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Advances in the ^{13}C NMR Microstructural Characterization of Propene Polymers

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ABSTRACT: This paper presents the main results of a high-resolution 150 MHz ^{13}C NMR characterization of polypropene samples prepared in the presence of a number of last-generation Ziegler–Natta catalyst systems. The configurational analysis of the polymers, in particular, was expanded from the pentad level (normally afforded by routine spectra) to the nonad level. This proved to be beneficial in mechanistic studies on the origin of the stereospecificity.

Introduction

In the stereochemical study of 1-alkene polymerization promoted by Ziegler–Natta catalysts, the ^{13}C NMR spectroscopical analyses of polymer microstructure provided the first real insights into the mechanisms of steric control exerted by catalytic species which remain (with only a few exceptions) unaccessible to a direct observation.[1]

In this framework, propene polymers represent a special case, in that their tremendous practical interest is concomitant with a resolution of the ^{13}C NMR spectra which is unique for poly(1-alkene)s: even in low-field experiments, indeed, the methyl resonance is split into components associated with the steric pentads.[2,3]

The experimental pentad distributions of the polymers can often be reproduced in terms of simple limiting statistical models. In particular, the "enantiomorphic-sites" model[4] has been shown to apply when the stereospecificity is dictated (only) by the chirality of the active metal center(s) (as found for all known highly isotactic polymers); Bovey's "chain-end" model,[5] instead, applies when the steric control is exerted (only) by the configuration of the last-inserted monomeric unit.

For polymers produced in the presence of catalysts with multiple types of active sites (as are most heterogeneous ones), combinations of the above two statistics may also lead to reasonable results (see e.g. refs 6 and 7).

In recent times, however, new catalysts have been developed, allowing the synthesis of polypropenes with distributions of configurations which cannot be reproduced in terms of the above cited statistical models. Particularly relevant are, within single-site systems, the syndiotactic-specific catalysts based on C_s-symmetric group 4 metallocenes;[8] among the heterogeneous multisite systems are a variety of $MgCl_2$-supported "high-yield" catalysts modified with Lewis bases leading to the formation of unusual elastomeric polypropenes made of *m*-rich and *r*-rich stereosequences in comparable amounts.[9]

The microstructural analysis of such polymers requires more sophisticated statistical models,[8,10] containing a higher number of adjustable parameters and taking into account, in some cases, the possibility of reversible interconversions between different types of active sites.[10] This makes it desirable, in turn, to expand the experimental basis for the calculations from the pentad level (with a maximum of nine independent data) to the heptad level at least.

To this end, we engaged in a high-resolution 150 MHz ^{13}C NMR characterization of polypropene samples obtained with the new catalysts.

The main results obtained are presented in this paper. They include assignments of the methyl resonances up to the nonad level and analyses of stereosequence distributions in terms of suitable statistical models.

Results and Discussion

Complete and unambiguous assignments of the methyl resonances (up to the tridecad level) in high-resolution ^{13}C NMR spectra of propene polymers have been reported so far in the literature for the special (and favorable) case of hemiisotactic polypropene.[11]

The additional assignments reported in this paper have been made by combining calculations of chemical shifts on the basis of the γ-gauche effect (Table 1)[12–14] with analyses of stereosequence distributions in the framework of appropriate statistical models (Table 2) (*vide infra*).

Description of the Characterized Polymer Samples. The spectra of two "reference" polymers (samples A and B) obtained in the presence of homogeneous single-site catalysts with a known mechanism of stereocontrol were used as a basis for facing more complex cases.

Sample A is a (predominantly) isotactic polypropene prepared with the catalyst system [*rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]$ZrCl_2$/MAO (MAO = methylaluminoxane).[15]

The isospecificity of the catalyst arises from the asymmetry of the transition metal centers, ensured by the chirality of coordination of the stereorigid aromatic ligand and leading to efficient discrimination between the two monomer enantiofaces, as a consequence of nonbonded interactions between the side group of the inserting monomer and the growing polymer chain.[16] Accordingly, the configurational statistics of 1-alkene polymers produced with this catalyst agrees with that predicted by the enantiomorphic-sites model (main type of stereodefects: ...*mmmmrrmmmm*...).[17]

