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Growing chain isomerizations in metallocene-catalyzed Ziegler–Natta 1-alkene polymerization ☆

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Abstract

A number of isomerization reactions of the growing polymer chain have been shown to compete with the process of 1-alkene polyinsertion promoted by Group 4 metallocene Ziegler–Natta catalysts.

The consequences of such reactions on the regioregularity and stereoregularity of the polymers are discussed for the class of isotactic-specific C_2-symmetric metallocene catalysts.

Keywords: Ziegler–Natta catalysts; Isomerization; Polymerization

1. Introduction

The new homogeneous metallocene-based Ziegler–Natta catalysts for 1-alkene polymerization [1] are certainly more suited to mechanistic studies than are their heterogeneous analogues [2], owing to the well-defined nature of the precursors and to the existence — for each catalyst system — of a single type of active site.

However, it is now being recognized that this attractive structural simplicity is partly balanced by a more complex reactivity. Indeed, a variety of isomerization reactions of the growing polymer chain, not observed normally in the presence of heterogeneous Ziegler–Natta catalysts, may compete with chain propagation promoted by metallocene catalysts; this is probably a consequence of a higher Lewis acidity of the transition metal [3–11].

In the present paper, this latter aspect is discussed, mainly on the basis of the latest experimental results achieved in our laboratory, for the class of C_2-symmetric metallocenes which catalyze the isotactic polymerization of 1-alkenes [1].

2. Results and discussion

2.1. Growing chain isomerizations at a regioirregular last-inserted monomeric unit

The first experimental evidence of growing chain isomerization events in 1-alkene polymerization catalyzed by Group 4 metallocenes was the observation of 3,1-propene enchainments in isotactic polypropene samples prepared in the presence of C_2-symmetric catalysts [3–5].

It was soon proposed [4,5] that the 3,1-propene units arise from the isomerization of regioirregular 2,1 last-inserted units [12].

Kinetic data confirmed this interpretation. In particular, it has been shown [9,13] that, for a given catalyst system, the total fraction of 2,1 and 3,1 units in the polypropene produced coincides with the fraction of 2,1-propene insertion events measured from hydro-oligomerization experiments. The ratio of 2,1 to 3,1 units, on the contrary, increases proportionally to the propene feeding pressure [9,13]; this has been explained in terms of competition between chain propagation (with a roughly first-order rate dependence on propene concentration) and isomerization (whose rate would be independent of propene concentration) at an active site with a 2,1 last-inserted unit.

☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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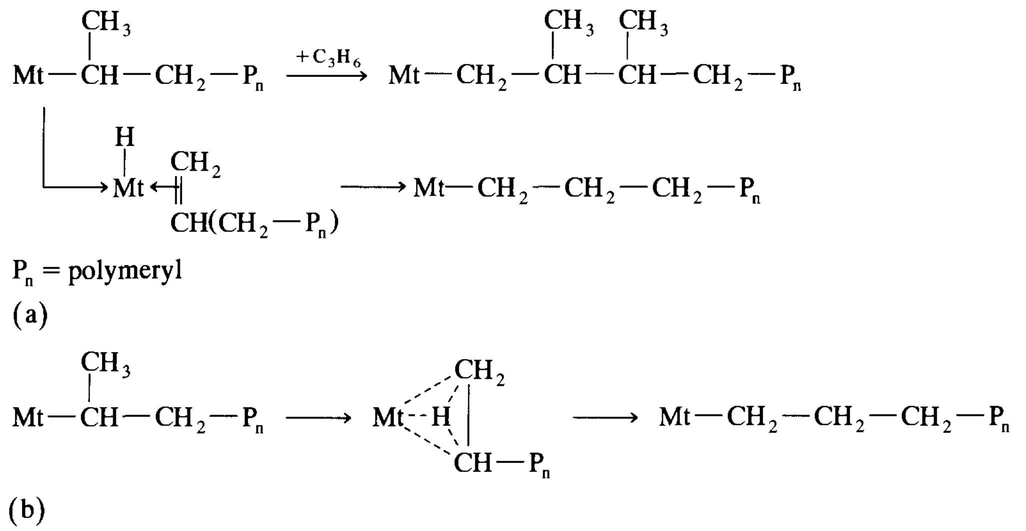


Scheme 1.

