FI Catalysts: A New Family of High Performance Catalysts for Olefin Polymerization

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Abstract: This paper reviews a new family of olefin polymerization catalysts. The catalysts, named FI catalysts, are based on non-symmetrical phenoxy-imine chelate ligands combined with group 4 transition metals and were developed using "ligand-oriented catalyst design". FI catalysts display very high ethylene polymerization activities under mild conditions. The highest activity exhibited by a zirconium FI catalyst reached an astonishing catalyst turnover frequency (TOF) of 64,900 s^{-1} atm^{-1}, which is two orders of magnitude greater than that seen with Cp_2ZrCl_2 under the same conditions. In addition, titanium FI catalysts with fluorinated ligands promote exceptionally high-speed, living ethylene polymerization and can produce monodisperse high molecular weight polyethylenes ($M_w/M_n < 1.2$, max. $M_n >$ 400,000) at 50 °C. The maximum TOF, 24,500 min^{-1} atm^{-1}, is three orders of magnitude greater than those for known living ethylene polymerization catalysts. Moreover, the fluorinated FI catalysts promote stereospecific room-temperature living polymerization of propylene to provide highly syndiotactic monodisperse polypropylene (max. [rr] 98%). The versatility of the FI catalysts allows for the creation of new polymers which are difficult or impossible to prepare using group 4 metallocene catalysts. For example, it is possible to prepare low molecular weight ($M_v \sim 10^3$) polyethylene or poly(ethylene-*co*-propylene) with olefinic end groups, ultra-high molecular weight polyethylene or poly(ethylene-*co*-propylene), high molecular weight poly(1-hexene) with atactic structures including frequent regioerrors, monodisperse poly(ethylene-*co*-propylene) with various propylene contents, and a number of polyolefin block copolymers [e.g., polyethylene-*b*-poly(ethylene-*co*-propylene), syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene), polyethylene-*b*-poly(ethylene-*co*-propylene)-*b*-syndiotactic polypropylene]. These unique polymers are anticipated to possess novel material properties and uses.

Keywords: block copolymer; group 4 transition metal catalyst; living polymerization; olefin polymerization; phenoxy-imine ligand; post-metallocene catalyst

Abbreviation: Al/Zr: molar ratio of aluminum in MAO and a Zr complex; Cp: cyclopentadienyl; DFT: density functional theory; EPR: ethylene-propylene rubber; *m*: meso-dyad; MAO: methylalumoxane; M_n: number-averaged molecular weight; M_v: viscosity-averaged molecular weight; M_w: weight-averaged molecular weight; PE: polyethylene; PP: polypropylene; *r*: racemo-dyad; sPP: syndiotactic polypropylene; TOF: turnover frequency

1 Introduction

The discovery of highly active olefin polymerization catalysts has been crucial to the creation of new polymers which impact our daily lives in countless beneficial ways. The first key discovery was made by Ziegler,[1] the combination of $TiCl_4$ and alkylaluminum, which displayed high ethylene polymerization activity under mild reaction conditions as opposed to a high-pressure and high-temperature free-radical polymerization process. Followed by Natta's stereoregular propylene polymerization,[2] the Ziegler–Natta catalysts resulted in the creation of new polymers such as high-density polyethylene and isotactic polypropylene.

The second important discovery in olefin polymerization catalysts was the introduction of $MgCl_2$ as a support to $TiCl_4$-based catalyst systems.[3] These $MgCl_2$-supported $TiCl_4$ catalysts exhibited activities two orders

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Terunori Fujita was born in November 1957 in Ehime, Japan. He received his Bachelors and Masters degrees in chemistry, natural product synthesis, from Hokkaido University working with Professors Takeshi Matsumoto and Haruhisa Shirahama. He obtained his Ph. D. degree in organic chemistry, anion coordination chemistry, from l'Universite Louis Pasteur de Strasbourg, France, in 1988 with Professor Jean-Marie Lehn. He joined Mitsui Petrochemical Industries, Ltd. (now Mitsui Chemicals, Inc.) in 1982, where he is now one of the three research fellows. Since 1988 his research interests have been focused on "synthesis of valuable organic materials with high efficiency using homogeneous and heterogeneous catalysis". Most recently, he has been working on the development of highly-active olefin polymerization catalysts and their applications for the preparation of polymers with new or enhanced material properties. He is a recipient of the Catalysis Society of Japan Award for Young Researchers for 2001.

of magnitude greater than Ziegler's original catalysts, and generated high performance high-density polyethylene, linear low-density polyethylene, and highly isotactic polypropylene, etc. In addition, it should be noted that these supported catalysts achieved important production process innovations. For polyethylene, the high catalyst efficiency circumvented the need to de-ash. For isotactic polypropylene, neither de-ashing nor removal of atactic-polypropylene was required due to the high catalyst efficiency and extremely high isospecificity ([*mmmm*] $> 98\%$). These simpler and more environmentally friendly processes still predominate in industry. However, it is difficult to control the microstructure of the polymers (and therefore optimize product properties) because of the heterogeneous and multi-site nature of these supported catalysts.

Shortly after the first reports on group 4 metallocenes, these well-defined complexes with alkylaluminum activators (e.g., Cp_2TiCl_2/AlR_nCl_{3-n}) found use as homogeneous olefin polymerization catalysts.[4,5] However, group 4 metallocenes activated with alkylaluminum were not considered as practical catalysts but instead were considered as soluble models of Ziegler–Natta catalysts because of their low activities. The discovery of the combination of group 4 metallocenes and methylalumoxane (MAO), partially hydrolyzed trimethylaluminum, by Sinn and Kaminsky in 1980 made the application of group 4 metallocenes as polymerization catalysts industrially practical.[6,7] The group 4 metallocenes, Cp_2ZrCl_2, combined with MAO led to a tremendous improvement in catalytic activity allowing the new system to rival $MgCl_2$-supported $TiCl_4$ catalysts. In addition, the homogeneous and well-defined nature of metallocenes allowed rational catalyst design to elucidate a qualitative relationship between catalyst structure and resulting polymer microstructure.[8] By virtue of elaborate catalyst design, metallocenes have created numerous polymers, which were unachievable using conventional Ziegler–Natta catalysts. These highly active metallocene catalysts have been used industrially to produce new or differentiated polymers such as linear low-density polyethylene, isotactic polypropylene, syndiotactic polypropylene (*s*PP), and syndiotactic polystyrene. Ever since, the great potential of well-defined transition metal complexes for olefin polymerization demonstrated by the group 4 metallocene catalysts has driven many researchers to investigate highly active post-metallocene catalysts.[9]

The first post-metallocene catalysts, which are truly comparable to the metallocene catalysts in terms of catalytic activities and polymer molecular weights, are probably the nickel complexes with diimine ligands discovered by Brookhart et al. in 1995.[10] Their discovery accelerated the research on post-metallocene catalysts, and in 1996, McConville et al. showed that titanium complexes bearing diamide ligands displayed high catalytic properties towards higher α-olefin polymerizations.[11] In 1998, Brookhart and Gibson reported that iron or cobalt complexes possessing diimine-pyridine ligands exhibited very high ethylene polymerization activities.[12] In the same year, nickel complexes with phenoxy-imine ligands (Grubbs et al.),[13] and group 4 transition metal complexes having phenoxy-imine ligands (Fujita et al.),[14] were reported as high performance olefin polymerization catalysts. These catalysts listed in Figure 1 show high activities comparable to or exceeding those of the group 4 metallocene catalysts. Beyond that, some behave as living polymerization catalysts of α-olefins,[10c,11b,14b] some produce branched polyethylenes without using comonomers,[10] and some promote copolymerization of ethylene or α-olefins with polar olefins to produce functionalized polyolefins.[10b,13] This article is not a comprehensive review of the post-metallocene catalysts because most of the catalysts in Figure 1 have already been covered in a number of excellent reviews.[15] In this article, we shall mainly highlight our work on the development of group 4 transition metal complexes featuring phenoxy-imine chelate ligands, named FI catalysts, and describe the concept behind the catalyst design, catalyst synthesis, catalyst structures, and unique olefin polymerization behavior. Moreover, we will discuss the preparation of new polymers with FI catalysts. FI catalysts are an important addition to the list of post-metallocene catalysts and have been exploited extensively by other research groups,[31] for example, with similar or modified ligands[31c, d,e, g] and different metals.[31f, j]

