailed propy-
lene polymerization mechanism with the Ti-FI catalyst/MAO systems will be described later (79).

While a Ti_FI catalyst on activation with i-Bu3Al/
Ph3CB(C6F5)_2 forms ultra-high molecular weight atac-
tic PPs (aPPs), Zr- and Hf-FI catalysts with the same
activators can induce isoselective propylene polymerization (89). For example, Zr- and Hf-FI catalysts 25
and 26 with i-Bu3Al/Ph3CB(C6F5)_2 at 25°C provide iPPs
with high molecular weights (25: M_w 209,000, M_w/M_n 2.42, mm 46%, T_m 104°C, 26: M_w 412,000, M_w/M_n 2.15,
mm 69%, T_m 124°C). As discussed, the active species
for these isoselective polymerizations are phenoxy-
amine complexes. Elaborate catalyst design
work focusing on the substituents at the R^1 and R^2 posi-
tions has resulted in the discovery of FI catalysts 29
and 30 that afford highly isotactic PPs that are comparable
to those produced with the best heterogeneous Ziegler-
Natta catalysts (25°C polymerization; 29 mmmmm 97%,
T_m 163°C, 30 mmmmm 97%, T_m 165°C) (86). The T_m and the isospecificity achieved by these FI catalysts repre-
sent some of the highest values for isotactic PPs ever synthesized with molecular catalysts. The isospecific propylene polymerization proceeds via a 1,2-insertion with a site-control mechanism.

The production of highly isotactic PPs with Zr- and
Hf-FI catalysts/i-Bu3Al/Ph3CB(C6F5)_2 (active species:
phenoxy-amine complexes, site-controlled polymeriza-

tion with 1,2-insertion) is in sharp contrast to that of
highly syndiotactic PPs with Ti-FI catalysts/MAO
(active species: phenoxy-imine complexes, chain-end
controlled polymerization with 2,1-insertion) (79).

4. 8. Highly Syndiotactic and Isotactic Polystyrenes

Interestingly, and importantly, fluorinated Ti-FI cata-
lysts are capable of producing isotactic polystyrenes
(iPSs) or syndiotactic polystyrenes (sPSs), or an iPS/
sPS mixture, by varying the reaction conditions. For
example, with MAO activation at 20°C, Ti-FI catalysts
3 and 4 form highly isotactic PSs (3; T_m 224°C, 4; T_m
213°C) (Table 7) (79). 13C NMR analyses for these iPSs showed practically perfect tacticity. These FI catalysts are not merely a notable addition to the limited list of molecular catalysts for iPS, but also the first examples of a catalyst with a nonbridged ligand that carries out isospecific styrene polymerization.

It should be noted that the same catalyst systems
polymerize propylene in a syndiospecific fashion, as
described above. Therefore, the formation of iPSs
with Ti-FI catalysts 3 and 4 may suggest that the pro-
posed site inversion between A and A for propylene poly-
merization does not take place for styrene polymer-
ization with 3 and 4 combined with MAO. The site-
version for propylene polymerization is probably

promoted by the presence of a secondary polypropylene growing chain due to its steric congestion\textsuperscript{57,78}, suggesting that styrene polymerization with the above Ti-FI catalysts would proceed \textit{via} a 1,2-insertion (which is suggested by DFT calculations). Altogether, we believe that the isospecific styrene polymerization with fluorinated Ti-FI catalysts \textit{via} site-control mechanism with 1,2-insertion without the site-inversion process.

Raising the polymerization temperature from 20°C to 40°C, Ti-FI catalyst \textbf{4} produces an sPS/sIPS mixture. The ratio of iPS/sPS can be varied by polymerization conditions. Surprisingly, treatment of \textbf{4} with MAO at 40°C or 60°C prior to a polymerization reaction (premix procedure) resulted in the exclusive formation of sPS. Under high polymerization temperature and/or premix conditions, Ti-FI catalysts are decomposed into mono(phenoxy-imine) Ti(III) species through the ligand transfer to alkylaluminums\textsuperscript{62}). This Ti(III) species is inactive toward isoselective styrene polymerization, probably due to their less electrophilic nature.

