Macromol. Symp. **2004**, *213*, 235-251

Polymerization of Propene by Post-Metallocene Catalysts

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Summary: In the last few years several non-metallocene catalysts have been disclosed as efficient catalysts for the stereospecific polymerization of propene.
In this paper we summarize some recent literature data and some new results concerning the stereochemical mechanism of propene polymerization promoted by late transition metal systems and group 4 metal bis(phenoxyimine) systems. NMR analysis of the fine structure of the polymers obtained, in some cases using isotopically enriched reagents, provides valuable information on the regiochemistry and stereochemistry of the polymerization.

Keywords: catalysis; microstructure; NMR; poly(propylene); stereochemical mechanism

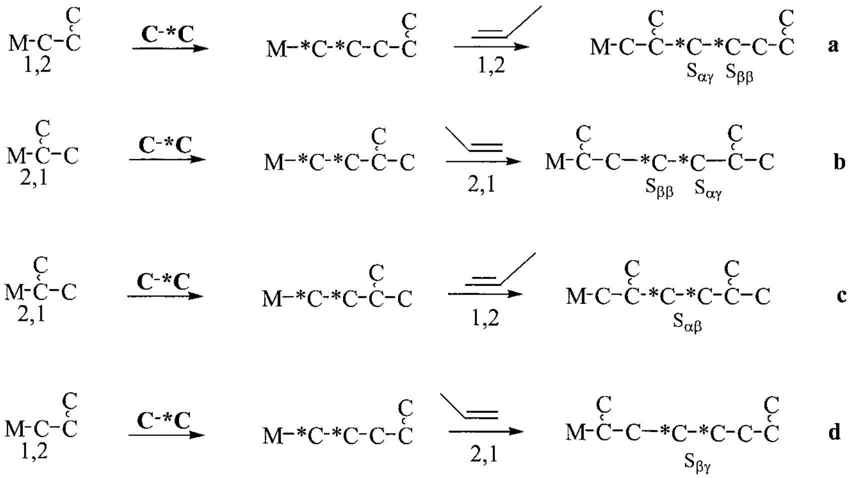
Introduction

The renaissance era of olefin polymerization catalysis has been mainly driven by the successful design and application of Group 4 metallocenes, some of which are now used in industrial processes.[1] While research in the metallocene area appears far from over, in the last years increasing interest has been directed toward the search for new class of catalysts, involving complexes of transition metals throughout the Periodic Table.[2] Examples of successful new classes of highly active non-metallocene catalysts include late-transition metal systems such as the Brookhart's Ni and Pd diimine catalysts,[3] and the Fe bis(imino)pyridyl catalysts, and group 4 metal bis(phenoxyimine) catalysts,[4] all of them showing a number of interesting peculiar features. One of the outcomes from these developments has been the expansion of stereospecific polymerizations.

In this paper we review some recent literature data and some new results concerning the

DOI: 10.1002/masy.200450922

stereochemical mechanism of propene polymerization promoted by "post-metallocene" catalysts, namely the above mentioned late-transition metal and bis(phenoxymine) systems. Most of the results discussed were achieved by using techniques, developed by Zambelli in the 70's, based on the NMR analysis of suitably labelled polymers obtained by employing isotopically enriched catalysts or monomers. In particular, ^{13}C can be introduced in different points of the polymer chain as a sort of magnifying lens to observe fine aspects of the microstructure, and to establish a chronology in the sequence of the monomer insertions. Thus, NMR analysis of ^{13}C enriched end groups provides information about the regiochemistry and the stereochemistry of the monomer insertion in the initiation steps. A useful method to investigate the chain propagation involves the synthesis of copolymers of propene containing isolated units of 1-^{13}C ethylene: NMR analysis provides information on the regiochemistry and the stereochemistry of propene insertion before and after ethylene entrance. When the ethylene unit bridges regioregular, either primary or secondary, polypropylene blocks, a three-methylene sequence is formed (see Scheme 1 a, b). An enriched two-methylene sequence can derive only from ethylene spanning propene units of opposite regiochemistry, according to scheme 1c. Finally, a four-methylene sequence can derive from the succession of insertions displayed in scheme 1d.

