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Award Accounts

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Propene Polymerization with Bis(phenoxy–imine) Group 4 Transition Metal Complexes

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Olefin polymerizations with group 4 transition metal complexes having two phenoxy–imine ligands (FI Catalysts) are reviewed with an emphasis on the characteristics and mechanisms of propene polymerization. The structures and properties of FI Catalysts can be easily modified by changing phenoxy–imine ligand structures. Such catalysts can be synthesized straightforwardly from readily available chemicals. An enormous library of FI Catalysts can be built up by combining a group 4 metal center and a variety of cocatalysts. The diversified library makes FI Catalysts so versatile that polyolefins with desired properties (molecular weight, molecular weight distribution, chain-end structure, tacticity, and so on) can be obtained sometimes predictably, by selecting the appropriate combination of ligand, metal, and cocatalyst. In propene polymerization, it remains a challenge to control the stereo- and regiochemistry of monomer enchainment in order to obtain commercially valuable products. FI Catalysts can produce *syndiotactic* and *isotactic* polypropene by Ti–FI catalysts/MAO and Zr– and Hf–FI catalysts/^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$, respectively. Because of the well-defined and tunable nature of the catalysts, the coordination environment around the metal center can be controlled by the ligand structures to achieve extremely high stereoregularities, comparable to those of heterogeneous Ziegler–Natta catalysts and metallocene catalysts. These *syndio-* and *isospecific* FI Catalysts have contrasting reaction mechanisms, i.e., the *syndiospecific* polymerization is mediated via 2,1-insertion under chain-end control, while *isospecificity* arises from 1,2-insertion and a site control mechanism. The observed *syndiospecificity* can originate from the inherent fluxionality of FI Catalysts between configurational isomers.

1. Brief History of Stereoregular Polypropene. The polyolefin industry has grown into a multi-billion dollar business because polyolefins possess excellent material properties, cost-effectiveness, and a broad product application ranging from common to specialized purposes.[1] Major polyolefin products include polyethenes, polypropenes, and elastic copolymers consisting of ethene and other olefins. Among them, polypropene is an interesting class of polymer for researchers in both industry and academia due to its high market values and the challenges of stereospecific polymerization.

In fact, before the discovery of transition metal catalysts, polypropene could only be produced as oily, low molecular weight products. Transition metal catalysts have enabled scientists to produce linear high molecular weight polypropenes, where the methyl groups are located on a polymer chain with enough regularity to form a crystalline polymer. Although several laboratories obtained crystalline polypropenes by means of transition metal catalysts in the early 1950s,[1,2] G. Natta addressed the significance of stereochemistry along a polymer chain and transition metal-mediated stereo- and regiospecific polymerizations,[3] for which he was awarded the Nobel Prize in chemistry in 1963 in company with K. Ziegler.

When polypropene is linear and pendant methyl groups are located on every other carbon of a polymer chain, each propene monomer is connected in a regioselective manner, where a secondary carbon is always bonded with a primary carbon (Fig. 1a). In addition to such regioselectivity, when all the methyl groups are oriented to one side of a polymer chain (assuming a straightened zigzag conformation of the main chain), the polypropene has stereospecificity and is called *isotactic* polypropene (Fig. 1b). If we look at the stereochemistry of methine carbons of *isotactic* polypropene, it would be either ···*RRRRRRRR*··· or ···*SSSSSSSS*···. Another type of stereoregularity, *syndiotacticity*, is defined as a type of sequence, ···*RSRSRSRSRS*···, where the methyl groups of polypropene are alternating (Fig. 1c). When there is no particular regularity of the methyl group orientation, the polypropene is *atactic*. Instead of using *R*, *S* representation for stereochemistry (because it is practically impossible to determine *R* or *S* for any methine carbons), the *isotactic* diad sequences, *RR* or *SS*, are named *meso* (*m*) and the *syndiotactic* ones, *RS* or *SR*, are called racemo (*r*) (Fig. 1d).[4] Thus, the *isotactic* and *syndiotactic* sequences are represented by ···*mmmmmmmm*··· and ···*rrrrrrrr*···, respectively.

The *isospecific* Ziegler–Natta catalysts have evolved after several generations into highly sophisticated heterogeneous catalysts supported on MgCl$_2$, which display high activity and (for propene polymerization) high *isospecificity* when

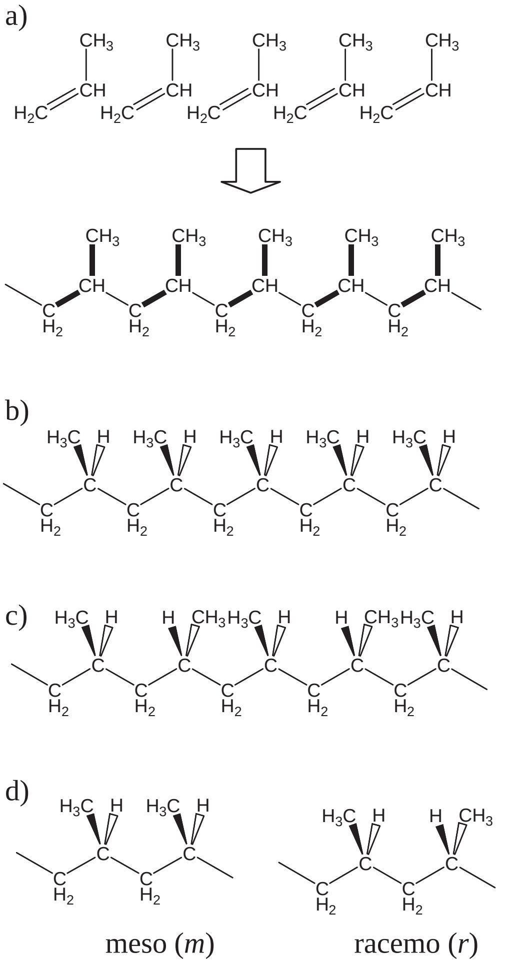
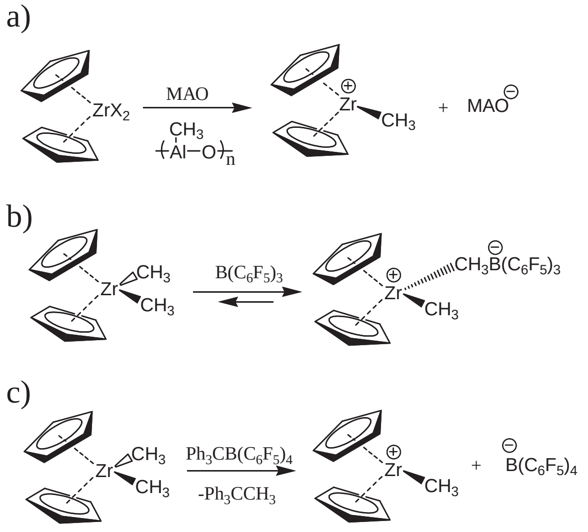


Fig. 1. Regio- and stereochemistry of polypropene.

combined with appropriate electron donors. The heterogeneous olefin polymerization catalyst employed in a real industrial process must have narrow distributions in size, shape, and density, because the catalyst powder is grown to polymer powder having the narrow distribution of the catalyst as if each polymer particle is a large replica of each catalyst particle.[1] Thus, the solid catalyst is magically transformed into white dense free-flowing polymer powder that can serve as a product without removal of catalyst residues or low crystalline byproducts. Despite the extremely complicated composition of the catalysts, the elementary steps of the polymerization reaction (initiation, propagation, chain-transfer, and termination reactions) have been fairly well understood through ingenious experiments and thorough analyses of polymer products. However, a true understanding of the catalytically active species remains elusive due to the heterogeneity of the catalyst and the multiple catalyst species.

Development of *syndiotactic* polypropene followed a different path from the huge commercial success achieved by *isotactic* polypropene. *Syndiotactic* polypropene was first produced by Natta in 1962 using vanadium compounds activated with R_2AlCl (R = alkyl).[5] The *syndioselective* vanadium catalysts are soluble in the polymerization medium and behave as a single-site catalyst (sometimes living catalysts)[6] as opposed to the heterogeneous *isospecific* titanium catalysts; unfortunately, polymerization activity was low and subambient temperatures (close to −78 °C) were required to achieve moderate *syndioselectivity*.



Scheme 1. Activation of metallocene catalysts.

Efforts to investigate homogeneous versions of Ziegler–Natta catalysts started shortly after the historical discoveries of Ziegler and Natta. Titanocene dichloride (Cp_2TiCl_2, Cp = cyclopentadienyl) when combined with R_2AlCl promotes ethene polymerization, but is followed by rapid deactivation.[7] The true discovery of metallocene catalysts relied on an appropriate cocatalyst, methylalumoxane (MAO), synthesized by partial hydrolysis of trimethylaluminum and usually represented by the general formula: $\left(Al(CH_3)O\right)_n$.[8] Although the structures remain unclear, MAO is thought to methylate a metallocene precursor and to generate a cationic methyl species by transforming itself into a weakly coordinating counteranion (Scheme 1a).[9] This process can be observed in a well-resolved manner by using tris(perfluoroaryl)borane, tetrakis(perfluoroaryl)borate salts (Scheme 1b, c) and many other related compounds as activators for metallocenes and non-metallocene catalysts.[9]

The metallocene catalyst displays high activity for olefin polymerization and produces polyolefins with narrow distribution owing to its singular nature of active species (single-site catalyst) contrary to the heterogeneous, multi-site Ziegler–Natta catalysts. The homogeneous nature of the metallocene catalyst also allows us to make significant progress in understanding the steric, electronic, and dynamic structures of active species, and the relationship between the active species and the polymer structures resulted.[10] Stereospecific polymerization of propene with the metallocene catalyst was thus achieved in a short period of time by bridging two Cp rings with appropriate substituents into a rigid ligand framework (*ansa*-metallocenes). The stereoselectivity of metallocene catalysts can be rationally understood in terms of the symmetry of complexes and a repulsive non-bonding interaction between ligands and a growing polymer chain (See below).

