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Comments on the paper titled: 'Error formation in ansa-zirconocene catalyzed isotactic propylene polymerization' (J. Organomet. Chem. 512 (1996) 131)

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In a recent communication to the Editor of the Journal of the American Chemical Society [1], we have shown that the stereospecificity of the new homogeneous C_2-symmetric metallocene catalysts for isotactic propene polymerization [2] decreases with decreasing monomer feeding pressure.

Symmetry considerations and ^{13}C-NMR analyses of polymer microstructures led us to conclude [1] that this trend is the result of a competition between propene polyinsertion, with a roughly first-order rate dependence with respect to the monomer, and a (comparatively slow) intramolecular reaction of epimerization of the growing polypropylene chain, involving the racemization of originally stereoregular last-inserted monomeric units. Understandably, the balance shifts towards chain epimerization when monomer concentration is lowered (but also, we found, when the temperature is increased, which gives reason for the decay of stereospecificity of most of these catalysts above 50–80°C) [1–5].

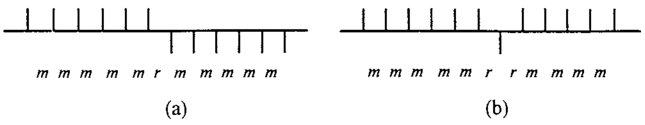
Direct and conclusive evidence in favour of this interpretation came from studies on the polymerization of selectively deuterated propenes, carried out in Brintzinger's [6] and our own laboratory [7]. These showed, in particular, that most stereoirregular monomeric units in isotactic polymers of (*E*)- and (*Z*)-propene-1-d [6] and of propane-1-d [7] prepared at low monomer concentration in the presence of a number of C_2-symmetric metallocene catalysts are deuterated at the methyl group, which proves that such stereoerrors arise from isomerizations of the growing chain end rather than from propene insertions with the 'wrong' enantioface.

Moreover, the large primary isotope effect observed in the polymerization of propene-2-d [7] indicated that the epimerization mechanism involves a rate-determining step of β-H migration, in accordance with our early proposal [1,7].

We are currently investigating the extent to which the stereospecificities of metallocene catalysts with different structures and symmetries are affected by growing chain epimerization.

Therefore, it was with great interest that we started reading the paper by Chien et al. referenced in the title, just appeared in the Journal of Organometallic Chemistry [8]. This interest, however, changed soon to surprise at the authors' assertion that, in our first paper on the subject [1], 'the possibility of interchange of propagating chains was frivolously waved aside' (sic).

As a matter of fact, we had obviously considered, inter alia, such an interchange between active species of opposite chirality in a racemic catalyst as a potential



Scheme 1.

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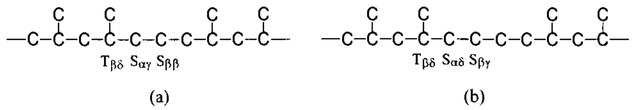

Scheme 2.

source of stereoirregularities, possibly becoming more relevant at low monomer concentration, but explicitly discarded it [1] because it would have required the formation of stereoerrors of the type ...*mmmmrmmmm*... (Scheme 1a); these were instead undetected in the ^{13}C-NMR spectra of all the characterized polypropylene samples, which showed only ...*mmmmrrmmmm*... stereodefects (Scheme 1b), as also found in subsequent independent investigations [6,9].

Surprisingly, in their paper [8] Chien et al. claim the presence of a high fraction of ...*mmmmrmmmm*... stereoerrors in a polypropylene sample (Sample 1) prepared at 0°C in the presence of a catalyst originated from the precursor *rac*-ethylene-(4,5,6,7-tetrahydro-1-indenyl)$_2$Zr(*O*-acetyl-(R)-mandelate)$_2$, whereas such stereoerrors are absent in a polypropylene sample (Sample 11) prepared similarly in the presence of a catalyst derived from the pure diastereomer with the chelating ligand in the (*S*,*S*) coordination mode. Moreover, the two samples would strongly differ also in regioregularity, the former having a much higher content of 2,1 and 1,3 monomeric units.

These findings, from which the authors concluded that the interchange of growing chains between enantiomorphic active species is a major source of stereoerrors when racemic catalysts are used, look awkward. Indeed, no reports of differences between the regio- and/or stereospecificities of C_2-symmetric metallocene catalysts in racemic and enantiomerically pure form have appeared to now in the literature [10], and in all known cases the configurational statistics of the produced polymers have been found to conform to that predicted by the enantiomorphic-site model (with ...*mmmmrrmmmm*... stereoirregularities) [2].