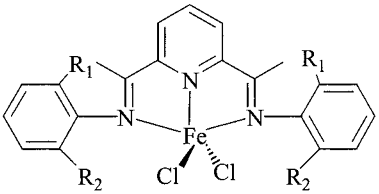


Scheme 1

Since the chemical shifts of the enriched methylenes[5] are affected by the stereochemical arrangements of the neighbouring propene units, valuable information on the mechanism of steric control can be obtained. In particular, if the steric control crosses intervening ethylene units, the stereochemistry of the insertion is controlled by the chirality of the active sites, while if it does not cross the intervening ethylene units, the stereospecificity of the insertion arises from the asymmetric induction by the last (propene) unit of the growing chain. The whole matter has been recently revisited analyzing, by high field NMR, several propene-enriched ethylene copolymers prepared with a variety of catalysts.[6]

1. Iron bis(imino) Pyridine Catalysts

Iron bis(imino)pyridine complexes, activated by MAO, were independently reported by Brookhart[7] and Gibson[8] as very active ethylene polymerization catalysts producing strictly linear, high-molecular weight polymers. These catalysts are moderately active in the polymerization of propene.[9-10] The bis(imino)pyridine complex with bulky isopropyl *ortho* substituents on the arylimino moieties (**Fe-1**, Scheme 2) is able to produce regioregular isotactic polypropylene with a 69% *mm* triad content at 0 °C.



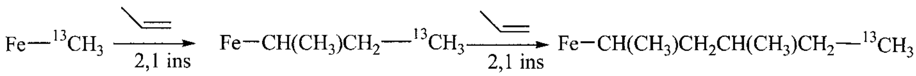
Fe-1: $R_1 = R_2 = CH(CH_3)_2$

Fe-2: $R_1 = CH_3$; $R_2 = CH(CH_3)_2$

Scheme 2

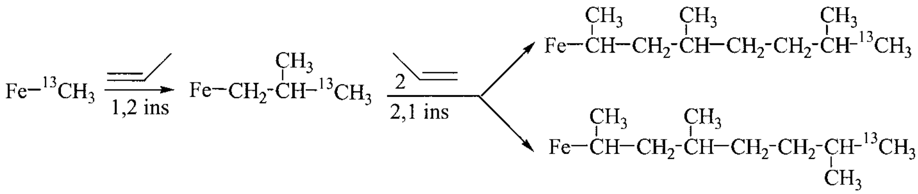
NMR analysis of the polypropylene microstructure suggested that a chain end mechanism of steric control is operative. Interestingly, this steric control is still effective above room temperature, *e.g.* at 50 °C (*mm*=60%).[11]

The regiochemistry of the monomer insertion in the initiation step was investigated by preparing a polymer sample bearing ^{13}C enriched end groups. [11] The major ^{13}C enriched end groups were *sec*-butyls, deriving from 2,1 insertions of propene into Fe-$^{13}CH_3$ bonds (Scheme 3).



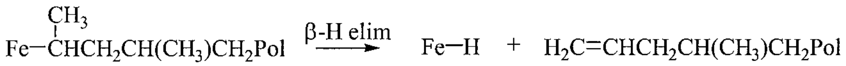
Scheme 3

Isopentyl end groups were also detected, deriving from initiation via 1,2 insertion followed by 2,1 insertion (Scheme 4).

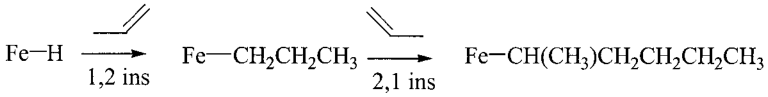


Scheme 4

Analysis of the natural abundance end groups showed the presence of unsaturated allyl groups deriving from β-H-elimination at the methyl of a secondary growing chain (Scheme 5) and *n*-butyl end groups, originating from 1,2 insertion of propene into Fe-H bonds followed by a 2,1 insertion (Scheme 6).



Scheme 5



Scheme 6

Since the polymer backbone is highly regioregular, the above end group analysis indicated that primary insertion is favoured into Fe-H bond, primary and secondary insertion have comparable probabilities into Fe-CH_3 bonds, while secondary insertion is preferred into Fe-alkyl bonds (for alkyl > CH_3). In conclusion secondary insertion is the most probable event during the propagation.

