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Solid-State ^{13}C NMR Approach to the Structural Investigation of Racemic and Optically Active Isotactic Poly(3-methyl-1-pentene)

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ABSTRACT: By ^{13}C NMR CP/MAS analysis it is shown that isotactic poly((*S*)-3-methyl-1-pentene) and poly((*RS*)-3-methyl-1-pentene) adopt similar chain conformations in the solid state. The strong tendency of polymer chains to form helices, even in the absence of crystallinity, is confirmed.

A recent ^{13}C NMR investigation[1] of the stereochemistry of polymerization of (*RS*)-3-methyl-1-pentene (3M1P) has shown that poly((*RS*)-3M1P) consists of a mixture of copolymer chains containing the *R* and *S* monomers in ca. 2.5:1 and 1:2.5 ratios, respectively, with a Bernoullian distribution. Therefore the optical purity of the enantiomorphic chains is rather low. A similar conclusion may be reached by comparing the broad resonances of the carbon atoms of poly((*RS*)-3M1P) with the sharp resonances of poly((*S*)-3M1P) observed in solution (Figure 1). In addition, previous X-ray studies[1,2] have indicated that poly ((*S*)-3M1P) and poly((*RS*)-3M1P) prepared in the presence of isotactic-specific catalysts have different crystalline structures. The crystal structure of poly((*RS*)-3M1P) has not been determined while poly((*S*)-3M1P) has been described in terms of a helical conformation with four monomer units per turn (i.e., a 4:1 helix)[3] (Figure 2).

The present communication reports preliminary CP (cross-polarization) and MAS (magic angle spinning) ^{13}C NMR results on isotactic poly((*S*)-3M1P) and poly((*RS*)-3M1P). The ^{13}C NMR solid-state spectra of the two polymers are shown in Figure 3a,b. The chemical shifts of the carbon resonances are summarized in Table I, where they are compared with the chemical shifts in solution for the benzene-soluble fraction of the same polymers. The signal assignment in the solid state was made on the basis of the previous assignment of the solution spectra obtained by using off-resonance decoupling and additivity rules.[4,5] By comparing the solution- and solid-state spectra (Figures 1 and 3, respectively) the most significant differences are observed for the chemical shift of the C_5 resonance, which, in the latter, overlaps with the $C_{3'}$ signal and in the line width of the resonances in poly((*RS*)-3M1P), which, in the solution spectrum, are even broader than those in the solid-state spectrum. In light of the results reported in this paper, the line broadening can be reasonably ascribed to the presence, in solution too, of secondary peaks which arise from carbons having different average conformations due to different stereochemical environments.

Table I
^{13}C Chemical Shifts of Isotactic Poly(3-methyl-1-pentene) in Solution and in the Solid State[a]

C atom[b]	solution poly-((*S*)-3M1P) and poly-((*RS*)-3M1P)	solid poly-((*S*)-3M1P)	solid poly-((*RS*)-3M1P)[c]
C_5	12.8	14.1	13.7
$C_{3'}$	13.8		(17.9)
C_4	28.6	29.0	28.9
			(22.8)
C_1	32.3	32.5	32.4
C_3	36.3	36.7	36.7
C_2	36.7	38.0	(40.6)

[a] Referred to TMS. [b] Carbons of the structural unit are numbered according to Figure 1a. [c] In parentheses are reported the chemical shifts of the smaller resonances, absent in poly((*S*)-3M1P) (see text).

Further work will be devoted to a deeper investigation of the influence that similar local environments can exert, in the solid state, in determining the chemical shifts of the chemically nonequivalent carbons $C_{3'}$ and C_5 and to a more detailed line-shape analysis. It must be noted that, despite the presence of two different conformations identified by X-ray diffraction, a single chemical shift was found for both C_3 and C_2 in poly((*S*)-3M1P). By accounting for the conclusions reached by Petraccone et al.,[3] this could mean that the exchange between the two isoenergetic species is fast on the NMR time scale, so producing a single averaged chemical shift.

