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Effects of Regiochemical and Stereochemical Errors on the Course of Isotactic Propene Polyinsertion Promoted by Homogeneous Ziegler–Natta Catalysts

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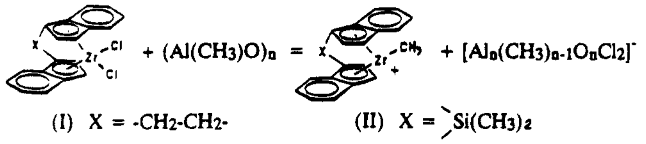
ABSTRACT: The effects of regiochemical and stereochemical errors on the kinetic course of isotactic propene polyinsertion promoted by two typical homogeneous metallocene catalysts are analyzed in detail. It is shown, in particular, that occasional *regioirregular* 2,1 insertions not only slow down chain propagation to a substantial extent—as already reported in a preliminary communication—but also practically inhibit chain transfer to the monomer and to the aluminum alkyl cocatalyst. Active centers bearing a growing chain with a 2,1 last-inserted propene unit are therefore trapped in a "dormant" state, in which the only feasible alternative to the formation of a sterically demanding head-to-head enchainment, at least at sufficiently high reaction temperatures, is 2,1 to 1,3 isomerization. Experimental data suggesting that chain propagation is hindered after a *stereoirregular* monomer insertion are also discussed.

Introduction

In the past decade, a new class of homogeneous Ziegler–Natta catalysts has been developed, able to promote the isotactic polymerization of 1-alkenes.[1] The catalyst precursors are stereorigid, chiral group IV metallocenes, such as, e.g., *rac*-(ethylene)bis(1-indenyl)-$ZrCl_2$ (**I**)[2] or its dimethylsilyl-bridged analogue (**II**),[3] from which cationic active species are formed by reaction with a suitable cocatalyst (typically, methylaluminoxane (MAO), Scheme 1).[1,4]

Scheme 1



Compared with the "classical" heterogeneous catalysts (i.e., $TiCl_3$ in a layered modification[5] or supported systems $MgCl_2/TiCl_4$[6]), the homogeneous ones are usually less regio- and stereospecific.[1] In particular, isotactic polypropene samples prepared in the presence of the latter catalysts typically contain ≈0.5–1 mol % of regioirregular monomeric units (2,1 and/or 1,3[1,7–10]), whereas the concentration of such defects in samples produced with most heterogeneous catalysts is below 0.1 mol %.[11,12]

The effects of constitutional and configurational errors on the crystallization behavior and on the physicochemical properties of the polymers have been widely investigated.[13–15] Much less information, conversely, can be found in the literature on the extent to which the "normal" kinetic course of chain propagation and transfer reactions is perturbed by a last-inserted regioirregular or stereoirregular monomeric unit.

In ref 12, a new method was introduced for the kinetic study of Zielger–Natta polyinsertions, combining ^{13}C NMR characterizations of polymers with GC–MS analyses of oligomers resulting from fast H_2-induced chain transfer. This approach allows the evaluation of the ratios between kinetic constants governing the formation of the various possible constitutional and configurational sequences.

In a preliminary communication[16] on propene polyinsertion promoted by the system I/MAO at 60 °C, the first quantitative kinetic data were presented, confirming the assumption[17,18] that chain propagation after a regioirregular 2,1 monomer enchainment is strongly slowed down, due to the high steric hindrance of the $Zr-CH(CH_3)CH_2-P_n$ moiety (P_n = polymeryl). It was found, indeed, that the great majority (≈90%) of the active centers in the quoted catalyst are trapped in a "dormant" state, so that the average apparent polymerization rate is an order of magnitude lower than the "true" rate of 1,2 polyinsertion.

In this paper, we present a more complete analysis on the kinetic consequences of regioirregular and stereoirregular insertion events on chain propagation, isomerization, and transfer based on comparative results of propene polyinsertion catalyzed by the two systems **I**/MAO, **II**/MAO under both hydrooligomerization and polymerization conditions.

Results and Discussion

For the sake of simplicity, the aspects connected with the regiospecificity and those concerning the stereospecificity will be treated separately.

