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Stereochemistry of First Monomer Insertion into Metal−Methyl Bond: A Tool for Evaluating Ligand−Monomer Interactions in Propene Polymerization with Metallocene Catalysts

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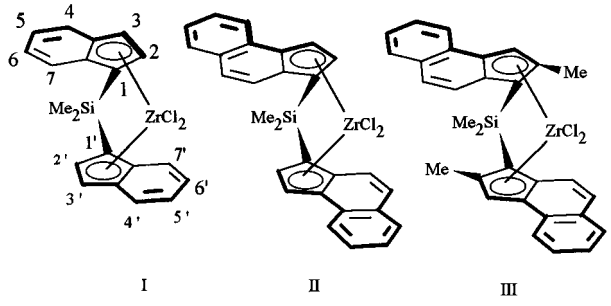
ABSTRACT: Propene has been polymerized with three different metallocene complexes: $Me_2Si(Ind)_2ZrCl_2$ (I), $Me_2Si(BenzInd)_2ZrCl_2$ (II), and $Me_2Si(MeBenzInd)_2ZrCl_2$ (III) by using ^{13}C-enriched cocatalyst MAO/$Al(^{13}CH_3)_3$. The stereochemical analysis of selectively ^{13}C-enriched methyl chain end groups has shown that, while a moderate first step enantioselectivity is present with catalyst I, the bulky benzannelated substituents (catalysts II and III) lead to an almost total lack of steric control on the first monomer insertion. The methyl substitution in the 2-position of cyclopentadienyl ring (catalyst III) does not seem to influence the choice of the face.

Since the discovery of the first soluble zirconocene/methylaluminoxane catalyst for the isotactic polymerization of propene,[1] much effort has been devoted to the question of how the mode and degree of stereospecificity could be explained.[2] The purpose of this paper is to report our contribution to understanding the mechanism of stereospecificity by focusing on the relationship between the position and the bulkiness of Cp-substituents and the steric control of monomer insertion. In the last few years the investigation, by ^{13}C NMR analysis, of the stereochemical structure of selectively ^{13}C-enriched chain end groups has been shown to be extremely informative on the contribution of the various ligands to steric control and also on the mutual interactions between the ligands, in heterogeneous Ziegler−Natta catalysis.[3] This method has been also successfully applied to the study of homogeneous metallocene-based systems.[4]

In the present paper a stereochemical study of the first monomer insertion into the ^{13}C-enriched $Zr-^{13}CH_3$ bond with three different metallocene complexes, $Me_2Si(Ind)_2ZrCl_2$, $Me_2Si(BenzInd)_2ZrCl_2$, and $Me_2Si(MeBenzInd)_2ZrCl_2$ (Chart 1), is presented.

Such an analysis is made possible by introducing ^{13}C-enriched CH_3 groups into the metallocene complex/MAO catalyst by alkyl exchange with $Al(^{13}CH_3)_3$. As has been extensively shown in previous papers,[3] the two possible resulting chain end groups are distinguishable and evaluable by ^{13}C NMR (Chart 2).[5]

Chart 1



Erythro (or isotactic) is the stereoisomer in which the first two monomeric units have the same configuration and threo (or syndiotactic) that in which the first two monomeric units have the opposite configuration. The signals of the enriched methyl carbons of the erythro and threo stereoisomers are at 20.4_4 and 21.7_5 ppm, respectively, downfield from hexamethyldisiloxane (HMDS). If e and t are the integrated peak areas of the enriched methyl resonances assigned respectively to the erythro and to the threo placements of the first propene unit, the molar fraction [e] of the erythro

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Chart 2

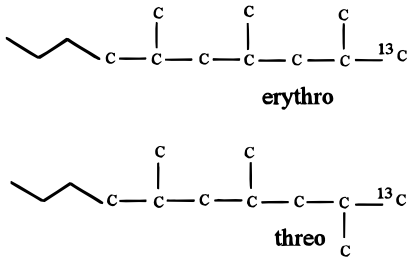

Table 1. Polymerization and Stereochemical Data

	catalyst	productivity, kg of PP/ (mol of Zr h)	[mmmm]	[e]	2,1-units (%)
I	$Me_2Si(Ind)_2ZrCl_2$	1900	0.78	0.60	0.4
II	$Me_2Si(BenzInd)_2ZrCl_2$	710	0.93	0.54	0.8
III	$Me_2Si(MeBenzInd)_2ZrCl_2$	840	0.93	0.54	0.5

