New Evidence on the Nature of the Active Sites in Heterogeneous Ziegler−Natta Catalysts for Propene Polymerization

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Received April 4, 1997
Revised Manuscript Received June 20, 1997

When, in the early 60s, pioneering studies of proton NMR provided the first information on the configuration of (partly) stereoregular vinyl polymers at the triad level,[1] two simple statistical models were developed for the interpretation of the observed stereosequence distributions. Known as "chain-end model"[1a] and "enantiomorphic-site model",[2] they correspond to the two limiting cases in which the stereocontrol of the polymerization is exerted, respectively, by the configuration of the last-added monomeric unit in the growing chain or by the intrinsic chirality of the catalytic species.[3]

In predominantly isotactic polymers, the two situations give rise to different types of stereoerrors (...*mmmmrmmmm*... in the case of chain-end control, ...*mmmmrrmmmm*... in case of enantiomorphic-site control) that can be distinguished from the triad distribution. This led to the first applications of the concept of polymer chain microstructure as a catalyst "fingerprint".

With the subsequent development of ^{13}C NMR, this concept has become the foundation for all stereochemical investigations of Ziegler−Natta and related transition metal catalyzed 1-alkene polymerizations.[3]

For these processes, relatively few cases of chain-end control (*1,3-like (lk)* or *1,3-unlike (ul)* asymmetric induction) have been documented.[3,4] In contrast, the observation of stereoerrors of the ...*mmmmrrmmmm*... type in all isotactic poly(1-alkene)s of practical interest has been taken as an indication of enantiomorphic-site control, and it has become common practice to adopt the homonymous statistical model for describing the stereosequence distribution of such polymers.[3,5]

However, a serendipitous application of this model to coordination polymerization catalysts is not advisable. Indeed, the assumption[2] that these catalysts can be described as racemic mixtures of enantiomorphous active sites and that opposite enantiofaces of a prochiral 1-alkene monomer are selected at active sites of opposite chirality is rather unlikely. The reason is that the transition metal *active species* at which the reaction occurs have necessarily two (*cis*) coordination positions available for the monomer and the growing polymer chain, and each of them can perform—at least in principle—as the *active site*;[3] as a matter of fact, the reaction path corresponding to the least nuclear motion is realized when the monomer and the growing chain exchange their coordination positions at each insertion step ("chain migratory insertion").[3,6,7]

Chart 1

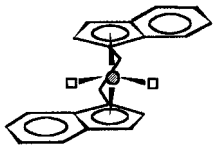


Chart 2

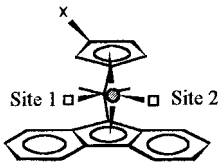
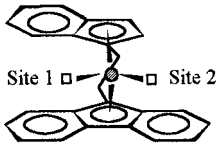


Chart 3



In view of the above, the only isotactic-selective catalysts to which the enantiomorphic-site model is unquestionably applicable are those deriving from Brintzinger-type C_2-symmetric group 4 *rac-ansa*-metallocenes,[3b] in which the two active sites of the chiral catalytic complex are *homotopic*[7c,8] (Chart 1).

An interesting example of predominantly isotactic polypropylenes with ...*mmmmrrmmmm*... stereodefects to which the enantiomorphic-site model should *not* be applied is instead that of polymers produced with C_1-symmetric *ansa*-metallocenes of the type sketched in Chart 2 (with X a bulky group such as, *e.g.*, *tert*-butyl or trimethylsilyl)[9] or Chart 3,[10] with two *diastereotopic* active sites[7c,8] (denoted in the charts as site 1 and site 2).

A rational explanation for the observed stereoselectivity has been provided by molecular mechanics calculations in the framework of the "growing chain orientation mechanism" of stereocontrol.[3,7,11] These indicated[7c,11] that, when the polymer chain is coordinated at the less hindered site 2, the conformation in which the first C−C bond points toward the unsubstituted side of the cyclopentadienyl ring in the more open quadrant is strongly preferred; this in turn favors, for steric reasons, the 1,2 insertion of a propene molecule coordinated at site 1 with the enantioface orienting the methyl substituent *trans* to the cited C−C bond. Conversely, when the growing chain occupies the more hindered site 1, the two conformations in which the first C−C bond is directed toward the substituted side of the cyclopentadienyl ring or toward the fluorenyl ring have comparable probabilities; therefore, there is no obvious reason for preferring propene insertion at site 2 with one or the other of its two enantiofaces.

