

C_2 -symmetric *ansa*-metallocene catalysts for propene polymerization: Stereoselectivity and enantioselectivity

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Abstract

Important similarities between the new homogeneous catalysts for 1-alkene polymerization based on C_2 -symmetric *ansa*-metallocenes of the 4th column and their heterogeneous Ziegler–Natta predecessors are unquestionable; in particular, the factors leading to the remarkable *enantioselectivity* of both catalyst classes have been proved to be strictly analogous. In the case of metallocene catalysts, however, an insidious side reaction of chain epimerization, unnoticed for a relatively long time, can undermine the *stereoselectivity* of the polymerization process; this recent finding and its mechanistic implications are discussed in the present paper. © 1998 Elsevier Science B.V.

1. Introduction

The fascinating story of Ziegler–Natta catalysis contains some of the nicest examples of lucky finds helping the progress of science [1].

Its very beginning in 1953, in Ziegler's laboratory at the Max Planck Institute in Mülheim, can be traced back to the fortuitous presence, in a reactor where ethene oligomerization promoted by $AlEt_3$ was being performed, of traces of colloidal Ni from a previous experiment acting as a polymerization catalyst. A systematic study of the effects of other transition metal compounds eventually led to the identification of a mixture of $TiCl_4$ and $AlEt_3$ as an efficient

catalyst system for the production of high molecular mass linear polyethylene [1–3].

Less than one year later, at the Polytechnic of Milan, Natta and coworkers had already proved the unpredictable ability of Ziegler's catalyst to polymerize propene to a partly crystalline isotactic polymer and related the stereoselectivity to the structural regularity of the surface-alkylated heterogeneous $TiCl_3$ phase which forms in situ when $TiCl_4$ and $AlEt_3$ react in hydrocarbon solvent [1,4–6]. Since then, pre-formed $TiCl_3$ in one of its layered 'violet' modifications [1,6] or, more recently, supported systems consisting of $TiCl_4$ epitactically chemisorbed on $MgCl_2$ (isostructural with violet $TiCl_3$) [7–9] represent the main components of what is probably the most efficient class of man-made catalysts, able to promote isotactic propene polymerization under mild conditions with a produc-

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tivity and a selectivity which rival those of enzymes.

Only in the early 1980s, thirty years after the discovery, elegant experimental studies [10–12] and molecular mechanics calculations on models of active sites [13–20] allowed to understand in depth the origins of the marvelous enantioselectivity of these catalysts [21].

Coordinatively unsaturated chiral Ti atoms are located on the side edges of the platelet-like TiCl_3 or MgCl_2 crystals, forming a racemic array of enantiomorphous sites (see models in Fig. 1). Two double Cl bridges in Λ or Δ arrangement bind each of them to two inner Ti(Mg) atoms and the two remaining *cis* positions of the coordination octahedron can be occupied by the growing polymer chain and a π -coordinated monomer molecule prior to its 1,2 (primary) *cis*-insertion in the Ti–C σ -bond. Non-bonded contacts with the crystal surface restrict the conformational freedom of the polymer chain, which assumes a chiral orientation; this, in turn, favors the attack of a prochiral 1-alkene molecule with the enantioface placing the alkyl substituent of the double bond *trans* to the first C–C bond of the growing chain (Fig. 2A) [13–21].

It should be noted that *cis*- TiL_2X_2 species, L being an anionic bidentate ligand (such as, for example, a β -diketonate) and X a halide, alkyl

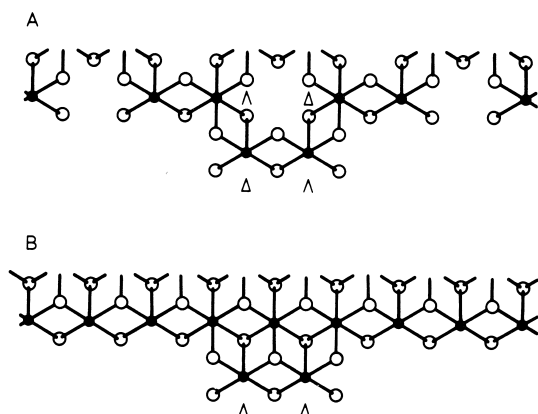


Fig. 1. Models of Ti_2Cl_6 reliefs on a (110) cut of 'violet' TiCl_3 (A) and on a (100) cut of MgCl_2 (B) [16], with indication of the chirality of the Ti atoms.

