# Stereochemistry of First Monomer Insertion into a Metal−Methyl Bond: Enantioselectivity and Diastereoselectivity in 3-Methyl-1-pentene Polymerization with Metallocene Catalysts

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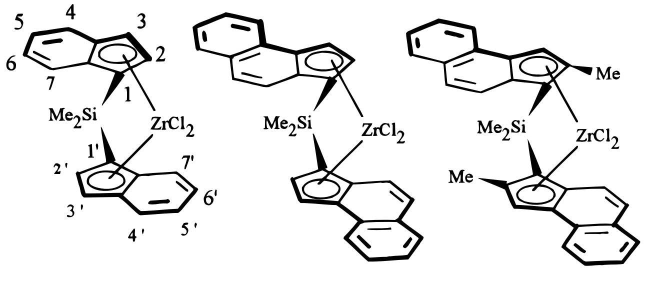
ABSTRACT: The stereochemistry of first monomer insertion in the polymerization of racemic 3-methyl-1-pentene ((*RS*)-3MP1) with three different metallocene complexes, $Me_2Si(Ind)_2ZrCl_2$ (**I**), $Me_2Si(BenzInd)_2ZrCl_2$ (**II**), and $Me_2Si(MeBenzInd)_2ZrCl_2$ (**III**), in the presence of MAO/$Al(^{13}CH_3)_3$ cocatalyst has been studied and the results have been compared to those previously obtained using the traditional isospecific $TiCl_3/Al(^{13}CH_3)_3$ heterogeneous catalyst. The highest enantioselectivity and diastereoselectivity are observed with the least hindered metallocene (catalyst **I**). While enantioselectivity decreases due to benzannelation of the ligand with catalyst **II**, the methyl substitution in the 2-position of the cyclopentadienyl rings with catalyst **III** causes an almost complete lack of diastereoselectivity.

## Introduction

The microstructure of poly-α-olefins obtained with isospecific metallocene-based catalysts is strongly influenced by the metal ligand structure. Variations of the basic structure of $(en)(Ind)_2ZrCl_2$, number and size of the atoms of the bridge as well as in size, positions, and combinations of the aromatic ring substituents, can produce often dramatic variations in isotacticity and in the number and type of misinsertions.[1] Many studies have been made to explain the relationship between ligand structure and polymer microstructure.[2] In order to get new information in this field, especially by focusing on monomer−ligand interactions, we have studied the stereochemistry of first monomer insertion in the polymerization of racemic 3-methyl-1-pentene ((*RS*)-3MP1) with three different metallocene complexes: $Me_2Si(Ind)_2ZrCl_2$ (**I**), $Me_2Si(BenzInd)_2ZrCl_2$ (**II**), and $Me_2Si(MeBenzInd)_2ZrCl_2$ (**III**) (Chart 1).

**Chart 1**



I II III

With respect to the simplest catalyst, **I**, catalysts **II** and **III** bear substituents in positions which have been shown to be decisive in propene polymerization. The addition of a 4,5-annelated aromatic ring results in a noticeable increase in isotacticity and in the frequency of regioinversions;[3] methyl substitution in the 2-position (α-methyl groups) is reported to lessen the number of chain terminations and misinsertions and to have a reinforcing effect on isotacticity.[3,4] All three metallocene complexes chosen can polymerize α-olefins branched in the 3-position, even if they have remarkably different activities.[3b]