[a] [e] = molar fraction of erythro (or isotactic) placement of first propene monomeric unit (error limits = ±0.01). Polymerization conditions: toluene = 50 mL; [Zr] = 4 μmol; [MAO/Zr] = 500; [Al($^{13}CH_3$)$_3$/Zr] = 100, T = 50 °C.

placement represents the extent of the first step stereoregularity. The peculiarity of this method is in the fact that it permits evaluation of the active center stereocontrol in the absence of the growing chain. In fact the conformation of the growing chain is recognized to have a fundamental role in the stereocontrol of the monomer insertion. The mechanism of stereocontrol generally accepted is that in which the asymmetric environment of the metal atom causes a unique chiral orientation of the first C−C bond of the chain in the most open sector of the ansa metallocene ligand framework.[2b−g] This orientation is an essential factor in determining the isospecificity since, in order to avoid repulsive interactions, that prochiral monomer approach will be favored which places the methyl group of the entering propene trans (on the opposite side) to the carbon atom of the growing chain in β position with respect to Zr. The study of the first monomer insertion into a Zr−methyl bond, by eliminating the dominant effect of the growing chain, allows us to estimate the direct effect of the ligand substituents on the enantioselectivity.

The three metallocene complexes chosen are appropriate for this study since they are isospecific and have the same coordination geometry at the Zr center: all three have a one-membered silicon bridge and have the same "coordination-gap" angle. Substitutions in the 4-positions (complexes II and III) and in 2-positions (complexes III) are reported to greatly influence yield, enantioselectivity, and molecular weights as well as the type and number of misinsertions in propene polymerization.[1] Table 1 summarizes polymerization and stereochemical data concerning propene polymerizations with the three complexes.

The stereochemical data are derived from polymerizations performed with the ^{13}C-enriched cocatalyst MAO/Al($^{13}CH_3$)$_3$ while the yields reported are average values of at least five experiments performed with natural abundance cocatalyst. The data regarding the yields are scarcely significant due to the fact that the polymerizations were not performed under optimum activity conditions and substantially differ from the trends reported in literature.[6] Indeed the MAO/Zr ratio was kept as low as possible in order to prevent dilution of the enriched methyls and consequent attenuation of the ^{13}C NMR signals of the enriched chain end groups.

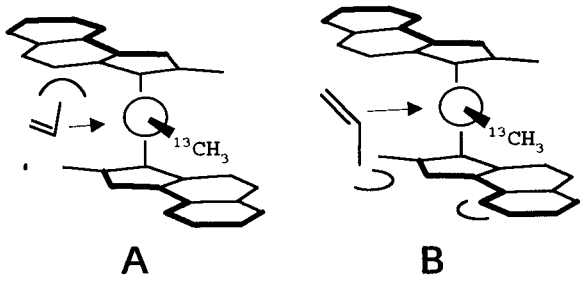

Figure 1. Schematic representation of propene insertion into the Zr−methyl bond: *si*-coordination (A) and *re*-coordination (B) of the monomer.

As expected there is a noticeable increase in propagation stereoregularity [mmmm] for catalysts II and III compared to catalyst I. In contrast to previous reports,[6] no increase of stereospecificity due to the methyl substitution in the 2-position is observed under our conditions on going from catalyst II to catalyst III. As to first step stereoregularity [e], a moderate selectivity (0.6) is observed with the least bulky catalyst I. A similar effect (0.66) was previously observed with (en)-$(Ind)_2ZrCl_2$ and it had been attributed to a direct influence of the metallocene ligands on the entering propene.[4c] It was proposed that repulsive interactions between the methyl group of propene and the β-Cp substituents were reinforcing the monomer orientation which leads to isotactic polymer.