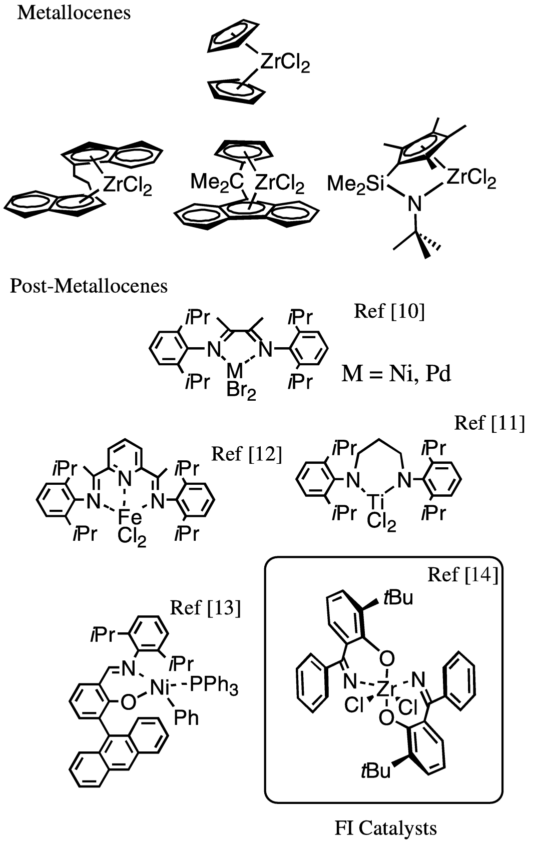
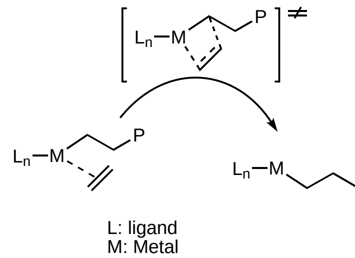


Figure 1. Examples of metallocene and post-metallocene catalysts.

2 Design and Discovery of FI Catalysts (Ligand-Oriented Catalyst Design)

Learning from history, we decided to pursue high activity because it would be the most fundamental prerequisite for olefin polymerization catalysts. In general, an olefin polymerization catalyst consists of a metal center, ancillary ligand(s), a growing polymer chain, and a monomer-coordination site (Scheme 1). It is very interesting to find out that the foregoing sentence sounds as if the metal is the center of catalysis and ligands are supplementary for the metal to do catalysis, for instance, holding the metal in a monomeric fashion, maintaining metal electrophilicity and oxidation state appropriately high, ensuring reaction space for incoming substrates, etc. Against this traditional viewpoint, we dared to think that ligands would work together with the metal in more positive and dynamic ways.[15c] In fact, DFT calculations performed on a metallocene catalyst show that electrons on the cyclopentadienyl ligand (Cp)



L: ligand
M: Metal
P: growing polymer chain

Scheme 1. Olefin insertion reaction in transition metal-catalyzed olefin polymerization.

move between the metal and the ligand along the reaction coordinate of ethylene insertion to a Zr–C bond. This means that ligands must be electronically flexible enough to receive electrons from the coordinating olefin through a metal and to release electrons whenever it is needed to expedite the olefin insertion reaction. We believe that this will be achieved by moderate electron-donating properties of ligands and will be the most important and common characteristic for a ligand to any metal. We conducted several calculations to estimate the electron-donating properties of ligands. For example, the negative charge on a ligand as estimated by PM3/MNDO may be employed as an index of electron-donating properties as shown in Figure 2.

Our basic strategy used to design a ligand is conceptually simple. A ligand must have:

i) moderate electron-donating properties estimated and categorized by several disparate calculations,
ii) a chelating structure to meet a demand for thermal stability,
iii) electron counting that fulfills the metal's requirement to form a complex of 16 electrons or less (pioneering work on the metallocene catalysts shows that the active species of metallocenes is a cationic species with 14 e and this would be one of the reasons for the high activity observed with metallocenes[16]). Additionally, we deliberately focused on ligands having
iv) non-symmetric chelating structures and
v) structural diversity and synthetic readiness (see Section 4 for this aspect).

When we were designing our ligands, non-symmetrical chelate ligands were less investigated as olefin polymerization catalysts[17] and we expected that such ligands might generate non-symmetrical reaction sites possessing non-symmetrical control over polymerization reactions to result in the formation of unique structure polymers.[18] This approach led us to many ligand candidates, and finally after continuous trial and error, we found that group 4 transition metal complexes having phenoxy-imine ligands displayed very high activity for ethylene polymerization at 25 °C under atmospheric ethylene pressure. Hence, complex **1**, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride, exhibited 519 kg-PE/mmol-Zr × h of activity, which is almost 20 times higher than the activities observed with Cp_2ZrCl_2/MAO (27 kg-PE/mmol-Zr × h) under the same polymerization conditions.[19] The activity displayed by complex **1** is one of the highest values observed for homogeneous olefin polymerization catalysts including the group 4 metallocenes at atmospheric pressure conditions (unless otherwise stated, the reaction conditions, ethylene at 1 atmospheric pressure and 25 °C, are applied for all polymerizations). Likewise, complex **2**, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]titanium(IV) dichloride, and complex **3**, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]hafnium(IV) dichloride, displayed very high activities of 3.3 kg-PE /mmol-Ti × h and 6.5 kg-PE /mmol-Hf × h, respectively.[19,20] The activities displayed by complexes **2** and **3** are some of the highest values achieved using titanium and hafnium complexes with non-Cp ligands. These results indicate that group 4 transition metal complexes possessing phenoxy-imine chelate ligands have good potential as olefin polymerization catalysts. Since these complexes were discovered as a result of ligand-oriented catalyst design, we named the newly-discovered complexes FI catalysts, following the Japanese pronunciation of the ligand "***F***enokishi-***I***min Haiishi" and, at the same time, FI catalysts stands for ***F***ujita group ***I***nvented catalysts.

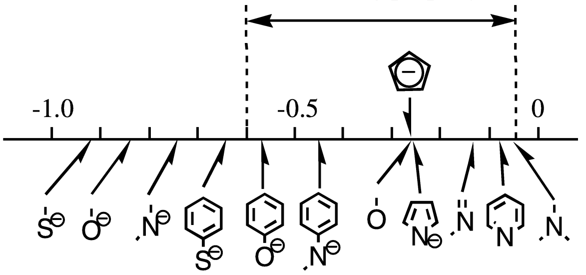
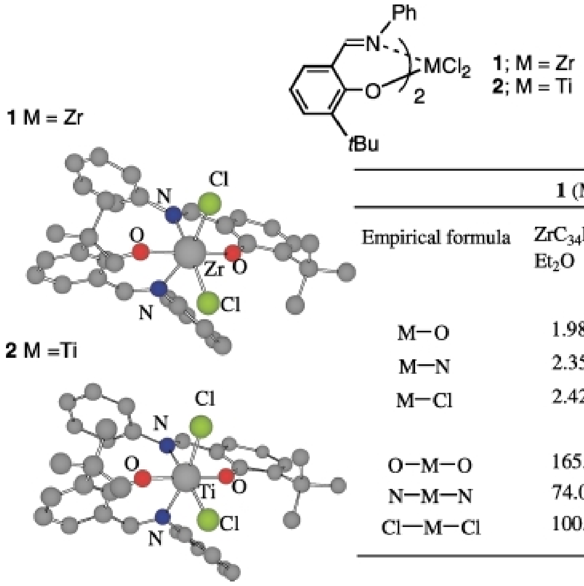


Figure 2. Calculated charge on coordinating atoms of representative ligands by PM3/MNDO.