Previously, polymerization of (*RS*)-3MP1 had been studied by Pino and co-workers[5] using the traditional isospecific $TiCl_3/AlR_3$-based heterogeneous catalyst. They discovered that polymerization of (*RS*)-3MP1 gives rise to a mixture of macromolecules, each of which consists prevailingly of *R* or *S* monomeric units. These results were explained by the fact that $TiCl_3$ heterogeneous catalyst consists of a racemic mixture of asymmetric centers in which, depending on the configuration, each reacts preferentially with either one or the other antipode of the monomer. Polymerization of (*RS*)-3MP1 was further investigated by Zambelli and co-workers[6] through $^{13}C$ NMR analysis of the selectively $^{13}C$-enriched chain-end groups, which come from the first monomer insertion into the $Ti-^{13}CH_3$ bond, when $Al(^{13}CH_3)_3$ is used as a cocatalyst. This method, which had previously supplied noticeable information on the polymerization stereochemistry of propene, permitted a better understanding of the mechanism of diastereoselective control on (*RS*)-3MP1 insertion and a quantitative evaluation of the first step diastereoselectivity. In Figure 1 the four diastereotopic faces of (*RS*)-3MP1 are shown: through the analysis of selectively enriched chain-end groups, it was pointed out that the *R′R* and *S′S* faces were about twice as reactive as the *S′R* and *R′S* faces (diastereoselectivity = 67%).

Figure 2 shows the modified Fisher projections of the eight possible diastereomeric environments of the $^{13}C$-enriched methyl groups which result from the incorporation of the two first monomeric units, taking into consideration both the backbone and the side chain asymmetric carbons.[7] Due to the fact that the metallocene complexes are racemic, eight more diastereomers are expected, but since they are mirror images of those considered, they are omitted.

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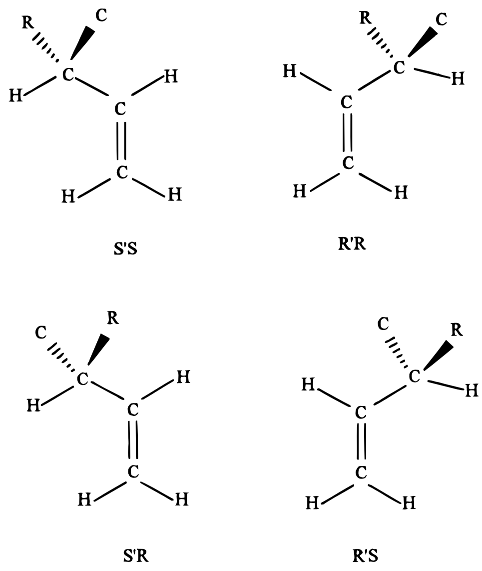


**Figure 1.** Diastereotopic faces of (*RS*)-3-methyl-1-pentene (R = $C_2H_5$). *R'* and *S'* indicate the absolute configuration of the prochiral carbon when the olefin is coordinated to a metal atom located below the plane of the figure.

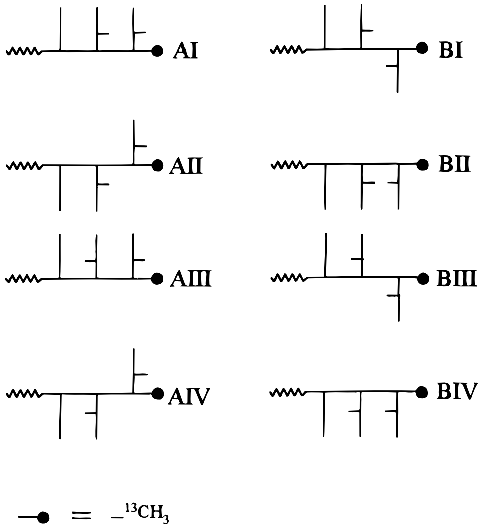


**Figure 2.** Modified Fisher projections of the eight possible stereochemical environments of the $^{13}$C-enriched methyl which result from the incorporation of two monomeric units.

