

On the mechanisms of growing-chain-end isomerization and transfer reactions in propylene polymerization with isospecific, C_2 -symmetric zirconocene catalysts

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Abstract

A new mechanism is proposed to explain the occurrence of primary-growing-chain-end epimerization, and the structure and frequency of olefinic end groups arising from primary β -hydride transfer, in low molecular weight isotactic polypropylenes produced with C_2 -symmetric zirconocenes. This mechanism, based on the reversible formation of a zirconocene allyl dihydrogen complex, accounts for both loss of catalyst stereospecificity and decrease of polypropylene molecular weights observed by lowering [propylene], and accommodates a number of previous and new experimental observations. Inter alia: (i) the formation of internal vinylidene unsaturations; (ii) the increase of catalyst activity induced by H_2 addition; (iii) the observed deuterium scrambling in the [1-D]propylene and [2-D]propylene polymerizations recently reported by Brintzinger. This new mechanism is discussed in the light of the polymerization results from two MAO-activated catalysts: *rac*- $C_2H_4(Ind)_2ZrCl_2$ and the novel, highly regiospecific *rac*- $Me_2C(3-t-Bu-Ind)_2ZrCl_2$. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metallocene catalysts polymerize α -olefins to linear polymers covering the whole range of molecular weights and stereoregularities [1,2]. Chiral, C_2 -symmetric zirconocenes are isospecific by virtue of their symmetry, producing isotactic polypropylenes (*i*-PP) that, in comparison to Ti-based heterogeneous catalysts, have narrower molecular weight distributions, isotacticities spanning from almost atactic to perfectly isotactic, incomplete regiospecificity (indicated by the detection of isolated secondary propylene insertions), a random distribution of stereo- and regioerrors in the polymer chain, and lower molecular weights, due to several facile β -hydride transfer reactions.

In addition to the strong influence of the *ansa*- π ligand structure, the microstructure of *i*-PP from chiral zirconocenes is also dependent on both polymerization temperature and propylene concentration.

In particular, and in contrast to the performance of Ti-based heterogeneous catalysts [3,4], isotacticity decreases when the concentration of propylene is lowered [5–9], due to the competing

reaction of unimolecular primary-growing-chain-end epimerization, which scrambles the chirality of the chirotopic methine of the metal-bound propylene unit in the growing chain.

Lowering propylene concentration also induces a non-linear decrease of the molecular weight of *i*-PP, due to β -hydride transfer after a primary insertion [9]. In addition, secondary propylene unit isomerization to tetramethylene sequences (2,1 \rightarrow 3,1 isomerization) is increased with bulkier ligands, lower propylene concentrations and higher polymerization temperatures [6,7,9–11].

In this work a possible mechanism is presented, which rationalizes the above observations, that is epimerization and chain transfer after primary insertion, and in addition accounts for a number of other experimental observations, such as H₂ evolution and formation of internal unsaturations.

2. Discussion

2.1. Primary growing chain epimerization

Leclerc and Brintzinger [12,13] have shown that unimolecular formation of primary insertion stereoerrors (primary-growing-chain-end epimerization) occurs with exchange of the methylene and methyl carbons of the stereoinverted unit:

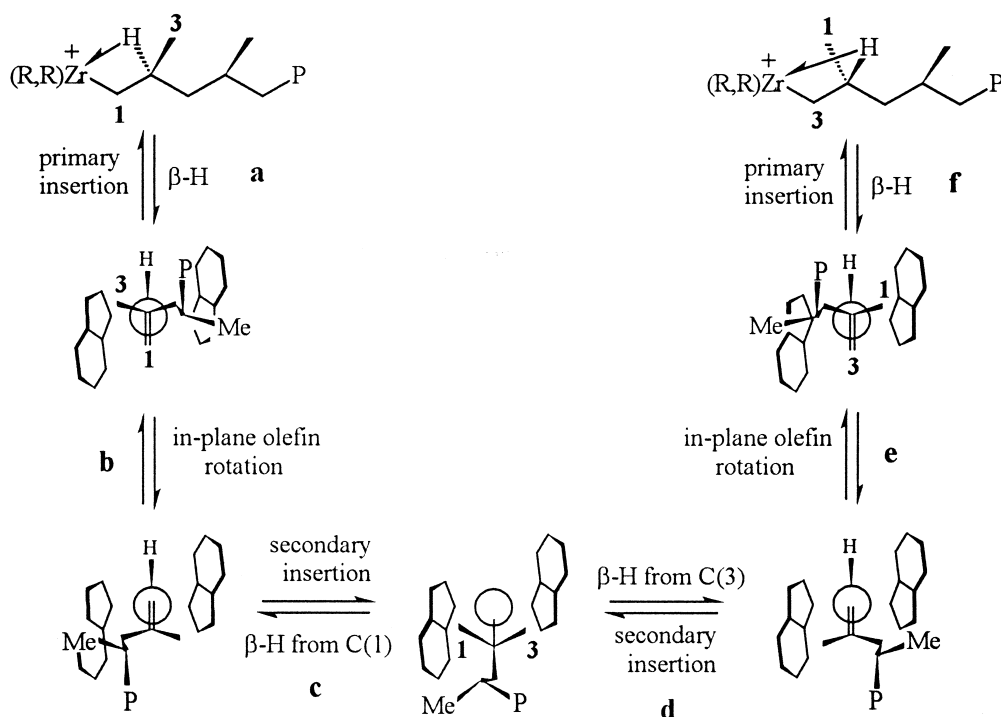


Busico and Cipullo [5–7] and Busico et al. [8] have proposed a mechanism that accounts for both the decrease of isospecificity occurring at decreasing concentrations of propylene, and the exchange of methylene with methyl in the epimerized unit. This mechanism, shown in its entirety in Scheme 1, appears flawed because of the requirements of rotation of the coordinated, α,α -disubstituted olefinic end group from *primary* to *secondary* (step b), and then its *secondary* insertion into the Zr–H bond (step c), which seems sterically unfeasible. In fact, Guo et al. [14] have shown that isobutene undergoes only primary insertion into the Zr–H bond of $(\text{MeCp})_2\text{ZrH}(\text{THF})^+$. In addition, secondary insertion of propylene into the Zr–H bond generated under hydroooligomerization conditions from $(-)-(R)\text{-C}_2\text{H}_4(\text{H}_4\text{Ind})_2\text{ZrMe}_2/\text{MAO}$ is not observed [15].

Before discussing a possible alternative mechanism for epimerization, a number of experimental observations available in the literature will be reviewed.

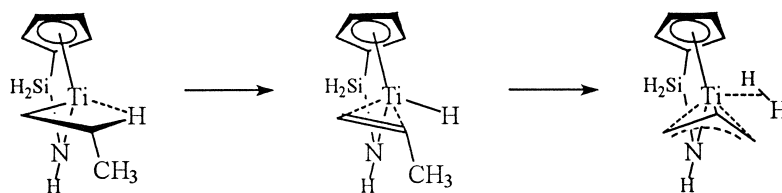
Neutral zirconocene(π -allyl)alkyl complexes are known [16–18]. Jordan et al. [19], Horton [20], Eshuis et al. [21] and Tjaden [22] have reported the synthesis of $(\text{Cp}')_2\text{Zr}(\eta^3\text{-allyl})$ cations ($\text{Cp}' = \text{MeCp}, \text{Me}_5\text{Cp}$) [23].¹ Richardson et al. [24] have observed the formation of the $[\text{Cp}_2\text{Zr}(\text{methallyl})]^+$ cation and H₂, from the reaction of $[\text{Cp}_2\text{ZrMe}]^+$ and propylene in the gas phase. More recently, in the gas-phase oligomerization of 1-butene catalyzed by the same methylzirconocene cation at higher pressure, Feichtinger et al. [25] observed the formation of a similar $[\text{Cp}_2\text{Zr}(\text{methallyl})]^+$ cation. Margl et al. [26,27] have theoretically shown that formation of the π -allyl-dihydrogen complex from the

¹ Also noteworthy is the work by Marks on $\text{Cp}_2^*\text{La}(\text{allyl})$ and $\text{Cp}_2^*\text{Nd}(\text{allyl})$, which were obtained by reaction of the hydrides with propylene, via intramolecular allylic C–H activation of a coordinated propylene molecule on $\text{Cp}_2^*\text{M}(\text{propyl})$, the first insertion product.



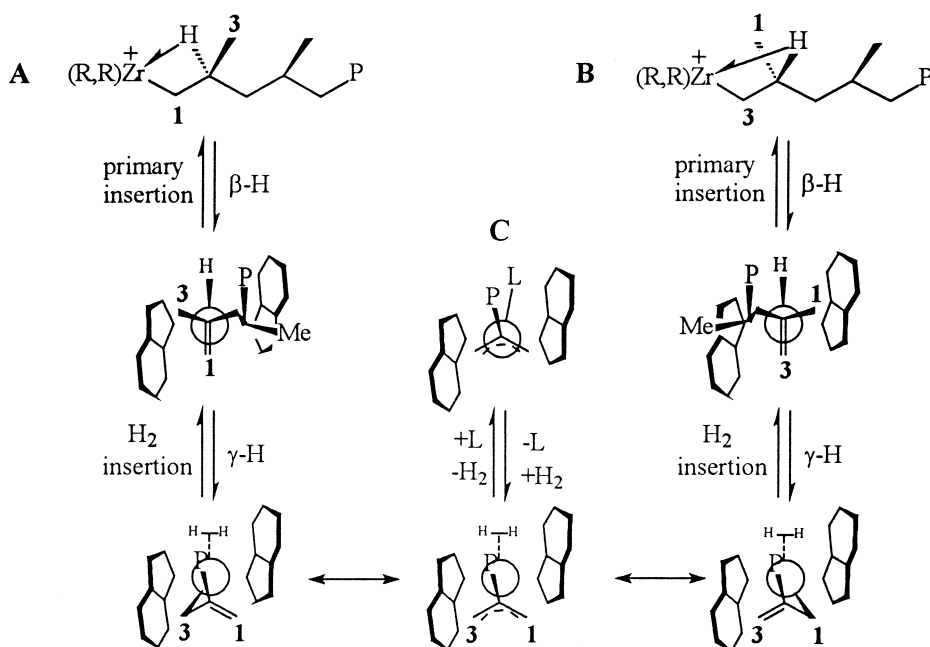
Scheme 1. Racemization of the growing-chain-end chirotopic methyne (epimerization) at an $(R,R)\text{-C}_2\text{H}_4(\text{Ind})_2\text{Zr}^+$ active center: extended form of the mechanism proposed in Ref. [3]. The ligand bridge is omitted for clarity.