Regiospecificity. (i) Chain Propagation and Isomerization. For chain propagation prevailingly via 1,2 (primary) monomer insertion (as is the case of the catalysts under study[1,7–10]) and with reference to the specific rates defined in Scheme 2, the fraction of regioirregular 2,1 (secondary) insertions is given by the ratio k_{ps}/k_{pp}. The fraction $x^*(d)$ of active centers in the "dormant" state due to regiochemical inversion, assuming stationary-state conditions and *in the limit of negligible chain transfer and 2,1 to 1,3 isomerization* (see further), tends to $x^*(d) = [1 + (k_{sp}/k_{ps})]^{-1}$.[12,16] The

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Scheme 2

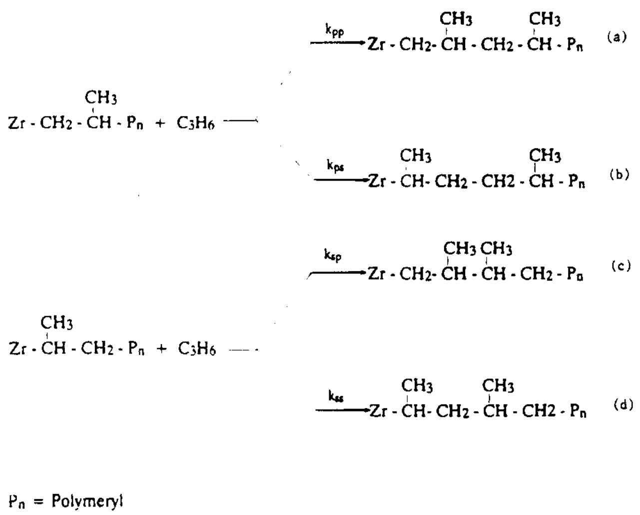


Table 1. Selected Results of Propene Hydrooligomerizations at 60 °C in the Presence of the Two Catalyst Systems under Study

catalyst system[a]	$\bar{X}_n$[b]	Q_p/Q_s[c]
I/MAO	36	1.7
	30	2.3
	27	2.8
	19	4.3
II/MAO	48	2.1
	32	3.5
	27	4.3
	21	5.6

[a] [Zr] = 2.25 × 10^{-5} mol/L in benzene; [Al]/[Zr] = 3.0 × 10^3 mol/mol. [b] Number-average degree of polymerization, measured by ^{13}C NMR. [c] Ratio between 1,2 (primary) terminated and 2,1 (secondary) terminated chains in the hydrooligomer, measured by GC.

Table 2. Regiospecificity of Propene Polyinsertion in the Presence of the Two Catalyst Systems under Study As Evaluated from Hydrooligomerization Experiments at 60 °C

catalyst system	k_{ps}/k_{pp} × 10^2	k_{sp}/k_{ps}	x^*(d)[a]
I/MAO	1.0	0.10 ± 0.05	0.90 ± 0.05
II/MAO	0.8	0.3$_5$ ± 0.05	0.7$_5$ ± 0.05

[a] Mole fraction of "dormant" centers.

values of k_{ps}/k_{pp}, k_{sp}/k_{ps}, and x^*(d) for the catalyst systems **I**/MAO and **II**/MAO, as estimated from propene hydrooligomerization experiments[12,16] at 60 °C by applying eq 16 of ref 12 to the data in Table 1, are given in Table 2 (in all tables, the accuracy of the data is ±1 in the last significant digit, unless differently indicated).

