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^{13}C NMR Evidence of the Copresence of *m*-Rich and *r*-Rich Sequences (Stereoblocks) in Polypropene Molecules

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ABSTRACT: The high resolution ^{13}C NMR microstructure of polypropene fractions containing *m*-rich and *r*-rich sequences, obtained by solvent extraction from polymer samples prepared in the presence of typical $MgCl_2$-supported Ziegler–Natta catalysts, was analyzed in terms of a Coleman–Fox type "two-site" statistical model taking into account the possibility (only postulated in the literature) of chemical junctions between the two different types of stereosequences. The results confirmed the copresence of *m*-rich and *r*-rich sequences (stereoblocks) in single polypropene molecules. This indicates the ability of isospecific and syndiospecific active centers to interconvert reversibly in times which are shorter than the average growth times of the polymer chains.

Introduction

It is known[1] that, on the surface of the heterogeneous Ziegler–Natta catalysts promoting the isotactic polymerization of propene, active centers are also present which may give rise to the formation of significant amounts of "*r*-rich" sequences (syndiotactic or "syndiotactoid"[2]). As a matter of fact, syndiotactic polypropene was isolated for the first time as an "impurity" from samples of isotactic polypropene prepared in the presence of catalyst systems such as, e.g., α- or γ-$TiCl_3$ in combination with $Al(C_2H_5)_2F$ or LiC_4H_9.[3]

The fraction of *r*-rich sequences is higher in polypropene samples obtained with $MgCl_2$-supported "high-yield" catalysts, particularly when suitable Lewis bases are added to the Al–alkyl cocatalyst.[4-6] Recently, high-yield catalyst systems have been disclosed which are able to produce polypropene samples containing up to one-third by weight of such sequences.[5]

The ^{13}C NMR spectroscopic characterization of propene homopolymers and copolymers with low amounts of [1-^{13}C]-ethene obtained with the above catalysts allowed us to prove that this type of (predominantly) syndiotactic chain propagation proceeds via 1,2 (primary) propene insertion[7] (as already known for the isotactic propagation[1]), under the steric control of the last-added monomeric unit.[4,7]

In these polymers, the fractions which are extractable with low-boiling solvents (e.g. diethyl ether, pentane, hexane) may be conceived, from the microstructural viewpoint, as mixtures of enantiomorphic-site-controlled isotactoid sequences and of chain-end-controlled syndiotactoid sequences.

In fact, the experimental distributions of the steric pentads, as evaluated from routine ^{13}C NMR spectra, can be reasonably reproduced within a simple "two-site" statistical model (see, e.g., refs 4, 8, and 9), with three adjustable parameters: σ (probability of formation of a *R*-(*S*-) unit at a *R*-(*S*-) preferring isospecific center), P_r (probability of formation of an *r* diad at a syndiospecific center), and *w* (weight fraction of the polymer formed at the isospecific centers).

However, some mismatch is usually observed in the region of the *mr*-centered pentads; this has been proposed to result from the presence of steric pentads arising from chemical junctions between isotactoid and syndiotactoid sequences (blocks).[7,9]

The pentad distribution, with (a maximum of) only nine independent data, is not an adequate basis for more sophisticated statistical calculations. On the other hand, with the availability of ^{13}C NMR spectrometers operating at very high magnetic fields, it is now possible to expand the microstructural determination on propene polymers to the heptad level at least.

This article presents the main results of a 150-MHz ^{13}C NMR characterization of polypropene fractions containing high amounts of syndiotactoid sequences, and of the statistical analysis of the spectroscopic data in terms of a Coleman–Fox type[10] "two-site" model taking into account the hypothesis of junctions between isotactoid and syndiotactoid sequences.

The results provide additional evidence in favor of this hypothesis.