3 Molecular Structure of FI Catalysts

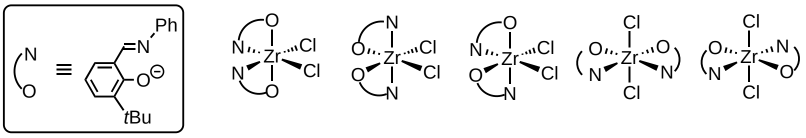
As shown in Figure 3, X-ray analyses of complexes **1** and **2** display distorted octahedral structures having two oxygen atoms in *trans*-positions and two nitrogen atoms and two chlorine atoms in *cis*-positions.[19,20] The larger ionic radius of Zr^{4+} (0.86 Å) than Ti^{4+} (0.68 Å) makes the Zr metal more exposed (away from the octahedral framework) as seen from the smaller O–Zr–O angle, while the Ti metal is more shielded and packed by the ligands.

DFT calculations on complex **1** support the same stereochemical structure obtained by X-ray analysis, which is the most stable of the possible isomers (Scheme 2). The calculations further revealed that when the two chlorine bound sites were turned into polymerization sites, in other words, a growing polymer chain site and an ethylene coordination site, the resulting cationic species retained the same stereochemistry as **1** (Scheme 3). The polymer chain and the ethylene monomer are still in *cis*-positions, which is indispensable for high polymerization efficiency. Furthermore, the theoretical calculations brought an interesting fact to light. The Zr–N bonds that lie in the same plane as polymerization sites expand and contract according to



	1 (M = Zr)	2 (M = Ti)
Empirical formula	$ZrC_{34}H_{36}Cl_2N_2O_2$/ Et_2O	$TiC_{34}H_{36}Cl_2N_2O_2$
	Bond Distances/ Å	
M—O	1.985(2)	1.852(4)
M—N	2.355(2)	2.236(4)
M—Cl	2.4234(9)	2.305(2)
	Bond Angles/ °	
O—M—O	165.5(1)	171.6(2)
N—M—N	74.0(1)	76.4(2)
Cl—M—Cl	100.38(5)	103.10(8)

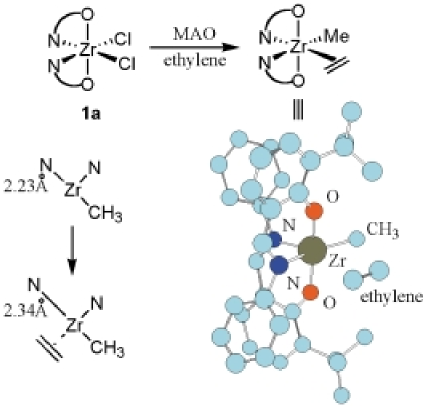
Figure 3. Perspective view of the molecular structures of complexes **1** and **2** and selected bond distances and bond angles. Hydrogen atoms and a diethyl ether molecule are omitted for clarity.



Isomers	1a	1b	1c	1d	1e
RFE/kJ mol^{-1}	0.0	25.3	19.5	33.3	37.3

Scheme 2. Relative formation energy (RFE) of the possible isomers of complex **1.**

the reaction coordinate of ethylene insertion (2.23 – 2.34 Å, Scheme 3), while the Zr–O bond length remains practically constant. We believe that this variable Zr–N bond length facilitates a smooth and flexible electron exchange between the metal and the ligands, which realizes the exceptionally high polymerization activity of FI catalysts.

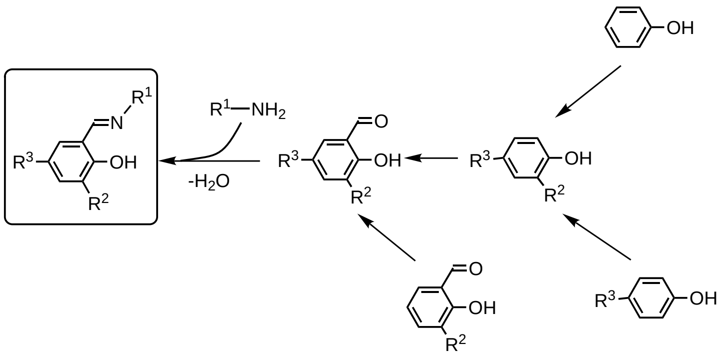


Scheme 3. DFT calculations on the possible active species of complex **1** and variable Zr–N bond length.

4 Synthesis of FI Catalysts

There is beautiful work on metallocene catalysts[8] that demonstrates how catalyst symmetry regulates the stereoregularity of the resulting polymers, how a substituent in a strategic position can disfavor β-hydride elimination and result in high molecular-weight polymers, and how subtle changes in bite angle affect activity and comonomer intake in copolymerization. These results exhibit that the diversity and tunability of a ligand framework are particularly important in the design and synthesis of new catalyst systems.

The phenoxy-imine ligands have the advantageous properties of diversity and tunability. Within the framework, there are three readily changeable substituents, which will sterically and electronically affect polymerization reactions (R^1 to R^3, Scheme 4). By retrosynthetic analysis, the phenoxy-imine ligands can be divided into two reactants; primary amines and phenol derivatives, both of which have rich inventories of commercially available compounds. The desired substituents on phenols can be introduced by electrophilic aromatic substitutions with electrophiles such as alcohols, olefins,



Scheme 4. Synthesis of FI ligands.

and silyl halides. Formylation at the 2-position of phenols can be performed using paraformaldehyde with many established methods in high yields (typically 70 to 80%). Salicylaldehydes and primary amines are condensed into Schiff bases under standard condensation conditions. Generally, the overall synthesis requires fewer steps and gives higher yields than those for metallocenes. Thus, FI catalysts allow us to examine a wide variety of substituents including functional groups that contain heteroatoms. Interestingly, recent research has revealed that each substituent, R^1 to R^3, has specific, independent, and additive effects on polymerization. Thus, appropriate combinations of R^1, R^2, and R^3 are responsible for the polymer molecular weight, polymerization activity, thermal stability of a complex, and so on. In the following sections, we will illustrate these unique characteristics of FI catalysts induced by the diversity of the ligand system.

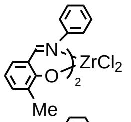
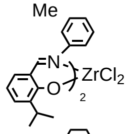
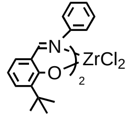
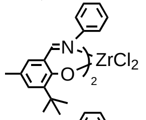
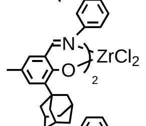
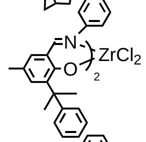
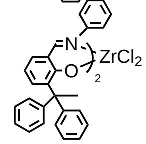
5 Polymerization with FI Catalysts

5.1 Zirconium FI Catalysts

5.1.1 Ethylene Polymerization Activity

Modifications in R^2 have a dramatic effect on the activity. Substituents less bulky than a *t*-butyl group significantly reduce ethylene polymerization activity (Table 1, Entries 1 – 3).[19b, c] The activity is directly correlated with the steric hindrance of R^2. For instance, in the sequence *t*-Bu < adamantyl < cumyl < 1,1-diphenylethyl, the activity increases from 519 kg-PE/mmol-Zr × h with **1** (R^2 = *t*-butyl) to 2383 kg-PE/mmol-Zr × h with **9** (R^2 = 1,1-diphenylethyl) (Table 1, Entries 3 – 7). With a cyclohexyl group as R^1, the R^2 effect is more pronounced (Table 2). Complex **10** (R^2 = *t*-butyl, R^3 = methyl) shows only 82 kg-PE/mmol-Zr × h of activity, while 1,1-diphenylethyl group as R^2 (**13**) raises the activity to 6552 kg-PE/mmol-Zr × h. This incredibly large activity corresponds to a catalyst turnover frequency (TOF) of 64,900 s^{-1} atm^{-1}, which is probably the largest of all known catalytic reactions.

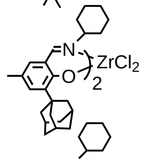
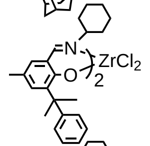
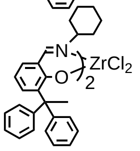
Table 1. Ethylene polymerization with zirconium FI catalysts.[a]

Entry	Zr complex	Activity/ kg-PE/mmol-Zr·h
1	**4**; 	0.4
2	**5**; 	0.9
3	**1**; 	519
4	**6**; 	331
5	**7**; 	714
6	**8**; 	2096
7	**9**; 	2383

[a] Polymerization conditions: toluene (250 mL), atmospheric ethylene (0.1 MPa), 25 °C, polymerization time = 5 or 10 min, MAO (1.25 mmol), Al/Zr = 250 (Entries 1 and 2) or 62,500 - 125,000 (Entries 3 - 7).