The higher value of k_{sp}/k_{ps} (and, consequently, the lower value of x^*(d)) for catalyst system **II**/MAO (Table 2) is indicative of a lower hindrance in the insertion of a 1,2 unit after a previous 2,1 insertion, most likely as a consequence of the wider "coordination gap aperture angle"[19] of the ligand framework ensured by the dimethylsilyl bridge. This may well explain the higher productivity of catalyst **II** compared with catalyst **I**.[3]

Table 3. Regioirregular Monomeric Units in Polypropene Samples Prepared with the Two Catalyst Systems under Study As Evaluated from ^{13}C NMR Spectra

catalyst system[a]	T (°C)	2,1 units (mol %)	1,3 units (mol %)	regioirregular units (total, mol %)
I/MAO	30	0.7	0.10 ± 0.05	0.8
	60	0.5	0.4	0.9
	80	0.3	0.5	0.8
II/MAO	30	0.5	nd[b]	0.5
	60	0.5	0.2	0.7
	80	0.3	0.4	0.7

[a] [Zr] = 2.25 × 10^{-5} mol/L in benzene; [Al]/[Zr] = 3.0 × 10^3 mol/mol; propene concentration, [M] = 1.2 ± 0.2 mol/L. [b] nd = not detected.

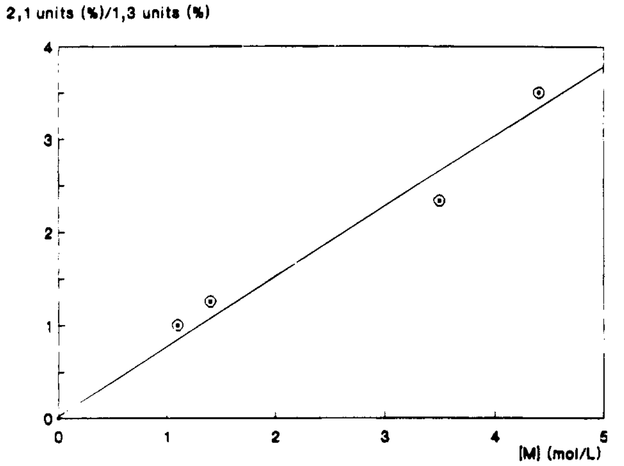
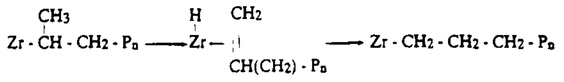


Figure 1. Ratio between 2,1 and 1,3 units (evaluated from ^{13}C NMR spectra) in polypropene samples prepared in the presence of the catalyst system I/MAO at 60 °C as a function of propene concentration, [M].

Scheme 3



In Table 3, we report the concentration of regioirregular units (2,1 and 1,3), determined from ^{13}C NMR spectra in polypropene samples prepared under corresponding experimental conditions, but in the absence of H_2, at 30, 60, and 80 °C. For both catalyst systems, the *total* concentration of regioirregularities does not seem to change much with the temperature in the examined ranged and is very close to the value of k_{ps}/k_{pp} (measured at 60 °C, Table 2). This latter finding agrees with the suggestion of Zambelli et al.[7] that the 1,3 units are formed via isomerization of 2,1 units (possibly according to Scheme 3[14]).

As a further kinetic argument in favor of the above interpretation, we found that the ratio between 2,1 and 1,3 units in polypropene samples prepared with each of the two metallocene catalysts at a given temperature is linearly dependent on monomer concentration, [M] (in the range [M] = 1−5 mol/L; Figure 1). This can be explained by admitting that the rate, $\bar{v}_{sp}$ of 1,2 propene insertion at an active center with a 2,1 last-inserted unit (Scheme 2c) has a first-order dependence on [M]:

$$\bar{v}_{sp} = k_{sp}C^*_s[M] \qquad (1)$$

whereas the rate, $\bar{v}_{is}$ of isomerization of a 2,1 to a 1,3 unit (Scheme 3) is independent of [M]:

$$\bar{v}_{is} = k_{is}C^*_s \qquad (2)$$

(C^*_s is the concentration of growing chains with a 2,1 last-inserted propene unit.)