products of β -hydride shift of both a ‘constrained geometry’ $\text{H}_2\text{Si}(\text{Cp})(\text{NH})\text{TiR}^+$ catalyst, and a zirconocene alkyl cation, is facile:



Karol [28], Karol et al. [29] and Wasserman et al. [30] have reported the formation of small amounts of hydrogen in the reactor gas phase of metallocene-catalyzed ethylene/ α -olefin copolymerizations, and relevant amounts (more than one per chain) of internal unsaturations in ethylene/1-butene and ethylene/1-hexene copolymers produced with the $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO}$ catalyst. In addition, they suggested that these internal *trans*-vinylenes could be formed via allyl formation after a $\beta\text{-H}$ elimination step, a process that releases H_2 . In addition, small amounts of H_2 have also been detected in the gas phase of batch liquid propylene polymerizations with *rac*- $\text{C}_2\text{H}_4(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ [31].

With only one additional hypothesis, that the formation of the allyl- H_2 complex is reversible, we can derive a likely and simple mechanism for primary-growing-chain-end epimerization, which is sketched in Scheme 2.



Scheme 2. Racemization of the growing-chain-end chirotopic methyne (epimerization) at an $(R,R)\text{-C}_2\text{H}_4(\text{Ind})_2\text{Zr}^+$ active center via reversible formation of a $\text{Zr}(\text{allyl})(\text{H}_2)$ cation. A \rightarrow B: epimerization; A \rightarrow C: deactivation. L = neutral or anionic ligand (e.g., solvent, AlR_3 , MAO, MAO^-). The ligand bridge is omitted for clarity.

By means of this mechanism, we can explain a number of experimental facts.

(i) As shown by Leclerc and Brintzinger, epimerization occurs with C(1)–C(3) exchange, and this is readily explained by the intervention of an η^3 -allyl intermediate; compared to the tertiary alkyl mechanism shown in Scheme 1 (which also accommodates C(1)–C(3) exchange) [5–7,12,13], the present one requires fewer steps and much less atomic motion.

(ii) If we assume that the $\text{Zr}(\text{allyl})(\text{H}_2)$ intermediate is less reactive towards insertion² than a $\text{Zr}(\text{primary-growing-chain})$, and that loss of coordinated H_2 will lead to an inactive $\text{Zr}(\eta^3\text{-allyl})$ species, we have a model for both reversible catalyst deactivation and hydrogen activation. In fact, it has been shown by Eshuis et al. [21] that the $\text{Cp}_2^*\text{Hf}(2\text{-methyl-allyl})^+$ species is inactive in the polymerization of propylene, but is reactivated by addition of H_2 . Allyl intermediates as possible cause for catalyst deactivation have been invoked in the case of heterogeneous Ti catalysts, although the $\text{Ti}(\text{allyl})$ species, in the model of Guyot et al. [32,33], is formed by allylic C–H activation of the coordinated monomer, not the polymer chain.

(iii) The exponential dependence of catalyst activity on propylene concentration:

$$R_p = k'_p [M]^\alpha \quad \text{with} \quad 1 \leq \alpha \leq 2$$

observed for stereospecific zirconocene catalysts [34–37] has been proposed to stem from the fact that a given single-center catalyst can exist in two interconverting states, a fast and a slow one, with their

² A dormant species, as defined by Busico, is a metallocene species bearing a secondary growing chain; this species requires a chemical transformation (be it 2,1 \rightarrow 3,1 isomerization or chain transfer) to regain the ability to insert monomer at appreciable rate. Similarly, our putative zirconocene allyl intermediate can still insert monomer, but at a (much) lower rate than a zirconocene σ -hydrocarbyl, possibly after an $\eta^3 \rightarrow \eta^1$ rearrangement. Note that $(\text{Cp}')_2\text{Zr}(\text{allyl})^+$ species have been reported active in the polymerization of ethylene (we assume with a lower intrinsic activity than a $(\text{Cp}^*)_2\text{ZrR}^+$ species) [19,22], but inactive towards insertion of propylene [21].

