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Mechanism of Propylene Insertion Using Bis(phenoxyimine)-Based Titanium Catalysts: An Unusual Secondary Insertion of Propylene in a Group IV Catalyst System

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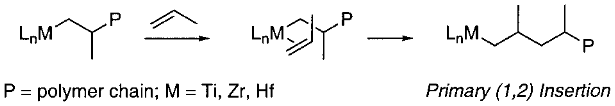
Abstract: A highly regioselective secondary enchainment of propylene in a group IV catalyst system is reported. End-group analysis of polypropylene formed using the phenoxyimine-based titanium catalysts revealed a reversal in the regioselectivity of insertion for this class of catalysts. To the best of our knowledge, bis(phenoxyimine)-based titanium complexes are the only known group IV catalysts that insert propylene with exclusive 2,1-regiochemistry. Insertion of propylene into the initiating titanium hydride occurs with high 1,2-regiochemistry. Subsequent insertions into primary titanium alkyls are regiorandom, while insertions into secondary titanium alkyls proceed with high 2,1-regioselectivity. Cyclopolymerization and ethylene/propylene copolymerization strategies are employed to support this proposal.

Introduction

Since their discovery in the 1950s,[1,2] Ziegler−Natta catalysts have evolved from multisite heterogeneous mixtures[3] to well-defined single-site homogeneous catalysts capable of remarkable control in olefin polymerization.[4−8] Sinn and Kaminsky[9] opened the door to a new era of olefin polymerization with the discovery that methylaluminoxane (MAO) activates group IV metallocenes for polymerization of olefins. This started the wave of homogeneous catalysts that has dominated the literature for the past 20 years. Along with impressive breakthroughs in control of stereochemistry,[4] these single-site catalysts have led to a greater understanding of the polymerization mechanism, providing the basis for the development of improved classes of catalysts. A coordinative insertion mechanism for olefin polymerization has been demonstrated for group IV Ziegler−Natta catalysts;[10] these reactions are generally agreed to proceed by coordination of an olefin to a vacant site,[11−13] followed by migratory insertion of the coordinated olefin into the growing polymer chain (Scheme 1). For heterogeneous Ziegler−Natta catalysts as well as metallocenes, α-olefin insertions into metal−alkyl bonds occur predominately with primary (1,2) regiochemistry, where the unsubstituted alkene carbon becomes bound to the metal. Theoretical studies by Morokuma predicted a clear preference for primary insertion due to both electronic and steric factors, in agreement with experimental observations.[14] However, small amounts (<1%) of regioerrors are commonly observed in polypropylenes (PPs) synthesized using metallocene catalysts, especially with isospecific zirconocenes.[5] In such polymerizations, 2,1-insertions typically lower catalyst activity and molecular weights of the polymers through competing chain release processes.[15] Because of the higher barrier to olefin insertion into the more bulky secondary metal-alkyl species, insertion rates are slowed, and β-hydride elimination and chain-end isomerization (1,3-insertion) become more competitive with chain growth.

Scheme 1



P = polymer chain; M = Ti, Zr, Hf

Primary (1,2) Insertion

Despite the clear preference for primary insertion, a few group IV catalysts have been shown to operate with higher levels of secondary insertion (Figure 1). One such example is the zirconocene *rac*-$C_2H_4(4,7\text{-}Me_2H_4Ind)_2ZrCl_2$ (**1**) of Spaleck,[16,17]

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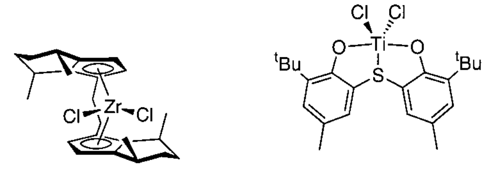
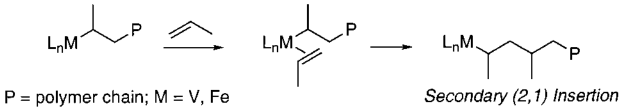


1
rac-$C_2H_4(Me_2H_4Ind)_2ZrCl_2$

2
(TBP)TiCl_2

Figure 1. Catalyst precursors for the synthesis of regioirregular polypropylenes.

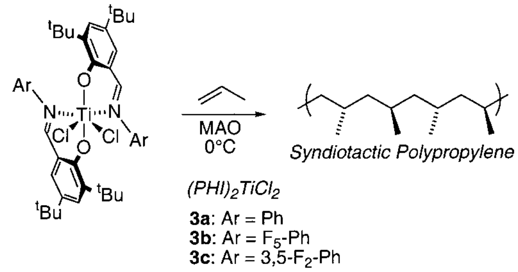
Scheme 2



which when activated with MAO polymerizes propylene with as high as 19% regioinversion. Kakugo and co-workers also discovered that the sulfur-bridged bisphenolate titanium catalyst (TBP)TiCl_2 (**2**) produced nearly completely regioirregular polypropylenes.[18] However, to the best of our knowledge, no system in the extensive literature on group IV catalysts has been reported to insert α-olefins with exclusive secondary regiochemistry.

