

Interfering Effects of Growing Chain Epimerization on Metallocene-Catalyzed Isotactic Propene Polymerization

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ABSTRACT: The stereoregularity of polypropylene produced with C_2 -symmetric group 4 *ansa*-metallocene catalysts results from the interplay of two competing reactions, namely isotactic monomer polyinsertion and a side process of epimerization of the polymer chain at its active end; therefore, for this class of homogeneous catalysts, at variance with the "classical" heterogeneous Ziegler–Natta ones, enantioselectivity and stereoselectivity are not (necessarily) coincident. In this paper, possible methods for the separate determination of these two parameters are introduced and applied to propene polymerization in the presence of the prototypical catalyst *rac*-ethylene–bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂. The results prove that the relatively poor stereoselectivity of this catalyst above room temperature is consequent primarily to chain epimerization; monomer insertion indeed is highly enantioselective up to at least 80 °C. Preliminary evidence for the existence of more than one epimerization mechanism is also presented; this complicates the measurements of enantioselectivity based on ¹³C NMR characterizations of *d*-labeled poly(propene)s.

Introduction

Transition-metal-catalyzed 1-alkene polymerization proceeds through sequential monomer *cis*-insertions in the σ -bond connecting the active metal atom and the growing polymer chain.^{1–4}

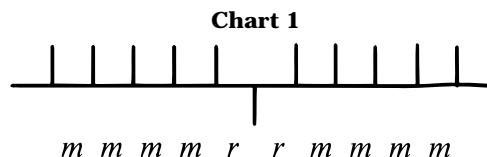
The formation of a (prevalingly) isotactic polymer requires that the prochiral monomer molecules react preferentially in the same orientation (either 1,2 or 2,1) with the same enantioface (*re* or *si* attack).¹

The main type of stereodefects in isotactic poly(1-alkene) samples produced with catalysts of practical interest are isolated *rr* triads^{1,4–6} (Chart 1). For a long time, they have been ascribed exclusively to occasional monomer insertions with the less reactive enantioface at intrinsically chiral active sites;^{1–3} if so, enantioselectivity and stereoselectivity would coincide.

This assumption, however, which seems to hold for the classical heterogeneous Ziegler–Natta catalysts,^{1–3,7} can be incorrect in other cases. In particular, in recent papers from this⁸ and other^{9,10} laboratories, it has been shown that the stereoselectivity of propene polymerization promoted by the new class of C_2 -symmetric group 4 *ansa*-metallocene catalysts⁴ is actually the result of an interplay of two competing reactions, namely isotactic monomer polyinsertion and a side process of epimerization of the polymer chain at its active end. A growing interference of the latter is responsible for the fade of stereoselectivity observed for most of these catalysts with decreasing monomer concentration and, at least in part, for that occurring with increasing temperature.^{4,8–10}

A plausible mechanism for chain epimerization, which agrees with the experimental results of propene, propene-1-*d*, and propene-2-*d* polymerization,^{8–10} is shown in Scheme 1 (P = Polymeryl).

Unfortunately, this side reaction also introduces randomly distributed stereoinverted monomeric units in the polymer (Chart 1).^{8–10} This complicates the separate evaluation of the stereo- and enantioselectivity, which requires a discrimination between "primary"



stereoerrors formed by monomer misinsertion and "secondary" ones resulting from the racemization of originally stereoregular monomeric units.

One possible method is based on the kinetics of the two concurrent reactions. The rate of monomer insertion (R_{ins}) depends on monomer concentration ($[M]$) according to the following approximate equation:

$$R_{\text{ins}} = k_{\text{ins}} C^* [M]^\alpha \quad (1)$$

where C^* is the concentration of active sites and $1 \leq \alpha \leq 2$, depending on the specific catalyst system.^{4,10,11} It should be stressed that eq 1 does not refer to an elementary process; as such, it is purely phenomenological, and its mechanistic implications are still unclear.⁴

Chain epimerization, on the other hand, is an intramolecular rearrangement, and its rate (R_{epim}) is independent of $[M]$:

$$R_{\text{epim}} = k_{\text{epim}} C^* \quad (2)$$

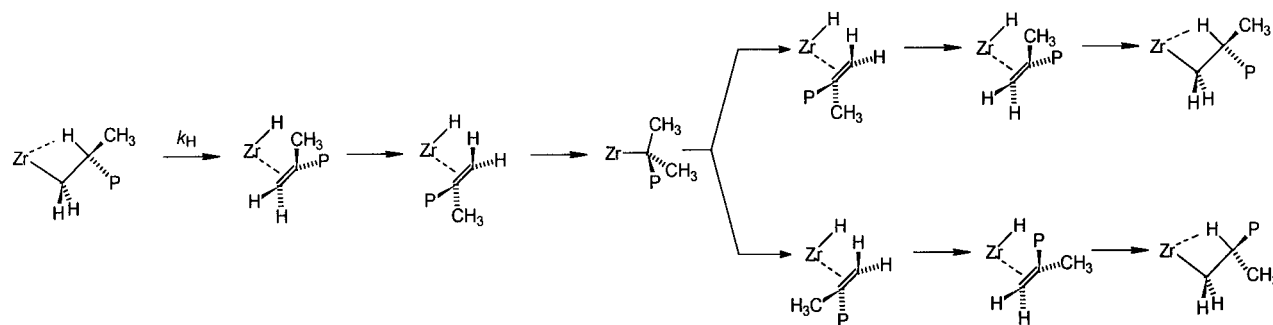
Hence, the probability that the last-inserted unit of a growing chain be *not* racemized before a new monomer insertion (in the approximation of negligible chain transfer) is given by

$$P_{\text{ins}} = R_{\text{ins}} / (R_{\text{ins}} + R_{\text{epim}}) = [M]^\alpha / ([M]^\alpha + k_{\text{epim}}/k_{\text{ins}}) \quad (3)$$