Results and Discussion

As representative examples for this presentation, we selected two different fractions (fraction A, diethyl ether-soluble; fraction B, hexane-soluble/pentane-insoluble) of a polypropene sample prepared in the presence of the catalyst system $MgCl_2/TiCl_4$–TMP/$Al(C_2H_5)_3$ (TMP = 2,2,6,6-tetramethylpiperidine; see Experimental Section).[4]

The methyl region of the 150-MHz ^{13}C NMR spectrum of fraction B is shown in Figure 1.

When not assigned in the literature,[11,12] the resonances were attributed on the basis of chemical shift calculations according to the γ-gauche effect[12] and by comparative analysis with the 150-MHz ^{13}C NMR spectra of samples of isotactic and syndiotactic polypropene prepared with homogeneous group IV metallocene-based catalysts,[13] as will be described in a separate paper.[14]

A complete resolution was achieved for the resonances arising from the *mmmm*-centered and *rr*-centered heptads, the latter showing a fine structure reaching the nonad or even the undecad level.

In the first column of Tables 1 and 2, we report the experimental stereosequence distributions of the two fractions, as evaluated from the spectral integration.

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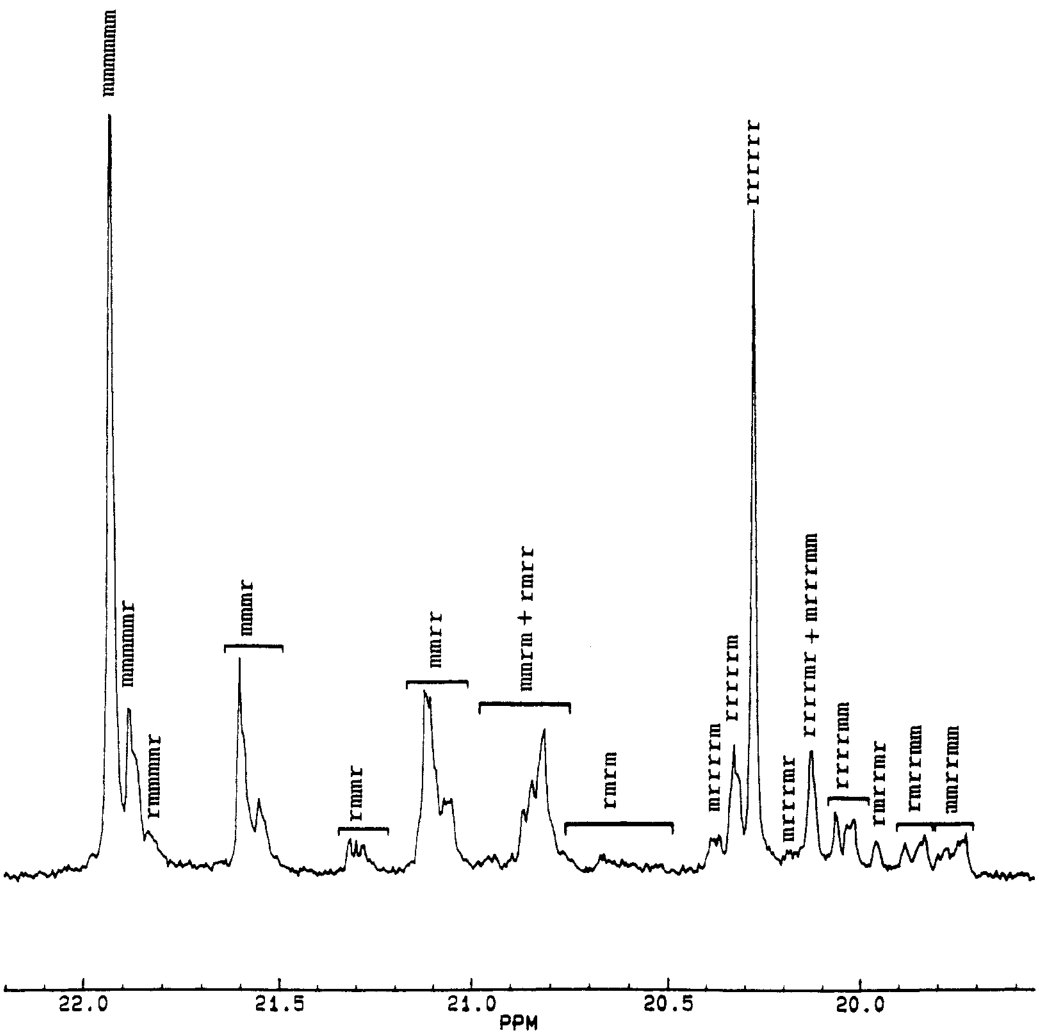

