

Development and Application of FI Catalysts for Olefin Polymerization: Unique Catalysis and Distinctive Polymer Formation

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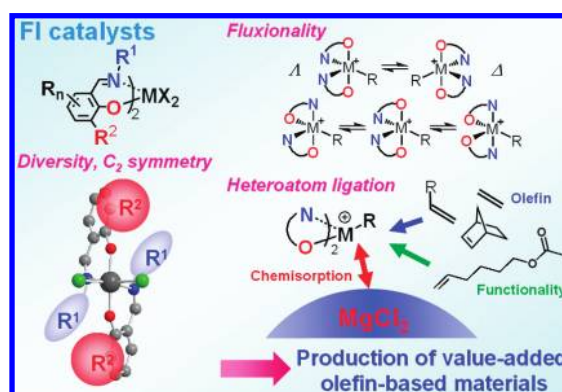
CON SPECTUS

Catalysts contribute to the efficient production of chemicals and materials in almost all processes in the chemical industry. The polyolefin industry is one prominent example of the importance of catalysts. The discovery of Ziegler–Natta catalysts in the 1950s resulted in the production of high-density polyethylenes (PEs) and isotactic polypropylenes (iPPs). Since then, further catalyst development has led to the production of a new series of polyolefins, including linear low-density PEs, amorphous ethylene/1-butene copolymers, ethylene/propylene/diene elastomers, and syndiotactic PPs (sPPs). Polyolefins are now the most important and the most produced synthetic polymers.

This Account describes a family of next-generation olefin polymerization catalysts (FI catalysts) that are currently being used in the commercial production of value-added olefin-based materials. An FI catalyst is a heteroatom-coordinated early transition metal complex that combines a pair of nonsymmetric phenoxy-imine $[O^-, M]$ chelating ligands with a group 4 transition metal. The catalytically active species derived from FI catalysts is highly electrophilic and can assume up to five isomeric structures based on the coordination of the phenoxy-imine ligand. In addition, the accessibility of the ligands of the FI catalysts and their amenability to modification offers an opportunity for the design of diverse catalytic structures.

FI catalysts exhibit many unique chemical characteristics: precise control over chain transfers (including highly controlled living ethylene and propylene polymerizations), extremely high selectivity for ethylene, high functional group tolerance, MAO- and borate-free polymerization catalysis, significant morphology polymer formation, controlled multimodal behavior, high incorporation ability for higher α -olefins and norbornene, and highly syndiospecific and isospecific polymerizations of both propylene and styrene. These reactions also occur with very high catalyst efficiency. The reaction products include a wide variety of unique olefin-based materials, many of which were previously unavailable via other means of polymerization. We have produced selective vinyl- and Al-terminated PEs, ultrahigh 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 ultrafine noncoherent PE particles.

FI catalysts are important from the organometallic, catalytic, and polymer science points of view, and the chemical industry is now using them for the production of value-added olefin-based materials. We anticipate that future research on FI catalysts will produce additional olefin-based materials with unique architectures and material properties and will offer scientists the chance to further study olefin polymerization catalysis and related reaction mechanisms.



A. Introduction

The discovery of single-site group 4 metallocene catalysts is considered to be one of the most significant breakthroughs within the modern chemi-

cal industry, not simply because of the superior properties shown by the metallocene polyolefins over conventional polyolefins but because on the horizon lies the prospect of fine-tuning molecular

catalysts by rational catalyst design, leading to a future array of new or differentiated polyolefins.¹

Indeed, much effort is currently being exerted into developing new single-site catalysts that will provide even higher catalyst efficiency and greater control over polymer microstructures. As a result of extensive studies, a number of diverse, highly active catalysts based on both early and late transition metals have been discovered.² Some of these catalysts can form new olefin-based materials with unique architectures, which include hyperbranched PEs and ethylene/methyl acrylate copolymers.^{3,4}

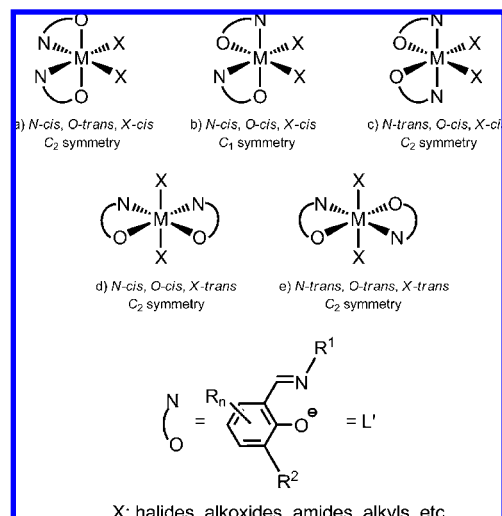
In our own work, we have discovered a number of highly active, new single-site catalysts featuring nonsymmetric ligands with electronically flexible properties that are based on ligand-oriented catalyst design.⁵ Most notable are the bis(phenoxy-imine) and bis(phenoxy-ketimine) group 4 transition metal complexes (now known as FI catalysts) that can achieve controlled (co)polymerization of olefinic monomers.^{5–7} We have reported on FI catalysts and their olefin polymerization characteristics since 1997 in the literature or patents,^{5–10} which has had the effect of stimulating further research on FI catalysts. In particular, recent research performed by Marks, Gibson, Bochmann, Cavallo, Coates, Talsi, Pellecchia, Busico, Müllhaupt, Repo, Scott, and others has contributed significantly to the further development of FI catalysts and other relevant catalysts.^{5–10}

In the previous reviews,^{6,7} we described catalytic behavior of FI catalysts, focusing on the polymerizations of ethylene, propylene, and higher α -olefins. In this Account, we would like to provide an overview of the key features of FI catalysts and how they lead to unique catalysis and distinctive polymer formation. Additionally, selected applications in the production of value-added olefin-based materials that illustrate the utility of FI catalysts will also be introduced.

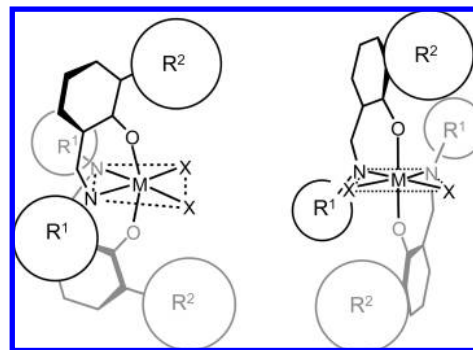
B. Key Features of FI Catalysts

1. Structural Features. A neutral FI catalyst is an octahedral complex bearing two bidentate phenoxy-imine ligands (L' ; FI ligand) and two nonspectator X ligands (Scheme 1). An important feature of FI catalysts is their straightforward synthesis, that is, Schiff base condensation of *ortho*-hydroxy aromatic aldehydes or ketones and primary amines, both of which have numerous synthetic recipes and rich inventories as commercially available compounds. This feature allows us to build enormous and diverse ligand libraries with a variety of substituents, including heteroatom-based functional groups. These ligand libraries have resulted in the remarkable versa-

SCHEME 1



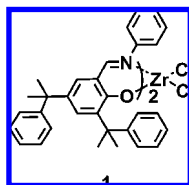
SCHEME 2



tility of FI catalysts and have also aided in systematic studies of the structure–reactivity relationships and reaction mechanisms.^{5–9}

Among the five possible isomers (Scheme 1), the crystallographically determined structures of FI catalysts, with a few exceptions,^{11,12} adopt a configuration in which the shortest M–O bonds (M = group 4 transition metal) are positioned *trans* to each other, and the nitrogen atoms and X ligands are in *cis*-positions, displaying overall C_2 symmetry (Scheme 1a).^{6,7} In this “ordinary” C_2 symmetric FI catalyst, the two imine-N’s are positioned in a plane defined by a metal M and two X ligands, and therefore, substituents on the imine-N’s (R^1) are on a plane at the backside of the X–M–X moiety, while substituents *ortho* to the phenoxy-O’s (R^2) are located above and below the X–M–X moiety (Scheme 2). Since the X–M–X moiety becomes a reaction site after activation (section B-3), these R^1 and R^2 substituents have the most pronounced effects on polymerization reactions, but each of the substituents work in a different manner due to their particular spatial arrangements, which will be described below.

