

Review

Fluorinated bis(phenoxy–imine) Ti complexes with MAO: Remarkable catalysts for living ethylene and syndioselective living propylene polymerization

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Abstract

Based on new results as well as the reported data, the ethylene and propylene polymerization behavior of bis(phenoxy–imine) Ti complexes (Ti–FI Catalysts) combined with MAO (particularly that of their fluorinated versions) is discussed, with an emphasis on the characteristics and mechanisms of living ethylene and syndioselective living propylene polymerization. Unlike common living olefin polymerization catalysts, fluorinated Ti–FI Catalysts with MAO display thermally robust living behavior and polymerize ethylene in a highly controlled manner at temperatures as high as 50 °C. Additionally, despite being C_2 -symmetric catalysts, fluorinated Ti–FI Catalysts/MAO mediate highly syndioselective living propylene polymerization. Fluorinated Ti–FI Catalysts that we developed are the first examples of catalysts that induce the living polymerization of both ethylene and propylene. In addition, they are also the first examples of living and, at the same time, highly stereoselective propylene polymerization catalysts. The versatile and robust living nature of the fluorinated Ti–FI Catalysts allows the preparation of a wide variety of unique living polymers; some of which can even be produced catalytically. On the basis of theoretical calculations as well as experimental results, we conclude that these unusual polymerization features of fluorinated Ti–FI Catalysts originate from an attractive interaction between the ligand and a growing polymer chain and/or the fluxional character of the catalyst coupled with 2,1-regiochemistry. This is in stark contrast to group 4 metallocene catalysts, which control olefin polymerization mainly by repulsive interactions based on the rigidly organized ligand frameworks.

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1. Introduction

The discovery of efficient and selective transition-metal-based catalysts for living olefin polymerization has been one of the important challenges in catalysis, organometallic chemistry and polymer science. This is because of the ability of these catalysts to enchain olefinic monomers without chain transfer or termination and, consequently, to provide unprecedented control over the molecular weight as well as the composition and architecture of a polymer. With living catalysts it is possible to synthesize polyolefinic materials with a variety of unique microstructures, including monodisperse (co)polymers, chain-end functionalized (co)polymers, star polymers and block copolymers. Therefore, a substantial amount of research has been conducted with a view to developing high performance catalysts for living olefin polymerization.

So far, a large number of high-performance molecular catalysts for olefin polymerization (represented by group 4 metallocene catalysts and constrained-geometry catalysts (CGCs)) have been developed, which can form a wide array of olefin-based polymers with well-defined, specific microstructures and narrower molecular weight distributions than heterogeneous Ziegler–Natta catalysts [1]. However, the polymerization of olefinic monomers with these molecular catalysts is frequently frustrated by facile chain transfer processes, especially β -alkyl and β -H transfer and chain transfer to an aluminum cocatalyst. Thus, these catalysts normally exhibit living character at low temperatures (typically below 0 °C), often when the use of alkylaluminum cocatalysts has been eliminated.

Impressive advances that have been made recently in the design and synthesis of transition metal complexes for olefin polymerization and in polymerization techniques have spurred the development of molecular catalysts that induce living olefin polymerization at relatively high temperatures [2]. As a result, a number of useful catalysts have been developed, which initiate the room-temperature living polymerization of 1-hexene or other higher α -olefins and the stereoselective living polymerization of 1-hexene and vinylcyclohexane [3–8]. There are, however, a limited number of examples of

catalysts that can carry out the living polymerization of ethylene and/or propylene at room temperature, in spite of the structural simplicity and industrial importance of ethylene- and propylene-based polymers [9–19]. Additionally, known catalysts normally promote the living polymerization of either ethylene or α -olefins but not both, resulting in limited success in the synthesis of polyolefinic block copolymers. Moreover, highly stereoselective living propylene polymerization has not yet been achieved, despite the fact that nearly perfect stereoselective polymerization of propylene can be performed with appropriately designed group 4 metallocene catalysts [1c,i]. Finally, living olefin polymerization catalysts afford extremely low productivity relative to common olefin polymerization catalysts. This is because a living catalyst can only create a single polymer chain during the polymerization reaction, in stark contrast to common catalysts that can produce thousands of polymer chains as a result of periodic chain transfer events, rendering living polymers economically unfavorable. Consequently, the development of high-performance living catalysts is a comparatively uncharted field, and hence there are still many important goals that remain to be realized in the field of living olefin polymerization catalysis and living polymer synthesis.

In our own efforts to develop new high-performance catalysts, we investigated well-defined transition metal complexes featuring non-symmetric bidentate and tridentate ligands [20] with an electronically flexible nature (“*ligand-oriented catalyst design research*”). In

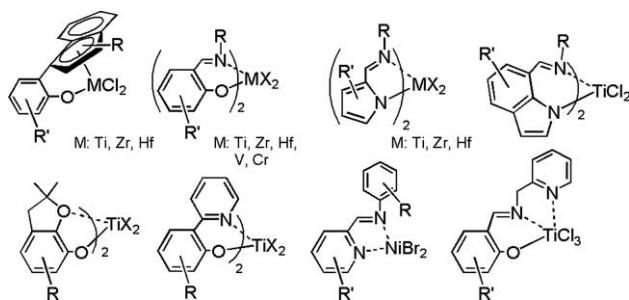
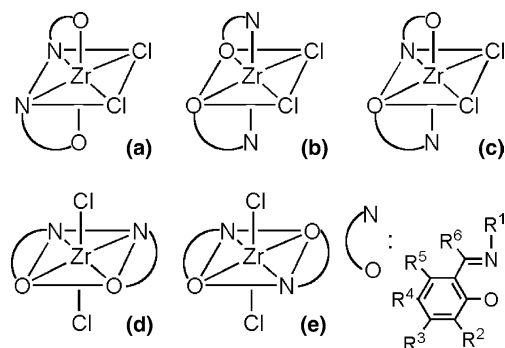


Fig. 1. Examples of new complexes for olefin polymerization, which were discovered based on ligand-oriented catalyst design research.

consequence, we found a number of families of transition metal complexes that incorporate, for example, phenoxy–cyclopentadienyl [21,22], phenoxy–imine [29–35], pyrrolide–imine [23,24], indolide–imine [17], phenoxy–ether [25], phenoxy–pyridine [26], imine–pyridine [27] and phenoxy–imine–pyridine [28] chelate ligands (Fig. 1). Upon activation with suitable cocatalysts, these complexes show high activities for the polymerization of ethylene.

Based on these discoveries, we have developed three families of living catalysts capable of producing unique polyolefinic materials that were unobtainable using conventional Ziegler–Natta catalysis. Bis(indolide–imine) Ti complexes (II Catalysts) promote room-temperature living ethylene polymerization and produce polyethylene (PE)-based block copolymers [17]. Pyrrolide–imine ligated Ti complexes (PI Catalysts) copolymerize ethylene and norbornene (NB) in a living fashion to form high molecular weight monodisperse cyclic olefin copolymers (COCs) [23c]. In addition, PI Catalysts can furnish ethylene- and NB-based block copolymers, such as PE-*b*-poly(ethylene-*co*-NB) [23g]. Alternatively, fluorinated bis(phenoxy–imine) Ti complexes (fluorinated Ti–FI Catalysts) carry out highly controlled living ethylene and highly syndioselective living propylene polymerization, in spite of the C_2 -symmetric nature of the catalysts [34,35]. Significantly, fluorinated Ti–FI Catalysts exhibit thermally robust living behavior, unlike common living olefin polymerization catalysts. The robust living nature allows the synthesis of many new block copolymers and chain-end functionalized (co)polymers from ethylene, propylene and higher α -olefins [30c,d]. Therefore, in recent years, there has been increasing interest in the research and development of FI Catalysts and closely related complexes [36–41].

