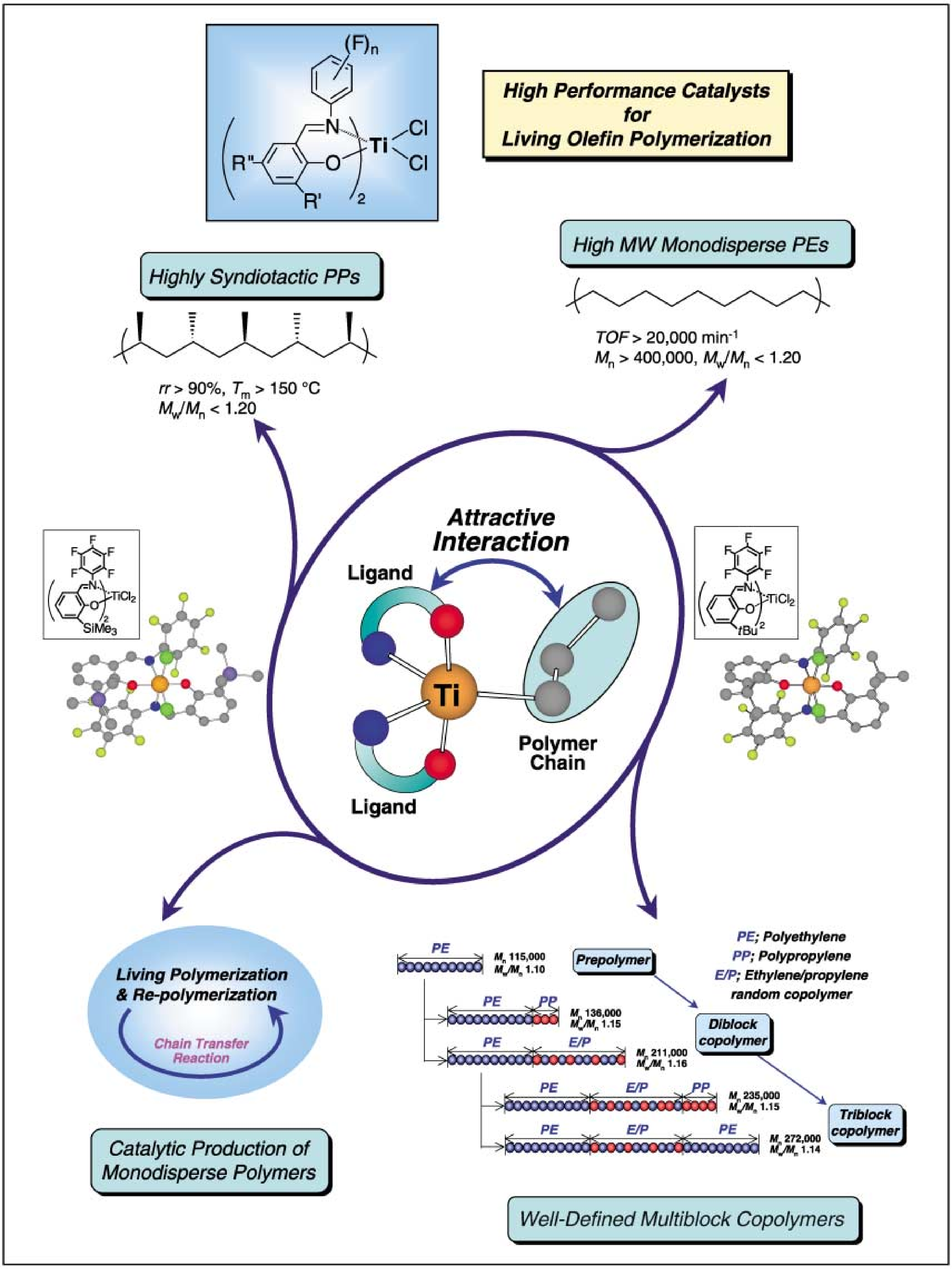

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Unprecedented Living Olefin Polymerization Derived from an Attractive Interaction between a Ligand and a Growing Polymer Chain

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Abstract: Ti complexes incorporating fluorine-containing phenoxy–imine chelate ligands (fluorinated Ti-FI catalysts) have been demonstrated to induce an unprecedented living polymerization effect with both ethylene and propylene, through an attractive interaction between the fluorine atom in the ligand and a β-hydrogen atom on the growing polymer chain. With the aid of this attractive interaction, highly controlled living ethylene polymerization, highly-syndiospecific living propylene polymerization, the synthesis of unique block copolymers from ethylene and propylene, and the catalytic production of monodisperse polyethylene and Zn-terminated polyethylene have been realized. The attractive interaction provides a conceptually new strategy for the achievement of controlled living olefin polymerization.