Rationalization of the R^2 effect would be i) steric protection of oxygen atoms from coordination of Lewis acids such as MAO or another molecule of the catalyti-

Table 2. Ethylene polymerization with zirconium FI catalysts.[a]

Entry	Zr complex	Activity/ kg-PE/mmol-Zr·h
8	**10**; 	82
9	**11**; 	434
10	**12**; 	4315
11	**13**; 	6552

[a] Polymerization conditions: toluene (250 mL), atmospheric ethylene (0.1 MPa), 25 °C, polymerization time = 5 min, MAO (1.25 mmol), Al/Zr = 6,250 - 625,000

cally active cationic complex which is supposed to be highly electrophilic. The coordination increases steric congestion near the reaction center, which at least hampers ethylene coordination to the metal. Even worse, it may cause catalyst deactivation by, for example, loss of the ligand. The bulky substituents may also help ii) effective ion-separation between an electrophilic active species and a counteranion, which allows more space for ethylene coordination to the metal and insertion into the carbon-metal bond. Moreover, electronically, the ion-separation enhances the degree of unsaturation associated with the catalytically active cationic species and therefore increases the reactivity towards ethylene.

Complex **1** exhibits a temperature-dependence of activity with a maximum at 40 °C (587 kg-PE/mmol-Zr × h). Above 40 °C activity decreases (100 kg-PE/mmol-Zr × h at 75 °C, Figure 4). Under ethylene pressurized conditions (0.9 MPa), the activity drops more rapidly above 50 °C from 1,192 kg-PE/mmol-Zr × h to 63 kg-PE/mmol-Zr × h at 90 °C. On the other hand, the activity maxima of metallocene catalysts generally lie in the industrially practical temperature range around 75 °C. The most straightforward approach to improve the activity decline at high temperature would be to enhance the thermal stability of the catalytically active cationic species derived from the complex **1**. We assume that the activity decrease at higher temperatures is due to the decomposition of the active species because of the loss of the ligand(s). Thus, to strengthen the metal-ligand bonds of complex **1**, electron-donating groups were introduced at the *para*-positions of phenyl groups which would have a large electronic influence on the zirconium metal while polymerization sites were retained in the same steric environment.[21] As expected, the activity ratio of 75 °C to 50 °C (A_{75}/A_{50}) was improved from 0.18 (R^1 = phenyl) to 0.61 (R^1 = 4-MeO-phenyl), 0.45 (R^1 = 4-Me_2N-phenyl) and 0.67 (R^3 = MeO) (Figure 5).

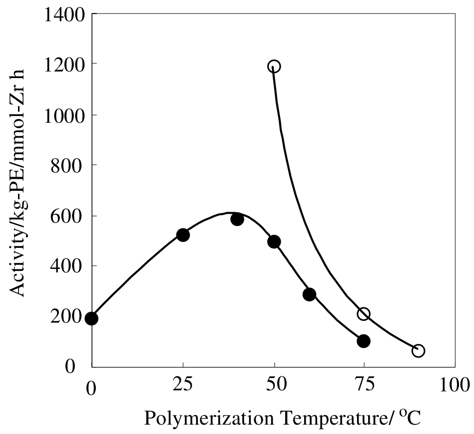


Figure 4. Temperature dependence of polymerization activity obtained with **1**/MAO. Conditions: ethylene (0.1 MPa), toluene (250 mL), MAO (1.25 mmol), polymerization time 5 min, Al/Zr = 1563 – 62,500 (●); ethylene (0.9 MPa), heptane (500 mL), MAO (1.25 mmol), polymerization time 15 min, Al/Zr = 2000 – 25,000 (○).

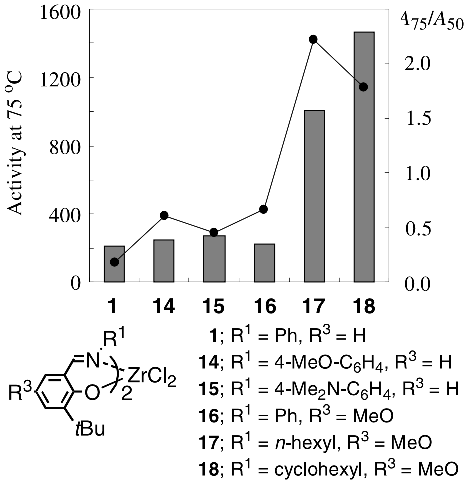
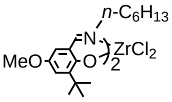
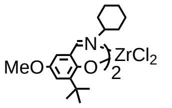
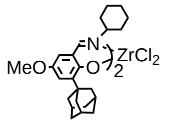
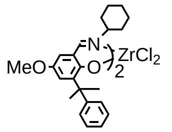
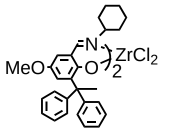


Figure 5. Effect of electron-donating substituents on activity at 75 °C (bar graph) and relative activity to 50 °C (A_{75}/A_{50}, line graph). Conditions: ethylene (0.9 MPa), heptane (500 mL), MAO (1.25 mmol), polymerization time 15 min, Al/Zr = 12,500 or 25,000.

In combination with alkyl groups as R^1 (*n*-hexyl: **17**, cyclohexyl: **18**), the effect of a methoxy group at the R^3 position became remarkable and the activities increased with polymerization temperature (A_{75}/A_{50} = 1.79 – 2.22) (Figure 5) and reached 1374 kg-PE/mmol-Zr × h (**17**) and 1697 kg-PE/mmol-Zr × h (**18**) at 90 °C. The elec-

Table 3. Ethylene polymerization with zirconium FI catalysts.[a]

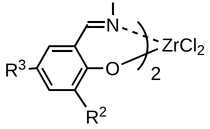
Entry	Zr complex	T_p[b]/ °C	Activity[c]
12	**17**; 	50	454
13		75	1008
14		90	1374
15	**18**; 	50	818
16		75	1462
17		90	1697
18	**19**; 	50	1898
19		75	3052
20	**20**; 	50	3665
21		75	7244
22	**21**; 	50	3986
23		75	9350

[a] Polymerization conditions: heptane (500 mL), ethylene (0.9 MPa), polymerization time = 15 min, MAO (1.25 mmol), Al/Zr = 25,000 - 250,000.

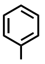
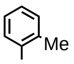
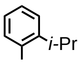
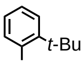
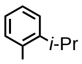
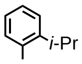
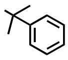
[b] Polymerization temperature.

[c] in kg-PE/mmol-Zr·h.

Table 4. Ethylene polymerization with zirconium FI catalysts.[a]



1; R^1 = Ph, R^2 = *t*-Bu, R^3 = H
22; R^1 = 2-Me-C_6H_4, R^2 = *t*-Bu, R^3 = H
23; R^1 = 2-*i*-Pr-C_6H_4, R^2 = *t*-Bu, R^3 = H
24; R^1 = 2-*t*-Bu-C_6H_4, R^2 = *t*-Bu, R^3 = H
25; R^1 = 2-*i*-Pr-C_6H_4, R^2 = adamantyl, R^3 = Me
26; R^1 = 2-*i*-Pr-C_6H_4, R^2 = cumyl, R^3 = cumyl

Entry	Complex	R^1	R^2	$M_v/10^4$	Activity[b]
24	**1**		*t*-Bu	1	519
25	**22**		*t*-Bu	32	40
26	**23**		*t*-Bu	113	58
27	**24**		*t*-Bu	274	0.1
28	**25**			153	23
29	**26**			220	43

[a] Polymerization conditions: heptane (500 mL), ethylene (0.9 MPa), 25 °C, polymerization time = 5 min, MAO (1.25 mmol), Al/Zr = 62,500 (Entry 24), 500 (Entry 26), 250 (Entry 27), 2,500 - 12,500 (other entries).

[b] In kg-PE/mmol-Zr·h.