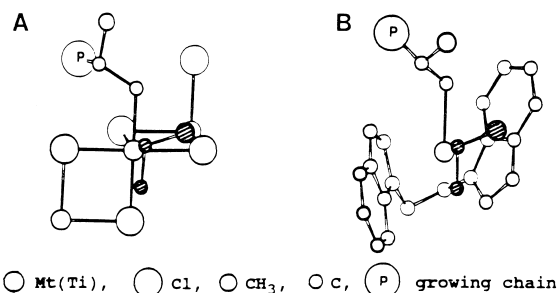


Fig. 2. Models of active sites for isotactic propene polymerization promoted by heterogenous Ziegler–Natta catalysts (A) and C_2 -symmetric metallocene catalysts (B), according to the 'growing chain orientation mechanism' of stereocontrol [19].

or aryl ligand, are fluxional in solution and undergo fast interconversion between Λ and Δ enantiomers [22]; for Ti_2Cl_6 reliefs on the surface of TiCl_3 and MgCl_2 this equilibrium seems instead to be 'frozen'.

Some 20 million tons per year of isotactic polypropylene are currently produced with highly efficient and environmentally clean processes based on catalysts strictly derived from first-generation Ziegler–Natta ones.

An inevitable feature of these systems is the disuniformity of the active sites (in spite of catalyst modification with suitable Lewis bases able to inhibit the active species of lower stereoselectivity); this complicates their mechanistic study as well as the efforts of tailoring catalyst structure to specific applications and ultimately results in a relatively broad distribution of polymer tacticity and molecular mass [7–9,21].

Therefore, a substantial research effort has been aimed at the synthesis of single-site catalysts with a well-defined structure and in particular of soluble complexes of early transition metals with a coordination environment of the metal mimicking that of Ti on the surface of the heterogeneous Ziegler–Natta systems.

When, however, in the early 80's, Brintzinger and coworkers isolated the first stereorigid *ansa*-metallocenes of the 4th column with C_2 -symmetry [23–25], shown to act as isotactic-selective catalysts for propene polymerization by Ewen [26] and Kaminsky [27], it was proba-

bly not clear to the same inventors how close to the original was the replica they had designed.

Nowadays, with the aid of computer modeling, it is easy to catch this similarity [19]. As an example, Fig. 2B shows a model of the cationic active site derived from the prototypical precursor *rac*-ethylene-bis(1-indenyl)MtCl₂, after activation with an appropriate co-catalyst (e.g., methylalumoxane (MAO)): the two halves of the aromatic ligand are locked by the ethylene bridge in an asymmetric conformation, with a local C₂ axis passing through the Mt atom and the growing polymer chain is constrained in a chiral orientation due to non-bonded contacts with one of the two C₆ rings. At the remaining coordination position, the *cis*-attack of a propene molecule (in orientation suitable for 1,2 insertion) with the enantioface directing the methyl group *trans* to the first C–C bond of the chain is favored; the analogy with the situation sketched in Fig. 2A is obvious [19].

The polymerization behaviors of the two classes of catalysts also seem strikingly similar. In particular, both produce isotactic polypropylene with occasional isolated stereoinverted units (...*mmmmrrmmmm*...; for metallocene catalysts see Refs. [26,28–30], for heterogenous catalysts see Refs. [31–34]) and, as expected on the basis of the ‘growing chain orientation’

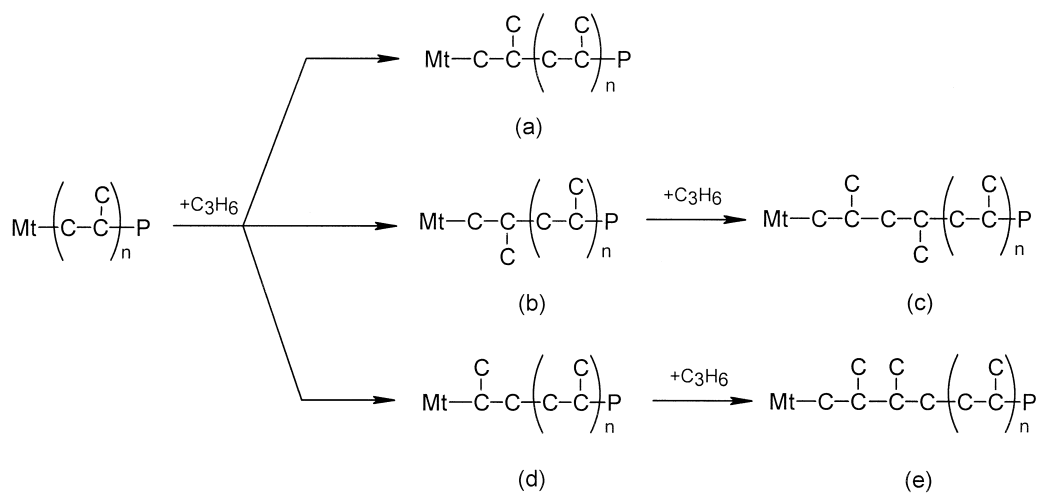
mechanism [13–20,35,36], both are not enantioselective when inserting propene in an initial Mt–CH₃ bond [10–12,37].