Keywords: block copolymers · fluorinated ligands · living polymerization · polyolefins · titanium

Introduction

Attractive noncovalent interactions, such as hydrogen bonding and electrostatic attraction, play a salient role in many catalytic processes, enabling us to achieve controlled catalysis with high selectivity and productivity.[1] Although repulsive interactions between the ligand and other components in the catalyst system have been shown to play a key role in increasing the stereoregularity and molecular weight of the resulting polymers, in the field of olefin polymerization catalysis[2] little is known about the attractive interactions[3] that contribute to the enhancement of the catalytic properties. Attractive interactions are intrinsically tunable and are more versatile than repulsive interactions, so if attractive interactions can be realized they are expected to provide facile and precise control over catalytic properties such as catalytic activity, polymer molecular weight, co-monomer incorporation, and polymer stereoregularity.

In our study, we focused on Group 4 transition-metal complexes featuring a pair of phenoxy–imine chelate ligands (named FI catalysts)[4, 5] for olefin polymerization; these are based on a ligand-oriented catalyst design concept.[6] FI catalysts can produce a variety of distinctive polymers with high efficiency, such as vinyl-terminated low molecular-weight polyethylenes (M_w 2000), ultra-high molecular-weight amorphous ethylene–propylene copolymers ($M_w = 10\,200\,000$), isotactic polypropylenes ($mm = 69\,\%$, T_m 124 °C), and stereo- and regio-irregular high molecular-weight poly(hex-1-ene)s, some of which are difficult or impossible to prepare using conventional catalysts.

Further studies aimed at developing higher performance FI catalysts resulted in the discovery of a new family of fluorinated Ti-FI catalysts for living olefin polymerization (Figure 1). The catalysts are capable of carrying out highly controlled living ethylene polymerization as well as highly syndiospecific living propylene polymerization at a remarkably elevated temperature of 50 °C, as introduced in our patent[7] and in a series of subsequent papers.[8] Unique block copolymers with a wide array of molecular architectures [e.g., polyethylene-*block*-poly(ethylene-*co*-propylene) (PE-*b*-EPR), PE-*block*-syndiotactic polypropylene (PE-*b*-sPP), sPP-*b*-EPR, PE-*b*-EPR-*b*-PE, PE-*b*-EPR-*b*-sPP] were synthesized from ethylene and propylene by using the catalysts, most of which were previously unobtainable with the use of Ziegler–Natta catalysts. Moreover, recent research has demonstrated that appropriately designed fluorinated Ti-FI catalysts are capable of producing monodisperse polymers catalytically by combination with chain-transfer agents, opening up a new methodology for the catalytic production of block copolymers and functional polyolefins.[9] Coates et al. have recently

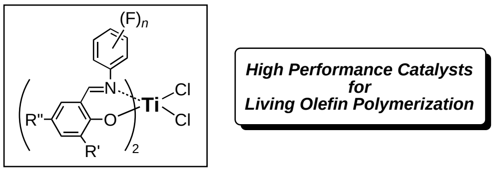

Figure 1. General structure of fluorinated Ti-FI catalysts.

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obtained a modified fluorinated Ti-FI catalyst by using combinatorial methods that can initiate syndiospecific living propylene polymerization at ambient temperatures and form sPP-*b*-EPR and sPP-*block*-poly(methylenecyclopentane-*co*-vinyl tetramethylene).[10]

Computational studies together with experimental results indicate that the attractive interaction of a fluorine atom in the ligand with a β-hydrogen on the growing polymer chain is responsible for the unprecedented living polymerization; this represents the first example of an attractive interaction between the ligand and other components in the catalyst system that significantly enhances the catalytic properties. In this article, we wish to describe the remarkable living olefin polymerization behavior of fluorinated Ti-FI catalysts originating from the attractive interaction of a ligand with a growing polymer chain. This attractive interaction has enabled us to achieve some of the long-standing challenges in the field of polymerization catalysis and polymer synthesis (i.e., highly controlled living ethylene polymerization, highly syndiospecific living propylene polymerization, the synthesis of unique block copolymers, and the catalytic production of monodisperse polymers).

Living Ethylene Polymerization

Living olefin polymerization[11] is of great importance in the production of precisely controlled polymers (e.g., monodisperse polymers, end-functionalized polymers, and block copolymers), all of which are anticipated to exhibit novel physical properties and, therefore, novel uses. Although FI catalysts display a unique catalytic behavior for the polymerization of ethylene and α-olefins, early FI catalysts did not polymerize such olefins in a living fashion owing to their exerting insufficient control over chain termination or transfer steps. Therefore, the precisely controlled polymers mentioned previously were inaccessible with early FI catalysts.