According to Rieger et al. [5], the isomerization could proceed via β-H elimination from the methyl group of a 2,1 unit, followed by anti-Markovnikov insertion of the terminally unsaturated polymer chain — still coordinated to the transition metal — into the Mt–H bond (Scheme 1(a)).

It should be noted that a sterically demanding olefin rotation in the wedge of the metallocene is required for a *cis* insertion geometry. Considering, however, that propene insertion into a growing polymer chain with a 2,1 last-inserted unit is exceedingly slow because of highly unfavourable non-bonded contacts at the hin-

Table 1

Regioregularity of isotactic polypropene samples prepared in the presence of a number of C_2-symmetric zirconocene catalysts (cocatalyst, MAO), evaluated by ^{13}C NMR

Catalyst [a]	Coordination gap aperture angle (°)	Relative productivity	$k_{sp}/k_{pp} \times 10^3$ [b]	[2,1 units] + [3,1 units] (mol.%)	[2,1 units] / ([2,1 units] + [3,1 units])
rac-$C_2H_4(indH_4)_2ZrCl_2$	86	0.4	< 1	1.1	< 0.1
rac-$C_2H_4(ind)_2ZrCl_2$	95	1	≈ 1	0.9	0.6
rac-$Me_2Si(ind)_2ZrCl_2$	99	3	3	0.7	0.8
rac-$Me_2Si(benz[e]ind)_2ZrCl_2$	100	9	3	1.0 ± 0.2	0.8

Polymerization conditions: benzene solvent; $[Zr] = 3.0 \times 10^{-5}$ mol L^{-1}; MAO/Zr, 4.0×10^3 mol Al (mol Zr)$^{-1}$; $[C_3H_6] = 2$ mol L^{-1}; $T_p = 60$°C. Hydro-oligomerization conditions: see [13,14].

[a] ind = 1-indenyl; $indH_4$ = 4,5,6,7-tetrahydro-1-indenyl.

[b] k_{sp}/k_{pp} is the ratio of the specific rate of 1,2 propene insertion at an active site with a 2,1 last-inserted propene unit to that at an active site with a 1,2 last inserted propene unit, measured at 60°C from propene hydro-oligomerization experiments [13,14].

Table 2

Regioregularity of isotactic polypropene and poly(1-butene) samples prepared in the presence of two different C_2-symmetric zirconocene catalysts (cocatalyst, MAO), evaluated by ^{13}C NMR

Catalyst [a]	Polypropene		Poly(1-butene)	
	[2,1 units] (mol.%)	[3,1 units] (mol.%)	[2,1 units] (mol.%)	[4,1 units] (mol.%)
rac-$C_2H_4(ind)_2ZrCl_2$	0.5	0.4	ND [b]	1.0
rac-$Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2ZrCl_2$	0.4	ND [b]	ND [b]	0.8

Polymerization conditions: benzene solvent; $[Zr] = 3.0 \times 10^{-5}$ mol L^{-1}; MAO/Zr, 4.0×10^3 mol Al (mol Zr)$^{-1}$; $[C_nH_{2n}] = 2$ mol L^{-1}; $T_p = 60$°C.

[a] ind = 1-indenyl.

[b] ND, not detected.

dered $Mt\text{–}CH(CH_3)\text{–}CH_2\text{–}P_n$ moiety [9,13,14], it is not surprising that an appreciable fraction of 2,1 last-inserted units may rather isomerize to 3,1 units.

Intuitively, the position of this balance is dependent inter alia on the structural features of the specific metallocene catalyst.