In **AI** to **AIV** the $^{13}$C-enriched methyl is in *erythro* configurational relationship with respect to the vicinal methyl of the monomer side chain. In **BI** to **BIV** the $^{13}$C-enriched methyl is in the *threo* configurational relationship with respect to the same methyl. As reported,[6a] the *erythro* arrangement arises from the attack at the *R'R* and *S'S* faces while the *threo* arrangement arises from the attack at the *S'R* and *R'S* faces. Among the *erythro* **AI** to **AIV** diastereomers, **AI** and **AIII** are those in which the first monomer insertion is in isotactic relationship with respect to the second one while in **AII** and **AIV** the first monomer insertion is in syndiotactic relationship to it. The same holds for **BII** and **BIV** with respect to **BI** and **BIII**. A nearly complete assignment of $^{13}$C NMR resonances of these chain end groups has been reported.[6a]

## Results and Discussion

In the present work the first-step diastereoselectivity in (*RS*)-3MP1 polymerization with catalysts **I**–**III** is evaluated by the same method used for heterogeneous catalysts, that is, through the $^{13}$C NMR analysis of the $^{13}$C-enriched methyl chain-end groups which come from the insertion of the first monomeric unit into the active Zr–$^{13}CH_3$ bond, which is in turn formed through alkyl exchange of the metallocene complex/MAO catalyst with $Al(^{13}CH_3)_3$.

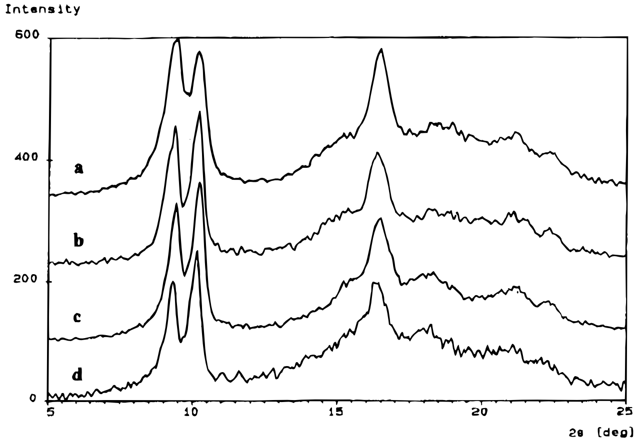


**Figure 3.** X-ray diffraction powder spectra of the samples of poly[((*RS*)-3-methyl-1-pentene] prepared with the traditional $TiCl_3$-based system (a) and with catalyst **I** (b), **II** (c), and **III** (d).

The X-ray spectra of poly[(*RS*)-3MP1] prepared with catalysts **I** (b), **II** (c), and **III** (d) and with the traditional $TiCl_3$-based system (a) are shown in Figure 3. The spectra are quite similar: the sample prepared with $TiCl_3$ appears slightly less crystalline, probably because of its higher molecular weight. These data indicate that the three metallocene-based catalysts produce poly[(*RS*)-3MP1] with highly isotactic structure as well as the traditional $TiCl_3$-based catalyst.

The complete $^{13}$C NMR spectra of poly[(*RS*)-3MP1] prepared with catalysts **I**–**III** in the presence of unenriched cocatalyst are shown in Figure 4b–d. The corresponding spectrum of the benzene soluble fraction of a sample of poly[(*RS*)-3MP1] prepared with the $TiCl_3$-based system is shown in Figure 4a as a point of reference. A fraction is used in this last case since poly[(*RS*)-3MP1] obtained with traditional heterogeneous catalysts is poorly soluble due to its high molecular weight. The assignment of the main carbon resonances is also shown. All the spectra present nearly the same broad resonances: since all the samples have been shown to be highly isotactic, the line broadening can be reasonably ascribed to the low optical purity of the chains. Even if it is not possible to evaluate polymerization diastereoselectivity from these spectra, the comparison allows us to deduce that the diastereoselectivity of the three metallocene catalysts is not higher than that of $TiCl_3$ catalyst.