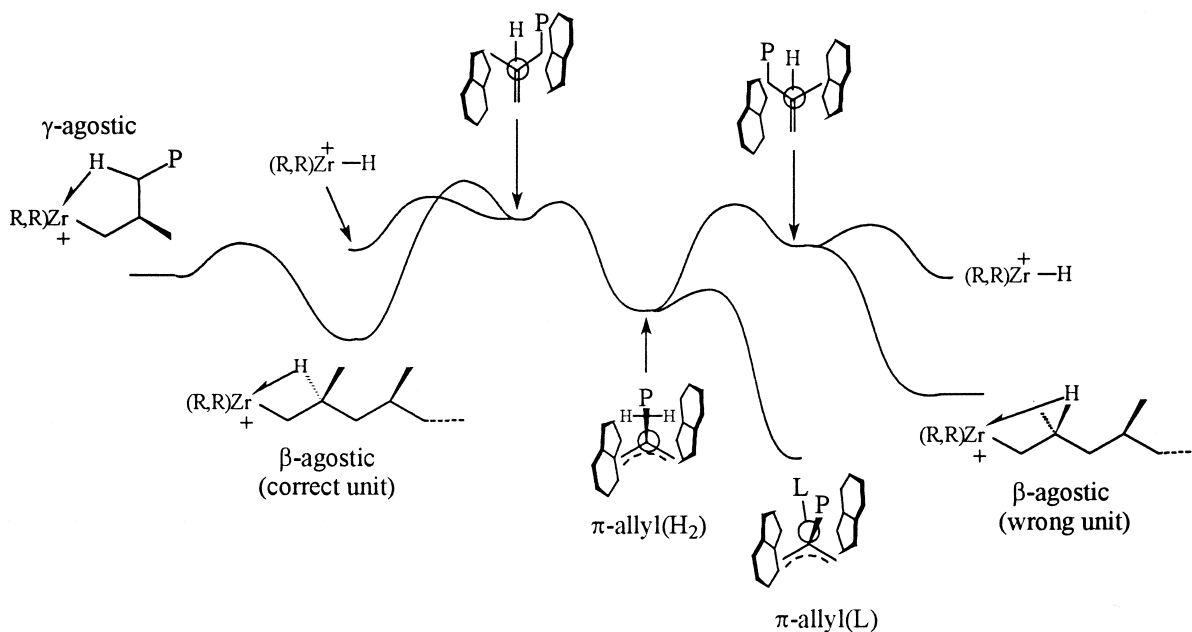


Fig. 1. Qualitative energy diagram showing epimerization and chain transfer. The rate-determining step is unimolecular β -hydride transfer to the metal.

molar fractions being dependent on propylene concentration [9,38,39]. The $\text{Zr}(\eta^3\text{-allyl})(\text{H}_2)$ intermediate could be either the slow state, or the product of an additional intramolecular reaction of the same slow state: according to Scheme 2, its concentration would be inversally dependent on [propylene], as propylene would inhibit the formation of a β -agostic hydrogen interaction, hence allyl formation.

(iv) D-scrambling, reported by Brintzinger and Leclerc, and (v) formation of internal vinylidenes and isobutenyl end groups can be accommodated by the allyl mechanism, and are discussed in Sections 3 and 4.

In addition, Scheme 2 provides a driving force to epimerization. In fact, β -H transfer from the last unit (previously generated by a correct insertion) of a primary growing chain generates the metallocene(olefin)cation with the olefin coordinated with the *least* favored enantioface. A qualitative energy diagram is shown in Fig. 1.

This also suggests that the generally low enantioselectivities observed for olefin hydrogenation with C_2 -symmetric zirconocenes might, in part, be due to enantioface inversion via the allyl mechanism [40].

3. Chain transfer reactions

The structure of unsaturated end groups observed in *i*-PP from C_2 -symmetric zirconocenes has been reported by us in some recent papers [9–11,41]. Here we focus on the presence of internal *vinylidene* unsaturations, which have been previously observed in most *i*-PP samples from C_2 -symmetric zirconocenes [41]. Fig. 2 shows the ^1H NMR (400 MHz) of the unsaturated end group region of two *i*-PP samples prepared with the *rac*-[ethylene(1-indenyl)] $_2\text{ZrCl}_2/\text{MAO}$ catalyst at 50°C , at two different propylene concentrations: 0.4 M in toluene and 11 M (liquid monomer). The inequality of the two vinylidene peaks of the sample prepared in liquid monomer clearly shows that there is an