In this contribution, we describe the ethylene and propylene polymerization behavior of bis(phenoxy–imine) Ti complexes (Ti–FI Catalysts), placing special emphasis on fluorinated Ti–FI Catalysts. These have achieved some of the crucial goals in the field of living polymerization catalysis and living polymer synthesis, probably with the aid of an attractive interaction between the ligand and a growing polymer chain and/or fluxionality of the catalysts combined with unusual 2,1-regiochemistry.



Scheme 1. Possible isomers for an FI Catalyst.

2. General introduction to FI Catalysts

FI Catalysts are one of the new catalyst families for use in olefin polymerization, and were developed in our laboratory using *ligand-oriented catalyst design*. An FI Catalyst consists of an early transition metal and a pair of non-symmetric chelating phenoxy–imine [O⁻, N] ligands (Fig. 2).

The molecular structures of group 4 metal FI Catalysts [(phenoxy–imine)₂ MCl₂, M = Ti, Zr, Hf] have been well-established by NMR, as well as by X-ray studies [31a,32g,h,35a,b,i,j,36c,37e,38c]. While an FI Catalyst has potentially five configurations ((a)–(e); Scheme 1) as a consequence of different binding geometries of two non-symmetric ligands, it normally possesses an approximately octahedrally coordinated metal center and C_2 symmetry, with a *trans*-O, *cis*-N and *cis*-Cl disposition in the solid state. Conversely, in solution, it generally exists as a mixture of the C_2 -symmetric isomer, with the *trans*-O, *cis*-N, *cis*-Cl arrangement (which is usually the predominant isomer) and the C_1 -symmetric isomer, with a *cis*-O, *cis*-N and *cis*-Cl disposition. It is important to note that group 4 metal FI Catalysts normally exhibit fluxional character in solution, which can lead to unique polymerization catalysis (e.g., controlled multimodal polymerization behavior) [32m,r]. Although the precise nature of the active species of an FI Catalyst with an MAO system has not been elucidated, DFT studies suggest that catalytically active species generally favor an octahedral geometry with a *trans*-O, *cis*-N and *cis*-polymer chain/coordinated olefin arrangement, displaying

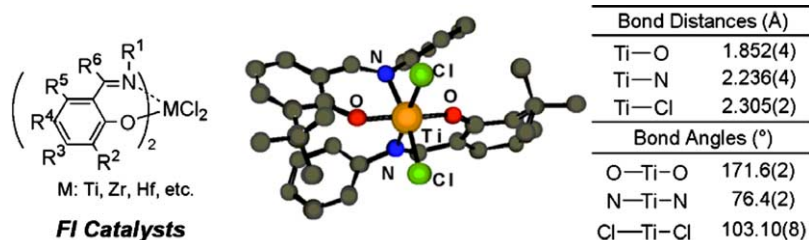
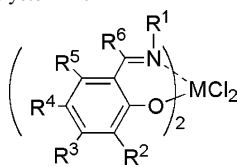


Fig. 2. General structure of an FI Catalyst (left) and X-ray structure of FI catalyst **1**. (M: Ti, R¹: Ph, R²: ^tBu, R³ = R⁴ = R⁵ = R⁶ = H).

Table 1
Structures of FI Catalysts 1–26



Catalyst	M	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
1	Ti	Ph	^t Bu	H	H	H	H
2	Zr	Ph	^t Bu	H	H	H	H
3	Hf	Ph	^t Bu	H	H	H	H
4	Ti	Ph	^t Bu	H	H	H	Et
5	Ti	Ph	^t Bu	H	^t Bu	H	Et
6	Ti	Ph	^t Bu	H	^t Bu	H	Ph
7	Zr	Pentafluorophenyl	^t Bu	H	H	H	H
8	Hf	Pentafluorophenyl	^t Bu	H	H	H	H
9	Ti	Pentafluorophenyl	^t Bu	H	H	H	H
10	Ti	Ph	Me	H	H	H	H
11	Ti	Ph	H	H	H	H	H
12	Ti	Pentafluorophenyl	ⁱ Pr	H	H	H	H
13	Ti	Pentafluorophenyl	Me	H	H	H	H
14	Ti	Pentafluorophenyl	H	H	H	H	H
15	Ti	2,4,6-Trifluorophenyl	^t Bu	H	H	H	H
16	Ti	2,6-Difluorophenyl	^t Bu	H	H	H	H
17	Ti	2-Fluorophenyl	^t Bu	H	H	H	H
18	Ti	3,4,5-Trifluorophenyl	^t Bu	H	H	H	H
19	Ti	3,5-Difluorophenyl	^t Bu	H	H	H	H
20	Ti	4-Fluorophenyl	^t Bu	H	H	H	H
21	Ti	2-Me-phenyl	^t Bu	H	H	H	H
22	Ti	2- ⁱ Pr-phenyl	^t Bu	H	H	H	H
23	Ti	Ph	^t Bu	H	^t Bu	H	H
24	Ti	Pentafluorophenyl	^t Bu	H	^t Bu	H	H
25	Ti	Pentafluorophenyl	SiMe ₃	H	H	H	H
26	Ti	2,4,6-Trifluorophenyl	Cumyl	H	Me	H	H

C₂ symmetry if one ignores the non-equivalence of the polymer chain and the coordinated olefin. The *cis*-relationship between the growing polymer chain and the coordinated olefin is potentially significant, since an indispensable requirement for a high-efficiency catalyst is that it possesses a pair of *cis*-located sites that are available for polymerization. In addition, the C₂-symmetric nature of the active species implies the capability for stereoselective polymerizations of α -olefins, considering the correlation of stereoselectivity with catalyst symmetry that has been established by group 4 metallocene catalysts [1c,i].

The group 4 metal FI Catalysts generally demonstrate high ethylene polymerization activities that are comparable to or even surpass those seen with early group 4 metallocene catalysts when activated [32g,i].

The highest activity that was exhibited by an FI Catalyst (M = Zr, R¹ = cyclohexyl, R² = 1,1-diphenylethyl, R³ = R⁴ = R⁵ = R⁶ = H) with MAO reached a record-breaking catalyst turnover frequency (TOF) value of 64900/s/atm, which is probably the highest observed so far, not only for olefin polymerization but also for any other catalytic reaction [30] (see Table 1).

A key feature of FI Catalysts is that their steric and electronic properties can easily be varied by systematically changing their ligand structures, which can be synthesized in a straightforward manner from readily available chemicals. Consequently, FI Catalysts possess a wide range of possibilities in terms of catalyst design, which has allowed us to examine a wide variety of substituents, including heteroatom-based species.

With the very high catalyst efficiency and readily varied steric as well as electronic properties of FI ligands, FI Catalysts combined with an appropriate cocatalyst (e.g., MAO, borates, clay minerals, hetero-poly compounds and MgCl₂) [31c,33] can exhibit many unique and practical features, such as the production of vinyl-terminated low molecular weight PEs [32j], ultra-high molecular weight amorphous ethylene/ α -olefin copolymers [32k], highly syndiotactic [32n,35i,j] and isotactic [32q] polypropylenes (PPs) with extremely high peak melting temperatures, stereo- and regioirregular high molecular weight poly(1-hexene)s [32d], well-defined and controlled multimodal PEs [32m,r] and very high molecular weight PEs with remarkable polymer particle morphologies [31c,33c,d]. Many of these polymers are either difficult or impossible to synthesize using conventional Ziegler–Natta catalysts. Recent reviews cover much of the unique catalysis of FI Catalysts and the distinctive polymer formation with FI Catalysts [30].