In the case of regular chain migratory propagation, the resulting polymer would be substantially hemiisotactic,[7c,8,11] as actually observed for catalysts of the type of Chart 2 with X = methyl.[12] When site 1 is more crowded, however, the calculations pointed out[11] a tendency of the polymer chain to occupy site 2, in order to avoid unfavorable steric contacts with the aromatic ligand framework. In consequence: (i) Monomer insertion occurs preferentially at site 1, the more so the lower is the insertion rate compared with that of chain "backskip" from site 1 to site 2. Chain propagation, therefore,

S0024-9297(97)00467-1 CCC: $14.00

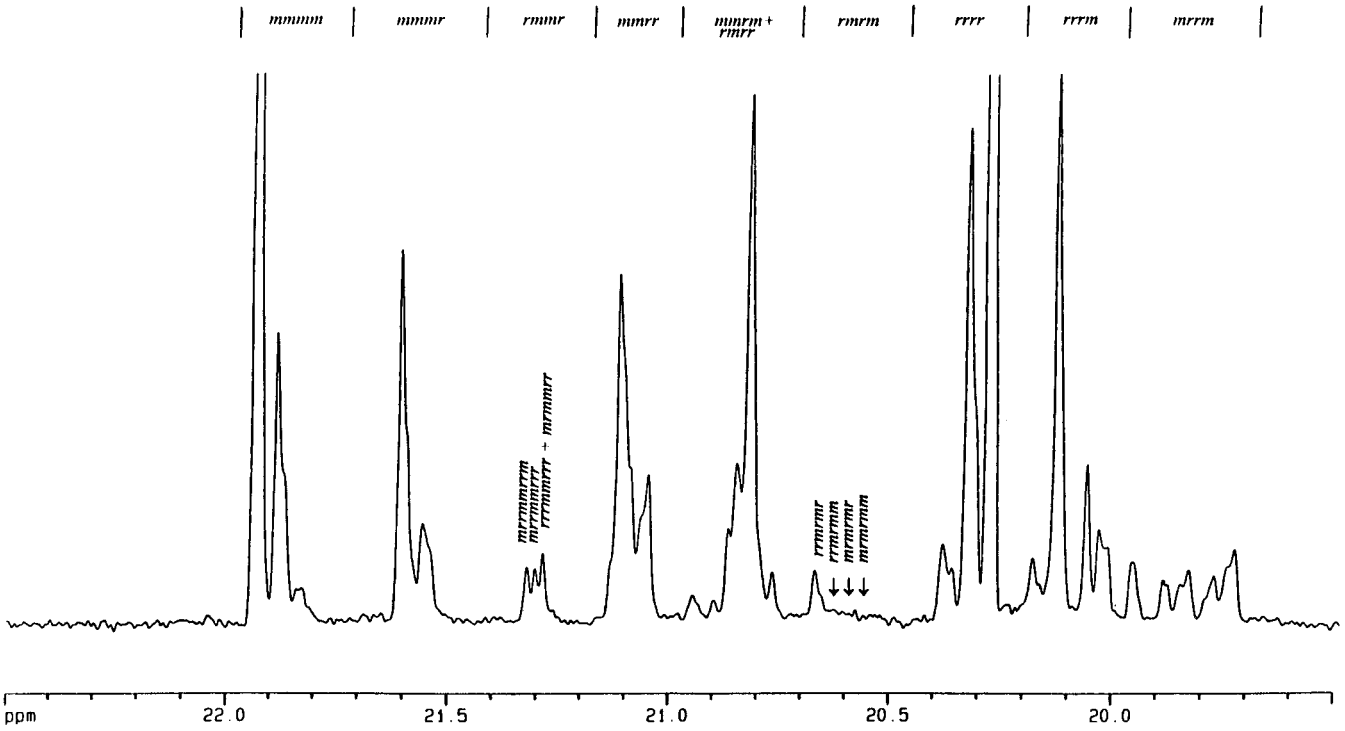


Figure 1. Methyl region of the 150 MHz ^{13}C NMR spectrum of the diethyl ether-insoluble/pentane-soluble fraction of a polypropylene sample prepared with the catalyst system $MgCl_2/TiCl_4-AlEt_3$/2,6-dimethylpyridine (δ scale in ppm downfield of TMS). All relevant resonance assignments[16,17] are indicated; the expected positions of the peaks corresponding to the *mrmrmm*, *mrmrmr*, and *rrmrmm* heptads (not observed, see text) are shown with arrows.

is predominantly isotactic, and the stereoselectivity tends to increase with decreasing monomer concentration.[10,11]

(ii) The probability of two consecutive monomer insertions at site 2 is virtually zero. Considering that site 1 is almost completely enantioselective,[7c,8,9,11,12] this actually means that the probability of two consecutive stereoerrors is also close to zero.

The resulting polymer stereosequence distribution is peculiar in that sequences with isolated *racemic* diads (*e.g.*, *...mmrm...*, *...rmrm...*) are "prohibited". This selection rule, well-known for hemiisotactic polypropylene,[8,12] does not seem to have been noted in the literature for predominantly isotactic polypropylenes produced with C_1-symmetric metallocene catalysts,[9,10] although it is clearly apparent, *e.g.*, from the ^{13}C NMR spectra reported in ref 9c.