Inspection of the solid-state spectra a and b of Figure 3 reveals a strong matching between most of the main resonances of poly((*S*)-3M1P) and poly((*RS*)-3M1P) and at least three substantial differences. (i) The resonance at 38.0 ppm, assigned to C_2 in poly((*S*)-3M1P) (Figure 3a), seems to overlap with the signal from C_3 at 36.7 ppm in poly((*RS*)-3M1P) (Figure 3b), as the increased intensity of this resonance suggests. The alternative possibility that the C_2 signal does not shift but disappears by broadening,

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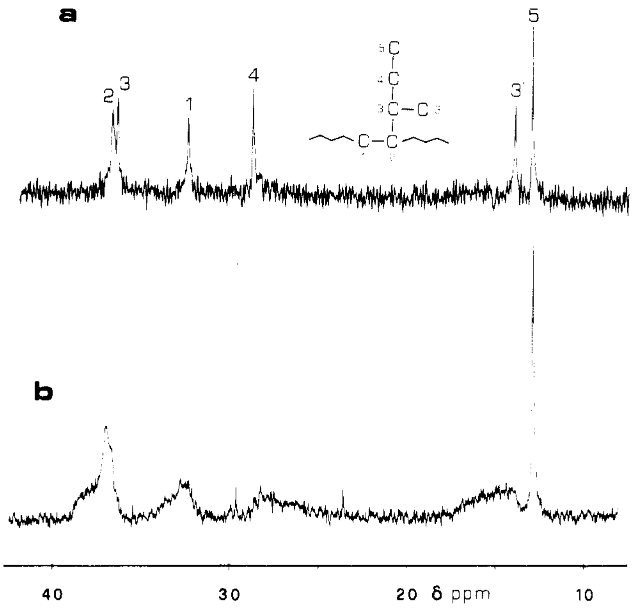

Figure 1. ^{13}C NMR solution spectra of the diethyl ether insoluble, benzene-soluble fraction of (a) poly((*S*)-3M1P) and (b) poly((*RS*)-3M1P).

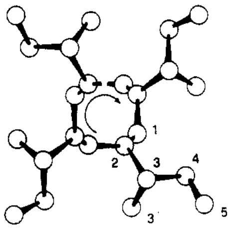

Figure 2. View of one of the two isomorphous conformations of isotactic poly((*S*)-3M1P), according to Petraccone et al.,[3] looking down the helix axis. Carbons of the structural unit are numbered according to Figure 1a and Table I.

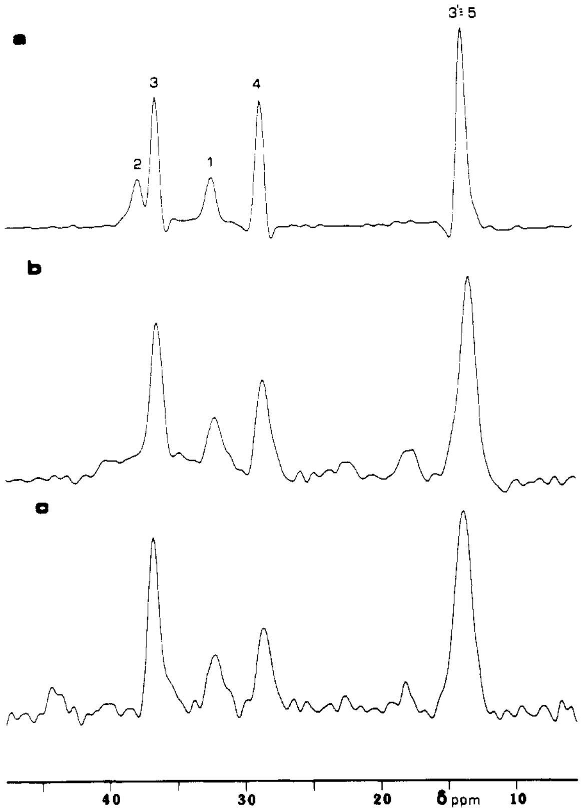

Figure 3. ^{13}C NMR solid-state spectra of the benzene-insoluble fractions of (a) poly((*S*)-3M1P), (b) poly((*RS*)-3M1P), and (C) poly((*RS*)-3M1P) after thermal degradation. For carbon numbering see Figure 1a. The resonance at 44.2 ppm was not assigned.

on going from poly((*S*)-3M1P) to poly((*RS*)-3M1P), cannot be ruled out. (ii) A significant broadening of all resonances is observed for poly((*RS*)-3M1P), whose spectrum exhibits line widths approximately twice as large as those of the corresponding resonances in the poly((*S*)-3M1P) spectrum. (iii) Three additional small resonances appear in the spectrum of poly((*RS*)-3M1P) at 17.9, 22.8, and 40.6 ppm, not observed in Figure 3a.