**4.9. Ultra-high Molecular Weight Atactic PPs and Regio- and Stereo-irregular High Molecular Weight Poly(higher \alpha-olefin)**

As described, the combination of an FI catalyst with \textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4} resulted in the generation of a phenoxy-amine-ligated complex as a catalytically active species, which can produce ultra-high molecular weight polymers. For example, Ti-FI catalyst \textbf{21} combined with \textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4} forms an ultra-high molecular weight aPP (\(M_w\) 8,286,000, no \(T_m\) with a somewhat broad molecular weight distribution (\(M_w/M_n 4.15\))\textsuperscript{95}). The molecular weight makes it one of the highest molecular weight aPPs ever synthesized. Ti-FI catalysts with \textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4} also display unique catalysis for the polymerization of higher \alpha-olefins\textsuperscript{98}). For instance, at 25°C Ti-FI catalyst \textbf{21} favors the 2,1-insertion of 1-hexene and affords high molecular weight (\(M_w 846,000, M_n/M_w 1.65\)) atactic poly(1-hexene) having ca. 50 mol\% of regio-irregular units with high efficiency (Table \textbf{8}).

Similarly, the same catalyst system forms high molecular weight atactic poly(1-octene) (\(M_w 906,000, M_n/M_w 1.68\))\textsuperscript{98}), poly(1-decene) (\(M_w 850,000, M_n/M_w 1.75\)) and poly(4-methyl-1-pentene) (\(M_w 1,450,000, M_n/M_w 1.71\)), all of which include frequent regio-errors (Table \textbf{8}). To the best of our knowledge, these molecular weights of the poly(higher \alpha-olefin)s described above are some of the highest encountered for homogeneus olefin polymerization catalysts. Additionally, ethylene/higher \alpha-olefin copolymers having a wide variety of higher \alpha-olefin contents were prepared with Ti-FI catalyst \textbf{21/\textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4}}.

Considering that 2,1-insertion normally encourages chain termination (which causes low molecular weights), the production of high molecular weight regio-irregular poly(higher \alpha-olefin)s is highly significant. These represent the first examples of stereo- and regio-irregular high molecular weight poly(higher \alpha-olefin) ("ultra-random polymers").

<table>
<thead>
<tr>
<th>Entry</th>
<th>FI catalyst</th>
<th>Activity ( \times 10^{-3} )</th>
<th>TOF [min(^{-1})]</th>
<th>Conv. [%]</th>
<th>( M_w )</th>
<th>( M_n/M_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5.21</td>
<td>257</td>
<td>12</td>
<td>846000</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>1.94</td>
<td>288</td>
<td>14</td>
<td>906000</td>
<td>1.68</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>0.56</td>
<td>308</td>
<td>15</td>
<td>850000</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>0.64</td>
<td>595</td>
<td>28</td>
<td>1450000</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Conditions: toluene, 25°C, 20 min, 0.1 MPa, monomer 0.211 mol, pretreated solution of FI catalyst \textbf{21} (5 \( \mu \)mol)/\textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4} 6 \( \mu \)mol, \textit{i-Bu}_3\textit{Al} 50 \( \mu \)mol. a) kg-polymer/mmol-cat./h. b) Turnover frequency. c) Calculated by (polymer yield (g)/total monomer (g)) \times 100. d) Determined by GPC.

Table \textbf{8} Higher \alpha-Olefin Polymerization Data for FI Catalyst \textbf{21} with \textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>Activity ( \times 10^{-3} )</th>
<th>TOF [min(^{-1})]</th>
<th>Conv. [%]</th>
<th>( M_w )</th>
<th>( M_n/M_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Hexene</td>
<td>1.30</td>
<td>257</td>
<td>12</td>
<td>846000</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>1-Octene</td>
<td>1.94</td>
<td>288</td>
<td>14</td>
<td>906000</td>
<td>1.68</td>
</tr>
<tr>
<td>3</td>
<td>1-Decene</td>
<td>2.59</td>
<td>308</td>
<td>15</td>
<td>850000</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>4-Methyl-1-pentene</td>
<td>3.00</td>
<td>595</td>
<td>28</td>
<td>1450000</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Conditions: \( n \)-heptane, 25°C, 20 min, 0.1 MPa, monomer 0.211 mol, pretreated solution of FI catalyst \textbf{21} (5 \( \mu \)mol)/\textit{i-Bu}_3\textit{Al/Ph}_3\textit{CB(C}_6\textit{F}_5)\textsubscript{4} 6 \( \mu \)mol, \textit{i-Bu}_3\textit{Al} 50 \( \mu \)mol. a) kg-polymer/mmol-cat./h. b) Turnover frequency. c) Calculated by (polymer yield (g)/total monomer (g)) \times 100. d) Determined by GPC.