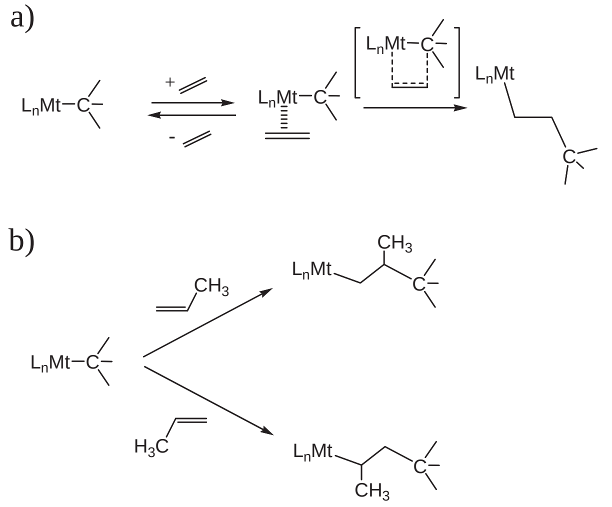
Research on well-defined transition metal complexes for olefin polymerization continues making progress and considerable research interest is currently being focused on non-metallocene complexes.[11] These complexes generally have oxygen and/or nitrogen (sometimes sulfur and phosphorus) as ligating atoms and most often those heteroatoms are incorporated into a chelate ligand structure. Learning from the knowledge obtained with metallocene catalysts, many electrophilic (cationic) complexes were investigated as olefin polymerization catalysts using early transition metals as well as late transition metals. Propene polymerization was examined if a complex fulfilled certain steric requirements with an expectation of stereospecific polymerization. These research activities yielded a wide variety of olefin polymerization catalysts with unique characteristics.

We have been engaged in the development of post-metallocene olefin polymerization catalysts since the mid 1990s with the precarious hope that new catalysts may provide new products possessing new structures/properties and new values. A pivotal output of the project is a series of early transition metal complexes having two phenoxy–imine chelate ligands (FI Catalysts).[12] FI Catalysts are readily varied in structures and properties by systematically changing the phenoxy–imine ligand structures, which can be synthesized straightforwardly from readily available chemicals. Combined with a central metal and a cocatalyst, an enormous library of FI Catalysts has been built up. This diversified library makes FI Catalysts so versatile that polyolefins with desired properties (molecular weight, molecular weight distribution, comonomer intake, chain-end structure, tacticity, and so on) can be obtained sometimes in a predictable way by selecting appropriate combinations of ligands, metal, and cocatalyst.

As an award account, this article is not intended to be a comprehensive review on the non-metallocene olefin polymerization catalysts nor even a review on FI Catalysts. The main objectives of this article are to obtain a general overview of FI Catalysts in order to discuss the unique propene polymerization behavior in a context of static and dynamic molecular structures of the active species, and to clarify generalities and specificities of FI Catalysts to other known catalysts.

2. Propene Polymerization by Transition Metal Catalysts. Olefin polymerization by transition metal catalysts is a two-fold process: i) monomer coordination to the metal center (Mt) of catalytically active species, and ii) insertion of the monomer into the Mt–C bond via σ-bond metathesis to generate a new vacant site for monomer coordination (chain-migratory insertion, Scheme 2a).[13] When a propagating species is schematically depicted as L_nMtR (L: an ancillary ligand; Mt: a transition metal; R: a growing polymer chain), a propene monomer can coordinate to Mt and be inserted into Mt–R in a way that the primary carbon is attached to the metal, resulting in Mt–$CH_2CH(CH_3)$–R (1,2-insertion or primary insertion, Scheme 2b upper path), or in the other opposite way, generating Mt–$CH(CH_3)CH_2$–R (2,1-insertion or secondary insertion, Scheme 2b lower path). To facilitate the insertion process, R and a propene coordinating site are usually positioned *cis* to one another.

Owing to the prochirality of a propene monomer, an asymmetric methine carbon is formed after each chain migratory insertion. For the sake of stereospecific polymerization, a chirality in proximity to the active species is required to discriminate two faces (*re*- or *si*-face) of an incoming propene monomer. In the case of transition metal catalyzed propene polymerization, there can be two chiral sources at the active species.[10] One is the asymmetric carbon of the last inserted monomer unit of a growing polymer chain. The other is chirality elements existing in the L_nMt fragment, which makes the *cis*-bound polymerization site either homotopic, enantiotopic, or diastereotopic. The two origins of stereospecificity can be easily distinguished by examining stereo-defects of polypropene by ^{13}C NMR spectroscopy.[14] When the former chirality dictates the stereochemistry of each monomer enchainment (i.e., chain-end control), a misinsertion reverses the stereochemistry of the following insertions, i.e., ···*RRRR**RS**SSSS*··· or ···*SSSS**SR**RRR*··· (···*mmmm**r**mmmm*···) for *isotactic* polymerization (Fig. 2a) and ···*RSRS**RR**SRSR*··· or ···*SRSR**SS**RSRS*··· (···*rrrr**m**rrrr*···) for *syndiotactic* polymerization (Fig. 2c), resulting in an isolated *m* or *r* diad defect. When the latter chilarity exercises site control, an insertion with incorrect stereochemistry is immediately corrected and the stereo-defects would be ···*RRRR**RSR**RRRR*··· or ···*SSSS**SRS**SSSS*··· (···*mmmm**rr**mmmm*···) for *isotactic* polymerization (Fig. 2b) and ···*RSRS**RRR**SRSR*··· or ···*SRSR**SSS**RSRS*··· (···*rrrr**mm**rrrr*···) for *syndiotactic* polymerization (Fig. 2d), causing a successive *mm* or *rr* triad defect. A chain-end control mechanism can be observed in ionic polymerizations and radical polymerizations as well as in coordination polymerization. In general, the selectivity of chain-end control largely depends on monomer structures, and usually low polymerization temperature is required to achieve even moderate stereoregularity. The site control is unique to transition metal catalyzed polymerization, and can reach a high regularity at higher polymerization temperature, and has plenty of room for deliberate control of stereoregulation by adjusting an L_nMt fragment sterically and electronically.



Scheme 2. Chain migratory insertions of a) ethene and b) propene with primary (upper path) and secondary (lower path) insertion.

Heterogeneous Ziegler–Natta catalysts are known to polymerize propene monomers into highly *isotactic* polypropene via a 1,2-monomer insertion into a Mt–C bond under a site control mechanism. The stereospecific insertion is observed when the growing polymer chain is larger than the methyl

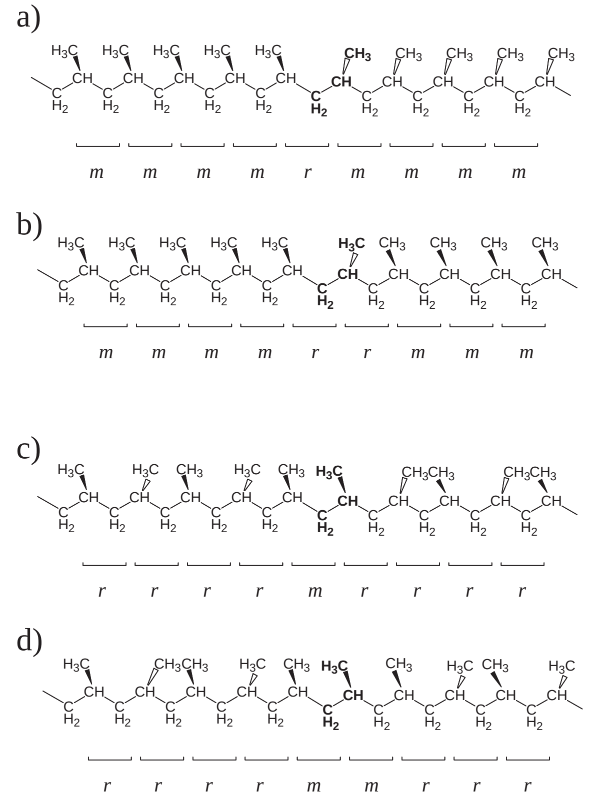


Fig. 2. Schematic representation of a mis-insertion in a) a chain-end controlled *isotactic* sequence; b) a site controlled *isotactic* sequence; c) a chain-end controlled *syndiotactic* sequence; d) a site controlled *syndiotactic* sequence.