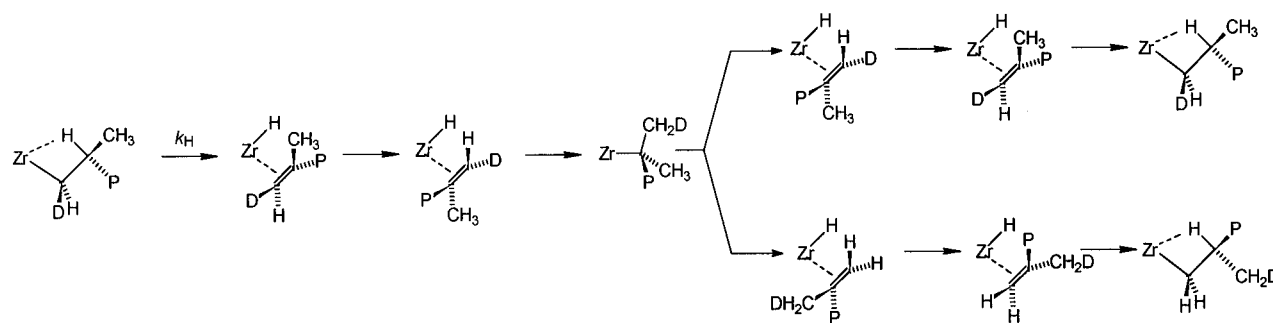
The probability that both units of a steric diad be *not* racemized is obviously (P_{ins}).² This leads to the following expression for polymer tacticity (measured as fraction of *meso* (*m*) diads, $[m]$) as a function of monomer concentration:

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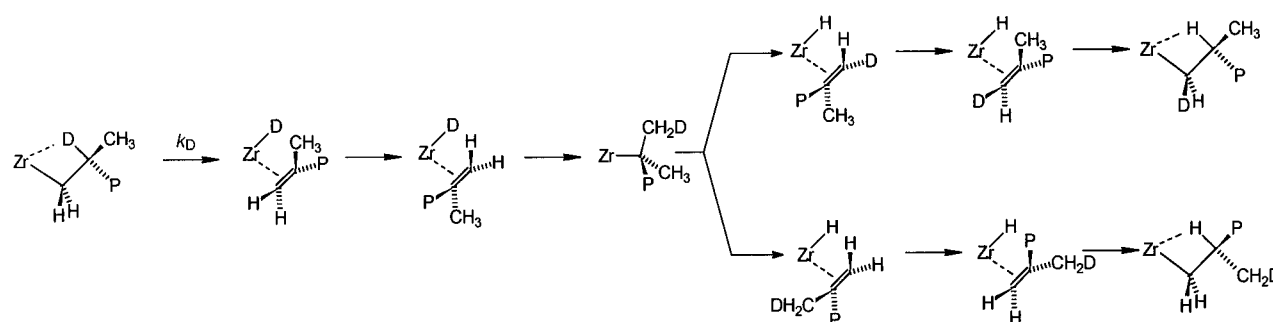
Scheme 1



Scheme 2



Scheme 3



$$[m] = [m^\circ](P_{\text{ins}})^2 + 0.5(1 - (P_{\text{ins}})^2) = 0.5 + \frac{([m^\circ] - 0.5)(P_{\text{ins}})^2}{([M]^\alpha + k_{\text{epim}}/k_{\text{ins}})^2} \quad (4)$$

where $[m^\circ]$, the fraction of m diads obtained in the limit $P_{\text{ins}} \rightarrow 1$ (i.e., for $k_{\text{ins}}[M]^\alpha \gg k_{\text{epim}}$), is a measure of the "true" enantioselectivity of the catalyst.

By interpolation of experimental points $\{[m], [M]\}$ in terms of eq 4, best-fit values of $k_{\text{epim}}/k_{\text{ins}}$ and $[m^\circ]$ can be obtained. The latter value is related to the fraction F_p of "primary" stereoerrors (i.e. of monomer misinsertions) according to the enantiomorphic-site statistics:¹²

$$F_p \approx 1 - [m^\circ]^{1/2} \quad (5)$$

A second way for identifying "primary" and "secondary" stereoerrors is to make use of d -labeled monomers. In particular, it has been shown^{8d,9} that, in poly(propene-1- d) and poly(propene-2- d) samples produced with C_2 -symmetric metallocene catalysts, (at least part of) the stereoirregular monomeric units formed by chain epimerization contain D in the methyl group (Schemes 2 and 3, respectively), whereas those deriving from monomer misinsertions obviously still have the D label in the original position. The fractions of constitutionally different units can be measured by ¹³C NMR in a relatively straightforward manner.^{8d,9}

In this paper, the two methods are applied and discussed comparatively for propene polymerization in the presence of the catalyst *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂ (short notation, (EBTHI)-ZrCl₂), known for its propensity to promote also the side reaction of chain epimerization.^{8,9}

The results prove that the enantioselectivity of this prototypical catalyst is close to that of modern C_2 -symmetric *ansa*-zirconocenes,¹³⁻¹⁵ and that the higher stereoselectivity of the latter in propene polymerization is due primarily to a (much) larger ratio between the rates of monomer insertion and of chain epimerization, the more so the higher is reaction temperature.