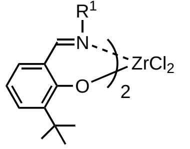
tron-donating effect was confirmed by the downfield-shifted imine proton signal in ^1H NMR [8.08 ppm (**1**) < 8.14 ppm (**17**) < 8.19 ppm (**18**)], the reduced net charge on zirconium calculated by RHF/PM3(tm) [2.001 (**1**) > 1.909 (**17**) > 1.852 (**18**)] and the crystallographically characterized shorter Zr–N bonds [2.355 Å (**1**) > 2.281 Å (**18**)]. Further modification of R^2 again displays a large activity-enhancing effect in accordance with steric bulkiness (Table 3, Entries 15 – 23). The activities displayed with the modified FI catalysts are some of the highest reported to date under industrially practical conditions. Noteworthy also are the additive properties of R^2 and R^3, in other words, R^2 enhances activity and the R^3 (MeO-) imparts thermal stability ($A_{75}/A_{50} = 1.61 - 2.35$ for R^3 = MeO, $A_{75}/A_{50} = 0.34 - 0.93$ for R^3 = Me).

5.1.2 Molecular Weight of Polyethylene

Polymer molecular weight can be controlled by R^1. Ligand modification was again started with complex **1**. Complex **1**, when activated with MAO, produces virtually linear polyethylene, indicated by IR and ^{13}C NMR analyses, having a viscosity-averaged molecular weight (M_v) of around 10×10^3. The polymer has almost equal numbers of vinyl and methyl groups as chain-end structures, suggesting that β-hydrogen elimination determines the molecular weight of the polymer. When an alkyl group was introduced at the *ortho*-position of the R^1-phenyl group the molecular weight of polyethylene increased as the steric bulk of the alkyl group increased (Table 4, Entries 24 – 27).[19] However, as the bulk of the alkyl group increases polymerization activity significantly decreases. This drawback can be minimized by the additive property of R^2. By combining a 2-isopropylphenyl group as R^1 with a bulky R^2, the catalytic activity can be kept at a certain level (23 – 58 kg-PE/mmol-Zr × h) while increasing polyethylene M_v from 1.13×10^6 to 2.20×10^6 (Table 4). DFT calculations indicate that the isopropyl group on the R^1-phenyl group makes the β-agostic interaction less favorable by 14 kJ/mol compared to complex **1**.

When R^1 is an alkyl group smaller than phenyl, the polymer molecular weights decrease which is consistent with the observation that an increase in R^1 bulk results in an increase in molecular weight. For example, the

Table 5. Ethylene polymerization with zirconium FI catalysts.[a]



Entry	complex	R^1	$M_v/10^3$	Activity[b]
30	**27**	*n*-Hexyl	11	45
31	**28**	Ethyl	5	38
32	**29**	Methyl	3	63

[a] Polymerization conditions: toluene (250 mL), atmospheric ethylene (0.1 MPa), 25 °C, polymerization time = 5 min, MAO (1.25 mmol), Al/Zr = 2,500 - 5,000.

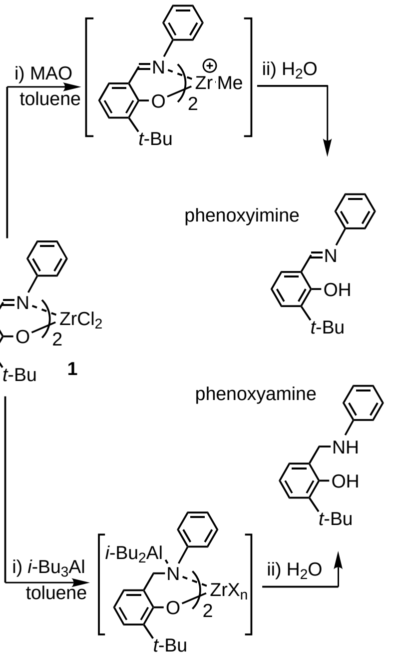
[b] in kg-PE/mmol-Zr·h.

molecular weight decreases in a sequence phenyl (10×10^3) > *n*-hexyl (1.1×10^3) > ethyl (0.5×10^3) > methyl (0.3×10^3) (Table 5). Chain-end analyses for these polymers display practically one chain-end vinyl group per polymer chain suggesting exclusive β-hydrogen elimination as the chain-termination step.

In addition to MAO, a combination of trityl tetrakis-(perfluorophenyl)borate [$Ph_3CB(C_6F_5)_4$] and trialkylaluminum can activate FI catalysts as well, but in a different fashion. The catalyst system, **1**/*i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$ afforded markedly high molecular-weight polyethylene ($M_v = 5.05 \times 10^6$) with an appreciable activity of 11 kg-PE /mmol-Zr × h. This is one of the highest molecular-weight polyethylenes ever prepared. The unusual difference by activators turned out to be a result of the imine reduction by *i*-Bu_3Al or its contaminant Al-H species. A hydroxybenzylamine was exclusively formed by the reaction of **1** and 30 equiv. of *i*-Bu_3Al after hydrolysis (Scheme 5).[19] This implies that the real active species in the system was bis(phenoxy-*amine*)titanium complex with Al attached on nitrogens. As shown, FI catalysts can produce polyethylene with an extremely wide range of molecular weight by modification of ligands or by selecting the appropriate activator. There is probably no example where a catalyst system can control such a broad range of polymer molecular weight without the aid of chain transfer reagents.

5.1.3 Propylene Homo- and Copolymerizations

Propylene polymerization conducted with **1**/MAO afforded an atactic oligomer (324 g-PP/mmol-Zr × h) and with **1**/*i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$ an isotactic polypropylene (68 g-PP/mmol-Zr × h, Tm = 101.6 °C, [mm] = 73.4%, $M_v = 0.2 \times 10^6$). The effect that the activator has on the polymer structure is not surprising because the active species derived from **1**/*i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$ is supposed to be sterically more congested due to the imine reduction by alkylaluminum. Ethylene-propylene copolymerizations were conducted with **1** in toluene at 50 °C for 5 min with a continuous gas flow at 50 L/h ethylene and 150 L/h propylene. Ethylene-propylene copolymers (EPR) having 20 – 30 mol % propylene contents were generated with high activities of about 6 kg-polymer/mmol-Zr × h with both activators, MAO and *i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$. Similar to ethylene homopolymerization, a marked difference of polymer molecular weight was found, i.e., 3×10^3 for MAO and 1.07×10^6 for *i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$. Encouraged by these results, large-scale pressurized reaction conditions were applied to the **1**/*i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$ catalyst, which resulted in ultra-high molecular weight EPR ($M_v = 2.11 \times 10^6$, 24.2 mol % propylene content, 11 kg-polymer/mmol-Zr × h).



Scheme 5. Possible reaction courses between complex **1** and alkylaluminums. X will be *i*-Bu, H, Cl, or possibly μ-(Cl, *i*-Bu, H)-Al complex.

5.2 Titanium FI Catalysts

In general, titanium FI catalysts demonstrate lower polymerization activity (but still appreciable) and produce higher molecular-weight polymers than the zirconium counterparts. Ligand modifications sometimes emphasize these characteristics. For example, chain termination rates can be reduced to the point where living polymerization results. Lower activity can also be rationally overcome by ligand modifications.

Some notable polymerization behavior with titanium FI catalysts is described here.