3. Ethylene polymerization behavior of group 4 metal FI Catalysts

A summary of ethylene polymerization results with group 4 metal FI Catalysts 1–4/MAO at 25 °C under atmospheric pressure is shown in Table 2, in order to highlight the nature of each catalyst vis-a-vis chain propagation and chain transfer [31a,32a,h,i,n,p,35b].

Zr–FI Catalyst 2 displays the highest activity (224 kg-PE/mmol-cat./h) followed by Hf–FI Catalyst 3 (21 kg-PE/mmol-cat./h) and Ti–FI Catalyst 1 (3 kg-PE/mmol-cat./h). The molecular weights of the products follow the opposite order; i.e., Ti–FI Catalyst (M_n 170000), Hf–FI Catalyst 3 (M_n 6000) and Zr–FI Catalyst 2 (M_n 4000). Considering that molecular weight is determined by the relative rates of chain propagation and chain transfer, Ti–FI Catalyst 1 exhibits the lowest chain transfer rate (relative rate; Zr–FI/Hf–FI/Ti–FI = 3200/200/1), though it demonstrates a considerable chain propagation rate (nearly equal to the catalytic activity for group 4

Table 2
Ethylene polymerization results with FI Catalysts 1–4/MAO

Entry	Catalyst	Temp. °C	Time (min)	Activity (kg-PE/mmol-cat./h)	M_n^a ($\times 10^3$)	M_w/M_n^a
1	1	25	5	3	170	1.61
2	2	25	5	224	4	1.88
3	3	25	5	21	6	3.01
4	1	25	1	3	52	1.12
5	1	50	1	5	65	1.17
6	4	25	1	0.3	8	1.05
7	4	50	1	0.3	9	1.08
8	1	50	5	4	132	1.83
9	4	50	5	0.3	24	1.46

Conditions: toluene 250 ml, cocat. MAO 1.25 mmol, ethylene 0.1 MPa.

^a Determined by GPC using polyethylene calibration.

metal FI Catalysts). In view of the fairly narrow molecular weight distribution (M_w/M_n) of 1.61 obtained with **1**/MAO in combination with the facts mentioned above, we postulated that a Ti–FI Catalyst might have potential as a catalyst for living ethylene polymerization.

Indeed, we found that Ti–FI Catalysts possess some characteristics of living ethylene polymerization and can form nearly monodisperse PEs (usually $M_n < 100\,000$, $M_w/M_n < 1.2$) under limited conditions (e.g., short polymerization time and/or controlled ethylene concentration in a polymerization medium) [1k,30d,31a,32n,35b]. These results indicate that a high ratio can be achieved for rate of chain propagation to chain transfer for ethylene polymerization with Ti–FI Catalysts, albeit under limited conditions.

For example, very narrow molecular weight distribution PEs can be synthesized with Ti–FI Catalysts **1** (1 min polymerization, atmospheric pressure, 25 °C; M_n 52 000, M_w/M_n 1.12; 50 °C; M_n 65 000, M_w/M_n 1.17) [32n]. In addition, phenoxy–ketimine type Ti–FI Catalyst **4** can also form nearly monodisperse PEs (1 min polymerization, atmospheric pressure, 25 °C; M_n 8000, M_w/M_n 1.05; 50 °C; M_n 9000, M_w/M_n 1.08), though with very low efficiency compared with the related phenoxy–imine type Ti–FI Catalysts [31a]. The inferior catalytic activity of a phenoxy–ketimine type Ti–FI Catalyst compared to a phenoxy–imine type FI Catalyst is a general trend, which probably originates from steric congestion near the polymerization center provided by the extra alkyl substituent on the imine-C for a phenoxy–ketimine type FI Catalyst. With these Ti–FI Catalysts, however, it is normally difficult to prepare high molecular weight and narrow molecular weight distribution PEs (e.g., 5 min polymerization, atmospheric pressure, 50 °C; **1**, M_n 132 000, M_w/M_n 1.83, **4**, M_n 24 000, M_w/M_n 1.46) [32a]. It has been reported that phenoxy–ketimine type Ti–FI Catalysts **5** and **6** can also afford PEs with very narrow molecular weight distributions (though with low efficiency) under controlled conditions (50 °C, 0.68 atm: **5**; 8 min, M_n 40,700, M_w/M_n 1.20, **6**; 1 min, M_n 24 000, M_w/M_n 1.14) [36m].

While these Ti–FI Catalysts can only induce (quasi)-living ethylene polymerization under limited conditions and do not initiate living propylene polymerization (see Section 5.1), we reasoned that Ti–FI Catalysts could become good catalysts for living α -olefin as well as ethylene polymerization when we consider the wide range of catalyst design possibilities.

4. Living ethylene polymerization with a perfluorinated Ti–FI Catalyst

In exploring new derivatives of FI Catalysts, we have studied FI Catalysts bearing halogen-containing ligands, which resulted in the discovery of the remarkably beneficial effects of a C_6F_5 group at the imine-N on the catalytic properties of FI Catalysts [30,31b,34,35a,e,f].

Since the electron-withdrawing nature of a ligand renders the metal center more electrophilic, and thus more reactive toward an olefin, we investigated perfluorinated Zr- and Hf–FI Catalysts **7** and **8** in an attempt to acquire higher activity FI Catalysts [32p]. As anticipated, the perfluorinated Zr- and Hf–FI Catalysts exhibited 40% to 50% increased catalytic activity compared with their non-fluorinated counterparts [7, 335 kg-PE/mmol-cat./h (non-fluorinated version 224 kg-PE/mmol-cat./h); **8**, 29 kg-PE/mmol-cat./h (non-fluorinated version 21 kg-PE/mmol-cat./h)].

Surprisingly, the perfluorinated Zr- and Hf–FI Catalysts formed tremendously enhanced (more than 20 times greater) molecular weight PEs, even though the increase in activity is merely 40–50%. Previous work established that β -H transfer is the predominant chain transfer mechanism for ethylene polymerization with non-fluorinated Zr–FI Catalyst **2**, whereas a chain transfer to aluminum is dominant in the case of the non-fluorinated Hf–FI Catalyst **3** [32p]. Therefore, the introduction of the C_6F_5 group diminishes the rates of both β -H transfer and chain transfer to aluminum, and simultaneously enhances the rate of chain propagation. It should also be

Table 3
Ethylene polymerization results with FI Catalysts 7–9/MAO

Entry	Catalyst	Temp. °C	Time (min)	Activity (kg-PE/mmol-cat./h)	$M_n^a(\times 10^3)$	M_w/M_n^a
1	7	25	5	335	83	1.90
2	8	25	5	29	152	2.70
3	9	50	1	36	424	1.13
4	9	75	1	27	329	1.15
5	9	90	1	14	167	1.30

Conditions: toluene 250 ml, cocat. MAO 1.25 mmol, ethylene 0.1 MPa.

^a Determined by GPC using polyethylene calibration.

pointed out that the fluorinated Zr- and Hf–FI Catalysts 7 and 8 exhibit increased incorporation capability for propylene and produce ethylene/propylene copolymers with a higher propylene content than the non-fluorinated congeners, representing an additional beneficial effect of the C₆F₅ group [32p]. These are rare examples of the introduction of a heteroatom-containing substituent that enormously enhances the catalytic properties (i.e., catalytic activity, molecular weight, comonomer incorporation). It is natural to think that the steric hindrance exerted by the introduced fluorines contributes to enhance the product molecular weight [30a,32g]; however, the magnitude of the increase observed (molecular weight increase ca. 20 times; catalytic activity increase ca. 1.5 times) suggests that the phenomenon cannot be accounted for by simply considering steric factors.