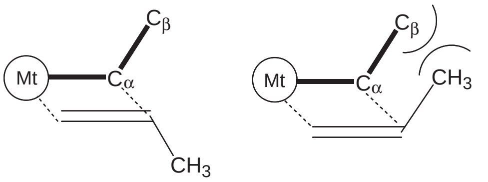


Fig. 3. Schematic representation of propene monomer coordination to a metal center.

group, in other words, the insertion to Mt–CH_3 is non-stereospecific.[15] The process of a stereospecific monomer insertion is thought to be as follows: The C_α–C_β bond of a growing polymer chain is firmly bound to one direction due to a repulsive interaction with ligands (chlorines in inorganic crystal lattice in most cases) of the chiral species. An incoming propene monomer approaches the species in the energetically most favorable way, that is, the double bond of the monomer is parallel to the Mt–C_α bond and the methyl group of the monomer is oriented away from the metal center (1,2-insertion) and *trans* to the C_α–C_β bond of the growing chain (Fig. 3) *irrespective of* stereochemistry of the methine (C_β) carbon (site control). After insertion, the resulting species is anticipated to have the same chirality as the original species and thus causes repetitive insertions under the same stereochemical environment (*isotactic* chain-growth). Note that the ligands of the chiral species do not directly participate in regulating an orientation of an incoming propene monomer but through an intermediacy of steric repulsion with the growing polymer chain.

The early metallocenes such as Cp_2ZrCl_2 are achiral and give *atactic* polypropene upon activation with MAO.[16] By bridging two Cp ligands and introducing appropriate substituents at strategic positions, one can create an asymmetric environment in a metallocene catalyst. Making the best use of homogeneous and well-defined nature of metallocenes, a clear and rational relationship between symmetry of a complex and stereospecificity shown by the complex was established.[10]

Chain growth with group 4 metallocenes involves the same successive 1,2-insertions of a propene monomer into a Mt–C bond of active species as the heterogeneous Ziegler–Natta catalyst, and the methyl group of a coordinating propene monomer is directed *trans* to the C_α–C_β bond by steric repulsion.[17] When a complex possesses C_2 symmetry, the C_α–C_β bond tends to be oriented in the less crowded two quadrants to avoid steric congestion and this orientation is further reinforced by a rigid triangle made by α-agostic interaction of Mt–H_α–C_α.[18] The orientation of the C_α–C_β bond, in turn, determines the coordinating face of a prochiral propene monomer in a way that the methyl group of propene becomes *trans* to the C_α–C_β bond. The homotopic nature of the species generates the identical environment after chain migratory insertion, which ensures successive *isotactic* propene monomer enchainments (Fig. 4a).

The two less crowded quadrants of a complex with C_s symmetry are related by symmetry of the mirror plane, i.e., they are enantiotopic. This leads to alternating face selection of a prochiral propene monomer (*syndiotactic* chain growth) under the conditions where coordination and insertion of propene monomers take place regularly at each site one after the other (Fig. 4b).[19,20] In this scheme, back-skip of the growing polymer chain before the next monomer coordination (site epimerization) causes an isolated *m* stereo-error (*rrrr**m**rrrr*), which in fact becomes more prominent at low monomer concentration.[20] Although chain-end controlled *syndiotactic* polypropene with vanadium catalysts has been known for years, the polymerization requires low temperature approximately below −50 °C, and the *syndiotacticity* is moderate. The *syndiospecific* propene polymerization under site control is one significant achievement with well-defined molecular catalysts. *Syndiotacticity* with metallocene catalysts approaches to 98% of [*rrrr*] and 154 °C of melting temperature even at a polymerization temperature of around 0 °C.[21]

The C_1-symmetric *ansa*-metallocene compounds can be an excellent *isospecific* catalysts when only one quadrant is open for the Mt–C_α–C_β bond and the growing polymer chain is supposed to flip back rapidly after chain migratory insertion to the open quadrant (Fig. 4c). Incoming propene monomers always coordinate to this fixed Mt–C_α–C_β arrangement, which leads to *isotactic* chain propagation.

According to the stereoregulating mechanism as described above, the reason is clear why Cp_2ZrCl_2 and *meso*-ethylene(indenyl)$_2ZrCl_2$ produce *atactic* polypropene.[16] These complexes have a mirror plane that includes Mt–C_α bond and cannot fix the C_α–C_β bond in one direction (Fig. 4d).

The dynamic nature of the active species also has a significant impact on stereospecificity of propene polymerization.

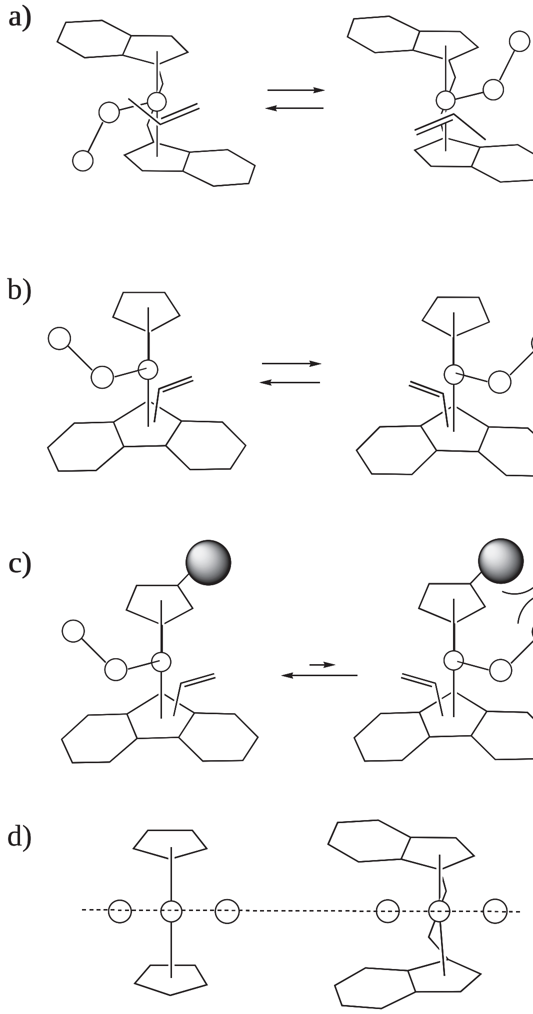
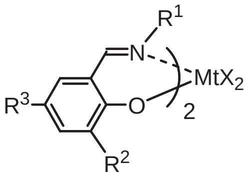


Fig. 4. Chain migratory insertions for stereospecific metallocene catalysts with a) C_2 symmetry; b) C_s symmetry; c) C_1 symmetry; and for aspecific metallocene catalysts with d) C_{2v} and C_s symmetry.

The chain back-skip (described above) causes inversion of chirality for the *syndioselective* C_s-symmetric complexes because the polymerization sites are enantiotopic (site epimerization). When the polymerization sites are diastereotopic (C_1-symmetric), two species isomerize into one another through chain-flipping, each of which might have different reactivity and selectivity. Another dynamic involved in olefin polymerization is the fluxional character of ancillary ligands, which sometimes causes structural changes in the active species. Such fluxional behavior includes, for example, rotation of an indenyl ring,[22] association and dissociation of a hemilabile ligand to the metal center,[23] or association and dissociation of electrophiles such as MAO to basic sites on the ligand.[24] If the rate of fluxional behavior is comparable to the propagation rate, the structural change of the species may be reflected on the sequence of the macromolecule. An ingenious use of this isomerization is the formation of stereoblock polymers. There are several examples of the formation of *isotactic–atactic* stereoblock polymers that exhibit properties as a thermoplastic elastomer.[22,23d]



Mt: group 4 transition metal; X: anion

Fig. 5. General formula of FI Catalysts.

General Features of FI Catalysts

1. Molecular Structures of FI Catalysts. A phenoxy–imine ligand can form a stable chelate complex with a wide array of metals, including scandium,[25] yttrium,[25] titanium,[26] zirconium,[27] hafnium,[28] vanadium,[29] chromium,[30] nickel,[31] and aluminum.[32] Among these, the most widely investigated is a family of group 4 complexes. Hereafter, we will focus on phenoxy–imine ligated group 4 transition metal complexes and refer to these complexes as FI Catalysts in a narrow sense (Fig. 5).

FI Catalysts possess two mono-anionic bidentate phenoxy–imine ligands with a general formula of L_2MtX_2 (L: phenoxy–imine ligand, Mt: group 4 transition metal, X: halogen or other anion). FI Catalysts have distorted octahedral structures having two oxygen atoms in *trans*-positions and two nitrogen atoms and two chlorine atoms in *cis*-positions for most of the complexes that were crystallographically characterized (Fig. 6a). This is consistent with the general tendency observed for similar group 4 complexes, where Mt–O bonds are considerably shorter than Mt–N bonds and Mt–O bonds tend to be in a *trans* orientation in order to avoid steric congestion.[33] However, this *cis*-N, *trans*-O, *cis*-Cl configuration is not a rigid requirement, especially in solution. Minor isomers are sometimes observable with the major *cis*-N, *trans*-O, *cis*-Cl isomer by NMR spectroscopy, even though a single crystal of *cis*-N, *trans*-O, *cis*-Cl isomer characterized by X-ray diffraction was used for the NMR experiment. There are five possible isomers for FI Catalysts if an octahedral framework is assumed (Fig. 6a–e).[12,27] Among them, the *cis*-N, *cis*-O, *cis*-Cl isomer is the only isomer whose two ligands are chemically non-equivalent; two sets of signals with identical intensities therefore appear in the NMR spectrum. This isomer seems to be fairly stable and is often observed as a minor isomer of FI Catalysts. These two non-equivalent ligands are found to be exchangeable on an NMR time scale for the zirconium FI Catalysts (Fig. 6b); bis[*N*-(3-*t*-butylsalicylidene)anilinato]zirconium(IV) dichloride (**1**), and bis{*N*-[3,5-bis(1-methyl-1-phenylethyl)salicylidene]anilinato}zirconium(IV) dichloride (**2**).[34] This reversible transformation presumably occurs via dissociation of an imine nitrogen from the metal, and the other isomers may be involved during the transformation in equilibrium.