5.2.1 Ethylene Polymerizations

The temperature dependence on polymerization activity and polymer molecular weight with complex **2**/MAO are shown in Figure 6.[20b] Maximum activity appeared around 50 °C, and catalyst deactivation at higher temperatures is less than what was seen with the corresponding zirconium complex (Figures 4 and 6). The use of *n*-heptane as a polymerization solvent slightly reduces the activities and the polymer molecular weights compared to those obtained using toluene. However, if the higher ethylene solubility in toluene and the higher dielectric constant of toluene are taken into account, the activity in *n*-heptane is considerable. In other words, the activity in toluene is much lower than that expected for an active species with ionic character.[22] Competitive coordination of ethylene and toluene as π-donors to the metal center may result in lower polymerization activity as is seen in the other electrophilic organotitanium complex.[11]

The lower catalytic activity has made titanium FI catalysts less attractive when compared to the zirconium counterparts or metallocene catalysts. Thus, ligand modification of complex **2** was started with the aim of increasing the catalytic activity. Unlike zirconium FI catalysts, a strong electron-withdrawing group at the R^1-phenyl group has a more pronounced effect on polymerization activity than R^2 groups. Ethylene polymerization results are summarized in Table 6.[23] Remarkable activity enhancement was observed when two or more F or CF_3 groups were introduced, although monosubstitution at the *para*-position had no significant effect on activity. The activity enhancement may be attributed to increased electrophilicity of the active Ti species. This observation is in sharp contrast to the behavior of metallocene catalysts for which activity is decreased by electron-withdrawing groups on Cp rings.[24] The activities displayed with the complexes, especially **32**, are substantially higher than those of simple metallocene compounds such as Cp_2MCl_2 (M = Ti and Zr) under the same conditions, and probably the highest for titanium-based ethylene polymerization catalysts reported to date.

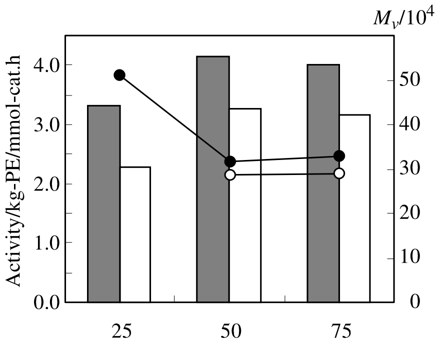
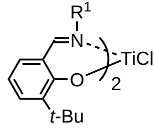
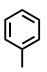
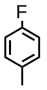
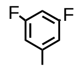
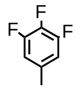
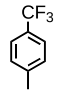
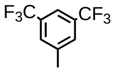


Figure 6. Ethylene polymerizations with **2**/MAO, polymerization activity in toluene (gray bars) and in *n*-heptane (white bars) and M_v in toluene (●) and in *n*-heptane (○). Conditions: ethylene (0.1 MPa), solvent (250 mL), MAO (1.25 mmol), polymerization time 5 – 30 min, Al/Zr = 25,000.

Table 6. Ethylene polymerization with fluorinated titanium FI catalysts/MAO.



Entry	Complex	R^1	$M_v/10^3$	Activity[b]
33	**1**		326	3.58
34	**30**		419	3.96
35	**31**		623	34.8
36	**32**		378	43.3
37	**33**		542	3.6
38	**34**		1,365	40.3
39	Cp_2TiCl_2		1,254	16.7
40	Cp_2ZrCl_2		1,040	27.9

[a] Polymerization conditions: toluene (250 mL), cat (0.5 - 5.0 mmol), MAO (1.25 mmol), polymerization time = 5 min, 25 °C, atmospheric ethylene (0.1 MPa).

[b] in kg-PE/mmol-cat·h.

5.2.2 1-Hexene Polymerization

The titanium FI catalyst **2** in conjunction with *i*-Bu_3Al/$Ph_3CB(C_6F_5)_4$ exhibits low activity towards ethylene and propylene polymerizations. The reduction of **2** with *i*-Bu_3Al or its contaminant Al-H species was again observed in the reaction. The resultant phenoxy-amine species turned out to display a distinctive polymerization behavior towards higher α-olefins.[25] In *n*-heptane,

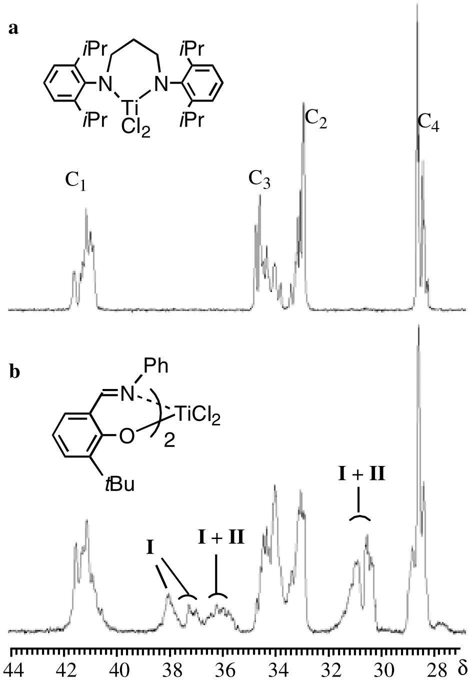
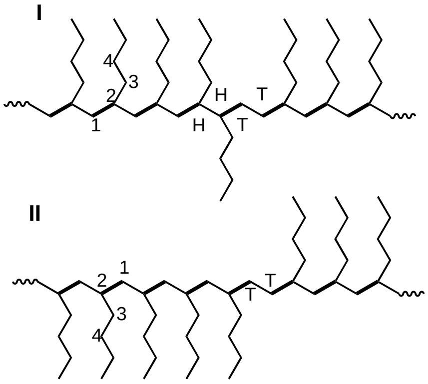


Figure 7. ^{13}C NMR spectra of poly(1-hexene) prepared by using (**a**) $[ArN(CH_2)_3NAr]TiCl_2$ (Ar = 2,6-di-*i*-Pr-C_6H_3) and (**b**) complex **2** with *i*-$Bu_3Al/Ph_3CB(C_6F_5)_4$. Conditions: heptane/1-hexene (60/40 mL), 25 °C, polymerization time 10 min, Ti/B = 1.2 – 2 (see Scheme 6 for the assignments).

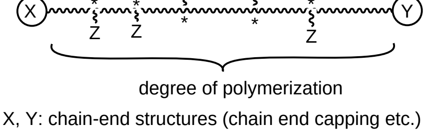
the catalyst system **2**/*i*-$Bu_3Al/Ph_3CB(C_6F_5)_4$ afforded high molecular-weight poly(1-hexene), $M_w = 592 \times 10^3$, which is one of the highest for poly(1-hexene)s prepared with homogeneous catalysts and is comparable to 619 × 10^3 obtained by McConville's titanium-diamide catalyst.[11] In addition to high molecular-weight polymers, there is an interesting resemblance between these titanium catalysts. Both the catalysts give no polymer in toluene, probably because the high electrophilicity of the species causes strong toluene coordination to the species relative to olefins.[11,25] Although these catalysts form similar molecular weight polymers, the polymer microstructures are remarkably different. In addition to atactic poly(1-hexene) sequence, several signals were observed for the polymer obtained with **2**/*i*-$Bu_3Al/Ph_3CB(C_6F_5)_4$ in the ^{13}C NMR spectrum, in striking contrast to the polymer obtained by the titanium-diamide catalyst (Figure 7). These signals originate from CH and CH_2 main-chain carbons in regioirregular head-to-head and tail-to-tail sequences (Scheme 6, **I** and **II**). From the integration, the polymer has 39 mol % tail-to-tail and 16 mol % head-to-head sequences together with 45 mol % regular head-to-tail sequence [ultra-random poly(1-hexene)]. This stereo- and regioirregular, high molecular-weight poly(1-hexene) is quite unusual, because, in general, a regioirregular 2,1-inserted monomer unit is prone to make the active species less reactive and cause chain termination through β-hydrogen elimination.



Scheme 6. Regioirregular structures in the polymer synthesized with **2**/*i*-$Bu_3Al/Ph_3CB(C_6H_5)_4$ (see Figure **6**, **b**).