FI catalysts have ligands that can be easily tailored synthetically from both an electronic and steric point of view, and hence they possess a wide range of catalyst design possibilities. The catalysts have allowed us to examine a wide variety of substituents including functional groups that typically contain heteroatoms. In exploring new derivatives of FI catalysts, we have investigated derivatives that contain halogen-substituted ligands. As a consequence, we discovered a Ti-FI catalyst with a perfluorophenyl group in the ligand that displayed unique catalytic behavior for the polymerization of ethylene (Table 1).[7, 8a,b] When FI catalyst **1** was activated with methylalumoxane (MAO), it was an order of magnitude more active (50 °C, atmospheric pressure: TOF = 21 500 min^{-1}) than the non-fluorinated congener (TOF = 3200 min^{-1}), and yielded high molecular-weight polyethylene (M_n = 412 000). It is reasonable to assume that a more electron-withdrawing ligand generates a more electrophilic Ti center. Therefore, the enhancement of activity as a result of introducing the perfluorophenyl group provides a clear demonstration that for the catalysts, the electrophilicity of the Ti center plays a predominant role in determining the catalytic activity. Remarkably, the high molecular-weight polyethylene displayed a narrow molecular-weight distribution (M_w/M_n = 1.13) and was free of olefinic end groups. These facts suggest that the catalyst **1**/MAO system may possess the characteristics of a living ethylene polymerization regime under the given conditions. The plots of the M_n and M_w/M_n values at 50 °C vs polymerization time are shown in Figure 2.

Table 1. Results of ethylene polymerization[a] with catalyst **1** and Cp_2ZrCl_2.

	Catalyst	T [°C]	t [min]	Yield [g]	TOF[b] [min^{-1}]	M_n[c] [10^3]	M_w/M_n[c]
1	**1**	50	0.5	0.172	24 500	257	1.08
2	**1**	50	1	0.302	21 500	424	1.13
3[d]	**1**	75	1	0.453	16100	272	1.15
4[e]	**1**	90	1	0.459	8200	167	1.30
5	Cp_2ZrCl_2	25	1	0.258	18400	157	1.73
6	Cp_2ZrCl_2	50	1	0.433	30900	136	2.26

[a] Conditions: catalyst (0.5 μmol), cocatalyst MAO (1.25 mmol), 1 atm. [b] Turnover frequency. [c] Determined by GPC using polyethylene calibration. [d] Catalyst **1** (1.0 μmol). [e] Catalyst **1** (2.0 μmol).

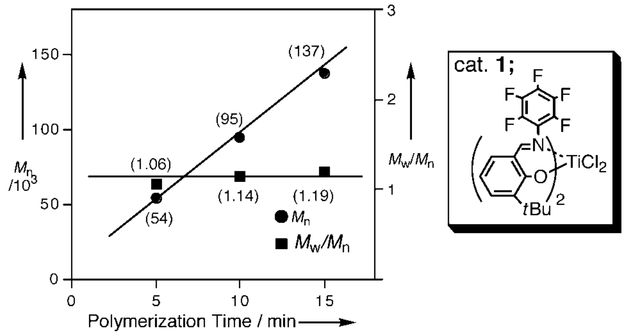


Figure 2. Plots of M_n and M_w/M_n as a function of polymerization time for ethylene polymerization with FI catalyst **1**/MAO at 50 °C. Conditions: **1** (1.0 μmol), cocatalyst MAO (1.25 mmol), 1 atm, ethylene/N_2 feed 2 L/50 L h^{-1}, 50 °C.

The M_n value increased proportionally with polymerization time, and the narrow M_w/M_n value (1.06–1.19) was retained for each run, indicating that the system is indeed living. This is the first example of living ethylene polymerization at a temperature as high as 50 °C. Considering that the MAO used as the activator is a potential chain-transfer agent and that living olefin polymerization can usually only be achieved using a borate cocatalyst in place of MAO, living ethylene polymerization with MAO at 50 °C is of great significance.

The M_n value of 412 000 represents one of the highest reported values to date for monodisperse polyethylenes. In addition, to the best of our knowledge, the activity (TOF = 21 500 min^{-1}) is the highest with regard to living ethylene polymerizations and is comparable to those found for early metallocenes such as Cp_2ZrCl_2 under the same conditions. Therefore, the introduction of the perfluorophenyl group had beneficial effects with respect to the suppression of chain termination as well as the enhancement of catalytic activity. Notably, at 75 °C and 90 °C, **1**/MAO produced high molecular-weight polyethylenes with fairly narrow molecular-weight distributions (75 °C: M_w/M_n = 1.15, M_n = 272 000; 90 °C: M_w/M_n = 1.30, M_n = 167 000). Therefore, highly controlled living ethylene polymerization has been achieved by using fluorinated Ti-FI catalyst **1**.