It should be concluded, therefore, that 2,1 to 1,3 isomerization (Scheme 3) competes with 1,2 over 2,1 monomer insertion (Scheme 2c). Accordingly, at a given temperature and propene concentration, when using catalyst system I/MAO, with a lower value of the ratio

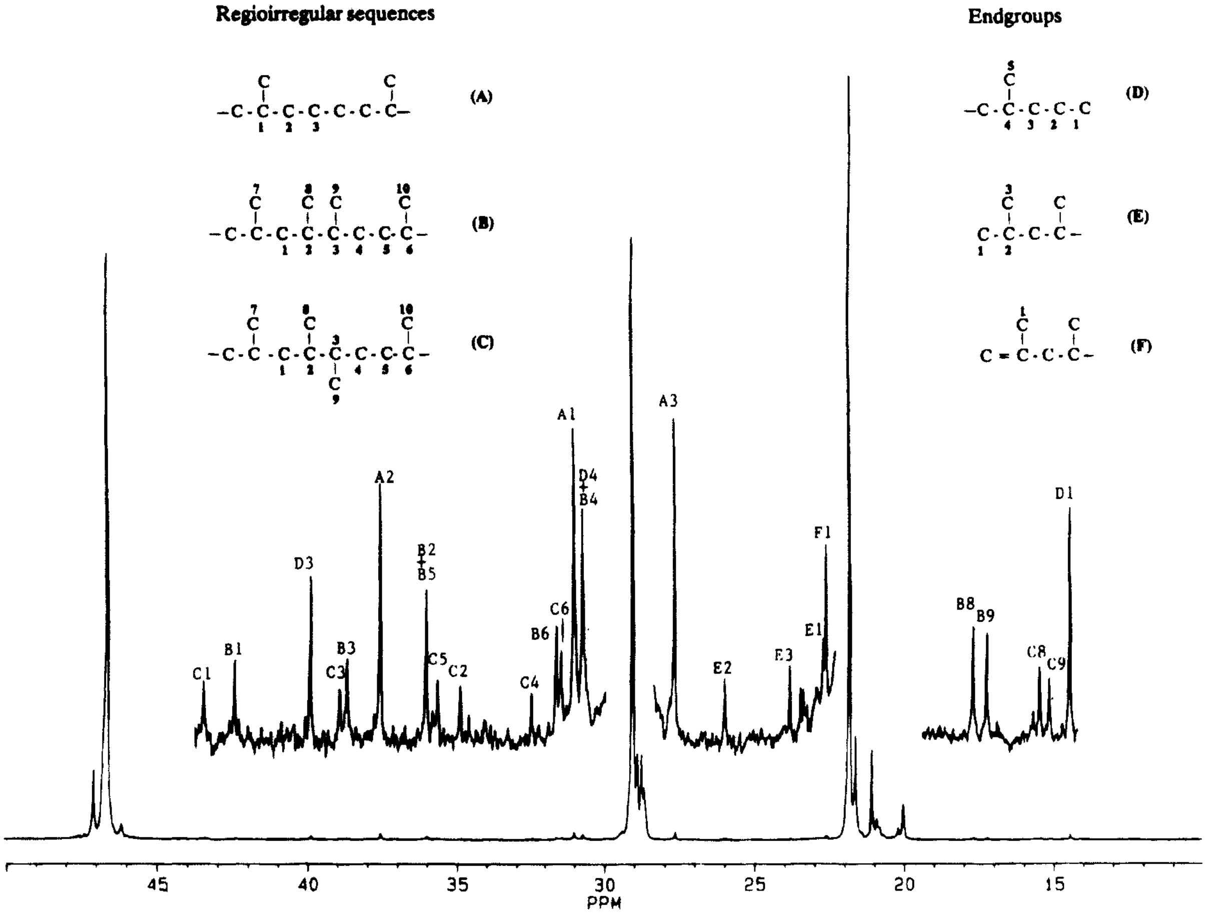


Figure 2. ^{13}C NMR spectrum of polypropene sample no. 7 in Table 4 (resonance assignments from refs 7 and 25).

k_{sp}/k_{ps} compared to system II/MAO (Table 2), a higher fraction of 2,1 units undergoes isomerization to 1,3 units (Table 3).