5.2.3 Living Polymerization

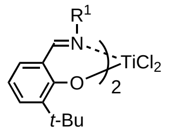
It is a goal for synthetic polymer chemists to synthesize polymers with completely defined structures. A chain of linear polyolefin has several elements to completely define its molecular structure, such as degree of polymerization, chain-end structures, stereochemistry of asymmetric carbons, and the number, types, and distribution of side-chains (Scheme 7). Living polymerization is known to control some of these elements, especially molecular weight and chain-end structures of polymer. Although there have been a number of transition metal catalysts which can polymerize ethylene or α-olefins in a living fashion,[26] there are few catalysts that are useful for both ethylene and α-olefins. Besides, most catalysts require a low polymerization temperature, usually below room temperature, to suppress chain-termination and therefore exhibit low activities and insufficient polymer molecular weights. The titanium FI catalyst bearing a perfluorophenyl group as R^1 (**35**) with MAO exhibited living polymerization with ethylene even at 50 °C to afford high molecular-weight polymer ($M_w = 424 \times 10^3$) having a narrow molecular weight distribution ($M_w/M_n = 1.13$) with exceptionally high TOF (21,500 min^{-1} atm^{-1}) (Ta-

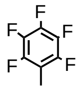
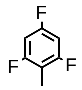
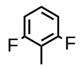
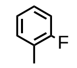
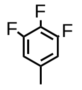
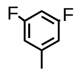
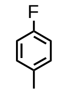


X, Y: chain-end structures (chain end capping etc.)
Z: side chains (block, alternating, random copolymerization)
*: asymmetric carbons (*R* or *S*, stereoregular polymerization)

Scheme 7. A schematic drawing of a polymer chain.

Table 7. Ethylene polymerization with fluorinated titanium FI catalysts/MAO.



Entry	Complex	R^1	$M_n/10^3$	M_w/M_n	TOF[b]
41	**35**		424	1.13	21500
42	**36**		145	1.25	1440
43	**37**		64	1.05	492
44	**38**		13	1.06	76
45	**32**		98	1.99	26500
46	**31**		129	1.78	19000
47	**30**		128	2.18	3160

[a] Polymerization conditions: toluene (250 mL), cat (0.5 - 5.0 mmol), MAO (1.25 mmol), polymerization time = 1 or 5 min, at 50 °C, atmospheric ethylene (0.1 MPa).

[b] In $min^{-1}atm^{-1}$.

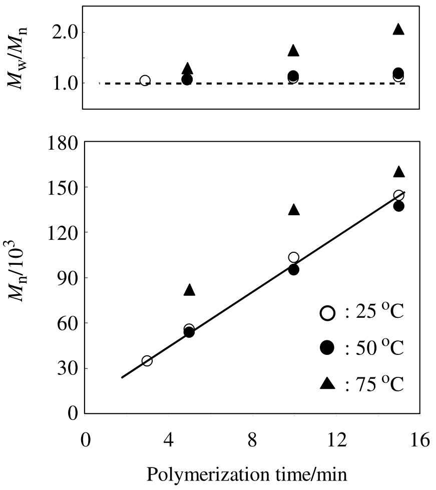


Figure 8. Plots of M_n and M_w/M_n as a function of polymerization time for ethylene polymerization with **35**/MAO. Conditions: **35** (1.0 μmol), MAO (1.25 mmol), ethylene/N_2 feed 2/50 L/h (25, 50 °C), 5/50 L/h (75 °C), toluene (250 mL).

ble 7, Entry 41).[27] The molecular weight is one of the highest observed for polyethylene produced through a living polymerization mechanism. The TOF is three orders of magnitude greater than those of known living ethylene polymerization catalysts[26] and is even comparable to those seen with highly active Cp_2ZrCl_2 under the same conditions. The catalyst exhibits living polymerization behavior over a wide range of temperature (Figure 8) even without ethylene monomer for at least 60 min at 25 °C, indicating a high potential for producing polyolefin block copolymers.

In order to investigate the mechanism of this unusual polymerization process, complexes which varied in the number and positions of fluorine atoms in the R^1-phenyl group were synthesized (**36–38, 30–32**). There is a clear difference in polymerization results depending on the fluorine substitution patterns. First of all, living polymerizations proceed only when at least one fluorine is located in the 2,6-positions of R^1-phenyl group (Table 7, Entries 41–44). Second, the activity of living systems is considerably lower than that of non-living systems (Table 7, Entries 41–44 compared to Entries 45–47). Finally, the activity increases with the number of fluorine atoms in both living and non-living systems (Table 7, Entries 41–44 and Entries 45–47). It is reasonable that electron-withdrawing fluorines enhance the electrophilicity and consequently the reactivity of the active centers. The lowered activity and "livingness" observed for complexes **35**, **36**, **37**, and **38** suggest that the *ortho*-fluorine(s) somehow participates in the polymerization reactions. DFT calculations on the complexes **35**, **36**, and **37** are consistent with the results of the X-ray analyses. Therefore, the calculations were extended to the cationic form of the complexes **35** to **38** bearing an *n*-propyl group which represent a model of a growing polymer chain. The calculations demonstrated that the *ortho*-fluorine substituent and a β-hydrogen of the *n*-propyl group were located at a distance of 2.276 to 2.362 Å which is well in the range of non-bonding interactions, and the $C{-}H_\beta$ bond elongation (1.113 Å) was observed in the calculation (Figure 9). According to the calculation, the interaction could be electrostatic between the negatively charged fluorine and the positively charged β-H. The electrostatic energy was estimated to be *ca.* –30 kJ/mol, which is large enough to overwhelm β-hydrogen transfer to the titanium center. In addition, the transition state of the β-hydrogen transfer to the titanium center will be disfavored by the fact that the β-hydrogen is positively charged and stabilized by the fluorine substituent, while the β-hydrogen should behave as a hydride in the β-hydrogen transfer process. This remarkable *ortho*-fluorine substituent effect represents a novel strategy for the design of a new transition metal complex for living olefin polymerization. Interestingly, a titanium FI catalyst having a chlorine at the 2-position of the R^1-phenyl group instead of fluorine, bis[*N*-(3-*tert*-butylsalicylidene)-2-chloroanilinato]titanium(IV) dichloride, also promoted ethylene polymerization at 25 °C to produce polyethylene having a narrow molecular weight distribution ($M_w/M_n = 1.23$), implying that the interaction with β-hydrogen is potentially achieved by any substituent possessing lone-pair electrons.

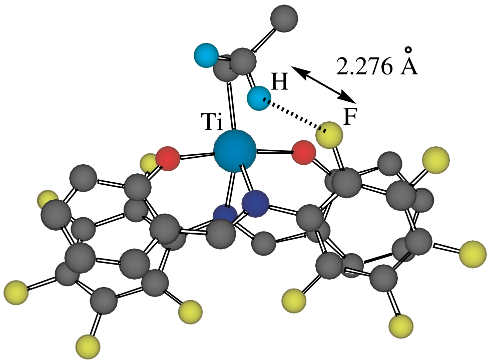
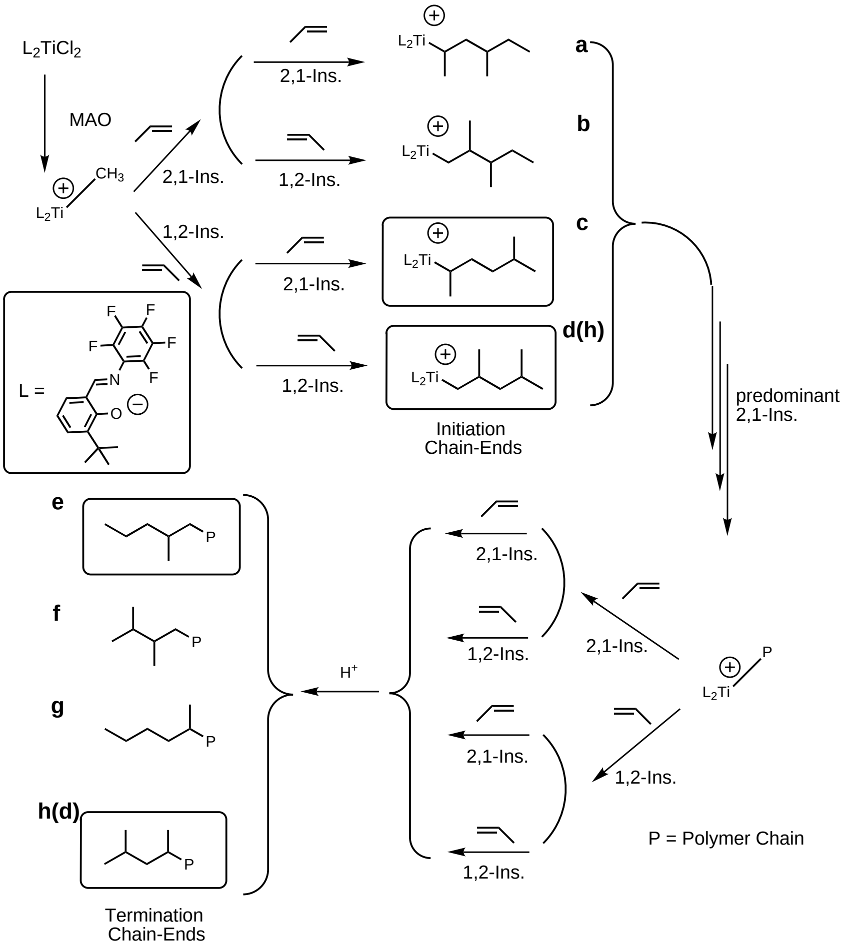


Figure 9. Calculated structure of a cationic form of complex **35** bearing an *n*-propyl group as a model of the polymer chain. Hydrogen atoms except those at the β-position of the *n*-propyl group and *t*-butyl groups are omitted for clarity.

