Stereospecific Polymerization of Propylene in the Presence of Homogeneous Catalysts: Ligand–Monomer Enantioselective Interactions

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ABSTRACT: Syndiotactic and isotactic polypropylene have been prepared in the presence of the catalytic systems *i*-PrCp-1-FluZrCl$_2$/MAO and Et(1-In)$_2$ZrCl$_2$/MAO. ^{13}C-enriched Al(CH$_3$)$_3$ has been added to the catalysts in order to observe the stereospecificity of the initiation on metal–CH$_3$ bonds. ^{13}C NMR analysis of the enriched end groups shows the contribution to the enantioselectivity of the direct interaction of the incoming monomer with the ligands of the transition metal of the true catalytic species.

According to the literature, stereospecific polymerization of α-olefins, in the presence of homogeneous catalysts based on proper group 4 metallocenes, is due to the π facial enantioselectivity of the catalytic complexes toward the incoming prochiral monomer[1–9] and the incorporation of the monomer into the reactive metal–carbon bond is a primary cis ligand migration.[10–12] Thus, stereorigid metallocene precursors belonging to the C_s symmetry group (e.g., isopropyl(cyclopentadienyl)(1-fluorenyl)zirconium(IV) dichloride (*i*-PrCp-1-FluZrCl$_2$)) promote syndiotactic-specific polymerization[11] and stereorigid precursors belonging to the C_2 symmetry group (e.g., *rac*-(ethylenebis(1-indenyl)zirconium(IV) dichloride (Et(1-In)$_2$ZrCl$_2$)) promote isotactic-specific polymerization.[13] The relative stereospecificity of a variety of bridged metallocene precursors in promoting propene polymerization has been semiquantitatively accounted for by considering that the π facial enantioselectivity is mainly governed by the chain end orientation enforced by the substituents of the cyclopentadienyl rings β to the bridge (β-CpR).[1–9] Direct contacts between the β-Cp-R substituents and the monomer methyl group might additionally reinforce (isotactic) or diminish (syndiotactic) stereoregulation.[10–14]

The stereoregulation coming from direct contact between the β-Cp-R substituent and the methyl of propene, although very small, can be evaluated from the relative amount of the diastereomeric end groups formed when chain propagation is initiated on active metal–^{13}CH$_3$ bonds, labeled **a** and **b** in Figure 1.

The relative amount of **a** and **b** can be easily evaluated by ^{13}C NMR because the geminal methyl substituents in **a** and **b** are diastereotopic and the chemical shift of the ^{13}C-enriched methyl is ~20.6 ppm in **a** and 21.6 ppm in **b** (the chemical shifts are referred to hexamethyldisiloxane).

The ^{13}C NMR spectrum of mainly syndiotactic polypropylene (sample 1), prepared as described in the Experimental Section at 70 °C in the presence of a catalyst consisting of *i*-PrCp-1-FluZrCl$_2$ and methylalumoxane (MAO), is given in Figure 2. The overall stereoregularity of the polymer can be evaluated from the relative areas of the resonances of the methyl stereochemical pentads (see Table I).

The relative amount of the **a** and **b** ^{13}C-enriched end groups can be evaluated from the relative areas of the resonances at 20.7 ppm (**a**) and at 21.4 ppm (**b**). While the mutual arrangement of the methyl substituents along the chains is prevalently syndiotactic, the arrangement of the two nonenriched methyls of the end groups is

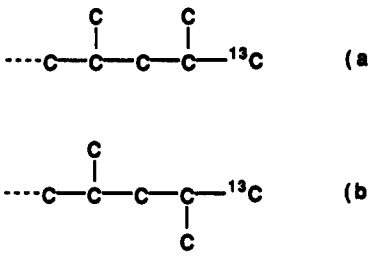

Figure 1. Fischer projection of diastereomeric end groups. The steric relationship between the methyls of two monomer units is *e* (isotactic) in **a** and *t* (syndiotactic) in **b**.[15]

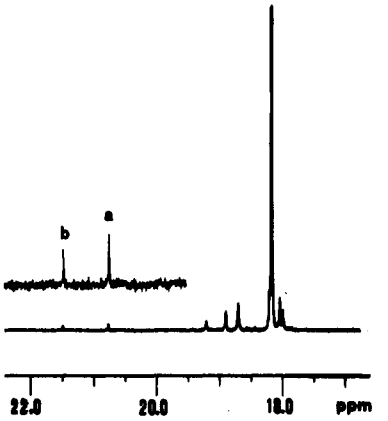

Figure 2. Methyl region of ^{13}C NMR spectrum of sample 1. HMDS scale. The signals labeled **a** and **b** are due to the ^{13}C-enriched methyls of the end groups given in Figure 1.

