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Propene Polymerization Promoted by C_2-Symmetric Metallocene Catalysts: From Atactic to Isotactic Polypropene in Consequence of an Isotope Effect

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In a recent communication from this laboratory,[1] it has been shown that the stereoregularity of isotactic polypropene obtained in the presence of C_2-symmetric group 4 metallocene catalysts[2] decreases with decreasing monomer feeding pressure. We explained this effect in terms of a competition between propene polyinsertion, with a roughly first-order rate dependence with respect to the monomer, and a (comparatively slow) intramolecular reaction of epimerization of the growing polypropene chain at a last-inserted monomeric unit. Understandably, the balance shifts toward chain epimerization when monomer concentration is lowered (but also, we found, when the temperature is increased, which gives reason for the decay of stereospecificity of most of these catalysts above 50−80 °C, indicatively[3]).

An elegant support to our interpretation has been provided recently by Leclerc and Brintzinger,[4] who observed that most stereoirregular monomeric units in isotactic polymers of (*E*)- and (*Z*)-propene-1-*d* prepared at low monomer concentration in the presence of a number of C_2-symmetric metallocene catalysts (such as *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-$ZrCl_2$) in combination with methylalumoxane (MAO) are deuterated *at the methyl group*; this clearly proves that such stereoerrors arise from isomerizations of the growing chain end rather than from propene insertions with the "wrong" enantioface.

Understanding the mechanism of this epimerization can contribute to the rational design of improved catalysts.

To this end, we studied the polymerization of propene-2-*d* promoted by the prototypical isotactic-specific catalyst system *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)$ZrCl_2$/MAO. In this communication, we report the results of our investigation, documenting a large isotope effect on the balance between polyinsertion and epimerization and, therefore, on the stereospecificity. The mechanistic implications of such results are also discussed.

Propene-2-*d* was polymerized under conditions (50 °C; monomer partial pressure, 0.6 bar) known[1,3] to result, for undeuterated propene (from here on, propene-d_0), in a highly epimerized, substantially *atactic* polymer (^{13}C NMR fraction of *m* diads, $[m] = 0.60 \pm 0.05$ only, to be compared with $[m] \approx 0.95$ for polymerizations in liquid propene at the same temperature). Quite surprisingly, a fairly *isotactic* poly(propene-2-*d*) (sample A) was instead obtained ($[m] \approx 0.85$; ^{13}C NMR distribution of the steric pentads: $[mmmm] \approx 0.65$, $[mmmr] \approx [mmrr] \approx 0.12$).

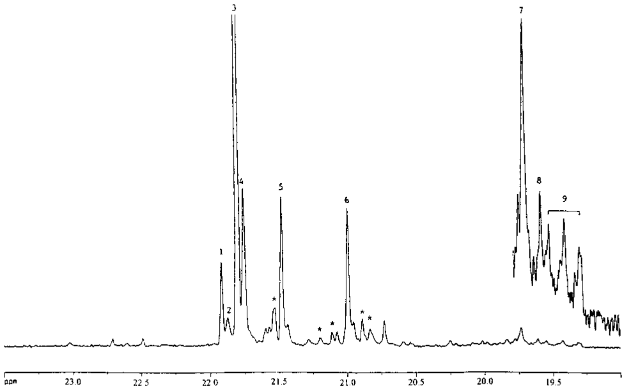

Figure 1. Methyl region of the 150 MHz ^{13}C NMR spectrum of sample B (chemical shifts are in ppm downfield of TMS). For main resonance attributions,[4−6] see Table 1; regions including resonances from chain end groups and/or regioirregular monomer sequences[5,16] are marked with asterisks.