The above represents an important difference with respect to the enantiomorphic-site statistics, according to which the distribution of configurations is Bernoullian and stereosequences of equal length containing an equal number of stereoerrors are equiprobable.[2] Of course, the difference tends to vanish with increasing polymer stereoregularity, and the two cases are virtually indistinguishable by ^{13}C NMR when the fraction of *meso* diads exceeds $[m] = 0.90$ (indicatively).

For a metallocene catalyst with a single type of active species deriving from a structurally well-defined precursor, it is relatively easy to identify the correct statistical model for the configurational description of the polymers produced.

The case of heterogeneous $TiCl_3$ and $MgCl_2/TiCl_4$ Ziegler–Natta catalysts for isotactic propene polymerization,[3a,13] on the other hand, is much more complicated. Indeed, active Ti species widely differing in selectivity (highly isotactic, weakly isotactic, syndiotactic) can be present on the catalyst surface, and their nature is still a matter of debate.[3a,13,14]

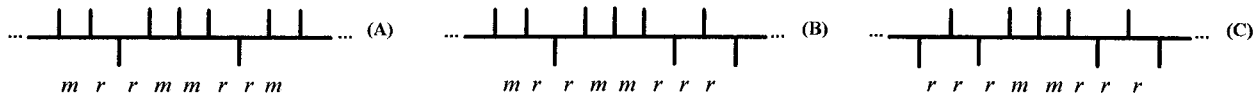
The occasional stereodefects in the polypropylene fraction of higher isotacticity (*e.g.*, insoluble in boiling heptane or in xylene) are of the *...mmmmrrmmmm...* type;[3a,13] this indicates that the stereocontrol must be traced back to the intrinsic asymmetry of the active species responsible for the production of this fraction.[3a,5]

Crystallochemical considerations on the layer lattices of "violet" $TiCl_3$ and of $MgCl_2$ have led to plausible models of surface Ti adducts in which the coordination environment of the transition metal is chiral.[3a,7a,c,15] Molecular mechanics calculations on such models in the framework of the "growing chain orientation mechanism" of stereocontrol have shown convincingly that part of them can give rise to isotactic-selective active species in propene polymerization.[7a,c,15] However, the detailed structure of such species and their local symmetry are still uncertain: the proposed models, indeed, range from locally C_2-symmetric species with two homotopic active sites to C_1-symmetric ones with two diastereotopic active sites (on this point, in particular, see ref 7c).