We reasoned that the fluorine atom(s) in the ligand is responsible for this highly controlled living polymerization because the corresponding non-fluorinated FI catalyst does not achieve the living polymerization of ethylene and provides classical unimodal polyethylene with an M_w/M_n value of about 2 under identical conditions.

To gain further insight into the role of the fluorine atom(s) in the realization of living polymerization, we examined the ethylene polymerization behavior of a series of fluorinated Ti-FI catalysts,[7, 8a,b] identified as catalysts **2**–**7**. A summary of the polymerization results is shown in Figure 3. The data indicate that only a Ti-FI catalyst that possesses fluorine atom(s) *ortho* to the imine-nitrogen could initiate living ethylene polymerization, showing that this is a requirement for living polymerization.

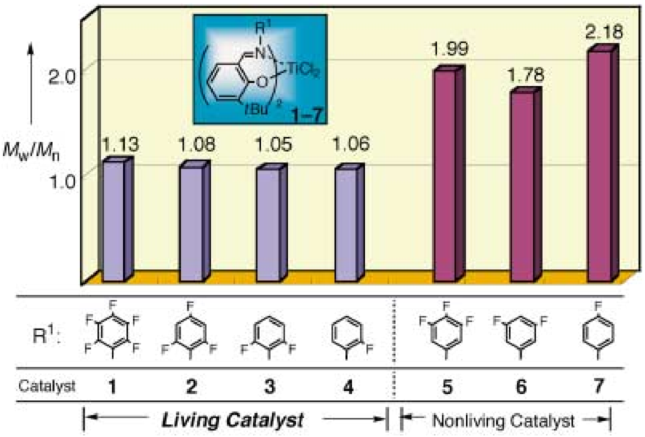


Figure 3. Ethylene polymerization results with FI catalysts **1**–**7**. Conditions: cocatalyst MAO, 1 atm, 1–5 min, 50 °C.

^{13}C NMR spectroscopy as well as IR analyses revealed that the polyethylenes formed from the nonliving-type FI catalysts **5**–**7** have a vinyl end-group ratio of about 0.1 per 1000 carbon atoms, indicating that β-hydrogen transfer plays a dominant role in chain termination for these complexes. These results clearly demonstrate that the *ortho*-fluorine suppresses the β-hydrogen transfer.

To gain insight into the role of the *ortho*-fluorine on living polymerization, DFT calculations[12] were performed on a catalytically active species derived from catalysts **1** and **2**–**4** (Table 2 and Figure 4, polymer chain model: *n*-propyl group). The calculations showed that the distance between the central metal and the fluorine atom *ortho* to the imine nitrogen atom (the nearest F) is too long to have an effective interaction (Ti–F distances: ca. 4 Å), indicating that there is practically no stabilization of the cationic metal center by the *ortho*-fluorine atom. Alternatively, the calculations indicated that the *ortho*-fluorine and the β-hydrogen atoms on a polymer chain are located at a distance of 2.276 to 2.362 Å apart, a distance that is well within the range of nonbonding interactions.

Table 2. F–H_β interactions calculated by DFT.

	Catalyst	r(F–H_β)[a] [Å]	q(F)[b]	q(H_β)[c]	ES[d] [kJ mol^{-1}]
1	**1**	2.276	–0.466	0.095	–27.1
2	**2**	2.362	–0.470	0.108	–29.9
3	**3**	2.346	–0.476	0.111	–31.2
4	**4**	2.324	–0.482	0.117	–33.6

[a] F–H_β distance. [b] Mulliken charge of the nearest *o*-F to H_β. [c] Mulliken charge of H_β. [d] Electrostatic energy for F–H_β interaction.

Additionally, elongation of the C–H_β bond (1.113 Å) was suggested by the calculations; this is probably the result of an attractive interaction between the *ortho*-fluorine and the β-hydrogen atoms. On the basis of the calculation results, the electrostatic energies between the negatively charged fluorine and the positively-charged β-hydrogen atoms are estimated to be approximately –30 kJ mol^{-1}. These electrostatic energies are large enough to mitigate the β-hydrogen transfer to the Ti metal and/or a reacting monomer. In addition, the transition state leading to the β-hydrogen transfer is probably disfavored by the fact that the β-hydrogen atom is positively charged and stabilized by the negatively charged *ortho*-fluorine atom, though the β-hydrogen should behave as a hydride in the β-hydrogen transfer process.

