# High-resolution solid-state $^{13}C$ nuclear magnetic resonance study of isotactic polypropylene polymorphs

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*(Received 11 May 1987; accepted 8 June 1987)*

High-resolution $^{13}C$ nuclear magnetic resonance spectra are reported for three solid samples of isotactic polypropylene (i-PP): (i) the α-crystalline form (monoclinic), (ii) the β-crystalline form (hexagonal), and (iii) the mesomorphic or smectic form of i-PP. These spectra were obtained using magic angle spinning, high-power proton dipolar-decoupling and cross-polarization techniques, and for the β- and smectic forms of i-PP constitute the first reported high-resolution solid-state spectra. The spectrum of the α-crystalline form shows well resolved splittings (1 ppm) of the methyl and methylene carbon resonances, as was reported previously by Bunn *et al.* These splittings are absent in the spectra observed for the β- and smectic forms of i-PP. Based on a comparison of the chemical shifts and $T_1$ relaxation times observed for the carbon resonances in these three forms of solid i-PP, we reach the following conclusions: (i) i-PP adopts the same $3_1$ helical conformation in each crystalline polymorph, (ii) the packing of i-PP helices in the β-form crystal is closer to the more distant of the two interhelical packings in the α-crystalline form, and (iii) the local packings of $3_1$ helices are very similar in the β- and smectic forms of i-PP.

**(Keywords: isotactic polypropylene polymorphs; $^{13}C$ n.m.r.; crystalline chain packing)**

## INTRODUCTION

Isotactic polypropylene (i-PP) is a stereoregular vinyl polymer that normally develops significant crystallinity below 200°C. The thermodynamically stable crystalline form, or α-form, consists of i-PP chains in the $3_1$ helical conformation (...*tgtgtg*...) packed in a monoclinic unit cell[1,2]. It is believed that left- and right-handed helices are in close proximity. The metastable β-form crystals of i-PP contain hexagonally packed $3_1$ helical chains, which are thought[2,3] to be arranged in groups of the same helical handedness (left or right) resulting in the distant packing of left- and right-handed chains.

The smectic form of i-PP is believed[1,4-10] to be only partially ordered compared to the α- and β-crystalline forms, though the i-PP chains in the smectic form remain in the $3_1$ helical conformation[1,4]. Smectic i-PP is therefore primarily disordered in the intermolecular packing of its chains.

It was the purpose of the present investigation to learn more about the structures of the crystalline regions in the α-, β- and smectic forms of i-PP. High-resolution $^{13}C$ n.m.r. spectroscopy of solid polymers[11-16] has revealed a sensitivity of the observed spectra to the microstructures of the polymer chains in the solid, including their intramolecular conformations and modes of interchain packings. Here we report the results of our investigation of three crystalline forms of i-PP using high-resolution $^{13}C$ n.m.r. as a structural probe.

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## EXPERIMENTAL

### *Sample preparation and characterization*

Isotactic PP in the smectic form was made by cryogenic grinding of a Hercules Profax-6523 i-PP sample[17] as described by Lovinger *et al.*[18] The α-form i-PP was obtained from the smectic sample by annealing for 1 h at 160°C. The β-form sample was made[19] by unidirectional crystallization at a growth rate of $10\,\mu m\,min^{-1}$ with a temperature gradient of $300°C\,cm^{-1}$.

X-ray diffractograms of all three i-PP samples were recorded before and after the $^{13}C$ n.m.r. experiments to ensure that the high-speed (3 kHz) magic angle spinning of the samples did not induce any solid–solid transitions. A Rigaku diffractometer at $1°\ (2\theta)\,min^{-1}$ under Ni-filtered Cu $K_\alpha$ irradiation was employed in the X-ray diffraction measurements.

Differential scanning calorimetry (d.s.c.) was used to estimate the crystallinity of our samples. A Perkin–Elmer DSC-4 instrument was employed at heating rates of 10 and $40°C\,min^{-1}$.

### *N.m.r. measurements*

$^{13}C$ n.m.r. spectra were recorded at ambient temperature on a Varian XL-200 spectrometer operating at a static field of 4.7 T. Magic angle sample spinning (MAS) at speeds of ~3 kHz was achieved with a Doty Scientific probe, which utilizes a double air bearing design. Isotactic PP samples were spun in aluminium oxide rotors with Kel-F (poly(chlorotrifluoroethylene)) end caps.