Complex **Fe-2** affords a polypropylene with a similar content of *mm* triads, although the polymer microstructure slightly deviates from the composition expected for a simple chain-end mechanism. Thus, a copolymer of propene containing about 1% of 1-^{13}C enriched ethylene was prepared with complex **Fe-2**.[6] NMR analysis of the copolymer showed only three-methylene sequences, in agreement with a highly regioregular secondary insertion of the monomer into any Fe-R bond (R > CH_3). Further information came from close examination of the fine structure of the enriched carbons (Figure 1). The relative areas of the resonances of the *m*-$S_{\alpha\gamma}$ and *r*-$S_{\alpha\gamma}$ enriched methylenes are the same as the molar fraction of *m* and *r* dyads inside the polypropylene blocks as determined from the methyl pentad resonances. This is again in agreement with the above mentioned mechanism since, for a secondary mode of propagation, the $S_{\alpha\gamma}$ carbon resonance is diagnostic of the stereochemical arrangement of the two propene units incorporated *before* the insertion of ethylene unit.

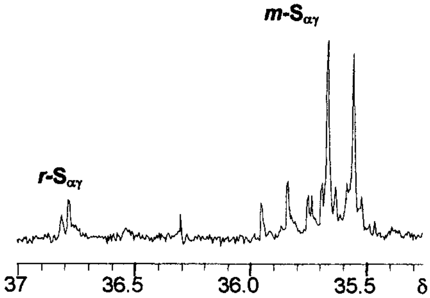
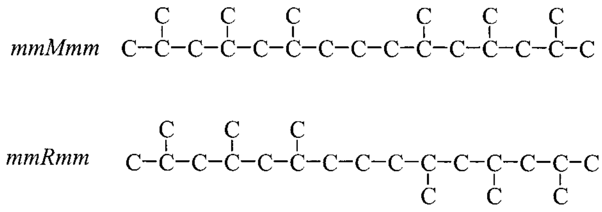


Figure 1. $S_{\alpha\gamma}$ region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 C) of a copolymer of propene with a little amount of 1-^{13}C-ethylene prepared with **Fe-2**-MAO. δ in ppm from hexamethyldisiloxane.

In the $S_{\beta\beta}$ region of the spectrum (Figure 2) two major resonances attributable to *mmMmm* and *mmRmm* pseudohexads were detected, [6] confirming a chain end mechanism of steric control, *i.e.* the steric control does not cross the intervening ethylene unit (see Scheme 7).



Scheme 7

A similar spectrum was observed for a copolymer prepared with the Ewen's achiral Cp_2TiPh_2-MAO catalyst which affords isotactic polypropylene via chain-end control at low temperature.[12]

On the contrary, only the *mmMmm* pseudohexad was observed for an isospecific C_2-symmetric *ansa*-zirconocene such as *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$[13] in agreement with an enanthiomorfic-site mechanism of steric control.[6]

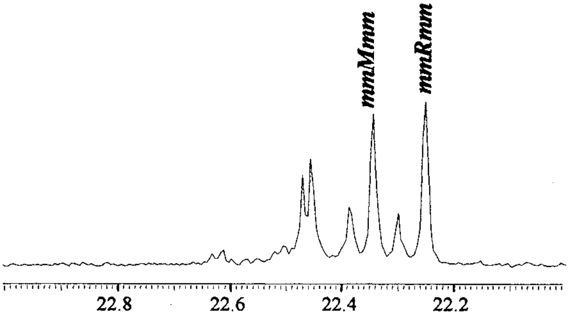
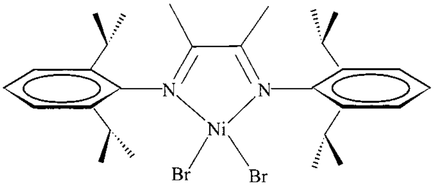


Figure 2. $S_{\beta\beta}$ region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propene with a little amount of 1-^{13}C-ethylene prepared with **Fe-2**-MAO. δ in ppm from hexamethyldisiloxane.

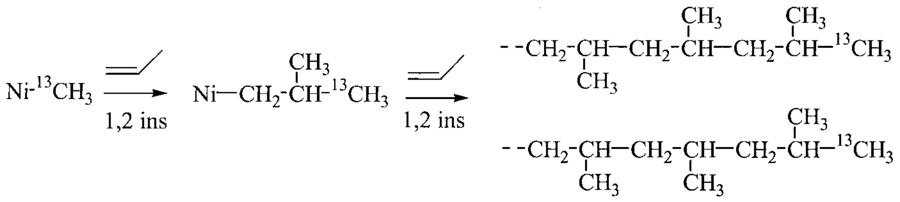
2. Nickel α-diimine Catalysts

Nickel α–diimine catalysts disclosed by Brookhart polymerize ethylene and α-olefins to high molecular mass polymers with activities comparable to early transition metal systems.[14] The polymer microstructure and properties are greatly dependent on the reaction conditions and on the ligand structure.[3] These catalysts are also moderately active in the polymerization of propene. The nickel complex displayed in Scheme 8 produces syndiotactic polypropylene at sub-ambient temperature, with a *rr* triad content up to 80% at -78°C.[15]