However, on inspection of Fig. 2 and Table 2 of ref. [8], it can be realized that such anomalous claims are simply the result of a misinterpretation of a ^{13}C-NMR polymer microstructure. Indeed, the ^{13}C-NMR spectrum of Sample 1 reported in the quoted Fig. 2 clearly indicates that the sample, for some reason, contains ethene units (ca. 6–7 mol%, as roughly estimated from the resonance intensities). These are mostly isolated and flanked by highly regio- and stereoregular propene homosequences, as shown by the sharp resonances of the $S_{\beta\gamma}$, $T_{\beta\delta}$ and $S_{\beta\beta}$ C's at ca. 38, 31 and 24 ppm (relative to TMS [11]; for the nomenclature, see Scheme 2a), in the correct 2:2:1 integral ratio [12]. Such resonances seem to have been attributed instead to the $S_{\alpha\delta}$, $T_{\beta\delta}$ and $S_{\alpha\gamma}$ C's in 1,3 propene units (Scheme 2b), expected at 37.2, 30.6 and 27.4 ppm in 1:1:1 ratio; on this basis, an unprecedented low regioregularity of the sample was estimated.

Moreover, unfortunately, in the methyl region of the spectrum, the resonances of the PPPPE, PPPEP and PEPEP sequences (P, propene; E, ethene), at 21.60, 20.90 and 20.04 ppm, respectively [12], were incorrectly assigned to PPPPP sequences in the *mmmr*, *mmrm* and *mrrm* configurations, occurring at 21.55, 20.76 and 19.82 ppm [11].

From the overall comonomer sequence distribution, the sample seems to be a mixture of isotactic polypropylene and of a propene/ethene copolymer (possibly resulting from a batch propene polymerization reaction in which minor amounts of ethene were initially present in the reactor). For comparison, in Fig. 1 we report the ^{13}C-NMR spectrum of a similar mixture (ca. 50 wt.% isotactic polypropylene; ca. 50 wt.% of a propene/ethene copolymer, average ethene content ca. 14 mol%) prepared by us at 0°C in the presence of the catalyst system *rac*-ethylene-(4,5,6,7-tetrahydro-1-indenyl)$_2$ZrCl$_2$/MAO (see Section 1); the strict similarity with the spectrum reported in Fig. 2 of ref. [8] is immediately apparent.

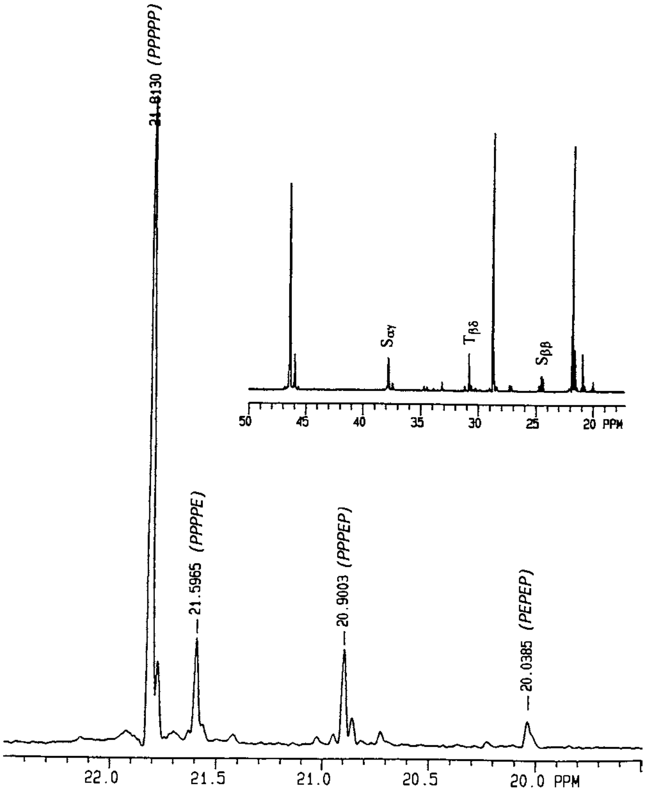

Fig. 1. ^{13}C-NMR spectrum, with enlargement of the methyl region ($\delta = 19.5$–22.5 ppm), of a mixture of isotactic polypropylene (ca. 50 wt.%) and a propene/ethene copolymer (ca. 50 wt.%; average ethene content, ca. 14 mol%) prepared at 0°C in the presence of the catalyst system *rac*-ethylene-(4,5,6,7-tetrahydro-1-indenyl)$_2$ZrCl$_2$/MAO. Chemical shift scale is in ppm downfield of TMS. The resonances relevant for the discussion are explicitly assigned (see text).