In particular, we have observed that widening the coordination gap aperture angle [1c] of the metallocene tends to release the steric constraints to chain propagation after a regioirregular (2,1)-inserted propene unit; this makes the isomerization of the latter into a 3,1 unit a less convenient alternative.

As an example, it can be seen that, for the series of homologous C_2-symmetric zirconocenes in Table 1, the decrease in propene insertion rate after a regioirregularity is lower the higher the value of the aperture angle (cf. the ratio k_{sp}/k_{pp} of specific rates); consequently, the ratio of 2,1 to 3,1 units in propene polymers produced at a given temperature and monomer concentration increases in the same direction.

On the contrary, some literature data [15] suggest that, for a given catalyst, the slowing-down effect of the regioirregularities is significantly higher in 1-butene than in propene polyinsertion; this should favour the isomerization of 2,1 last-inserted 1-butene units.

In fact, we have found that metallocenes well able to incorporate 2,1 monomeric units in polypropene chains promote instead their complete isomerization to 4,1 units in growing poly(1-butene) chains (Table 2) [6].

The undetectability, in the examined poly(1-butene) samples, of 3,1 enchainments puts the question whether the isomerization mechanism of Scheme 1(a) can be extended from propene to 1-butene (Scheme 2(a)) or a more concerted isomerization pathway, such as the direct metal-assisted hydride shift in Scheme 2(b), should be imagined [16] (an analogous possibility for 2,1- to 3,1-propene unit isomerization is shown in Scheme 1(b)).

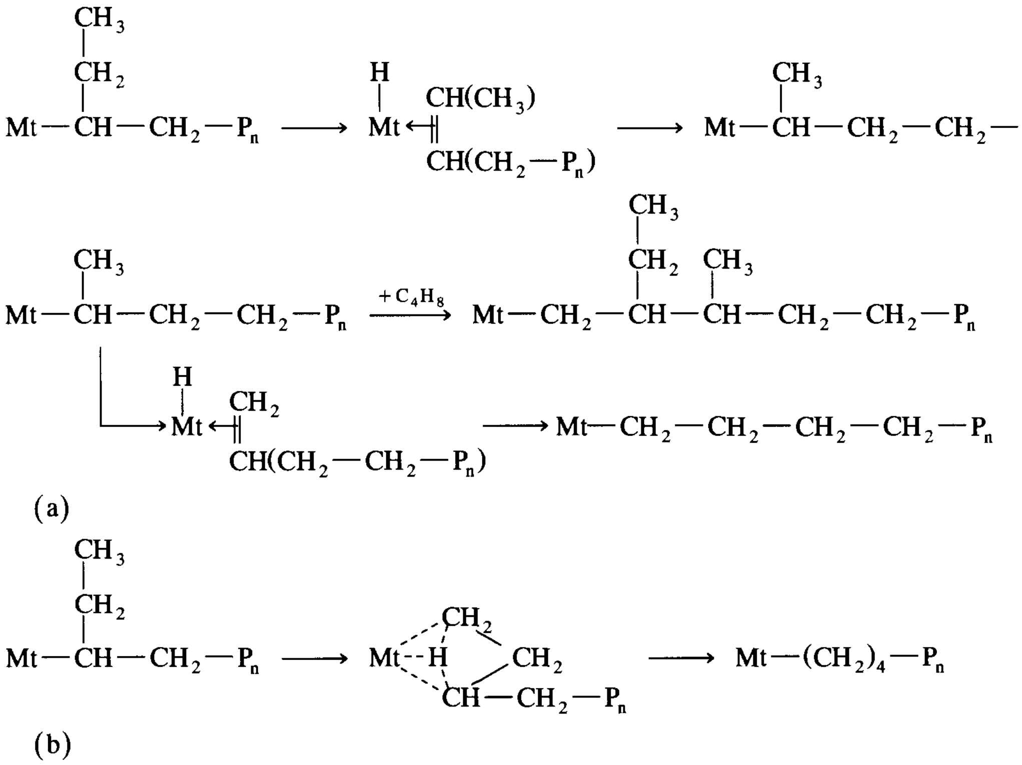
The investigation of the behavior of higher 1-alkenes, which may help to answer that question, proved unfortunately to be very complicated [7].

