Solid-state High-resolution ^{13}C N.m.r. Spectra of Polypropene

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Summary The high-resolution ^{13}C n.m.r. spectra of solid isotactic and syndiotactic polypropene are reported and a novel confirmation of the specific helical nature of syndiotactic polypropene previously deduced from *X*-ray diffraction studies is given.

SCHAEFER and STEJSKAL[1] combined the heteronuclear dipolar-decoupling and cross-polarisation techniques[2] with magic-angle sample rotation[3] to demonstrate that ^{13}C n.m.r. spectra of organic solids could be obtained with high resolution. In this communication we describe some preliminary results from isotactic and syndiotactic polypropene in the solid state. The spectra were obtained using a home-built spectrometer operating at 22·6 MHz for ^{13}C with a magic-angle rotation speed of *ca.* 2·3 kHz.[4,5]

The ^{13}C n.m.r. spectrum of a solid rotor of the α-form[6] of isotactic polypropene showed three resonance peaks assigned to methyl, methine, and methylene carbons (see Table). The chemical shifts differ from those found for the same polymer in the solution state where the molecules are thought to exist as random coils. In contrast, the crystalline regions of isotactic polypropene are known to be composed of regular arrays of helical molecules.[6] The unit cell contains four polymer molecules where each molecule is in the form of a helix having three monomer units per complete turn. *X*-Ray studies showed that the polypropene rotor used in this work was approximately 75% crystalline. However, the total helical content was shown[7] by i.r. spectroscopy to be *ca.* 85%. We believe that the solid-state chemical shifts found for isotactic polypropene are largely dependent on intramolecular effects. Thus, the helical nature of the polymer is more important than the packing of the helices in the crystalline regions in determining the chemical-shift values observed. However, as noted elsewhere,[5] the widths of the resonance lines from the different carbons in isotactic polypropene are not the same. In addition, determination of the spectrum by a pulse sequence in which the ^{13}C contact pulse is delayed by various amounts following the spin-locking of the protons produces considerable changes in these line shapes, even resulting in splittings for certain other, related, polymers. We believe that these observations relate to the fact that a polymer such as isotactic polypropene contains amorphous regions, and that finer details of the crystal structure may lead to structure on the individual resonances from the crystalline region. Future publications will amplify these observations and deal with polyolefins in general.

Figure 1 shows the ^{13}C n.m.r. spectrum of solid syndiotactic polypropene in powder form, packed into a hollow glass rotor.[5] Solution-state ^{1}H n.m.r. spectroscopy at 220 MHz showed the material to be highly syndiotactic (> 95% racemic dyads). The chemical shifts observed for resonances in the solid-state spectrum are significantly different from those obtained in the solution state (see Table) but by far the most important difference between the spectra taken in the two states is the doubling of the methy-

TABLE. The ^{13}C chemical shifts of isotactic and syndiotactic polypropenes in solution and solid states.

Material	δ_C/p.p.m.					
	Methyl		Methylene		Methine	
	Solution[a]	Solid	Solution[a]	Solid	Solution[a]	Solid
Isotactic	21·58	22·5	45·54	44·5	27·86	26·5
Syndiotactic	19·90	21·0	46·14	39·6 and 48·3	27·45	26·8

[a] Since the chemical shifts of polypropene are temperature-dependent,[12] the values quoted are obtained from atactic polypropene, which is soluble in *o*-dichlorobenzene at room temperature, in contrast to the other forms which require considerably elevated temperature to form a solution.