A thorough ^{13}C NMR stereosequence analysis of the polymerization products can help to clarify the picture. However, as already noted above, indicative results can be expected only for polymers in which the concentration of *m* diads is low enough to result in appreciable fractions of short stereosequences with at least two stereoerrors (*e.g.*, at the pentad level, *rmmr*, *rmrr*, *rmrm*).

Unfortunately, polypropylene samples produced with heterogeneous catalysts that contain isotactic sequences of low stereoregularity invariably also contain significant amounts of predominantly syndiotactic sequences.[14] This results in very complicated ^{13}C NMR spectra, in which the resonances associated with stereoerrors in isotactic and syndiotactic stretches are largely overlapped.[14] Moreover, the two types of stereosequences are—at least in part—chemically linked within stereo-

Chart 4



block chains,[16] and the resonances arising from stereoblock junctions are an additional source of complexity.

In this context, quantitative analyses of stereosequence distribution at the pentad level normally afforded by routine ^{13}C NMR spectra,[14] looking for possible deviations of the predominantly isotactic sequences from the enantiomorphic-site statistics, should be regarded as unfeasible.

On the other hand, the problem is perfectly within the reach of high-field ^{13}C NMR. In particular, our recent assignment[16,17] of the methyl region in 150 MHz ^{13}C NMR spectra of polypropylene has given access to the stereosequence distribution of this polymer at the heptad/nonad level.

The stereoregularity of polypropylene produced with $MgCl_2$-supported catalysts is largely dependent on the electron donors present in the catalyst system.[3a,13b−d,14] With certain "external donors",[18] in particular, stereoblock polypropylene fractions of rather low stereoregularity but with high average block length can be obtained. From the ^{13}C NMR point of view, such samples can be regarded as mixtures of predominantly isotactic and syndiotactic chains, the concentration of stereoblock junctions being negligible; this circumstance, along with the high resolution, makes it possible to identify, in their 150 MHz ^{13}C NMR spectra, the resonances pertaining to isotactic and syndiotactic sequences practically on inspection.

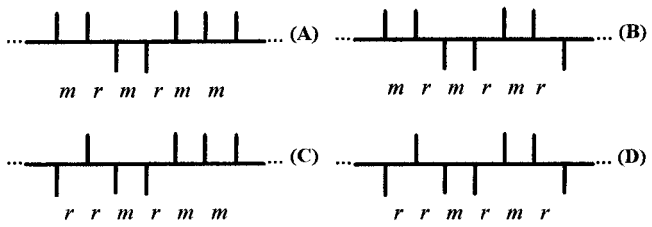
The methyl region of one such spectrum, obtained from the diethyl ether-insoluble/pentane-soluble fraction of a polypropylene sample prepared with the catalyst system $MgCl_2/TiCl_4-AlEt_3$/2,6-dimethylpyridine, is shown in Figure 1. In the following, its main features are discussed without making use of best-fit calculations of stereosequence distribution, in order to avoid the risk of drowning in numbers the essence of the stereochemical message (a complete quantitative analysis of the 150 MHz ^{13}C NMR spectra of stereoblock polypropylenes, covering also the methylene and methine regions, will be presented in a separate article[19]).

The presence of comparable amounts of predominantly isotactic and syndiotactic sequences in the sample is clearly indicated by the two intense resonances of the *mmmm* and *rrrr* pentads (which reveal their fine structure at the heptad level). The multiplets associated with the *mmmr*, *mmrr*, and *mrrm* pentads, with integral ratios close to 2:2:1, are largely due to isolated ...*mmmmrrmmmm*... stereoerrors in isotactic stretches; those corresponding to the *rmrr* and *rrrm* pentads, in roughly a 1:1 integral ratio, mostly arise from isolated ...*rrrrmrrrr*... stereoerrors in syndiotactic stretches (which indicates a chain-end control[4f,16]).

For this discussion, however, the most important peaks are the weak ones associated with (*rmmr*)-centered and (*rmrm*)-centered stereosequences, containing two or more stereoerrors.