Scheme 8

Analysis of pentad region of the ^{13}C NMR spectrum suggested a chain end mechanism of steric control, since isolated *m* diads are the major stereodefects. A significant amount of regioirregular monomer units was also detected (about 12%). The whole picture is similar to the case of the classical V-based sydiospecific catalyst.[16-17] A significant difference emerged from investigation of the regiochemistry of the monomer insertion. The insertion in the initiation steps was determined using a ^{13}C enriched catalyst, producing a polypropylene with enriched isobutyl end groups indicating a primary (1,2) monomer insertion (Scheme 9). Also, only two of four possible diasteroisomers were observed indicating that steric control becomes active when the first chiral carbon is generated in the growing chain,[18] while in the case of vanadium the steric control is effective only when monomer insertion turns from primary to secondary.[19]



Scheme 9

A primary (1,2) monomer insertion as the main propagation mode was confirmed by analyzing the end groups formed in the termination step, in which a deuterium label was introduced by quenching the polymer with deuteriated trifluoromethanol[20] (Scheme 10).

The formation of a deuteriated methyl group of an isobutyl was confirmed by ^{13}C and ^{2}H NMR analysis, while in the case of vanadium catalyst the same experiment led to a deuteriated methylene of a n-propyl.[21]

$$\mathrm{Ni{-}CH_2CH(CH_3)CH_2CH(CH_3)Pol} \xrightarrow{D^+} \mathbf{D}\mathrm{{-}CH_2CH(CH_3)CH_2CH(CH_3)Pol} \qquad \mathbf{a}$$

$$\mathrm{V{-}CH(CH_3)CH_2CH(CH_3)CH_2Pol} \xrightarrow{D^+} \mathrm{CH_3CH}\mathbf{D}\mathrm{CH_2CH(CH_3)Pol} \qquad \mathbf{b}$$

Scheme 10

A copolymer of propene with trace amounts of ^{13}C enriched ethylene was prepared also with the nickel catalyst (see the ^{13}C NMR spectrum in figure 3). In this case sequences of two, three and also four methylenes were observed in comparable amount, in agreement with the poor regioregularity of the system.

The ratio r-$S_{\alpha\gamma}$/m-$S_{\alpha\gamma}$ (6:4) is lower than the *r*/*m* ratio in the main chain (~8:2): this is not surprising considering that, since the propagation is prevailing 1,2, the $S_{\alpha\gamma}$ carbon resonance is diagnostic of the two propene units incorporated *after* the enriched ethylene unit, and that the chain end control can be affected by the presence of a less bulky chain.

In this case the region of $S_{\beta\beta}$ carbons (Figure 3) is less informative; in fact, a sharp peak at 22.50 ppm emerges from a broad band of resonances: this is the same resonance found in the case of a copolymer prepared with a highly syndiospecific C_s symmetric metallocene[6] but in no sample examined up to now there is evidence of any detectable splitting of the resonances for the *rrRrr* and *rrMrr* pseudohexads, which would allow one to establish if the steric control crosses or not the intervening ethylene unit.[6] Theoretical calculations and analysis of model compounds suggest that in this case the chemical shift difference should be significantly lower than in the case of *mmMmm* and *mmRmm* pseudohexads.