A 45 kHz r.f. field strength was used for dipolar

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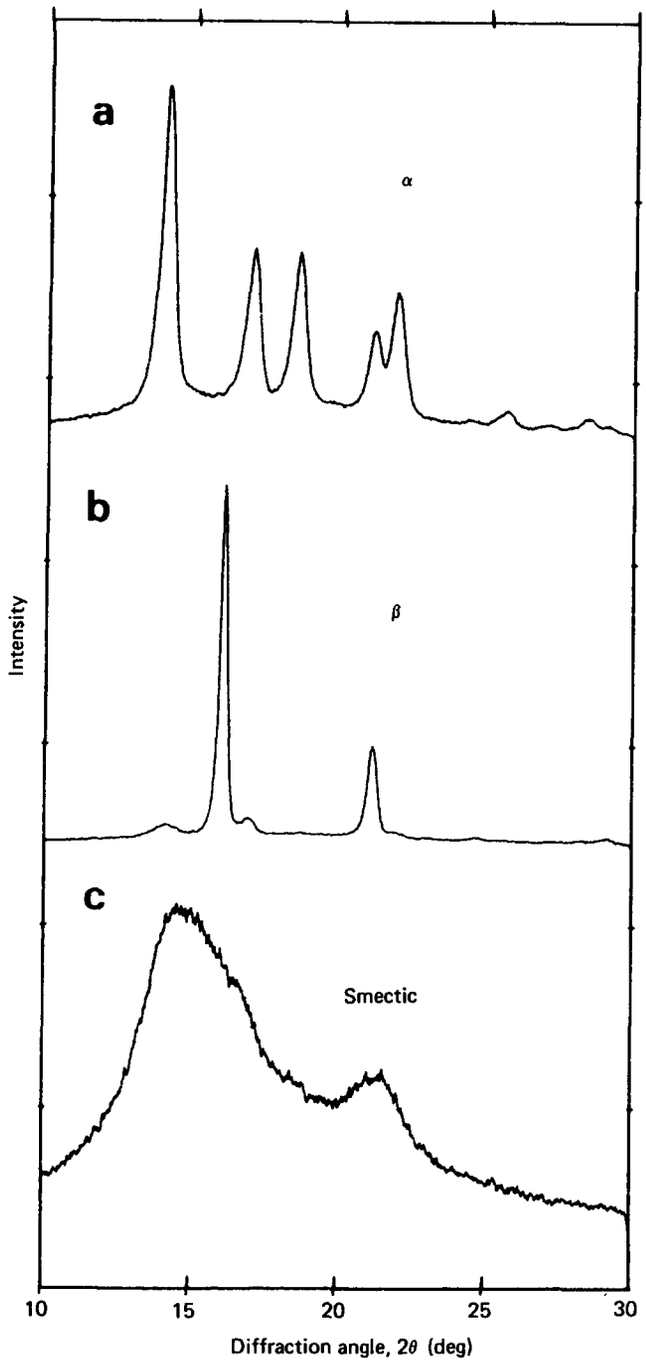


**Figure 1** X-ray diffractograms of i-PP at 24°C in (a) α-form, (b) β-form and (c) smectic-form crystalline states

decoupling (DD), with a decoupling period of 200 ms. The optimal cross-polarization (CP) contact times for the methine and methylene carbons and for the methyl carbon were found to be 1000 μs and 3000 μs, respectively, and the former value was employed.

No attempt was made to record the absolute chemical shifts of the observed resonances. Instead spectra of all three i-PP samples were recorded consecutively on the same day without adjustment of the magnetic field. Relative chemical shifts were obtained by direct comparison of the spectra and were confirmed by recording the spectra of mixtures of the i-PP samples. The most upfield resonance of each carbon type was assigned a chemical shift of 0 ppm, and the chemical shifts of the remaining resonances were referred to these most shielded resonances.

Spin–lattice relaxation times, $T_1$, were measured for each carbon in all three i-PP samples under the CP condition by application of the pulse sequence developed by Torchia[20]. In addition, the usual inversion–recovery method[21,22] for obtaining $T_1$ was employed without CP, but with DD, to estimate the $T_1$ values of the amorphous carbons.

## RESULTS

### *X-ray and d.s.c. characterization of i-PP samples*

The diffractograms of our i-PP samples are presented in *Figure 1*. The α-form i-PP has a monoclinic unit cell[1], with a measured fibre period of 6.5 Å. Five strong reflections at $2\theta = 14.0$ (1 1 0), 16.8 (0 4 0), 18.6 (1 3 0), 21.1 (1 1 1) and 21.7° ($\bar{1}$ 3 1, 0 4 1) characterize its diffractogram. The β-form i-PP is arranged in a hexagonal unit cell[1-3] with a similar assumed $3_1$ helical fibre period. Its diffractogram is dominated by two strong reflections at $2\theta = 16.1$ (3 0 0) and 21.2° (3 0 1). Two diffuse reflections centred at $2\theta = 15.2$ and 21.3° are characteristic of our smectic i-PP sample, where the individual chains are also believed[1,4] to assume the $3_1$ helical conformation.