Significantly, Chan et al.[13] have recently reported the first NMR spectroscopic and X-ray structural evidence for an attractive interaction between a fluorine atom in the ligand and a hydrogen atom on a benzyl group attached to the central metal for Group 4 transition-metal complexes, potentially indicating the generality of the attractive interaction between the functionalized ligand and the polymer chain. Interestingly, DFT calculations show that an active species generated from the chlorinated counterpart of catalyst **4** also exhibits an attractive interaction between the chlorine and the β-hydrogen of a growing polymer chain (polymer chain model: *n*-propyl group, *ortho* Cl–H_β distance: 2.683 Å, electrostatic energy: –5.6 kJ mol^{-1}), and in fact the chlorinated FI catalyst produced polyethylene with a reasonably narrow molecular-weight distribution (50 °C: $M_n = 106\,000$, $M_w/M_n = 1.21$). These results imply that interaction with a β-hydrogen atom can potentially be achieved by any substituent possessing lone-pair electrons.

The attractive interaction between the functionalized ligand and the polymer chain provides a new breakthrough for achieving highly controlled living ethylene polymerization and may be extended to the living polymerization of propylene, since a growing polypropylene chain includes a β-hydrogen. Indeed, DFT calculations indicate that the *ortho*-fluorine of the active species generated from catalyst **1** during propylene polymerization can interact with the β-hydrogen of a growing polypropylene chain (polymer chain model: isobutyl and *sec*-butyl) derived from either 1,2-insertion or 2,1-insertion (1,2-insertion; *ortho* F–H_β distance 2.251 Å, electrostatic energy –46.84 kJ mol^{-1}: 2,1-insertion; *ortho* F–H_β distance 2.262 Å, electrostatic energy –30.70 kJ mol^{-1}: for ethylene polymerization; *ortho* F–H_β distance 2.276 Å, electrostatic energy –27.1 kJ mol^{-1}), suggesting that the catalyst may also exhibit living behavior for propylene polymerization.

Living Propylene Polymerization

Single-crystal X-ray analysis revealed that catalyst **1** has a six-coordinate center in a distorted octahedral geometry with a

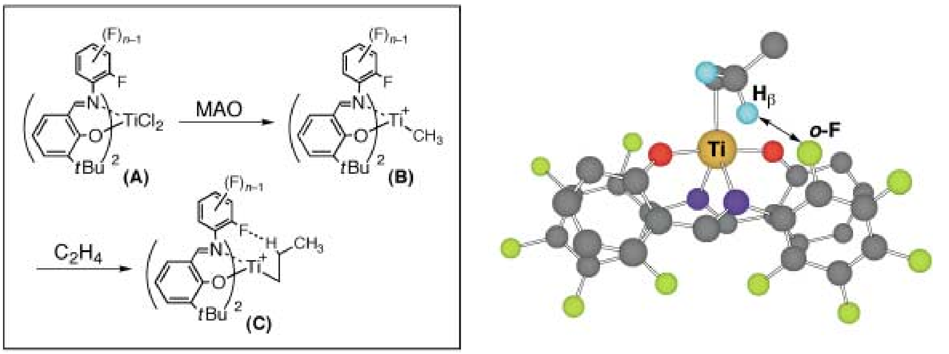


Figure 4. Structure of an active species derived from **1** calculated by DFT (Model C). *t*Bu groups are omitted for clarity.

trans-O, *cis*-N, and *cis*-Cl arrangement; thus it possesses approximate C_2 symmetry.[8b] This molecular structure implies that **1** combines living enchainment with isospecific control of polymer stereochemistry. Ti-FI catalyst **1** with an MAO activator is able to polymerize propylene to crystalline polypropylene with an increased M_n of 28500 and an enhanced TOF of 87 h^{-1} (25 °C, 5 h, 1 atm; Figure 5) compared with those for the corresponding non-fluorinated FI catalysts. As anticipated, the polypropylene exhibited an extremely narrow M_w/M_n of 1.11, and olefinic resonances were absent from the NMR spectrum of the polymer. The living nature of the polymerization was confirmed by the linear relationship between M_n and polymerization time as well as by the narrow M_w/M_n values observed. Therefore, it was demonstrated that the catalyst promotes room-temperature living propylene polymerization, as predicted by DFT calculations. Catalyst **1** is the first example of a polymerization catalyst that displays living behavior for the polymerization of both ethylene and propylene. These results suggest that the attractive interaction capable of suppressing chain termination probably sets a standard for controlled living polymerization of simple olefins through insertion chemistry.

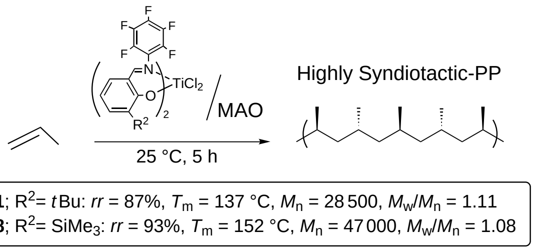


Figure 5. Propylene polymerization with FI catalysts.