The fluxional nature of catalysts can result in multiple characters in olefin polymerization. In fact, complex **2**, which interestingly has a fluxional *cis*-N, *cis*-O, *cis*-Cl arrangement as the major isomer, produces polyethenes with uni-, bi-, and trimodal molecular weight distribution depending on polymerization temperature when activated with MAO.[34]

2. Activation of FI Catalysts. The active species of FI

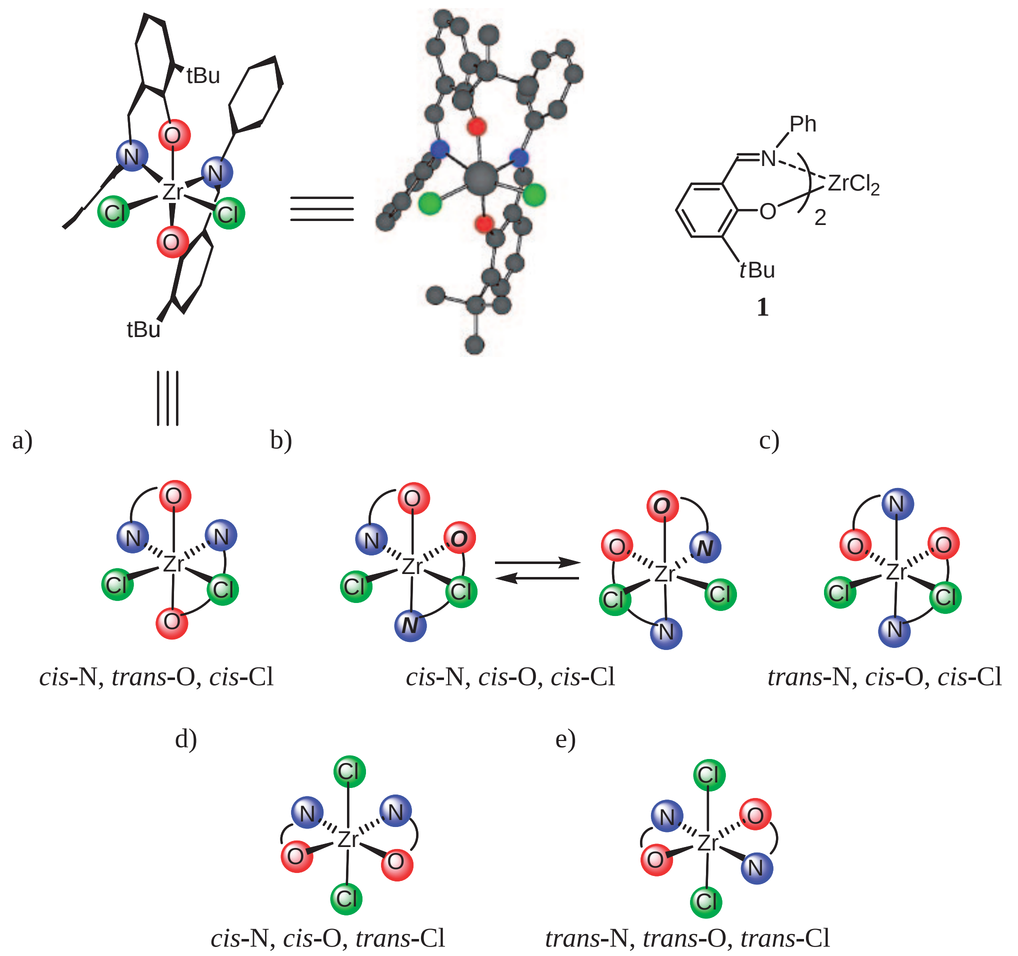


Fig. 6. The solid state structure of a Zr–FI catalyst (**1**) and its possible isomers (b–e).

Catalysts generated by MAO is considered to be a cationic methyl species with a general formula of $[L_2Mt–CH_3]^+$, as is generally accepted for metallocenes and most other well-defined non-metallocene catalysts. However, it has been rather difficult for those cationic methyl species to be identified and characterized by any spectroscopic means in a well resolved manner because of a disturbance of large $Al–CH_3$ signals in MAO, complex equilibria existing in the reaction mixture, and the inherent instability of the species.[35] Taking advantage of a relatively simple ^1H NMR spectrum of bis[*N*-(3-*t*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**3**) and the robust living nature of the species generated from **3** and MAO, a reaction of **3** with MAO was monitored by ^1H NMR spectroscopy in toluene-d_8.[36] One species that immediately formed has a set of downfield shifted ligand signals compared to those of the neutral dichloride (**3**), implicating that the two ligands are chemically equivalent on the NMR time scale and that the species is highly electrophilic (Fig. 7). In addition to these ligand signals, there is one broad signal at δ 1.97 integrated to 3H relative to 2H of the imine signal, which is attributable to the methyl group bound to the titanium metal center. In fact, the addition of a small amount of ethene (1.4 to 7 equiv. of Ti) allows chain growth of polyethene $(\!-CH_2-\!)_n$ at δ 1.32 and $–CH_2–CH_3$ at δ 0.97 as triplet) in exchange for the disappearance of the signal at δ 1.97. Thus, the processes, formation of $[L_2Mt–CH_3]^+$ and a living ethene polymerization to $[L_2Mt(\!-CH_2CH_2-\!)_nCH_3]^+$, are actually seeable for this catalyst. Together with the results of DFT calculations on the cationic methyl species, the species are assumed to have the same *cis*-N, *trans*-O configuration as the neutral **3** with a *cis*-bound methyl group and a vacant site for polymerization reaction.

MAO usually contains 20–30 mol% of $Al(CH_3)_3$ as a contaminant. Some care should be paid to the content of $Al(CH_3)_3$ in MAO because $Al(CH_3)_3$ can act as a reducing agent for the tetravalent metal center to less- or non-reactive lower oxidation states, especially for titanium. Another deactivation pathway caused by $Al(CH_3)_3$ is ligand transfer from $[L_2Mt–CH_3]^+$ onto trimethylaluminum to form $LAl(CH_3)_2$, CH_4, and the remaining uncharacterized group 4 metal compound, which is less reactive toward olefin insertion.[36] The ligand transfer reaction probably involves coordination of aluminum to the phenoxy-oxygen, followed by activation of H–C bond in $Al(CH_3)_3$ with $M–CH_3$ species (Scheme 3a). The ligand transfer reaction seems to occur for both Ti– and Zr–FI catalysts, though the species that has a longer polymer chain, $[L_2Mt–polymer]^+$, seems to be more robust to this side reaction for steric reasons.[36] Because of these deactivation pathways, premixing of FI Catalysts and MAO in the absence of an olefin monomer sometimes deteriorates polymerization activity, while removal of $Al(CH_3)_3$ under vacuum from MAO generally gives good results in terms of activity.

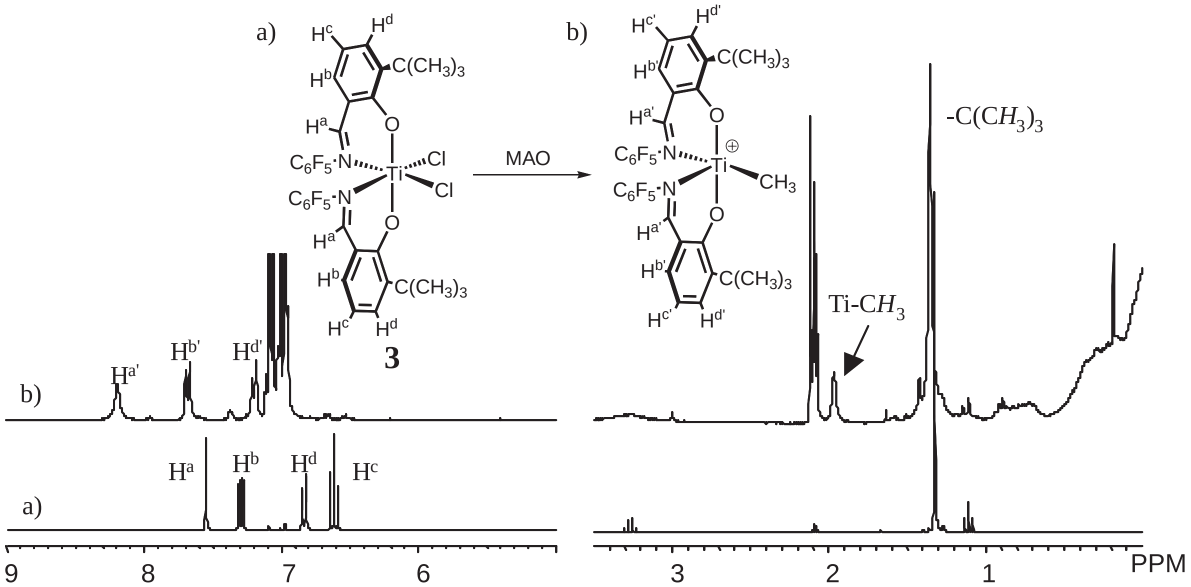
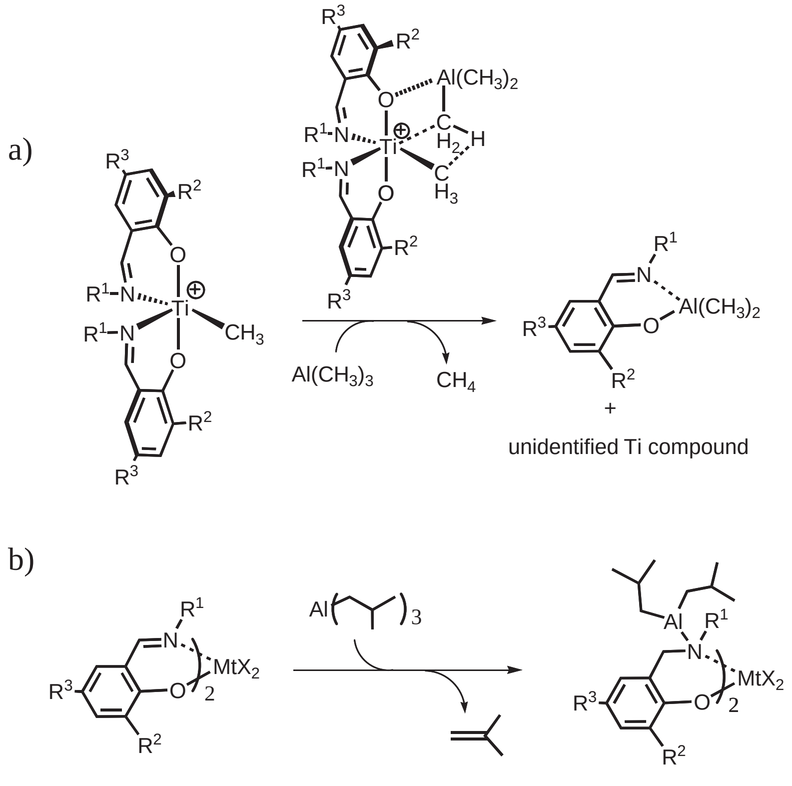