This background belief has been immanent in the research of the last decade aimed at improving the inadequate regio- and stereoselectivity of the first metallocene catalysts. Ironically, as we discuss in Section 2, it is only now being realized that the great success achieved [25,38] has been based, at least in part, on wrong premises and that, in a way, a major similarity with Ziegler–Natta catalysis is, once again, good luck!

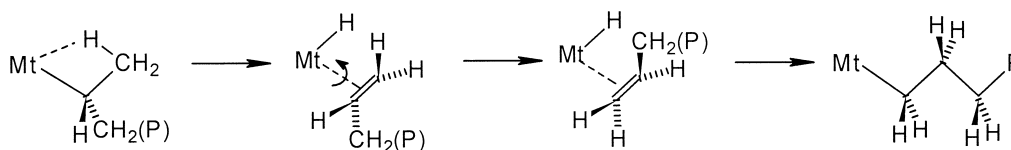
2. Results and discussion

Due to the four possible reaction modes of the monomer, (at least) sixteen different propagation steps should be considered in the kinetic scheme of propene polymerization [21].

However, from the ¹³C NMR microstructure of the polymers produced with all isotactic-selective coordination catalysts of practical interest, consisting of isotactic sequences interrupted by randomly-distributed isolated stereo- and regioerrors [25,26,28–34], a simplified description of the polyinsertion process can be derived (Scheme 1; P = polymeryl).



Scheme 1.



Scheme 2.

If one assumes that regioirregular and stereoirregular units are formed exclusively by monomer insertions with the ‘wrong’ enchainment or enantioface, respectively, catalyst regio- and stereoselectivities can be evaluated simply by measuring the concentration of such units from the ^{13}C NMR spectra of the polymers produced (the only practical difficulty being, in some cases, the low sensitivity of natural abundance ^{13}C NMR).

Actually this practice, used routinely for the heterogeneous Ziegler–Natta catalysts since the early 1970’s [21], has been extended tout-court to the new homogeneous metallocene-based ones. The higher concentration of regio- and/or stereoerrors in propene polymers prepared with most of the latter catalysts [25,38] has been explained in terms of a lower regio- and enantioselectivity of polyinsertion and the more or less significant decrease of the stereoselectivity with increasing polymerization temperature [25,38] (not observed when using heterogeneous systems [7–9]) has been ascribed mainly to an inadequate stereoridity of the metallocene ligand framework.

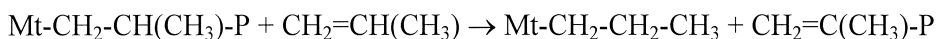
However, the reality is not that simple, as might have been suspected as soon as the first detailed ^{13}C NMR characterizations of isotactic polypropylene prepared in the presence of C_2 -symmetric metallocenes pointed out the presence in some samples of 3,1 monomer enchainments [28,29] and it was realized that these derive from the isomerization of *regioirregular*

2,1 last-inserted monomeric units [39,40]. As a matter of fact, monomer insertion in a growing chain ending with a 2,1 unit is exceedingly slow [40–43], and the rearrangement of the latter to a 3,1 unit can be a convenient alternative to the sterically demanding formation of a head-to-head enchainment (Scheme 1e).

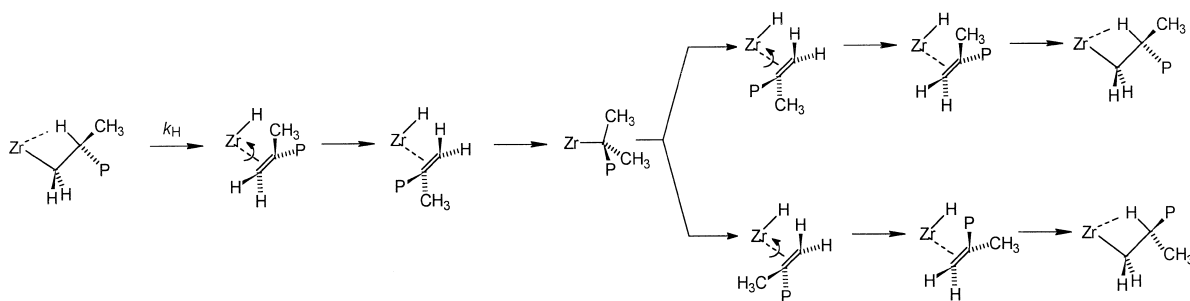
The fraction of 2,1 units that actually undergo isomerization depends on a number of variables: it is larger the more hindered is the active metal, and increases with decreasing monomer concentration and with rising temperature [25,38–40,44]. Obviously, ^{13}C NMR measurements of catalyst regioselectivity must consider the cumulative fraction of 2,1 and 3,1 units.

The commonly accepted isomerization mechanism [39,40] is shown in Scheme 2; it moves from the known propensity of the metallocene catalysts to promote β -H migration, due to the tendency of the highly electrophilic transition metal center in the cationic active species to establish a β -agostic interaction with the growing chain [25].