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Table 1. Assignments of the Methyl Resonances in the ^{13}C NMR Spectra of Figure 1

resonance no.	Δδ (exptl)	stereosequence assgnt	Δδ (calcd) isotactic chain	Δδ (calcd) syndiotactic chain	Δδ (calcd) isotactic/syndiotactic block junction
(A) *mm*- and *mr*-Centered Stereosequences; *mmmmmm* Resonance Used as Reference Line for the Δδ Values					
1	0[a]	*mmmmmm*	0		
2	−0.05	*mmmmmr*	−0.11		−0.11
3	−0.11	*rmmmmr*	−0.21		
4	−0.33 ÷ −0.34	*mmmmrr*	−0.28		−0.31
5	−0.38	*rmmmrr*	−0.39		
6	−0.62	*mrrmmrrm*	−0.57		
7	−0.63	*mrrmmrrr*		−0.60	
8	−0.65	*rrrmmrrr*		−0.61	
9	−0.81 ÷ −0.86	*mmmrrm*	−0.74		
		mmmrrr	−0.79		−0.79
		rmmrrm	−0.85		
10	−0.86	*mmmrmr*	−0.89		
11	−0.88	*rmmrrr*		−0.91	
12	−1.06	*mrrmrrmm*	−1.04		
13	−1.08	*rrrmrrmr*		−1.09	
14	−1.12	*rrrmrrrr*		−1.12	
15	−1.21 ÷ −1.44	*rmrm*	−1.21 ÷ −1.42	−1.25 ÷ −1.31	
(B) *rr*-Centered Stereosequences; *rrrrrr* Resonance Used as Reference Line for the Δδ Values					
16	+0.10	*mrrrrm*	+0.12	+0.09	
17	+0.05	*rrrrrrmr*		+0.05	
18	+0.03	*rrrrrrmm*	+0.08	+0.06	+0.07
19	0[b]	*rrrrrr*		0	
20	−0.09	*rmrrrmrr*		−0.11	
21	−0.15	*rrrrrmrr*		−0.16	
22	−0.21	*rrrrrmmr*		−0.22	
23	−0.24	*rrrrrmmm*			−0.25
24	−0.25	*mrrrrmmm*	−0.26		
25	−0.32	*rrmrrmrr*		−0.34	
26	−0.39	*rrmrrmmr*		−0.40	
27	−0.43 ÷ −0.45	*rrmrrmmm*	−0.44		
28	−0.49	*mmmrrmmr*	−0.50		
29	−0.51 ÷ −0.53	*mmmrrmmm*	−0.53		

[a] 21.94 ppm downfield from TMS. [b] 20.28 ppm downfield from TMS.

Table 2. Stereosequence Distributions in Samples A−C, Evaluated from the ^{13}C NMR Spectra of Figure 1, and Best-Fitting Calculated Ones in the Framework of Suitable Statistical Models (See Text)

	sample A (Figure 1A)		sample B (Figure 1B)		sample C (Figure 1C)	
stereosequence	% (exptl)	% (calcd)	% (exptl)	% (calcd)	% (exptl)	% (calcd)
mmmmmm	41.$_5$	41.7			4.6	4.4
mmmmmr					3.4	3.9
rmmmmr					0.9	0.9
mmmr	16.$_6$	16.1			7.5	8.5
rmmr	2.1	1.8	1.0	0.9	3.1	2.8
mmrr + *mmmrmr*	16.$_0$	18.2	2.1	1.8	12.$_6$	12.2
mmmrmm + *rmmrmr* + *rmmrmm* + *rmrr*	5.6	5.1	4.4	4.1	16.$_3$	14.9
rmrm	3.9	3.6			2.7	5.0
rrrrrr			80.$_3$	80.2	17.$_9$	17.7
rrrrrm	0.5	0.5	5.7	5.7	7.0	8.8
mrrrrm	0.9	1.1			2.3	1.5
mrrrmr	≈1	1.5			1.4	2.0
rrrrmr + *mrrrmm*			4.4	4.2	7.5	8.3
rrrrmm	2.8	2.2	2.0	1.9	5.5	4.7
rrrrrmmr					2.4	1.4
rrrrrmmm					1.7	1.8
mrrrrmmm					0.9	0.9
rmrrmr	2.6	2.4			1.9	0.9
rmrrmm					3.1	1.9
mmrrmm	6.7	5.6			2.1	1.6
		$\sigma = 0.84$		$\sigma = 0.99$		$\sigma = 0.76$
				$P_{sk} = 0.024$		$P_r = 0.87$
						$P_{i/s} = 0.094$
						$P_{s/i} = 0.084$