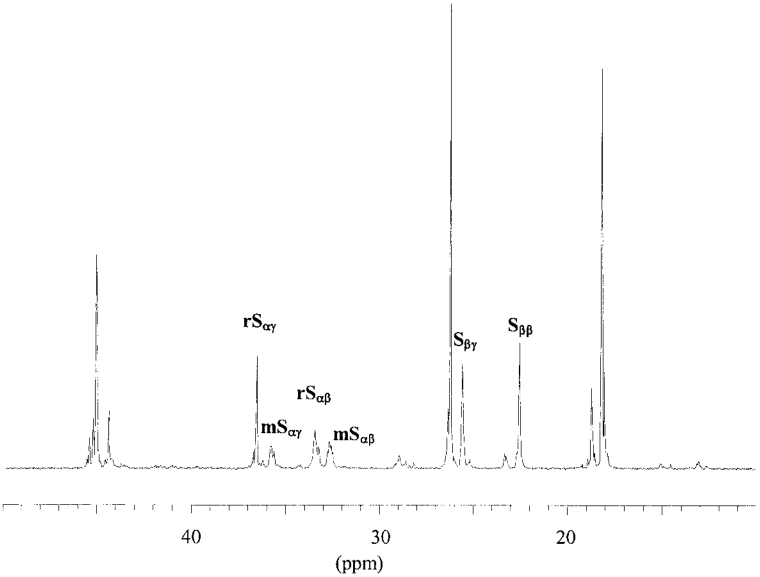
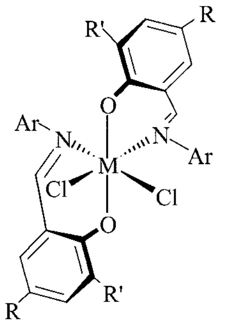


Figure 3. 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 C) of a copolymer of propene with a little amount of 1-^{13}C-ethylene prepared with the nickel catalyst-MAO. δ in ppm from hexamethyldisiloxane.

3. Bis(phenoxyimine) Group 4 Metal Catalysts

The octahedral C_2 symmetric bis(phenoxyimine) Group 4 metal complexes (Scheme 11), developed by the group of Fujita,[22] are able to produce polyethylene with activities comparable to or even exceeding those of metallocene catalysts. Production of syndiotactic polypropylene using a titanium complex of this class was first reported in the scientific literature by Coates;[23] microstructural analysis of the resulting polymer suggested that a chain-end mechanism was responsible for the observed stereocontrol.[23,24,25] The polymer stereoregularities range from moderate to high, depending on the precatalyst structure and the polymerization conditions.[26] The use of perfluorinated N-aryl groups improves the catalyst performances, concerning both activities, stereospecificity and polymer molecular weights. Very interestingly, titanium complexes bearing fluorinated N-aryl groups polymerize ethylene and propene in a living fashion, allowing the synthesis of a variety of block copolymers.[24,25,26]

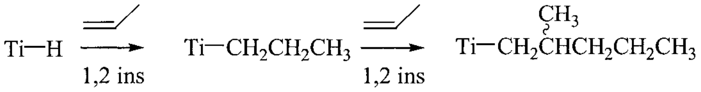


Complex **1**: R = *t*-Bu; Ar = C_6H_5
Complex **2**: R = H; Ar = C_6H_5
Complex **3**: R = H; Ar = C_6F_5
Complex **4**: R = *t*-Bu; Ar = C_6F_5
Complex **5**: R = *t*-Bu; Ar =3,5-F_2-C_6H_3
M = Ti; R' = *t*-Bu

Complex **6**: M = Zr
Complex **7**: M = Ti
R' = Me; R = H; Ar = C_6F_5

Scheme 11

We studied the regiochemistry and the stereochemistry of propene polyinsertion in the presence of complex **2** (Scheme 11) *via* NMR analysis of the natural abundance polymer end-groups.[27] The polymer is prevailingly syndiotactic, the content of *rr* triads being 81%, with few regioirregularly arranged monomer units (<2%). As observed in the case of the iron catalyst (see Scheme 5), allyl end groups originated from β-hydrogen elimination at the methyl of the growing chain-end after a 2,1 insertion were detected. In the saturated region of the spectrum, resonances attributable to *n*-propyl and *n*-butyl end groups were observed. The latter originates from 1,2 monomer insertion into Ti-H bonds, followed by an insertion with opposed (2,1) regiochemistry, again as observed for the iron catalyst (Scheme 6), while the former arises from at least two consecutive 1,2 monomer insertions into Ti-H bonds (Scheme 12).