2.2. Growing chain isomerizations at a regioregular last-inserted monomeric unit

In the previous section we have seen that, in the presence of C_2-symmetric metallocene catalysts, side reactions of chain isomerization may compete with the process of polyinsertion when this slows down as a consequence of an occasional regioirregularity.

The polyinsertion rate can also be lowered in a controlled way by lowering monomer concentration. It is not surprising therefore that "parasitic" isomerization reactions of regioregular last-inserted monomeric units have been recently revealed [8–11] which interfere with chain propagation when the polymerization is performed at low monomer concentration.

We have shown [8] indeed that the stereospecificity of the C_2-symmetric metallocenes in propene polymerization decreases with decreasing propene feeding pres-



Scheme 2.

sure, as a result of a side reaction of epimerization of last-inserted 1,2 monomeric units, whose rate appears to be low but independent of propene concentration.

The disturbing effects of this epimerization on the stereoregularity of the produced polymers are understandably more apparent, coeteris paribus, for catalysts with an intrinsically low propagation rate. From Fig. 1, it can be seen that such effects are appreciable only at exceedingly low propene concentrations for "fast" metallocenes (usually having a high value of the coordination gap aperture angle, see Table 1), whereas they can be dramatic even at relatively high propene concentrations for "slow" metallocenes (with a low value of aperture angle); this may explain why, at least at moderate propene feeding pressures, C_2-symmetric metallocenes with a highly crowded environment of the active site can be less isotactic specific than more "open" and active metallocenes [1].

As an example, Leclerc and Brintzinger [11] have shown that most stereoirregularities present in polypropene samples produced at low propene concentration with the catalyst system *rac*-C_2H_4(4,5,6,7-tetrahydro-1-indenyl)$ZrCl_2$–MAO (MAO = methylaluminoxane) derive from epimerization events of stereoregularly inserted monomeric units, rather than from propene insertions with the "wrong" enantioface.