It might be objected that, alternatively to the proposed subsequent steps of rotation and reinsertion in the Mt-H bond, the terminally unsaturated polymer chain can be eliminated; however, this has also been shown to be a slow process [45–50]. Chain transfer, indeed, proceeds primarily via associative displacement involving a monomer molecule (Scheme 3), unless the active metal is sterically hindered by



Scheme 3.



Scheme 4.

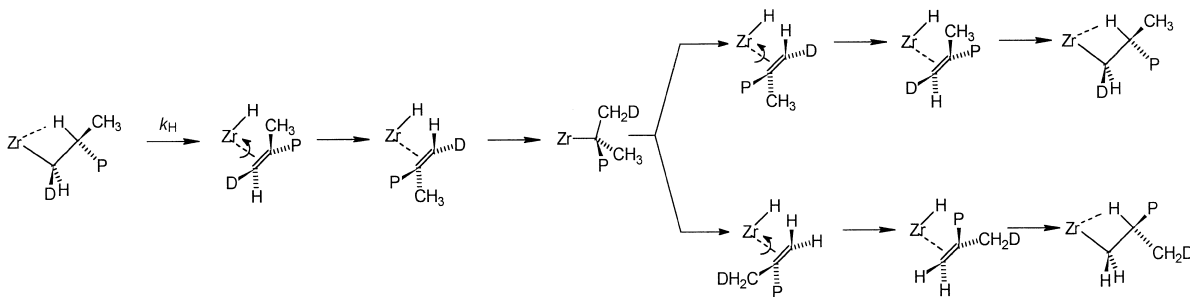
substituents at specific locations of the ligand framework [45] or in consequence of a last-inserted 2,1 unit [40,43].

The possibility of related isomerization reactions taking place at *regioregular* last-inserted units, particularly at low monomer concentration when chain propagation and transfer to the monomer are slow, would have been a logical guess. On the contrary, these processes have been overlooked for a decade, until they have been invoked as the only plausible explanation for the unexpected and puzzling dependence of the stereoselectivity of C_2 -symmetric metallocene catalysts in propene polymerization on monomer concentration [51].

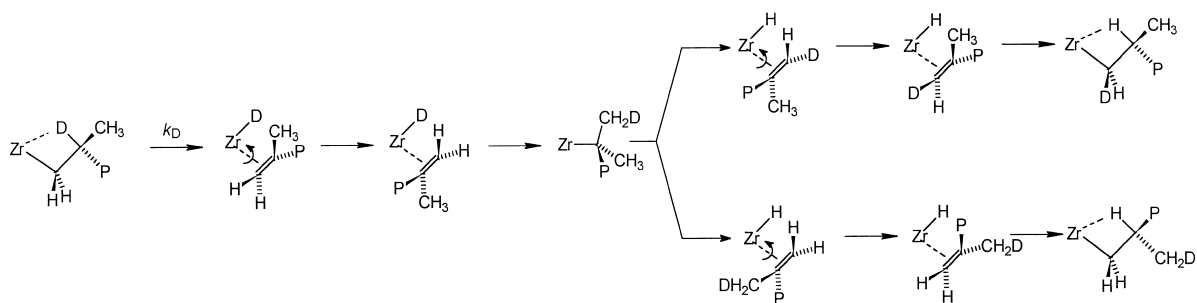
Indeed, in this [44,51–53] and other laboratories [54–56] it has been proved that, for such catalysts, isotactic monomer polyinsertion competes with an intramolecular side process of

epimerization of the polymer chain at its active end; the loss of stereoselectivity with decreasing monomer concentration observed for most of these catalysts is due to a growing interference of the latter reaction. As a result, enantioselectivity and stereoselectivity do not coincide and in extreme cases truly atactic polymers are obtained in the presence of highly enantioselective catalysts [51–53,56].

A possible mechanism of chain epimerization [51–53], conceptually related to that proposed for the generation of the 3,1 enchainments (Scheme 2), is shown in Scheme 4. Recent results of propene-1-*d* [54,55] and propene-2-*d* [53–55] polymerization seem to support it (Schemes 5 and 6): the ^{13}C NMR observation, in both cases, of *stereoirregular* monomeric units with the D label in the methyl group; the 2H NMR detection, in poly(propene-2-*d*), of



Scheme 5.



Scheme 6.

stereoregular monomeric units with D in the methylene group; the large primary isotope effect slowing down epimerization compared with polyinsertion in the case of propene-2-*d*.

