High-Resolution Solid State ^{13}C Nuclear Magnetic Resonance Spectrum of Form I of Syndiotactic Poly(1-butene)

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Introduction

The polymorphism of syndiotactic poly(1-butene) (s-PB) has been recently described.[1] The crystallization of s-PB is a very slow process; indeed by cooling from the melt or by precipitation or casting from polymer solutions, amorphous samples are generally obtained.[1] However, crystallization in form I occurs if amorphous samples are maintained at room temperature for several days.

Form I is characterized by chains in helical conformation of the kind (TTGG)$_2$ with line repetition symmetry $s(2/1)2$ and identity period $c = 7.73$ Å.[1] The chains are packed in an orthorhombic unit cell with $a = 16.81$ Å, $b = 6.06$ Å, and $c = 7.73$ Å.[2] The space group proposed for the limit-ordered structure, in which all the helical chains are isoclined, is $C222_1$.[2] The presence of some degree of disorder corresponding to the departure from the fully isochiral packing of the helices has been suggested.[2]

Form II of s-PB was obtained in oriented fibers of s-PB, drawn at a high draw ratio.[1] It is characterized by chains in helical conformation of the kind ≈TTGG with $s(5/3)2$ symmetry and identity period $c = 20$ Å.[1]

The main feature of the model proposed for the $s(2/1)2$ chain conformation of form I is the "double" gauche conformation of the lateral group.[1] Indeed methyl carbons have been assigned in a gauche arrangement to both neighboring methylene groups on the basis of conformational energy calculations, as well as of a comparison between the X-ray diffraction fiber pattern and the calculated Fourier transform of isolated model chains.[1,3]

In this paper amorphous and crystalline form I samples of s-PB were examined by solid state high-resolution ^{13}C NMR spectroscopy using cross polarization/magic angle spinning (CP-MAS), in order to test the conformational assignment of the lateral groups proposed for the form I.[1−3]

The observed chemical shifts in CP-MAS ^{13}C NMR spectra of solid polymer provide information concerning the conformation of polymer in the crystalline state. Conformationally sensitive γ-gauche effect shielding[4] has been observed in isotactic poly(1-butene) (5) and syndiotactic poly(propylene),[6,7] polystyrene,[8,9] and poly(*p*-methylstyrene).[10]

Experimental Section

The s-PB sample was supplied by Himont Italia. The amount of *rrrr* pentads is 93%. Amorphous sample of s-PB was obtained by compression molding of the as-prepared polymer, while semicrystalline sample in form I was obtained by crystallization of the amorphous sample at room temperature for 2 weeks. X-ray powder diffraction patterns were obtained with an automatic Philips diffractometer using nickel-filtered Cu Kα radiation.

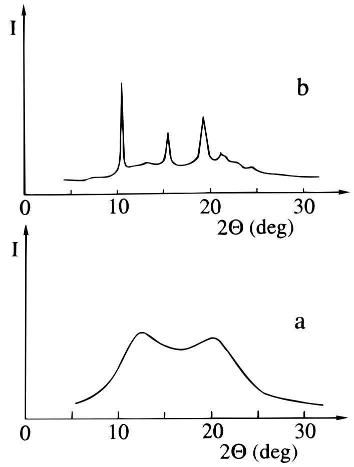

Figure 1. X-ray powder diffraction patterns of amorphous (a) and form I (b) samples of s-PB.

Table 1. Solid State ^{13}C NMR Chemical Shifts (ppm from TMS) of s-PB

	side chain carbons		backbone carbons	
	CH$_3$	CH$_2$	CH	CH$_2$
form I	11.0	27.2	31.4	32.3, 41.4
amorphous	11.9	broad resonance 20−45		

CP-MAS ^{13}C NMR spectra were recorded at room temperature on a AM 250 Brucker spectrometer operating at 62.89 MHz for ^{13}C. The samples (100 mg) were spun in a Zirconia rotor at a speed of 4500 Hz. For each spectrum about 1500 transients were collected using the following acquisition parameters: 3 s delay between pulses, 90° pulse of 5.4 μs, and contact time of 1 ms. Crystalline poly(ethylene) was used as external reference at 33.6 ppm from tetramethylsilane (TMS).

Results and Discussion

The X-ray powder diffraction patterns of amorphous and semicrystalline form I samples of s-PB are reported in Figure 1a,b, respectively. The corresponding CP-MAS ^{13}C NMR spectra are reported in Figure 2a,b, respectively. The assignment of the observed resonances are reported in Table 1.

It is apparent that two resonances of the backbone methylene carbons appear, at $\delta = 32.3$, and 41.4 ppm, in the spectrum of form I (Figure 2b). The total area of these two resonances is about equal to that of the methine carbons at $\delta = 31.4$ ppm. The difference of chemical shift between the two methylene resonances is ≈9 ppm, which corresponds to the shielding effects produced by two γ-gauche effects.[4]

This splitting can be accounted for by considering that the proposed conformation of the chains of s-PB in the form I is an $s(2/1)2$ helix[1,2] (reported in Figure 3), characterized by sequences of torsion angles TTGG. In this helix the backbone methylene carbons are conformationally distinct. The methylene carbons in conformational environments of the backbone of the kind GT•TG (where the dot represent the methylene carbon), those lying along the helix interior, are in a gauche arrangement with both the methine carbons in γ -position, while the methylene carbons in conformational environments of the kind TG•GT, the exterior methylenes, are *trans* to both the methine carbons in γ-position.