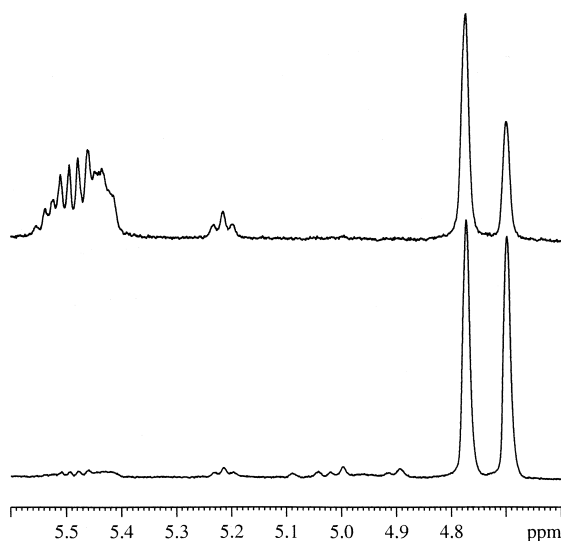
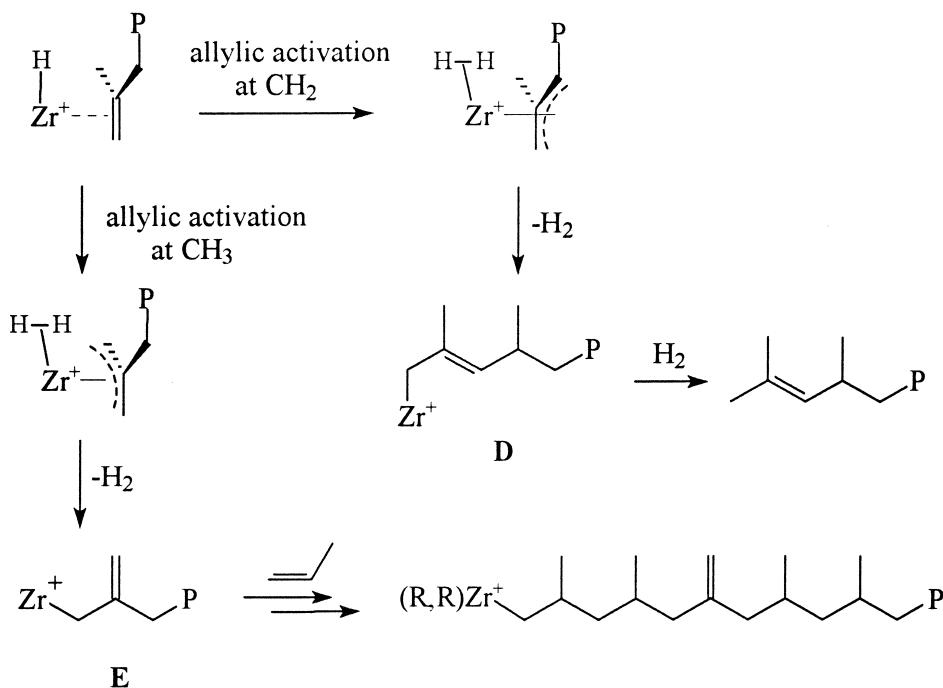


Fig. 2. Olefin region of the ^1H NMR spectra of two *i*-PP samples prepared with the rac -[ethylene(1-indenyl)] $_2\text{ZrCl}_2$ /MAO catalyst at 50°C : in liquid propylene (top) and at 1 bar propylene in toluene (bottom).

additional, symmetrical vinylidene overlapping the lower field vinylidene peak. A possible origin of this unsaturation (different from that suggested in Ref. [41]) is shown in Scheme 3.

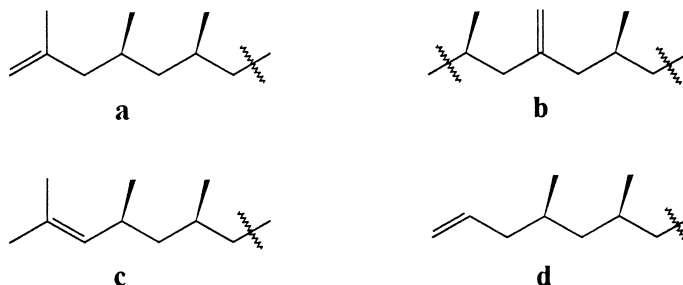
Note that, according to this mechanism, and as it is the case of the internal *trans*-butenyl group formation proposed by Karol et al. [29] and Wasserman et al. [30], *internal vinylidene formation is not, per se, a chain transfer reaction.*



Scheme 3. Formation of internal vinylidene by propylene insertion at the η^1 -allyl intermediate **E**. Insertion of monomer at the η^1 -allyl intermediate **D** could not be detected.