CHART 1. FI Catalyst 1



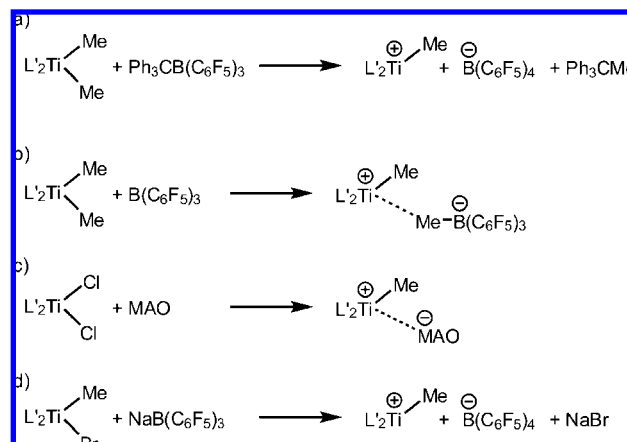
In solution, FI catalysts often exist as a mixture of isomers.¹³ These isomers are usually fluxional and interchangeable with each other on an NMR time scale.^{11–13} The PEs with temperature-dependent trimodal molecular weight distributions produced with **1**/MAO (Chart 1), which appeared to be formed with three chemically distinctive active species, may be associated with this fluxionality of FI catalysts that can generate multiple single-site catalysts.⁷ Also, fluxional isomerization between two enantiomers (Δ/Δ racemization) was proposed by calculations for a syndioselective propylene polymerization (section C-5),¹⁴ and has been suggested by VT-NMR for a cationic monobenzyl Hf–FI catalyst.¹⁵ Thus, the fluxionality of FI catalysts will be an important feature in understanding their polymerization characteristics.^{7,9}

2. Electronic Features. FI catalysts have another distinctive feature vs metallocenes, that is, M–ligand bonding characteristics. The presence of FI ligands with heteroatom donors renders the complex more electrophilic, a requirement for an active olefin polymerization catalyst,¹⁶ as supported by DFT calculations, which demonstrated that the Mulliken charge at the metal center (in au) in three cationic species increases in the following order, $(C_5H_5)_2TiMe^+$ (1.417) < CGC $(Me_2Si(C_5Me_4)-tBu-N)TiMe^+$ (1.599) < $(Ph-N=CH-C_6H_3-2-O-3-tBu)_2TiMe^+$ (1.741).

The heteroatom ligation also renders the M–L' bonding properties of FI catalysts more ionic or polarized relative to those of metallocenes, which may cause the stark differences between these two catalysts for two other important characteristics. The first of these concerns their interaction with solid surfaces, which needs to be considered when a supported molecular catalyst is required. Probably owing to the polarized M–L' bonding, FI catalysts are more strongly chemisorbed on the surface of, for example, $MgCl_2$ than metallocenes are, to the degree that $MgCl_2$ can serve as an activator/support (section C-6).^{7,10}

The second significant characteristic is functional group tolerance, which must be addressed when (co)polymerizations of polar olefins are undertaken. As a measure of functional tolerance, the energy differences (ΔE) between carbonyl-coordinated and ethylene-coordinated complexes were estimated by DFT calculations, using 5-hexen-1-yl acetate or ethylene as

SCHEME 3



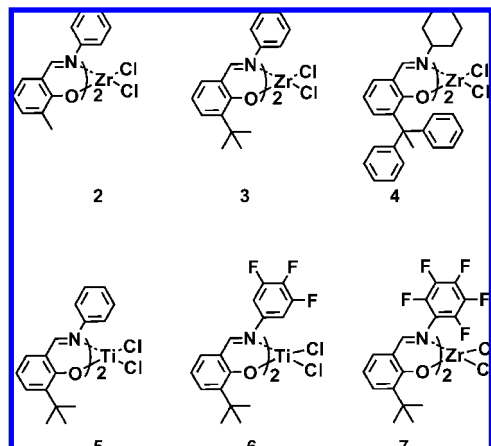
monomers. The ΔE values for Ti–FI catalysts (37–61 kJ/mol) were substantially smaller than those of metallocenes and CGC (>100 kJ/mol),¹⁷ making the FI catalysts viable candidates for the (co)polymerization of polar olefins (section C-4).

3. Activation Methods and Active Species. Like metallocenes, FI catalysts (L'_2MX_2) are believed to be transformed into coordinatively and electronically unsaturated monoalkyl cationic complexes (L'_2M^+-R) upon activation (Scheme 3), and in fact, the monoalkyl cationic species of some FI catalysts were observed by NMR.^{15,18–21} Since these cationic species of FI catalysts exhibited only one set of ligand signals, the species still possess C_2 symmetry in solution at room temperature, although these are likely to be time-averaged dynamic structures on an NMR time scale (sections C-1, -2, and -5).^{15,21}

When FI catalysts are activated by triisobutylaluminum (iBu_3Al) and $Ph_3CB(C_6F_5)_4$ instead of MAO, a new species is generated in situ, where the imine is reduced to an amine by iBu_3Al with the concurrent formation of isobutene.^{6,7} The resulting phenoxy-amine complexes exhibited various interesting polymerization characteristics owing to their unusual iBu_2Al-N donors, which will be bulkier and weaker as donors than the imine-N's (section C-5).

In summary, FI catalysts contain a pair of nonsymmetric phenoxy-imine ligands, which inevitably results in (a) enormous structural diversity, stemming from a wide array of ligand varieties due to ligand accessibility and amenability to modification, (b) isomers arising from ligand coordination arrangements in an octahedral framework, and (c) potential fluxionality among these isomers. The phenoxy-imine ligands also make FI catalysts highly electrophilic, chemically adsorbable, and functional group tolerant, presumably due to the heteroatoms that are present and their M–L' bonding characteristics. Additionally, the high reactivity of the imine moieties allows in situ ligand modification by a choice of

CHART 2. FI Catalysts 2–7



activation methods. In the following sections, we will discuss how these unique features of FI catalysts are associated with their polymerization characteristics.

C. Olefin Polymerizations with FI Catalysts

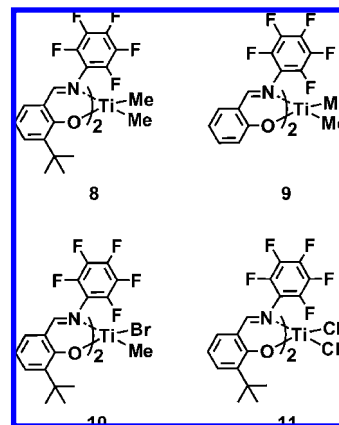
1. Catalyst Efficiency. FI ligands were deliberately selected and designed to have an electronically flexible nature, which we believe is a primary reason for the remarkably high ethylene polymerization activities of FI catalysts.^{5,7}

A clear relationship between the ethylene polymerization efficiency and the size of R² substituents was observed for Zr–FI catalysts. For example, the difference in activity between **2** and **3** (R² = Me and ^tBu, Chart 2) reaches more than 10³-fold (0.4 and 519 kg of PE/[mmol of Zr]·h). To this end, the activity of 6552 kg of PE/[mmol of Zr]·h was achieved with **4**/MAO (R² = C(Me)Ph₂, Chart 2), which is one of the highest catalyst efficiencies ever reported for any catalytic reaction.^{5–7} The observed activity enhancement is likely due to the R² substituents that provide steric protection for the metal center or the phenoxy-O's to prevent side reactions (Scheme 2, see also section C-2).