The methyl region of the ^{13}C NMR spectrum of sample A (Figure 1A) is somewhat complicated by the occurrence of weak resonances arising from chain end groups and regioirregularities (the latter mainly of the 1,3 type);[18–20] in the figure, such resonances are marked with asterisks.

Sample B, instead, is a syndiotactic polypropene produced in the presence of the catalyst system [Me$_2$C(Cp)(Flu)]ZrCl$_2$/MAO (Cp = cyclopentadienyl; Flu = fluorenyl).[8]

The syndiospecificity of the polymerization is the result of a "chain migratory" insertion mechanism,[8] in which the incoming monomer and the growing polymer chain exchange regularly at each insertion step between the two enantiotopic coordination positions available at the Zr atom.[16,21] Occasional failures of this mechanism

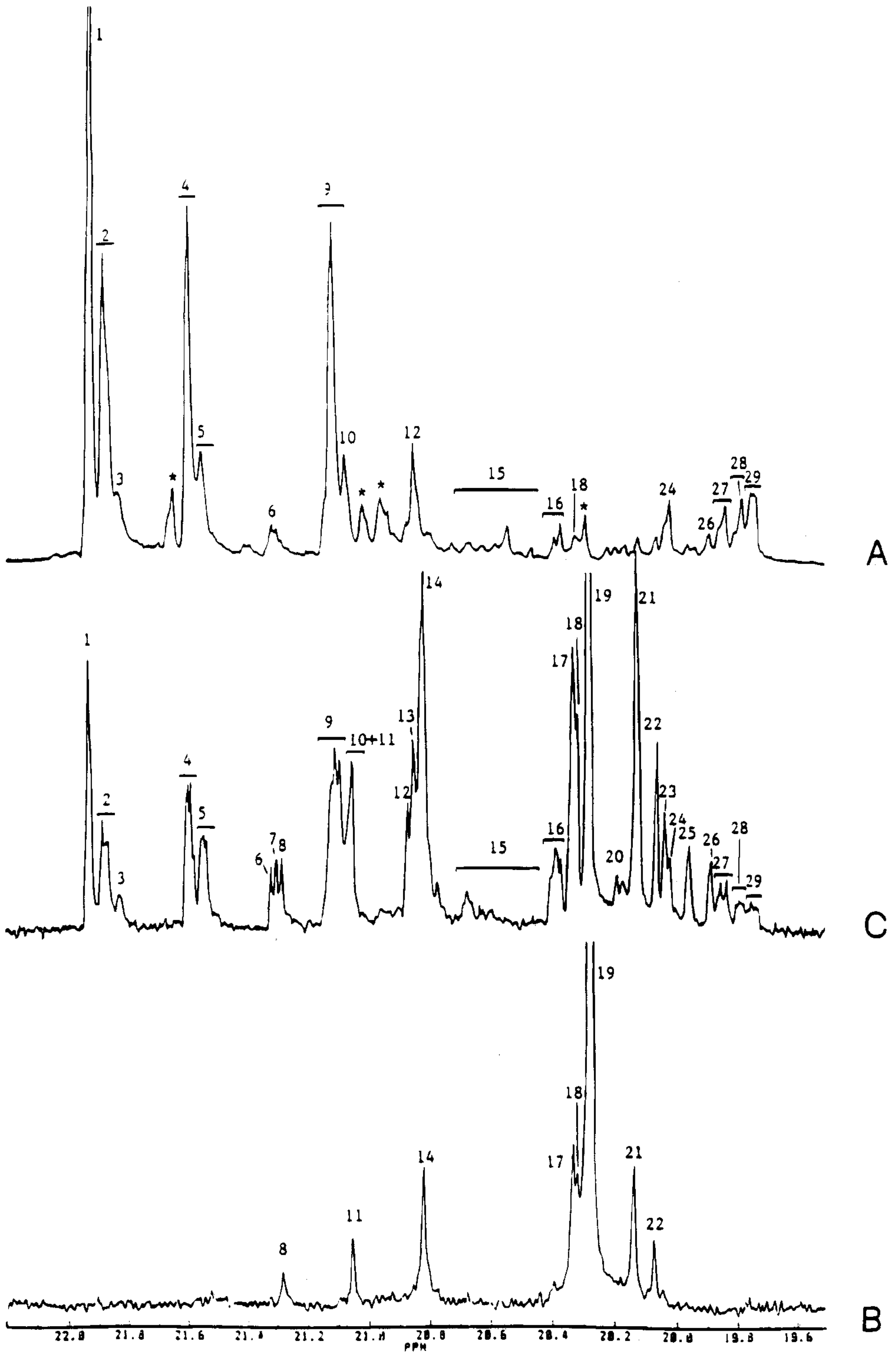

Figure 1. Methyl region of the 150 MHz ^{13}C NMR spectra (at 70 °C) of sample A (A), sample B (B), and sample C (C). The scale is in ppm downfield from TMS. For resonance attributions, see Table 1. Starred peaks in Figure 1A indicate resonances arising from chain end groups or regioirregular sequences.

("skipped insertions") lead to the formation of *...rrrrmrrrr...* stereodefects, which sum up to the *...rrrrmmrrrr...* ones arising from monomer insertions with the "wrong" enantioface,[8] as clearly shown by the ^{13}C NMR spectrum in Figure 1B.

As an example of a less clear-cut case, we selected for this presentation the diethyl ether-soluble fraction of a polypropene sample prepared with a $MgCl_2$/dioctyl phthalate/$TiCl_4$–$AlEt_3$ catalyst system modified with 2,6-dimethylpyridine[9] and containing "*m*-rich" and "*r*-rich" sequences in roughly equal amounts (sample C).

Previous investigations on similar samples[7,10] proved that the distribution of configurations in the *m*-rich sequences conforms to the enantiomorphic-sites statistics, whereas that in the *r*-rich sequences is in better agreement with Bovey's chain-end model. They also pointed out[10] that the two kinds of stereosequences are, at least in part, chemically bound within individual macromolecules.

The methyl region of the ^{13}C NMR spectrum of sample C is shown in Figure 1C.