Also, if the mechanism of formation of internal symmetrical vinylidene shown in Scheme 3 is correct, one might expect that the amount of this unsaturation changes with the structure of the ligand (as we have shown in Ref. [41]) and monomer concentration, due to different positions of the equilibrium: η^3 -allyl (*inactive*) \rightarrow η^1 -allyl (*active*). In fact, as shown in Fig. 2, the internal vinylidene is clearly observed in the *i*-PP sample obtained in liquid monomer (internal:terminal = 0.6:1) while there is practically none of this group at lower propylene concentration (higher epimerization rate).

Based on this mechanism, one would also expect that excess H_2 should suppress the formation of both the internal vinylidene and the isobutenyl end groups. Indeed, it does; when liquid propylene is polymerized with *rac*- $Me_2C(3-t-Bu-Ind)_2ZrCl_2/MAO$ ($50^\circ C$, 1 h), we observe four end groups: terminal vinylidene (a), internal vinylidene (b), isobutenyl (c) and allyl (d).



The terminal vinylidene, internal vinylidene, and isobutenyl are in the ratio of a:b:c = 1:1.8:0.8, with frequencies (unsaturations per monomer unit) $a = 1.3 \times 10^{-4}$, $b = 2.3 \times 10^{-4}$, $c = 1 \times 10^{-4}$;