The expanded methyl region of the $^{13}$C NMR spectra of the samples of poly[(*RS*)-3MP1] prepared with catalysts **I**–**III** with the enriched cocatalyst MAO/$Al(^{13}CH_3)_3$ is shown in Figure 5b–d. The corresponding spectrum of the benzene soluble fraction of the sample prepared with the heterogeneous $TiCl_3/Al(^{13}CH_3)_3$ catalyst is shown in Figure 5a. In all the spectra the same four $^{13}CH_3$ resonances are observed. The resonances at 14.97 and 15.09 ppm had been previously assigned to **AI** and **AII**, respectively, in which $^{13}CH_3$ is in the *erythro* relationship with the vicinal methyl substituent, and the resonances at 13.26 and 13.02 ppm to **BI** and **BII**, in which $^{13}CH_3$ is in the *threo* relationship. The extent of diastereoselectivity of the first monomer insertion can

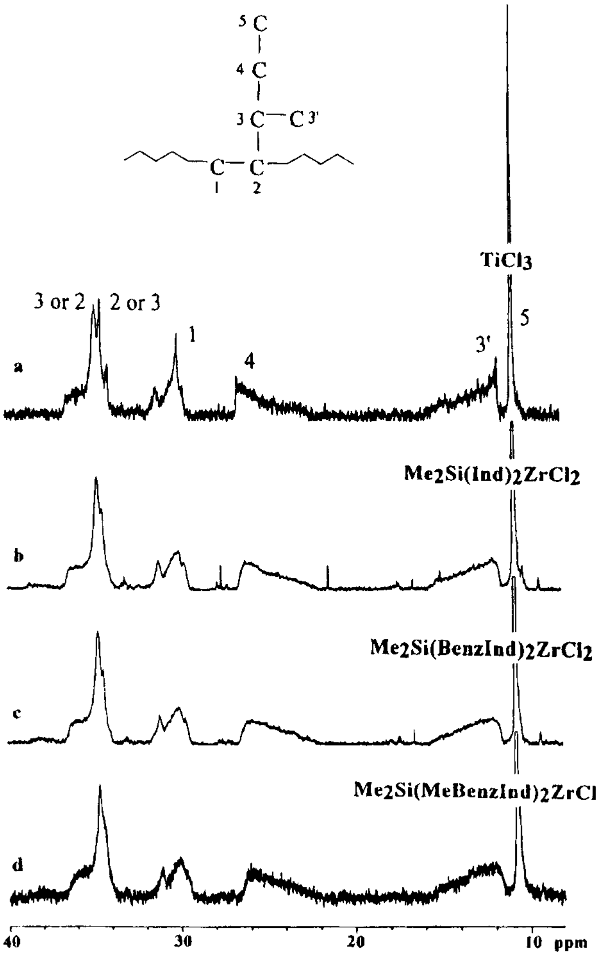


**Figure 4.** $^{13}$C NMR spectra of benzene soluble fraction of poly[(*RS*)-3-methyl-1-pentene] prepared with the traditional $TiCl_3$-based system (a) and of samples of poly[(*RS*)-3-methyl-1-pentene] prepared with catalyst **I** (b), **II** (c), and **III** (d).