The data in Table 3, on the other hand, show that—in the presence of each catalyst—the proportion of 1,3 units increases rapidly with increasing temperature (at constant [M]). From an Arrhenius plot of such data for the catalyst system I/MAO, it can be evaluated that $[\Delta E^{\ddagger}(\mathrm{is}) - \Delta E^{\ddagger}(\mathrm{sp})]$ is of the order of 10 kcal/mol and that $\ln[A(\mathrm{is})/A(\mathrm{sp})]$ is of the order of 15. This indicates that, relative to 1,2 insertion after a 2,1 last-inserted unit, the isomerization of the latter into a 1,3 unit is strongly disfavored for enthalpic reasons but may come into play at sufficiently high temperatures due to a highly favorable entropy factor.

(ii) Chain Transfer. A second way through which an active center with a 2,1 last-inserted unit may escape from its "dormant" state is, in principle, a chain transfer event.

Actually, in the presence of H_2, growing polypropene chains with a 2,1 last-inserted unit are readily terminated (Scheme 4b) and, at the resulting Mt–H species, 1,2 propagation is restored.[16,18] Accordingly, H_2 is a strong activator of the isotactic-specific metallocene catalysts.[16,18]

When H_2 is not used, however, the picture is different. The predominant chain end groups which could be detected by ^{13}C NMR in polymers prepared in the absence of H_2 (Figure 2) were isobutenyl and *n*-propyl, corresponding to chain termination and initiation by, respectively, β-hydrogen elimination from a 1,2 last-inserted unit (Scheme 5a) and 1,2 propene insertion into a Zr–H bond (Scheme 5c).

In addition, isobutyl chain end groups were detected, arising from transfer to $Al(CH_3)_3$ (in equilibrium with MAO) of growing chains with a 1,2 last-inserted unit (Scheme 6a) and subsequent chain initiation via 1,2 propene insertion into a $Zr-CH_3$ bond (Scheme 6c).[20] The fraction of isobutyl end groups tends to increase with decreasing propene concentration.

Scheme 4

(*a*) $Zr-CH_2-CH(CH_3)-P_n + H_2 \xrightarrow{k_{pH}} Zr-H + CH_3-CH(CH_3)-P_n$

(*b*) $Zr-CH(CH_3)-CH_2-P_n + H_2 \xrightarrow{k_{sH}} Zr-H + CH_3-CH_2-CH_2-P_n$

(*c*) $Zr-H + C_3H_6 \longrightarrow Zr-CH_2-CH_2-CH_3$

Resonances indicative of termination events involving chains with a 2,1 last-inserted unit were hardly detected, in spite of the fact that the majority of the growing chains are in that state (Table 2). *This means that, in the absence of H_2, chain transfer at "dormant" centers is negligible.*

If it can be accepted that the approach of an Al–alkyl molecule to a $Zr-CH(CH_3)CH_2-P_n$ moiety (Scheme 6b) is hindered for steric reasons, it would be difficult to understand the low rate of chain transfer via β-hydrogen elimination from a 2,1 last-inserted unit (Scheme 5b), unless it is admitted that the detachment of the unsaturated chain is slow without the "assistance" of a monomer molecule (Scheme 7).[21] In fact, chain transfer to the monomer, which seems to be not viable at a sterically hindered 2,1 last-inserted unit (Scheme 7b), is the main transfer pathway for growing chains with a 1,2 last-inserted unit (Scheme 7a). A simple kinetic proof for this latter statement is given in Table 4, showing that the average molecular weight of polypropene samples obtained with the investigated catalyst systems is independent of propene concentration [M] for

Scheme 5

(*a*) $Zr\text{-}CH_2\text{-}CH(CH_3)\text{-}P_n \longrightarrow Zr\text{-}H + CH_2{=}C(CH_3)\text{-}P_n$

(*b*) $Zr\text{-}CH(CH_3)\text{-}CH_2\text{-}P_n \longrightarrow Zr\text{-}H + x\,CH_2{=}CH\text{-}CH_2\text{-}P_n + (1\text{-}x)\,CH_3\text{-}CH{=}CH\text{-}P_n$

(*c*) $Zr\text{-}H + C_3H_6 \longrightarrow Zr\text{-}CH_2\text{-}CH_2\text{-}CH_3$