Chemical Shift Calculations. A list of all methyl resonances observed in the ^{13}C NMR spectra of samples A–C at 70 °C (the lowest temperature allowing complete dissolution of all three samples) is given in the first two columns of Table 1. The reproducibility of the experimental chemical shifts was ±1 Hz, roughly corresponding to ±0.002 ppm.

Theoretical values of chemical shifts *at the same temperature* for the resonances of the central methyl C atoms in different stereosequences were calculated (columns 4–6 of Table 1) in terms of the γ-gauche effect,[12–14] by applying the rotational isomeric state method[14] and the five-state conformational model of Suter and Flory.[22]

For relatively short stereosequences (such as heptads or nonads), these values can be somewhat dependent on the tacticity of a longer segment of the macromolecule. Therefore, for each of the investigated polypropene samples, the calculations were made by taking into account its (predominant) tacticity.

As an example, in the (predominantly) isotactic sample A, with a distribution of configurations conforming to the enantiomorphic-sites statistics, the *rmmmmr* heptad was assumed to be located (mainly) in a ...*mmmrrmmmmrrmmm*... stereosequence.

The calculated set of chemical shifts (and in particular their sequential order) was used as a first guide for the assignments reported in Table 1. These were then checked by quantitative analyses of stereosequence distributions, as described below.

Statistical Analysis of the ^{13}C NMR Stereosequence Distributions. The application of statistical methods to the configurational analysis of propene polymers has been thoroughly discussed (see e.g. refs 3, 8, 23, and 24).

In most cases, however, best-fitting calculations have been limited to distributions of steric pentads, as evaluated from "routine" ^{13}C NMR spectra. The low number (≤ 9) and the relatively high uncertainty of the experimental data discouraged the use of chain propagation models with more than three adjustable parameters; the latter were evaluated by solving, in the least-squares sense, the overdetermined set of (usually cumbersome) equations, giving the probability of occurrence of each observable pentad.