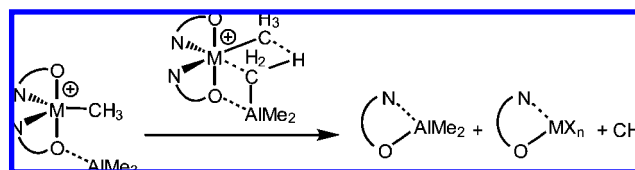
Catalytic efficiency can also be increased by electronically manipulating the active species. Electron-withdrawing R¹ substituents significantly enhance the activities (**5**, 3.58; **6**, 43.3; **3**, 224; **7**, 334 kg of PE/[mmol of M]·h, Chart 2).^{6,7} The introduction of an electron-donating methoxy group *para* to the phenoxy-O's (R³) was found to increase the thermal stability of FI catalysts, making them available for polymerizations at industrially practical higher temperatures.^{6,7}

Ionic character of the active species can also have an impact on the activity as is well-known in metallocene chemistry.¹⁶ The reaction mixtures of a dimethyl complex (**8** or **9**, Chart 3) and an activator (Ph₃CB(C₆F₅)₄ or B(C₆F₅)₃) were pre-

CHART 3. FI Catalysts 8–11



SCHEME 4



cipitated out as an oil (~10 mM [Ti] in toluene), indicating a strong ionic character of the resulting monomethyl cationic species (Scheme 3).²⁰ All the species maintained C₂ symmetry (as was evidenced by only one set of ligand signals) in bromobenzene-*d*₅, which suggested that the counteranions were not strongly associated with the cationic species, even for the ion pair of sterically unencumbered **9** and the more nucleophilic CH₃B(C₆F₅)₃[−]. Furthermore, the proton chemical shifts of CH₃B(C₆F₅)₃[−] for **8**/B(C₆F₅)₃ and **9**/B(C₆F₅)₃ were insensitive to solvent polarity (toluene-*d*₈ or BrC₆D₅), the size of R² (^tBu or H), and titanium-bound alkyls (Me or polymeryl) and always appeared at around 0.8–0.9 ppm, which is comparable to a Li⁺CH₃B(C₆F₅)₃[−] salt, or a weakly associating ion pair at most.^{16,20} The high catalytic efficiency of FI catalysts may be attributed in part to this inherent ionic character.

2. Catalyst Deactivation. An FI catalyst can be deactivated by ligand transfer to AlMe₃ in MAO, yielding an Al–FI complex (L'AlMe₂), a methane molecule, and an inactive group 4 metal compound with, we believe, one FI ligand remaining (Scheme 4, see also section C-5).^{18,19,21} This deactivation path can be effectively blocked by large R² groups, which is consistent with the R²-size-dependent activity. The ligand transfer reaction for a living Ti–FI catalyst is also significantly retarded when the metal-bound alkyl group is a polymeryl group.¹⁸ The intramolecular 1,2-migratory insertion of M-benzyl to the electrophilic N=C moiety has often been observed, which is also detrimental to olefin polymerization catalysis.²²

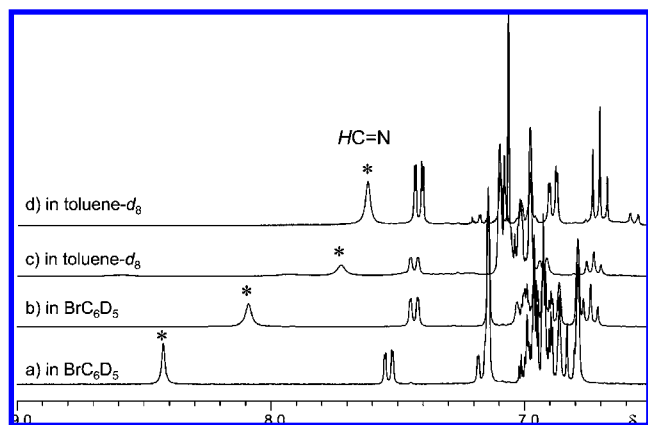


FIGURE 1. ^1H NMR spectra of (a) **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, (b) **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ /**10**, (c) **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ /**10**, (d) **10**/ $\text{NaB}(\text{C}_6\text{F}_5)_4$.

SCHEME 5



The situation where highly electrophilic $\text{L}'_2\text{Ti}^+\text{Me}$ and neutral $\text{L}'_2\text{TiX}_2$ coexist often leads to the formation of a dinuclear complex that is considered to be an inactive dormant species.¹⁶

The species derived from **10**/ $\text{NaB}(\text{C}_6\text{F}_5)_4$ (envisaging Scheme 3d) exhibited a less cationic character (upfield shifted imine-H, Figure 1d) and significantly lower activity for ethylene and propylene polymerizations than the species generated by **11**/MAO or **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (Figure 1a).²⁰ This can be because stoichiometric excess of **10** (Chart 3) caused by the limited solubility of $\text{NaB}(\text{C}_6\text{F}_5)_4$ allows for the situation above, yielding a Br-bridged dinuclear complex (Scheme 5). To test this postulation, neutral **10** was added to $\text{L}'_2\text{Ti}^+\text{Me}$ generated by **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (Figure 1b,1c). The NMR spectra of **10**/ $\text{NaB}(\text{C}_6\text{F}_5)_4$ and **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ /**10** exhibited very similar upfield shifts of the imine signals, which supports the hypothesis. The species in Figure 1 exhibited only one set of ligand signals at ambient temperature, implying the equilibrium shown in Scheme 5. A similar situation would result if **8** was employed in excess to $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$. Under such conditions, the imine-H of the resulting species appeared as a broad singlet in between the imine-H of **8** and **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (1/1 m.r.) (Figure 2), which suggests the formation of a methyl-bridged dinuclear complex equilibrated with the mononuclear cationic species (Scheme 5).

It is reasonable to assume, therefore, that large R^2 substituents would benefit the catalytic activity by shifting the equilibrium to the mononuclear species for these dinuclear complexes (Scheme 2).

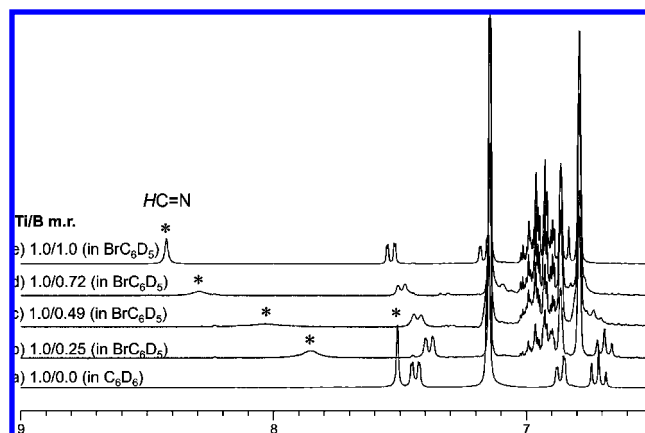
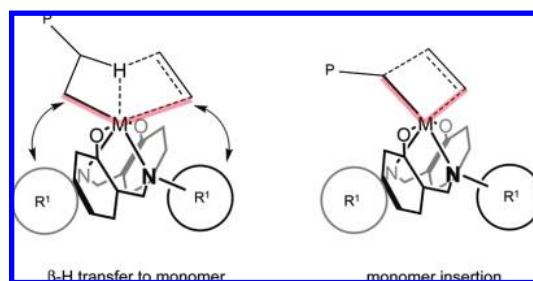


FIGURE 2. ^1H NMR spectra of the species derived from **8**/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ with varied molar ratios.