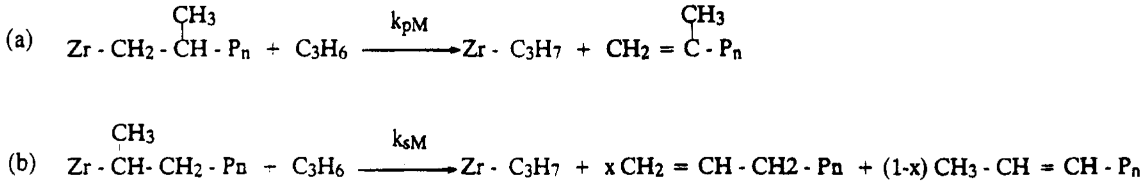
Scheme 6

(a) $Zr\text{-}CH_2\text{-}CH(CH_3)\text{-}P_n + Al(CH_3)_3 \xrightarrow{k_{p,Al}} Zr\text{-}CH_3 + P_n\text{-}CH(CH_3)\text{-}CH_2\text{-}Al(CH_3)_2$

(b) $Zr\text{-}CH(CH_3)\text{-}CH_2\text{-}P_n + Al(CH_3)_3 \xrightarrow{k_{s,Al}} Zr\text{-}CH_3 + P_n\text{-}CH_2\text{-}CH(CH_3)\text{-}Al(CH_3)_2$

(c) $Zr\text{-}CH_3 + C_3H_6 \longrightarrow Zr\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$

Scheme 7



(a) $Zr\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}P_n + C_3H_6 \xrightarrow{k_{pM}} Zr\text{-}C_3H_7 + CH_2{=}\overset{CH_3}{C}\text{-}P_n$

(b) $Zr\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}P_n + C_3H_6 \xrightarrow{k_{sM}} Zr\text{-}C_3H_7 + x\,CH_2{=}CH\text{-}CH2\text{-}P_n + (1\text{-}x)\,CH_3\text{-}CH{=}CH\text{-}P_n$

Table 4. Average Molecular Weight of Polypropene Samples Prepared in the Presence of the Catalyst System I/MAO at 30 and 60 °C

T (°C)	[M][a] (mol/L)	$\bar{M}_v$[b] (amu × 10^{-4})	sample no.
30	7.1	2.8	1
	3.4	2.7	2
	2.2	2.5	3
	1.1	1.7	4
60	6.7	1.5	5
	3.5	1.5	6
	1.1	1.2	7

[a] Propene concentration. Other polymerization conditions: [Zr] = 2.25×10^{-5} mol/L in benzene; [Al]/[Zr] = 3.0×10^3 mol/mol. [b] Viscosity-average molecular weight.

[M] > 2 mol/L.[21,22] At lower [M] values, the decrease of average molecular weight with decreasing [M] is mainly due to a nonnegligible chain transfer to the Al–alkyl, as shown by the ^{13}C NMR analysis of the end groups and in accordance with eq 3:

$$\bar{x}_n \approx \bar{v}_p/\bar{v}_t \approx k_{pp}[M]/\{k_{pM}[M] + k_{p,Al}[Al(CH_3)_3]^{\alpha}\} \quad (3)$$

($\bar{x}_n$ = number-average degree of polymerization; for definition of the kinetic constants, see Schemes 2, 6, and 7).

Stereospecificity. The isotactic-specificity of the C_2-symmetric metallocene catalysts is due to the asymmetry of the cationic complex arising from the coordination mode of the aromatic ligand.[1,23] Accordingly, the distribution of the stereoirregularities in the polymers produced conforms to that predicted by the enantiomorphic-sites statistical model.[1,10]

As a result, active species with a given chirality of ligand coordination and opposite configurations at the tertiary C atom in the last-inserted monomeric unit of the growing chain are diastereoisomeric and, in principle, have a different reactivity. Experimental evidence that this difference may be appreciable seems to be provided by the comparative analysis of the stereoregularity of propene polyinsertion products obtained using the two investigated catalysts in the presence and in the absence of H_2.