\textit{Note}: \( T_m \) determined by \textit{d}SC. \\
\textit{Table 7} Styrene Polymerization Data for FI Catalysts \textbf{3, 4, 21} and \textbf{28} with MAO
toward sterically larger olefins due to steric congestion. This highly unusual behavior can be explained as follows: a sterically bulkier side chain originating 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. One of the amine-donors of the phenoxy-amine ligands is suggested by DFT calculations to be detached during 1-hexene coordination and insertion, providing a wider space for polymerization.

It should be emphasized that the polymerization rate has practically a zeroth-order dependence on the concentration of the monomer, which is a rare example for a group 4 metal-based catalyst. Although the reason for the zeroth-order dependence is unclear at the current time, this unusual observation can be explained by assuming either a higher α-olefin-coordinated complex as a resting state or the dissociation of the amine-donor as the rate-determining step.

4.10. Monodisperse Polymers (living polymers)

We discovered that Ti_FI catalysts having fluorine(s) ortho to the imine-N (ortho-fluorinated Ti_FI catalysts) can mediate thermally robust living ethylene and highly syndiospecific living propylene polymerizations \(^{59,94,99} - 102\). Well-established experimental results along with DFT calculations have allowed us to conclude that the attractive interaction of a fluorine atom with a β-hydrogen on a growing polymer chain (which effectively curtails chain transfer) is responsible for the unprecedented living polymerization. This is the first example of an attractive interaction between the ligand and other components in the catalyst system that greatly enhances the catalytic performance \(^{50} - 58,103\).

For example, Ti_FI catalyst 3 mediates living ethylene polymerization at the very high temperature of 50°C and forms very high molecular weight monodisperse PEs with extremely high activities \((M_\text{n}/M_\text{w} 1.13, M_\text{n} 424,000, \text{TOF} 21,500 \text{ min}^{-1} \text{ atm}^{-1})^{99,100,102}\). This \(M_\text{n}\) value of 424,000 is one of the highest reported values to date for monodisperse PEs. To our surprise, at 90°C, FI catalyst 3 gives PEs with a fairly narrow molecular weight distribution \((M_\text{n}/M_\text{w} 1.30, M_\text{n} 167,000)\). Significantly, the same catalyst system carries out highly syndiospecific, chain-end controlled living propylene polymerization at 25°C via predominant 2,1-regiochemistry to produce highly syndiotactic monodisperse PPs \((M_\text{n}/M_\text{w} 1.11, M_\text{n} 29,000, \text{rr} 87\%, T_\text{m} 137°C)^{94,101,102}\). FI catalyst 3 is the first example of a catalyst that promotes living, and at the same time, highly stereoselective propylene polymerization. Additionally, this FI catalyst is the first example of a catalyst that carries out the living polymerization of both ethylene and propylene. Coates and coworkers reported on a similar Ti_FI catalyst 31 that promotes syndiospecific living propylene polymerization in combination with MAO \(^{104}\).

In addition, we have demonstrated that ethylene- and propylene-based telechelic polymers are also available with the ortho-fluorinated Ti_FI catalyst 3 if a functionalized monomer \([e.g., \text{CH}_2 = \text{CH}-(\text{CH}_2)_n-\text{OSiMe}_3, \text{CH}_2 = \text{CH}-(\text{CH}_2)_n-\text{OAlMe}_2, \text{CH}_2 = \text{CH}-(\text{CH}_2)_n-\text{N(SiMe}_3)_2\)] is used during the initiation and termination steps \([e.g., \text{HO}_{-}\text{SPP-OH}, M_\text{n} 9600, M_\text{n}/M_\text{w} 1.08, T_\text{m} 143°C^{105}]\).

