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# *Communications to the Editor*

## Influence of Monomer Concentration on the Stereospecificity of 1-Alkene Polymerization Promoted by $C_2$-Symmetric *ansa*-Metallocene Catalysts

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An influence of monomer concentration on the stereospecificity of group 4 *ansa*-metallocene catalysts for the polymerization of 1-alkenes[1] has been pointed out for $C_s$-symmetric syndiotactic-specific catalysts.[1–3]

In particular, Ewen reported[1,3] that the stereoregularity of syndiotactic polypropene samples prepared in the presence of catalyst systems such as, e.g., [isopropyl(1-fluorenyl)(cyclopentadienyl)]$MtCl_2$/MAO (Mt = Zr, Hf; MAO = methylaluminoxane) decreases significantly with decreasing monomer concentration.

This has been explained[1,3] in terms of a "chain migratory" polymerization mechanism, in which the incoming monomer and the growing polymer chain exchange *at each insertion step* between the two available enantiotopic coordination positions.[4] Occasional failures of this mechanism ("skipped insertions") lead to the formation of stereoirregularities (...*rrrrmrrrrr*...); intuitively, the probability of skipped insertions is higher the lower is propene concentration.[1,3]

No similar effects of monomer concentration have been described so far for $C_2$-symmetric isotactic-specific catalysts.[1,5] In these catalysts, the two coordination positions available to the monomer and the growing polymer chain are homotopic,[4] so that monomer insertion from the same enantioface is preferred at each of the two positions for a catalytic complex with a given chirality of coordination of the aromatic ligand.

Quite surprisingly, we found that the isotacticity of propene polymers prepared at a given temperature (50 °C) in the presence of a number of $C_2$-symmetric *ansa*-zirconocenes (Table 1; cocatalyst: MAO) is also dependent on propene concentration, $[C_3H_6]$ (Figure 1).

Starting from bulk polymerization conditions, with decreasing $[C_3H_6]$ (in benzene) the fraction of *m* diads, [*m*], remains at first fixed within experimental error at an upper limit (in the range 0.90–0.96, depending on the catalyst) and begins then to decrease.

For each catalyst, this effect was found to be independent of Zr concentration (in the normal[1] range of $1 \times 10^{-4}$ to $1 \times 10^{-6}$ mol/L) and concomitant with a strong reduction of the productivity (Table 2), which prevented us from extrapolating the lower limit for [*m*]. At least for catalyst I, however, from Figure 1 it seems plausible to assume that [*m*] tends to 0.5 (atactic polymer) in the limit of $[C_3H_6] = 0$.

Table 1. Tested Metallocene Catalysts

| catalyst | short notation | ref |
|---|---|---|
| *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)$ZrCl_2$ | I | 11 |
| *rac*-ethylenebis(1-indenyl)$ZrCl_2$ | II | 12 |
| *rac*-dimethylsilylbis(1-indenyl)$ZrCl_2$ | III | 13 |
| *rac*-dimethylsilylbis(1-benzindenyl)$ZrCl_2$ | IV | 14 |

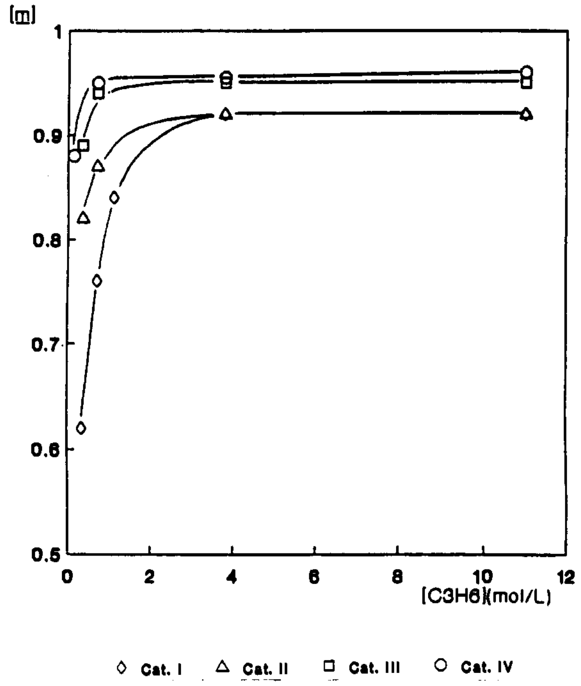

**Figure 1.** Fraction of *m* diads, [*m*], in polypropene samples obtained at 50 °C in the presence of the investigated catalysts (Table 1) as a function of propene concentration, $[C_3H_6]$.

The $^{13}C$ NMR distribution of the stereosequences in all polypropene samples obtained was reasonably reproduced in terms of the enantiomorphic-sites statistics[1,6] (Table 3).

One possible explanation for the above results is that a slow reaction of epimerization of the last-inserted monomeric unit competes with that of chain propagation. It should be admitted that the reaction order with respect to $[C_3H_6]$, which is ≈1 for chain propagation,[7] is 0 for epimerization.