Table 5. Effect of H_2 Pressure on the Stereoregularity of Propene Polyinsertion Products Obtained with the Two Catalyst Systems under Study

catalyst system[a]	T (°C)	$p(H_2)$ (bar)	$[r]$[b]	$\bar{X}_n$[c]
I/MAO	30	0	0.04	6×10^2
		40	0.020	58
	60	0	0.08	1.7×10^2
		10	0.058	51
		20	0.041	36
		40	0.035	27
	80	0	0.15	1.2×10^2
		40	0.077	13
II/MAO	60	0	0.06	2.2×10^2
		10	0.060	48
		20	0.037	32
		40	0.022	27

[a] [Zr] = 2.25×10^{-5} mol/L in benzene; [Al]/[Zr] = 3.0×10^3 mol/mol; propene concentration, [M] = 1.2 ± 0.2 mol/L. [b] Fraction of r diads, measured by ^{13}C NMR and by GC (for $p(H_2) \geqslant 10$ bar). [c] Number-average degree of polymerization, measured by ^{13}C NMR.

In Table 5 we report the average concentration, $[r]$ of r diads (evaluated from ^{13}C NMR and/or GC data) in products prepared at different H_2 partial pressures for given values of reaction temperature and propene concentration. It can be seen that, for both catalysts, $[r]$ tends to decrease with increasing $p(H_2)$.

It should be noted that, upon chain transfer to H_2, the chirality of the tertiary C atom in the last-inserted unit of the growing chain is lost (see Scheme 4a). The experimental trend in Table 5 can thus be explained if it is admitted that the probability of undergoing hydrogen transfer is higher for a growing chain with a stereoirregular last-inserted propene unit.

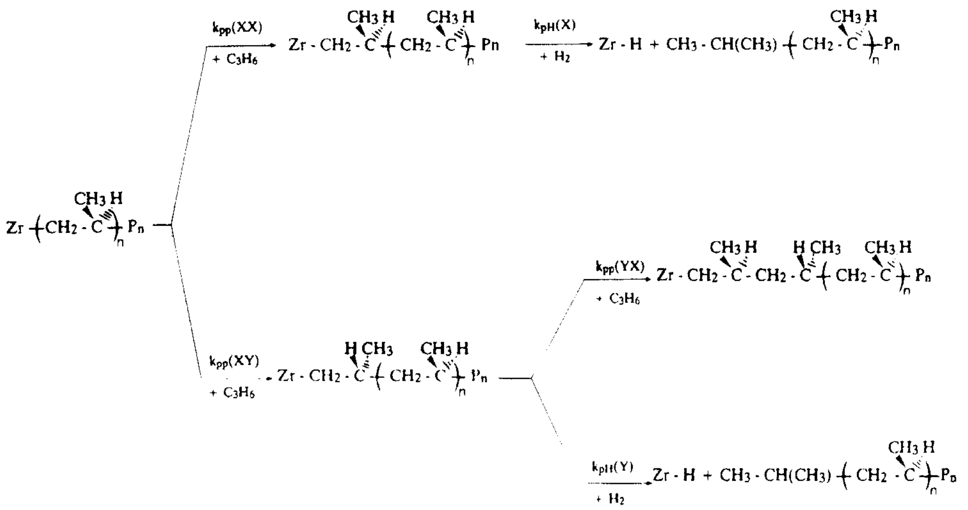
More quantitatively and with reference to the kinetic constants defined in Scheme 8

$$k_{pp}(XX)/k_{pH}(X) > k_{pp}(YX)/k_{pH}(Y) \quad (4)$$

(since $k_{pp}(XX) \gg k_{pp}(XY)$ and $k_{pp}(YX) \gg k_{pp}(YY)$).

For a given catalyst system, the values of the kinetic constants of chain transfer to H_2 seem to be relatively insensitive to differences in the chemical structure of the growing polymer chain,[12,16] so that it can be as-

Scheme 8[a]



[a] For a catalytic complex with (*R,R*) coordination of the aromatic ligand, X corresponds to *re* propene insertion (favored[23]), and Y to *si* propene insertion. The opposite holds for a catalytic complex with (*S,S*) coordination of the aromatic ligand.