The introduction of the C₆F₅ group to Ti–FI Catalyst 1 had more pronounced effects on its catalytic performance [31b,34,35a,f]. We found that fluorinated Ti–FI Catalyst 9 carries out highly controlled living ethylene polymerization at 50 °C and affords very high molecular weight, nearly monodisperse, PE with strikingly high activity (M_w/M_n 1.13, M_n 424 000, TOF 21 500/min/atm) [34,35a]. The living nature was confirmed by the linear relationship between M_n and the polymerization time, as well as the narrow M_w/M_n values observed. The molecular weight (M_n) of the PE that was formed is close to that calculated from the monomer/catalyst ratio obtained from the mass of the PE produced, suggesting substantially quantitative catalyst efficiency. Considering that the MAO used as the cocatalyst is a potential chain transfer agent, and that living olefin polymerization can normally only be achieved using a borate cocatalyst instead of MAO, the fact that living ethylene polymerization with MAO was exhibited by the system is highly significant. Because of the highly controlled living nature of 9/MAO, a living propagating species can be observed with ¹H NMR spectroscopy [–(CH₂)_n– at δ 1.32 ppm and –CH₂–CH₃ at δ 0.97 ppm as a triplet in toluene-*d*₆] [35f].

We revealed that, even in the absence of ethylene, there is virtually no chain termination or transfer operation in the fluorinated Ti–FI Catalyst 9/MAO system for at least 60 min at room temperature, further con-

firmed the highly controlled living nature. Significantly, at 75 °C and 90 °C, Ti–FI Catalyst 9/MAO formed PEs with very narrow molecular weight distributions (75 °C, M_w/M_n 1.15, M_n 329 000, 90 °C; M_w/M_n 1.30, M_n 167 000). The thermally robust living behavior of 9 with MAO is highly unusual, since a common living olefin polymerization catalyst normally operates well at low temperatures and loses its living nature at elevated temperatures, implying that steric factors do not play a salient role in the realization of the living polymerization with 9/MAO (see Table 3).

5. Origin of highly controlled living ethylene polymerization

5.1. Ethylene polymerization behavior of a series of Ti–FI Catalysts

To obtain information about the origin of the highly controlled, thermally robust living ethylene polymerization achieved by Ti–FI Catalyst 9/MAO, comparative ethylene polymerization experiments were conducted using both fluorinated and non-fluorinated Ti–FI Catalysts 10–14, which incorporate a series of substituents (Pr, Me, H) *ortho* to the phenoxy-Os (Table 4) [31b,32n,35e]. It can be seen that non-fluorinated Ti–FI Catalysts 10, 11 form PEs with classical molecular weight distributions (M_w/M_n 1.54–3.13). Interestingly, in the case of non-fluorinated Ti–FI Catalysts, the *ortho*-substituent (R²) has a considerable effect on the product molecular weight, and the reduction in the steric bulk of the substituent R² results in a marked decrease in the molecular weight of the PE that is produced [32n]. In sharp contrast, independent of the magnitude of the steric bulk of R², fluorinated Ti–FI Catalysts provide extremely narrow molecular weight distribution PEs (M_w/M_n 1.08–1.16), which is indicative of living ethylene polymerization [35e]. It is noted that, though R² is located in close proximity to the active site, the steric hindrance stemming from R² exerts no significant influence on the living nature of the fluorinated Ti–FI Catalysts. These results indicate that the combination of the C₆F₅ group and the ^tBu group is not responsible for living

Table 4
Ethylene polymerization results with FI Catalysts **10–22**/MAO

Entry	Catalyst	Temp. (°C)	Time (min)	Activity (kg-PE/mmol-cat./h)	M_n^a ($\times 10^3$)	M_w/M_n^a
1	10	25	30	0.2	402	1.54
2	11	25	30	0.04	66	3.13
3	12	25	1	4	51	1.10
4	13	25	1	6	75	1.16
5	14	25	1	3	44	1.08
6	15	25	5	2	145	1.25
7	16	25	5	1	64	1.05
8	17	25	5	0.1	13	1.06
9	18	25	1	45	98	1.99
10	19	25	1	32	129	1.78
11	20	25	5	5	128	2.18
12	21	25	30	0.3	355	2.14
13	22	25	30	0.2	296	1.29

Conditions: toluene 250 ml, cocat. MAO 1.25 mmol, ethylene 0.1 MPa.

^a Determined by GPC using polyethylene calibration.

polymerization, but the C_6F_5 group itself plays a decisive role in the achievement of living ethylene polymerization [35e].

To provide some insight into the role of the C_6F_5 group in this unprecedented living polymerization, we investigated the ethylene polymerization behavior of fluorinated Ti–FI Catalysts **15–20** with various F-numbers and F-substitution patterns [30c,35b]. As summarized in Table 4, Ti–FI Catalysts with *ortho*-F(s) produce PEs with extremely narrow molecular weight distributions (M_w/M_n 1.05–1.25) whereas FI Catalysts possessing no *ortho*-F generate PEs with M_w/M_n of ca. 2 under the conditions examined. These results demonstrate that the *ortho*-F is a requirement for living polymerization.¹ IR and ¹³C NMR analysis of the end-groups of PEs produced using non-living-type FI Catalysts show the presence of nearly equal amounts of vinyl and methyl chain-end groups, indicating that the predominant mechanism for chain termination with non-living type FI Catalysts is by β -H transfer. These results show that the *ortho*-F suppresses the β -H transfer.

Important information on the role of the *ortho*-F was obtained from an ethylene polymerization experiment using Ti–FI Catalyst **21**, which bears a sterically more-encumbered *ortho*-substituent than F (i.e., a methyl group) [32n]. Interestingly, it turned out that the *ortho*-Me Ti–FI Catalyst **21** does not carry out liv-

ing ethylene polymerization under the conditions where the singly *ortho*-F version promotes living ethylene polymerization. This fact unambiguously indicates that steric factors do not play a vital role in the achievement of living ethylene polymerization, which in turn means that the *ortho*-F is most probably involved electronically in the realization of the living polymerization.²

In summary, the well-established experimental results suggest that the living nature of Ti–FI Catalyst **9**/MAO originates not from the combination of the C_6F_5 group on the imine-N and the ^tBu group *ortho* to the phenoxy-O (though both substituents are located near the polymerization center) but from the C_6F_5 group itself. In addition, they also show that the *ortho*-F is responsible for living polymerization in which the *ortho*-F is involved electronically.

5.2. DFT studies on active species

So far, we have established that the presence of the *ortho*-F accounts for living polymerization by mitigating β -H transfer, probably through electronic participation. DFT calculations were performed on an active species originating from **9**/MAO (polymer chain model: ⁿpropyl group) to elucidate how the *ortho*-F is involved electronically in the realization of living polymerization [30c,35b]. Since the attractive interaction

¹ It has recently been reported that only a single *ortho*-F is required in order to achieve living propylene polymerization, which is the same as for living ethylene polymerization. This result probably suggests that steric factors do not play a key role in living propylene polymerization in addition to living ethylene polymerization with fluorinated Ti–FI Catalysts [37e].