Fig. 7. ^{1}H NMR spectra of a) a Ti–FI catalyst (**3**) and b) **3**/MAO.



Scheme 3. Possible reactions of FI Catalysts and alkylaluminum.

For metallocenes and related complexes, a cationic alkyl species can be generated by $B(C_6F_5)_3$, $EB(C_6F_5)_4$ (E = Ph_3C, $PhN(CH_3)_2H$, $(CH_3CH_2)_2OH$, etc.) or related compounds, and the species formed are similar in character to those which are generated with MAO.[9] When FI Catalysts are activated by $^i Bu_3Al/Ph_3CB(C_6F_5)_4$, polymerization characteristics are strikingly different from those which are observed for MAO activation.[27,37] This is because the imine groups of FI Catalysts, –CH=NR^1, are susceptible to attack by electrophiles and are easily reduced, in this case, by addition of $^i Bu_3Al$ to form $–CH_2–NR^1–Al^iBu_2$ with concurrent formation of isobutene (Scheme 3b). This is supported by the fact that hydrolysis of a catalyst solution treated with $^i Bu_3Al/Ph_3CB(C_6F_5)_4$, gives a phenoxy–amine ligand, while the imine function is intact after activation with MAO and hydrolysis under the same conditions.[27] The reduced species is, in general, lower in polymerization activity than the corresponding MAO-activated species, but tends to polymerize ole-

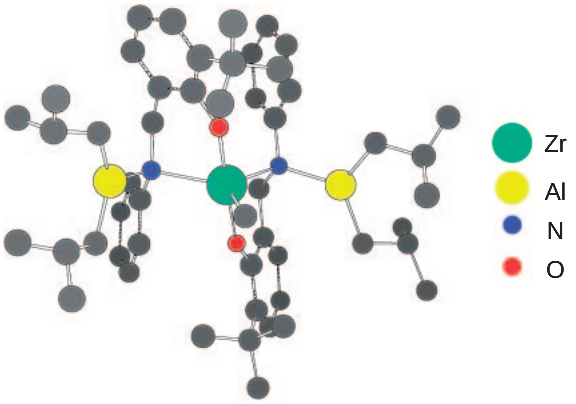


Fig. 8. The calculated cationic methyl species of a Zr–FI catalyst (**1**) reduced by ^{i}Bu$_3$Al.

fins into extremely high molecular weight polymers. At first sight, it can be recognized that the phenoxy–amine ligand is sterically larger but probably less basic than the phenoxy–imine ligand because of Al^{i}Bu$_2$ moiety on the nitrogen (Fig. 8). Although relatively low in polymerization activity, the reduced species exhibits a number of interesting polymerization characteristics. For example, the polymerization activities of a Ti–FI catalyst constantly increase for larger monomers, (1-hexene $<$ 1-octene $<$ 1-decene $<$ 4-methyl-1-pentene),[37c] and the polymers obtained possess very high molecular weight and a large amount of regioirregular units. Even though the reduced species looks sterically crowded, the weaker Mt–N bond could be elongated or the nitrogen could be completely dissociated from the metal to adapt these large α-olefins. The unusual polymerization characteristics of the catalysts may be attributed to the adaptable nature of the ligands.

FI Catalysts sometimes display a multiple-site character in the polymer produced depending on the cocatalyst used in the polymerization and on other reaction conditions (e.g., monomer concentration or solvent choice).[38] This can be attributed to these side reactions, i.e., the reduction of metal or imine functions with alkylaluminum and the formation of unidentified group 4 species after the ligand transfer reaction to aluminum metal, as well as to equilibrium between configurational isomers as described in the previous section.

3. Structural Variation of Phenoxy–Imine Ligands. Ligand modification of FI Catalysts can be done most effectively by varying substituents at R^1, R^2, and R^3 sterically and electronically (Fig. 5).[39] The substituent on the imine nitrogen (R^1) can be incorporated from the corresponding aliphatic or aromatic primary amine. An obvious trend is observed in the relationship between steric bulk of R^1 and molecular weight of polymer, i.e., bulkier R^1 tends to afford a higher molecular weight polymer.[27] In most cases, the molecular weight of polyethene produced with FI Catalysts is slightly affected by monomer concentration, which implies that the main chain transfer reaction has the same reaction order in monomer as the propagation reaction, i.e., that most chains are terminated by β-hydrogen transfer to a coordinating ethene monomer. As shown in Fig. 9, the R^1 substituents are situated in a skewed position at the backside of a *cis*-bound MtX$_2$ polymerization site in a *cis*-N, *trans*-O, *cis*-X octahedral configuration. Thus, a sterically larger R^1 makes an angle of MtX$_2$ fragment narrower by a repulsive non-bonding interaction, which is crystallographically confirmed for a series of Zr–FI catalysts.[40] Since a six-membered ring transition state of the β-H transfer reaction requires a wider angle of the MtX$_2$ fragment than the compact four-membered ring transition state of propagation reaction, it is most likely that large R^1 substituents discourage chain transfer relative to propagation by making a polymerization site more compact, which results in higher molecular weight polymers.

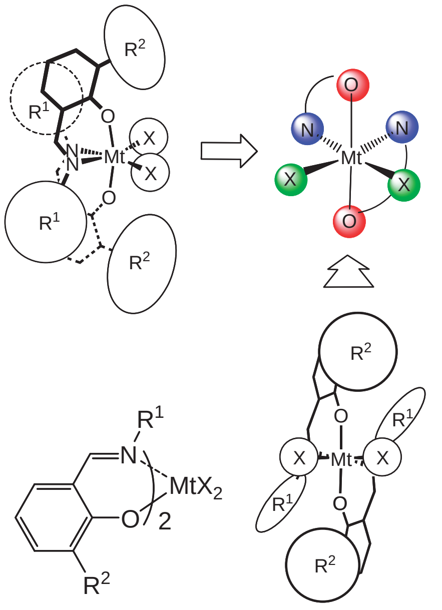


Fig. 9. Steric arrangement of R^1 and R^2 in FI Catalysts having *cis*-N, *trans*-O, *cis*-X configuration.

The R^2 substituents of FI Catalysts protrude above and below the MtX$_2$ plane of a *cis*-N, *trans*-O, *cis*-X octahedral configuration (Fig. 9). Because the *cis*-bound X groups turn to a polymerization site upon activation, one can easily imagine that R^2 substituents would directly participate in a polymerization reaction. In fact, the bulkiness of R^2 affects polymerization activity, comonomer incorporation ability, and polypropene stereoregularity. As discussed in the previous section, one deactivation pathway proceeds through a ligand transfer reaction from FI Catalysts to alkylaluminum, which involves an Mt–O bond cleavage, presumably preceded by Al(CH$_3$)$_3$ coordination to a phenoxy-oxygen.[36] Bulky R^2 substituents effectively prevent deactivation, and there is a clear positive relationship between the bulkiness of R^2 and the ethene polymerization activity.[27] The bulky R^2 may also enhance ion-separation between a cationic active species and a counter anion, making the species more electrophilic. Not surprisingly, this steric protection is felt by an incoming α-olefin monomer and has a significant effect on ethene/α-olefin copolymerization behavior. Thus, FI Catalysts with bulkier R^2 substituents usually display lower α-olefin intake in copolymerization with ethene.[41] The bulkiness of R^2 substituents also influences stereoregularity in *syndiospecific* propene polymerization by FI Catalysts,[26] which will be discussed later.