On the other hand, in a thorough ^{13}C NMR investigation of poly(propene-1-*d*) and poly(propene-2-*d*) samples prepared at low (< 2 mol/l) monomer concentration with a number of C_2 -symmetric zirconocenes [55], Leclerc and Brintzinger have shown that the distribution of D in the chain end-groups is consistent with the hypothesis of chain transfer by $\beta\text{-H(D)}$ elimination taking place alternatively to epimerization at a $\text{Zr-C}(\text{CH}_3)(\text{CH}_2\text{D})(\text{P})$ moiety, but have also pointed out the presence of unexpectedly high amounts of *stereoregular* monomeric units with D in the methyl group¹; at present, it is not clear whether such units derive from additional side reactions of chain (or monomer) isomerization, or indicate that the mechanism proposed in Schemes 4–6 has to be modified.

What is certain, however, is that the epimerization of predominantly isotactic chains introduces stereoirregularities of the ... *mmmmrrm*-

mmm... type [51–56], identical to those formed by monomer misinsertion². This complicates the separate evaluation of the stereo- and enantioselectivity, which requires to discriminate between the two sources of stereoerrors.

In principle, one possibility would be to make use of D-labelled monomers. As discussed above, one may assume that, in predominantly isotactic samples of poly(propene-1-*d*) and poly(propene-2-*d*) produced with C_2 -symmetric metallocene catalysts, stereoirregular monomeric units with D in the methyl group are ‘secondary’ ones formed by epimerization (Schemes 5 and 6), whereas ‘primary’ ones deriving from monomer misinsertion obviously still have the D label in the original position; the constitutionally different units can be recognized by ^{13}C NMR in a relatively straightforward manner [53–55]. The weak point of this approach is that it relies on the assumptions that the mechanism of Schemes 4–6 is correct and that it represents the only active epimerization pathway.

In Table 1, we compare the fractions of stereoirregular units with unshifted D label in samples of poly(propene-1-*d*) and poly(propene-2-*d*) prepared at low monomer concentration in the presence of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO at 30 and

¹ According to Schemes 5 and 6, stereoregular $-\text{CH}_2-\text{CH}(\text{CH}_2\text{D})-$ units in poly(propene-1-*d*) and poly(propene-2-*d*) might derive from repeated epimerization events involving the same monomeric unit. Their fraction could be appreciable if it is admitted, for example, that the ratio between the rates of chain propagation and epimerization at stereoirregular units is (much) lower than that at stereoregular ones; however, in the case of propene-2-*d* (Scheme 6), this hypothesis would require the formation of stereoirregular $-\text{CHD}-\text{CH}(\text{CH}_3)-$ units, which instead have not been detected by ^2H NMR in poly(propene-2-*d*) samples [53].

² In our investigation [51–53,61], we found no ^{13}C NMR evidence of *mmrm* stereoerrors, whose presence in polypropylene prepared with *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO at 0°C and $[\text{Zr}] \geq 2.5 \mu\text{mol/l}$ has been claimed in Ref. [57]. For a possible explanation of this disagreement, see Ref. [58].

Table 1

Fractions of stereoirregular units with unshifted D label, measured by ^{13}C NMR, in samples of poly(propene-1-*d*) and poly(propene-2-*d*) prepared at low monomer concentration in the presence of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO

Monomer	$T = 30^\circ\text{C}$	$T = 50^\circ\text{C}$
(<i>E</i>)-Propene-1- <i>d</i> ^a	0.016	0.044
(<i>Z</i>)-Propene-1- <i>d</i> ^a	0.014	0.059
Propene-2- <i>d</i> ^b	0.010	0.017

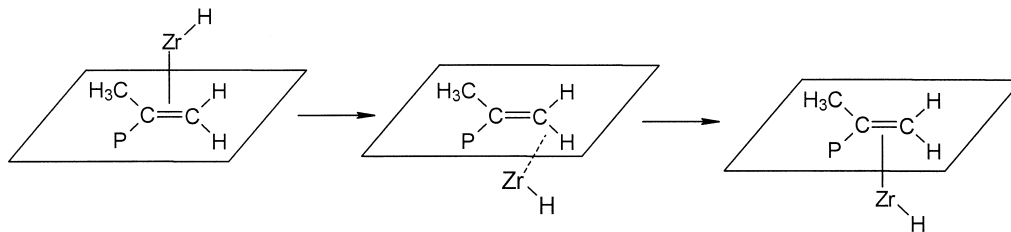
^aData from Ref. [55].

^bData from Ref. [61].

50°C. In the hypothesis that these can be identified with ‘primary’ stereoerrors, their concentration in polymer samples prepared at the same temperature should be equal within the experimental error; in contrast, from Table 1 it can be seen that this is not so and that, particularly at 50°C, the fraction of such units is definitely higher in poly(propene-1-*d*) than in poly(propene-2-*d*).

In our opinion, these findings suggest the existence of (at least) one additional process of chain epimerization, slower than that postulated in Schemes 4–6, which does not imply the migration of D in propene-1-*d* and propene-2-*d* monomeric units subjected to epimerization but does involve a rate-determining step of β -H (β -D) abstraction; due to the isotope effect, the incidence of such a process on the stereoselectivity would be larger for the polymerization of propene-1-*d* than for that of propene-2-*d*.