Such an approach becomes impractical when data for longer stereosequences or more sophisticated statistical models are handled. Moreover, it does not allow one to take into account the hypothesis of reversible switches between different types of stereocontrol.

Therefore, we developed new computational methods in which the traditional analytical treatment is replaced by conceptually simpler matrix multiplication techniques, as is preliminarily described in the Appendix to this paper.

In Table 2, the experimental stereosequence distributions for the three investigated polypropene samples, evaluated from the ^{13}C NMR spectra by full deconvolution of the methyl region (Figure 2), are compared with best-fitting ones calculated in the framework of appropriate statistical models. The experimental data for sample A were corrected to take into account the presence of chain end groups and regioirregularities.[20]

It should be noted that, whenever the separate evaluation of the integrals pertaining to partly overlapped resonances appeared to be to some extent discretional, cumulative integrals were used in the calculations.

The cases of samples A and B, formed in the presence of catalyst systems with a single type of active site, are relatively straightforward.

For the (predominantly) isotactic sample A, indeed, we adopted the enantiomorphic-sites model requiring, as the only adjustable parameter, the probability, σ of generating an R (S) monomeric unit at an R(S)-preferring active site.[4]

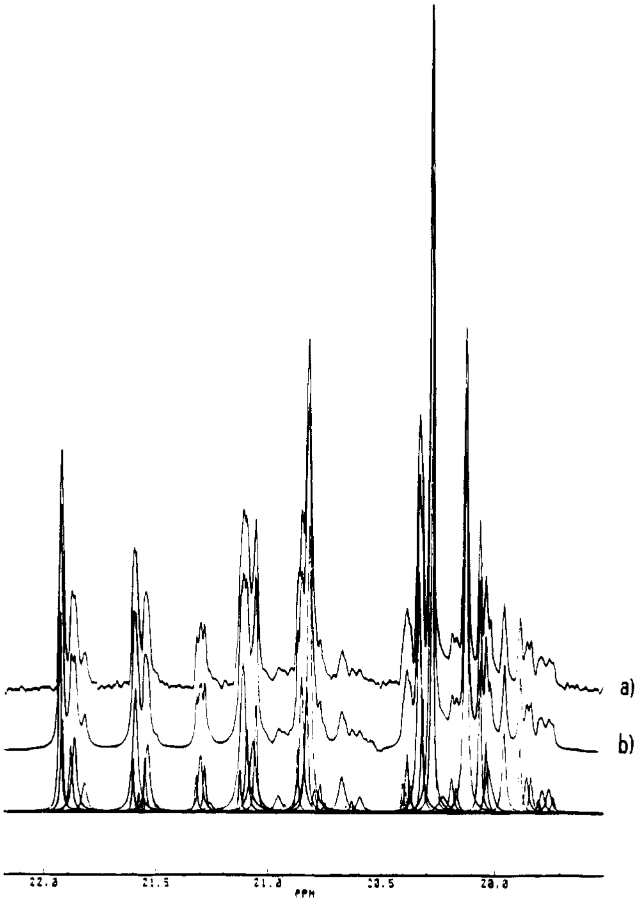

Figure 2. Full deconvolution of the methyl region for the ^{13}C NMR spectrum of sample C: (a) experimental spectrum; (b) simulated spectrum.

The stereosequence distribution in sample B was reproduced in terms of a two-parameter model assuming the chain migratory insertion mechanism for syndiotactic propagation proposed by Ewen.[8] According to this model, σ is the probability of selecting the preferred enantioface of the prochiral monomer at each of the two enantiotopic coordination positions available at the transition metal atom;[16,21] P_{sk} is the probability of a back-skip of the growing polymer chain to its original coordination position prior to further monomer coordination and insertion.[8]

The agreement between experimental and calculated integrals is good (Table 2) and lends support to the resonance assignments (Table 1 and Figure 1A,B).

The statistical model adopted for reproducing the stereosequence distribution in sample C, instead, is necessarily more sophisticated.