The effects of the R^3 substituents are relatively subtle and essentially function electronically through chemical bonds. One practically important example is that the methoxy group can improve the thermal stability of Zr–FI catalysts enough to bear industrially practical polymerization conditions at >75 °C.[42] The stereospecificity of Ti–FI catalysts can also be slightly altered by R^3 substituents.

4. Group 4 Transition Metals. It is almost always true that the elements of the second and third transition series are appreciably different from those of the first transition series. This is also true for FI Catalysts, and the differences are striking. FI Catalysts having titanium as a central metal (Ti–FI catalysts) generally give higher molecular weight polymer but lower activity than the zirconium or hafnium congeners when activated with MAO. This general tendency of Ti–FI catalysts can be extended to living polymerization, where practically no chain transfer and no termination reactions are involved. The living nature of Ti–FI catalysts/MAO is especially pronounced when the complexes have phenyl groups as R^1 substituents, possessing at least one fluorine atom at the ortho-position.[26f,26i,43] Complex **3**, with perfluorophenyl group as R^1, defies the common behavior of living olefin polymerization. First, the catalyst can polymerize both ethene and propene in a living manner at far higher activity than the known living catalysts. Second, the living nature of the polymerization is maintained even at 50 °C, and third, the polypropene obtained is moderately to highly *syndiotactic*. The robust living nature of Ti–FI catalysts allows the synthesis of many new block copolymers[43] and chain-end functionalized polyolefins.[44] As a rationale for this unusual behavior, we proposed, based on DFT calculations, that the ortho-fluorine atom has an attractive interaction (electrostatic in nature) with β-hydrogen on a growing polymer chain, which could place strong restraint on chain transfer reactions.[26f,43] This hypothesis is in accord with the observation that the similar fluorinated Zr– and Hf–FI catalysts afford higher molecular weight polyethenes than the corresponding non-fluorinated Zr- and Hf-complexes by a factor of about 20, while the activity enhancement (nearly equal to enhancement of propagation rate) is merely ×1.3–1.9.[28a]

Zr– and Hf–FI catalysts afford relatively low molecular weight polyolefins because of frequent β-hydrogen transfer reactions that result in the formation of terminal double bonds. The molecular weights of polyethenes and chain-end structures are controllable by deliberate molecular design of a catalyst.[27] As described above, by increasing the bulkiness of R^1 substituents, the molecular weight of polyethene can be predictably increased at the cost of reduced activity. However, the effect of bulky R^2 on activity enhancement seems to be additive in this case, and a balance of molecular weight and polymerization activity are satisfactorily obtained by appropriate combinations of R^1 and R^2. Under the conditions where chain transfer to alkylaluminum is suppressed, e.g., by protection with suitable R^2 and/or removal of Me_3Al from MAO, exclusive introduction of vinyl groups at a chain end of a polyethene molecule can be realized (>95 mol%). This can be used as a reactive polymer having desired molecular weight. The differences between Ti–FI and Zr–/Hf–FI catalysts are even greater in the polymerization of propene, as demonstrated in the section below.

Propene Polymerization with FI Catalysts

1. FI Catalysts Activated with MAO. Despite the fact that most of the FI Catalysts are considered to have a C_2-symmetric *cis*-N, *trans*-O, *cis*-Cl configuration as the main isomer, they behave in a quite different way from the *isospecific* C_2-symmetric metallocene complexes in propene polymerization. Ti–FI catalysts with MAO polymerize propene monomers in a moderately to highly *syndiotactic* manner,[26] whereas the corresponding Zr– and Hf–FI catalysts/MAO afford *atactic* to slightly *syndiotactic* polypropene (Table 1).[28b,45] The stereoerror in the *syndiotactic* polypropenes obtained with Ti–FI catalysts is an isolated *m*-type (···*rrrr**m**rrrr*···), indicating that the *syndiospecific* enchainment is mediated via a chain-end control (Fig. 10).[26c,26e,26j,43] Molecular weights of the polypropenes obtained are also strongly affected by the group 4 metal center and follow the same general trend observed for ethene polymerization. Low molecular weight polymers or oligomers having double bonds at one chain-end via β-H transfer are mainly obtained by Zr– and Hf–FI catalysts[28b,45] and much higher molecular weight polypropenes are produced by Ti–FI catalysts. When perfluorophenyl groups are applied as R^1, the catalysts exhibit a robust living nature for propene polymerization with much enhanced *syndioselectivity* relative to the corresponding non-fluorinated catalysts (Table 1, Fig. 10).[26c,26e,26j,43] This may again indicate participation of the ortho-fluorine in realization of the robust living polymerization as well as in the process of stereospecific propene enchainment. The fundamental difference between Ti–FI and Zr/Hf–FI catalysts when activated with MAO may be the regiochemistry of propene insertion. Regarding Ti–FI catalysts as generalized in Scheme 4, a propene molecule is inserted into Ti–R exclusively in a 1,2-fashion (primary insertion) when R is –H[46b,46c] and $–CH_3$.[26j,43,46] Primary insertion of propene is also favored after ethene insertion, i.e., $R = –CH_2CH_2–$.[46b,46c] However, when R becomes $–CH_2CH(CH_3)–$ after primary insertion of a propene monomer, the regioselectivity of primary insertion seems to be comparable with or slightly less energetically favored than the opposite 2,1-type insertion (secondary insertion) depending on catalyst structures and polymerization conditions.[46b,46c,46d] Once secondary insertion begins, which sets in a structure of $–CH(CH_3)CH_2–$ to the chain-end of the active species, the subsequent insertion is preferentially secondary. As a whole, the regioselectivity described above ends up with prevailing secondary insertion and exclusive 1,2-insertion at the initiating chain-end.[46] Propene polymerization via secondary insertion is highly unusual for group 4 transition metal-mediated olefin polymerization and could be a crucial feature for the observed *syndiospecificity*. Despite the fact that the polypropenes obtained with Ti–FI catalysts have a significant amount of regio-error units, the melting temperature of the polypropenes is very high comparable to the highly regio-regular *syndiotactic* polypropenes prepared by metallocene catalysts.[26h] This interesting feature may stem from the subtle balance of regioselectivity toward $Ti–CH_2CH(CH_3)–$, which sometimes causes a considerable length of 1,2-enchained sequences, resulting in regio-block structures (Scheme 4).[26j,43] In contrast, the Zr– and Hf–FI catalysts polymerize propene monomers mostly via ordinary primary insertion.[28b,45]

Table 1. Propene Polymerization with FI Catalysts Activated by MAO

Run	R^1	R^2	R^3	Mt[a) /µmol	P[b) /MPa	T_p /°C	Time /h	A[c)	M_n[d) /×10^4 g mol^{-1}	M_w/M_n[d)	T_m /°C	[rr][e)	Ref.
1	C_6F_5	^{t}Bu	H	Ti, 10	0.1	0	5	2.9	2.36	1.05	137		26e
2	C_6F_5	^{t}Bu	H	Ti, 10	0.1	25	5	3.7	2.85	1.11	137	87	26e
3	C_6F_5	^{t}Bu	H	Ti, 10	0.1	50	5	3.0	1.64	1.37	136		26e
4	C_6F_5	^{t}Bu	CH_3	Ti, 10	0.1	0	5	2.0	1.68	1.04	143		26j
5	C_6F_5	^{t}Bu	CH_3	Ti, 10	0.1	25	5	2.3	1.65	1.11	140		26j
6	C_6F_5	^{t}Bu	CH_3	Ti, 10	0.1	50	5	2.3	1.57	1.48	124		26j
7	C_6F_5	^{t}Bu	^{t}Bu	Ti, 10	0.1	0	5	2.2	1.92	1.05	141		26j
8	C_6F_5	^{t}Bu	^{t}Bu	Ti, 10	0.1	25	5	4.4	2.98	1.15	135	86	26j
9	C_6F_5	^{t}Bu	^{t}Bu	Ti, 10	0.1	50	5	5.3	3.13	3.19	127		26j
10	C_6F_5	H	H	Ti, 10	0.1	25	5	30.7	18.9	1.51	n.d.[f)	43	26j
11	C_6F_5	CH_3	H	Ti, 10	0.1	25	5	68.8	26.0	1.22	n.d.[f)	50	26j
12	C_6F_5	^{i}Pr	H	Ti, 10	0.1	25	5	31.1	15.4	1.16	n.d.[f)	75	26j
13	C_6F_5	$SiMe_3$	H	Ti, 10	0.1	0	5	3.0	2.47	1.08	156	94	26j
14	C_6F_5	$SiMe_3$	H	Ti, 10	0.1	25	5	5.9	4.70	1.08	152	93	26j
15	C_6F_5	$SiMe_3$	H	Ti, 10	0.1	50	5	4.7	3.51	1.23	149	90	26j
16[h)	C_6H_5	H	H	Ti, 100	0.37	0	6	0.4	74/1.5[i)	2.93/1.51[i)	n.d.[f)		38a
17[h)	C_6H_5	CH_3	H	Ti, 100	0.37	0	6	6.7	6.87	1.47	n.d.[f)		38a
18[h)	C_6H_5	^{t}Bu	H	Ti, 100	0.37	0	6	1.0	0.43	1.38	97	62.9[g)	38a
19[h)	C_6H_5	$SiMe_3$	H	Ti, 100	0.37	0	6	1.6	8.09	1.73	140	83.7[g)	38a
20[h)	C_6H_5	^{t}Bu	CH_3	Ti, 100	0.37	0	6	0.9	0.50	1.39	101	66.4[g)	38a
21[h)	C_6H_5	^{t}Bu	^{t}Bu	Ti, 100	0.37	0	6	2.1	0.71	1.55	107	68.8[g)	38a
22	C_6F_5	^{t}Bu	H	Zr, 5	0.1	0	0.5	372	0.15	2.22	n.a.[j)		28b
23	C_6F_5	^{t}Bu	H	Zr, 5	0.1	25	0.5	428	0.13	2.34	n.a.[j)		28b
24	C_6F_5	^{t}Bu	H	Zr, 5	0.1	50	0.5	328	0.13	2.23	n.a.[j)		28b
25	C_6F_5	^{t}Bu	H	Hf, 10	0.1	0	1.5	333	3.19	2.29	n.d.[f)	37	28b
26	C_6F_5	^{t}Bu	H	Hf, 10	0.1	25	1.5	380	0.99	2.73	n.d.[f)	44	28b
27	C_6F_5	^{t}Bu	H	Hf, 10	0.1	50	1.5	123	0.22	2.65	n.d.[f)	42	28b
28	C_6H_5	^{t}Bu	H	Zr, 5	0.1	0	0.5	308	0.02	1.31	n.a.[j)		28b
29	C_6H_5	^{t}Bu	H	Zr, 5	0.1	25	0.5	688	0.02	1.55	n.a.[j)		28b
30	C_6H_5	^{t}Bu	H	Zr, 5	0.1	50	0.5	84	n.d.	n.d.	n.a.[j)		28b
31	C_6H_5	^{t}Bu	H	Hf, 10	0.1	0	1.5	25	0.05	1.70	n.a.[j)		28b
32	C_6H_5	^{t}Bu	H	Hf, 10	0.1	25	1.5	59	0.04	1.62	n.a.[j)		28b
33	C_6H_5	^{t}Bu	H	Hf, 10	0.1	50	1.5	6	n.a.[j)	n.a.[j)	n.a.[j)		28b