Figure 1. Methyl region of the 150-MHz ^{13}C NMR spectrum of fraction B (δ scale in ppm downfield from TMS).

For a few broad and partly overlapped resonances, in spite of the chemical shift calculations,[11,12,14] the separate evaluation of the integrals appeared to be somewhat discretional; in such cases, we preferred to consider the cumulative integral. This led to a total of 14 independent data to be used in the statistical calculations.

In the second column of Tables 1 and 2, the experimental data are compared with the best-fitting ones calculated in the framework of a simple "two-site" model.[4,8,9]

The agreement between the two sets is reasonable (and lends support to the main features of the model). It can be seen, however, that the *mmrr* pentad and the *rrrrmm* heptad are significantly underestimated in the calculations, whereas the cumulative integral of the *mmrm*, *rmrr*, and *rmrm* pentads is instead overestimated.

It should be noted that the *rrrrmm* heptad is not likely to arise from stereochemical errors in the isotactoid sequences (mainly of the ...*mmmrrmmm*... type) nor in the syndiotactoid ones (mostly ...*rrrmrrr*...);[1,4,7] conversely, it is expected to occur in the case of chemical junctions between isotactoid and syndiotactoid sequences (...*mmmmmrrrrr*...), contributing to the *mmrr* pentad as well.

Therefore, we elaborated on a Coleman–Fox type[10] "two-site" model, taking into account the possibility of reversible switches between an enantiomorphic-site-controlled isospecific and a chain-end-controlled syndiospecific chain propagation.[14,15] Four adjustable parameters are now required: in addition to σ, P_r, and w (coincident with those of the simple "two-site" model), it is necessary to consider the probability $p_{i/s}$ that a propagating isospecific center changes into a syndiospecific one (the probability $p_{s/i}$ for the reverse change is given by $p_{s/i} = p_{i/s}[w/(1 - w)]$).

For the two characterized polypropene fractions, the best-fitting stereosequence distributions calculated on the basis of this model are reported in the last column of Tables 1 and 2.

The improvement of the match with the experimental data is apparent already on inspection (this is, of course, better noted for fraction A, with a higher estimated concentration of junctions). In fact, the decrease in the standard deviation resulting from the use of the four-parameter model in the place of its three-parameter version is well beyond the threshold for statistical significance (as shown by the values of the Ω parameter[16] in Tables 1 and 2).

The best-fitting values of the adjustable parameters obtained for both fractions in the framework of the two statistical models are also reported in the tables.

A first obvious remark is that, when the presence of junctions between stereosequences is not taken into account, the calculated values of the two probabilities σ and P_r for a given sample tend to be underestimated, the more so the higher is the concentration of the junctions, part of the steric sequences across the junctions being interpreted as stereoirregularities.