The polypropylene formed with catalyst **1**/MAO system displays a peak melting temperature (T_m) of 137 °C, indicative of a high degree of stereo control. To our surprise, microstructural analysis by ^{13}C NMR spectroscopy revealed that the resulting polymer is highly syndiotactic polypropylene (*rr* 87 %), and that a chain-end control mechanism was responsible for the observed stereo control. It should be noted that **1** exhibits higher syndioselectivity compared with the non-fluorinated version (*rr* 79 %). Accordingly, the introduction of the perfluorophenyl group contributed to the enhancement of stereoselectivity in addition to the suppression of chain termination and the increase in catalytic activity. Although the exact cause for the unexpected and very high syndiospecificity through chain-end control is not clear at present, the syndiospecificity can be explained by the combination of a rapid site inversion proposed by Cavallo et al.[14] and the attractive interaction of the ligand with the growing polymer chain discussed herein.

Catalyst **1** is unique in its ability to generate a highly stereoregular polymer through a chain-end control mechanism at room temperature; usually chain-end control operates well at very low to subambient temperatures and loses its stereoregulating ability at elevated polymerization temperatures. In fact, the *rr* triad (87 %) was the highest degree of chain-end control yet observed in a propylene polymerization when it was discovered. Also, the *rr* triad was among the highest reported for monodisperse syndiotactic polypropylenes. As disclosed in our patent filed in January 2000,[7] catalyst **1** is the first example of a living and, at the same time, highly stereoselective catalyst for propylene polymerization. The unique catalytic properties of the catalyst for living propylene polymerization are thought to stem from the attractive interaction between the fluorinated ligand and the growing polymer chain.

^{13}C NMR analyses of the chain-end groups of low molecular-weight polypropylenes ($M_n = 2000$, 3300, and 9700) derived from catalyst **1** demonstrated that syndiospecific propylene polymerization is initiated exclusively by 1,2-insertion followed by 2,1-insertion as the principal mode of polymerization.[8e] As far as we are aware, this is the first example of a predominant 2,1-insertion mechanism for chain propagation displayed by a Group 4 metal-based catalyst. Recently, the generality of this highly unusual propylene polyinsertion mode with Ti-FI catalysts has been confirmed by other research groups.[10c, 15, 16]

Further efforts aimed at developing improved versions of existing FI catalysts for living propylene polymerization led to the discovery of catalyst **8**, which forms much higher tacticity monodisperse polymers with extremely high T_ms by a chain-end control mechanism.[8f] Thus, catalyst **8**, which has a trimethylsilyl group *ortho* to the phenoxy oxygen atom, furnished highly syndiotactic monodisperse polypropylene (25 °C: $rr = 93\,\%$, $M_n = 47000$, $M_w/M_n = 1.08$) with a very high T_m (152 °C). Such an extremely high level of chain-end control is unprecedented in propylene polymerization. The syndiotactic polypropylene arising from **8** at 0 °C has an exceptionally high T_m of 156 °C, which represents the highest T_m value ever observed among syndiotactic polypropylenes.

Surprisingly, at 50 °C, catalyst **8** promoted living propylene polymerization and yielded monodisperse syndiotactic polypropylene with a very high T_m of 150 °C. This is the first example of living propylene polymerization at a temperature as high as 50 °C. Additionally, the T_m of 150 °C for polymerization at 50 °C is the highest value observed for syndiotactic polypropylenes produced under the same or similar polymerization conditions.

Synthesis of Unique Multiblock Copolymers

An attractive feature of living olefin polymerization catalysts is their ability to create polyolefinic multiblock copolymers, which have potential uses for a broad spectrum of applications including compatibilizers, elastomers, and composite materials. However, known catalysts can promote the living polymerization of either ethylene or α-olefins but not both, resulting in limited success in the preparation of polyolefinic block copolymers. As discussed, fluorinated Ti-FI catalysts are capable of initiating highly controlled living ethylene polymerization and highly syndiospecific living propylene polymerization by an unprecedented interaction of the fluorine in the ligand and the growing polymer chain. We have thus demonstrated the utility of these catalysts through the syntheses of both ethylene- and propylene-based di- and tri-block copolymers in a controlled fashion,[7, 8b,d] most of which were previously unavailable with Ziegler–Natta catalysts. These unique multiblock copolymers consist of crystalline and amorphous segments and/or two different kinds of crystalline segments.