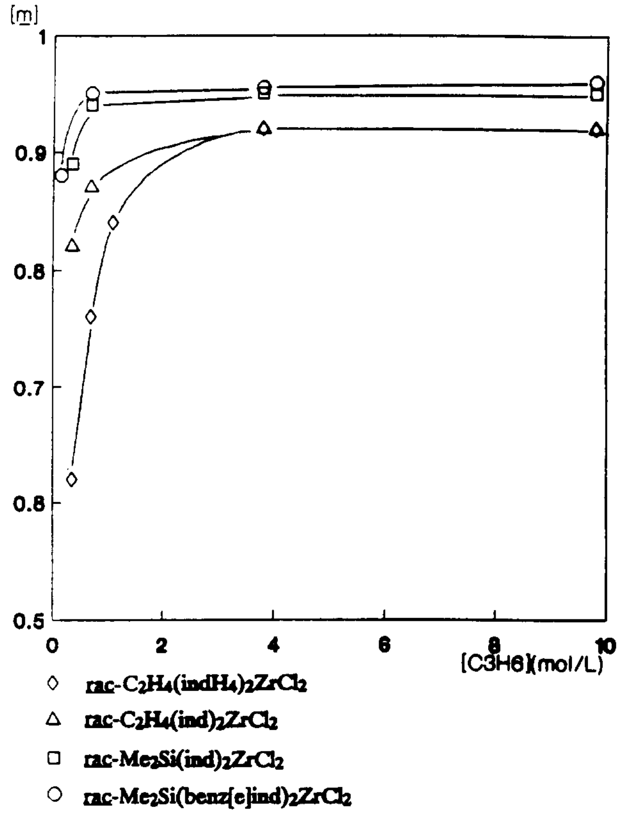
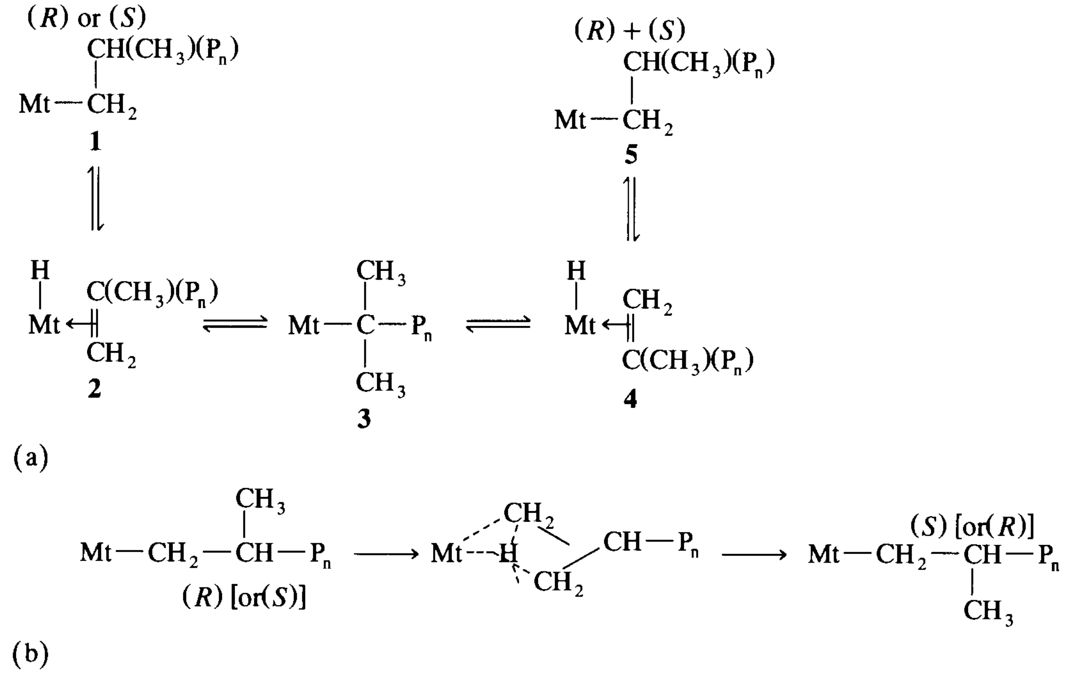


Fig. 1. Fraction [*m*] of *m* diads in polypropene samples obtained at 50°C in the presence of a number of C_2-symmetric zirconocene catalysts (cocatalyst, MAO) as a function of propene concentration $[C_3H_6]$.

It should also be noted that the polymerization temperature has an important effect on the extent to which, for a given catalyst and at a given propene concentration, the stereoregularity of the polymer is affected by the epimerization reaction, the balance between chain propagation and epimerization being shifted towards the latter with increasing temperature (Fig. 2). This may be the reason for the strong temperature effect on the stereospecificity of most metallocene catalysts (not observed instead for typical heterogeneous Ziegler–Natta catalysts) [8,9].



Scheme 3.