Three main components are detected in the region of the *rmmr* pentad: from lower to higher field, they must be attributed[17] to the *mrrmmrrm*, *mrrmmrrr*, and *rrrmmrrr* nonads (the last overlapped with the broad peak of the *mrmmrr* heptad). The main contribution to the *mrrmmrrm* nonad comes from isotactic sequences with (at least) two nonconsecutive stereoirregularities,

Chart 5



as in Chart 4A; that to the *rrrmmrrr* nonad, from syndiotactic sequences with two consecutive stereoerrors (Chart 4C); finally, both "isotactic" and "syndiotactic" sequences containing (at least) three stereoerrors, as in Chart 4B, contribute to the *mrrmmrrr* nonad (as well as to the *mrmmrr* heptad).

Let us now turn our attention to the region of the *rmrm* pentad. The clear peak corresponding to the *rrmrmr* heptad[16,17] is mainly due to syndiotactic sequences with (at least) two nonconsecutive stereoerrors, as in Chart 5D; its integral is roughly twice that of the *rrrmmrrr* nonad,[20] in agreement with the chain-end statistics.[1a] Quite surprisingly, on the other hand, the peaks arising from the *mrmrmm*, *mrmrmr*, and *rrmrmm* heptads (Chart 5A−C), expected in the range of $\delta = 20.50-20.65$ ppm,[16,17] are not observed (which means that their individual integrals are below 0.2% of the total methyl integral).

Particularly revealing is the undetectability of the *mrmrmm* heptad (Chart 5A), which would arise mainly from isotactic sequences with two *consecutive* stereoerrors: in the case of applicability of the simple enantiomorphic-site statistics,[2] its fraction would be roughly twice that of the *mrrmmrrm* nonad (Chart 4A), whose peak is well observable as noted above.

This indicates that, for the sample examined, the distribution of configurations in the predominantly isotactic sequences does not correspond to that predicted by the enantiomorphic-site model[2] *but, instead, is analogous to that observed for predominantly isotactic polypropylene samples obtained in the presence of C_1-symmetric ansa-metallocene catalysts.*[9,10]

Now the questions are, (i) is this spectroscopic evidence sufficient to conclude that the mechanism of stereocontrol in the generation of such sequences resembles that for C_1-symmetric metallocenes, and, if so, (ii) how general is this conclusion—or, in other words, can it be extended to all classes of isotactic-selective active species in heterogeneous Ziegler−Natta catalysts?

In order to answer these questions, we investigated the effect of monomer concentration on the stereoselectivity of a number of these catalysts[13c,d] in propene polymerization. In this Communication, we give a preliminary account of the results obtained.

Propene polymerization experiments were run at different monomer concentrations (from 0.05 to 3.5 mol/L in heptane slurry). The reaction conditions ($T =$ 50 °C, no added H_2) were chosen so as to obtain polymers having appreciable contents of stereochemical inversions, even with catalyst systems (such as, *e.g.*, $MgCl_2$/1,3-diether/$TiCl_4-AlEt_3$[13d]) that under different conditions (higher temperature and with H_2 present) are highly stereoselective.[21]

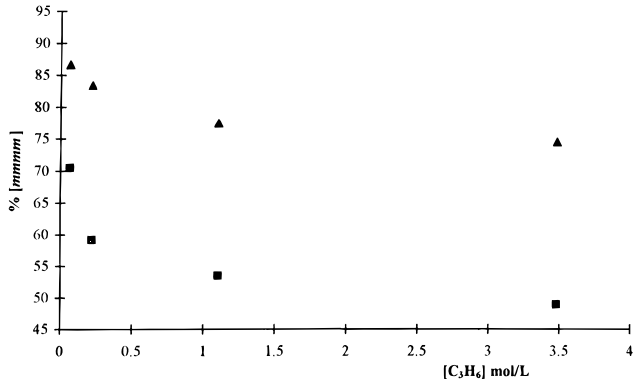


Figure 2. Content of *mmmm* pentads in polypropylene samples obtained with the catalyst system $MgCl_2/TiCl_4-AlEt_3$ (■) and in the xylene-insoluble fraction of such samples (▲), as a function of propene concentration.