SCHEME 6

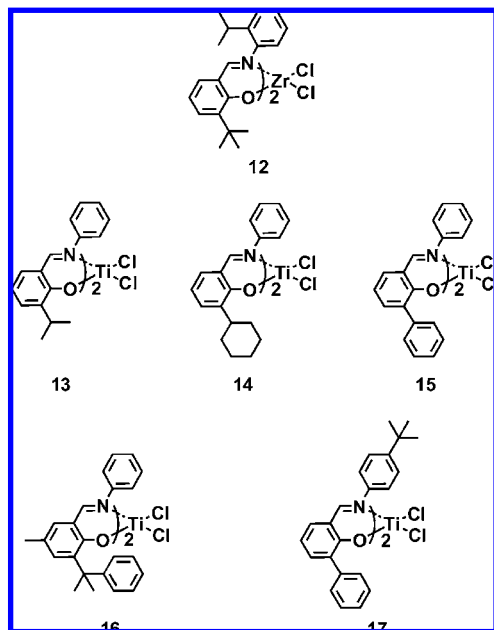


3. Control of Molecular Weight. The molecular weights of polymers will, on average, be statistically determined by the ratio of the chain growth and the chain-terminating reactions. Therefore, it is essential to understand chain transfer reactions in order to control polymer molecular weights (and chain-end structures). Thanks to their structural diversity, FI catalysts possess an exceptionally wide range of molecular weight control from 10^3 to 10^7 without adding any chain transfer agents, for which the R^1 substituents are mostly responsible.^{5–7}

DFT calculations on the reaction intermediates suggested that the large R^1 groups located at the backside of the reaction site would destabilize a sterically encumbered six-centered transition state for β -hydrogen transfer to a coordinating ethylene to a greater extent than the compact four-centered transition state for the ethylene insertion reaction (Scheme 6). The X-ray structures of FI catalysts revealed narrower Cl-Zr-Cl bond angles as the R^1 groups became larger, which is also consistent with this scenario.⁵

When bulky R^1 substituents shut down the β -H transfer reaction, a chain transfer to alkylaluminums can become more prominent. FI catalyst **12** (Chart 4), which has a 2-isopropylphenyl group as a sterically demanding R^1 substituent, yields almost exclusively an alkylaluminum-terminated PE upon acti-

CHART 4. FI Catalysts 12–17



vation with MAO/(trimethylaluminum) (M_w 1000–720 000; M_w/M_n 2.0–2.6).⁵

Finally, it is important to discuss living olefin polymerizations as the ultimate molecular weight control, where any chain-terminating reactions are absent by definition. Although nonfluorinated Ti–FI catalysts possess some characteristics of living ethylene polymerization,^{7,9} we discovered that a series of *ortho*-fluorinated *N*-aryl Ti–FI catalysts polymerize ethylene or propylene in a versatile and highly controlled living manner.^{5–9} Another group also reported on similar Ti–FI catalysts that promote living propylene polymerization.²³

Due to the robust livingness, the active propagating species of the Ti–FI catalysts can be observed at ambient temperatures. We have been successful in the syntheses of dimethyl Ti–FI catalysts (**8**, **9**) that were difficult to synthesize using conventional methods due to the susceptibility of the imine moiety toward the nucleophilic alkylating agents and the readily reduced Ti(IV) metal center.²⁰ The dimethyl Ti–FI catalysts can be stoichiometrically activated with known borate activators to well-defined monomethyl cationic species, which allows us to observe the species without any disturbance caused by the large signals of MAO. The monomethyl cationic species can be grown into “living” propagating species by adding ethylene in NMR tubes, and the propagating species also possess C_2 symmetry with two well-resolved multiplets assignable to diastereotopic α -methylene protons of the growing polymer chain (L'_2Ti-CH_2-), indicating that Λ/Δ isomerization assumed for syndioselec-

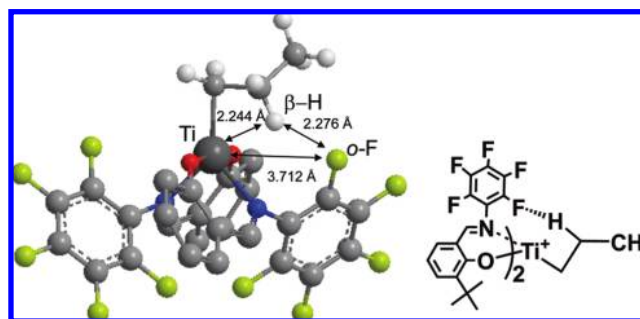


FIGURE 3. DFT-optimized structure of a cationic *n*-propyl species derived from **8** (see the inset figure). Phenolic aryl groups are simplified for clarity.

tylene polymerizations is slow (if it occurs at all) at ambient temperature (section C-5).^{20,24}

Living FI catalysts have expanded the scope of living polymerization processes (including a catalytic living process that is nonstoichiometric in terms of catalysts and polymer chains)^{7,9} and created olefin-based polymers with well-defined architectures, that is, a wide variety of monodisperse polymers, chain-end functionalized polymers (including telechelics), and block copolymers from ethylene, propylene, HAO, cyclic olefins, and styrene.^{5–9,23} It should be noted that this living polymerization with the Ti–FI catalysts again underlines the importance of R^1 substituents for controlling chain transfer reactions, that is, at least one *ortho*-fluorine at the R^1 aryl groups is a requirement to achieve this unprecedented living polymerization, for which we proposed, based on DFT calculations, weak attractive and electrostatic interactions between the *ortho*-F and β -H. Such attractive interactions can stabilize the chain-transfer-prone β -H of the cationic polymeryl-titanium and avert unwanted β -H transfer reactions (Figure 3).^{5–7,9}

The proposed noncovalent C–H \cdots F–C interactions have recently been observed by NMR spectroscopy and X-ray and neutron crystallography for relevant neutral Zr and Ti complexes in the solid state and in solution.²⁵ Additionally, a similar Ti enolatoimine complex bearing an *ortho*-F(s) *N*-aryl group was reported to perform living ethylene polymerization, whereas the corresponding complexes having *ortho*-methyl substituted or unsubstituted *N*-aryl groups were reported not to perform.²⁶

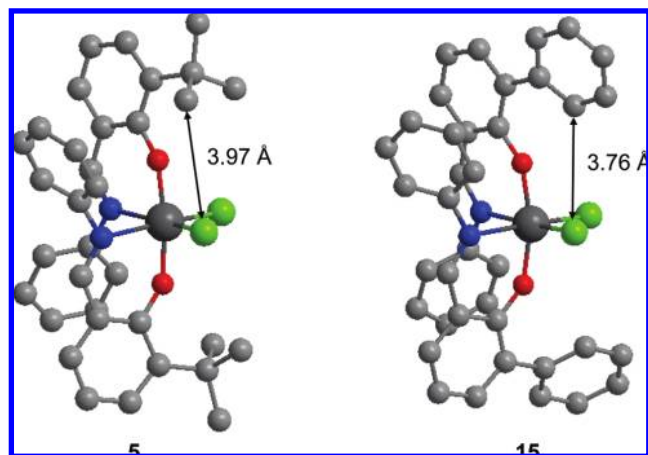
Although still remaining controversial, a weak electronic/attractive interaction between a ligand and a growing polymer chain may open up the prospect of a new catalyst design strategy to manipulate olefin polymerizations in tandem with conventional steric/repulsive interactions.^{5–9}

4. Control of Comonomer Uptake. The ethylene polymerization results obtained with FI catalysts/MAO (Table 1) show

TABLE 1. Ethylene/Propylene Copolymerization with Ti–FI Catalysts/MAO^a

entry	complex	activity ^b	C ₃ content ^c	M _w /10 ^{3d}	M _w /M _n ^d
1	13	0.18	17.7	48.8	1.29
2	5	0.65	6.8	302	1.85
3	14	0.45	20.2	136	1.35
4	15	3.42	47.7	456	3.26
5	16	0.38	3.8	30.5	1.92

^a Toluene 250 mL; complex 5.0 μmol; 50 °C; 10 min; ethylene 50 L/h; propylene 150 L/h; MAO 1.25 mmol. ^b Kilograms of polymer per millimole of catalyst per hour. ^c Propylene content (mol %) determined by IR. ^d Determined by GPC (PScalibration).