² Interestingly, the *ortho*-ⁱPr Ti–FI Catalyst **22** forms relatively narrow molecular weight distribution PE (M_w/M_n 1.29, M_w/M_n 29,600) with very low efficiency, which suggests that the introduction of considerable steric congestion *ortho* to the imine-N can realize a relatively high ratio for the rates of propagation-to-chain transfer, but at the cost of reduced catalyst efficiency [32n].

Table 5
F–H_β interactions estimated by DFT calculations

FI Catalyst	9	12	13	14	15	16	17
$r(\text{F}-\text{H}_\beta)^{\text{a}}$	2.276	2.311	2.260	2.302	2.362	2.346	2.324
$q(\text{F})^{\text{b}}$	-0.466	-0.46	-0.46	-0.46	-0.470	-0.476	-0.482
$q(\text{H}_\beta)^{\text{c}}$	0.095	0.09	0.09	0.08	0.108	0.111	0.117
$\text{ES}(\text{F}-\text{H}_\beta)^{\text{d}}$	-27.1	-26.3	-25.5	-23.6	-29.9	-31.2	-33.6

^a F–H_β distance (Å).

^b Mulliken charge of the nearest *ortho*-F to H_β.

^c Mulliken charge of H_β.

^d Electrostatic energy for F–H_β interaction (kJ/mol).

between a cationic group 4 metal center and an F in a phenyl ring is well established [44], we thought at first that the living nature stemmed from the stabilization of the Ti center by the *ortho*-F through electronic interaction. However, the calculations indicate that the distance between the Ti and the nearest *ortho*-F is about 4 Å. Thus, it turned out that there is substantially no interaction between the Ti center and the *ortho*-F. Instead, unexpectedly, the calculations demonstrate that the *ortho*-F interacts electronically with a β-H on a growing polymer chain (*ortho*-F/β-H distance: 2.276 Å) [35b,j,42]. The electrostatic energy between the negatively charged *ortho*-F and the positively charged β-H is estimated at 27.1 kJ/mol, which is large enough to place restraint on β-H transfer to the Ti metal and/or a reacting monomer. Interestingly, a degree of C–H_β bond elongation (1.113 Å) was suggested by the calculations, which is probably the result of an attractive interaction between the *ortho*-F and the β-H. DFT studies suggest the presence of an attractive interaction between the *ortho*-F and the β-H (23.6–33.6 kJ/mol) for all *ortho*-fluorinated Ti–FI Catalysts (i.e., living FI Catalysts) independent of the phenoxy–imine ligand structures, confirming the generality of the unusual attractive interaction for *ortho*-fluorinated Ti–FI Catalysts (Table 5). It should be noted that a similar, but much weaker, interaction has been suggested for the corresponding fluorinated Zr- and Hf–FI Catalysts **7** and **8** (*ortho*-F/β-H distance, **7**; 2.484 Å, **8**, 2.480 Å, electrostatic energy, **7**; -3.1 kJ/mol, **8**, -2.3 kJ/mol) [32p]. Although these FI Catalysts do not induce living ethylene polymerization, they form extremely enhanced molecular weight PEs compared to their non-fluorinated congeners, as described previously. These results indicate that the attractive interaction, even if it is weak, is highly effective in reducing the rate of chain transfers (see Fig. 3, Scheme 2).

For chain propagation, ethylene can approach and coordinate to the cationic active species (e.g., that derived from **9**, Fig. 4) from either the reverse-side (I) or the front-side (II) with respect to the *ortho*-F/β-H interacting space. The former scheme, leading to (I), can maintain the F–H interaction, whereas the latter

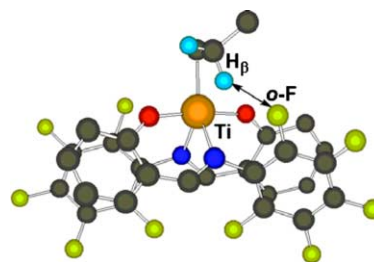


Fig. 3. Calculated structure of an active species (c; Scheme 2) derived from FI Catalyst **9**. 'Bu groups are omitted for clarity.

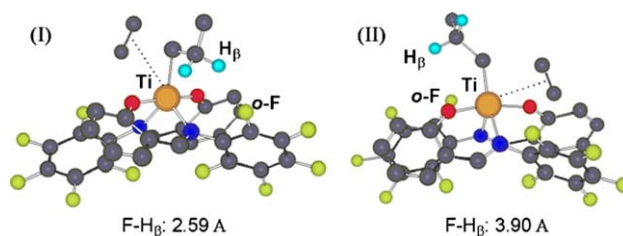
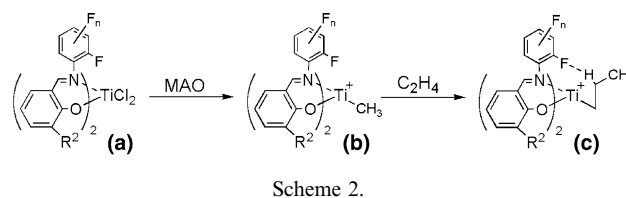


Fig. 4. Ethylene coordination to the Ti center (FI Catalysts) from the back-side (I) or front-side (II) F–H_β interacting space. ('Bu groups are omitted for clarity.)

scheme, which results in (II), breaks the interaction. Considering the strong attractive F–H interaction (27.1 kJ/mol), it seems reasonable that access to the active site by ethylene from the front-side of the F–H interacting space is less favorable than access from the back-side. The relative formation energies estimated by DFT calculations suggest that (I) is more stable than (II) by 14.3 kJ/mol.

On the basis of the above discussions, we concluded that ethylene approaches and coordinates to the Ti center from the back-side to the F–H interacting space, resulting in the formation of the chain-transfer-wise

stable ethylene-coordinated species (I). For ethylene-coordinated species, the transition state of the β -H transfer is probably disfavored by the fact that the β -H is positively charged and is stabilized by the negatively charged *ortho*-F, whereas the β -H should behave as a hydride in the β -H transfer process.

The attractive interaction as a whole is thought to control the approach and coordination of the ethylene. It prevents β -H transfer, resulting in living polymerization. The attractive interaction probably sets a standard for the highly controlled, thermally robust living polymerization of ethylene and α -olefins through insertion chemistry.

The presence of the attractive interaction between the *ortho*-F and the β -H indicates that a growing polymer chain is fixed by the *ortho*-F, which should also reduce the rate of chain transfer to the aluminum cocatalyst, as well as the rate of chain propagation. In fact, we note that *ortho*-F Ti–FI Catalysts display lower activities than the estimated values based on the electron-withdrawing properties of the ligands [32i,35b].

6. Syndioselective propylene polymerization with C_2 -symmetric Ti–FI Catalysts

6.1. Propylene polymerization behavior of group 4 metal FI Catalysts

As seen before, a group 4 metal FI Catalyst normally assumes a C_2 -symmetric *trans*-O, *cis*-N and *cis*-Cl configuration as the predominant isomer. Additionally, DFT calculations suggest that a catalytically active species derived from a group 4 metal FI Catalyst favors a C_2 -symmetric configuration with a *trans*-O, *cis*-N and *cis*-polymer chain/coordinated olefin disposition. We therefore reasoned that FI Catalysts might be viable catalysts for isoselective propylene polymerization (in the case of fluorinated Ti–FI Catalysts; isoselective living propylene polymerization) with a site-control mechanism.