Preliminary evidence for the existence of more than one epimerization pathway is also presented.

Results and Discussion

Evaluation of the Enantioselectivity of (EBTHI)-ZrCl₂ in Propene Insertion. (i) Dependence of Polymer Tacticity on Monomer Concentration. In principle, this is the simplest approach: a number of polymerization runs at different $[M]$'s are performed, the fraction $[m]$ of *meso* diads in the polymers is measured by ¹³C NMR, and, from a best-fit procedure on the experimental points $\{[M], [m]\}$, $[m^\circ]$ and F_p are calculated in terms of eqs 4 and 5.

$[M]$ can be varied approximately in the range 0.1–10 mol/L: the higher limit is imposed by the concentration

Table 1. Effect of Catalyst Concentration, [Zr], and of the Mole Ratio [Al]/[Zr] on the Fraction of *m* Diads, [*m*], in Polypropylene Samples Prepared with (EBTHI)ZrCl₂/MAO at 50 °C ([M] = Propene Concentration in Toluene)

entry no.	[Zr] (mol/L)	[Al]/[Zr]	[M] (mol/L)	[<i>m</i>]
1	5 × 10 ⁻⁶	5 × 10 ³	2.1 ₆	0.92 ₀
2	5 × 10 ⁻⁵	5 × 10 ³	2.1 ₆	0.91 ₅
3	5 × 10 ⁻⁶	5 × 10 ³	0.30	0.68
4	5 × 10 ⁻⁵	5 × 10 ³	0.30	0.67
5	5 × 10 ⁻⁴	5 × 10 ³	0.30	0.68
6	5 × 10 ⁻⁵	5 × 10 ²	2.1 ₆	0.91 ₄

of pure liquid propene at practical temperatures (typically, 30–80 °C), whereas below 0.1 mol/L the productivity of the catalyst becomes too low and/or it is difficult to measure and control accurately monomer concentration.

In practice, however, it is virtually impossible to run all experiments under identical conditions (apart from the value of [M]), as would be desirable.

Indeed, at high [M], catalyst concentrations of the order of 1 μmol/L are advisable for a good control of the reaction temperature; at low [M], on the other hand, values of [Zr] > 100 μmol/L may be needed in order to obtain enough polymer for the characterizations in a reasonable time using a lab-scale reactor. Moreover, if methylalumoxane (MAO) is used as the cocatalyst, maintaining the "optimum" value of (3–5) × 10³ for the mole ratio [Al]/[Zr]¹⁶ when [Zr] exceeds 100 μmol/L would correspond to an impractically high [Al].

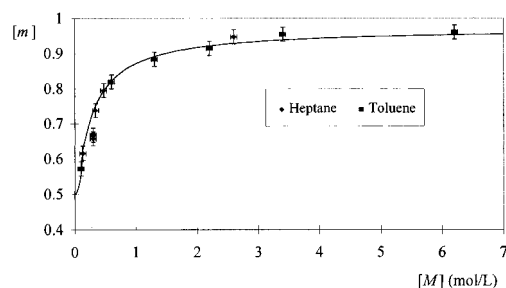
We found, however, that the stereoselectivity of propene polymerization promoted by the catalyst system (EBTHI)ZrCl₂/MAO is practically invariant when changing—*coeteris paribus*—[Zr] in the range 5 × 10⁻⁶ to 5 × 10⁻⁴ mol/L (Table 1, entries 1–5) and [Al]/[Zr] in the range 5 × 10² to 5 × 10³ (Table 1, entries 2 and 6), so that, in the present investigation, these two variables were freely adjusted to the needs within such ranges.

We are aware that the above findings conflict with those reported in ref 17, claiming a decrease of the stereoselectivity of (EBTHI)ZrCl₂ with increasing [Zr] in the range 2.5–25 μmol/L at T ≤ 0 °C, due to an unprecedented^{4,6,8–10} formation of ...*mmmmrmmmm*... stereodefects. On the other hand, we have tried in vain to reproduce the data of ref 17: indeed, under the cited conditions, we have invariably obtained highly isotactic polypropylene samples, with just traces of ...*mmmmrmmmm*... stereodefects, in line with the expectations;^{4,6,8,9,15} for a possible explanation of this disagreement, see ref 18.

Another source of irreproducibility potentially affecting the stereoselectivity of the ionic⁴ catalyst system is the polarity of the reaction medium, necessarily subjected to changes along the series of experiments moving from conditions of diluted propene in a suitable solvent (typically, toluene) to pure liquid propene. That this is not so for the investigated system is indicated by the fact that the same plot {[M], [*m*]} (within the experimental error) was obtained for propene polymerization at 50 °C using as a solvent toluene (more polar than propene) and heptane (less polar than propene) (Figure 1 and Table 2, entries 7–18).