A possible mechanism might involve, for instance, the equilibration of diastereomeric π -complexes of the terminally unsaturated polymer chain (Schemes 4–6) via a σ -bond complex [59] (Scheme 7 for propene-*d*₀).



Scheme 7.

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. [44,60], it seems difficult to propose a reaction pathway analogous to that of Scheme 4.

Although the overall picture is still partly undefined, it can be safely concluded that the previous approach tends to underestimate catalyst enantioselectivity, particularly when propene-1-*d* is used and the more so the higher is the temperature.

A viable alternative is offered by the kinetics of the two concurrent reactions [61]. The rate of monomer insertion (R_{ins}) indeed is a function of monomer concentration ($[\text{M}]$):

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

where C^* is the concentration of active sites and $1 \leq \alpha \leq 2$, depending on the specific catalyst system [25,62,63]. It should be stressed that Eq. (1) does not refer to an elementary process and as such it is merely phenomenological, its mechanistic foundations being still unclear [25].

Chain epimerization instead is an intramolecular rearrangement, and its rate (R_{epim}) is independent of $[\text{M}]$:

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

Hence, the probability that the last-inserted unit of a growing chain is *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 given diad have *not* been epimerized is then $(P_{\text{ins}})^2$. This leads to the following expression for polymer tacticity (measured as a fraction of *meso* (m) diads, $[m]$):

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

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 catalyst enantioselectivity.

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 is related to the fraction F_p of ‘primary’ stereocenters (i.e. of monomer misinsertions) according to the enantiomorphic-site statistics [64]:

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

We have recently applied this method [61] to propene polymerization promoted by the catalyst system *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO, known [51–55] for its propensity to promote also the side reaction of chain epimerization.

Plots of $[m]$ versus $[M]$ obtained at temperatures of 30, 50 and 80°C are shown in Fig. 3. The experimental points can be interpolated satisfactorily in terms of Eq. (4) (with $\alpha = 1.2$), as shown by the solid curves. The corresponding best-fit values of $k_{\text{ins}}/k_{\text{epim}}$ and $[m^\circ]$ are reported in Table 2.

Rising the temperature from 30 to 80°C results in a large decrease of $k_{\text{ins}}/k_{\text{epim}}$, whereas $[m^\circ]$ remains almost unchanged. This means that the corresponding drop of stereoselectivity (Fig.

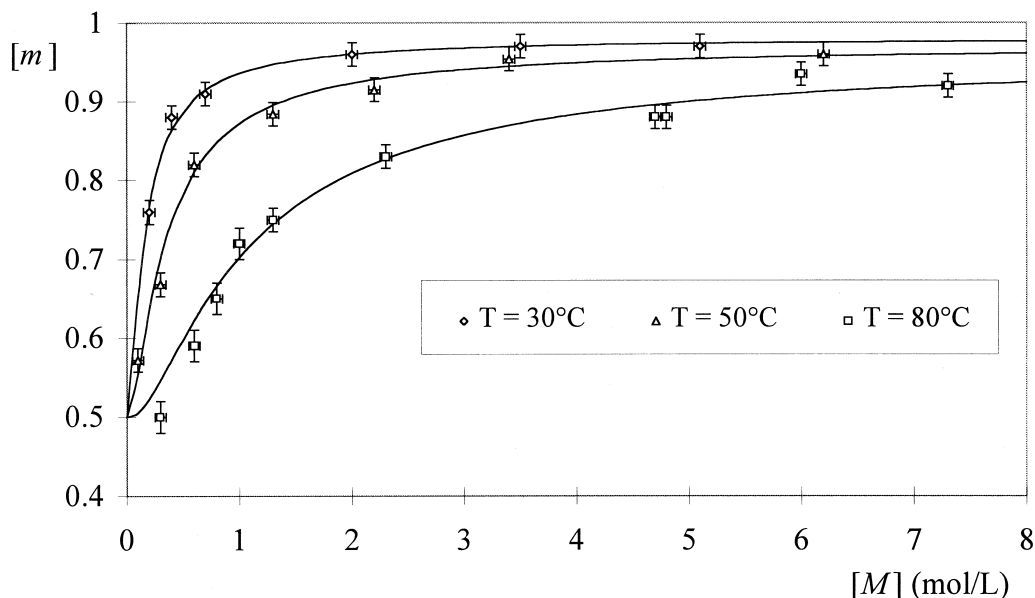


Fig. 3. Fraction of m diads, $[m]$ versus propene concentration, $[M]$ in toluene for polypropylene samples prepared in the presence of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO at three different temperatures.