Further investigations into the propylene polymerization behavior of ortho-fluorinated Ti_FI catalysts have revealed that the steric bulk of the R² substituent is ortho to the phenoxy-O controls the syndioslectivity of the polymerization, as demonstrated by the linear relationship between the steric bulk of the R² substituent and the syndioselectivity \((rr: H, 43\%, \text{Me}, 50\%, \text{i-Pr}, 75\%, \text{t-Bu}, 87\%, \text{Me}_3\text{Si}, 93\%, 25°C\) polymerization) \((\text{Fig. 12}^{94})\). A striking feature observed is that despite the chain-end control mechanism, the ligand structure has a dramatic effect on the tacticity and the sterically encumbered R² substituent results in the production of highly syndiotactic PPs. Therefore, we have given the name “ligand-directed chain-end controlled polymerization” to this type of chain-end controlled polymerization that is evidently governed by the ligand structures \(^{50} - 58,94\). With ligand-directed chain-end controlled polymerization, atactic- to highly-syndiotactic PPs can now be prepared in a living manner with ortho-fluorinated Ti_FI catalysts. The PPs produced possess regio-block structures, which are classified into two types; one involving consecutive regio-irregular units (highly syndiotactic PPs) and the other having isolated regio-irregular units (atactic to syndiotactic-rich PPs) \(^{94}\).

On the basis of the theoretical calculation studies performed by Cavallo and coworkers \(^{63,106}\) along with our experimental data described above (ligand-directed chain-end controlled polymerization behavior), we have concluded that a site inversion between propylene insertions \((i.e., \text{fluxional isomerization between the A})

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Fig. 12 Plots of rr Triad Values as a Function of the Calculated Volume of the R² Substituent
Δ forms at a rate which is faster than chain propagation) that gives enaniomeric sites is responsible for this ligand-directed chain-end controlled polymerization that is capable of forming highly syndiotactic PPs despite a C2 symmetric nature (Fig. 13).

The sPP produced with Ti_FI catalyst 4/MAO at 25°C exhibits an exceptionally high $T_m$ of 152°C ($r_r$ 93%, $M_n$ 47,000, $M_w/M_n$ 1.08)$^{33,54}$, which is one of the highest $T_m$ values among sPPs ever synthesized at room temperature. Notably, FI catalyst 4 in combination with MgCl2/i-Bu-Al(OR)$_3$-a (MgCl2-supported catalyst) at 25°C yields highly syndiotactic PP with an exceptionally high $T_m$ of 155°C ($r_r$ 97%), which is higher than the sPPs obtained with the corresponding MAO activation system$^{107}$. This behavior is significant because supported transition metal complexes generally exhibit lower stereoselectivity and $T_{mobs}$ than those complexes of solution-phase analogues. The formation of sPP with FI catalyst 4/MgCl2/i-Bu-Al(OR)$_3$-a suggests that the immobilization of the Ti_FI catalyst onto MgCl2/i-Bu-Al(OR)$_3$-a does not mitigate the site-inversion process, indicative of the fluxionality of the FI catalyst after immobilization.

In addition, another research group has revealed that Ti_FI catalyst 32 bearing a phenyl group on the imine-C can induce isoselective living propylene polymerization and form moderately isotactic and nearly monodisperse PPs (0°C polymerization; $M_n$, $M_w$ 1.11, $M_n$ 27,900, $M_w/M_n$ 53%, $T_m$ 69.5°C), probably because of the suppression of the site-inversion process by the steric congestion provided by the phenyl group on the imine-C$^{108,109}$. The corresponding Ti_FI catalysts bearing a sterically encumbered group at the R2 position (which may produce higher tacticity PPs) exhibit virtually no reactivity toward propylene.

Recently, we have succeeded in the catalytic production of monodisperse PEs and Zn-terminated PEs using a combination of Ti_FI catalyst 33 and H$_2$ or 34 and Et$_2$Zn$^{56,58,110}$, opening opportunities for the catalytic synthesis of polyolefinic block copolymers and block copolymers containing polyolefin and polar polymer segments. In fact, the catalytic production of a PE-b-poly(ethylene-co-propylene) block copolymer was achieved with 33/MAO.