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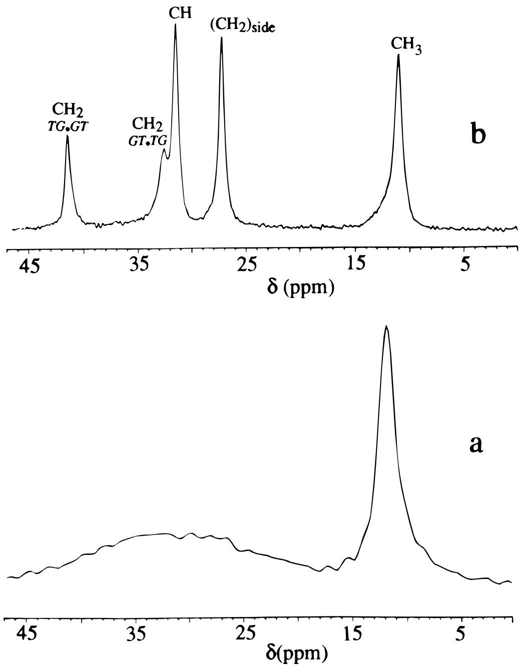


Figure 2. Solid state CP-MAS ^{13}C NMR spectra of amorphous (a) and crystalline form I (b) samples of s-PB.

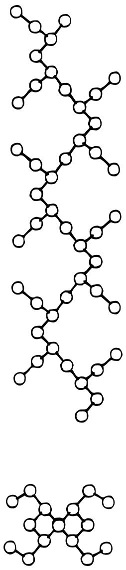
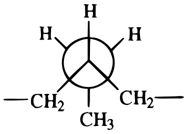


Figure 3. Projections of the chain of s-PB in form I. Views are in a plane containing the chain axis (A) and in a plane perpendicular to the chain axis (B).

It is worth noting that each of the two different kinds of methylene carbons, GT·TG and TG·GT, have two methyl carbons in γ-position, both in gauche arrangement (Figure 3). Hence the resonances of the backbone methylene GT·TG and TG·GT carbons are expected to be separated by two γ-gauche effects (9−10 ppm), as actually found (Figure 2b).

As far as the methyl carbons are concerned, we note that in the spectra of Figure 2 the resonance of the methyl carbons in the crystalline form I is shifted upfield (at $\delta = 11.0$ ppm) with respect to that of the methyl carbons in the amorphous phase (at $\delta = 11.9$ ppm). This difference of chemical shift can be accounted for by the conformation assumed by the side groups in the crystalline state in the form I. As proposed in ref 1, on the basis of conformational energy calculations and comparison between X-ray diffraction fiber patterns and calculated Fourier transforms of isolated model chains, and confirmed in ref 2 by the complete structure determination of form I, the methyl carbons should be in a gauche arrangement to both neighboring backbone methylene carbons (see also Figure 3). The alternative conformation about the $CH-CH_2CH_3$ bond, in which the methyl carbon is gauche to one neighboring methylene carbon and *trans* to the other, may occur in the amorphous phase. The "double" gauche conformation of the side groups in the form I would be expected to move the resonance of the crystalline methyl carbons upfield relative to that of the methyls in the amorphous phase, as observed (Figure 2).



It is worth noting that the contrary occurs in the CP MAS ^{13}C NMR spectra of the amorphous and crystalline forms of isotactic poly(1-butene).[5] As shown in ref 5, the resonance of the methyl carbons of the amorphous sample of isotactic poly(1-butene) (i-PB) is shifted upfield relative to that of the methyls of the crystalline polymorphs. This was explained[5] considering that in the three crystalline forms of i-PB (forms I−III) the lateral groups assume a conformation with the methyl carbon in gauche arrangement to one neighboring methylene carbon and *trans* to the other. The alternative conformation, in which the methyl carbons are gauche to both neighboring methylene carbons, may occur in the amorphous phase and produces the upfield shift of the amorphous methyl resonance.[5] The opposite shift found in the spectra of s-PB confirms the "double" gauche conformation of the side groups in the form I proposed in refs 1−3.

In conclusion, the CP-MAS ^{13}C NMR analysis of form I of s-PB supports the model of refs 1 and 2 for the *s*(2/1)2 chain conformation and the "double" gauche conformation of the side groups.

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References and Notes

(1) De Rosa, C.; Venditto, V.; Guerra, G.; Pirozzi, B.; Corradini, P. *Macromolecules* **1991**, *24*, 5645.
(2) De Rosa, C.; Venditto, V.; Guerra, G.; Corradini, P. *Makromol. Chem.* **1992**, *193*, 1351.
(3) Corradini, P.; De Rosa, C.; Guerra, G.; Pirozzi, B.; Venditto, V. *Gazz. Chim. Ital.* **1992**, *122*, 305.
(4) Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection;* VCH: New York, 1989.
(5) Belfiore, L. A.; Schilling, F. C.; Tonelli, A. E.; Lovinger, A. J.; Bovey, F. A. *Macromolecules* **1984**, *17*, 2561.
(6) Bunn, A.; Cudby, E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *Chem. Commun.* **1981**, 15.
(7) Sozzani, P.; Simonutti, R.; Galimberti, M. *Macromolecules* **1993**, *26*, 5782.
(8) Grassi, A.; Longo, P.; Guerra, G. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 687.
(9) Gomez, M. A.; Tonelli, A. E. *Macromolecules* **1990**, *23*, 3385.
(10) Guerra, G.; Iuliano, M.; Grassi, A.; Rice, D. M.; Karasz, F. E.; Mac Knight, W. J. *Polym. Commun.* **1991**, *32*, 430.

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