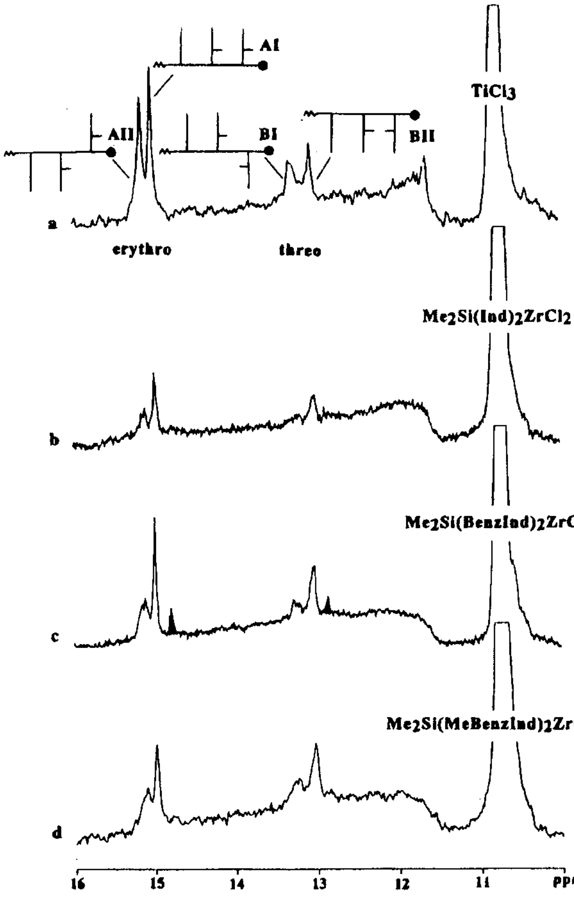


**Figure 5.** Expanded methyl region of the $^{13}$C NMR spectra of benzene soluble fraction of poly[(*RS*)-3-methyl-1-pentene] prepared with the traditional $TiCl_3$-based system (a) and of samples of poly[(*RS*)-3-methyl-1-pentene] prepared with catalyst **I** (b), **II** (c) and **III** (d). The dashed signals, which are detected only in spectrum c, are not assigned. However, they do not seem related to first monomer insertion.

**Table 1. First Monomer Enantio- and Diastereoselectivity Data**

| catalyst[a] | *t* (h) | yield (%) | enantio-selectivity[b] | diastereo-selectivity[c] |
|---|---|---|---|---|
| $TiCl_3$[6a] | 144 | 61 | 0.51 | 0.67 |
| $Me_2Si(Ind)_2ZrCl_2$ (**I**) | 48 | 47 | 0.63 | 0.70 |
| $Me_2Si(BInd)_2ZrCl_2$ (**II**) | 48 | 46 | 0.57 | 0.64 |
| $Me_2Si(MeBInd)_2ZrCl_2$ (**III**) | 48 | 7 | 0.57 | 0.52 |

[a] Polymerization conditions: toluene = 25 mL; [Zr] = 4 $\mu$mol; MAO/Zr = 500; $Al(^{13}CH_3)_3$/Zr = 100; $T$ = 50 °C. [b] Molar fraction of isotactic first monomer insertion evaluated from $^{13}$C NMR integrated peak areas according to the relationship ([**AI**] + [**BII**])/([**AI**] + [**AII**] + [**BI**] + [**BII**]) × 100. [c] Molar fraction of diastereoselective first monomer insertion evaluated from $^{13}$C NMR integrated peak areas according to the relationship ([**AI**] + [**AII**])/([**AI**] + [**AII**] + [**BI**] + [**BII**]) × 100.

be evaluated as molar fraction of *erythro* isertion [([**AI**] + [**AII**])/([**AI**] + [**AII**] + [**BI**] + [**BII**]) × 100]. Moreover, in **AI** and **BII**, the first monomeric unit is in isotactic relationship with respect to the next one, while in **AII** and **BI** the first monomeric unit is in syndiotactic relationship to it. Consequently first monomer enantioselectivity can be evaluated also and it is expressed as the molar fraction of isotactic first monomer insertion [([**AI**] + [**BII**])/([**AI**] + [**AII**] + [**BI**] + [**BII**]) × 100].

In Table 1 the enantioselectivity and diastereoselectivity values of first monomer insertion for all the samples are listed along with polymerization data.

**(A) First Step Enantioselectivity.** The most obvious datum is the difference between the $TiCl_3/Al(CH_3)_3$ catalyst and the three metallocene-based catalysts. With $TiCl_3$ the first monomer insertion was completely nonspecific. The enantioselectivity of this heterogeneous catalyst is generally accepted to arise from repulsive interactions between the $\beta$-carbon atom of the growing polymer chain and the incoming monomer.[8] Therefore, in the first insertion step into the Ti—methyl bond (where there is no growing chain) no enantioselectivity would be expected. The same behavior was observed for propene, 1-butene, and all the other α-olefins studied.