The results from the bulkier catalyst II are more surprising. In fact, the increased bulk of the substituent in the 4-position, which greatly increases propagation stereoregularity, leads to an almost total lack of steric control on the first monomer insertion ([e] = 0.54). This means that, in this case, the bulky benzannelated substituents have similar repulsive interactions with the methyl on either prochiral face of the incoming propene.

Our hypothesis is, as shown in Figure 1, that the monomer can interact with different parts of the ligand framework depending on faciality of the monomer's coordination. When the monomer is coordinated to its *si*-face (Figure 1A) there is an interaction between the monomer methyl group and the benzo ring belonging to the indenyl system. On the other hand, when propene is coordinated to its *re*-face (Figure 1B), there could be an interaction between this methyl group and one of the hydrogen atoms on the benzo ring. So both prochiral faces are almost equally favored.

In contrast, during chain propagation, the bulkier benzoannelated substituents force the growing chain into a more constrained conformation which in turn favors a higher steric control. The gain in stereospecificity due to the growing chain effect largely compensates for the lack of any direct orientation effect of the ligand on the monomer, and therefore we observe an overall higher propagation isotacticity ([mmmm] = 0.93).

Methyl substitution at the 2-position (catalyst III) does not influence the first insertion, which still is almost completely aspecific ([e] = 0.54). Evidently these methyls are far away from the methyl of either prochiral face of the entering propene and so do not have steric interaction with it. Methyl substitution in the 2-position has been observed to reinforce the catalyst isospecificity. This reinforcing effect has been attributed to interactions between the 2-methyl substituents and the methyl groups on silicon, which would contribute to the rigidity of the ligand framework.[6a] The lack of ste-

reospecificity in the first monomer insertion shows that this increase in rigidity does not assist in giving any direct control over the entering monomer but rather that it may further increase the indirect controlling force of the chain conformation.

Conclusions

The stereochemical analysis of selectively ^{13}C-enriched methyl chain end groups has shown that the two stereochemical controlling factors, that is, the chiral fixed orientation of the first segment of the growing chain and the direct effect of the metallocene ligands on the entering propene, are influenced in different ways by varying bulk and position of the ligand substituents. In the simplest catalyst I ($Me_2Si(Ind)_2ZrCl_2$) both the effect of the growing chain ([mmmm] = 0.78) and the direct effect of the ligand framework ([e] = 0.6) on the entering monomer lead to preference of the same enantiotopic face of propene. On the contrary, the increasing bulk of the ligand in catalysts II and III ($Me_2Si(BenzInd)_2ZrCl_2$ and $Me_2Si(MeBenzInd)_2ZrCl_2$) produces a noticeable increase of propagation stereoselectivity ([mmmm] = 0.93) and a nearly complete lack of first step stereoselectivity ([e] = 0.54). Methyl substitution in the 2-position does not have any noticeable direct effect on steric control of first monomer insertion since [e] = 0.54 for both catalysts II and III.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere by using glove box and Schlenk line techniques. Nitrogen and propene used 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.[6b] MAO (Witco, 30% (w/w) in toluene) was dried under vacuum (ca. 0.1 mmHg) for 12 h at room temperature 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.[3b]

Polymerization. To 45 mL of anhydrous toluene in a 100 mL round bottom flask equipped with a magnetic stirrer 2 mmol of MAO (1.1 M solution in toluene) and 0.4 mmol of ^{13}C-enriched TMA were added. A solution of 0.004 mmol of metallocene is transferred into the mixture via syringe.

The polymerization is carried out at atmospheric propene pressure, at 50 °C for 1 h.

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 in 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 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 27 s, and 4500 free induction decays were stored in 32 000 data points using a spectral window of 4950 Hz.

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(5) Only the two resonances corresponding to the two stereoisomers shown in Chart 2 are detected since with isospecific Ziegler−Natta catalysts the second inserted units have the same configuration as the successive ones. Otherwise we should detect four methyl chain end groups resonances corresponding to the four possible stereoisomers formed after the insertion of the first two monomeric units. This last datum demonstrates that the insertion into the Mt−isobutyl group is as enantioselective as the propagation steps.[3,4]

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