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^{13}C CP/MAS NMR Analysis of Isotactic Poly(3-methyl-1-butene)

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Introduction

Isotactic polymers of 1-alkenes CH$_2$=CHR in which R is a branched or cyclic alkyl group can be obtained in the presence of a number of Ziegler−Natta catalyst systems.[1−3]

Remarkably high melting points (e.g., ca. 310 °C for poly(3-methyl-1-butene); 370 °C for poly(vinylcyclohexane); 420 °C for poly(4,4-dimethyl-1-pentene)),[4] coupled with a good thermal stability, make some of these polymers of potential interest for high-temperature applications.

As a part of a structural reinvestigation of this class of poly(1-alkenes), in the present note we report on a solid-state cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR characterization of isotactic poly(3-methyl-1-butene) (from here on, P3MB1).

Results and Discussion

Several X-ray diffraction studies of the crystal structure of P3MB1 have been reported in the literature.[5−8]

A general agreement exists on a 4_1 helical conformation of the chains (Figure 1), whereas different packing models have been proposed. In ref 8, however, all previous suggestions were shown to be inconsistent with the experimental data, which were interpreted instead in terms of a monoclinic unit cell with a = 9.55 Å, b = 17.08 Å, c = 6.8 Å, γ = 116°30′, and space group $P2_1/b$ (Figure 2).

The ^{13}C CP/MAS NMR spectrum of P3MB1 is shown in Figure 3. The resonance assignments (see also Table 1) were easily made by comparison with the solution spectrum.[9] At variance with the latter, however, the two methyl carbon atoms in the monomeric unit (labeled as C4 and C5) are not equivalent and give a doublet, separated by roughly 6 ppm, centered around the chemical shift of the single resonance observed in solution. The slow decay observed for both resonances in a dipolar dephasing experiment (Figure 4) confirmed that they arise from methyl C's.[10]

The nonequivalence of C4 and C5 is fully consistent with the proposed conformation of the polymer chains. Indeed, from Figure 1, showing a projection of the chain along its axis, it can be easily realized that C4 has two methylene carbon atoms in the γ position, one of which (C1) is in a *gauche* arrangement and the other of which (C1′) is in a *trans* arrangement; the same methylene carbon atoms C1 and C1′, on the other hand, are both in a *gauche* arrangement with respect to C5. C4 and C5 are therefore shielded by 1 and 2 γ-*gauche* effect(s), respectively; according to the literature,[11] the resonance of C5 is then expected to occur at 5−6 ppm upfield from that of C4, as actually found.

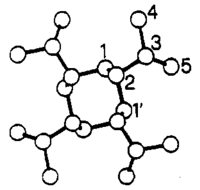

Figure 1. Projection along the chain axis of a chain of P3MB1 in a 4_1 helical conformation.

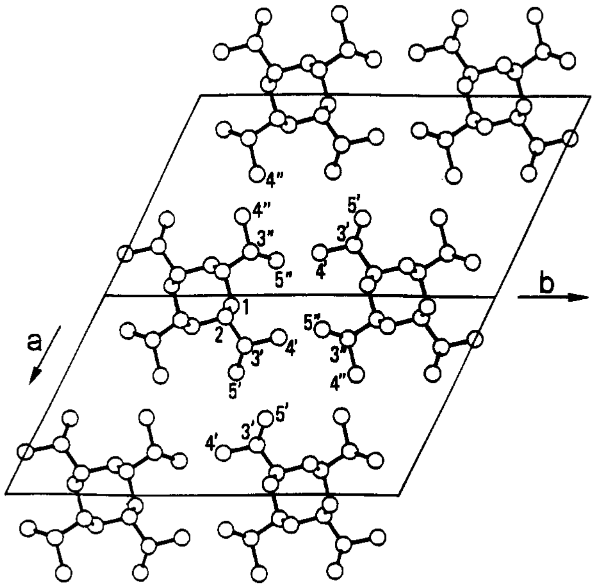

Figure 2. Chain packing model of P3MB1, space group $P2_1/b$, as proposed by Corradini et al.[8]

Table 1. Chemical Shifts of the Resonances Observed in the ^{13}C CP/MAS NMR Spectrum of Figure 3 (for C Atom Labels, Refer to Figure 1)

	δ (ppm from TMS)
methyl C5	15.7, 16.7
methyl C4	23.0
methine C3	28.5, 29.8
methylene C1	32.7
methine C2	40.7

In addition, finer splittings (≈1 ppm) are seen in the CP/MAS spectrum for the resonances of C5 and of the side group tertiary C atom (C3). These should be traced back to packing effects[11,12] and provide a chance of testing the packing model proposed in ref 8 (Figure 2).

As a consequence of the monoclinic symmetry of this model, each chain has two nonequivalent methyl groups of type 5, indicated in Figure 2 as 5′ and 5″. Indeed, methyl 5″ has two critical contact distances with methyls 5″ and 4 of an adjacent chain along b (at 3.6 and 3.54 Å, respectively, according to ref 8), while methyl 5′ has three critical contact distances with methyls 5′ and 4 and with methine 3 of an adjacent chain (at 3.84, 4.15, and 3.85 Å, respectively, again according to ref 8).

Similarly, two nonequivalent methine groups of type 3, having different environments due to the different contact distances with atoms of adjacent chains, can be recognized (3′ and 3″ in Figure 2).

All this accounts well for the splittings of the pertaining resonances.