With the homogeneous catalytic systems we observe a different behavior: a small but definite first step enantioselectivity can be detected for all three catalysts: the least hindered complex (**I**) shows the highest enantioselectivity (0.63), while with the benzannelated catalysts (**II** and **III**) there is only a slight preference for one enantiotopic face (0.57).

A similar trend in first step enantioselectivity was previously observed in propene polymerization with the same three catalysts.[10] With $Me_2Si(Ind)_2ZrCl_2$, a moderate enantioselectivity was observed (0.60), and it was ascribed to repulsive direct interactions between the monomer and the ligand framework.[9,10] However, in the case of propene, such enantioselectivity almost completely vanishes (0.54) due to benzannelation of the ligand (catalyst **II**). The unexpected finding that both enantiotopic faces are almost equally favored by the bulkier benzo ligand was explained by the fact that the monomer interacts with different parts of the ligand framework depending on the faciality of its coordination. When the monomer is coordinated to one of its enantiotopic faces, there is an interaction between the propene methyl group and the indenyl benzo ring. On the other hand, when propene is coordinated to the other enantiotopic face, there could be an interaction between the propene methyl group and one of the hydrogen atoms on the benzo ring.

A similar explanation could also account for the decrease of first step enantioselectivity in (*RS*)-3MP1 polymerization with catalyst **II**: the increased bulkiness of the ligand generates similar repulsive interactions with both enantiotopic faces of (*RS*)-3MP1. The residual enantioselectivity, which is still detected in the case of (*RS*)-3MP1, could be ascribed to the fact that the two different monomers bear substituents which have different bulkiness and geometry, and therefore, it is likely that the substituent interactions with the ligand framework are different as well.

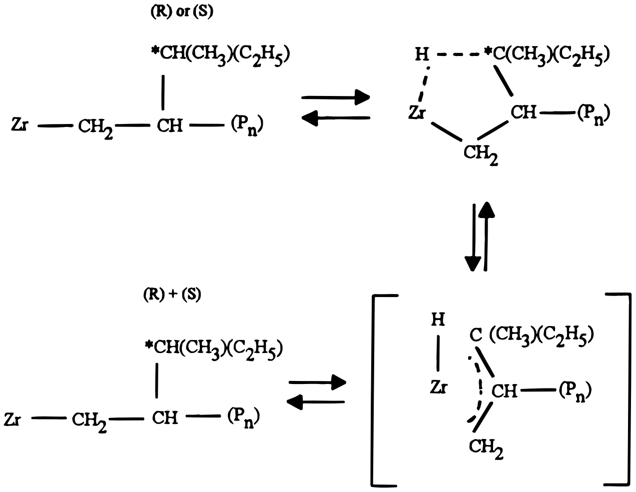
The introduction of the α-methyl groups at the cyclopentadiene rings (catalyst III) does not influence the first step enantioselectivity of either (*RS*)-3MP1 or propene.[10] Evidently, these methyls are far away from the incoming monomer and do not have any direct steric interaction with it.

**(B) First Step Diastereoselectivity.** The first step diastereoselectivity observed with the simplest $Me_2Si(Ind)_2ZrCl_2$ catalyst (0.70) is rather similar to that observed with $TiCl_3$ (0.67), indicating that the *S′S* and *R′R* faces of the monomer are about twice as reactive as the *S′R* and *R′S* faces with both catalysts. The trend of diastereoselectivity observed by passing from the least to the most hindered metallocene catalyst is quite interesting. With the bulkier benzindenyl ligand (catalyst **II**), a slight decrease of diastereoselectivity is observed while the yield does not vary significantly. The methyl substitution in the 2-position (catalyst **III**) causes an almost complete lack of diastereoselectivity. Here the yield is also noticeably lower than with catalysts **II** and **III**.