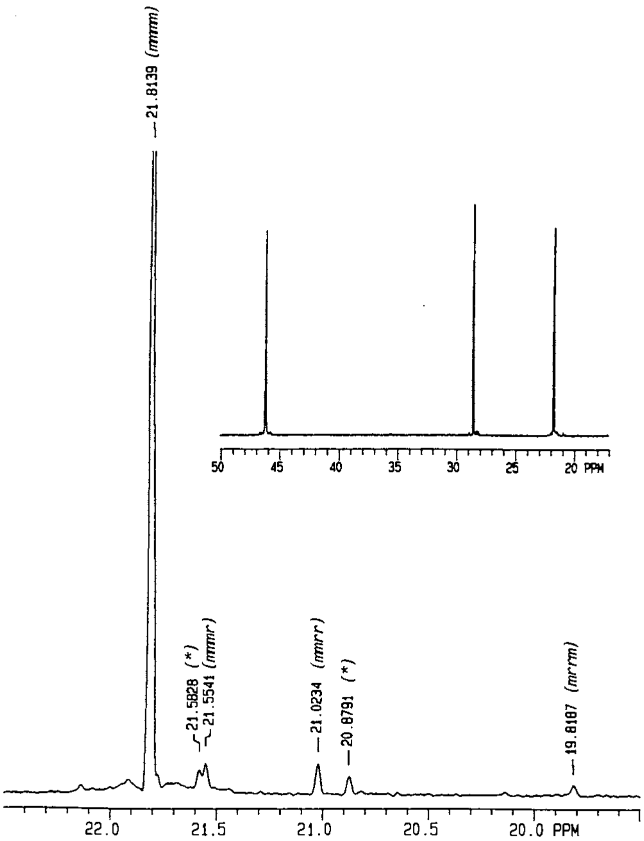

Fig. 2. ^{13}C-NMR spectrum, with enlargement of the methyl region ($\delta = 19.5$–22.5 ppm), of a sample of isotactic polypropylene prepared at 0°C in the presence of the catalyst system *rac*-ethylene-(4,5,6,7-tetrahydro-1-indenyl)$_2$ZrCl$_2$/MAO. Chemical shift scale is in ppm downfield of TMS. The weak methyl resonances associated with ...*mmmmrrmmmm*... stereoerrors are explicitly assigned; that of the *mmrm* pentad, indicative of ...*mmmmrmmmm*... stereoerrors (see text), is not detectable. All other minor peaks in the spectrum arise from regioirregular sequences containing 2,1 and 1,3 monomeric units (total amount, ca. 1 mol%); in the methyl region, in particular, the resonances of regio- and stereoregular units flanking 1,3 units are marked with an asterisk

The consequence of the above misguess is a gross underestimate of the regio- and stereoregularity of Sample 1. In particular, when the data in Table 2 of ref. [8] (which, inter alia, violate the pentad conservation law) are corrected taking into account the presence of the ethene units, the isotacticity of the propene homosequences in Sample 1 is estimated to be close to 100%.

This latter result is consistent with what is normally observed when propene is polymerized at 0°C in the presence of catalyst systems based on *rac*-ethylene-(4,5,6,7-tetrahydro-1-indenyl)$_2$ZrL$_2$ complexes [13]. As an example, in Fig. 2 we show the ^{13}C-NMR spectrum of a polypropylene sample prepared by us with the catalyst system *rac*-ethylene-(4,5,6,7-tetrahydro-1-indenyl)$_2$ZrCl$_2$/MAO under experimental conditions close to those used in ref. [8] for the synthesis of Sample 1; from the spectrum, it can be seen that the polymer is highly isotactic, with only traces of stereodefects of the ...*mmmmrrmmmm*... type (Scheme 1b).

The high stereospecificity of the quoted catalyst at low temperature is due to the fact that the disturbing effect of the side process of growing chain epimerization becomes significant only above ambient temperature, as already noted in a number of papers [2–5].