In contrast to group IV systems, catalysts based on other metals have been shown to polymerize α-olefins by secondary insertion (Scheme 2). In the 1960s, Natta and Zambelli reported a series of homogeneous vanadium-based catalysts that polymerized propylene to give syndioenriched polymers.[19] Further study revealed that the monomer was enchained with secondary regiochemistry, and stereocontrol was derived from a chain-end mechanism.[20] More recently, iron-based catalysts discovered by Brookhart[21] and Gibson[22] have been shown to polymerize propylene by secondary insertion to produce polymers that are moderately isotactic through a chain-end control mechanism.[23−25]

Scheme 3



In an effort to expand the field of nonmetallocene catalysts for stereoselective α-olefin polymerization,[7] we recently discovered a new family of catalysts for the syndiospecific polymerization of propylene (Scheme 3).[26] Further investigation into this lead resulted in a complex capable of the highly syndiospecific and living polymerization of propylene, as well as the synthesis of ethylene and propylene-based block copolymers.[27] These titanium chlorides **3a**−**c** bearing phenoxyimine (PHI) ligands, based on a class of compounds explored extensively by Mitsui for ethylene polymerization,[28−35] were initially targeted by us as catalysts for the isospecific polymerization of propylene. As with the chiral C_2-symmetric metallocenes discovered by Ewen[36] and Brintzinger and Kaminsky,[37] we reasoned that **3a**−**c**/MAO might be capable of isospecific enantiomorphic site control in the polymerization. To our surprise, these compounds produced polypropylenes that were highly syndiotactic.[38] Since this discovery, we have been working to uncover the mechanism by which these chiral C_2-symmetric catalysts perform a syndiospecific polymerization instead of producing isotactic polymers like the symmetrically related *ansa*-metallocenes. In our initial report,[26] we proposed that the selectivity was derived from chain-end control enhanced by a secondary mechanism of enchainment. We based our proposal on the high level of chain-end control of stereochemistry typical of such a mechanism, as well as on the unusually high activity for ethylene polymerization, modest activity for propylene polymerization, and inactivity for 1-hexene polymerization. Fujita and co-workers have recently reported the first evidence consistent with our proposal; end groups of polypropylenes formed using complexes similar to **3b** were consistent with elimination following 2,1-insertion of propylene.[39] Herein we provide additional evidence for our proposal through analysis of polymer end groups, copolymerization, and a new propagation-based strategy for regiochemistry elucidation.

As we previously reported, ^{13}C NMR revealed that a chain-end control mechanism was responsible for the observed stereocontrol in the polymerization.[26,27] Isolated *m*-dyads were identified as the lone source of stereoerrors ($[mrrr] = [rmrr]$), consistent with a chain-end control mechanism. However, such an extremely high level of chain-end control was unprecedented

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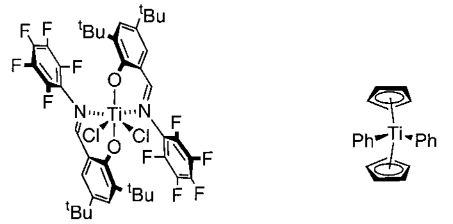
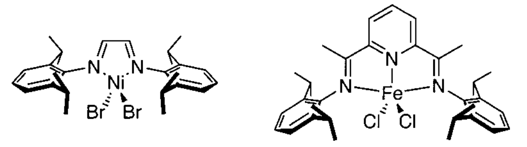


3b **4**

Syndiotactic Polypropylene [*rrrr*] = 0.96 at 0°C

Isotactic Polypropylene [*mmmm*] = 0.52 at −45°C



5 **6**

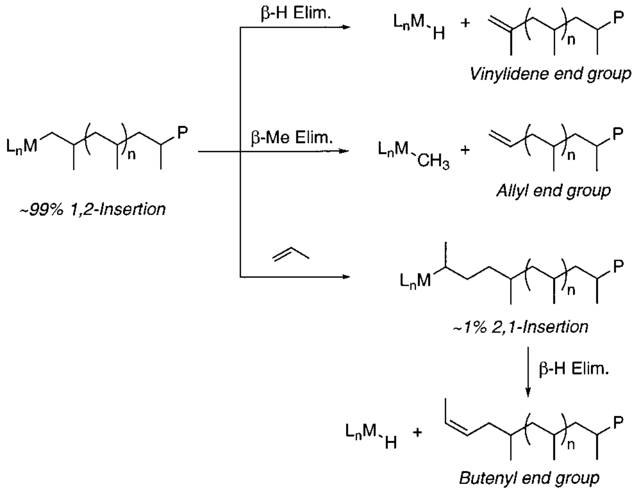
Syndiotactic Polypropylene [*rrrr*] = 0.64 at −78°C

Isotactic Polypropylene [*mmmm*] = 0.62 at −20°C

Figure 2. Catalyst precursors for the synthesis of stereoregular polypropylenes by chain-end control mechanisms.