As was outlined for isotactic polypropylene,[6] the helical nature of the polymer chain is more important than the packing of the helices in the crystalline state in determining the observed chemical shift values. Therefore, the remarkable coincidence of chemical shifts between the two spectra suggests similar intramolecular effects for both polymers; i.e., isotactic poly((*RS*)-3M1P) and poly((*S*)-3M1P) are likely to adopt similar chain conformations in the solid state. Hence, as previously hypothesized,[7] the *R* and *S* *sec*-butyl substituent groups are isomorphous to a large extent. Consequently, the presence in poly((*RS*)-3M1P) of as much as 25–30% of *S* monomer in a macromolecule mainly formed of *R* monomer units and vice versa is not sufficient to hinder the chains from organizing in the same helical structure as the optically pure poly((*S*)-3M1P).

The line broadening of the main resonances of poly((*RS*)-3M1P), in comparison with those from poly((*S*)-3M1P), could in principle be attributed to the presence of regions structurally less organized (amorphous) in poly((*RS*)-3M1P). In fact, when the X-ray spectra of the highly isotactic fractions of both polymers are compared, poly((*RS*)-3M1P) shows an appreciable lowering of crystallinity. In order to check the correlation between crystallinity and line width, a sample of poly((*RS*)-3M1P) was thermally degraded. Such treatment nearly completely destroyed the crystalline structure of the polymer (>90% amorphous by X-ray analysis). After the treatment, nevertheless, the ^{13}C solid-state spectrum (reported in Figure 3c) appears basically unchanged with respect to spectrum 3b both in chemical shifts and in line widths. Therefore, the line broadening in poly((*RS*)-3M1P) must not arise from amorphous regions but can be interpreted as a chemical shift dispersion due to the presence of sequences of monomer units of different chirality.

Moreover, the basically unchanged spectrum of the polymer after thermal degradation confirms the conclusion that the tendency of poly(3M1P) chains to form helical structures strongly persists even when crystallinity is essentially absent. This result is in agreement with the intrinsic tendency of the optically active isotactic poly(α-olefin) chains to form helices, even in dilute solution and in the molten state, previously observed by Pino et al.[8,9]

Finally, the observed resonances of lower intensity in poly((*RS*)-3M1P) at 17.9, 22.8, and 40.6 ppm, which are absent in poly((*S*)-3M1P), must arise from carbons that monitor different intramolecular interactions, due to the presence of *R* units in macromolecules mainly formed of *S* units and vice versa, when the helical structure of the chain remains substantially unchanged. On the basis of semiquantitative conformational considerations (three-bond intramolecular effects),[10] these resonances are those expected for $C_{3'}$, C_4, and C_2, respectively, when the methyl and ethyl groups bonded to the asymmetric C_3 carbon interchange, i.e., when the configuration of C_3 changes from *S* to *R*, the conformation of the helix remaining the one appropriate for the *S* chain, and vice versa. Therefore, these resonances give further qualitative evidence for the low optical purity of the chains and could in principle be used for a quantitative evaluation. However an in-depth quantitative analysis requires completion of a detailed relaxation study.

Experimental Section

Polymerizations were performed at 50 °C for 3 days, using (*S*)- or (*RS*)-3-methyl-1-pentene (4 mL), $TiCl_3$ (3.2 mmol), $Al(CH_3)_3$ (1.7 mmol), and $Zn(CH_3)_2$ (1.4 mmol) in 7 mL of toluene. The yield of poly((*S*)-3M1P) and poly((*RS*)-3M1P) was 1.3 and 1.2 g, respectively.

Polymers were fractionated with boiling solvents as described in the literature.[8] The use of $Zn(CH_3)_2$—which is a fast transfer agent—resulted in regular benzene-soluble fractions. In fact, the solubility results from the low molecular weight of the fractions, rather than from the lack of stereoregularity.