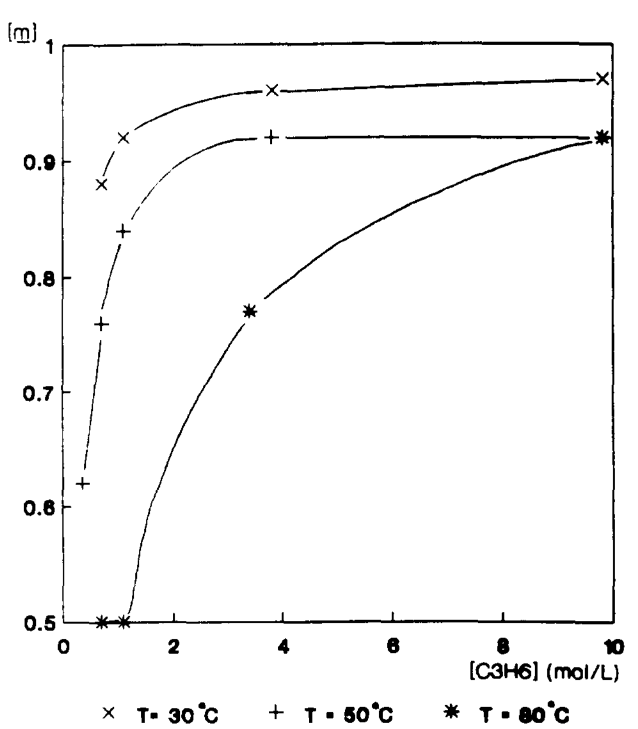


Fig. 2. Fraction [*m*] of *m* diads vs. propene concentration [C_3H_6] in polypropene samples obtained in the presence of *rac*-C_2H_4(4,5,6,7-tetrahydro-1-indenyl)$_2$$ZrCl_2$–MAO at three different temperatures.

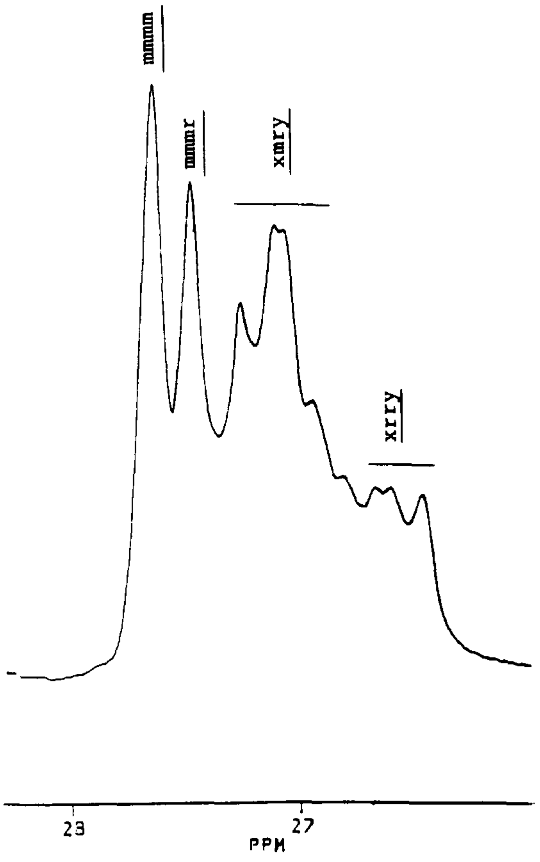


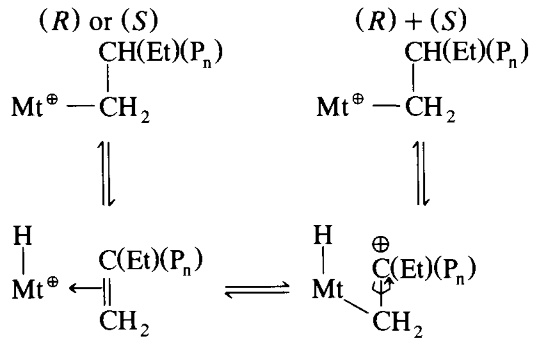
Fig. 3. ^{13}C NMR spectrum (side group methylene resonance; parts per million scale downfield of tetramethylsilane) of a poly(1-butene) sample prepared in the presence of *rac*-C_2H_4(4,5,6,7-tetrahydro-1-indenyl)$_2$$ZrCl_2$–MAO at 80°C ([$C_4H_8$] ≈ 2 mol l^{-1}). The poor stereoregularity of the polymer is immediately apparent.