A more interesting observation concerns the values of the two probabilities $p_{i/s}$ and $p_{s/i}$. These are simply related to the number average length of the isotactoid and syndiotactoid sequences ($\langle L_i \rangle$ and $\langle L_s \rangle$, respectively):

Table 1. Experimental Stereosequence Distribution for Fraction A and Best-Fitting Distributions Calculated According to the Two Statistical Models Described in the Text

stereosequence	% (exptl)	% (calc, "two-site")	% (calc, "Coleman–Fox two-site")
mmmmmm	8.8	10.2	8.4
mmmmmr + *rmmmmr*	6.6	7.5	7.4
mmmr	11.0	11.7	12.1
rmmr	3.6	3.0	3.0
mmrr	15.1	12.8	14.1
mmrm + *rmrr* + *rmrm*	19.5	21.5	19.4
rrrrrr	8.6	8.9	8.5
rrrrrm + *mrrrrm*	7.4	6.3	7.8
mrrrmr	1.5	1.8	1.8
rrrrmr + *mrrrmm*	5.6	5.9	5.7
rrrrmm	5.1	3.0	5.1
rmrrmr	1.2	1.8	1.6
rmrrmm	3.2	2.3	2.4
mmrrmm	2.8	3.3	2.7
		$\sigma = 0.76$	$\sigma = 0.80$
		$P_r = 0.81$	$P_r = 0.86$
		$w = 0.69$	$w = 0.65$
			$p_{i/s} = 0.088$
			$(p_{s/i} = 0.17)$
		$10^3\Sigma^a = 2.1$	$10^3\Sigma^a = 0.48$
		$10^4\Omega^b = 1.9$	$10^4\Omega^b = 0.48$

[a] $\Sigma = \sum(y_i - y_i^\circ)^2$. [b] $\Omega = \sum(y_i - y_i^\circ)^2/(n - m)$ where n (=14) is the number of independent experimental data and m is the number of adjustable parameters.

Table 2. Experimental Stereosequence Distribution for Fraction B and Best-Fitting Distributions Calculated According to the Two Statistical Models Described in the Text

stereosequence	% (exptl)	% (calc, "two-site")	% (calc, "Coleman–Fox two-site")
mmmmmm	17.9	18.1	17.6
mmmmmr + *rmmmmr*	8.3	8.6	8.5
mmmr	10.0	11.5	11.5
rmmr	2.4	1.8	1.7
mmrr	13.6	12.0	12.4
mmrm + *rmrr* + *rmrm*	13.6	14.3	13.1
rrrrrr	14.1	14.1	14.0
rrrrrm + *mrrrrm*	5.3	5.3	6.3
mrrrmr	0.7	0.9	0.9
rrrrmr + *mrrrmm*	4.1	4.7	4.6
rrrrmm	4.3	2.2	3.5
rmrrmr	1.0	0.9	0.8
rmrrmm	1.5	1.7	1.7
mmrrmm	3.2	3.9	3.4
		$\sigma = 0.82$	$\sigma = 0.84$
		$p_r = 0.88$	$p_r = 0.90$
		$w = 0.70$	$w = 0.67$
			$p_{i/s} = 0.028$
			$(p_{s/i} = 0.057)$
		$10^3\Sigma^a = 1.1$	$10^3\Sigma^a = 0.67$
		$10^4\Omega^b = 1.0$	$10^4\Omega^b = 0.67$

[a] $\Sigma = \sum(y_i - y_i^\circ)^2$. [b] $\Omega = \sum(y_i - y_i^\circ)/(n - m)$ where n (=14) is the number of independent experimental data and m is the number of adjustable parameters.

$$\langle L_i \rangle = 1/(p_{i/s}) \qquad \langle L_s \rangle = 1/(p_{s/i})$$

The estimated values of $\langle L_i \rangle$ and $\langle L_s \rangle$ are 11 and 6 monomeric units, respectively, for fraction A and 40 and 20 monomeric units (indicatively) for fraction B.

It appears, therefore, that one reason for the lack of crystallinity in fraction A (Figure 2A) is the short length of the stereosequences. In the case of fraction B, conversely, at least part of the isotactoid and syndiotactoid sequences (stereoblocks) are long enough to crystallize (Figure 2B).