**FIGURE 4.** X-ray structures of **5** and **15**.

that the R² substituent is located at a strategic position capable of controlling propylene incorporation. As already described, the R² substituent significantly affects catalytic activity, and thus this substituent plays a key dual role for polymerization.^{6,7} A striking feature is that a sterically encumbered R² substituent induces extremely high selectivity for ethylene, which is unachievable with metallocene catalysts. In fact, FI catalyst **16** (R², cumyl; Chart 4), is approximately 300 times more reactive to ethylene relative to propylene, as estimated by the monomer molar ratio in a reaction medium and in copolymer composition. This unprecedented feature has resulted in the production of value-added polymers (i.e., ultra-high molecular weight linear PEs and PE-based multiblock copolymers, see section D-2).⁵

Generally, an FI catalyst bearing a sterically unencumbered R² substituent promotes higher propylene incorporation, while such substituent leads to decreased catalytic activity. Of particular note is the exceptional behavior of FI catalyst **15** (R², Ph; Chart 4), which achieves high propylene incorporation and simultaneously high catalytic activity. The X-ray structures in Figure 4 show FI catalyst **15** with the phenyl group at the R² position possessing a sterically more encumbered environment around the Cl-bound sites (potential polymerization sites) than FI catalyst **5**,¹⁷ which appears contradictory to the copoly-

TABLE 2. Ethylene/Norbornene Copolymerization^a

entry	complex	activity ^b	M _w ^c /10 ³	M _w /M _n ^c	T _g ^{d,e} /°C
1	5	0			
2	15	2.02	198	1.13	129
3	Cp ₂ TiCl ₂	5.93	1048	2.80	e
4	CGC	3.31	617	2.14	65

^a Toluene 250 mL; complex 1.0 μmol; NB 10 g; 25 °C; 5 min (entries 2, 4) or 10 min (entries 1, 3); ethylene 0.1 MPa; MAO 1.25 mmol (entries 1–3); ^b Bu₃Al 0.25 mmol/Ph₃CB(C₆F₅)₄ 6 μmol (entry 4). ^c Kilograms of polymer per millimole of catalyst per hour. ^d Determined by GPC (PS calibration). ^e Not detected.

merization behavior. However, DFT calculations on cationic methyl complexes derived from FI catalysts **5** and **15** revealed that the phenyl group provides a sterically more open active site than the ^tBu group because it rotates to evade steric congestion. With this unique feature, FI catalysts containing the phenyl group at the R² position can be high-performance catalysts for the copolymerization of ethylene with cyclic olefins or polar monomers, as well as higher α-olefins.

Electronically, norbornene (NB) is unique because it possesses a more nucleophilic nature than that possessed by ethylene and α-olefins. As described, the active species derived from FI catalysts possess higher electrophilicity than those derived from the metallocene catalysts, suggesting the high potential of FI catalysts for ethylene/NB copolymerization.

Ethylene/NB copolymerization results are presented in Table 2.²⁷ Although FI catalyst **5** with MAO was a poor catalyst for this copolymerization, FI catalyst **15** in combination with MAO produced a copolymer with a very high T_g of 129 °C (NB content 48.4 mol %), higher than that formed with CGC (T_g 65 °C, NB content 33.6 mol %), which is well-known for achieving the high incorporation of sterically encumbered olefinic monomers.

One major untapped area for early transition metal catalysts is the copolymerization of ethylene with polar comonomers. The high oxophilicity of the early metals precludes their use in this application. FI catalysts, however, are highly active heteroatom-coordinated complexes, and in a sense, they are already poisoned. Thus, FI catalysts have much higher functional group tolerance than metallocene catalysts, though both are group 4 metal catalysts (section B-2).

Ethylene/5-hexen-1-yl acetate (HA) copolymerization results are tabulated in Table 3.¹⁷ As expected, Cp₂TiCl₂ and CGC displayed no reactivity under the given conditions. However, FI catalysts **5**, **15**, and **17** (Chart 4) afforded high molecular weight copolymers of narrow molecular weight distributions with very high activity. The data in Table 3 indicates that the phenyl group gives rise to higher HA incorporation and catalytic activity, further confirming the beneficial effect of the

TABLE 3. Ethylene/5-Hexene-1-yl Acetate (HA) Copolymerization^a

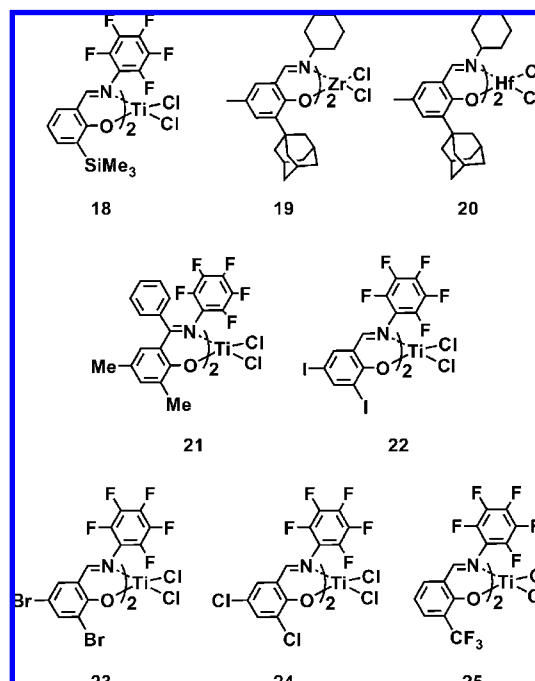
entry	complex	HA feed	activity ^b	HA content ^c	$M_w^d/10^3$	M_w/M_n^d
1	5	1.00	86	0.13	497	2.1
2	15	1.00	337	0.81	269	2.2
3	17	1.00	341	0.90	273	2.2
4	15	2.00	68	1.97	59	1.8
5	17	2.00	71	1.90	69	1.7
6	15	5.25	11	2.45	20	1.8
7	17	5.25	15	3.20	23	1.6

^a Toluene 250 mL; complex 20 μ mol; 25 °C; 10 min; ethylene 0.1 MPa; cocatalysts, MAO 5.0 mmol. ^b Kilograms of polymer per mole of catalyst per hour. ^c Determined by ¹H NMR. ^d Determined by GPC (PS calibration).

phenyl group at the R² position. Notably, FI catalysts **15** and **17** furnished copolymers even in the presence of an excess amount of HA to MAO. These results may open the door to polar monomer copolymerization with early transition metal catalysts.