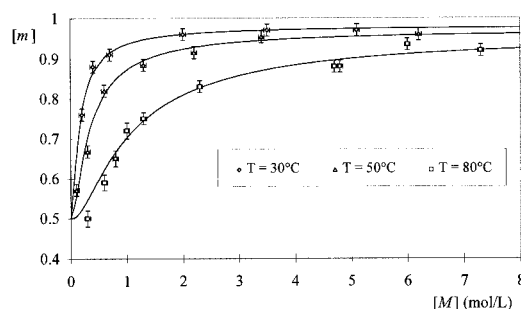
It appears, therefore, that experimental plots {[M], [*m*]} for propene polymerization in the presence of (EBTHI)ZrCl₂/MAO can be used confidently for the determination of [*m*°].

Three such plots, obtained as described in the Experimental section for reaction temperatures of 30, 50,

**Figure 1.** Fraction of *m* diads, [*m*], vs. propene concentration, [M], for polypropylene samples prepared at 50 °C in the presence of (EBTHI)ZrCl₂/MAO in two different solvents. The experimental points are interpolated in terms of eq 4 (text).**Table 2.** Fraction of *m* Diads, [*m*], in Polypropylene Samples Prepared with (EBTHI)ZrCl₂/MAO as a Function of Propene Concentration, [M]^a

entry no.	T (°C)	solvent	[M] (mol/L)	[<i>m</i>]
1	30	toluene	0.21	0.76
2			0.38	0.88
3			0.70	0.91 ₀
4			2.0 ₄	0.95 ₇
5			3.5 ₁	0.96 ₇
6			5.1 ₀	0.96 ₇
7	50	heptane	0.13	0.62
8			0.30	0.66
9			0.34	0.74
10			0.47	0.80
11			2.5 ₄	0.94 ₇
12			0.10	0.57
13			0.30	0.67
14			0.51	0.82
15			1.2 ₇	0.88
16			2.1 ₆	0.91 ₅
17			3.4	0.95 ₄
18			6.2	0.96 ₀
19	80	toluene	0.20	0.5 ₀
20			0.55	0.59
21			0.72	0.65
22			1.0 ₀	0.72
23			1.2 ₇	0.75
24			2.2 ₅	0.83
25			4.7	0.88
26			4.8	0.88
27			6.0	0.93 ₅
28			7.3	0.92 ₀

^a Other experimental conditions: [Zr] = 1 × 10⁻⁶ to 5 × 10⁻⁵ mol/L; [Al]/[Zr] = 1 × 10³ to 5 × 10³.

**Figure 2.** Fraction of *m* diads, [*m*], vs. propene concentration, [M], in toluene for polypropylene samples prepared in the presence of (EBTHI)ZrCl₂/MAO at three different temperatures.

and 80 °C and based on the data in Table 2 (entries 1–6, 12–18, and 19–28), are shown in Figure 2.

The experimental points in Figure 2 can be interpolated satisfactorily in terms of eq 4 (with α = 1.2¹⁹), as shown by the solid curves. The corresponding best-fit values of the adjustable parameters *k*_{ins}/*k*_{epim} and [*m*°] are reported in Table 3.

Table 3. Best-fit Values of $k_{\text{ins}}/k_{\text{epim}}$ and $[m^*]$ Obtained by Interpolation of the Experimental Points in Figure 2 in Terms of Eq 4, and Corresponding Fraction of "Primary" Stereoerrors, F_p (Eq 5)

T (°C)	$k_{\text{ins}}/k_{\text{epim}}$ (L/mol)	$[m^*]$	F_p
30	20 ± 3	0.98	0.010 ± 0.005
50	8	0.97	0.015 ± 0.005
80	2.0 ± 0.2	0.96	0.020 ± 0.005

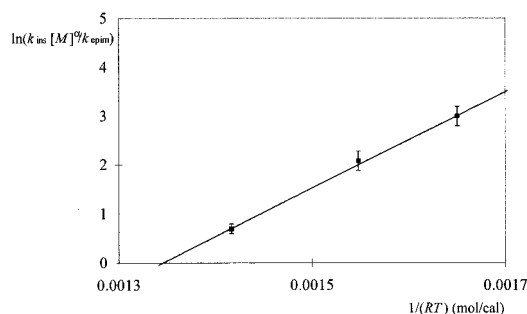


Figure 3. Plot of $\ln(k_{\text{ins}}[M]^{\alpha}/k_{\text{epim}})$ (with $[M] = 1$ mol/L) vs $1/RT$ based on the data of Table 3 (see text).

Table 4. ^{13}C NMR Methyl Pentad Distribution for Poly(propene-2-*d*) Samples Obtained with (EBTHI)ZrCl₂/MAO at Three Different Temperatures ($[M]$ = Monomer Concentration in Toluene)

T (°C)	$[M]$ (mol/L)	$[mmmm]$	$[mmmr] =$ $[mmrr]$	$[mrrm]_{2-d}$ CD(CH ₃)	$[mrrm]_{3-d}$ CH(CH ₂ D)
30 ^a	0.42	0.95	0.02	0.01	<0.005
50 ^b	0.25	0.70	0.10	0.013	0.039
80 ^b	0.71	0.59	0.13	0.018	0.047

^a Data from ref 9b. ^b $[\text{Zr}] = 4 \times 10^{-5}$ mol/L; mole ratio $[\text{Al}]/[\text{Zr}] = 5 \times 10^3$.