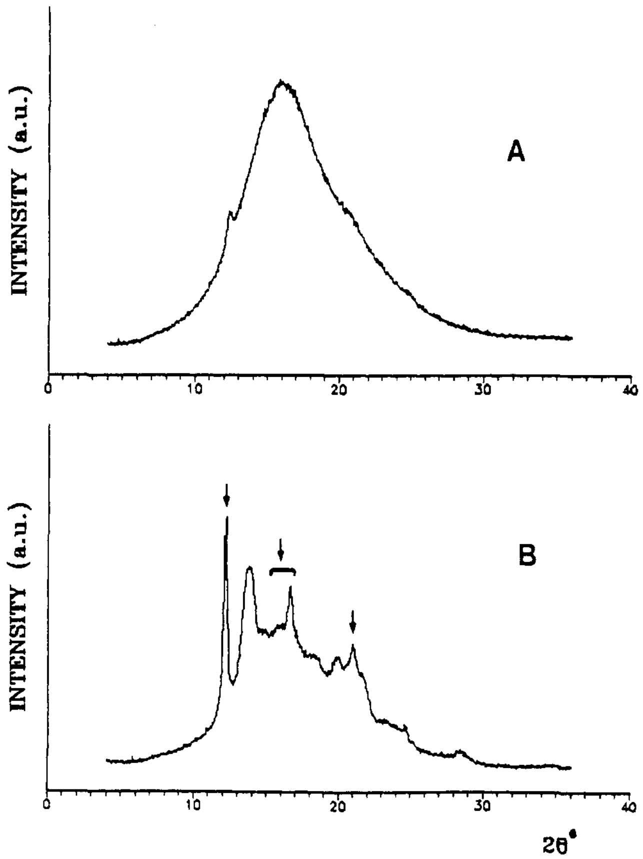

Figure 2. Powder X-ray diffraction spectra of fraction A (A) and of fraction B (B). The positions of reflections from syndiotactic polypropene are indicated with arrows.

These findings seem to be quite general. Indeed, we obtained very similar results for a number of polypropene samples prepared with different heterogeneous catalysts, both violet-$TiCl_3$-based and $MgCl_2$-supported, as will be reported in more detail in following papers.[14,17]

Interestingly, (low amounts of) syndiotactoid sequences may be present even in boiling-heptane-insoluble fractions conventionally taken[1] as "isotactic polypropene". This is proved by the observation, in the ^{13}C NMR spectra of such samples, of weak but unquestionable resonances associated with the *rrrr*, *rrrm*, and *rmrr* pentads.[17,18] According to a statistical analysis of the microstructure in the framework of the Coleman–Fox type "two-site" model introduced above, in that extreme case, which is thoroughly discussed in a separate paper,[17] the macromolecules are made of long (>10^2 monomeric units) isotactic blocks spaced by much shorter (10–20 monomeric units, indicatively) syndiotactoid sequences.

The overall picture, therefore, seems to indicate that the active metal centers on the surface of most heterogeneous Ziegler–Natta catalysts (including the highly isospecific ones) may change reversibly their environment in times which are shorter (or even much shorter) than the average growth times of the polymer chains.

Structural models of active sites that could switch from an isospecific to a syndiospecific control can be found, e.g., in refs 9 (Figure 1), 19 (Figure 4), 20 (Figure 5).

The influence of Lewis base molecules on the surface equilibria between different chlorinated transition metal species, considered to be precursors of active sites of different stereospecificities, on the edges of $MgCl_2$ platelets has been preliminarily discussed in refs 17, 20, and 21.

Experimental Section

Catalyst preparation, polymerization conditions, and polymer fractionation procedures were as described in ref 4.