Fluorinated and non-fluorinated group 4 metal FI Catalysts 1–3 and 7–9 were investigated for their potential as propylene polymerization catalysts (Table 6)

[31a,b,32n,35f,h–k]. An inspection of the data summarized in Table 6 indicates that product molecular weights are strongly affected by the nature of the metal center and the presence or absence of the F atoms, and follow the same general trend observed for ethylene polymerization. For both the non-fluorinated and the fluorinated group 4 metal FI Catalysts examined, Zr–FI Catalysts demonstrate the highest activity (2, 310 kg/mol-cat./h, 7, 370 kg/mol-cat./h) followed by Hf–FI Catalysts (3, 25 kg/mol-cat./h, 8, 333 kg/mol-cat./h) and Ti–FI Catalysts (1, 1 kg/mol-cat./h, 9, 3 kg/mol-cat./h.) [32n,35j,k]. Additionally, considerable effects of the C_6F_5 on increasing product molecular weight have also been observed with Zr- and Hf–FI Catalysts [Zr complex 7, M_n 1500 (non-fluorinated version M_n 200); Hf complex 8, M_n 32000 (non-fluorinated version M_n 500)].

The oligo- and polypropylene produced with Zr–FI Catalysts 2, 7, Hf–FI Catalysts 3, 8 and Ti–FI Catalyst 1 possess molecular weight distributions (M_w/M_n) values of 1.31–2.29, suggesting non-living polymerization. The M_w/M_n values obtained with 2 (1.31) and 3 (1.70) may be decreased from the real values by the loss of some volatile low molecular weight materials during isolation of the products. As anticipated, fluorinated Ti–FI Catalyst 9 affords an extremely narrow molecular weight distribution PP (M_w/M_n 1.05), indicative of living propylene polymerization [31b,34,35f,j]. The living nature was confirmed by the linear increase in M_n with polymerization time, coupled with the narrow molecular weight distributions observed. For propylene polymerization with the fluorinated Ti–FI Catalyst 9, the calculated attractive interaction between the *ortho*-F and the β -hydrogen is 46.8 kJ/mol (1,2-insertion) or 30.7 kJ/mol (2,1-insertion) depending on the insertion mode [35j]. Therefore, the attachment of C_6F_5 to the imine-N has been demonstrated to induce the living polymerization effect, not only with ethylene, but also with propylene with the aid of the attractive interaction. Ti–FI Catalyst 9 is the first example of a catalyst that mediates the living polymerization of both ethylene and propylene [30c,d,31b,34].

Although the molecular weights of the products formed from Zr–FI Catalysts 2, 7, and Hf–FI Catalyst

Table 6
Propylene polymerization results with FI Catalysts 1–3 and 7–9/MAO

Entry	Catalyst	Temp. (°C)	Time (h)	P (MPa)	Activity (kg-PP/mmol-cat./h)	M_n^a ($\times 10^3$)	M_w/M_n^a
1	1	1	6	0.37	1	6	1.38
2	2	0	0.5	0.1	310	0.2	1.31
3	3	0	1.5	0.1	25	0.5	1.70
4	7	0	0.5	0.1	370	1.5	2.22
5	8	0	1.5	0.1	333	32	2.29
6	9	0	5	0.1	3	24	1.05

Conditions: toluene 350 ml (entry 1), 250 ml (entries 2, 4, 6), 500 ml (entries 3, 5), cocat. MAO 15 mmol (entry 1), 2.5 mmol (entries 2, 4, 6), 5.0 mmol (entries 3, 5).

^a Determined by GPC using polypropylene calibration.

3 are too small to meaningfully discuss the degree of stereochemistry, fluorinated Hf–FI Catalyst **8** turned out to be a non-stereoselective catalyst and furnished atactic PP [35k]. To our surprise, both fluorinated and non-fluorinated Ti–FI Catalysts **1** and **9** yield moderately and highly syndiotactic PPs (sPPs) (**1**, *rr* 79%, 1 °C polymerization, **9**, *rr* 87%, 25 °C polymerization) despite the C_2 -symmetric nature of the catalysts [32n,35f]. The unexpected formation of sPPs by using C_2 -symmetric Ti–FI Catalysts suggests that catalyst symmetry is not a strict requirement for determining polymer stereochemistry. Ti–FI Catalyst **9** is the first example of a simultaneous living and highly stereoselective catalyst for the polymerization of propylene [30c,d,31b,34].

It is worth noting that Ti–FI Catalyst **9**, which incorporates a C_6F_5 group, displays higher syndioselectivity than the corresponding non-fluorinated version. Therefore, the introduction of the C_6F_5 group contributes to the enhancement of stereoselectivity, as well as to the realization of living propylene polymerization. The increase in stereoselectivity as a result of the introduction of C_6F_5 is a general trend that might be induced by the *ortho*-F/ β -H interaction. This has an influence on the approach and coordination of the propylene to the Ti center, and possibly the transition state of its insertion into the Ti–C bond.

Ti–FI Catalysts **23** and **24** combined with MAO have been reported to initiate syndioselective propylene polymerization (**23**, *rr* 88%, **24**, *rr* 98%) [36e,37b]. The reported stereoselectivity is very high compared with our previous data obtained under analogous conditions (*rr* 83%, *rr* 86%) [31,32n,35j]. While the reason for this discrepancy is unclear at the present time, the difference in the syndioselectivity could stem from the fact that propylene polymerization with a Ti–FI Catalyst is very sensitive to the reaction conditions employed (e.g., cocatalyst, solvent, propylene concentration) [32n,38a,d].

The sPPs arising from Ti–FI Catalysts **1** and **9** contain isolated *m*-dyad errors (*[rrmm]* and *[rmrr]*, a stereochemical error is propagated) in the methyl pentad region, indicating that the syndioselective enchainment is mediated via chain-end control. The syndioselectivity obtained with Ti–FI Catalysts is very high for a chain-end control mechanism.

We revealed that syndioselective propylene polymerization is exclusively initiated by 1,2-insertion followed by 2,1-insertion as the principal mode of polymerization [35h]. This is the first example of a predominant 2,1-insertion mechanism for chain propagation observed for a group 4 metal-based catalyst. The generality of this highly unusual propylene poly-insertion mode with Ti–FI Catalysts has been confirmed by other research groups [37c,38a,40]. It should be pointed out that Zr- and Hf–FI Catalysts **7** and **8** polymerize propylene prevalently via a 1,2-insertion mechanism and generate atactic- to slightly syndiotactic PPs [35k,38c]. The un-

sual preference for 2,1-regiochemistry exhibited by the Ti–FI Catalysts (unlike the Zr- and Hf–FI Catalysts) is evidently inconsistent with the crystallographically characterized structures, which show that the Ti is more shielded by the phenoxy–imine ligands, and therefore possesses higher steric compression near the polymerization center. At this point, it is not clear why Ti–FI Catalysts favor 2,1-regiochemistry. Recently, QM/MM calculation results vis-à-vis the regiochemistry of propylene polymerization with Ti- and Zr–FI Catalysts have been reported, which suggest that secondary propagation is favored after a 2,1-insertion for both Ti- and Zr–FI Catalysts [40]. While the calculation results for Ti–FI Catalysts are fairly consistent with the experimental data, they seem to be out of accord with the experimental results for Zr–FI Catalysts, which favor 1,2-regiochemistry rather than 2,1-regiochemistry, albeit with considerable regioerrors [35k].