in a propylene polymerization; when activated by MAO, the pentafluoro-catalyst **3b** produces PP with a *rrrr*-pentad[5] content of 0.96 at 0 °C ($P_r = 0.99$).[27] Moderate to high degrees of chain-end control have been observed for several C_{2v}-symmetric catalyst precursors (Figure 2). In the 1980s, Ewen found that the Cp_2TiPh_2(**4**)/MAO catalyst system produced partially isotactic polypropylene at low temperatures ($P_m = 0.85$, [*mmmm*] = 0.52 at −45 °C).[36] However, stereocontrol was completely diminished at elevated temperatures as the resulting polymer was completely atactic ($P_m = 0.50$ at 25 °C). Outside the phenoxyimine-based catalyst **3b**, the highest previously observed degree of chain-end control in a syndiospecific propylene polymerization was reported by Pellecchia, who found that the diimine-ligated nickel complex **5**/MAO produced polypropylene with an *r*-dyad content of 89% ([*rrrr*] = 0.64) at −78 °C.[40] Mechanistic analysis confirmed that the polymerization proceeded predominately by a primary insertion mechanism, as in metallocene systems.[41−43] Again, polymerization at ambient temperatures produced an atactic polymer having a highly irregular microstructure due to chain walking. Similarly, Brookhart reported that the iron-based catalyst **6** bearing bis(imino) pyridyl ligands produced isotactic polypropylene at −20 °C with a high degree of specificity ($P_m = 0.91$, [*mmmm*] = 0.69).[25] These catalysts are unique in their ability to produce stereoregular polymers through a chain-end mechanism at ambient temperatures; while the above examples required low temperatures to achieve high levels of stereocontrol, the iron-based systems produced isotactic-enriched polymers even at 20 °C ($P_m = 0.81$, [*mmmm*] = 0.43).[24] As mentioned above, this phenomenon was attributed to an unusual 2,1-insertion mechanism. In the polymerization, the pendant chiral center of the growing polymer chain is placed in closer proximity to the metal center, thus exerting a greater influence on the next monomer insertion. This phenomenon is also responsible for the observed stereocontrol in vanadium-based catalysts, which produce moderately syndiotactic polypropylenes by chain-end control enhanced by secondary propylene insertion.[20] With these leads, it seemed reasonable that the extremely high levels of stereoregularity in polypropylenes produced by **3b**/MAO might be the result of a similar secondary insertion process.[26]

Scheme 4



Results and Discussion

End-Group Analysis. In an effort to elucidate the mechanism of polymerization, ^{13}C NMR spectra of polypropylenes from the Ti-based catalysts were evaluated to detect end groups formed by initiation and chain termination processes. Typical metallocene catalysts produce polypropylenes with characteristic end groups resulting from chain release reactions, primarily *β*-hydride and/or *β*-methyl transfer (Scheme 4).[15] In processes that compete with chain growth, these catalysts participate in different types of chain release, generating a free polymer chain along with an active metal-hydride or metal-alkyl species capable of propagating a new polymer chain. Three such processes are typically observed in propylene polymerizations with metallocene catalysts. *β*-Hydride transfer following a primary insertion releases a vinylidene-terminated PP, while *β*-methyl elimination after a primary insertion yields PP bearing an allyl end group. A third important chain release process is *β*-hydride transfer following a 2,1-insertion; as discussed above, a misinsertion of this type generates a secondary chain end into which monomer insertion is slowed, making chain release or chain-end isomerization more competitive. Indeed, this process is responsible for lowering the molecular weight of polymers produced by catalysts that operate with higher levels of misinsertion. For the metallocenes, this *β*-hydride transfer has been shown to occur from the internal methylene, producing 2-butenyl end groups typically of cis-configuration.[15] With the iron-based catalyst **6**, which propagates exclusively by a secondary insertion mechanism, *β*-hydride transfer is also the main type of chain release but it occurs exclusively from the terminal methyl, generating allyl-terminated PPs.[24,25]

Although evaluation of the olefinic end groups provides mechanistic information, this method can be misleading because it gives evidence solely of the final insertion event before chain release and is often not representative of the propagation process.

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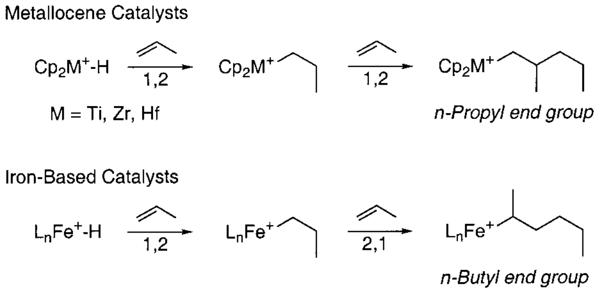
Scheme 5



Excellent examples of this are propylene polymerizations with metallocene catalysts in which the main mode of insertion is primary but a small amount of misinsertion (∼1%) serves to lower catalytic activity and the molecular weight through competitive chain release. In polymers synthesized with the C_2-symmetric *ansa*-zirconocenes, for example, butenyl end groups often become more prominent than vinylidene end groups even in the presence of low amounts of regioerrors.[15] To gain a more representative picture of the mechanism of propagation, end groups arising from the initiation process were also evaluated.

As stated above, the common types of chain release in olefin polymerizations generate, respectively, metal-hydride or metal-methyl species capable of growing a new polymer chain. For metallocene catalysts, insertions into the metal-hydride are primary and produce *n*-propyl initiated PP (Scheme 5).[5] Similarly, primary insertions into the metal-methyl species account for the presence of isobutyl end groups. Polypropylenes from the iron-based catalyst **6**, however, contained saturated end groups not observed in PPs from metallocene catalysts (*n*-butyl end groups are however observed in the case of hydrogenolysis after 2,1-insertion of propylene).[24,25] This catalyst generates a PP initiated by an *n*-butyl species as the result of the unusual secondary insertion mechanism (Scheme 5). As described above, chain release is through β-hydride elimination, leaving a metal-hydride species. Insertion into this hydride is exclusively primary, but the second insertion into this iron-*n*-propyl species is highly specific and secondary, yielding *n*-butyl initiated PP. The presence of this end group, along with labeling studies, was instrumental in demonstrating the unusual secondary monomer enchainment insertion in this system.