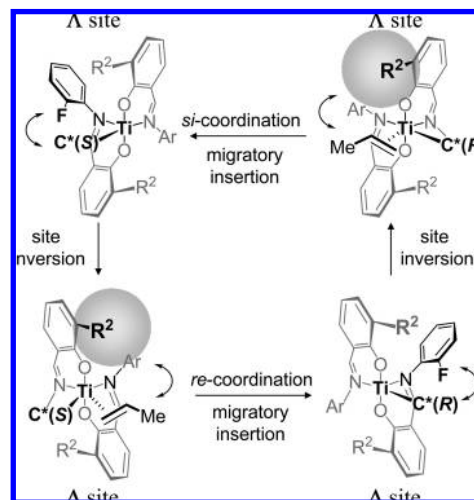
5. Control of Stereoselectivity. Many studies on metallocene catalysts have revealed the general relationship between the catalyst symmetry and the resulting stereoselectivity and how the chiral reaction sites of the metallocenes achieved stereoselective monomer enchainment via the site-control mechanism.^{1,24,28} Despite the C₂ symmetry and homotopic X–M–X moieties as described above, Ti–FI catalysts with MAO or MgCl₂ display moderate-to-exceptionally high syndioselectivity toward propylene polymerizations.^{5–10,23,24} Microstructural analyses of the sPPs produced with Ti–FI catalysts revealed that each monomer was enchainment by consecutive 2,1-insertions and also that the syndioselectivity relied on the stereochemistry of the asymmetric methine carbon (α -carbon) in the last-inserted propylene (chain-end control).^{6–9,23,24} Furthermore, the syndioselectivity of the Ti–FI catalysts is in direct proportion to the sizes of the R² substituents, despite the apparent chain-end controlled stereoregulating mechanism.^{6–9,24} Although chain-end stereocontrol usually works only at a subambient temperature (typically down to –60 °C) and results in poor-to-moderate selectivity,²⁸ the syndioselectivity of **18** (Chart 5)/MgCl₂/i-Bu_nAl(OR)_{3–n} ([*rrr*] 97%; T_m 155 °C) compared favorably with the best syndioselective metallocene catalysts that were operative via the site-control mechanism.^{7,9,10}

A model was proposed to explain this unexpected syndioselective polymerization by C₂ symmetric FI catalysts, which assumed the chirality inversion of C₂ symmetric FI catalysts through fluxional Λ/Δ isomerization (Figure 5).¹⁴ This model also predicted that the monomer face selection was achieved by steric repulsion between the methyl group of the propylene and the R² substituent, which is consistent with the observed R² dependence of the syndioselectivity.^{7,9,24} The free energy barriers (ΔG^\ddagger) for the Λ/Δ isomerization of related cat-

CHART 5. FI Catalysts **18–25**

ionic Hf benzyl complexes were experimentally estimated to be between 10–14 kcal/mol.¹⁵ The Λ/Δ isomerization could be facilitated by the bulkier secondary alkyl polymer chain derived from the secondary insertion faster than the Λ/Δ isomerization for the Ti–FI catalyst bearing a polyethylene chain mentioned above, which proved to be slow.²⁴

Isoselective propylene polymerizations are also made possible by selecting appropriate FI catalysts and activators.^{6–9,24} The isoselectivity of propylene polymerizations controlled by **19** or **20** (Chart 5) activated by ^tBu₃Al/Ph₃CB(C₆F₅)₄ reached [*mmmm*] 96.9% (**19**) and [*mmmm*] 96.8%, T_m 165.1 °C (**20**), one of the highest numbers ever reported, including the best

**FIGURE 5.** The proposed model for the syndioselectivity of Ti–FI catalysts.

heterogeneous Ziegler–Natta catalysts. The imine $R^1N=CH-$ moiety is probably reduced to $(iBu_2Al)N(R^1)CH_2-$ under these conditions (section B-3) and the NMR analyses of the obtained polymers suggested that propylene monomers were isoselectively enchaind by repetitive 1,2-insertions via an enantiomorphic site-control mechanism.^{7,9,24}

Recently, a fluorinated Ti–FI catalyst **21** (Chart 5), which has a phenyl group on the imine-C, was described to perform moderately isoselective living propylene polymerization ($[mmmm]$ 0.73).^{9,23} Additionally, fluorinated Ti–FI catalysts bearing I, Br, Cl, or CF_3 at the R^2 position (**22–25**, Chart 5) were reported to form prevailing isotactic PPs via an enantiomorphic site control mechanism in a nonliving fashion.⁹ In these isoselective polymerizations, the Λ/Δ isomerization was supposed to be slow relative to propylene insertion, probably due to steric or electronic reasons or the 1,2-insertion mode.^{9,23,24}

The *ortho*-fluorinated *N*-aryl Ti–FI catalysts can also afford highly isotactic or highly syndiotactic polystyrenes (PSs) or a mixture of both, depending on the reaction conditions.²⁹ Styrene polymerizations at 20 °C with **11**/MAO or **18**/MAO produced iPSs with virtually no stereoerrors (T_m 213–224 °C). Given the C_2 -symmetry of these FI catalysts and by a comparison with the syndioselective propylene polymerizations described above, it is reasonable to postulate that 1,2-insertion (supported by DFT calculations), enantiomorphic site control, and no Λ/Δ isomerization are operating in order to explain the observed isoselectivity. By raising the polymerization temperatures or mixing the FI catalysts with MAO before polymerization, one can observe the concurrent formation of syndiotactic PSs along with isotactic PSs. Under these conditions, the FI catalysts will be decomposed into mono(phenoxy-imine) Ti(III) species through ligand transfer to alkylaluminums, as described above (section C-2). This NMR-silent Ti(III) species can form sPSs because many cationic Ti(III) species that are stabilized by a monoanionic ligand are assumed to be active species with respect to other known syndioselective catalysts for styrene, for example, $CpTiX_3/MAO$. The related nonfluorinated Ti–FI catalysts were inactive toward isoselective styrene polymerizations and only yielded sPSs.²⁹

In stark contrast to the isoselective polymerizations with Zr– or Hf–FI catalysts, Ti–FI catalysts activated with $iBu_3Al/Ph_3CB(C_6F_5)_4$ afforded high molecular weight regio- and stereoirregular polymers of higher α -olefins (HAO; ultrarandom polymers).^{5–7} For example, **5**/ $iBu_3Al/Ph_3CB(C_6F_5)_4$, supposedly modified in situ to $[(iBu_2Al)N(Ph)CH_2-C_6H_3-2-O-3-(iBu)_2Ti]^+-R$, afforded such polymers from 1-hexene, 1-octene, 1-decene,

TABLE 4. Ethylene Polymerization with Ti–FI Catalysts Using $MgCl_2/iBu_nAl(OR)_{3-n}$ or MAO as an Activator^a

entry	complex	activator	activator composition		activity ^b	$M_w^c/10^4$	M_w/M_n^c
			Mg/ mmol	Al/ mmol			
1	5	$MgCl_2/iBu_nAl(OR)_{3-n}$	0.40	2.40	36.3	50.9	2.66
2	26	$MgCl_2/iBu_nAl(OR)_{3-n}$	0.40	2.40	20.8	59.6	2.67
3	15	$MgCl_2/iBu_nAl(OR)_{3-n}$	0.40	2.40	36.0	23.1	2.40
4	27	$MgCl_2/iBu_nAl(OR)_{3-n}$	0.40	2.40	26.2	117	3.51
5	5	MAO	0	1.25	44.6	46.4	2.38
6	26	MAO	0	1.25	21.4	62.5	2.74
7	15	MAO	0	1.25	99.1	22.9	2.07
8	27	MAO	0	1.25	68.0	42.2	4.74