The clear and relatively intense resonance (no. 23 in Figure 1C) assigned to the *rrrrrmmm* nonad (Table 1) is diagnostic for the presence of (regioregular) junctions ...*mmmmmrrrrr*... between *m*-rich and *r*-rich sequences. This implies the ability of the two types of active sites at which such stereosequences are formed to interconvert reversibly at a rate faster than that of chain growth.[7,10]

The simplest approach to this case is to adopt the Coleman–Fox type[25] "two-site" model introduced in ref 10, with four adjustable parameters: σ, the probability of generating an R (S) monomeric unit at an R(S)-preferring isospecific site, according to the enantiomorphic-sites statistics; P_r, the probability of forming an r diad at a syndiospecific site, according to Bovey's chain-end model; $P_{i/s}$, the probability of switching from a (predominantly) isotactic to a (predominantly) syndiotactic chain propagation; $P_{s/i}$, the probability of the reverse switch.

It should be noted, in particular, the ability of this model to fit the resonances associated with the *rrrrmm*-centered nonads (last two columns of Table 2), largely arising from junctions between *m*-rich and *r*-rich sequences and, as such, not accounted for by a simple "two-site" model[6,7] (for a more thorough discussion, see ref 10).

Conclusions

In this investigation, we have shown the advantages of high-resolution (150 MHz) ^{13}C NMR in the microstructural characterization of polypropene samples prepared in the presence of Ziegler–Natta catalyst systems.

Expanding the determinations of stereosequence distribution from the pentad level (normally afforded by routine spectra) to the nonad level proved to be beneficial in mechanistic studies of catalyst stereospecificity based on the configurational analysis of the polymers.

As an example, we reported the first direct spectroscopical evidence of the coexistence of *m*-rich and *r*-rich sequences in single polypropene molecules formed in the presence of $MgCl_2$-supported "high-yield" catalysts, this implying the presence of interconverting active sites with different stereospecificities on the surface of such catalysts.[10]

It seems advisable to extend this approach to other complex cases as are, in general, multisite and interconverting-site catalyst systems, or hybrid mechanisms of stereocontrol for single-site catalysts.

Experimental Section

Polymer Preparation. Sample A. A 1.1 mL aliquot of a 30% (w/v) solution of MAO in toluene (Schering) and 1.0 μmol of [*rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]$ZrCl_2$[15] were dissolved in benzene (200 mL, freshly distilled over Na/K alloy). The solution was charged into a 300 mL stainless steel reactor (Brignole AU-300), thermostated at 50 °C and pressurized under stirring (1000 rpm) with propene at the (constant) partial pressure of 1.0 bar. After 1 h, the reaction was stopped by monomer degassing. The product was coagulated with acidified methanol (2 L), filtered out, and dried *in vacuo*; yield, 1.6 g.

Sample B. A 1.0 mL aliquot of a 30% (w/v) solution of MAO in toluene (Schering) and 1.5 μmol of $Me_2C[(Cp)(Flu)]ZrCl_2$[8] were mixed and kept at 20 °C for 6 h. The solution was then diluted with toluene (200 mL, freshly distilled over Na), transferred into a 1 L stainless steel reactor (Brignole AU-1), thermostated at 60 °C, and pressurized under stirring (1000 rpm) with propene at the (constant) partial pressure of 5.0 bar. After 15 min, the reaction was stopped by monomer degassing. The product was coagulated with acidified methanol (1 L), filtered out, and dried *in vacuo*; yield, 10.3 g.

Sample C. A glass vial containing 35 mg of a $MgCl_2$/dioctyl phthalate/$TiCl_4$ catalyst[26] (sealed under argon in a Vacuum Atmospheres glovebox) was placed in a 2 L stainless steel reactor (Brignole AU-2) equipped with a vial holder/breaker. Then 300 mL of heptane (freshly distilled over Na) containing 0.60 mL (4.4 mmol) of $AlEt_3$ and 0.052 mL (0.45 mmol) of 2,6-dimethylpyridine were charged into the reactor, thermostated at 80 °C, and pressurized under stirring (1000 rpm) with H_2 and propene at the partial pressures of 0.2 and 7.0 bar, respectively. The polymerization was started by breaking the catalyst vial, allowed to proceed at constant propene pressure for 1 h, and stopped by quick monomer degassing. The product was coagulated with acetone (2 L), filtered out, and dried *in vacuo*; yield, 190 g. From a 10 g portion of the polymer, 4.1 g of the diethyl ether-soluble sample C was obtained by exhaustive Kumagawa extraction.