^{13}C NMR spectra were recorded on a Bruker AMX 600 spectrometer operating at 150.9 MHz, on polymer solutions (8 mg/mL) in 1,2-dideuteriotetrachloroethane at a temperature of 70 °C, using the following parameters: spectral width, 80 ppm; time domain, 64K; size, 128K (zero filling); relaxation delay, 2 s; 45° pulse (corresponding to the optimum Ernst angle[22]). Broad band proton decoupling was achieved with the WALTZ sequence.[23]

Under the above conditions, quantitative spectra are obtained.[18] The resonances were integrated by full simulation of the experimental spectrum, using the GLINFIT program from the Bruker ABACUS library.[24]

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References and Notes

(1) (a) Corradini, P.; Busico, V.; Guerra, G. *Comprehensive Polymer Science*; Pergamon Press: Oxford, U.K., 1988; Vol. 4, pp 29–50. (b) Pino, P.; Giannini, U.; Porri, L. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley & Sons: New York, 1987; Vol. 8, pp 147–220.

(2) The terms "isotactoid" and "syndiotactoid" are used hereby to indicate macromolecules or sequences of monomeric units with statistical distributions of configurations such that the content of *m* diads or of *r* diads, respectively, is significantly higher than 50% (typically, in the interval 70–90%), but not equal or nearly equal to 100% (in which cases the terms "isotactic" and "syndiotactic" can be applied).

(3) Natta, G.; Pasquon, I.; Corradini, P.; Peraldo, M.; Pegoraro, M.; Zambelli, A. *Rend. Fis. Acc. Lincei* **1960**, *28*, 539.

(4) Busico, V.; Corradini, P.; De Martino, L.; Graziano, F.; Iadicicco, A. M. *Makromol. Chem.* **1991**, *192*, 49.

(5) Job, R. C. (Shell Oil Co.). Int. Pat. Appl. WO 90/12816, 19 April 1990.

(6) Ohnishi, R.; Tsuruoka, M.; Funabashi, H.; Tanaka, A. *Polym. Bull.* **1992**, *29*, 199.

(7) Busico, V.; Corradini, P.; De Martino, L. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 49.

(8) Van der Burg, M. W.; Chadwick, J. C.; Sudmeijer, O.; Tulleken, H. J. A. F. *Makromol. Chem., Theory Simul.* **1993**, *2*, 399.

(9) Doi, Y. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 635.

(10) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.

(11) Di Silvestro, G.; Sozzani, P.; Savaré, B.; Farina, M. *Macromolecules* **1985**, *18*, 928.

(12) Hayashi, T.; Inoue, Y.; Chujo, R.; Doi, Y. *Polymer* **1989**, *30*, 1714.

(13) 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.

(14) Busico, V.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. Manuscript in preparation.

(15) The applicability of a Coleman–Fox type model to propene polymerization was demonstrated by Zambelli for homogeneous V-based catalysts at low temperatures; see, e.g.: Ammendola, P.; Shijing, X.; Grassi, A.; Zambelli, A. *Gazz. Chim. Ital.* **1988**, *118*, 769.

(16) Gans, P. *Data Fitting in the Chemical Sciences*; John Wiley & Sons: Chichester, U.K., 1992; Chapter 6.

(17) Busico, V.; Cipullo, R.; Corradini, P.; De Biasio, R. Submitted for publication to *Macromol. Chem. Phys.*

(18) Martuscelli, E.; Avella, M.; Segre, A. L.; Rossi, E.; Di Drusco, G.; Galli, P.; Simonazzi, T. *Polymer* **1985**, *26*, 259.

(19) Albizzati, E. *Chim. Ind. (Milan)* **1993**, *75*, 107.

(20) Busico, V.; Corradini, P. In *Transition Metal Catalyzed Polymerizations*; Quirk, R. P., Ed.; Cambridge University Press: New York, 1988; pp 551–562.

(21) Corradini, P.; Barone, V.; Fusco, R.; Guerra, G. *Gazz. Chim. Ital.* **1983**, *113*, 601.

(22) Ernst, R. R.; Bodenhousen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in one and two dimensions*; Clarendon Press: Oxford, U.K., 1987; Chapter 4, pp 124–125.

(23) Reference 22, Chapter 8, pp 474–475.

(24) GLINFIT, by A. D. Bain, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada, 1989.