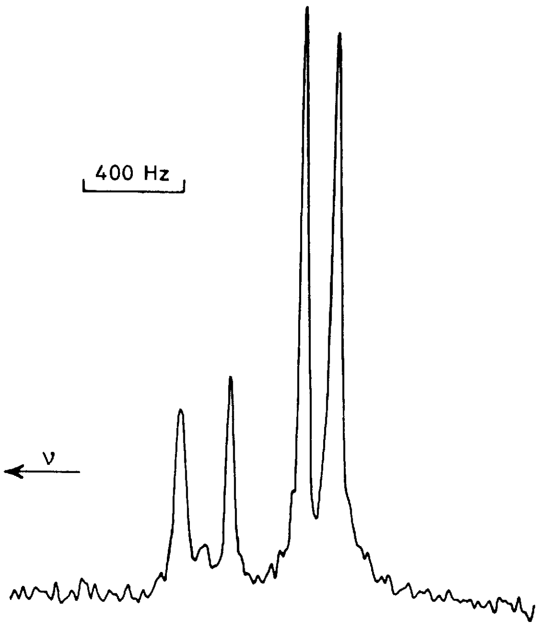

FIGURE 1. The ^{13}C n.m.r. spectrum of *ca.* 70 mg of powdered syndiotactic polypropene at *ca.* 300 K. The spectrum was obtained by co-adding 5×10^4 free-induction decays generated by cross-polarisation using a single contact pulse of 1 ms per ^1H spin-locking and a recycle time of 1 s. Magic-angle rotation at *ca.* 2·3 kHz was employed.

lene carbon resonance in the solid-state spectrum. The magnitude of the chemical-shift difference between the two methylene peaks is a larger effect than has been reported for any other polymer system.[8,9] We suggest that the reason for the two methylene resonances in the solid-state spectrum of syndiotactic polypropene lies in the conformation of the polymer molecule in the solid. Corradini *et al.* suggested from *X*-ray diffraction studies that the conformation of syndiotactic polypropene is an involuted helix having the appearance of a figure-of-eight when viewed down the helix axis[10] (Figure 2). Examination of this structure shows that there are two equally probable, distinct, sites for methylene carbons, one lying on the axis of the helix (numbers 4 and 8 in Figure 2), the other on the periphery of the helix (2 and 6 in Figure 2), whereas there are only single sites for methine and methyl carbons. The number of peaks in the spectrum is therefore consistent with this structure. The chemical-shift difference of 8·7 ± 0·5 p.p.m. observed between the two methylene-carbon resonances is considered to arise largely from 3-bond interactions (the γ-effect).[11] The internal methylene carbons (4 and 8 in Figure 2) have two *gauche* γ-carbons, whereas the outer methylenes (2 and 6 in Figure 2) have two *trans* γ-carbons. Recently published data[12] indicate that the *γ-gauche* shielding effect in polypropene is *ca.* 4 p.p.m. Our measurements give a value of 4·4 p.p.m. for this effect, assuming it to be the dominant cause of the observed splitting. If the γ-effect is the cause of the difference in the chemical shift of the two methylene resonances then the resonance at $\delta_C = 39{\cdot}6$ p.p.m. is assigned to the internal methylene carbons (4 and 8 in Figure 2). In support of this, the other methylene resonance at 48·3 p.p.m. is broader than that at 39·6 p.p.m., and shows evidence of asymmetry and even splitting under higher scale-expansion. As noted above we believe that such effects may arise from details of the solid-state structure related, at least in part, to interchain effects and it would be reasonable that those atoms on the periphery of the helical chain would be more subject to such perturbations.

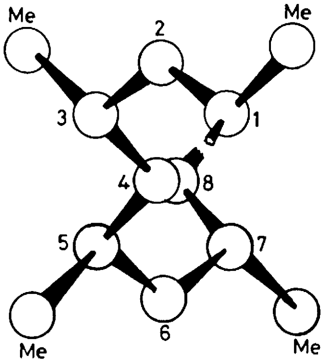

FIGURE 2. A view of the conformation of syndiotactic polypropene, according to Corradini *et al.*,[10] looking down the helix axis. The backbone methine and methylene carbons are numbered sequentially for clarity with the methyl carbons labelled Me. The two non-equivalent sites for the methylene carbons are clear, being typified by atoms 2 and 6, and 4 and 8 respectively.

We feel that the major features of these spectra are explicable in terms of the known structures and γ-shielding effects, and it should be noted that, on such a basis, the resonance arising from the methylene carbon in α-isotactic polypropene should occur at a chemical shift midway between those for the two different methylenes of the syndiotactic form. This is indeed the case and confirms that the main effects determining the chemical shifts are intramolecular in origin. The question of the finer structure of the resonance lines will be pursued in more detail elsewhere.

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