On raising the temperature from 30 to 80 °C, a strong decrease of $k_{\text{ins}}/k_{\text{epim}}$ was observed (as expected^{8b,9b}), with only a smooth concomitant decline of $[m^*]$. This means that the corresponding drop of stereoselectivity (Figure 2) must be attributed primarily to an increasing incidence of growing chain epimerization, the enantioselectivity being very high ($[m^*] \geq 0.96$, $F_p \leq 0.020$) in the whole temperature range.

It should be noted that the effect of chain epimerization becomes negligible, indicatively, for $[M] > 3$ mol/L at 30 °C and for $[M] > 6$ mol/L at 50 °C; at 80 °C, on the other hand, even for polypropylene samples obtained from bulk polymerizations, the value of $[m]$ is appreciably lower than that of $[m^*]$.

The $k_{\text{ins}}/k_{\text{epim}}$ values of Table 3 can be used to build an Arrhenius plot in terms of eqs 1 and 2, assuming $[M]$ constant; at $[M] = 1$ mol/L, the estimated values of $(E_{a,\text{epim}} - E_{a,\text{ins}})$ and $\ln(A_{\text{epim}}/A_{\text{ins}})$ are of the order of 10 kcal/mol and 13, respectively (Figure 3); it thus appears that, in spite of a much higher activation energy, chain epimerization can compete with monomer insertion already at relatively low temperature due to a largely favorable entropy factor. For similar metallocene catalysts, analogous observations have been reported²⁰ for the competition, at a last-inserted regioirregular 2,1 propene unit, between monomer insertion and isomerization to a 3,1 unit;^{6b,20,21} the latter process is also believed to involve a first step of β -H abstraction.^{20,21}

(ii) ^{13}C NMR Analysis of Selectively Deuterated Poly(propene)s. As already noted in the Introduction, it has been proved that, in (prevailing) isotactic poly(propene-1-*d*) and poly(propene-2-*d*) samples prepared in the presence of C_2 -symmetric metallocene catalysts, part of the stereoirregular monomeric units are deuterated at

the methyl group, as a result of chain epimerization^{8d,9} (Schemes 2 and 3). In the hypothesis that the stereoirregular units with unshifted D derive instead exclusively from monomer misinsertions, their fraction, which can be easily evaluated by ^{13}C NMR, coincides with that of "primary" stereoerrors and can thus be used as a measure of catalyst enantioselectivity.

Compared with the approach illustrated in the previous section, this method looks appealing because, in principle, it requires the characterization of one single polymerization product, with no need for high-pressure polymerization facilities and accurate reaction control. However, its basic assumption needs to be verified; moreover, the monomers are not easily available commercially and have to be synthesized on purpose.

In this investigation, we used propene-2-*d* because, in addition to the fractions of "primary" and "secondary" stereoirregular units, we were also interested in measuring the isotope effect in the rate-determining β -H (β -D) abstraction step of the epimerization process (cf. Schemes 1 and 3).^{8d,9b}

Propene-2-*d* was thus polymerized in the presence of (EBTHI)ZrCl₂/MAO at various temperatures, and the polymers obtained were characterized by ^{13}C NMR.

In ref 8d, we reported the attributions of the methyl resonances in the ^{13}C NMR spectra of poly(propene-2-*d*) samples produced with this catalyst system. The fractions F_{2-d} and F_{3-d} of stereoirregular $[\text{CH}_2\text{-CD}(\text{CH}_3)]$ and $[\text{CH}_2\text{-CH}(\text{CH}_2\text{D})]$ units can be evaluated from the normalized integrals, in quantitative spectra at zero NOE, of the methyl resonances of such units (respectively, singlet at 0.11 ppm upfield and triplet at 0.31 ppm upfield of the *mrrm* methyl resonance of poly(propene-*d*₀), Figure 4), according to the enantiomorphic-site statistics.¹²

Table 4 gives the ^{13}C NMR pentad distribution for two poly(propene-2-*d*) samples prepared by us at 50 and 80 °C, along with data at 30 °C taken from ref 9b. In Table 5, the derived values of F_{2-d} and F_{3-d} are compared with the fractions F_p and F_s of "primary" and "secondary" stereoerrors in samples of poly(propene-*d*₀) prepared under corresponding experimental conditions.

From Table 5, it can be seen that F_{2-d} tends to increase smoothly with increasing temperature, as already observed for F_p (Table 3); the two fractions coincide, within the experimental error, at 30 and 50 °C, whereas at 80 °C F_{2-d} is slightly larger than F_p .

It is interesting to compare these results with analogous ones for (*E*)- and (*Z*)-propene-1-*d* polymerization promoted by the same catalyst system at 30 and 53 °C, recently published by Leclerc and Brintzinger^{9b} and also included in Table 5. In this latter case, the fraction F_{1-d} of stereoirregular $[\text{CHD-CH}(\text{CH}_3)]$ units in poly(propene-1-*d*)—supposedly coincident with that of "primary" stereoerrors—is indeed very close to F_p at 30 °C but significantly higher already at 53 °C.