In an effort to elucidate the mechanism by which our catalysts polymerize propylene with extremely high syndiospecificity under mild reaction conditions, we performed end-group analysis by evaluating the ^{13}C NMR of PPs synthesized by **3b**/MAO. However, the very nature of polymerization of propylene with this catalyst made the analysis difficult because of the absence of chain release. In the living polymerization, β-transfer reactions are effectively suppressed, resulting in a polypropylene without the common olefinic end groups typically present in polymers produced by other catalysts. To perform the analysis, we turned to PP produced by a catalyst that was not living but instead operated with an appreciable amount of chain release. A catalyst that proved exceptional for this task was the complex derived from 3,5-difluoroaniline (**3c**). This complex proved to be more active than **3a** and **3b**, but the increase in activity was accompanied by an increase in chain transfer, producing low molecular weight syndiotactic PP ($M_n = 3600$, PDI = 2.5, [*rrrr*] = 0.81) with readily observable end groups. Given the similarities in syndiospecificity of **3a**−**c**, we concluded that these catalysts operate by similar insertion mechanisms. ^{13}C NMR of this polymer revealed a spectrum with resonances in the olefinic region at δ 137.7 and 115.5 ppm, attributable to the unsaturated carbons of allylic end groups (Figure 3). As stated above, these end groups could result from either β-hydride elimination from the terminal methyl following a secondary insertion or exclusive β-methyl elimination following a primary insertion. These processes can easily be distinguished by considering the events that would follow the two types of release. Insertion into the Ti-hydride or the Ti-methyl results in distinct saturated end groups that can be easily identified. Further evaluation of the NMR spectrum reveals resonances at δ 14.1 and 14.6 ppm in an approximately equal ratio (Figure 3). The resonance at 14.6 is characteristic of the terminal methyl of *n*-propyl initiated PP, a common end group in metallocene polymers. However, the resonance at 14.1 ppm is attributable to an *n*-butyl end group, which is not observed with metallocenes but is seen in PPs synthesized with iron-based catalysts.[24,25] Peaks corresponding to either isobutyl or ethyl end groups that would arise from insertions into a titanium-methyl species are notably absent from the spectrum; therefore, β-methyl elimination and chain transfer to aluminum can be ruled out as the main sources of chain release. Resonances between 18 and 15 ppm which are consistent with the methyls of regioirregular tail-to-tail linkages are also present in the polymer; interestingly, these defects occur with opposite (meso) enantiofacial selectivity relative to the principle mode of enchainment (rac). However, these resonances are not observed in PPs from **3b**/MAO, consistent with highly regioregular 2,1-insertions.

The presence of both *n*-propyl and *n*-butyl end groups indicates the existence of two distinct initiation events in the polymerization, which can be explained by considering the insertion events of metallocenes and iron-based catalysts. In these systems, the first insertion occurs mainly into a metal-hydride with exclusive primary regiochemistry. While the second monomer insertion is highly regioregular in these systems (primary in metallocenes, secondary for iron systems), monomer addition into the titanium-*n*-propyl species generated in this phenoxyimine-based system appears to be highly irregular and accounts for the two types of saturated end groups. Primary insertion into this species explains the presence of *n*-propyl initiated PP, while a secondary insertion results in the *n*-butyl end group. From the NMR spectrum, it appears that these two processes occur with roughly equal probability, indicating random regiochemistry of propylene insertion into primary Ti-alkyls in this system. Also, an insertion into the titanium-propyl in a 1,2-fashion generates another primary metal-alkyl species, into which the next insertion is also random. In this case, propagation becomes secondary after one or more primary insertions. However, the largely regioregular nature (∼99%) of the PP indicates that insertion into a secondary titanium-alkyl is highly regular and secondary.

These data allow postulation of a unique mechanistic cycle of initiation, propagation, and chain release for propylene polymerization by the phenoxyimine-based catalyst system **3**/MAO (Scheme 6). Again, initiation occurs mainly through primary insertion into a Ti-hydride, generating a Ti-*n*-propyl species. Chain propagation reactions of propylene on the titanium-alkyl species can then be considered as four distinct processes: (a) primary insertion into a primary metal-alkyl, (b)

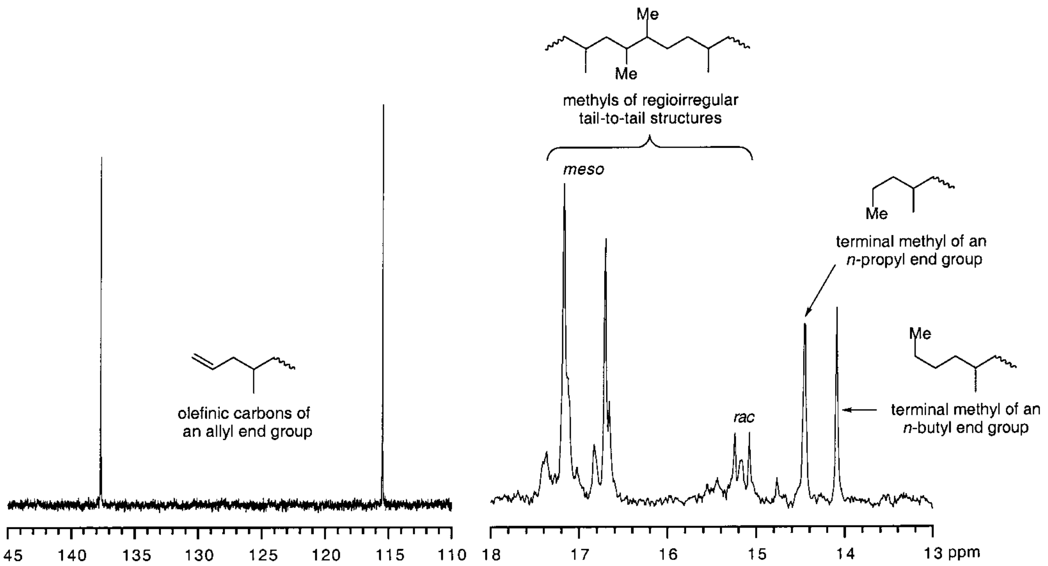
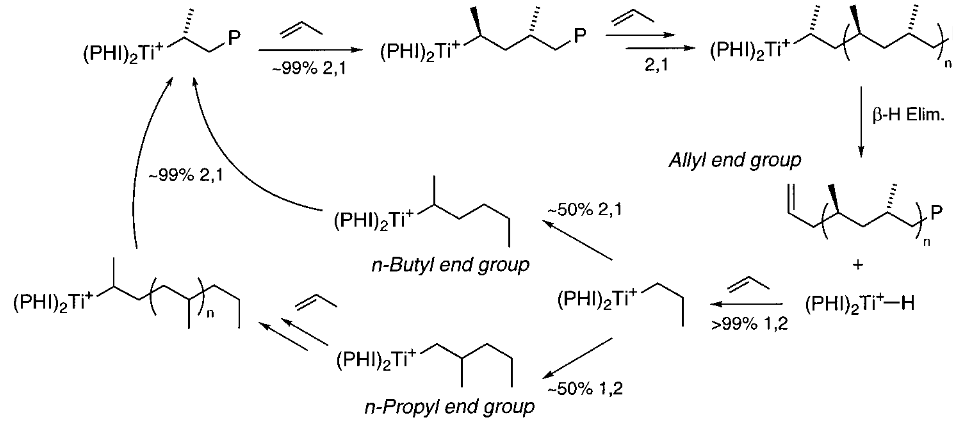