Interestingly, we found that ortho-fluorinated Ti_FI catalyst 35 bearing a CF3 group at the R2 position, with MAO activation, carries out non-living ethylene polymerization (0°C polymerization, 0.5 min, $M_n$ 346,000, $M_w/M_n$ 1.66). The corresponding Ti_FI catalyst 36 having a methyl group at the R2 position mediates room-temperature living ethylene polymerization ($M_n$ 75,000, $M_w/M_n$ 1.16)$^{111}$. The reason for the non-living behavior of 35/MAO is not clear at the present time. Moreover, Mazzeo et al.$^{46}$, as well as ourselves, have discovered the fact that ortho-fluorinated Ti_FI catalysts such as 35 and 37, which incorporate electron-withdrawing substituents (e.g., CF3, Cl, Br) at the R2 positions, with MAO activation, induce non-living propylene polymerization and yield iPPs (35: 0°C polymerization, mm 54%, $M_w/M_n$ 2.02) via a site-control mechanism. These results may suggest that the electron-withdrawing R2 substituents discourage the living nature of the Ti_FI catalysts, and mitigate the site-inversion process for propylene polymerization.

4. 11. Block Copolymers

The highly controlled living nature of ortho-fluorinated Ti_FI catalysts for both ethylene and propylene polymerizations has enabled us to synthesize both ethylene- and propylene-based diblock and multi-block copolymers comprised of crystalline and amorphous segments and/or two different kinds of crystalline segments$^{56,58,100,112}$. For example, FI catalyst 3 with MAO forms PE-b-poly(ethylene-co-propylene), PE-b-poly(ethylene-co-propylene)-b-PE, sPP-b-poly(ethylene-co-propylene), PE-b-sPP, and PE-b-poly(ethylene-co-propylene)-b-sPP by the sequential addition of the corresponding monomers (Table 9). A sPP-b-poly(ethylene-co-propylene) similar to that listed above has been synthesized by Coates and coworkers using Ti_FI catalyst 31 in combination with MAO$^{53}$. The ortho-fluorinated Ti_FI catalysts (e.g., 36) also allow access to block copolymers composed of PE and ethylene/higher α-olefin copolymer segments (Table 9)$^{111}$. The block copolymers consisting of PE and amorphous ethylene/1-hexene copolymer segments possess a good combination of extensibility and toughness$^{111}$. Most of the block copolymers that we synthesized were previously unavailable from Ziegler-Natta catalysis.

As an extension of the living behavior of ortho-fluorinated Ti_FI catalysts to block copolymer synthesis,
Coates, Mühlaupt, Thomas and their co-workers prepared sPP-b-poly(propylene-co-methylene-1,3-cyclopentane-co-3-vinyl tetramethylene), PE-b-poly(ethylene-co-pentene), poly(ethylene-co-propylene)-b-poly(ethylene-co-norbornene), poly(methylene-1,3-cyclopentane-co-3-vinyl tetramethylene)-b-(ethylene-co-norbornene), iPP-b-poly(ethylene-co-propylene), PE-b-PS, and poly(ethylene-co-propylene)-b-PS, further demonstrating the utility of ortho-fluorinated Ti-FI catalysts.

Notably, researchers at Dow Chemical have demonstrated that non-living-type FI catalysts can also contribute to the production of PE-based block copolymers. Namely, and regarding the extremely high selectivity displayed by FI catalysts for ethylene relative to \( \alpha \)-olefins, they have successfully produced multi-block copolymers comprised of crystalline and amorphous segments using FI catalyst 38 combined with arlyphosphinidohafnium catalyst 39 and dialkyl zinc (Fig. 14). FI catalyst 38 bearing sterically encumbered R\(^1\) and R\(^2\) substituents selectively yields high molecular weight PEs even in the co-presence of ethylene and 1-octene, while the Hf catalyst 39 produces amorphous ethylene/1-octene copolymers, leading to the production of multi-block copolymers through a reversible chain transfer mediated by dialkyl zinc. The AFM image is displayed in Fig. 14, which contains two molecules of the block copolymer, demonstrating the formation of a well-defined multi-block copolymer. The black moiety corresponds to a PE segment, and the white part is an amorphous copolymer segment. Unlike random copolymers of similar densities, these block copolymers display a 40°C higher melting temperature (\( T_m \) ca. 120°C), while maintaining excellent elastic properties. It was the development of an FI catalyst with extremely high ethylene selectivity and a reversible chain-transfer nature that made it possible to produce these unique and useful new polymers.