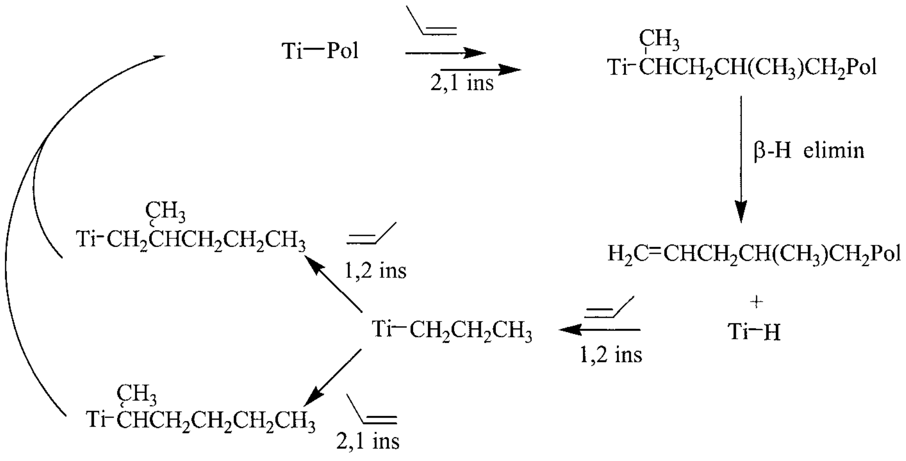


$$\mathrm{Ti{-}H} \xrightarrow[\text{1,2 ins}]{} \mathrm{Ti{-}CH_2CH_2CH_3} \xrightarrow[\text{1,2 ins}]{} \mathrm{Ti{-}CH_2\overset{CH_3}{C}HCH_2CH_2CH_3}$$

Scheme 12

No incorporation of deuterium in the polymer was observed when the polymerization run was terminated by adding a mixture of deuteriated alcohols, therefore ruling out the production of a significant amount of *n*-propyl and *n*-butyl end groups by hydrolysis of polymer chains bound either to Ti or Al in the termination step.

The above end group analysis suggested that β-hydrogen elimination is the main termination process, generating allyl-terminated macromolecules and Ti-H bonds, into which primary insertion of propene is favoured, and is followed either by a primary (60%) or a secondary (40%) propene insertion (see Scheme 13).



Scheme 13

Similar conclusions were reported by Coates,[28] from end group analysis of a *s*PP sample produced with complex **5** and also on the basis of the results of cyclopolymerization of 1,6-heptadiene.

The regiochemistry of polymerization has been studied also for the catalytic system based on the perfluorinated complex **3**. In this case the living nature of the polymerization made the analysis difficult, because of the absence of chain release. Low molecular weight polymer samples, suitable for ^{13}C NMR analysis of chain-end groups in natural abundance, were obtained by Fujita,[26b] quenching the reactions after short times. Only saturated end-groups were distinguished: *n*-propyl (34 %), isobutyl (33 %) and isopentyl (33 %). Isopentyl chain-end groups would originate in the initiation step from 1,2 insertion into a Ti-Me bond followed by 2,1 insertion, while *n*-propyl chain-end groups would derive from hydrolysis of a secondary growing chain. Isobutyl groups would be generated either in the initiation (*via* two consecutive propene primary insertions into a Ti-Me bond) or in the termination steps (*via* hydrolysis of a primary growing chain).

From the relative ratio of the chain-end groups formed during the initiation step (i.e. isobutyl and isopentyl) and during the termination step, Fujita estimated that 2,1 insertion is only about 70 % and proposed that the polypropylenes possess regio-block structures consisting of consecutive 2,1-insertion and 1,2-insertion segments.

Further information came from analysis of a propene-1-^{13}C-enriched ethylene copolymer prepared by catalyst **3**-MAO.[27]

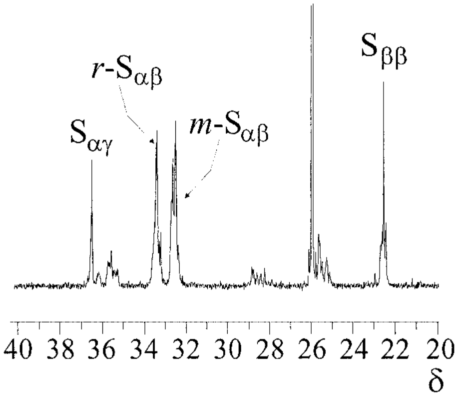
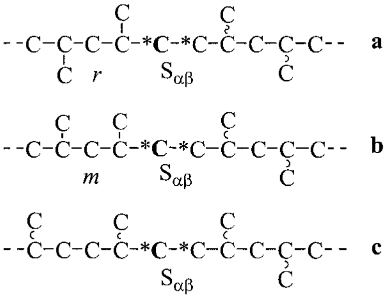


Figure 4. Aliphatic region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 C) of a copolymer of propene with a little amount of 1-^{13}C-ethylene prepared with **3**-MAO. δ in ppm from hexamethyldisiloxane.