The relative proportion of α- and β-form present in our β-form sample of i-PP was estimated from the X-ray diffractogram (see *Figure 1b*) by comparison of the heights of the three strong equatorial α-form peaks with the strong β-form peak (3 0 0)[3,23]. On this basis, 90% of the crystallinity in our β-form sample of i-PP is of the β-form.

The calorimetric measurements are summarized in *Table 1*, where the melting temperatures and endotherms are presented for each i-PP sample. Degrees of crystallinity were estimated by comparing the observed melting enthalpies to those presented in the literature[24,25] for the completely crystalline polymorphs obtained via extrapolation.

A heating rate of 40°C min$^{-1}$ was used specifically for our β-form sample to avoid recrystallization to the α-form[25]. An intermediate value of the enthalpy of fusion[24] was chosen from the wide range of values reported in the literature for α-form i-PP. Only a single enthalpy of fusion has been reported[25] for β-form i-PP.

No enthalpy of fusion has been detected for the smectic form (see *Figure 2c*), only a recrystallization to the α-form accompanied by a small exotherm and followed by the melting of the newly created α-form crystals. In our estimation of the percentage crystallinity for the smectic-

**Table 1** Calorimetric properties of i-PP crystalline modifications

| i-PP sample | Heating rate (°C min$^{-1}$) | $T_m$ (°C) | $H_{obs}$ (cal g$^{-1}$) | $H_f^a$ (cal g$^{-1}$) | Crystallinity (%) |
|---|---|---|---|---|---|
| α-form | 10 | 169.7 | 24.0 | 50.0 | 48 |
| | 40 | 176.0 | 23.3 | 50.0 | 47 |
| β-form | 40 | 160.7 | 24.2 | 46.1 | 53 |
| smectic form | 10 | 162[b] | 18.5[b] | 50.0 | 37 |
| | 40 | 165.8[b] | 18.4[b] | 50.0 | 37 |

[a] Obtained from refs. 24 and 25

[b] Melting temperatures and enthalpies of the α-form crystals that result from the conversion of the ordered smectic chains upon heating (see *Figure 2*)

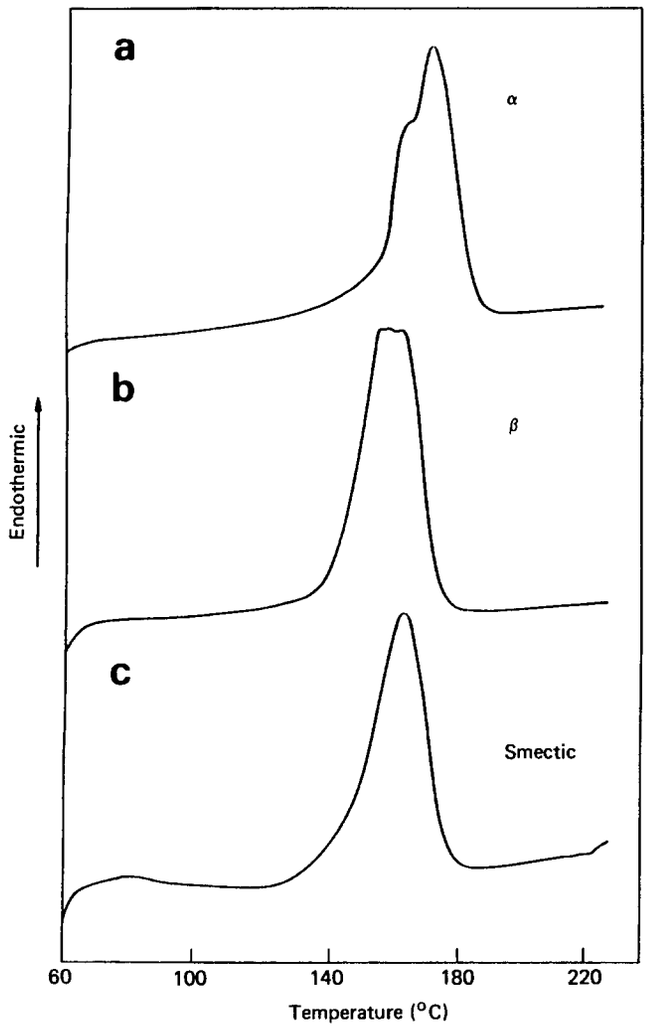


**Figure 2** D.s.c. scans at 40°C $min^{-1}$ for i-PP (a) α-form, (b) β-form and (c) smectic-form

form sample, we have assumed that all of the α-form crystals that are produced in the heating of this sample are a result of the exclusive conversion of the ordered smectic chains and do not result from the amorphous portions of the sample.