^a Toluene 500 mL, complex 0.5 μ mol, 50 °C, 30 min, ethylene 0.9 MPa. ^b Kilograms of polymer per millimole of catalyst per hour. ^c By GPC.

and 4-methyl-1-pentene. Interestingly, the catalyst exhibited higher activities for bulkier monomers (TOF in min^{-1} for 1-hexene 257, 1-octene 288, 1-decene 308, 4-methyl-1-pentene 595) and a zeroth-order activity dependence on monomer concentration. The DFT calculations on $[(iBu_2Al)N(Ph)CH_2-C_6H_3-2-O-3-(iBu)_2Ti]Me^+$, demonstrated an approximate C_2 symmetric *N-cis,O-trans* geometry. Upon coordination with a 1-hexene monomer, one of the N donors dissociated adopting a square-pyramidal configuration with the methyl group at the apical site.^{5,7} This coordinatively and electronically unsaturated state of the metal center will make the species extremely electrophilic. The observation of activities that are dependent on monomer size but independent of monomer concentration can be explained by assuming either an olefin-coordinated complex as a resting state or the dissociation of the N donor as the rate-determining step.⁵

6. MAO- and Borate-Free Catalyst Systems. FI catalysts can form highly active catalysts in combination with $MgCl_2/R'_nAl(OR)_{3-n}$, heteropoly compounds/ R_3Al , and clays/ R_3Al ,^{7,10} in addition to the MAO and borates that are typically used for the activation of metallocenes. In particular, $MgCl_2/R'_nAl(OR)_{3-n}$ can activate and simultaneously immobilize FI catalysts (thus working as an activator/support), resulting in the realization of MAO- and borate-free-supported single-site catalysts. The roles of $MgCl_2$ and $R'_nAl(OR)_{3-n}$ for the activation and immobilization of FI catalysts have been described in previous papers.^{7,10}

Selected ethylene polymerization results with FI catalysts/ $MgCl_2/iBu_nAl(OR)_{3-n}$ [OR = 2-ethyl-1-hexoxy group] are collected in Table 4.¹⁰ The activities seen with these catalyst systems are comparable to the activities for the well-established MAO activation catalysts. Notably, the PEs formed from the FI catalyst/ $MgCl_2/iBu_nAl(OR)_{3-n}$ systems possess narrow molecular weight distributions, implying single-site catalysis. Further evidence of single-site behavior was obtained under ethylene/propylene copolymerization with the above catalyst systems, which provided copolymers with a narrow molecu-

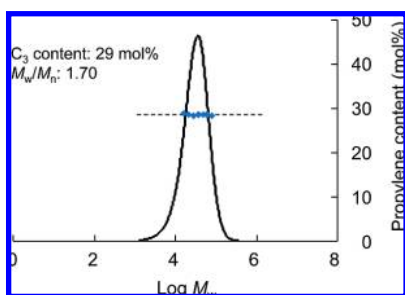
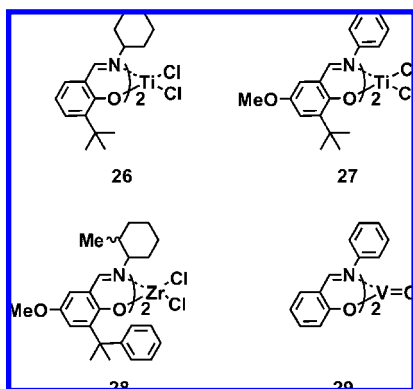


FIGURE 6. GPC-IR chart of the ethylene/propylene copolymer obtained with **15**/MgCl₂/Bu_nAl(OR)_{3-n}.

CHART 6. FI Catalysts **26–29**

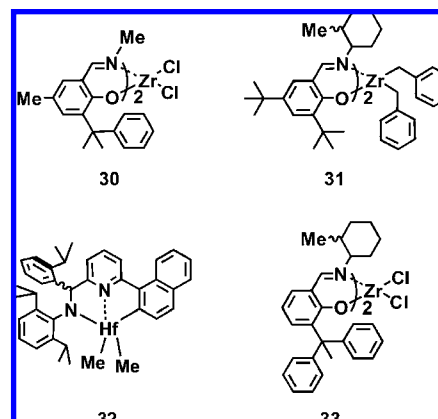


lar weight distribution and the uniform incorporation of propylene (e.g., **15**/MgCl₂/Bu_nAl(OR)_{3-n}, see Figure 6).¹⁰

The PEs produced by the FI catalyst/MgCl₂/Bu_nAl(OR)_{3-n} systems show morphologies characterized by well-defined particles, indicating that the combination of FI catalysts and MgCl₂/Bu_nAl(OR)_{3-n} form supported catalysts, which possess the technological advantages of good morphology control, high polymer bulk density, and little reactor fouling.^{7,10} The FI catalyst/MgCl₂/Bu_nAl(OR)_{3-n} systems that we have developed represent the first examples of MAO- and borate-free, highly active, group 4 metal-based catalysts capable of controlling polymer morphology.

The success of the MgCl₂/R'_nAl(OR)_{3-n} activator/support was not limited to Ti–FI catalysts. Zr–FI catalysts combined with MgCl₂/R'_nAl(OR)_{3-n} converted ethylene to very good morphology PEs with strikingly high productivity (e.g., **28** (Chart 6)/MgCl₂/Bu_nAl(OR)_{3-n}, 0.9 MPa, 50 °C, activity 1819 kg of PE/(mmol of Zr)·h), which is the highest reported activity for MAO- and borate-free olefin polymerization catalysts.^{7,10} Additionally, unlike ordinary V catalysts, the combination of V–FI catalysts with MgCl₂/R'_nAl(OR)_{3-n} generated high activity ethylene polymerization catalysts at elevated temperatures (e.g., **29** (Chart 6)/MgCl₂/Et_nAl(OR)_{3-n}, 0.1 MPa, 75 °C, activity 65 kg of PE/(mmol of V)·h), representing the first examples of highly active, thermally robust, single-site V catalysts, which

CHART 7. FI Catalysts **30, 31,** and **33** and Hf Pyridylamide Complex **32**



satisfy an extremely desirable industrial goal regarding V catalysts.^{7,10}

MgCl₂/R'_nAl(OR)_{3-n} can also effectively activate and immobilize early to-late transition metal complexes incorporating heteroatom-containing ligands, which include diimine-ligated Ni complexes and diimine–pyridine-ligated Fe complexes, suggesting that transition metal complexes bearing heteroatom-based ligands can achieve high catalytic performance without using MAO or borate activators, unlike metallocene catalysts.^{7,10}

D. Selected Applications in the Production of Value-Added Olefin-Based Materials

1. Vinyl-Terminated PEs and Their Derivatives. PEs with vinyl end groups (vinyl-terminated PEs) possess high reactivity and high melting temperatures (>120 °C), which allow them to act as reactive PEs or distinctive intermediates.^{5–7} Although the originally discovered FI catalysts for vinyl-terminated PEs showed diminished activities at increased polymerization temperatures, elaborate catalyst design work focusing on the substituents at the R¹ and R³ positions have allowed for the development of FI catalysts capable of producing vinyl-terminated PEs (*M_w* 1400–15 000) with high efficiency under solution polymerization conditions (sections C-1,3). For instance, FI catalyst **30** (Chart 7) with MAO at 150 °C under 3 MPa ethylene pressure afforded PEs (*M_w* 2000) having predominant vinyl chain ends (>95%) with high productivity (>200 kg of PE/(mmol of Zr)).

Starting from the vinyl-terminated PEs formed with FI catalysts, we have successfully synthesized epoxy- and diol-terminated PEs.^{5,7} Figure 7 demonstrates the ¹H NMR spectra of these end-functionalized PEs, indicating the production of well-defined structures.