Table 2

Best-fit values of $k_{\text{ins}}/k_{\text{epim}}$ and $[m^\circ]$ obtained by interpolation of the experimental points in Fig. 3 in terms of Eq. (4) and corresponding fraction of ‘primary’ stereoregions, F_p (Eq. (5))

T (°C)	$k_{\text{ins}}/k_{\text{epim}}$ ((l/mol) $^\alpha$)	$[m^\circ]$	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

3) must be attributed primarily to an increasing incidence of chain epimerization, the enantioselectivity being very high ($[m^\circ] \geq 0.96$, $F_p \leq 0.02$) 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, while at 80°C the value of $[m]$ is appreciably lower than that of $[m^\circ]$ even for polypropylene samples obtained from bulk polymerizations.

We are presently extending this approach to other C_2 -symmetric metallocenes. Preliminary results at 80°C for the catalyst systems *rac*-ethylene-bis(1-indenyl)ZrCl₂/MAO and *rac*-

Me₂Si-bis(1-indenyl)ZrCl₂/MAO are compared with those for *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO in Fig. 4.

The experimental points have been interpolated in terms of Eq. (4), with $\alpha = 1.5$ for *rac*-ethylene-bis(1-indenyl)ZrCl₂/MAO [65] and 1.4 for *rac*-Me₂Si-bis(1-indenyl)ZrCl₂/MAO [62]; the best-fit values of $k_{\text{ins}}/k_{\text{epim}}$ and $[m^\circ]$ are given in Table 3.

From these estimates, it appears that at 80°C the ‘old’ *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂ is the most enantioselective of all three catalysts (which is not surprising, since it is also the most sterically hindered [25]). Its comparatively poor stereoselectivity is the result of a lower $k_{\text{ins}}/k_{\text{epim}}$ ratio; as a matter of fact, this ratio tends to increase with increasing ‘opening’ of the aromatic ligand framework [25,51,55].

It is also worthy of note that the two zirconocene precursors with the same bis-indenyl ligand give rise to catalysts with a rather similar fade of enantioselectivity with increasing temperature: F_p indeed increases from 0.011 at 0°C [38] to 0.05 at 80°C for *rac*-ethylene-bis(1-inde-

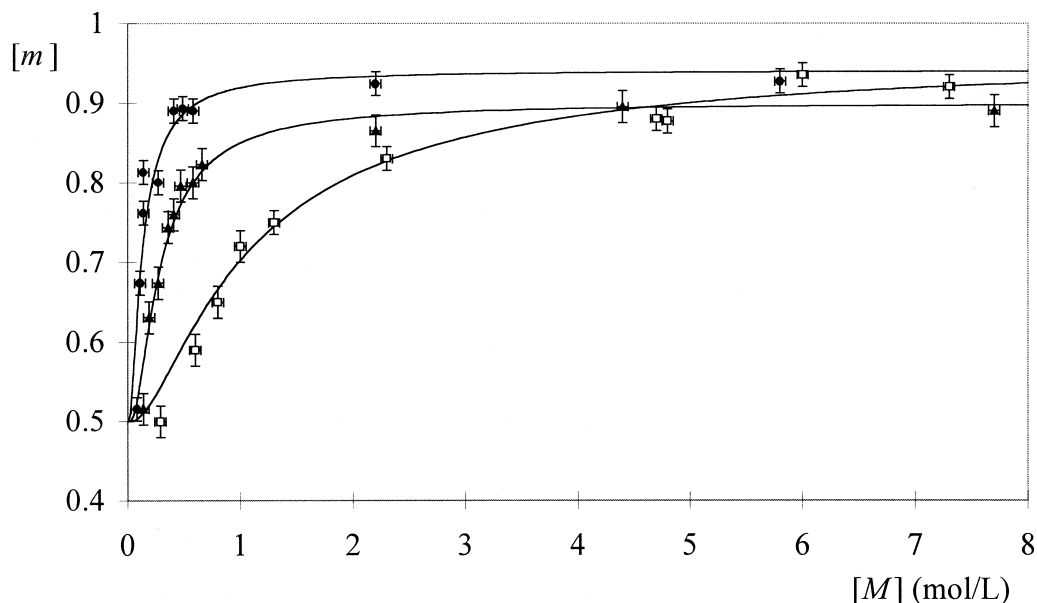


Fig. 4. Fraction of m diads, $[m]$ versus propene concentration, $[M]$ in toluene for polypropylene samples prepared at 80°C in the presence of the catalyst systems *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO (\square), *rac*-ethylene-bis(1-indenyl)ZrCl₂/MAO (\blacktriangle) and *rac*-Me₂Si-bis(1-indenyl)ZrCl₂/MAO (\bullet).