Figure 3. Selected regions of the ^{13}C NMR spectrum (100 MHz, $C_2D_2Cl_4$, 100 °C) of PP synthesized by **3c**/MAO.

Scheme 6



secondary insertion into a primary metal-alkyl, (c) primary insertion into a secondary metal-alkyl, and (d) secondary insertion into a secondary metal-alkyl. In this system, processes a and b are important only in the initial stages of polymerization and occur in roughly equal amounts, while process c accounts for ca. 1% of total propylene enchainments. Despite the aspecific nature of insertion into the primary titanium-alkyl species, statistics dictate that a secondary titanium-alkyl be generated, after which propagation becomes exclusively secondary (d). Chain release then occurs exclusively by β-hydride transfer from the terminal methyl, giving PP with allylic end groups. To our knowledge, this type of chain transfer has not been observed for metallocenes, in which elimination occurs from the internal methylene to give butenyl end groups, but is the principle source of termination with iron-based systems. Again, chain propagation is highly secondary in this system, a phenomenon that has been observed for the aforementioned vanadium[20] and iron-based[24,25] systems but not group IV propylene polymerization systems.

Regiochemistry from Cyclopolymerization. Because of the highly unusual and unprecedented secondary monomer enchainment proposed above for propylene polymerization by bis(phenoxyimine) titanium complexes, we targeted new methods to probe the polymerization mechanism. In the past, termination-based techniques have played a critical role in determining the mode of monomer enchainment. The vanadium systems, for example, were shown to propagate by 2,1-insertion by quenching the active species to give unique functionalized polymer end groups.[44−46] However, these methods only determine the regiochemistry of the last inserted monomer and are not necessarily representative of propagation as a whole. We reasoned that cyclopolymerizations[47] of α,ω-diolefins would provide evidence more relevant to the important chain propagation reactions, in contrast to previously employed initiation- and termination-based techniques. To this end, we decided to compare polymers derived from 1,6-heptadiene synthesized using **3b**/MAO with those from metallocene-based catalysts.[48] With *rac*-ethylenebis(indenyl) zirconium dichloride/MAO, 1,6-heptadiene was polymerized through a primary insertion, primary cyclization mechanism to give poly(methylene-1,3-cyclohexane) (PMCH) with a cis ring content of 50% when

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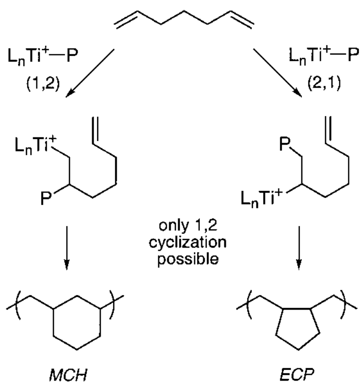
Scheme 7



polymerized at room temperature (Scheme 7).[48] Because the formation of these rings relies on monomer enchainment with 1,2-regiochemistry, we reasoned that the secondary mechanism operating in the phenoxyimine-based systems would give diene polymers with different microstructures. With 1,6-heptadiene, a secondary insertion and cyclization would in principle generate the same microstructure as given by metallocenes, but ring formation in this fashion is sterically prohibited due to the length of the aliphatic chain separating the olefins. However, cyclization with primary regiochemistry following an initial 2,1-insertion involves a favorable intermediate geometry. Ring closing of this type generates a primary Ti-alkyl species, into which subsequent insertions will be regiorandom as demonstrated by end-group analysis. Therefore, the initial insertion of the diene may be primary or secondary, resulting in a polymer with equal amounts of methylene-1,3-cyclohexane (MCH) and ethylene-1,2-cyclopentane units (ECP) (Scheme 7).