6.2. Highly syndioselective propylene polymerization with fluorinated Ti–FI Catalysts

Further investigations aimed at developing higher performance FI Catalysts for living propylene polymerization led to the discovery of an exceptional Ti–FI Catalyst [35i,j]. Ti–FI Catalyst **25**, which incorporates a trimethylsilyl group *ortho* to the phenoxy-O, affords highly syndiotactic monodisperse PP (25 °C, *rr* 93%, M_n 47000, M_w/M_n 1.08) with an extremely high T_m (152 °C) via a chain-end control mechanism. Moreover, the polymer produced at 0 °C displays a T_m of 156 °C (*rr* 94%), which is among the highest values reported for sPPs. Surprisingly, at 50 °C, **25** yields highly syndiotactic PP with a very narrow molecular weight distribution (M_w/M_n 1.18) and a very high T_m of 150 °C. The formation of high T_m sPPs is remarkable in view of the tremendous technological significance of such sPPs.

The high syndioselectivity displayed by the fluorinated Ti–FI Catalysts through chain-end control at

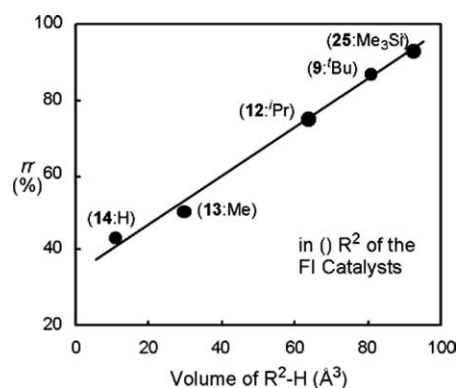


Fig. 5. Plots of *rr* triad values as a function of calculated R^2 -H volume.

Table 7
Propylene polymerization results with FI Catalysts **9**, **12–14**, **23–25**/MAO

Entry	Catalyst	Temp. (°C)	Activity (kg-PP/mmol-cat./h)	M_n^a ($\times 10^3$)	M_w/M_n^a	<i>rr</i>	T_m^b (°C)
1	9	25	4	29	1.11	87	137
2	12	25	31	154	1.16	75	n.d. ^c
3	13	25	69	260	1.22	50	n.d. ^c
4	14	25	31	189	1.51	43	n.d. ^c
5	23	25	2	11	1.55	83	107
6	24	25	4	30	1.15	86	135
7	25	0	3	25	1.08	94	156
8	25	25	6	47	1.08	93	152
9 ^d	25	50	5	26	1.18	90	150

Conditions: toluene 250 ml, cat. 0.01 mmol, cocat. MAO 2.50 mmol, propylene 0.1 MPa, 5 h.

^a Determined by GPC using polypropylene calibration.

^b Melting temperature determined by DSC.

^c Not detected.

^d Polymerization time 3h.

room temperature or above is highly unusual, since chain-end control normally only works well at very low to sub-ambient temperatures and rapidly loses its stereo-regulating capability at elevated temperatures.

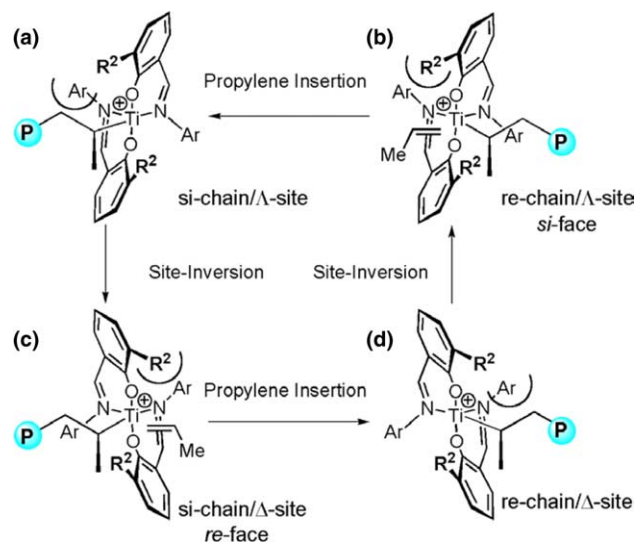
Further research into the propylene polymerization behavior of Ti–FI Catalysts has revealed that the steric bulk of the substituent that is *ortho* to the phenoxy-O controls the syndioselectivity of the polymerization, as clearly demonstrated by the linear correlation of the volume of the *ortho*-substituent with the syndioselectivity [**14** (H): *rr* 43%, **13** (Me): *rr* 50%, **12** (^tPr): *rr* 75%, **9** (^tBu): *rr* 87%, **25** (Me₃Si): *rr* 93%, 25 °C polymerization, Fig. 5] [35j]. A striking feature that is observed is that despite the chain-end control mechanism, in which the stereochemistry is governed by the asymmetry of the last-inserted monomer unit, the ligand structure has a dramatic effect on the tacticity, while the sterically encumbered *ortho*-substituent results in highly syndioselective, thermally robust living propylene polymerization. Therefore, we have given the name “ligand-directed chain-end controlled polymerization” to this type of chain-end controlled polymerization, which is evidently governed by the ligand structure [30c–e,35i,j]. With ligand-directed chain-end controlled polymerization, atactic- to highly syndiotactic living PPs can now be prepared with fluorinated Ti–FI Catalysts (see Table 7).

7. Mechanism for ligand-directed chain-end controlled propylene polymerization

The propylene polymerization behavior of *C*₂-symmetric Ti–FI Catalysts (syndioselective polymerization via a chain-end control mechanism with 2,1-monomer insertion) is totally different from that of *C*₂-symmetric group 4 metallocene catalysts (isoselective polymerization via a site-control mechanism with 1,2-monomer insertion). At the same time, we recognize that the

behavior is apparently similar to that of classical homogeneous V catalysts such as V(acac)₃, which induce moderately syndioselective propylene polymerization under chain-end control with 2,1-insertion [10,43f]. There may be a similarity between the polymerization mechanisms exhibited by the Ti–FI and V catalysts.

Approximately 20 years ago, a molecular mechanics study suggested the use of a unique mechanism based on the fluxionality of an octahedral active species for syndioselective propylene polymerization with V catalysts [43a], although it was not supported by experimental evidence. Considering that we often observe fluxional character for FI Catalysts in solution, and that some FI Catalysts with MAO can form well-defined uni-, bi- and trimodal PEs simply by varying the temperature of polymerization [32m,r], it is unsurprising that a fluxionality-based mechanism is involved in propylene polymerization with Ti–FI Catalysts [30e] (see Scheme 3).



Scheme 3. Site-inversion mechanism for propylene polymerization promoted by FI Catalysts.

In fact, on the basis of QM/MM calculations, a site-inversion mechanism has recently been proposed in an effort to explain ligand-directed chain-end-controlled syndioselective propylene polymerization with C_2 -symmetric Ti–FI Catalysts [30e,35i,j,41]. According to the proposal, an octahedral active species with a *trans*-O and *cis*-N configuration is subject to fluxional isomerization between the Λ and Δ forms (site-inversion) at a rate which is faster than chain propagation. The fluxional isomerization is driven by the repulsive interaction between a growing polymer chain and the substituent on the imine-N, which is induced by the stereochemistry of the α -carbon in the last-inserted propylene unit. The energetically favorable diastereomers [re-chain/ Λ -site (b) and si-chain/ Δ -site (c)] control the stereochemistry in terms of propylene coordination and insertion, which is essentially directed by steric hindrance between the substituent *ortho* to the phenoxy-O and the methyl group of the propylene [Λ -site/si-face (b) and Δ -site/re-face (c)]. Therefore, the stereochemistry of the α -carbon dictates the face-selectivity of the pro-chiral propylene monomer [re-chain/si-face (b) and si-chain/re-face (c)] via a phenoxy–imine ligand on the catalyst as an intermediary, resulting in chain-end control that works in concert with the site-control effects. The proposal has not been without criticism, with the objection being that, although fluxional isomerization for a neutral group 4 transition metal complex is known, a highly electrophilic cationic Ti–FI Catalyst apparently disfavors site-inversion that probably proceeds via the dissociation of the imine-N donor of the ligands.