^{13}C NMR Characterization. ^{13}C NMR spectra were run on a Bruker AMX-600 spectrometer operating at 150.9 MHz on dilute[27] polymer solutions in 1,2-dideuteriotetrachloroethane at 70 °C. A 2 s relaxation delay with a 2.2 s acquisition time and a pulse angle of $\approx 45°$ were applied, so to attain conditions close to the maximum signal-to-noise ratio[28] and far from any saturation.

Proton broad-band decoupling was achieved with a Waltz 16 sequence.[29] Due to the high number of resonances, at least 25K scans were collected on a 64K time domain.

After zero filling, Fourier transformation was performed either without any further correction or after the application of a weak enhancing function.[30]

It has been shown[30,31] that spin–lattice relaxations are very similar for chemically equivalent groups differing only in tacticity. It is thus reasonable to assume, in particular, that all resonances of CH_3 groups in fully regioregular polypropene sequences (far from the chain ends) have basically the same NOE, so that quantitative data of stereosequence distributions can be obtained from an accurate resonance integration.

This was performed by full deconvolution of the experimental spectrum using the "GLINFIT" program from the "ABACUS" library.[32]

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Appendix

Let us consider an ideally infinite chain of events taking place at a catalytic site, each event corresponding to the insertion of a propene unit into a growing polypropene chain.

We assume that the stereochemistry of each insertion event can be controlled either by the intrinsic chirality of the catalytic site (site control) or by the configuration of the last-inserted monomeric unit (chain-end control).

We explicitly include the possibility that the nature of the steric control changes reversibly between these two limiting mechanisms along the chain of events.

In order to devise a versatile evaluation scheme for the fractional abundance of monomer stereosequences of any length, we write the following 2 × 2 stochastic matrices:

$$\mathbf{E} = \begin{array}{c|cc|} & S & R \\ S & \sigma & 1-\sigma \\ R & \sigma & 1-\sigma \end{array}$$

$$\mathbf{C} = \begin{array}{c|cc|} & S & R \\ S & 1-P_r & P_r \\ R & P_r & 1-P_r \end{array}$$

The rows of **E** and **C** are indexed to the chirality (*S* or *R*) of the last-inserted monomeric unit in the growing chain, whereas the columns are indexed to the possible chirality of the new unit to be inserted.

Matrix **E** applies to site control,[4] σ being the probability of insertion of a monomeric unit with the preferred chirality (arbitrarily assumed here to be *S*).

Matrix **C** holds in the case of chain-end control,[5] P_r being the probability of formation of a racemic (*r*) diad.

E and **C** can be combined then in the 4 × 4 matrix:

$$\mathbf{A} = \begin{array}{c|cccc|} & S & R & S & R \\ S & \mathbf{E}(1-q_{EC}) & & \mathbf{C}q_{EC} & \\ R & & & & \\ S & \mathbf{E}q_{CE} & & \mathbf{C}(1-q_{CE}) & \\ R & & & & \end{array}$$

where q_{EC} is the probability of a change from site control to chain-end control and q_{CE} the probability of the reverse change.

It should be noted that, in this simple formulation, (i) the two probabilities q_{EC} and q_{CE} are assumed to be independent of the chirality of the last-inserted monomeric unit and (ii) the same preferred chirality of monomer insertion is always restored following a change from chain-end to site control. More complex hypotheses, however, can be easily handled in the framework of our scheme by suitably modifying the above matrices and/or by using higher-order matrices, as will be discussed in more detail in a separate paper.[33]

For the calculations of stereosequence distributions, we now define the matrices $\mathbf{A}_{\mathrm{m}}$ and $\mathbf{A}_{\mathrm{r}}$ as the matrices $[a_{ij}] = \mathbf{A}$ in which all the elements a_{ij} with $(i + j)$ odd or with $(i + j)$ even, respectively, are set equal to zero.