As anticipated, reaction of 1,6-heptadiene with **3b**/MAO produced a polymer with no observable unsaturation, indicating quantitative cyclization. The microstructure of the polymer as revealed by ^{13}C NMR displayed resonances consistent with poly(methylene-1,3-cyclohexane) with 80% cis rings (Figure 4); however, the spectrum also contained new peaks at 44−43, 31, 29, and 23 ppm which matched those of the anticipated poly(ethylene-1,2-cyclopentane) prepared independently by ring-opening metathesis polymerization (ROMP) of bicyclo[3.2.0]hept-6-ene and subsequent hydrogenation.[49] As predicted, the cyclopolymer contains equal amounts of MCH and ECP repeat units, demonstrating the random nature of insertions into primary Ti−alkyl bonds. Because steric constraints permit only 1,2-cyclization, a primary Ti-alkyl is generated with each cyclization. Insertions into these primary Ti-alkyls are regiorandom, consistent with the findings of end-group analysis. The presence of both MCH and ECP units in the polymer clearly demonstrates the high occurrence of secondary insertion in this catalytic system, as the ECP units can only form following an insertion of 2,1-regiochemistry.

Ethylene/Propylene Copolymerizations. In addition to this new cyclopolymerization technique for probing propagation events in olefin polymerization, information about the selectivity of insertions into primary and secondary titanium-alkyl species can also be obtained by evaluating the microstructure of ethylene-propylene copolymers (EP) synthesized by **3b**/MAO. Unlike typical AB-copolymers in which a sequence can be explained by a succession of monomers A and B (e.g., AAB, ABA, etc.), EPs typically possess a more complicated microstructure. In the presence of regiorandom propylene insertion, EPs contain three types of repeat units: ethylene, propylene, and inverted propylene. Therefore, an alternate approach to explain the microstructure of these copolymers has been proposed.[50−52] This method considers an EP copolymer as a succession of methylene and methine carbons, thus eliminating the problems of propylene inversion. In the ^{13}C NMR spectrum, resonances arising from methylene carbons of specific structural sequences can be used to calculate the monomer sequence distribution.[50−52] These peaks depend on the proximity of the nearest methyl branches to a carbon atom, with unique resonances arising from methylene sequences of one to five carbons and another corresponding to longer sequences. In this fashion, the relative concentration of methylene sequences of length one to five, as well as six and longer, can be determined. By evaluating the relative number fractions of uninterrupted methylene sequences of length n (χ_n), regioregularity of insertions can be probed.

The feasibility of this technique can be demonstrated by considering consecutive insertion events (Scheme 8). For example, a primary propylene insertion followed by m ethylene insertions (where $m \geq 0$) and a subsequent primary propylene insertion generate a methylene sequence between tertiary carbons of length $n = 2m + 1$; the same sequence also results from a secondary propylene insertion followed by m ethylenes and another secondary propylene. Therefore, regioregular propylene insertions produce a polymer with high number fractions of odd numbered methylene sequences ($n = 1, 3, 5...$). However, an even numbered sequence of length $n = 2m + 2$ arises from a primary propylene insertion followed by m ethylenes terminated by a secondary insertion of propylene, while an opposite sequence of insertions gives an EP with a sequence length $n = 2m$. Therefore, regioirregular insertion of propylene gives a polymer with high concentrations of even numbered sequences ($n = 2, 4, 6...$). As a consequence of the highly regioregular primary propylene insertion, both heterogeneous titanium catalysts[53] and titanium-based metallocenes[54] produce EPs with high fractions of odd numbered methylene sequences ($n = 1, 3, 5$); resonances corresponding to the even numbered sequences of length two and four are not observed ($\chi_2 = \chi_4 \approx 0$) (Figure 5). However, EPs synthesized by vanadium catalysts contain higher fractions of even numbered methylene sequences ($\chi_2 = 0.14$, $\chi_4 = 0.08$) due to a high number of propylene inversions.[45,51,52,55] EPs from the Ti-based catalyst **3b** should also contain high fractions of even numbered methylene sequences due to the highly aspecific nature of propylene insertions into a primary Ti-alkyl. As anticipated, ^{13}C NMR of these copolymers reveals exceptionally high levels of even numbered methylene sequences ($\chi_2 = 0.26$, $\chi_4 = 0.09$), which are the result of regioirregular propylene insertions. The large number fraction of such sequences clearly demonstrates the high number of propylene inversions due to the aspecific nature of insertions