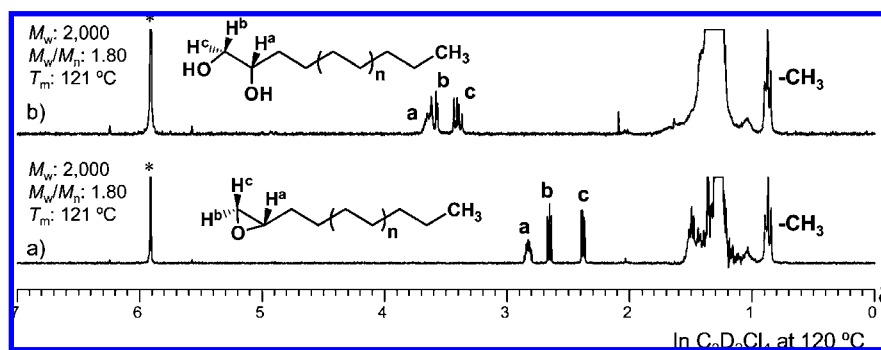


FIGURE 7. ^1H NMR spectra of (a) epoxy- and (b) diol-terminated PEs.

A series of well-defined PE/poly(ethylene glycol) (PEG) block copolymers with different molecular architectures (A₄B-, AB-, AB₂-, and AB₃-type block copolymers), and PE/polyester or PE/polyurethane block copolymers composed of polyester or polyurethane main chains and PE side chains (comb-shaped polymers) were successfully prepared using these well-defined and highly reactive end-functionalized PEs.⁵ The above end-functionalized PEs and PE/polar polymer hybrid materials possess unique macromolecular structures and associated properties, and thus many potential applications exist across a broader range of fields.

2. Ultrahigh Molecular Weight Linear PEs and Block Copolymers. One application of the high selectivity shown by FI catalysts for ethylene relative to α -olefins (and vinyl-terminated macromonomers) in regard to the formation of value-added polymers is their ability to produce ultrahigh molecular weight linear PEs.^{5–7} FI catalysts bearing sterically encumbered R¹ and R² substituents (meaning a combination of the ability to form ultrahigh molecular weight PEs and the ability to display high selectivity for ethylene) can produce ultrahigh molecular weight linear PEs that are ideal high strength materials.

For example, FI catalyst **28** supported on MAO/SiO₂ at 80 °C under 0.8 MPa ethylene pressure afforded with high efficiency (560 kg of PE/(mmol of Zr)) ultrahigh molecular weight PEs (M_v 4 400 000) that exhibited morphologies consisting of well-defined spherical particles. ¹³C NMR studies, together with the rheological properties of these PEs, indicated the production of PEs with neither short nor long branches along the polymer backbone, unlike the ultrahigh molecular weight PEs formed with heterogeneous Ziegler–Natta catalysts. These ultrahigh molecular weight linear PEs can be used for artificial bones, artificial legs, and bulletproof vests.

Another application of high ethylene selectivity with respect to value-added materials was demonstrated by

researchers at Dow Chemical.³⁰ FI catalysts bearing sterically encumbered R¹ and R² substituents are capable of yielding ultrahigh molecular weight PEs from an ethylene and α -olefin mixture. As a result, they succeeded in the production of multiblock copolymers composed of crystalline and amorphous segments using FI catalyst **31** combined with arylpyridylamidohafnium catalyst **32** (Chart 7) and R₂Zn. FI catalyst **31** selectively generates PEs even in the presence of ethylene and 1-octene, whereas **32** provides amorphous copolymers, resulting in the production of multiblock copolymers through a reversible chain transfer mediated by R₂Zn. 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.⁵

3. Noncoherent Particulate PEs. The combination of an FI catalyst and isolated MgCl₂/R'_nAl(OR)_{3–n} has brought forth an extraordinary opportunity for the preparation of noncoherent particulate PEs that display excellent polymer morphology.^{7,10} With this effective production technique in hand, noncoherent, size-controllable microparticle PEs with high bulk densities and extremely narrow particle size distributions were successfully prepared. Because of FI catalysts' unique and versatile polymerization catalysis,^{5–9} a wide variety of particulate PEs can be made with very-low to ultrahigh molecular weights and with saturated end groups and vinyl end groups.

For example, FI catalyst **33** (Chart 7) coupled with isolated MgCl₂/Et_nAl(OR)_{3–n} [OR = 2-ethyl-1-hexoxy group] at 80 °C under 0.8 MPa ethylene pressure enabled us to produce spherical particle PEs (diameter ~120 μm , productivity 360 kg of PE/(mmol of Zr)) with very high molecular weight (M_v 3 000 000) and with an exceptionally high bulk density of 0.50 g/mL (Figure 8a), which is probably the highest bulk density ever achieved for a PE.^{7,10}

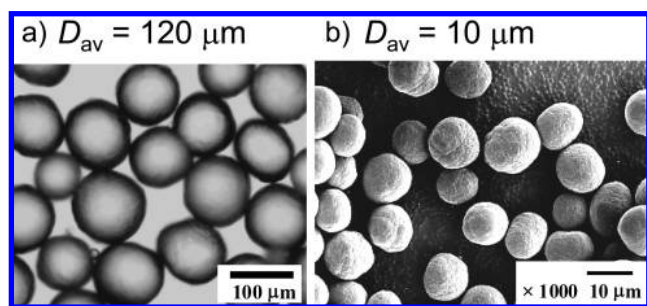


FIGURE 8. (a) Photograph and (b) SEM image of the spherical particle PEs.

Importantly, the combination of an FI catalyst with an ultrafine particle MgCl_2 -support allowed us to produce ultrafine, noncoherent PE particles.^{5,7,10} For instance, FI catalyst **33** supported on isolated $\text{MgCl}_2/\text{Bu}_n\text{Al}(\text{OR})_{3-n}$ (particle size $1.5 \mu\text{m}$) formed very high molecular weight PEs (M_v 3 100 000) consisting of noncoherent, spherical particles of $10 \mu\text{m}$ in diameter (Figure 8b). Additionally, noncoherent PE particles of $3 \mu\text{m}$ were also prepared using this technology. Moreover, with a technology that allows for the production of ultrafine noncoherent particle PEs in our possession, functionalized PE particles that are dispersible in water were synthesized by either chemical or physical surface modifications.¹⁰ The ultrafine particulate materials described above are new and thus should expand the utility of polyethylenic materials (e.g., sintered sheets and filters, resin modifiers, light diffusion films, cosmetics, etc.).

E. Conclusion

The ligand-oriented catalyst design concept has resulted in the discovery of highly active FI catalysts for the controlled (co)polymerization of olefinic monomers. An FI catalyst is a group 4 transition metal complex bearing a pair of nonsymmetric and potentially reactive phenoxy-imine ligands that possess electronically flexible properties. Additionally, an FI catalyst normally has a C_2 -symmetric nature, but is potentially fluxional. Importantly, FI catalysts allow for an extremely wide-ranging catalyst design capability, derived from the readily varied steric and electronic properties of the phenoxy-imine ligands. With these features, FI catalysts (after activation) exhibit unique and versatile polymerization catalysis, leading to the production of a wide variety of value-added olefin-based materials.

Therefore, FI catalysts are very important from the organometallic, catalysis, and polymer science points of view, and they are now being used commercially for the production of value-added olefin-based materials. It is anticipated that future research on FI catalysts will produce additional olefin-based

materials with unique architectures and material properties and will offer scientists the chance to further study olefin polymerization catalysis and related mechanisms.

BIOGRAPHICAL INFORMATION

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