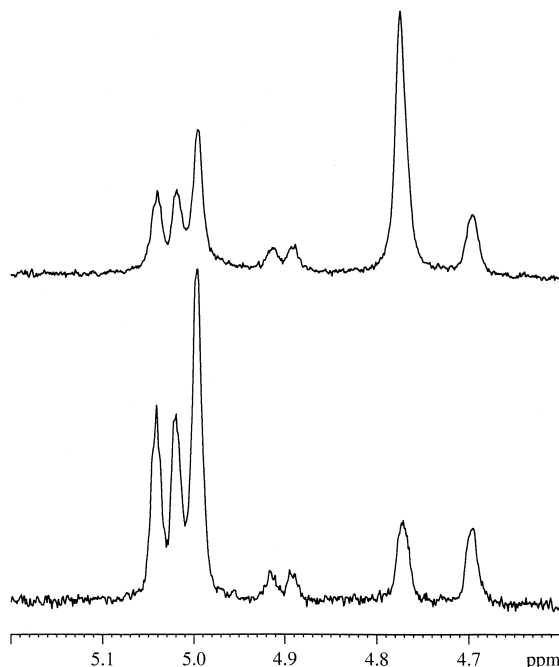
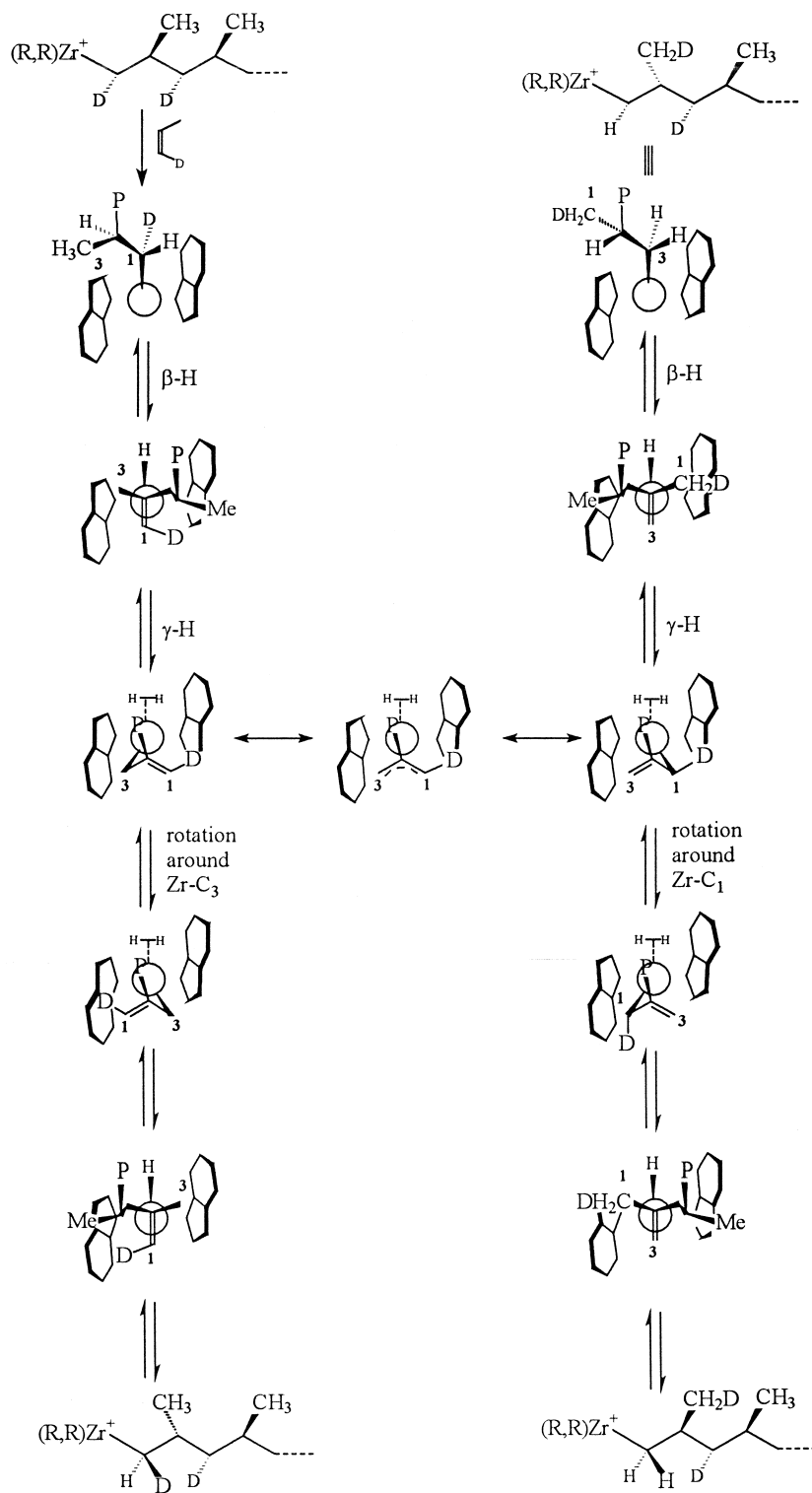
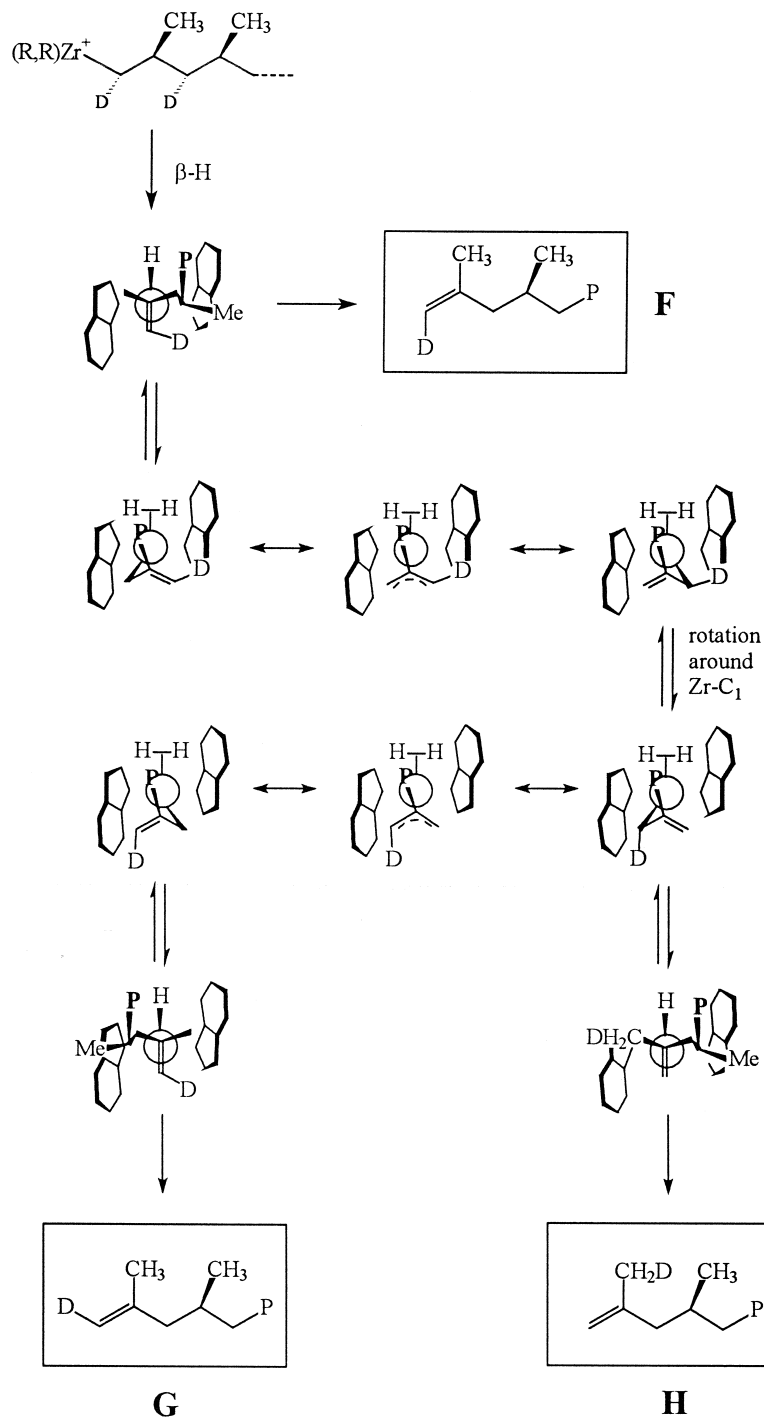


Fig. 3. Olefin region of the 1H NMR spectra of two *i*-PP samples prepared with the *rac*- $[Me_2C(3-t-Bu-1-Ind)]_2ZrCl_2/MAO$ catalyst at $50^\circ C$ in liquid propylene: without hydrogen (top) and with 4 bar H_2 in toluene (bottom).