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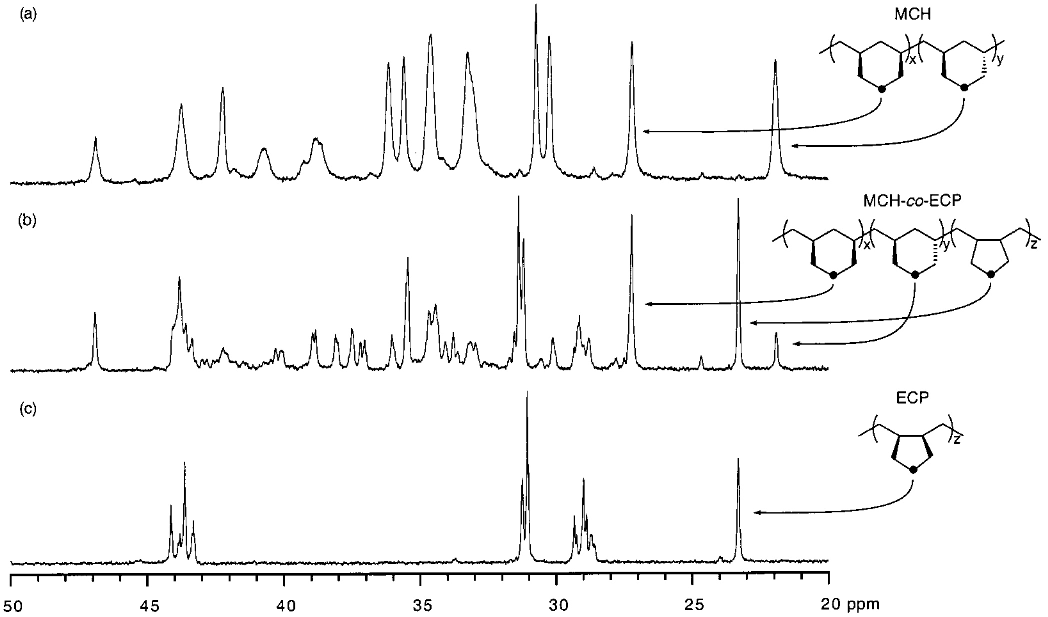
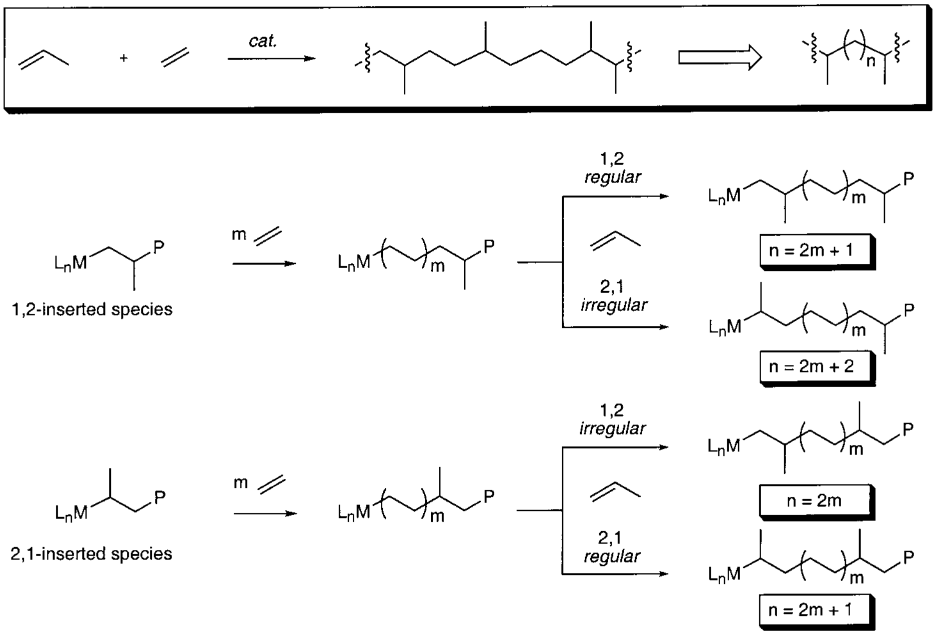


Figure 4. ^{13}C NMR spectra (100 MHz, $C_2D_2Cl_4$, 100 °C) of 1,6-heptadiene cyclopolymers synthesized from (a) *rac*-ethylene-bis(indenyl) zirconium dichloride/MAO, (b) **3b**/MAO, and (c) hydrogenation of the atactic ROMP polymer of bicyclo[3.2.0]hept-6-ene.

Scheme 8



into a primary Ti-alkyl, thus confirming the findings of end-group analysis and cyclopolymerization.

Conclusions

In summary, we have discovered a highly unusual mechanism of insertion in propylene polymerizations using the phenoxy-imine-based titanium catalyst system. Chain propagation was shown to occur with highly regular secondary regiochemistry, a phenomenon never observed for a group IV catalyst system. Although the dominant reaction was 2,1-insertion of propylene into a secondary Ti-alkyl, end-group analysis revealed that insertions into the Ti-hydride were exclusively primary, while insertions into the primary Ti-alkyl proceeded with random regiochemistry. The origin of this regiochemistry is not currently clear; our present thought is that the sterically congested titanium center alleviates hindrance in the transition state of olefin insertion by placing the methyl of the reacting propylene in an open region of the active species. For this species, this happens to result in a significant amount of 2,1-enchainment when inserting propylene into a Ti-primary carbon bond. Ensuing enchainment occurs, and once a 2,1-insertion takes place, alkene insertion into the Ti-secondary carbon end group causes additional steric congestion and results subsequently in exclusive 2,1-insertion. The nature of this unusual insertion was further validated by 1,6-heptadiene polymerization and ethylene/propylene copolymerization, demonstrating new and powerful techniques for mechanistic elucidation in olefin polymerization as well as producing polymers with new and interesting microstructures. Such an insertion could play an important role in the polymerization of functional monomers, as β-elimination can potentially be avoided by placing functionality on the α

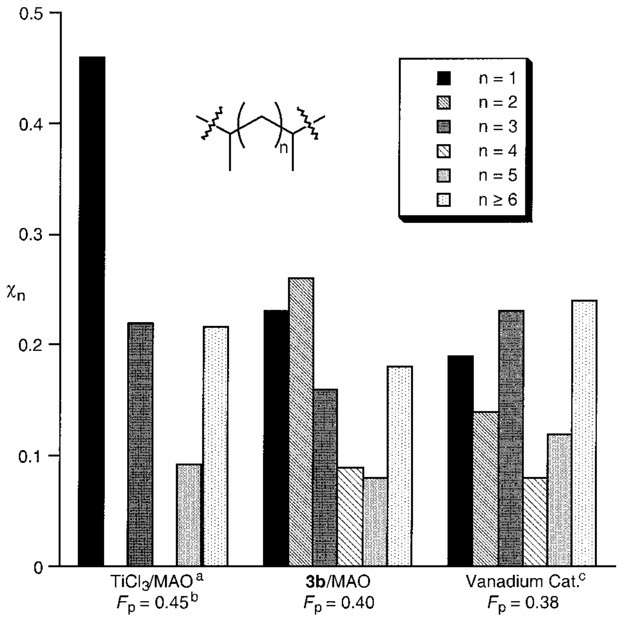


Figure 5. Number fractions (χ_n) of uninterrupted methylene sequences for ethylene/propylene copolymers. [a]From ref 53. [b]F_P is defined as the mole fraction of propylene. [c]From ref 55.

carbon of the propagating polymer.[56] Future work will center on more detailed methods for elucidating the mechanisms of insertion and stereochemical control in this important class of compounds.