Table 3

Best-fit values of k_{ins}/k_{epim} and $[m^2]$ obtained by interpolation of the experimental points in Fig. 4 in terms of Eq. (4) and corresponding fraction of 'primary' stereoregions, F_p (Eq. (5))

Catalyst system ^a	k_{ins}/k_{epim} ((l/mol) ^α)	$[m^2]$	F_p
(I)/MAO	2.0 ± 0.2	0.96	0.020 ± 0.005
(II)/MAO	15 ± 5	0.90	0.05
(III)/MAO	40 ± 15	0.94	0.03

^a (I) = *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO; (II) = *rac*-ethylene-bis(1-indenyl)ZrCl₂/MAO; (III) = *rac*-Me₂Si-bis(1-indenyl)ZrCl₂/MAO.

nyl)ZrCl₂/MAO and from 0.008 at 0°C [38] to 0.03 at 80°C for *rac*-Me₂Si-bis(1-indenyl)ZrCl₂/MAO. Hence, the higher conformational flexibility of the ethylene bridge compared with the dimethylsilyl one [25,38,66] seems to have only a marginal effect on the temperature dependence of the enantioselectivity.

We are now enlarging the number of investigated systems, including zirconocenes with substituents in positions 2 and/or 4 of the indenyl ligands [25,38,67].

3. Conclusions

In the last decade, a tremendous progress has been achieved in isotactic propene polymerization promoted by C₂-symmetric metallocene catalysts.

The first reported high-performance catalyst system, namely *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂/MAO [27], is able to yield a polymer with a *mmmm* pentad content higher than 95% at 0°C, but its stereoselectivity becomes disappointingly low at temperatures of practical interest (50–80°C) [25,38]. A systematic investigation of the effects associated with changes in the structure of the aromatic ligand has led in a relatively short time to the isolation of a number of metallocene precursors giving rise to catalysts which maintain an exceedingly high stereoselectivity up to 80°C [25,38,67].

This search has been by far more rational than that, almost entirely based on the trial-

and-error approach, which in the 1970's resulted in the evolution of the heterogeneous catalysts from TiCl₃ to MgCl₂/TiCl₄ 'high-yield' systems [7–9]; indeed, basic relationships between catalyst performance and metallocene structure (e.g. nature of the interannular bridge, different substitutions of the aromatic rings) have been identified [25]. However, the existence of a side reaction of chain epimerization and the notion that stereoselectivity and enantioselectivity for metallocene catalysts are not necessarily coincident were totally ignored.

Nowadays we know that the enantioselectivity of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂ is comparable to that of the most stereoselective metallocenes based on dimethylsilyl-bridged-bis(2,4-substituted-1-indenyl) ligands [38,67] and that what makes the difference is its higher vulnerability to chain epimerization.

If the former catalyst had been tested at low propene concentration and high temperature only (a condition that is quite normal in academic laboratories), it might have been concluded that it represented just one more failure in the long series of frustrating attempts to prepare a stereoselective homogeneous catalyst for propene polymerization [1]. It is hard to decide if this is an overstatement or a paradox: how many selective catalysts have been masked by 'silent' side reactions and are waiting for rehabilitation?

4. Experimental section

Samples of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl₂, *rac*-ethylene-bis(1-indenyl)ZrCl₂ and *rac*-Me₂Si-bis(1-indenyl)ZrCl₂ were received from Witco.

Propene polymerizations were carried out in a 2 l magnetically stirred (1000 rpm) stainless steel reactor (Brignole AU-2) equipped with a glass vial holder-breaker. Anhydrous toluene and MAO (Witco, 10 wt% solution in toluene)

were introduced into the reactor, brought to the desired temperature and pressurized with propene at the appropriate concentration (total volume of liquid phase, 0.5 l). The reaction was started by breaking a glass vial containing a catalyst solution in toluene, allowed to proceed at constant monomer concentration (i.e. partial pressure) for a suitable time and stopped by quick monomer degassing. Typical reaction conditions: $[Zr] = 5 \times 10^{-5} - 5 \times 10^{-6}$ mol/l, $[Al]/[Zr]$ mole ratio = 5×10^3 . The polymers were coagulated with methanol (0.5 l) added to 10 ml HCl (aq. conc.), filtered and vacuum-dried at 50°C.

Quantitative $^{13}C\{^1H\}$ NMR spectra of all polypropylene samples 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 100–130°C, under the following conditions: 5 mm probe; $\approx 80^\circ$ pulse; acquisition time, 1.2 s; relaxation delay, 1.5 s; 10–15 K transients.

The fraction $[m]$ of m diads in the polymers was derived from the triad distribution, measured by integration of the methyl region. 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 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 [68,69]; 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-groups [70] and/or of the $S_{\alpha\delta}$ C's in 3,1 monomeric units [29,68,69]; a good agreement between the three estimates was always observed.

The synthesis and polymerization procedures of propene-2- d and the ^{13}C and 2H NMR characterizations of poly(propene-2- d) have been described in Refs. [53,61].

5. Note added in proof

The mechanistic hypotheses on chain epimerization presented in this paper have been substantially validated by a theoretical study based on Density Functional Theory (DFT) calculations [71].

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