Our Fig. 2 also proves a high regioregularity of the sample, with ca. 1 mol% of regioirregular (2,1 and 1,3) units, as expected [13].

It should be noted that the spectrum of Fig. 2 in the present paper is practically coincident with that reported in Fig. 3 of ref. [8] for a sample (Sample 11) prepared using the (*S*,*S*) enantiomer of the same catalyst; this proves that no significant differences of regio- and stereospecificity exist for propene polymerization promoted at 0°C by the quoted catalyst in racemic and enantiomerically pure form [14].

In conclusion, we are pleased to confirm all our previous findings and interpretations on the mechanisms of stereoerror formation in isotactic propene polymerization promoted by C$_2$-syrnmetric metallocene catalysts [1,3–5,7], and to exclude any ‘frivolous’ conclusion on the subject from our side.

1. Experimental

1.1. Propene homopolymerization

In a 100 ml Pyrex bottle, 25 ml of toluene (freshly distilled over Na) was added to 4.5 ml of a 10% (w/v) solution of MAO in toluene (Witco GmbH) and 1.2 µmol of *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl$_2$ (Witco GmbH) and saturated at 0°C with propene at the partial pressure of 1.0 bar. The polymerization was allowed to proceed at constant monomer pressure for 1.5 h, after which it was stopped by monomer degassing. The product was coagulated with acidified methanol (200 ml), filtered out and dried at 50°C under vacuum (yield, 0.4 g).

1.2. Propene/ethene copolymerization

In a 100 ml Pyrex bottle, 25 ml of dry toluene was added to 4.5 mL of a 10% (w/v) solution of MAO in toluene and saturated at 0°C with a propene/ethene mixture (propene, 30 mol% in the gas phase) at a total monomer pressure of 1.0 bar. The polymerization was initiated by injecting 1 ml of toluene containing 1.2 µmol of *rac*-ethylenebis(4,5,6,7-tetrahydro-l-indenyl)ZrCl$_2$ and allowed to proceed at the constant monomer pressure of 1.0 bar by feeding propene only. After 3 h, the reaction was stopped by monomer degassing. The product was coagulated with acidified methanol (200 ml), collected by filtration and dried at 50°C under vacuum (yield, 1.3 g).

1.3. NMR characterizations

The polymer samples were characterized by ^{13}C-NMR with a Varian XL200 spectrometer operating at 50.3 MHz, on 10% (w/v) solutions in tetrachloroethane-1,2-d_2 at 120°C under the following instrumental conditions: 5 mm probe; ca. 70° pulse; acquisition time, 1.0 s; relaxation delay, 1 s; 15–20 K transients.

2. Note added in proof

The processing of this paper has been unusually long. In the meantime, the following other papers from our laboratory on the same or related subjects, making reference to the present one, have already been published: (a) V Busico, D. Brita, L. Caporaso, R. Cipullo, M. Vacatello, Macromolecules 30 (1997) 3971. (b) V. Busico, R. Cipullo, L. Caporaso, G. Angelini, A.L. Segre, J. Mol. Catal. Part A 128 (1998) 53.

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[9] L. Resconi, A. Fait, F. Piemontesi, M. Colonnesi, H. Rychlicki, R. Zeigler, Macromolecules 28 (1995) 6667.

[10] Polypropylene samples of virtually identical regio- and stereoregularities were obtained, e.g. when polymerizing propene in the presence of the catalyst dimethylsilyl-bis(2-methyl-4-*t*-butyl-cyclopentadienyl)$ZrCl_2$ in racemic and enantiomerically pure form (co-catalyst, MAO); H.H. Brintzinger, A. Reinmuth, personal communication.

[11] In our spectra, run at 120°C, the methyl resonance corresponding to the *mmmm* pentad occurs at 21.74 ppm downfield of TMS; however, for comparative purposes, we adjusted slightly the δ scale so to have such a resonance at 21.81 ppm, as in ref. [8].

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[13] W. Kaminsky, K. Kulper, H.H. Brintzinger, F.R.W.P. Wild, Angew Chem. Int. Ed. Engl. 24 (1985) 507.

[14] The observed DSC melting point of both samples is ca. 150°C. The lower melting points reported in Table 1 of ref. [8] for samples prepared with the catalyst in racemic form are probably due to copolymerized ethene units or to other impurities; unfortunately, the DSC curves, that would have been more informative in this respect, were not reported.