Experimental Section

General Methods. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun Labmaster drybox or standard Schlenk line techniques. Routine small-molecule ^1H and ^{13}C NMR spectra were recorded on a Bruker AF300 (^1H, 300 MHz) and a Varian Inova (^1H, 400 MHz, ^{13}C, 100 MHz) spectrometer and referenced versus residual nondeuterated solvent shifts. ^{13}C NMR spectra of the polymers were recorded on a Varian VXR-400 (100 MHz) spectrometer and referenced versus residual nondeuterated solvent shifts. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 (TCE) in a 5 mm o.d. tube by heating to 120 °C in an oil bath. For quantitative analysis, an inverse gated decoupling sequence was employed with a 30° pulse width over a 160 ppm spectral width at a 2.0 s acquisition.

Molecular weights (M_n and M_n) and polydispersities (M_w/M_n) were determined by high temperature gel-permeation chromatography (GPC). All analyses were performed with a Waters Alliance 2000 liquid chromatograph equipped with a Waters DRI detector and a Jordi styrene-divinylbenzene linear mixed-bed column. The GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) containing 0.1 wt % Irganox 1010 at 140 °C at 1.0 mL/min and were calibrated using 23 monodisperse polystyrene standards. Polymer samples were typically placed in a 140 °C oven for 24 h to eliminate supermolecular aggregates prior to molecular weight measurements.

Materials. Benzene, benzene-d_6, diethyl ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Hexane was distilled from CaH_2 under nitrogen. Chloroform and methylene chloride were distilled from P_2O_5 under nitrogen. Titanium tetrachloride was purchased from Aldrich and distilled prior to use. Propylene (Matheson, polymer grade) was purified through a mixed bed column (R&D Separations, BOT-4). Ethylene (polymer grade) was purchased from Matheson and used as received. Methylaluminoxane (PMAO-IP, 12.9 wt % Al in toluene, Akzo Nobel) was concentrated in vacuo to dryness (10^{-3} mmHg) at 40 °C for 18 h to remove residual trimethylaluminum, providing a solid white powder. 3,5-Difluoroaniline was purchased from Fluorochem and used as received. $(F_5\text{-PHI})_2TiCl_2$ **3b** and $(3,5\text{-}F_2\text{-PHI})_2TiCl_2$ **3c** were synthesized according to published procedures.[27] Bicyclo[3.2.0]hept-6-ene, its ROMP polymer poly(vinylene-*alt*-1,2-cyclopentane), and poly(ethylene-*alt*-1,2-cyclopentane) were synthesized according to literature procedures.[49] *rac*-Ethylenebis(indenyl) zirconium dichloride was purchased from Strem and used as received. All other chemicals were commercial materials and were used as received.

Propylene Polymerization Using 3c. In a typical polymerization experiment, a 6 ounce Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was first conditioned under dynamic vacuum and high temperature and then charged with a desired amount of PMAO (0.60 g, 10 mmol) and toluene (150 mL). The reactor was equilibrated at 0 °C, and the atmosphere was exchanged three times with propylene. The solution was then saturated under pressure (20 psi). Complex **3c** (0.041 g, 0.051 mmol, [Al]/[Ti] = 200) was dissolved in toluene (6 mL) at room temperature under nitrogen. The solution was then added to the reactor via gastight syringe to initiate the polymerization. After 4 h, the reactor was vented and the polymer was precipitated in copious methanol/HCl, filtered, washed with methanol, and then dried in vacuo to constant weight (2.11 g, $M_n = 3600$, PDI = 2.5).

1,6-Heptadiene Polymerization. A dry Schlenk-type flask under nitrogen was charged with the diene (1.00 g, 10.4 mmol), PMAO (0.87 g, 15 mmol), and toluene (100 mL). After this solution was equilibrated at room temperature, a toluene solution (4 mL) of **3b** (0.046 g, 0.050 mmol, [Al]/[Ti] = 300) was added via syringe. After 48 h, the polymer was precipitated in methanol/HCl, filtered, washed with methanol, and dried in vacuo to constant weight (1.00 g).

Ethylene/Propylene Copolymerization. A 6 ounce Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was first conditioned under dynamic vacuum and high temperature and then charged with PMAO (0.31 g, 5.3 mmol) and toluene (100 mL). The reactor was then equilibrated at 0 °C. At this point, the reactor atmosphere was exchanged with propylene three times, and then the solution was saturated under propylene pressure (30 psi). An overpressure of ethylene (33 psi) was introduced to the reactor, and a toluene solution (4 mL) of **3b** (0.009 g, 0.01 mmol, [Al]/[Ti] = 500) was added via syringe. After 1 h, the reactor was vented, and the polymer was precipitated in methanol/HCl, filtered, washed with methanol, and then dried in vacuo to constant weight (2.33 g, $M_n = 192\,000$, PDI = 1.19).

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Supporting Information Available: ^{13}C NMR spectra of PP synthesized by **3c**/MAO and the EP copolymer from **3b**/MAO (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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