Concerning the reaction mechanism, by analogy with the pathway proposed in [5] for the isomerization of a 2,1 last-inserted propene unit to a 3,1 unit and already discussed (Scheme 1(a)), the epimerization could proceed according to Scheme 3(a). β-Hydrogen elimination from a growing polymer chain with a 1,2 last-inserted unit **1**, followed by Markovnikov addition of the metal hydride to the coordinated olefin **2**, would lead to the intermediate **3** (olefin rotation being required if a *cis* attack is assumed). Further β-H elimination from either of the two CH_3 groups of **3** and subsequent anti-Markovnikov insertion of the unsaturated species **4** into the Zr–H bond would allow epimerization of **1** into **5** without intermediate detachment of the growing polymer chain from the Zr atom (it should be noted indeed that, even at low values of propene concentration, the monomer is in large excess with respect to the polymer chains produced).

A mechanism involving a direct Mt-assisted hydride shift similar to that presented in Schemes 1(b) and 2(b) for the isomerization of 2,1 to *n*,1 1-alkene units can also be imagined (Scheme 3(b)).

Both reaction schemes are compatible with the results of the spectroscopic characterization of poly(1-deuteriopropene)s reported in [11], proving the presence of D in the methyl group of the epimerized propene units. The mechanistic hypothesis of Scheme 3(a), however, is also consistent with the very first results of a study of 2-deuteriopropene polymerization catalyzed by C_2-symmetric metallocenes (at present in progress in our laboratory), which seem to indicate D scrambling in polypropene samples prepared at low monomer concentrations.

In contrast, it seems hard to adapt either mechanism to the case of growing poly(1-butene) chains, which do undergo epimerization in conditions similar to those described for polypropene (Fig. 3). For this (and higher) 1-alkene(s), one could propose for example the mecha-



Scheme 4.

nism of Scheme 4 [17], which in turn cannot be substitutive for those presented in Schemes 3(a) and 3(b) in the case of polypropene, in view of the cited spectroscopic results of [11].

It is worth noting, however, that the three reaction pathways in Schemes 3(a), 3(b) and 4 (as well as other conceivable pathways) are not necessarily mutually exclusive.

3. Conclusions

In this paper, we have discussed how side reactions of isomerization of the growing polymer chain may affect the regiospecificity and stereospecificity of 1-alkene polyinsertion promoted by C_2-symmetric Group 4 metallocene catalysts.

Such reactions, which may be traced back to the known tendency of the electrophylic transition metal center in these catalysts to establish agostic interactions with the last-inserted monomeric unit [11,18], can help an active site to escape from a "dormant" state [13,14] (as in the case of 2,1-to-*n*,1 isomerization) or, conversely, worsen its performance by inverting the configuration of a stereoregularly inserted monomeric unit.

We feel that this topic has considerable importance in the mechanistic study of this (and related) class(es) of homogeneous Ziegler–Natta catalysts, as well as in the rational search for better catalysts.

4. Experimental section

Propene and 1-butene polymerization conditions have been indicated in the tables; for propene hydrooligomerization procedures, see [13,14]. Schering MAO (30% w/w solution in toluene) was used as received.

Quantitative proton-decoupled ^{13}C NMR spectra were recorded with a Bruker AC-270 spectrometer operating at 67.93 MHz, on polymer solutions (10% w/v) in 1,2-dideuteriotetrachloroethane (also used as an internal standard) at 70–100°C. The instrumental conditions were as follows: 5 mm probe; 56.25° pulse (5.0 μs pulse width); acquisition time, 1.2 s; relaxation delay, 4 s; 15 K transients.