### Table 9: Examples of the Polyolefinic Block Copolymers Formed with ortho-Fluorinated Ti-FI Catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>First Segment</th>
<th>( M_w )</th>
<th>( M_n/M_w )</th>
<th>( T_m )</th>
<th>Second Segment</th>
<th>( M_w )</th>
<th>( M_n/M_w )</th>
<th>( \text{P or H content} )</th>
<th>( T_m )</th>
<th>Third Segment</th>
<th>( M_w )</th>
<th>( M_n/M_w )</th>
<th>( \text{P or H content} )</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>PE</td>
<td>115000</td>
<td>1.10 (133)</td>
<td>sPP</td>
<td>136000</td>
<td>1.15</td>
<td>16.1</td>
<td>131</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>PE</td>
<td>115000</td>
<td>1.10 (133)</td>
<td>E/Pd)</td>
<td>211000</td>
<td>1.16</td>
<td>6.4</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PE</td>
<td>115000</td>
<td>1.10 (133)</td>
<td>E/Pd)</td>
<td>211000</td>
<td>1.16</td>
<td>6.4 (123)</td>
<td></td>
<td></td>
<td>sPP</td>
<td>235000</td>
<td>1.15</td>
<td>14.1</td>
</tr>
<tr>
<td>4</td>
<td>PE</td>
<td>115000</td>
<td>1.10 (133)</td>
<td>E/Pd)</td>
<td>161000</td>
<td>1.51</td>
<td>40.3</td>
<td>127</td>
<td></td>
<td>PE</td>
<td>272000</td>
<td>1.14</td>
<td>6.6</td>
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<tr>
<td>5</td>
<td>sPP</td>
<td>27000</td>
<td>1.13 (137)</td>
<td>E/Pd)</td>
<td>80000</td>
<td>1.21</td>
<td>15.0</td>
<td>130</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>PE</td>
<td>38000</td>
<td>1.11 (135)</td>
<td>E/H)</td>
<td>80000</td>
<td>1.21</td>
<td>15.0</td>
<td>130</td>
<td></td>
<td></td>
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a) Determined by GPC. b) Determined by DSC. c) Overall propylene (P) or 1-hexene (H) content, determined by \(^1\)H NMR. d) Poly(ethylene-co-propylene). e) Poly(ethylene-co-1-hexene).
5. Conclusion

The ligand oriented catalyst design concept has led to the discovery of a new generation of olefin polymerization catalysts, now known and referred to as FI catalysts. An FI catalyst is a heteroatom-coordinated early transition metal complex that is based on a pair of phenoxy-imine ligands combined with an early transition metal. Due to the coordination of the electron withdrawing, nonsymmetric phenoxy-imine ligand, the catalytically active species stemming from FI catalysts possess a highly electrophilic, polarized nature and can potentially assume five structural isomers. Additionally, the accessibility of the FI ligands and their amenability to modification offers a wide range of catalyst design possibilities leading to diversified catalyst structures. These characteristics have given rise to the remarkable versatility of FI catalysts and have facilitated systematic studies of the structure-reactivity relationships and reaction mechanisms.

Because of the above characteristics, FI catalysts display many unique features such as precise control over chain transfers (including highly controlled living ethylene and propylene polymerizations), extremely high selectivity for ethylene, high functional group tolerance, versatility vis-à-vis activator selection, MAO- and borate-free polymerization catalysis, significant morphology polymer formation, controlled multimodal behavior, high incorporation ability for α-olefins and norbornene, and highly syndiospecific and isospecific polymerizations of both propylene and styrene.

These features have yielded a wide variety of unique olefin-based materials, many of which were previously unavailable via other means of polymerization. The materials include selective vinyl- and Al-terminated PEs, ultra-high molecular weight linear PEs, regio- and stereoirregular high molecular weight poly(higher α-olefin)s, ethylene- and propylene-based telechelic polymers, a wide array of polyolefinic block copolymers from ethylene, propylene and higher α-olefins, and ultra-fine, non-coherent PE particles.

Therefore, the development and application of FI catalysts has had a significant impact on recent polymerization catalysis and polymer synthesis, and has also given us industrial opportunities to produce value-added olefin-based materials of great benefit to mankind. Future research on FI catalysts will produce additional olefin-based materials with unique microstructures and associated material properties and give us further insight into olefin polymerization catalysis.

Acknowledgment

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発表の第1報告としてシンドイエンポリマーの合成と生活エチレンおよびプロピレンポリマーの合成にF1触媒の使用について述べた。