Table 1. Attributions of the Methyl Resonances in the ^{13}C NMR Spectrum of Sample B (Figure 1)

peak no.	δ (ppm)[a]	chemical structure	stereochemical structure	integral (%) exptl[c]	integral (%) calcd[d]
1	21.92	−CH(CH$_3$)−	*mmmmmm*	4.5	59.2
2	21.87	−CH(CH$_3$)−	*mmmmmr*	2.7	
3	21.81	−CD(CH$_3$)−	*mmmmmm*	43	
4	21.76	−CD(CH$_3$)−	*mmmmmr*	9	
5	21.48	−CD(CH$_3$)−	*mmmr*	13	13.1
6	21.00	−CD(CH$_3$)−	*mmrr*	13	13.1
7	19.72	−CH(CH$_3$)−	*mrrm*	2.7	6.6
8	19.61	−CD(CH$_3$)−	*mrrm*	0.9	
9	19.41 (t)[b]	−CH(CH$_2$D)−	*mrrm*	2.7	

[a] Downfield of TMS. [b] Triplet; $J(^{13}C, ^2H) = 18.9$ Hz. [c] Of total methyl integral, in a spectrum at zero NOE. [d] According to the enantiomorphic-sites statistics, with $[m] = 0.82$.

In view of the steep dependence of the catalyst stereospecificity on propene concentration when operating at low monomer feeding pressure,[1,3] we decided to confirm this result by polymerizing propene-2-*d* in the presence of a minor amount of propene-d_0 used as an internal standard.

The methyl region of the 150 MHz ^{13}C NMR spectrum of a copolymer of propene-2-*d* (90 mol %) and propene-d_0 (10 mol %) (sample B) is shown in Figure 1 (for resonance assignments[4−6] and integration,[7] see Table 1).

The copolymer is predominantly isotactic ($[m] \approx 0.82$), with a distribution of configurations conforming to that foreseen in terms of the enantiomorphic-sites statistics[8] (as also shown in Table 1). Of the ≈10 mol % stereoirregular monomeric units, moreover, ≈4 mol % are propene-d_0 ones; this means that the epimerization took place extensively at the few propene-d_0 units (coherently with the results of refs 1 and 3) and only marginally at the propene-2-*d* ones.

Interestingly, *≈$^3/_4$ of the stereoirregular (C_3H_5D) monomeric units in samples A and B bear the D atom on the methyl carbon (Figure 1 and Table 1).* The amount of "genuine" stereoirregular propene-2-*d* insertions can thus be estimated as 1−2 mol %, in good agreement with ref 4.

From the above results, it can be concluded that the epimerization of a growing polypropene chain involves a rate-

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(1) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329.

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(7) From ^{13}C NMR spectra at zero NOE.

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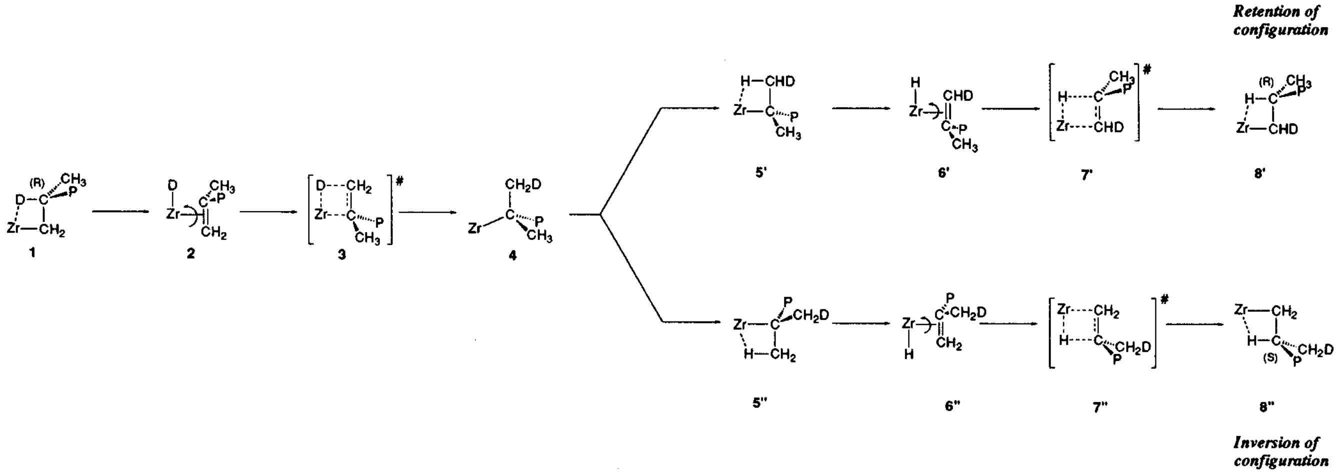
Scheme 1



determining migration of the methine hydrogen in a last-inserted monomeric unit (most likely induced by a β-agostic interaction with the Zr atom[4,9]) and that, due to a primary isotope effect,[10] the process is significantly slower when it requires the cleavage of a C−D bond instead of a C−H one.[10,11]