NMR analysis (see Figure 4) indicated the presence of two-methylene and three-methylene sequences. The methylene pairs outnumber the three-methylene sequences, in agreement with the previous conclusion concerning the prevailing 2,1 regiochemistry insertion of propene during the "normal" propagation, and the observation that 1,2 insertion is slightly favoured into metal-primary carbon bond.

In addition, in this case the fraction of the r-$S_{\alpha\beta}$ (Scheme 14a) enriched carbons is unexpectedly low (45%) if compared to the r diad content inside the polypropylene blocks (98%). On the basis of literature data,[29] the m-$S_{\alpha\beta}$ (Scheme 14b) resonance probably overlaps with the $S_{\alpha\beta}$ carbon flanking a regioirregular propene diad (Scheme 14c). Since two methylene sequences can derive only from a ^{13}C-enriched ethylene inserted after a secondary polypropylene block and followed by a primary propene insertion (see above, Scheme 1c), and since the secondary block is highly syndiotactic, one may conclude that either 1,2 insertion is highly isotactic or that it is prevailingly followed by a 2,1 insertion, ruling out the presence of significant amount of primary blocks. [30]



Scheme 14

The main resonance of the $S_{\beta\beta}$ carbons is the same observed in all the previous mentioned *s*PP prepared by either C_s symmetric group 4 metallocene or Ni diimine based catalysts (see above), thus not providing any additional information on the origin of the enantioselectivity.

Very recently we synthesized a zirconium(IV) complex bearing two N-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroaniline and two Cl ligands (complex **6** in Scheme 11).[31] X-ray analysis (see Figure 5) indicates that **6** adopts a distorted octahedral structure with a *trans*-O, *cis*-N, and *cis*-Cl arrangement, similarly to previously reported complexes of this class.

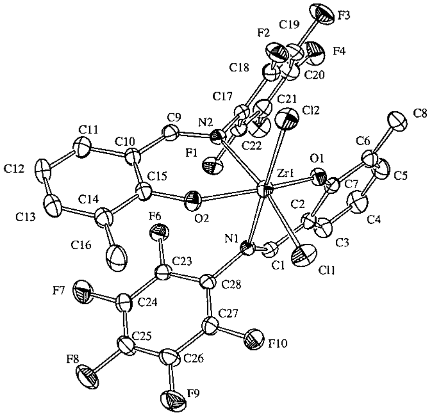
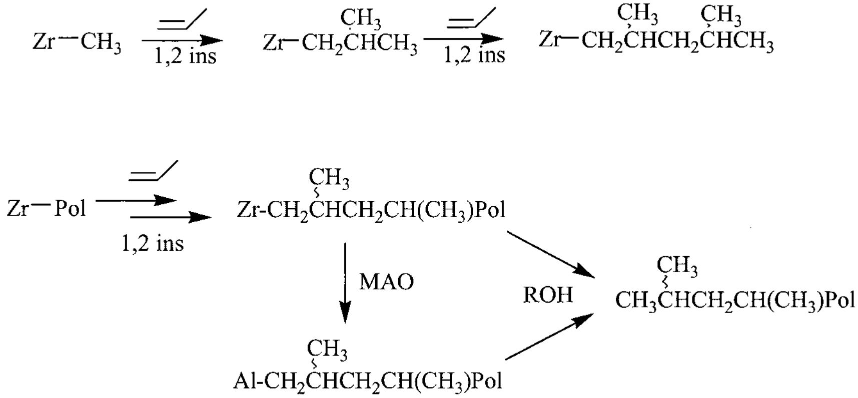


Figure 5. Ortep drawing of the molecular structure of compound **6**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 20% probability level.

Polymerization of propene at room temperature in the presence of **6** resulted in the production of a poorly stereoregular, prevailingly syndiotactic polypropylene ($P_r = 0.67$). The polymer microstructure is in agreement with a chain-end mechanism of steric control. End group analysis showed the almost exclusive presence of isobutyl end groups, indicative of a primary (1,2) propene insertion operating both in the initiation and the termination steps. The formation of isobutyl end groups during the termination step was confirmed by the presence of $CH_2\mathit{D}CH(CH_3)CH_2$-- end groups in the ^2H NMR spectrum of a polypropylene sample prepared with the same deuterium labelling technique used in the case of the nickel catalyst (see above, Scheme 10 a).

The reasonable polymerization mechanism involves (see Scheme 15) primary propene insertion into Zr-CH_3 bonds, followed by prevailingly primary insertion during the propagation, and termination *via* chain transfer of the primary growing chain to MAO (or to $Al(CH_3)_3$ present in the MAO solution) generating a new Zr-CH_3 bond for reinitiation.