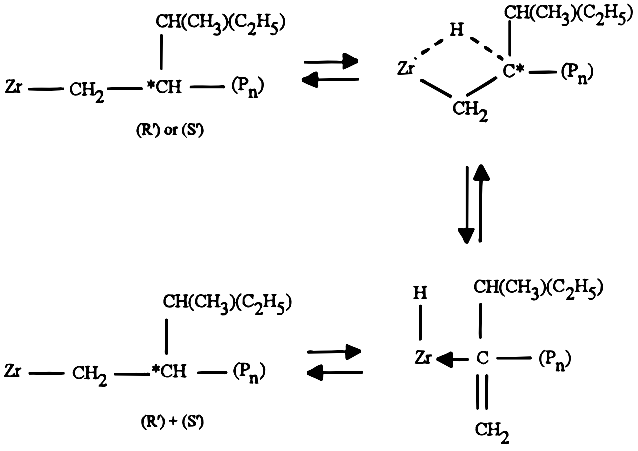
It is not easy to explain the observation that the methyl substituents on the cyclopentadienyl rings in position next to the silicon bridge have such dramatic effects on first step diastereoselectivity. The α-methyl substituents do not have any effect on first step enantioselectivity with either (*RS*)-3MP1 or propene, that is, they do not seem to affect the choice of the enantiotopic monomer faces. Therefore, they should not have any direct influence on the choice of the diastereotopic face either. However, steric interactions have been shown to occur between the two α-methyl substituents and the methyl groups on silicon, which increase the rigidity of the ligand framework.[3a] Similar repulsive interactions could then take place between the more rigid ligand framework and the two diastereotopic monomer faces. As a result, the insertion reactions of the two diastereotopic faces *R′R* and *R′S* (or *S′S* and *S′R*) would be equally disfavored. In this case the two α-methyl substituents would exert an indirect effect on diastereoselectivity. This could account for the low propagation rate also.

An alternative explanation for the above results is that a side reaction of racemization of the chiral carbon of the last inserted unit competes with the propagation reaction and that it prevails when, as in the case of catalyst III, the interactions between the monomer and the rigid ligand framework strongly slow down the propagation rate. Such a racemization would proceed through a $\gamma$-H elimination from the last inserted unit substituent, followed by an intermediate stage, such as an hypothetical allylic species, as represented in Scheme 1.

Scheme 1



Scheme 2



Similar epimerization reactions of the last inserted unit have been suggested to occur in propene[11] and 1-butene[12] polymerization with metallocene catalysts, when the propagation rate is low. However, under conditions in which the epimerization reactions are appreciable, a decrease of isotacticity is always observed, also as a result of $\beta$-H elimination, which becomes more probable when the propagation rate decreases, as in Scheme 2.

Therefore, if this second explanation was valid, poly-(*RS*)-3MP1 produced with the slower catalyst **III** should result less isotactic than that produced with the faster catalysts **I** and **II**. The fact that this polymer is highly isotactic (as the X-ray analysis indicates) seems to reinforce the first explanation, which considers the actual loss in the diastereoselective effect as due to an indirect effect of the increased ligand rigidity. Further experimental and theoretical work is in progress to clarify this point.

## Concluding Remarks

The comparison between the data regarding the stereochemical structure of the enriched methyl chain-end groups in (*RS*)-3-methyl-1-pentene polymerization in the presence of three isospecific metallocene catalysts and those previously obtained with “classical” heterogeneous catalyst $TiCl_3/Al(CH_3)_3$ allows us to draw the following conclusions.

(i) In (*RS*)-3MP1 polymerization with the heterogeneous $TiCl_3$-based catalyst the first monomer insertion was completely aspecific, as expected. On the contrary, with the least hindered metallocene catalyst **I**, a moderate enantioselectivity of first monomer insertion is observed, which decreases, although without vanishing, as a consequence of the addition of the bulky 4,5-annelated aromatic ring in catalysts **II** and **III**.