For example, a novel A-B diblock copolymer composed of crystalline and amorphous segments, PE-*block*-poly(ethylene-*co*-propylene) (PE-*b*-EPR), was prepared from ethylene and ethylene/propylene (see Figure 6). Addition of **1**/MAO to a toluene solvent saturated with ethylene at 25 °C resulted in the rapid formation of the first polyethylene block segment ($M_n = 115\,000$, $M_w/M_n = 1.10$). The ethylene/propylene (1:3) feed produced a sequential poly(ethylene-*co*-propylene) (EPR) segment. The resulting high-molecular-weight well-defined PE-*b*-EPR block copolymer ($M_n = 211\,000$, $M_w/M_n = 1.16$) contained 6.4 mol % of propylene.

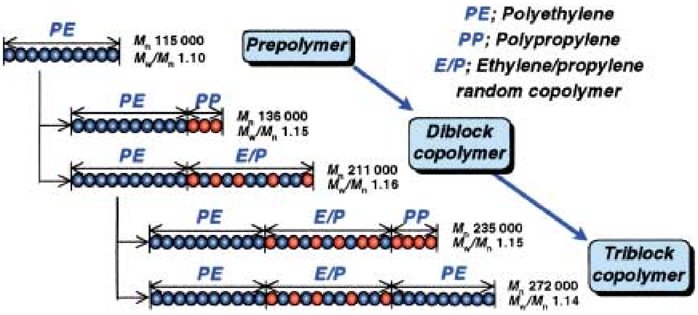


Figure 6. Synthesis of various block copolymers by using catalyst **1**.

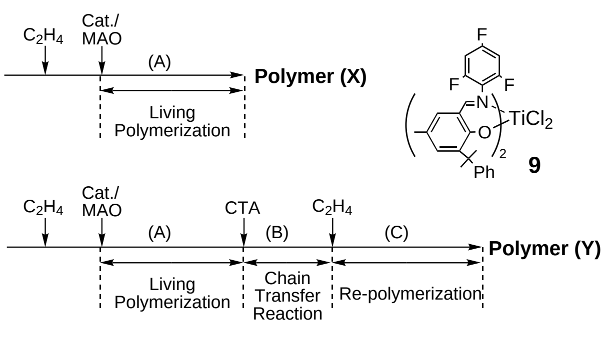
Similarly, PE-*b*-sPP, sPP-*b*-EPR, PE-*b*-EPR-*b*-sPP, and PE-*b*-EPR-*b*-PE block copolymers were also synthesized with the **1**/MAO system by the sequential addition of the corresponding monomers. Some of the new block copolymers derived from the catalysts were analyzed by AFM (atomic force microscopy)[17] and TEM (transmission electron microscopy)[8d] to demonstrate their considerable potential as new materials. The powerful strategy of well-defined multiblock copolymer formation based on FI catalyst living polymerization technology is being further applied to the preparation of block copolymers with novel architectures.

Catalytic Production of Monodisperse Polymers

Fluorinated Ti-FI catalysts have achieved some important goals with respect to living olefin polymerization (i.e., highly controlled living ethylene polymerization, highly syndiospecific living propylene polymerization, and the synthesis of unique block copolymers) with the aid of the attractive interaction between the ligand the polymer chain. A crucial goal that still remains to be realized is the catalytic production of precisely controlled polymers, such as monodisperse polymers and block copolymers, because each molecule of the catalyst can only produce one polymer chain during the polymerization reaction; this results in an extremely low yield relative to common olefin polymerization catalysts. One solution to this problem is to develop FI catalysts that can incorporate monomers without termination, even in the presence of a chain-transfer agent (CTA) and which undergo chain transfer only in the absence of a reacting monomer. Such FI catalysts, if developed, will provide a new strategy for the catalytic production of the precisely controlled polymers.

With the high catalytic performance of fluorinated Ti-FI catalysts for living olefin polymerization already established, we considered these catalysts to be viable catalysts for the production of multiple polymer chains per unit of catalyst. Initial attempts were unsuccessful because of catalyst decomposition and/or undesirable chain termination induced by the chain-transfer agent employed. However, elaborate catalyst design work focusing on the substitution pattern of fluorines in the phenyl group on the imine nitrogen atom as well as in the substituent *ortho* to the phenoxy oxygen atom, has allowed for the development of FI catalysts capable of catalytically producing monodisperse polymers in combination with chain-transfer agents.[9]

The catalytic production of monodisperse polyethylenes was achieved by catalyst **2**, which has a trifluorophenyl group on the imine nitrogen atom. The polymerization procedures are summarized in Scheme 1. Firstly, saturation of the reaction



Scheme 1. Polymerization procedure for catalytic production of monodisperse polyethylene.