prevalently isotactic (i.e., **a** > **b**). This is agreement with facial selectivity governed by counteracting contacts of the methyl of the monomer with, respectively, the growing chain end and the β-Cp-R substituent, as proposed by Ewen.[16]

Considering that on the whole the polymerization is 85% (in diads) syndiospecific, excepting the insertion step on metal–CH$_3$, one can evaluate the difference of the activation free energies for syndiotactic versus isotactic insertion on metal–CH$_3$ at 70 °C (i.e., the driving force of the steric control coming from direct contact of the methyl of propylene with the β-Cp-R).

$$\ln((\mathbf{b})/(\mathbf{a})) \approx \Delta E_s/RT \qquad \Delta E_s \approx -0.2 \text{ kcal/mol}$$

The spectrum of isotactic polypropylene (sample 2) prepared in similar conditions in the presence of Et(1-In)$_2$ZrCl$_2$ and MAO is given in Figure 3. The relative

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Table I
Stereochemical Pentad Compositions of Sample 1 and Sample 2[a]

sample	mmmm	mmmr	rmmr	mmrr	rmrr + mrmm	mrmr	rrrr	rrrm	mrrm
1	nd	nd	0.03	0.05	0.08	nd	0.73	0.11	nd
2	0.78	0.09	nd	0.09	nd	nd	nd	nd	0.04

[a] nd, not detected.

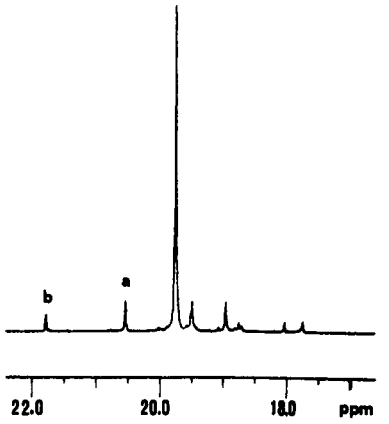

Figure 3. Methyl region of ^{13}C NMR spectrum of sample 2. HMDS scale. The signals labeled **a** and **b** are due to the ^{13}C-enriched methyls of the end groups given in Figure 1.

amount of the **a** and **b** end groups is ~2, and consequently, the difference of the activation free energies at 70 °C for isotactic versus syndiotactic insertion on metal–CH_3 is

$$\ln((\mathbf{a})/(\mathbf{b})) \approx \Delta E_i/RT \qquad \Delta E_i \approx 0.5 \text{ kcal/mol}$$

As anticipated by Ewen, in this case the steric control coming from the direct contact of CH_3 with β-Cp-R reinforces that due to the growing chain. The stereochemical pentad compositions of the isotactic polypropylene are also reported in the table.

In conclusion, the direct contacts of the methyl of the incoming monomer with the β-Cp-R substituent provide a very small but definite face selectivity, opposite to that provided by the orientation of the growing chain end for the syndiotactic-specific catalytic system and a small reinforcing face selectivity in the presence of the isotactic-specific catalytic system.

It is worth noting that, as reported in a previous paper,[4] direct contact with the β-Cp-R does not seem to provide any face selectivity in the presence of the isotactic-specific catalyst Et(1-In)$_2$TiCl$_2$/MAO/Al($^{13}CH_3$)$_3$.

Experimental Section

i-PrCp-1-FluZrCl$_2$, Et(1-In)$_2$ZrCl$_2$, MAO, and Al($^{13}CH_3$)$_3$ were prepared according to the literature.[11,17,18]

Sample 1 was prepared at 70 °C, introducing into a glass autoclave 9×10^{-6} mol of *i*-PrCp-1-FluZrCl$_2$, 58 mg of MAO (10 mmol), and 0.75 mmol of Al($^{13}CH_3$)$_3$ in 80 mL of toluene. The mixture was fed with propylene at a constant pressure of 5 atm. Polymerization was stopped after 18 h by injecting acidified ethanol and the polymer was coagulated in alcohol, recovered by filtration, washed twice with ethanol, and dried in vacuo. Yield 6.0 g; mp 120 °C.

Sample 2 was prepared under the same conditions as sample 1, utilizing Et(1-In)$_2$ZrCl$_2$ as catalyst precursor. The polymerization time was 1.5 h. Yield 1.0 g; mp 122 °C.

The ^{13}C NMR spectra were recorded on AM 250 Bruker spectrometer, at 120 °C, by using an inverse-gated mode of decoupling in order to obtain signals without NOE. The samples were dissolved in tetrachlorodideuterioethane containing hexamethyldisiloxane (HMDS) as internal chemical shift reference.

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