By analogy with the pathway commonly accepted for the isomerization of a 2,1 last-inserted unit to a 1,3 unit,[8,9] the epimerization could proceed as in Scheme 1. β-Hydrogen elimination from a growing polymer chain with a 1,2 last-inserted unit **1**, followed by Markovnikov attack 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 the low values

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(1) For a recent review, see, e.g.: Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253.

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**Table 2.** Selected Results of $C_3H_6$ Polymerizations at 50 °C in the Presence of Catalyst I/MAO

| sample no. | $[Zr]^a$ (mol/L) | $[C_3H_6]$ (mol/L) | productivity$^b$ (kg(PP) $[Zr]^{-1}$ $[C_3H_6]^{-1}$ $h^{-1}$) | $[m]^c$ | $\bar{M}_n^d \times 10^{-3}$ (amu) |
|---|---|---|---|---|---|
| 1 | $5 \times 10^{-5}$ | 3.8 | 760 | 0.92 | 8.4 |
| 2 | $5 \times 10^{-5}$ | 1.1 | 25 | 0.84 | 6.7 |
| 3 | $5 \times 10^{-5}$ | 0.7 | 11 | 0.76 | 3.4 |
| 4 | $5 \times 10^{-5}$ | 0.35 | 0.95 | 0.62 | 1.7 |
| 5 | $5 \times 10^{-6}$ | 3.8 | 1900 | 0.92 | 9.2 |
| 6 | $5 \times 10^{-6}$ | 0.7 | 40 | 0.76 | 4.2 |

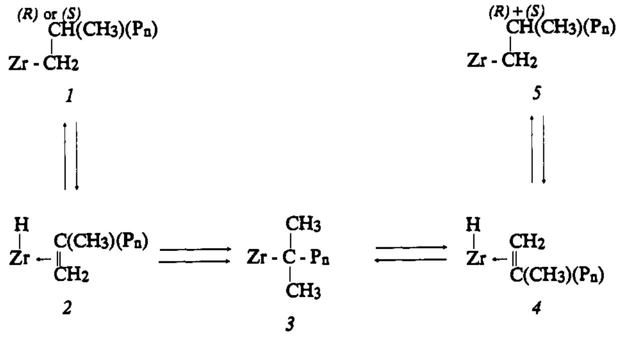
[a] In benzene (200 mL); $[Al]/[Zr] = 5 \times 10^3$ mol/mol. [b] Averaged over 2 h. [c] Fraction of meso diads in the polymer, measured by $^{13}C$ NMR. [d] Number average molecular weight, measured by $^{13}C$ NMR.

**Table 3.** $^{13}C$ NMR Pentad Distribution of Two Polypropene Samples (Numbers 2 and 3 in Table 2) Prepared in the Presence of Catalyst I/MAO and Best-Fitting Values (in Parentheses) According to the Enantiomorphic-Sites Statistical Model

| sample | fractions of stereochemical pentads in % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *mmmm* | *mmmr* | *rmmr* | *mmrr* | *mmrm* + *rmrr* | *rmrm* | *rrrr* | *rrrm* | *mrrm* |
| 2 | 63 | 13 | *a* | 13 | 2 | *a* | *a* | *a* | 6 |
| | (63) | (12) | (0.6) | (12) | (3) | (1) | (0.6) | (1) | (6) |
| 3 | 46 | 17 | 1 | 15 | 7 | 2 | 1 | 3 | 8 |
| | (46) | (16) | (1) | (16) | (6) | (3) | (1) | (3) | (8) |

[a] Resonance not detected or too weak for accurate integration.

**Scheme 1**



($P_n$ = polymeryl)

of $[C_3H_6]$ used in this investigation, the monomer is in large excess with respect to the polymer chains produced).

Alternative explanations based on the hypotheses of active site isomerization or of transfer events of polymer chains between active sites of opposite chirality, as possibly favored by a low monomer concentration, seem to be ruled out by the polypropene microstructural data in Table 3, indicating the occurrence of (...*mmmmrrmmmm*...) rather than of (...*mmmmrmmmm*...) stereodefects.

Further studies on the subject are in progress. They include the investigation of 1-alkenes other than propene and of MAO-free catalyst systems,[1] as well as an analysis of solvent and temperature effects. In this latter respect, a competition between chain propagation and epimerization could give reason for the strong temperature dependence of the stereospecificity of the investigated catalysts[9] (not observed for typical heterogeneous Ziegler–Natta systems[10]).

It should also be noted that the described effect of propene concentration may well explain apparent disagreements between different laboratories in the evaluation of the stereospecificity of this class of homogeneous Ziegler–Natta catalysts and suggests caution in the interpretation of results of mechanistic studies performed at low monomer concentrations, possibly resulting in "anomalous" polymerization behaviors.

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