Table 1. Fraction of *mmmm* Pentad, Measured by ^{13}C NMR, in Polypropylene Samples Prepared with a Number of $MgCl_2$-Supported Catalyst Systems at Two Different Propene Concentrations[a] (See Text)

catalyst system	$[C_3H_6]$ (mol/L)	% [*mmmm*]
$MgCl_2/TiCl_4-AlEt_3$	0.06	71
	3.5	49
$MgCl_2$/diisobutyl phthalate/$TiCl_4$–phenyltriethoxysilane/$AlEt_3$	0.09	94
	3.5	80
$MgCl_2$/2-isopropyl-2-isopentyl-1,3-dimethoxypropane/$TiCl_4-AlEt_3$	0.09	93
	3.5	83

[a] Other experimental conditions: T = 50 °C; Al/Ti = 50−100 mol/mol; heptane solvent.

In all cases, a significant increase in the stereoregularity of the isotactic part of the polymers was observed with decreasing propene concentration. As an example, in Figure 2 we plot, as a function of $[C_3H_6]$, the ^{13}C NMR fraction of *mmmm* pentads in polypropylene samples obtained with the simple catalyst system $MgCl_2/TiCl_4-AlEt_3$, and that in the xylene-insoluble fraction of the same samples. The two sets of data show the same trend; therefore, in this respect, the behavior of highly isotactic-selective and weakly isotactic-selective active species appears to be similar.

Analogous results were obtained for all investigated $MgCl_2$-supported systems, including last-generation ones containing 1,3-diethers as internal donors[13d] (Table 1).

For all these systems, the dependence of the stereoselectivity on monomer concentration, along with the high-field ^{13}C NMR observations discussed above, indicates a mechanism of isotactic propagation similar to that for C_1-symmetric metallocene catalysts,[9,10] in the sense that monomer insertion at a weakly enantioselective active site competes with chain back-skip followed by monomer insertion at a highly enantioselective active site.[11]

It is worth noting that models of unsymmetrical active species for heterogeneous Ziegler−Natta catalysts with two diastereotopic coordination sites corresponding to the features discussed above have already been proposed in the literature.[7a,c,15] Models postulating a local C_2-symmetry of the catalytic complex and two homotopic active sites,[7c,15] on the other hand, seem to be less compatible with the new experimental data and may need to be critically reconsidered.

Experimental Section. Propene polymerizations were performed in a 1 L stainless steel reactor (Brignole AU-1) equipped with a magnetic stirrer (1000 rpm). Typically, a heptane slurry (200 mL) containing the appropriate amounts of catalyst (50−150 mg), $AlEt_3$ (Al/Ti = 50−100 mol/mol), and "external donor", ED (when required; ED/Al = 0.05 mol/mol) was introduced in the reactor, thermostated at 50 °C, and saturated with propene. The reactions were allowed to proceed at constant monomer concentration (in the range 0.05−3.5 mol/L) for 15−60 min and stopped by monomer degassing. The polymers were coagulated with methanol (1 L), filtered off, and vacuum-dried.

Polymer fractionations were made by exhaustive Kumagawa extraction with boiling solvents, or by fractional crystallization after dissolution in xylene.[21]

The high-resolution $^{13}C\{^1H\}$ NMR spectrum of Figure 1 was recorded with a Bruker AMX 600 spectrometer operating at 150.9 MHz, on a 5 mg/mL polymer solution in tetrachloroethane-*1,2-*d_2 at 70 °C, under the conditions described in ref 16b.

The fractions of *mmmm* pentad in Table 1 were evaluated from quantitative $^{13}C\{^1H\}$ NMR spectra recorded with a Bruker AC-270 spectrometer operating at 67.9 MHz, on 10% w/v polymer solutions in tetrachloroethane-*1,2-*d_2 at 130 °C, under the following conditions: 5 mm probe; ≈80° pulse; acquisition time, 1.2 s; relaxation delay, 1.5 s; 10−15 K transients.

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MA9704673