a) group 4 transition metal (Al/M = 250); b) propene pressure; c) activity in g-PP/mmol•h; d) determined by GPC; e) determined by ^{13}C NMR; f) not detected; g) [$rrrr$]; h) Al/M = 150; i) bimodal; j) not applicable.

The observations made with Ti–FI catalysts are obviously different from those for the *isospecific* C_2-symmetric metallocenes, which polymerize propene in 1,2-insertion via a site-control mechanism, but apparently similar to those for soluble vanadium catalysts, where the monomer insertion is secondary and the polypropene with low to moderate *syndiotacticity* is formed via a chain-end control mechanism.[47] Because of the well-defined nature of FI Catalysts relative to the classical vanadium catalysts, intriguing results were obtained by systematically changing molecular structures. A steric modulation of R^2 substituents gives a sharp increase in *syndioregularity* proportional to the volume of the R^2, up to 94% of rr triad for the Me_3Si group (Table 1, Run 13).[26h,26j] If one compares between C_6H_5 and C_6F_5 as R^1, the fluorinated complex tends to give higher *syndioregularity* if the R^2 and R^3 are identical. The effect of R^3 is more subtle and complicated. For $R^1 = C_6F_5$ and $R^2 = {}^t$Bu, the *syndioregularity* is on the order of $R^3 = CH_3 >$ ^{t}Bu > H at 0 °C polymerization temperature, CH_3 > H > ^{t}Bu at 25 °C, and H > ^{t}Bu > CH_3 at 50 °C, showing that the *syndioregularity* is more rapidly deteriorated at higher polymerization temperature for the complexes having alkyl groups as R^3, while the complex with R^3 = H exhibits almost constant *syndioregularity* in this temperature range.[26j] All the results obtained here are rather unexpected in view of traditional chain-end control, in which stereospecificity is governed by the asymmetry of the last inserted monomer unit, while the chain-end controlled *syndioselectivity* with FI Catalysts is obviously affected by the ligand structures. The observed chain-end controlled *syndioselectivity* was theoretically explained on the hypothesis that the FI Catalysts are fluxional between Δ

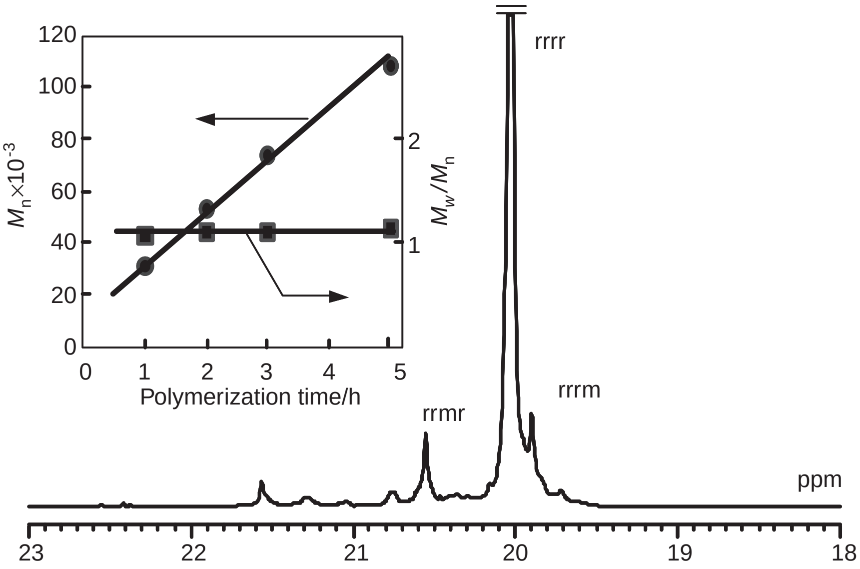
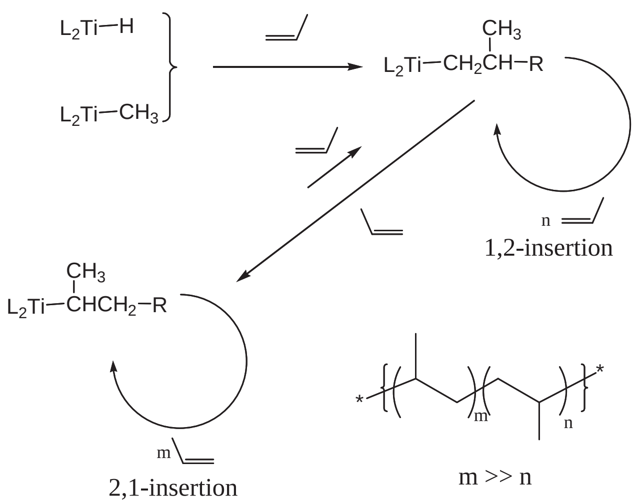


Fig. 10. Expanded ^{13}C NMR spectrum of a polypropene obtained with **3**/MAO. Inset: The relationship between molecular weight and molecular weight distribution vs polymerization time in a propene polymerization with **3**/MAO.

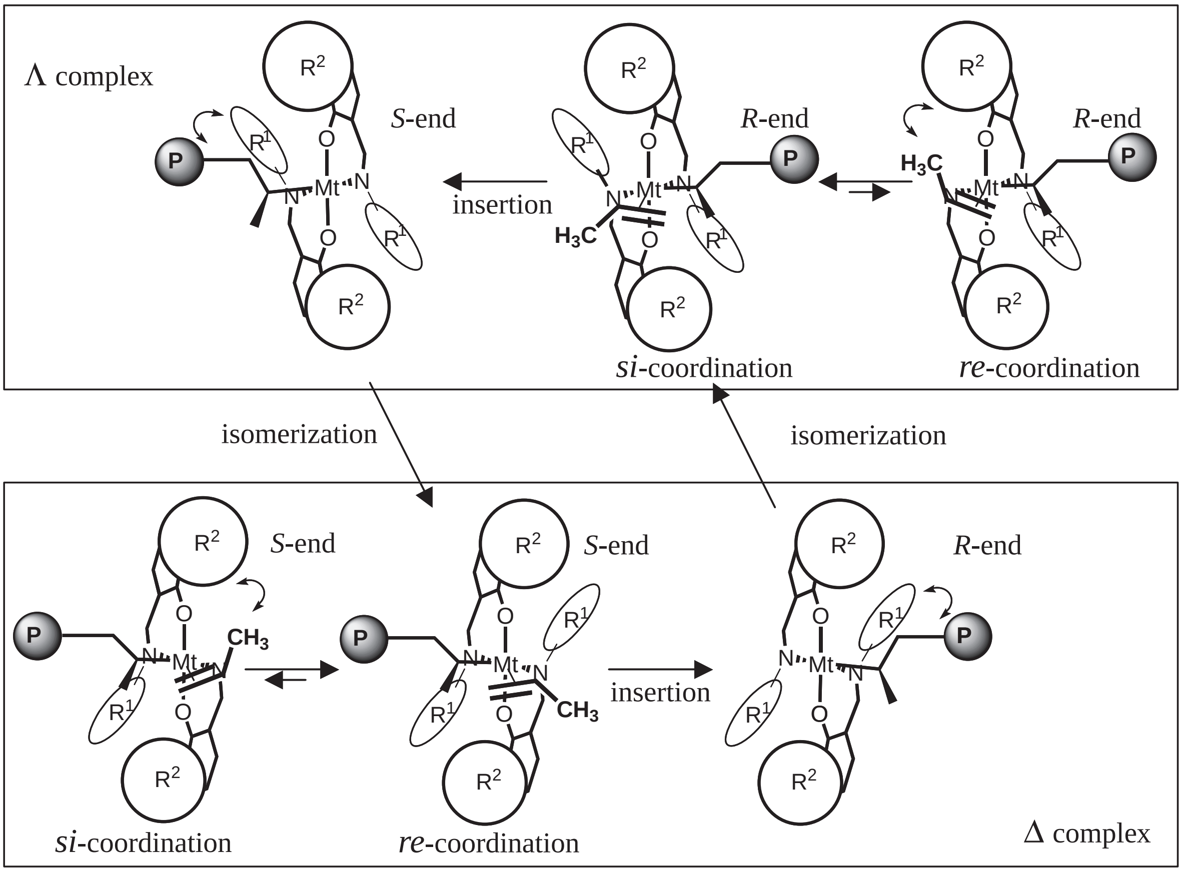


Scheme 4. Regioselectivity observed for Ti–FI catalysts.