medium with ethylene occurs, followed by living ethylene polymerization (A). Next comes the addition of hydrogen to the reaction medium (B), and then ethylene polymerization once again (C). Quenching the reaction after (B) yielded monodisperse polyethylene ($M_n = 37500$, $M_w/M_n = 1.04$, Figure 7), whereas quenching following the complete sequence provided an approximately double yield of polyethylene with practically the same molecular weight and molecular-weight distribution ($M_n = 37900$, $M_w/M_n = 1.15$, Figure 7). This is the first example of the catalytic production of monodisperse polymers. We confirmed that the catalytic cycle could be repeated at least ten times with virtually no loss of productivity. These results suggest that, in principle, the catalysts are capable of producing block copolymers catalytically by using H_2 as a chain-transfer agent, and, in fact, the catalytic creation of PE-*b*-EPR block copolymers was accomplished for the first time by using catalyst **2**.

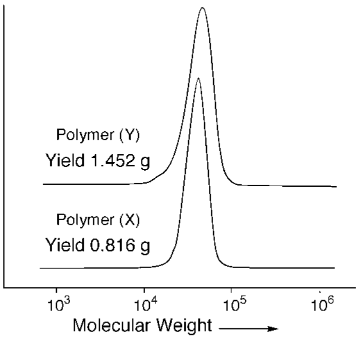


Figure 7. GPC profile of polyethylenes obtained by FI catalyst **2** (CTA; H_2). Polymer (X); M_n 37,500, M_w/M_n 1.04, Polymer (Y); M_n 37,900, M_w/M_n 1.15.

Likewise, with catalyst **9**, which has a trifluorophenyl and a cumyl group in the ligand, catalytic production of Zn-terminated polyethylenes was accomplished by using $ZnEt_2$ as a chain-transfer agent (80 equiv to **9**). Similar procedures to those listed above followed by quenching formed monodisperse polyethylene ($M_n = 36700$, $M_w/M_n = 1.20$, Figure 8) and approximately a double yield of monodisperse polyethylene ($M_n = 37100$, $M_w/M_n = 1.31$, Figure 8), respectively. These results indicate there is practically no chain transfer in the presence of $ZnEt_2$. This chemistry provides a convenient and efficient route to catalytically prepare monodisperse Zn-terminated polyolefins; this in turn opens countless opportunities for the synthesis of functionalized polyolefins or block copolymers containing polyolefins and polar polymer segments.

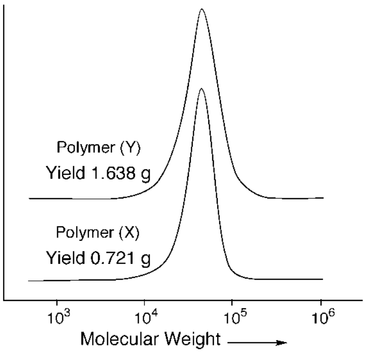


Figure 8. GPC profile of polyethylenes obtained by catalyst **9** (CTA; Et_2Zn). Polymer (X); $M_n = 36700$, $M_w/M_n = 1.20$, Polymer (Y); $M_n = 37100$, $M_w/M_n = 1.31$.

Conclusion

The catalytic behavior of Ti complexes incorporating fluorine-containing phenoxy–imine chelate ligands (fluorinated Ti-FI catalysts) for the polymerization of ethylene and propylene has been summarized. The use of these catalysts with an MAO activator is capable of polymerizing both ethylene and propylene in a living fashion. The living nature originates from the attractive interaction between a fluorine atom in the ligand and the β-hydrogen atom of a growing polymer chain; this curtails β-hydrogen transfer. The attractive interaction provides a conceptually new strategy for achieving living olefin polymerization and has permitted us to perform highly controlled living ethylene polymerization at the remarkably high temperature of 50 °C. In addition, such an interaction has realized highly-stereospecific, thermally robust, living propylene polymerization and has created highly syndiotactic monodisperse polypropylenes with an exceptionally high T_m.

The versatility of the fluorinated Ti-FI catalysts induced by the attractive interaction has allowed for the synthesis of unique block copolymers, previously unavailable with Ziegler–Natta catalysts. Moreover, the interaction has enabled us to develop new versions of the catalysts that can catalytically synthesize monodisperse polyethylenes and Zn-terminated polyethylenes by the combination with H_2 or $ZnEt_2$ as a chain-transfer agent, opening up the possibility of the catalytic synthesis of block copolymers and functional polymers.

We believe that the attractive interaction capable of suppressing chain termination sets a standard for the controlled living polymerization of simple olefins through insertion chemistry, and that the results described herein will activate research into the attractive interaction between the functionalized ligand and the growing polymer chain; this will probably result in the discovery of additional hitherto-unknown polymerization catalysis.

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