In our opinion, these findings indicate the existence of (at least) one additional process of chain epimerization—slower than that postulated in Schemes 1–3—which does not imply the migration of D in propene-1-*d* and propene-2-*d* monomeric units subjected to racemization but does involve a rate-determining step of β -H (β -D) abstraction. In fact, due to the isotope effect,^{8d,9b} the incidence of such a process on the stereoselectivity is larger for the polymerization of propene-1-*d* than for that of propene-2-*d* (Table 5).

A possible mechanism might involve, for instance, the equilibration of diastereomeric π -complexes of the ter-

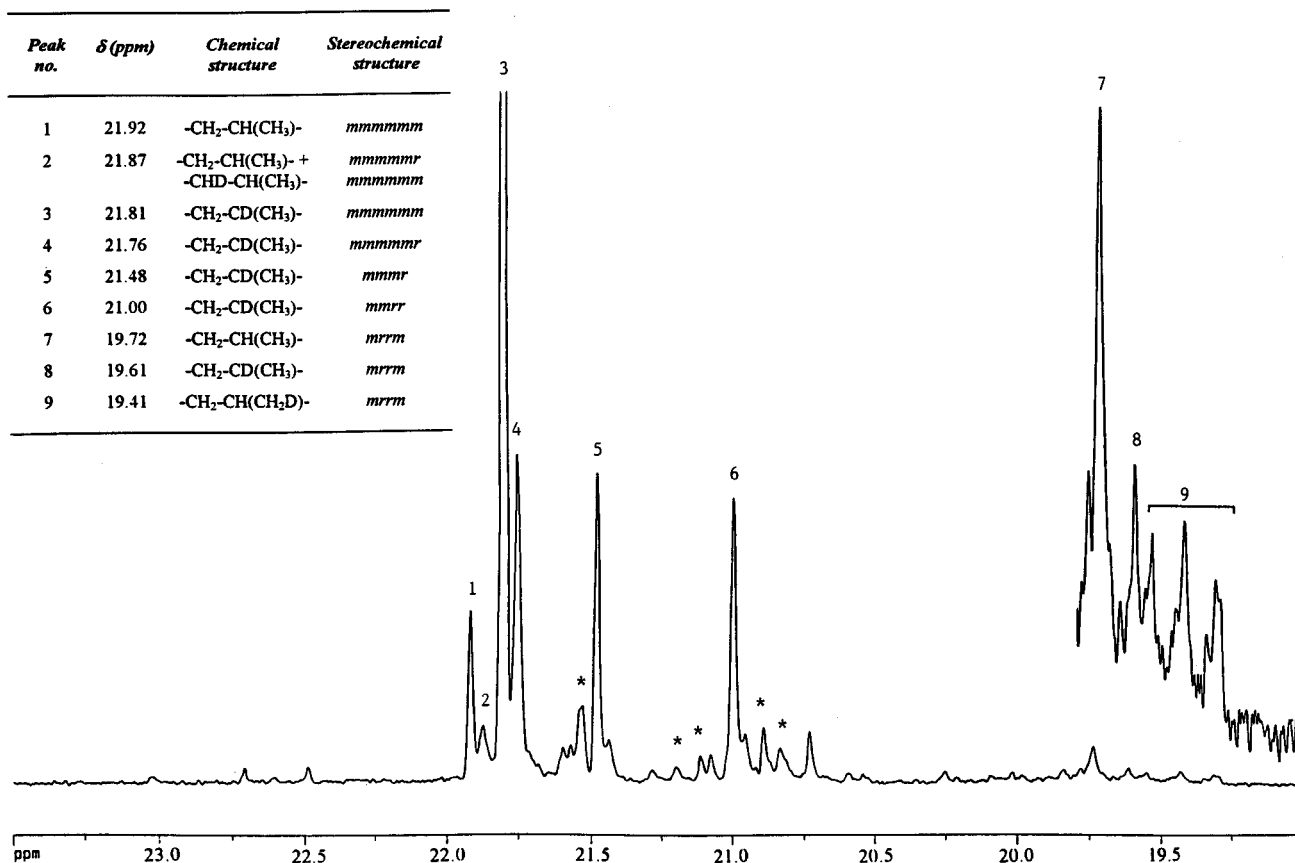


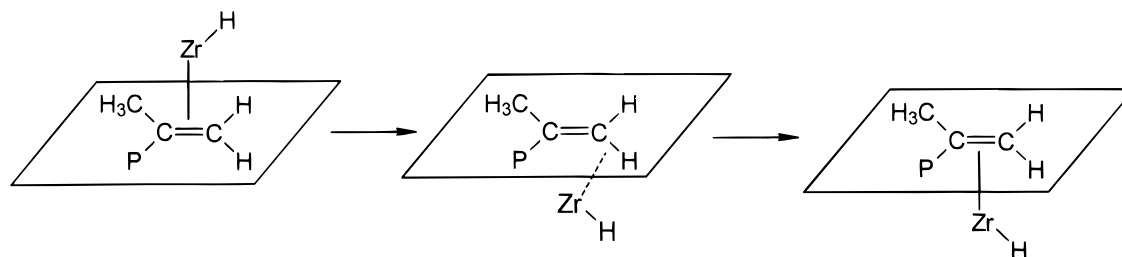
Figure 4. Attributions of the methyl resonances in the 150 MHz ¹³C NMR spectrum of poly(propene-2-d) (from ref 8d); the sample contains 10 mol % *co*-(propene-*d*₀) units for internal reference. Regions including resonances from chain end groups and/or regioirregular sequences are marked with asterisks.