Under the assumption that site-inversion mechanism is operating in propylene polymerization with Ti–FI Catalysts, the steric bulk of the substituent *ortho* to the phenoxy-O should exercise a significant influence on the syndioselectivity of the polymerization, being consistent with our experimental results that are described in Section 5.2 [30e,35i,j]. Additionally, the highly syndioselective and thermally robust living nature of the catalyst, despite the chain-end control mechanism, can also be explained by a site-inversion mechanism, since the stereoselectivity is governed in practical terms by the ligand structure, and more specifically by the steric bulk of the substituent that is *ortho* to the phenoxy-O [30e,35i,j].

Therefore, our experimental results (ligand-directed chain-end controlled polymerization) and the predicted catalytic properties derived from the site-inversion mechanism are mutually compatible, though the postulated inversion between the Λ and Δ forms is not experimentally supported. The site-inversion mechanism leads to the concept that if chain propagation is faster than site-inversion (i.e., site-inversion is slower than chain propagation), a C_2 -symmetric FI Catalyst with sufficient steric bulk *ortho* to the phenoxy-O can be an isoselective

catalyst for propylene polymerization via a site-control mechanism. Reduction in the site-inversion rate may be achieved by ligand modifications that suppress the site-inversion, such as bridging the ligands and/or the introduction of a steric obstacle. Investigations are underway along this research direction to develop an FI Catalyst that initiates isoselective (living) propylene polymerization [30b,e,32l,q,35j].

Considering that the structurally similar and probably fluxional Zr- and Hf–FI Catalysts that favor 1,2-monomer insertion produce atactic to slightly syndiotactic PPs, then fluxionality alone seems insufficient to accomplish syndioselective propylene polymerization [32m,r,35j,38c]. Therefore, a combination of fluxionality and 2,1-regiochemistry probably accounts for the achievement of syndioselective propylene polymerization with C_2 -symmetric Ti–FI Catalysts [30e].

8. Preparation of living polymers

Having established the living nature of ethylene and propylene with fluorinated Ti–FI Catalysts, we decided to explore the creation of living polymers from ethylene, propylene and higher α -olefins [30c,d,31b,35a,b,e,g]. With the fluorinated Ti–FI Catalysts **9**, **13**, **14** and **25**, high molecular weight monodisperse PEs ($M_n > 400\,000$, $M_w/M_n < 1.2$), ethylene-propylene copolymers (EPRs, $M_n > 80\,000$, M_w/M_n 1.07–1.13, propylene content 15–48 mol%), ethylene-1-hexene ($M_n > 150\,000$, M_w/M_n 1.08–1.15, 1-hexene content 12–23 mol%), ethylene-1-octene ($M_n > 170\,000$, M_w/M_n 1.10–1.17, 1-octene content 9–21 mol%) and atactic to highly syndiotactic PPs (e.g., *rr* 94%, T_m 156 °C) were obtained [30c,d,31b,35a,b,e,g].

In addition, the highly controlled living nature allowed the synthesis of a number of chain-end functionalized polyolefinic materials if a functionalized monomer [e.g., $\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{OSiMe}_3$] was used during the initiation and/or termination step(s). With **9**/MAO, we successfully prepared ethylene- and/or α -olefin-based monodisperse (co)polymers that possessed terminal reactive groups such as –OH and –NH₂ [e.g., (HO–sPP–NH₂)_s, M_n 9600, M_w/M_n 1.08] [31d,e].

Moreover, the fluorinated Ti–FI Catalysts permitted us to create a wide variety of ethylene- and α -olefin-based block copolymers composed of crystalline and amorphous segments and/or two different kinds of crystalline segments. For example, ethylene- and propylene-based block copolymers; PE-*b*-EPR (M_n 211 000, M_w/M_n 1.16), PE-*b*-sPP (M_n 136 000, M_w/M_n 1.15), sPP-*b*-EPR (M_n 161 000, M_w/M_n 1.51), PE-*b*-EPR-*b*-sPP (M_n 235 000, M_w/M_n 1.15) and PE-*b*-EPR-*b*-PE (M_n 272 000, M_w/M_n 1.14) were synthesized with the **9**/MAO system using a sequential addition polymerization procedure [31b,35b,g]. Likewise,

ethylene- and higher α -olefin-based block copolymers such as PE-*b*-poly(ethylene-*co*-1-hexene), PE-*b*-poly(ethylene-*co*-1-octene) and PE-*b*-poly(ethylene-*co*-1-decene) were obtained using **13**/MAO [31b,35e]. We revealed that PE-*b*-poly(ethylene-*co*-higher α -olefins) display unique tensile properties with a good combination of extensibility and toughness compared to the corresponding blend and random (co)polymers [35e]. An extension of the living behavior of fluorinated Ti–FI Catalyst **24** to block copolymer synthesis using cyclopentene or 1,5-hexadiene has resulted in the production of PE-*b*-poly(ethylene-*co*-cyclopentene) and sPP-*b*-poly(methylenecyclopentane-*co*-vinyl tetramethylene) [36j,37d].

Finally, with the robust living nature, the combination of elaborately designed Ti–FI Catalysts and suitable chain transfer agents offered a new strategy for the catalytic production of living polymers [30c,d,35c]. For instance, with Ti–FI Catalyst **26**, the catalytic formation of monodisperse Zn-terminated PEs was accomplished using Et₂Zn as a chain transfer agent. Additionally, the association of Ti–FI Catalyst **15** with H₂ enabled us to prepare monodisperse PEs, EPRs and PE-*b*-EPR catalytically. The realization of the catalytic production of living polymers results from the fact that carefully designed Ti–FI Catalysts can incorporate monomers without termination, even in the co-presence of a chain transfer agent, and only undergo chain transfer in the absence of a reacting monomer. This strategy is expected to render the displacement of some of the existing olefin-based materials by high performance living polymers economically viable. The discovery of fluorinated Ti–FI Catalysts has created new opportunities for the syntheses of a wide array of living polymers, some of which can even be produced catalytically. Many of the living polymers formed with the fluorinated Ti–FI Catalysts were previously unavailable by other methods.

9. Conclusion

The unique catalysis of fluorinated Ti–FI Catalysts for the polymerization of ethylene and propylene has been described. The versatility of Ti–FI Catalysts is derived from their controllable reactivity and selectivity due to diversified ligand structures. The most remarkable degree of control was attained by fluorinated versions in thermally robust living ethylene polymerization and highly syndioselective living propylene polymerization, which ensures easy access to various unique block copolymers and chain-end functionalized (co)polymers. Theoretical calculations as well as experimental data suggest that the attractive interaction between the ligand and the growing polymer chain, and the fluxionality of an octahedral framework together

with 2,1-regiochemistry, play a pivotal role in the achievement of thermally robust living polymerization and highly syndioselective (living) propylene polymerization behavior. These features of fluorinated Ti–FI Catalysts are totally different from those of group 4 metallocene catalysts, which mainly control olefin polymerization by repulsive interactions based on rigidly organized ligand frameworks. We believe that the attractive interaction between a ligand and a growing polymer chain and the fluxionality of a catalyst will provide a conceptually novel strategy for realizing controlled and selective polymerizations of olefinic monomers, leading to the creation of additional value-added polyolefinic materials [30c,d,e].

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