The fractional abundance of a given stereosequence $\mathrm{d}_1\mathrm{d}_2...\mathrm{d}_n$, with $\mathrm{d}_i = m$ for meso diads and $\mathrm{d}_i = r$ for racemic diads, is then given by

$$\mathbf{f}(\mathrm{d}_1\mathrm{d}_2...\mathrm{d}_n) = \mathbf{f}_{\mathrm{o}}^{\mathrm{T}}\, \mathbf{A}_1\mathbf{A}_2...\mathbf{A}_n\, \mathbf{J}$$

where $\mathbf{A}_i = \mathbf{A}_{\mathrm{m}}$ when $\mathrm{d}_i = m$ and $\mathbf{A}_i = \mathbf{A}_{\mathrm{r}}$ when $\mathrm{d}_i = r$, $\mathbf{J} = |1\ 1\ 1\ 1|^{\mathrm{T}}$, and $\mathbf{f}_{\mathrm{o}}^{\mathrm{T}}$ is the vector of the stationary probabilities of the four states, evaluated by numerically solving the system of equations

$$\mathbf{f}_{\mathrm{o}}^{\mathrm{T}}\mathbf{A} = \mathbf{f}_{\mathrm{o}}^{\mathrm{T}}$$

The overall probability w that monomer insertion takes place under site control, coincident with the sum of the first two elements of $\mathbf{f}_{\mathrm{o}}^{\mathrm{T}}$, is given by

$$w = q_{\mathrm{CE}}/(q_{\mathrm{EC}} + q_{\mathrm{CE}})$$

A special case arises when $q_{\mathrm{EC}} = q_{\mathrm{CE}} = 0$ (i.e. when the steric control exerted by each catalytic site is not allowed to change during chain growth). In such a case, which can be used to treat a mixture of catalytic sites—part of which impose an (enantiomorphic-)site(s) control, the other a chain-end control—w is an independent parameter; of course, $w = 1$ and $w = 0$ correspond to the limiting cases of pure (enantiomorphic-)site(s) control and of pure chain-end control, respectively.

In the paper, this simplified approach has been applied to the cases of samples A (with the independent parameter $w = 1$) and C; in this latter case, the two probabilities q_{EC} and q_{CE} have been denoted in the text as $P_{\mathrm{i/s}}$ and $P_{\mathrm{s/i}}$, respectively, in order to conform to a notation already introduced in the literature.[10] We checked that a more rigorous treatment for sample C, requiring the use of higher-order matrices,[33] does not lead to appreciable improvements in the agreement between calculated and experimental data.

Our method can be easily extended to other mechanisms of steric control. In particular, the chain-migratory syndiotactic propagation mechanism proposed by Ewen[8] and suited to the case of sample B can be treated by replacing the matrix $\mathbf{A}$ in the previous equations with the matrix $\mathbf{A}_{\mathrm{CM}}$:

$$\mathbf{A}_{\mathrm{CM}} = \begin{array}{c|cccc|} & S & R & S & R \\ S & \sigma P_{\mathrm{sk}} & (1-\sigma)P_{\mathrm{sk}} & (1-\sigma)(1-P_{\mathrm{sk}}) & \sigma(1-P_{\mathrm{sk}}) \\ R & \sigma P_{\mathrm{sk}} & (1-\sigma)P_{\mathrm{sk}} & (1-\sigma)(1-P_{\mathrm{sk}}) & \sigma(1-P_{\mathrm{sk}}) \\ S & \sigma(1-P_{\mathrm{sk}}) & (1-\sigma)(1-P_{\mathrm{sk}}) & (1-\sigma)P_{\mathrm{sk}} & \sigma P_{\mathrm{sk}} \\ R & \sigma(1-P_{\mathrm{sk}}) & (1-\sigma)(1-P_{\mathrm{sk}}) & (1-\sigma)P_{\mathrm{sk}} & \sigma P_{\mathrm{sk}} \end{array}$$

The elements of $\mathbf{A}_{\mathrm{CM}}$ are such that, when $P_{\mathrm{sk}} = 0$, the chain of events corresponds to a sequence of monomer insertions in which the preferred chirality of insertion inverts regularly at each insertion step, as a consequence of the migration of the growing chain between two enantiotopic coordination positions available at the catalytic site. P_{sk} represents the probability of a back-skip of the growing chain to its original coordination position prior to a new monomer insertion; this results in two consecutive insertions with the same preferred chirality ("skipped" insertion, see text).

References and Notes

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