A sample (0.6 g) of benzene-insoluble fraction of highly isotactic poly((*RS*)-3M1P) was thermally degraded under high vacuum about 500 °C, and the degradation products were collected in a trap at liquid nitrogen temperature.

^{13}C NMR spectra of highly isotactic diethyl ether insoluble, benzene-soluble fractions of poly((*RS*)-3M1P) and poly((*S*)-3M1P) were obtained at 140 °C on a Bruker HX-90 spectrometer operating at 22.63 MHz in the PFT mode. The pulse width was 3.6 μs (the pulse width for a 90° pulse is 15 μs). Dwell time of 200 μs was used with 16K of computer memory for the interferogram. Samples were prepared by dissolving the polymers in 1,2,4-trichlorobenzene and by adding 1% of hexamethyldisiloxane (HMDS) as an internal standard. The chemical shifts were converted to the Me_4Si scale.

^{13}C CP/MAS NMR spectra of benzene-insoluble fractions of poly((*RS*)-3M1P) and poly((*S*)-3M1P) and of thermally degraded poly((*RS*)-3M1P) were obtained on a Bruker CXP-300 spectrometer operating at 75.46 MHz, with magic angle rotation speed of 4.3 kHz. Free induction decays were generated by cross-polarization using a single contact pulse of 3 ms per ^1H spin locking and a recycle time of 5 s. The chemical shifts were referred to external Me_4Si.

Acknowledgment. Thanks are due to Dr. H. Forster (Bruker Analytische Messtechnik GMBH) for recording the ^{13}C CP/MAS NMR spectra and to Dr. D. R. Ferro for helpful discussion.

Registry No. Isotactic poly[(*S*)-3-methyl-1-pentene] (homopolymer), 28575-86-2; isotactic poly[(*RS*)-3-methyl-1-pentene] (homopolymer), 88611-18-1.

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Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. 4. Solid-State Spectra of Poly(3-methyl-1-pentene)

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Received April 7, 1983

ABSTRACT: A semiquantitative analysis of the solid-state ^{13}C NMR spectra of poly(3-methyl-1-pentene) is presented. The analysis is based on an empirical scheme for the computation of the chemical shifts of hydrocarbons, which takes into account conformational effects. The calculations provide a structural interpretation of the differences between the spectra of the optically active and the racemic polymers observed by Sacchi et al.[1] The effects of distortions of the helical structure from perfectly staggered conformations are also discussed.

The solid-state ^{13}C NMR spectra of racemic and optically active isotactic poly(3-methyl-1-pentene) ((poly(3M1P), shown schematically in Figure 1) have recently been studied by Sacchi et al.,[1] who also put forward an interpretation of the differences between the resonances observed for the two polymers in terms of the conformational structure of such polymeric chains.

In the present article we show a semiquantitative analysis of the ^{13}C chemical shifts observed by Sacchi et al.,[1] on the basis of an empirical scheme devised in this laboratory[2] for the computation of ^{13}C NMR chemical shifts of hydrocarbons.

Method of Calculation

The method applied here for computing the ^{13}C chemical shifts is a generalization of the well-known formula of Lindeman and Adams,[3] modified in order to account for conformational effects. According to our scheme, the chemical shift of a given carbon atom, characterized by a certain constitutional environment and by a certain average conformational state, can be computed as

$$\nu = \alpha_i + \sum_{j=2}^{4}\sum_{r} P'_{jr}\beta_{ij}(\phi'_r) + \sum_{j=2}^{4}\sum_{k=2}^{4}\sum_{r}\sum_{s} P_{jkrs}\gamma_{ijk}(\phi'_r,\phi_s) + (\delta \text{ effects} + \ldots) \quad (1)$$

where the parameters α_i, β_{ij}, and γ_{ijk} represent additive effects due to substituents in positions α, β, and γ, respectively, with respect to the observed atom C*. The index *i* is the number of carbons bonded to atom C*, the index *j* is the number of carbons bonded to an α carbon, and the index *k* is the number of carbons bonded to a β carbon. Finally the indexes *r* and *s* refer to the rotational states allowed for bonds $C^*–C^\alpha$ and $C^\alpha–C^\beta$, respectively.

The parameters β_{ij} and γ_{ijk} are conformation dependent. Thus the β contribution to the chemical shift of carbon

0024-9297/84/2217-0485$01.50/0