Propylene polymerization with the complex **35**/MAO at room temperature also turned out to be living and produced polypropylene with a controlled molecular weight, a narrow molecular weight distribution ($M_w/M_n = 1.07 - 1.14$), and surprisingly high syndiotacticity (rr = 87%, 98%).[28] Microstructural analysis of the polymer by ^{13}C NMR exhibited that the first propylene monomer was inserted into the Ti–Me bond in a 1,2-fashion, which was followed predominantly by repetitive 2,1-insertions (Scheme 8).[29] To our knowledge, this is the first example of the domination of the 2,1-insertion mechanism for chain propagation displayed by a group 4 metal-based catalyst. Very recently, the generality of this unusual propylene polyinsertion mode with Ti FI catalysts was confirmed by other research groups.[31i, l] The isolated *m*-dyad errors in the polymer chain mean that chain-end stereocontrol is operating in the course of polymerization. The high syndioregularity at room temperature by chain-end control is quite unusual



Scheme 8. Possible chain-end structures: propyl (**e**), 1.6 mol % isobutyl (**d** + **h**); 1.5 mol % isopentyl (**c**); 1.5 mol % by ^{13}C NMR.

because generally chain-end control loses stereoregulating capability at higher temperatures. As a result of the interaction between the *ortho*-F and a β-H, a polymer chain is possibly forced to be oriented in one direction and fixed firmly in one conformation. The rigid conformation of the polymer chain will help the stereochemical information of the α-carbon transfer to the incoming propylene monomer, thus resulting in high syndioregularity even at room temperature ("ligand-directed chain-end control"). Coates et al. have obtained similar FI catalysts based on combinatorial methods,[31d] one of which promotes the syndiospecific living polymerization of propylene.[31h]

The catalysts are well-suited for the synthesis of a number of unique olefinic block copolymers such as polyethylene-*b*-poly(ethylene-*co*-propylene), syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene), and polyethylene-*b*-poly(ethylene-*co*-propylene)-*b*-syndiotactic polypropylene (Table 8)[27,30] because of the excellent living processes observed with both ethylene and propylene. Transmission electron microscopy (TEM) is a technique for the assessment of the structure of the semicrystalline polymers. Thus, TEM was applied to elucidate the morphology differences between the *s*PP-*b*-poly(ethylene-*co*-propylene) and the corresponding *s*PP/poly(ethylene-*co*-propylene) blend polymer (blend conditions; toluene, 100 °C, 1 h). As a result, the TEM micrograph of the press-sheet made from the block copolymer shows well-defined morphology of microphase separation (Figure 10). In Figure 10 (A), white domains corresponding to the *s*PP segment form a very fine and uniform nanostructure consisting of about 10 nm diameter domains, while those for the blend polymer [Figure 10 (B)] display coarse and non-uniform domains. Therefore, the block copolymer is suggested to have good potential as a compatibilizer.

Table 8. Synthetic examples of block copolymer based on ethylene and propylene.

Block copolymer	Total		1st block		Propylene content/mol %
	$M_n/10^3$	M_w/M_n	$M_n/10^3$	M_w/M_n	
Diblock					
PE-*b*-sPP	136	1.15	115	1.10	14.6
PE-*b*-EPR	211	1.16	-	-	6.4
sPP-*b*-EPR	161	1.51	27	1.13	40.3
Triblock					
PE-*b*-EPR-*b*-sPP	235	1.15	-	-	14.1
PE-*b*-EPR-*b*-PE	272	1.13	-	-	6.6

6 Other Catalysts Developed using Ligand-Oriented Catalyst Design

Ligand-oriented catalyst design research has resulted in the introduction of a number of highly active catalysts for ethylene polymerization, aside from FI catalysts. As shown in Scheme 9, titanium complexes with pyrrolide-imine ligands (PI catalysts),[32] indolide-imine ligands (II catalysts),[33] imine-phenoxy ligands (IF catalysts)[34] or phenoxy-pyridine ligands (FP catalysts)[35] have been made. These complexes display not only high ethylene polymerization activities but also unique polymerization behavior. Thus, for example, PI catalysts and FP catalysts produce exceptionally high molecular-weight polyethylene. II catalysts promote room-temperature living polymerization of ethylene to provide polyethylene with extremely narrow molecular weight distributions, and moreover create polyethylene-*b*-poly(ethylene-*co*-propylene) [M_n(total) = 31.4×10^3, M_w/M_n (total) = 1.17; M_n (PE block) = 15.2×10^3, M_w/M_n (PE block) = 1.05; propylene content (EPR block) = 19.5 mol %]. IF catalysts exhibit high activities at high polymerization temperatures.

7 Conclusion

Ligand-oriented catalyst design research has led us to the discovery of highly-active group 4 transition metal complexes featuring phenoxy-imine chelate ligands, named FI catalysts, for ethylene (living) polymerization. As anticipated, the highly-active FI catalysts have created new polymers which are unobtainable with

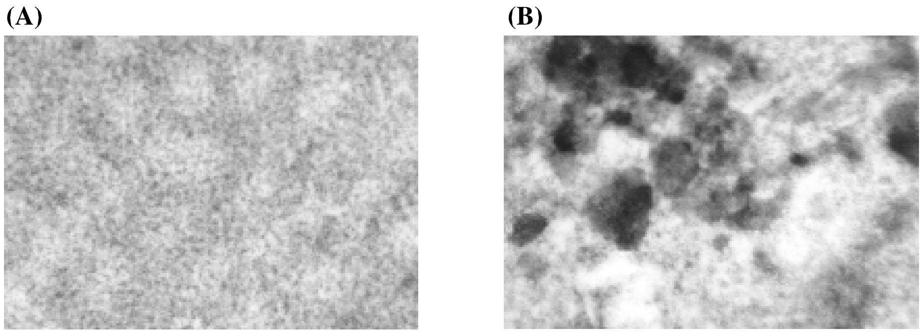
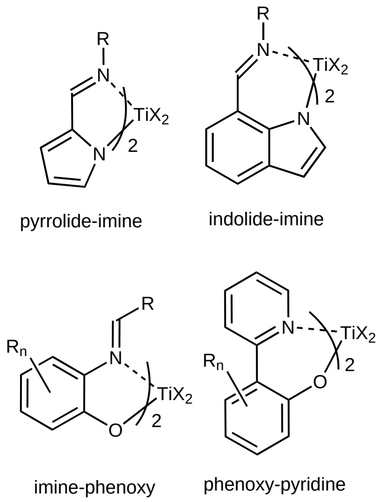


Figure 10. TEM micrographs of (**A**) sPP-*b*-poly(ethylene-*co*-propylene) and (**B**) sPP and poly(ethylene-*co*-propylene) blend polymer.



Scheme 9. Other highly active olefin polymerization catalysts generated by ligand-oriented catalyst design.

conventional Ziegler–Natta catalysts. We have used these new catalysts to produce very low molecular-weight polymers with olefinic end-groups, high molecular-weight poly(1-hexene)s with unique structure, and various block copolymers with high efficiency. These polymers are expected to have novel material properties and uses. Thus, FI catalysts represent a notable addition to the list of high performance single-site catalysts for olefin polymerization. We hope that the results introduced herein will rejuvenate research on group 4 metal catalysts, especially those with non-symmetrical ligands, for olefin polymerization.

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