From Figure 2, nonequivalent methyl groups of type 4 can also be envisaged, but the difference in their chemical environments is quite small. Accordingly, a

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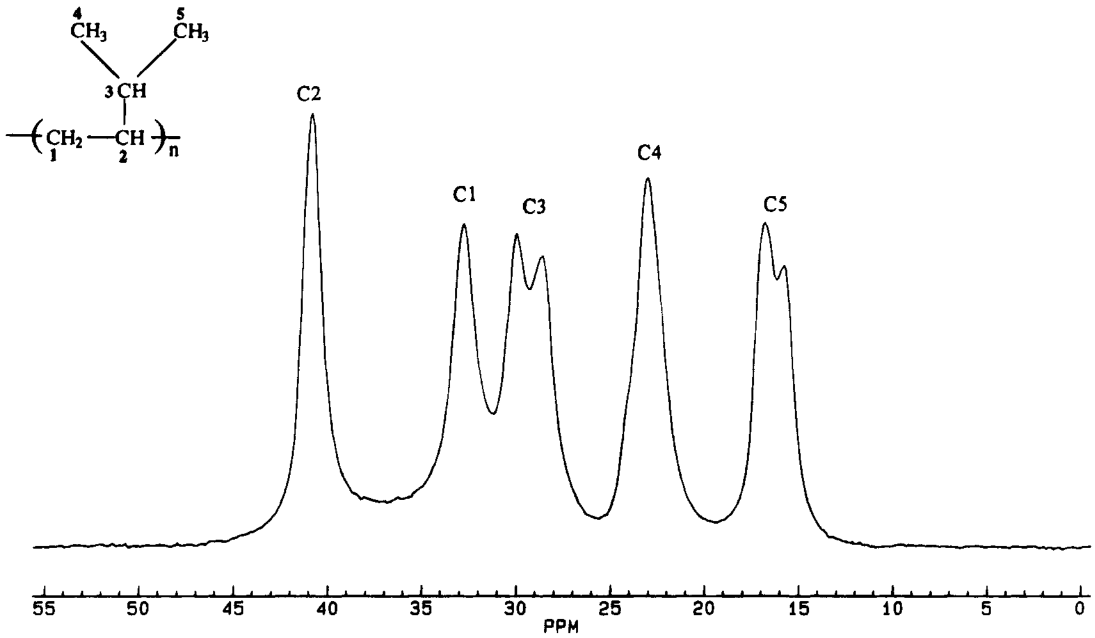

Figure 3. ^{13}C CP/MAS NMR spectrum of P3MB1.

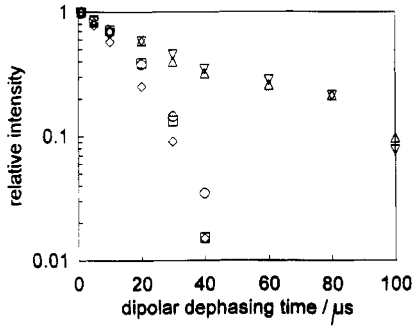

Figure 4. Relative intensities of the resonance lines from C1 (32.7 ppm, ◇), C2 (40.7 ppm, □), C3 (29.8 and 28.5 ppm, ○), C4 (23.0 ppm, △), and C5 (16.7 and 15.7 ppm, ▽) in a ^{13}C CP/MAS dipolar dephasing experiment on P3MB1.

single but broad resonance with a clear downfield shoulder is observed (Figure 3).

In conclusion, the ^{13}C CP/MAS NMR analysis of P3MB1 supports the model of ref 8 for the crystal structure of this polymer. In spite of the 4_1 helical symmetry of the isolated chain, the lower symmetry of the monoclinic lattice accounts for the splittings of the resonances observed in the solid-state ^{13}C NMR spectrum.

Experimental Section

3-Methyl-1-butene was polymerized in a 300-mL magnetically stirred stainless steel reactor (Brignole AU300) in the presence of the catalyst system $TiCl_3$ (Solvay)/$AlMe_3$. Polymerization conditions were as follows: $T = 60$ °C; $TiCl_3$, 300 mg in heptane slurry (80 mL); $AlMe_3$, 0.8 mL; 3-methyl-1-butene, 30 g; polymerization time, 3.5 h; yield, 5 g.

The ^{1}C CP/MAS NMR spectrum of Figure 3 was obtained on an isotropic powder sample using the following parameters: ^{13}C resonance frequency, 75.468 MHz; Hartmann–Hahn and decoupling field strength, 55.5 kHz; MAS frequency, 3 kHz; contact time, 2 ms; recycle delay, 2 s; number of transients, 3350.

For the dipolar dephasing experiment of Figure 4, the same experimental conditions were used with the exception of a decoupling delay of variable length between contact time and acquisition.

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References and Notes

(1) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.
(2) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985.
(3) Corradini, P.; Busico, V.; Guerra, G. In *Comprehensive Polymer Science*; Pergamon Press: Oxford, 1989; Vol. 4, pp 29–50.
(4) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.
(5) Natta, G.; Corradini, P.; Bassi, I. W., *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1955**, *19*, 404.
(6) Turner-Jones, A.; Aizlewood, J. M. *J. Polym. Sci.* **1963**, *B1*, 471.
(7) Huguet, M. G. *Makromol. Chem.* **1966**, *94*, 305.
(8) Corradini, P.; Ganis, P.; Petraccone, V. *Eur. Polym. J.* **1970**, *6*, 281.
(9) Asakura, T.; Nakayama, N. *Polymer Commun.* **1991**, *32*, 213.
(10) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.
(11) Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH: New York, 1989.
(12) See, e.g.: (a) Gomez, M. A.; Tanaka, H.; Tonelli, A. E. *Polymer* **1987**, *28*, 2227. (b) Sozzani, P.; Simonutti, R.; Galimberti, M. *Macromolecules* **1993**, *26*, 5782.

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