(ii) With $TiCl_3$, the *S′S* and *R′R* diastereotopic faces of the monomer were shown to be twice as reactive as the *S′R* and *R′S* faces. From our results with the metallocene catalysts, we see the same preference of these diastereotopic faces with catalyst **I** and a slightly smaller one with catalyst **II**, whereas a dramatic loss of first step diastereoselectivity occurs as a consequence of the presence of the α-methyl substituents in catalyst **III**.

(iii) The fact that first step enantioselectivity (that is, the choice between the two enantiotopic monomer faces) and diastereoselectivity (that is, the choice among the four diastereotopic monomer faces) seem to be guided by different repulsive interactions with the ligand framework confirms that enantioselectivity and diastereoselectivity are independent effects, with metallocene catalysts as well as with $TiCl_3$.

Further work will be devoted to identify the actual steric interactions which generate the two kinds of selectivity.

## Experimental Section

**General Procedures.** All operations were performed under a dry nitrogen atmosphere by using glovebox and conventional Schlenk line techniques. The monomer (*RS*)-3MP1 was dried by refluxing over $LiAlH_4$. Toluene was freshly distilled after refluxing over sodium. Nitrogen and propene were purified by passage through columns of BASF RS-11 (Fluka), Linde 4-Å molecular sieves, and calcium chloride. The metallocene complexes $Me_2Si(Ind)_2ZrCl_2$, $Me_2Si(BenzInd)_2ZrCl_2$, and $Me_2Si(MeBenzInd)_2ZrCl_2$ were prepared according to literature procedures.[1g] MAO (Witco, 30% w/w in toluene) was dried to remove solvent and unreacted TMA and stored under nitrogen. The cocatalyst solutions were freshly prepared by dissolving solid MAO in anhydrous toluene. $^{13}$C-Enriched TMA was prepared according to literature procedures.[4b]

**Polymerizations.** To 25 mL of anhydrous toluene in a 100 mL round-bottom flask equipped with a magnetic stirrer were added 2 mmol of MAO (1.1 M solution in toluene), 0.4 mmol of $^{13}$C-enriched TMA, and 2mL of (*RS*)-3MP1. A solution of 0.004 mmol of metallocene was transferred into the mixture via syringe.

The polymerizations were carried out at 50 °C for 2 days. The polymer was precipitated by pouring the mixture into 500 mL of ethanol acidified with 6 mL of concentrated hydrochloric acid. The precipitated polymer is stirred for 1 h, filtered, and dried under vacuum.

**$^{13}$C NMR Analysis.** The NMR samples were prepared by dissolving 100−150 mg of polymer in 2 mL of $C_2D_2Cl_4$ (which is also used as a lock solvent) in a 10-mm o.d. tube, and hexamethyldisiloxane (1%) was added as an internal chemical shift reference. All the spectra were obtained by using a Bruker AM-270 spectrometer operating at 67.89 MHz in the PFT mode, at 107 °C. In all measurements CPD was used to remove $^{13}$C−$^{1}$H couplings, the pulse angle was 90°, the pulse repetition time was 27s, and 4500 free induction decays were stored in 32 000 data points using a spectral window of 4950 Hz.

**X-Ray Analysis.** X-Ray spectra of unoriented samples were obtained with a Siemens D-500 instrument, using a Cu Kα graphite-monochromated radiation, divergence and receiving apertures of 0.3° and 0.05°, respectively, step width ($2\theta$) of 0.04°, and $2\theta$ range of 5°−35°.

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(7) For the sake of simplicity, in Figure 2 the enriched methyls are represented in chain-end groups of polymer chains in which, from the second monomer insertion on, the asymmetric carbons of the backbone have the same configuration. From the third monomer insertion on, the configuration of the asymmetric carbon of the side chain is not indicated. A rigorous definition of these eight diastereomers has been reported in a previous paper.[6a]

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