Scheme 4. Polymerization of (Z)-[1-D]propylene.

when the same polymerization is carried out in the presence of 4 bar H_2 , internal vinylidenes are no longer detectable, and the isobutenyl group is diminished: a:c = 1.8, with frequencies a = 1×10^{-4} , c = 7×10^{-5} . The two 1H NMR spectra are compared in Fig. 3.



Scheme 5.

4. Deuterium scrambling

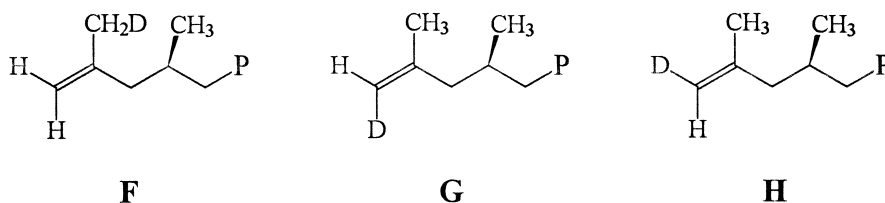
Leclerc and Brintzinger have reported a detailed microstructural analysis of poly-(*Z*)-[1-D]propylene, poly-(*E*)-[1-D]propylene, and poly-[2-D]propylene [13]. The main findings can be summarized as follows.

(a) Poly-(*Z*)-[1-D]propylene: at low monomer concentration, most errors contain a D atom on the methyl group of the stereoirregular unit; in addition, a similar amount of CH₂D is found in stereoregular units. This second finding cannot be explained by Busico's mechanism, but is easily accommodated by the allyl mechanism, assuming both $\eta^1 \rightarrow \eta^3$ and rotation with enantioface exchange to be facile. The distribution of D atoms is shown in Scheme 4.

(b) Poly-[2-D]propylene: again, stereoerrors mostly have a D atom in the methyl group. In addition, as it is the case for (*Z*)-[1-D]propylene, a similar amount of CH₂D is found in stereoregular units. Again, this second finding cannot be explained by Busico's mechanism, and is accommodated by the allyl mechanism.

Note that the allyl mechanism also predicts D scrambling in the CH₂ (for poly-(*Z*)-[1-D]propylene) and CH (for poly-[2-D]propylene) groups.

D scrambling is also observed in the terminal vinylidene end groups, and for poly-(*Z*)-[1-D]propylene, the following end groups have been observed [13]:



with $F > G > H$. In the case of poly-(*E*)-[1-D]propylene, the same end groups were observed, but in the order $F > H > G$.

The allyl mechanism accounts for the formation of all the three end groups, by olefin dissociation from the different Zr-(α -Me- α' -P-olefin) intermediates. E.g., for poly-(*Z*)-[1-D]propylene, as shown in Scheme 5, end groups F and H arise from the zirconium(olefin) intermediates shown in Scheme 4, and group H can be generated by syn-anti proton exchange of the allyl intermediate [42], a process already documented for a cationic zirconocene(allyl) species [19].

5. Conclusions

A new mechanism for primary-growing-chain-end epimerization in propylene polymerization with C₂-symmetric zirconocenes is proposed. This mechanism requires reversible formation of a zirconocene (allyl) dihydrogen complex, and is based on the results of gas-phase ionization experiments reported by Richardson [24] on the theoretical calculations on related systems by Margl et al. [26,27] and on the detection of chain unsaturations and hydrogen evolution in ethylene/ α -olefin copolymerizations reported by Karol [28], Karol et al. [29] and Wasserman et al. [30]. This novel mechanism correlates the loss of catalyst stereospecificity to the decrease of polypropylene molecular weights observed by lowering [propylene], predicts the formation of internal vinylidenes and their dependence

on both [propylene] and [H₂], and provides a driving force to epimerization, as the barrier to olefin insertion into the metal hydride bond is lowered by olefin enantioface exchange. A number of other experimental observations are explained, such as: (i) catalyst activity increase by adding H₂; (ii) the observed deuterium scrambling in the [1-D]-propylene and [2-D]-propylene polymerizations. In addition, one could speculate also that 1-butene 4,1-insertion [43] can be explained by the intervention of an allyl(H₂) intermediate, and also likely, propylene 3,1-insertion [44–48]. In the latter case, however, other, possibly simpler, mechanisms can be invoked [49–51]. We are currently investigating this latter isomerization reaction.

Acknowledgements

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