Table 6. Calculated[a] Values of the Ratio $k_{pp}(XX)/k_{pp}(YX)$ (Scheme 8) for Propene Polyinsertion in the Presence of the Two Catalyst Systems under Study (See Text)

catalyst system	*T* (°C)	$k_{pp}(XX)/k_{pp}(YX)$
I/MAO	30	60
	60	45
	80	30
II/MAO	60	45

[a] For a three-state first-order Markov process with transition probabilities expressed by the stochastic matrix

$$\begin{array}{c|ccc|} & X & Y & T \\ \hline X & \sigma/(1+P_1) & (1-\sigma)/(1+P_1) & P_1/(1+P_1) \\ Y & \sigma/(1+P_2) & (1-\sigma)/(1+P_2) & P_2/(1+P_2) \\ T & \sigma & 1-\sigma & 0 \end{array}$$

States X and Y are as defined in Scheme 8; state T is chain transfer to H_2. The value of the probability σ was determined from ^{13}C NMR spectra of polypropene samples prepared in the absence of H_2 in the framework of the enantiomorphic-sites statistical model: for the catalyst system **I**/MAO $\sigma = 0.98$ at 30 °C, 0.96 at 60 °C, and 0.92 at 80 °C; for the catalyst system **II**/MAO $\sigma = 0.97$ at 60 °C (Table 5). With reference to Scheme 8, $k_{pp}(XX)/k_{pp}(YX) = P_2/P_1$ for $k_{pH}(X) = k_{pH}(Y)$.

sumed that $k_{pH}(X) \approx k_{pH}(Y)$. If so, inequality 4 reduces to

$$k_{pp}(XX) > k_{pp}(YX) \qquad (5)$$

This would mean that chain propagation is considerably slower after a stereoirregular monomer insertion. In Table 6 we report the values of the ratio $k_{pp}(XX)/k_{pp}(YX)$ that, *within the previous assumptions*, would lead to the experimental results in Table 5 for $k_{pH}(X)/k_{pH}(Y) = 1$.

Different and/or additional explanations, however, cannot be ruled out, so that $k_{pp}(XX)/k_{pp}(YX)$ in Table 6 may well be overestimated.

Conclusions

In this paper, we have presented an analysis of the effects of regiochemical and stereochemical errors on the kinetic course of isotactic propene polyinsertion promoted by two prototypical homogeneous metallocene catalysts. We have shown, in particular, that occasional *regioirregular* 2,1 insertions not only slow down chain propagation to a substantial extent—as preliminarily discussed in a previous communication[16]—but also practically inhibit chain transfer to the monomer and to the aluminum alkyl cocatalyst. Active centers bearing a growing chain with a 2,1 last-inserted propene unit are therefore trapped in a "dormant" state, in which the only feasible alternative to the formation of a sterically demanding head-to-head enchainment, at least at sufficiently high reaction temperatures, is 2,1 to 1,3 isomerization.[7,14]

The fraction of dormant centers, however, is critically dependent on the structure of the metallocene. For the two examined catalyst systems, indeed, a wider coordination gap aperture angle of the bis(indenyl) ligand was found to result in a lower fraction of dormant centers (and therefore in a higher average productivity).

We have also reported experimental data possibly suggesting that isotactic chain propagation may be hindered at a *stereoirregular* last-inserted unit. This effect, likely due to steric repulsions between the growing polymer chain and the inserting olefin, could be at the origin of the weak isotactic *chain-end* control observed in propene polymerization promoted by some *achiral* metallocene catalysts at low temperature.[24]

Experimental Section

rac-(Ethylene)bis(1-indenyl)$ZrCl_2$ and *rac*-(dimethylsilyl)bis(1-indenyl)$ZrCl_2$ were prepared according to the literature.[2,3] Commercial MAO (Schering, 30 wt % solution in toluene) was used as received.

Propene polymerization and hydrooligomerization experiments were performed in benzene (freshly distilled over Na/K alloy) following the general procedures described in refs 12 and 16, to which we refer also for details on the GC–MS and ^{13}C NMR characterization of the reaction products.

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