and Λ form of their *cis*-N, *trans*-O, *cis*-Cl configuration (Scheme 5).[48] In this C_2-symmetric environment, two diagonal quadrants are less crowded relative to the other two where R^2 substituents are situated. There are four possible stereoisomers in combination with enantiomers of the complexes (Δ and Λ) and the asymmetric carbon of the last secondarily inserted monomer unit (*R* and *S*, or *re*-chain and *si*-chain). Because asymmetry at α-carbon is situated in an inner sphere of the active center and has larger interaction with ligands of the active center, Δ/*si*-chain (and Λ/*re*-chain) is differentiated in energy by 1.4 kcal/mol from Δ/*re*-chain (and Λ/*si*-chain) because of a repulsive non-bonding interaction between growing polymer chain and R^1 substituents. This energy difference may be sufficiently large to drive the isomerization from Δ/*re*-chain (Λ/*si*-chain) to Λ/*re*-chain (Δ/*si*-chain). If we start with a stable Δ/*si*-chain, a propene monomer coordinating at the *re*-face takes precedence over *si*-face coordination due to steric repulsion between the methyl group of the coordinating propene and the R^2 substituents on the ligands. A subsequent chain-migratory insertion leads to Δ/*re*-chain, which is subject to the isomerization to Λ/*re*-chain. The Λ/*re*-chain is the mirror image of the Δ/*si*-chain at the beginning and prefers *si*-face to *re*-face coordination. The opposite preference of *re*-chain to *si*-face and vice versa leads to overall *syndioselective* chain propagation. This scenario, which was originally proposed for the soluble vanadium catalysts,[49] is in good accordance with the observation that the steric bulk of R^2 has pronounced effect on *syndioselectivity*.[26h,26j] Although the postulated inversion between Δ and Λ form is not experimentally supported, FI Catalysts are likely to be fluxional in solution, as was already reported for some Zr–FI catalysts[34] and related complexes,[33] probably via dissociation of an Mt–N bond.

Propene polymerization with FI Catalysts activated with MAO in comparison with other representative catalysts is summarized in Table 2. The key features in common between Ti–FI catalysts and vanadium catalysts to afford *syndiotactic* polypropenes under chain-end control would be an octahedral geometry of the active species, secondary insertion observed in propene polymerization, and possible fluxionality between enantiomers (Δ and Λ form). The fluxionality alone seems insufficient to achieve the *syndioselectivity*, because the structurally similar and likely fluxional Zr– and Hf–FI catalysts are only slightly stereoselective.[28b,45] Chirality at β-carbon, resulting from 1,2-insertion of Zr– and Hf–FI catalysts, has much smaller interaction with the ligands, which would cause rather random Δ/Λ isomerization. It should also be pointed out that the *isospecific* catalysts, either *ansa*-metallocenes or heterogeneous Ti catalysts, have rigid and non-fluxional ligand frameworks.

2. FI Catalysts Activated with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$. The active species of FI Catalysts generated by ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ is assumed to be reduced at the imine function by ^{i}Bu$_3$Al, as already introduced in the section above.[27] The postulated species, therefore, has –CH$_2$–NR^1–Al^{i}Bu$_2$ instead of –CH=NR^1 (Fig. 8) and generally displays lower activity to-



Scheme 5. A proposed mechanism for the chain-end controlled *syndiospecific* propene polymerization with Ti–FI catalysts activated with MAO.

Table 2. Comparison of the Catalyst Structures and Propene Polymerization Characteristics

	Heterogeneous Ziegler–Natta	*ansa*-Metallocene	Homogeneous vanadium	Ti–FI/MAO	Zr– or Hf–FI/Borate[a)]
Geometry	octahedral[b)]	tetrahedral	octahedral[b)]	octahedral	octahedral[b)]
Insertion	primary	primary	secondary	secondary	primary
Tacticity	*isotactic*	*iso-/syndiotactic*[c)]	*syndiotactic*	*syndiotactic*	*isotactic*
Fluxionality	no	no	possible	possible	not clear

a) $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$; b) presumably; c) depending on the catalyst structure.

ward polymerization but gives higher molecular weight polyolefins than the corresponding MAO-activated FI Catalysts.[26g,27]

Propene polymerization with the reduced species follows this general trend, but marked differences of polymerization characteristics for different metal centers and ligand substituents are observed just as for the MAO-activated FI Catalysts but in an opposite selectivity. A Ti–FI catalyst, bis[*N*-(3-*t*-butylsalicylidene)anilinato]titanium(IV) dichloride (**4**), yields ultra-high molecular weight *atactic* polypropene with a significant amount of regioirregular units upon activation with $^{i}Bu_3Al/Ph_3CB(C_6F_5)_4$.[37b] On the other hand, the corresponding Zr– and Hf–FI catalysts afford rather *isotactic* polypropenes with *mmmm* tacticity of 36% for the Zr and 56% for the Hf.[37b] In these polymerizations, the product obtained with the Ti catalyst **4** exhibits relatively broad molecular weight distribution ($M_w/M_n = 4.15$), indicating multiple active species, while the Zr and the Hf catalysts demonstrate single-site polymerization characteristics. The *isospecificity* of the catalyst can be improved by changing ligand substituents. Bulkiness of R^2 substituents has tremendous impact on *isotacticity* of the polypropene produced, with the best results obtained thus far using a combination of $R^1 = $ cyclohexyl, $R^2 = $ adamantyl, and $R^3 = CH_3$.[37d] Although these catalysts exhibit multiple-site character, *isotacticity* in *mmmm* pentad reaches 97% with a melting temperature of 165 °C for the polymer after fractionation with boiling hexane. Microstructural analyses of these *isotactic* polypropenes suggested that the polymerization proceeds via a site control mechanism with primary insertion of propene monomers.[37d] Although the structure of the active species remains elusive, there might be two possibilities to rationalize the observed *isospecificity*. The first possible explanation is that the presumed phenoxy–amine species possesses a C_2-symmetric octahedral *cis*-N, *trans*-O, *cis*-Cl con-

Table 3. Qualitative Polymerization Characteristics of FI Catalysts

		MAO	^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$
Ti–FI	Polymer MW	high (livingness)	extremely high
	Stereospecificity	moderately to highly *syndiotactic*	*atactic*
	Regiospecificity	secondary insertion	regioirregular
Zr/Hf–FI	Polymer MW	low in general (β-H transfer)	extremely high
	Stereospecificity	*atactic* to slightly *syndiotactic*	moderately to highly *isotactic*
	Regiospecificity	primary insertion	primary insertion

figuration similar to the non-reduced phenoxy–imine (Fig. 8). However, fluxional inversion of chirality may be inhibited by the large substituents on the amine nitrogen. The second possibility is the incomplete reduction of imine function by ^{i}Bu$_3$Al, which may result in C_1-symmetric (phenoxy–imine)(phenoxy–amine)M–R species. In either case, an *isospecific* polymerization can occur via primary insertion of propene monomers in a similar mechanism for the C_2- and C_1-symmetric metallocene catalysts.

Conclusion

phenoxy–imine ligands can generate highly active olefin polymerization catalysts in conjunction with group 4 transition metals (FI Catalysts), and the catalysts display a number of interesting polymerization characteristics. General features of olefin polymerization with FI Catalysts are briefly summarized in Table 3. With FI Catalysts, we have acquired a high degree of freedom for the design and synthesis of a wide array of polyolefins with well-defined molecular architectures in molecular weight, molecular weight distribution, monomer sequence, stereo- and regiochemistry of α-olefin units, chain-end structures, etc. The versatility of FI Catalysts seems to be derived from i) diversified and tunable ligand structures, ii) large and characteristic differences between Ti and Zr/Hf as metal centers, iii) susceptibility to electrophiles of coordinating heteroatoms in the ligands, and iv) fluxionality between configurational isomers. The proposed fluxional behavior, together with the intriguing ortho-fluorine effect to realize the robust living and highly *syndiotactic* polymerization, might provide new tools for highly controlled olefin polymerizations.

In this article, we have correlated the molecular features and the polymerization characteristics of FI Catalysts, albeit at a primitive stage. We believe that further understanding of the mechanistic aspects of FI Catalysts will provide tremendous opportunities for the development of new catalysts and value-added polymer products with improved performance.

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