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References and notes

[1] See for example (a) J.A. Ewen, M.J. Elder, R.L. Jones, L. Haspeslagh, J.L. Atwood, S.G. Bott and K. Robinson, *Makromol. Chem., Makromol. Symp., 48–49* (1991) 253; (b) W. Röll, H.H. Brintzinger, B. Rieger and R. Zolk, *Angew. Chem., Int. Edn. Engl., 29* (1990) 279; (c) K. Hortmann and H.H. Brintzinger, *New J. Chem., 16* (1992) 51; (d) U. Stehling, J. Diebold, R. Kirsten, W. Röll, H.H. Brintzinger, S. Jüngling, R. Mülhaupt and F. Langhauser, *Organometallics, 13* (1994) 964.

[2] See for example P. Corradini, V. Busico and G. Guerra, in *Comprehensive Polymer Science*, Vol. 4, Pergamon, Oxford, 1988, pp. 29-50.

[3] K. Soga, T. Shiono, S. Takemura and W. Kaminsky, *Makromol. Chem., Rapid Commun., 8* (1987) 305.

[4] A. Grassi, A. Zambelli, L. Resconi, E. Albizzati and R. Mazzocchi, *Macromolecules, 21* (1988) 617.

[5] B. Rieger, X. Mu, D.T. Mallin, M. Rausch and J.C.W. Chien, *Macromolecules, 23* (1990) 3559.

[6] ^{13}C NMR evidence of 4,1 monomer enchainments in isotactic poly(1-butene) samples prepared with metallocene catalysts has been given by V. Busico, R. Cipullo and A. Borriello, *Macromol., Rapid Commun.*, in press.

[7] G.N. Babu, R.A. Newmark and J.C.W. Chien, *Macromolecules, 27* (1994) 3383.

[8] V. Busico and R. Cipullo, *J. Am. Chem. Soc., 116* (1994) 9329.

[9] V. Busico, R. Cipullo, *Macromol. Symp.*, in press.

[10] G. Balbontin, A. Fait, F. Piemontesi, L. Resconi and H. Rychlicki, *Int. Sympo. on Stereospecific Polymerization, Milan, 6–10 June 1994.*

[11] M. Leclerc and H.H. Brintzinger, *J. Am. Chem. Soc., 117* (1995) 1651.

[12] In view of this consideration, the notation "3,1 unit" should be used instead of "1,3 unit", frequently adopted in the literature, however.

[13] V. Busico, R. Cipullo, J.C. Chadwick, J.F. Modder and O. Sudmeijer, *Macromolecules, 27* (1994) 7538.

[14] (a) P. Corradini, V. Busico and R. Cipullo, *Makromol. Chem., Rapid Commun., 13* (1992) 15; (b) V. Busico, P. Corradini and R. Cipullo, *Makromol. Chem., Rapid Commun., 14* (1993) 97.

[15] (a) N. Kashiwa and M. Kioka, *Polym. Mater. Sci. Eng., 64* (1991) 43; (b) M. Kioka, A. Mizuno, T. Tsutsui and N. Kashiwa, in E.J. Vandenberg and J.C. Salamone (eds.), *Catalysis in Polymer Synthesis*, American Chemical Society, Washington, DC, 1992, p. 72.

[16] See for example (a) H. Rabaa, J.-Y. Saillard and R. Hoffmann, *J. Am. Chem. Soc., 108* (1986) 4327; (b) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, *J. Am. Chem. Soc., 109* (1987) 203.

[17] (a) T.S. Peng and J.A. Gladysz, *J. Chem. Soc., Chem. Commun.*, (1990) 902; (b) O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc., 103* (1981) 4308.

[18] See for example (a) H. Krauledat and H.H. Brintzinger, *Angew. Chem., Int. Edn. Engl., 29* (1990) 1412; (b) M.H. Prosenc, C. Janiak and H.H. Brintzinger, *Organometallics, 11* (1992) 4036; (c) C. Janiak, *J. Organomet. Chem., 452* (1993) 63, and references cited therein.