Table 5. Fractions of Stereoirregular Monomeric Units with Different Constitutions,^a Evaluated from ¹³C NMR Data,^b in Samples of Poly(propene-2-d) and of Poly(propene-1-d) Prepared with (EBTHI)ZrCl₂/MAO at Various Temperatures ([M] = Monomer Concentration in Toluene)^c

<i>T</i> (°C)	[M] (mol/L)	propene-2-d ^d		<i>(E)</i> -propene-1-d ^e		<i>(Z)</i> -propene-1-d ^e		propene- <i>d</i> ₀	
		<i>F</i> _{2-d}	<i>F</i> _{3-d}	<i>F</i> _{1-d}	<i>F</i> _{3-d}	<i>F</i> _{1-d}	<i>F</i> _{3-d}	<i>F</i> _p ^f	<i>F</i> _s ^g
30	0.42	0.01 ₀	<0.005	0.016	0.026	0.014	0.036	0.010	0.18
50	0.25	0.017	0.053					0.015	0.20
53	0.33			0.044	0.11	0.059	0.12		
80	0.71	0.028	0.074					0.020	0.21

^a *F*_{1-d}: [CHD-CH(CH₃)]; *F*_{2-d}: [CH₂-CD(CH₃)]; *F*_{3-d}: [CH₂-CH(CH₂D)]. ^b *F*_{*j*-d} (*j* = 1, 2, or 3) $\approx (1 - [mmmm]^{1/5})[mrrm]_{j-d}[mrrm]$. ^c The fractions *F*_p and *F*_s of "primary" and "secondary" stereoregularities in samples of poly(propene-*d*₀) prepared under identical experimental conditions are also added for comparison. ^d Based on the ¹³C NMR pentad data in Table 4. ^e Based on the ¹³C NMR pentad data in ref 9b (renormalized). ^f From Table 3. ^g Evaluated from Figure 2 at the appropriate [M], according to the following relation: $[m] = (F_p + F_s)^2 + [1 - (F_p + F_s)]^2$.

Scheme 4



minally unsaturated polymer chain (Schemes 1–3) via a σ -bond complex²² (Scheme 4, adapted to propene-*d*₀ from ref 22).

We note that a similar mechanism may also be invoked for the epimerization of growing poly(1-butene) chains, for which—as remarked in refs 8c and 23—it seems difficult to propose a reaction pathway analogous to that of Scheme 1.

A rough estimate of the isotope effect in chain epimerization can be obtained from the amounts of "secondary" stereoregularities in samples of poly(propene-*d*₀) and of poly(propene-2-d) prepared under the same experimental conditions (in Table 5, *F*_s and *F*_{3-d}, respectively); indeed, it can be assumed^{9b} that the ratio *k*_H/*k*_D (for definitions, see Schemes 1 and 3) coincides with the ratio *F*_s/*F*_{3-d}. From the data in Table 5, this

ratio turns out to be approximately 3.8 at 50 °C (in substantial agreement with ref 9b) and 2.8 at 80 °C.

In view of the above, it can be concluded that the approach introduced in this section tends to underestimate catalyst enantioselectivity, particularly when propene-*l-d* is used and the more so the higher the polymerization temperature.

Conclusions

The stereoregularity of polypropylene produced with C_2 -symmetric group 4 *ansa*-metallocene catalysts results from a balance between isotactic monomer polyinsertion and a side process of epimerization of the polymer chain at its active end.^{4,8–10}

In this paper, we have presented two basic approaches for the separate evaluation of stereoselectivity and enantioselectivity: one based on the quantitative analysis of the dependence of polymer tacticity on monomer concentration and another based on the ¹³C NMR characterization of *d*-labeled poly(propene)s.

The two methods, applied to propene polymerization promoted by the "classic" catalyst system *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO, have given consistent results, although the existence of more than one epimerization pathway, which emerged in this investigation, imposes caution in the interpretation of results for *d*-labeled monomers.

Ethylene-bis(4,5,6,7-tetrahydro-1-indenyl) is one of the ligands used in the first published syntheses of group 4 *ansa*-metallocenes with C_2 -symmetry.^{4,24} However, 1-alkene polymerization catalysts based on this ligand^{4,6b,15,25,26} and on its fully aromatic analogue ethylene-bis(1-indenyl)^{4,6,15,21,27} were soon abandoned, mainly because of their low stereoselectivity at practical reaction temperatures (>50 °C), tentatively ascribed to an inadequate stereorigidity of the ligand framework.^{4,15,28}

The search for improved metallocene precursors has been highly successful, and a number of catalysts affording highly isotactic polypropylene up to 80 °C have been disclosed.^{4,13–15} In most cases, the two halves of the aromatic ligand are linked by a dimethylsilyl bridge, considered to reduce the conformational freedom allowed by the ethylene bridge.^{4,15,28,29}

Ironically, it is now being realized that this progress has been achieved on the basis of a partly wrong premise. Indeed, the results presented in this paper prove that the lower stereoselectivity of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂, compared with that of the new, sterically more open C_2 -symmetric zirconocenes,^{13–15,29} is not due to a lower enantioselectivity in monomer insertion (as is also suggested by common sense and in agreement with the indications of molecular mechanics calculations³⁰) but to a (much) lower ratio k_{ins}/k_{epim} between the specific rates of monomer insertion and of chain epimerization at temperatures of practical interest.