Further support to the whole picture came from copolymerization of propene with a small amount of ^{13}C ethylene enriched C1 (see the spectrum in Figure 6a). In this case the three methylene sequences outnumber the methylene pairs (79 % vs 21 %), in agreement with a prevailingly primary regiochemistry: this result is unexpected in view of the opposite regiochemistry observed for related bis(phenoxyimine)titanium catalysts. In order to



Scheme 15

discriminate the role played by the nature of the metal in determining the regiochemistry of propene insertion from any ligand effect, we tested the titanium complex (complex **7** in Scheme 11) bearing the same ligands. The polypropylene produced was very similar to that obtained with the corresponding Zr compound, according to recent literature data.[26c] End groups analysis, also confirmed by deuterium labelling data, revealed in this case the presence of *n*-propyl and isobutyl end groups. As discussed above, these data suggest that the polymerization is prevailingly initiated by at least two consecutive 1,2-insertions into a Ti-CH_3 bond (generating the isobutyl end groups), while the main termination step is the hydrolysis of titanium-bound secondary growing chains (generating *n*-propyl end groups). Conclusive results came from the structure of a copolymer of propene with a low amount of 1-^{13}C-ethylene. NMR analysis (see the spectrum in Figure 6b) showed that in this case methylene pairs outnumber the three methylene sequences (90 % vs 10 %), suggesting that 2,1 insertion of propene is the “normal” mode of propagation, and that 1,2 insertion becomes preferred after the insertion of an ethylene unit, which generates a metal-primary carbon bond.

In conclusion, zirconium and titanium complexes bearing the same ligands afford prevailingly syndiotactic polypropylenes having very similar structures, but *via* opposite regiochemistries.

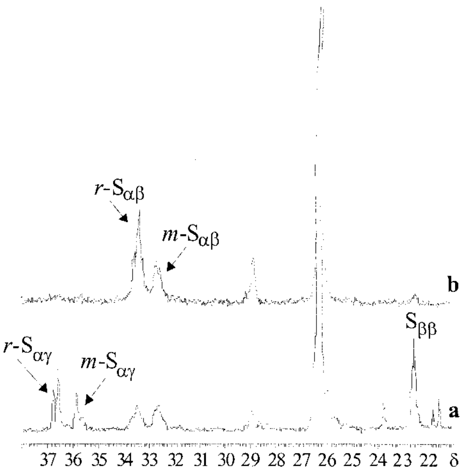


Figure 6. Aliphatic region of the 100.6 MHz ^{13}C NMR spectra ($C_2D_2Cl_4$, 100 C) of two copolymers of propene with a little amount of 1-^{13}C-ethylene prepared with a) **6**-MAO and b) **7**-MAO. δ in ppm from hexamethyldisiloxane.

Conclusions

One of the main achievements of research on metallocene catalysts involves a detailed understanding of the mechanism of stereospecific polymerization of propene and α-olefins, including a precise insight in the relationships between the precatalyst structure and the microstructure of the polymer obtained. In the last few years, several non-metallocene catalysts have been shown to afford either isotactic or syndiotactic polypropylenes, in addition to the classical syndiospecific V-based catalysts disclosed by Natta and Zambelli in the early 1960s. While the mechanistic details of the stereospecific polymerization promoted by these new catalysts are less defined, some facets have been elucidated, showing some peculiar features with respect to metallocenes. E.g., while polymerization of propene by metallocene catalysts predictably involves primary (1,2) monomer insertion as the preferential mode of propagation, practically all possible combinations of regiochemistries and stereochemistries have been observed in propene polymerization by non-metallocene catalysts. Thus, Fe(II) bis(imino)pyridine catalysts afford isotactic polypropylene via a *chain-end* mechanism of steric control and a prevailingly secondary regiochemistry of monomer insertion. On the other hand, Brookhart's Ni(II) diimine catalysts are able to produce prevailingly syndiotactic polypropylene at sub-ambient temperature through a *chain-end* control mechanism operating via primary monomer insertion. Finally, octahedral C_2-symmetric bis(phenoxyimine) titanium complexes are highly syndiospecific and living propene polymerization catalysts operating via a secondary mode of monomer insertion. Surprisingly, analogous zirconium catalysts can afford moderately syndiotactic, low molecular weight polypropylenes via primary monomer insertion.

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