Consistently with this interpretation, in the ^{13}C NMR spectra of samples A and B, only vinylidene and ($-CH_2CHDCH_3$) end groups were observed (number-average degree of polymerization, $\bar{X}_n \approx (1.7 \pm 0.2) \times 10^2$ and 1.1×10^2, respectively), the concentration of ($-CH_2CD_2CH_3$) end groups being too low for detectability; this is a further indication of a lower rate of β-D relative to β-H elimination.[11,12]

The ^{13}C and ^{2}H NMR spectra of samples A and B revealed also [$-CHDCH(CH_3)-$] monomeric units in isotactic arrangement (≈4 mol %).[13] It appears therefore that, in the propene-2-*d* monomeric units subjected to isomerization, the D atom originally bound to the methine C was almost equally distributed between the methyl and the methylene group: in the former case, the original configuration of the tertiary C atom was inverted; in the latter case, conversely, it was retained.

In ref 1, we proposed a tentative mechanism for the epimerization of a growing polypropene chain. This mechanism, applied to propene-2-*d* in Scheme 1, is fully consistent with the experimental data achieved in this investigation (as well as with those in ref 4 on the polymerization of propene-1-*d*; this latter demonstration is left to the reader).

We wish to stress that, in Scheme 1, **2**, **6′**, and **6″** should be inteded as formal representations of transient species rather than true intermediates. We also note that β-D elimination from **4** was regarded as unlikely, compared with β-H elimination, owing to the discussed isotope effect; this agrees with the slight excess of [$-CH_2CH(CH_2D)-$] units over [$-CHDCH(CH_3)-$] ones observed in samples A and B.

A detailed analysis of the effects of changes in temperature, solvent, type of cocatalyst, and catalyst and cocatalyst concentration on the extent of chain epimerization for propene polymerization in the presence of representative C_2-symmetric metallocene catalysts will be presented in a subsequent article.

Propene-2-*d* was prepared from $CH_2{=}C(CH_3)Li$ and D_2O (Aldrich; 99.9+% isotopic purity) in diethyl ether according to ref 14 and purified by bubbling through a solution of Al(*i*-Bu)$_3$ in toluene (25% by weight) followed by vacuum distillation.

The polymerizations were performed at 50 °C in a 50 mL Pyrex pressure bottle, under the following conditions: toluene solvent, 10 mL; *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-$ZrCl_2$,[15] 5 μmmol; MAO, 0.96 g of solid product recovered from a toluene solution (Schering, 30% w/v) after vaccum distillation; monomer partial pressure constant at 0.60 ± 0.05 bar.

$^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker AMX 600 spectrometer operating at 150.9 MHz on dilute polymer solutions (<5 mg/mL) in tetrachloroethane-1,2-d_2 at 70 °C. A 5 s relaxation delay with 2.2 s acquisition time and 90° pulse angle were applied so as to be far from saturation. For quantitative measurements of sequence distributions, the spectra were run with an inverse-gated decoupling sequence, considering that proton-bearing C atoms have spin−lattice relaxation and NOE quite different from partly or fully deuterated ones.

^{2}H spectra were recorded with the same spectrometer operating at 92.13 MHz on polymer solutions (1 mg/mL) in 1,1,2,2-tetrachloroethane at 70 °C (at least 128 scans without any lock system).

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[13] The concentration of stereoregular [$-CHDCH(CH_3)-$] units was evaluated unambiguously from the methine ^{13}C NMR resonance of such units in *mm* arrangement (0.08 ppm upfield from the corresponding resonance of stereoregular [$-CH_2CH(CH_3)-$] units); in the ^{2}H spectra, no resonance at 1.03 ppm (downfield of TMS) was observed, diagnostic of −CHD− groups in *r* diads (see, e.g., Bovey, F. A.; Jelinski, L. W. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, NY, 1982; Chapter 3, pp 75−78).

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