As an example, we have preliminarily estimated, for propene polymerization in the presence of *rac*-dimethylsilyl-bis(1-indenyl)ZrCl₂/MAO^{11a,29} at 50 °C, a value of $k_{ins}/k_{epim} \approx 70$ (L/mol)^{1.4}, to be compared with $k_{ins}/k_{epim} \approx 8$ (L/mol)^{1.2} only for *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO (Table 3); on the other hand, the fraction F_p of "primary" stereoerrors in polypropylene samples prepared with the two catalyst systems is of the order of 0.015 and 0.020, respectively.

These findings can provide a key for rationalizing, at least *a posteriori*, the stereoselective behavior of this

new class of homogeneous catalysts for isotactic 1-alkene polymerization. We are extending our investigation to other metallocenes within the same class, as well as to the related class of syndiotactic-specific metallocene catalysts with C_5 -symmetry.^{4,31}

Experimental Section

Polymerization of Propene-*d*₀. All polymerization experiments were carried out in a 2 L magnetically stirred stainless steel reactor (Brignole AU-2) equipped with a glass vial holder-breaker. The appropriate amounts of anhydrous solvent (toluene or heptane) and of MAO (Witco GmbH, 10 wt % solution in toluene, evaporated to dryness and redissolved in toluene or heptane) were introduced in the reactor, which was thermostated at the desired temperature and pressurized with propene at the chosen concentration (total volume of liquid phase, 0.5 L). The reaction was started by breaking a glass vial containing a (toluene or heptane) solution of (EBT-HI)ZrCl₂ (Witco GmbH), allowed to proceed at constant monomer concentration (*i.e.* partial pressure) for a suitable time, and stopped by quick monomer degassing. The polymers were coagulated with methanol (0.5 L) added with 10 mL of concentrated HCl, filtered, and vacuum-dried at 50 °C.

The propene concentration in the reacting phase, [M], was calculated from the following approximate equation:³²

$$[M] = p_M A \exp(B/RT) \quad (6)$$

with p_M = monomer partial pressure (in atm). According to ref 32, for the system propene/heptane, $A = 2.72 \times 10^{-3}$ mol/(L atm) and $B = 3260$ cal/mol; we verified that the same A and B values can be used also for the system propene/toluene in the temperature range 30–80 °C up to (at least) [M] = 6 mol/L.

Synthesis and Polymerization of Propene-*2-d*. Propene-*2-d* was prepared by reacting CH₂=C(CH₃)Li with D₂O (Aldrich; 99.9+% isotopic purity) in diethyl ether according to refs 8d and 33.

Polymerization experiments were run in a 50 mL glass reactor (Büchi MiniClave) with magnetic stirring. The reactor was charged, under nitrogen atmosphere, with 20 mL of anhydrous toluene and 3 mL of a 10 wt % MAO solution in the same solvent (Witco GmbH). The system was then thermostated at the desired temperature and pressurized with propene-*2-d* (at the partial pressure 0.6 bar at 50 °C or 2.6 bar at 80 °C). The polymerization was started by syringing in the reactor, through a silicone rubber septum, 0.4 mg of (EBT-HI)ZrCl₂ dissolved in 2 mL of toluene, and it was allowed to proceed at constant monomer pressure for 2 h, after which it was stopped by injecting 10 mL of methanol. The polymers were coagulated with acidified methanol (0.2 L), filtered, and vacuum-dried at 50 °C.

¹³C NMR Characterization of Poly(propene-*d*₀). Quantitative³⁴ ¹³C{¹H}NMR spectra were recorded with a Bruker AC-270 spectrometer operating at 67.9 MHz, on 10% w/v solutions in 1,1,2,2-tetrachloroethane-*d*₂ at 100–120 °C, under the following conditions: 5 mm probe; ≈80° pulse; acquisition time, 1.2 s; relaxation delay, 1.5 s; 10–15K transients.

The fraction $[m]$ of *m* diads in the polymers was evaluated from the triad distribution, measured by integration of the methyl region:

$$[m] = [mm] + \frac{1}{2}[mr]$$

It should be noted that the resonances of methyl C's in stereoregular monomeric units adjacent to chain end groups and to 3,1 regioirregular units and that of the methylene C-2 in *n*-propyl end groups occur in the regions of methyl peaks corresponding to regioregular sequences in *mr* and *rr* stereochemical arrangement, respectively;^{9b,35} this must be taken into account when the concentration of end groups and/or of 3,1 units is not negligible, as was the case for most of the investigated polypropylene samples. Independent measurements of triad distribution were also made using the resonance

of the methylene C-3 in *n*-propyl end groups³⁶ and/or of the S_α C's in 3,1 monomeric units;^{6b,35a} a good agreement between the three estimates was always observed.

¹³C NMR Characterization of Poly(propene-2-*d*). Quantitative ¹³C{¹H}NMR spectra at zero NOE were recorded with a Bruker AMX 600 spectrometer operating at 150.9 MHz on dilute polymer solutions (<5 mg/mL) in 1,1,2,2-tetrachloroethane-*d*₂ at 70 °C, with the acquisition parameters described in ref 8d.

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