### $^{13}C$ n.m.r. spectra

*Figure 3* presents the CPMAS/DD spectra of the three forms of i-PP recorded at ambient temperature. Spectra obtained without CP are presented in *Figure 4*. *Table 2* contains the observed solid-state $^{13}C$ n.m.r. chemical shifts. $^{13}C$ spin–lattice relaxation times, $T_1$, measured in the solid state at ambient temperature, are given in *Table 3*. In addition, the $T_1$ values measured[22] for i-PP in solution are also presented in *Table 3* for comparison.

## DISCUSSION

A comparison of the CPMAS $^{13}C$ n.m.r. spectra in *Figure 3* and the relative chemical shifts presented in *Table 2* lead to several observations. First, both the methylene and methyl carbon resonances in α-form i-PP are split by ~1 ppm, as first reported by Bunn *et al.*[14] The ratio of intensities of the downfield to the upfield component is ~2:1 for both carbon types. Bunn *et al.*[14] interpreted this splitting as due to the inequivalent sites, A and B, produced by pairing of helices of opposite handedness[1] (see *Figure 5a*), which are also present in the ratio A:B=2:1. Note that the A sites correspond to a separation of 5.28 Å between helical axes, while for the B sites the helices are 6.14 Å apart.

In the spectrum of β-form i-PP (see *Figure 3b*), on the other hand, each carbon exhibits a single resonance. The β-form methylene and methyl resonances are close to the upfield member of each pair of the same resonances in the α-form, which were attributed to the B sites (see *Table 2*). *Figure 5b* indicates the interchain packing proposed[2] for β-form i-PP. Unlike the α-form packing[1], $3_1$ i-PP helices of the same handedness are packed together in groups in the β-form crystals. The interhelical separation[3] is 6.36 Å, very similar to the smallest interhelical separation involving the B sites of α-form crystals. Thus, the near-coincidence of the $^{13}C$ chemical shifts in β-form i-PP with those corresponding to the B sites in the α-form can be understood on the basis of similar interhelical separations in both packing modifications.

At this point it should be mentioned that Bunn *et al.*[14] have also reported the $^{13}C$ n.m.r. CPMAS spectrum of β-form i-PP. They found, in opposition to our results, that the chemical shifts of the A site methylene and methyl carbon resonances in α-form i-PP were closer than the B

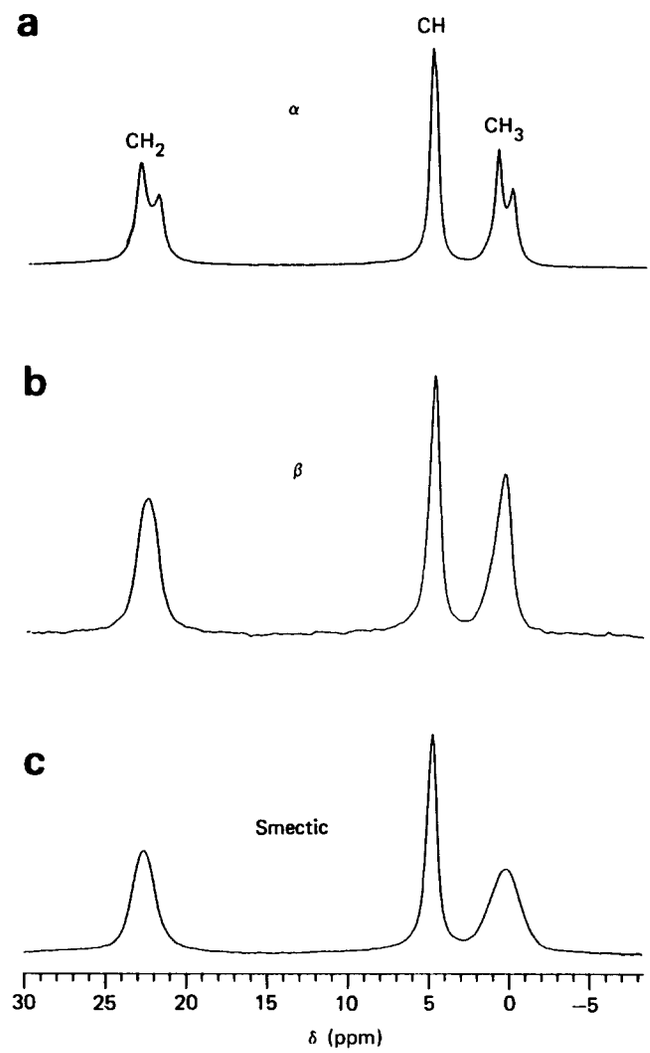


**Figure 3** CPMAS spectra of i-PP in (a) α-form, (b) β-form and (c) smectic form. Spectra were recorded at ambient temperature with no reference employed

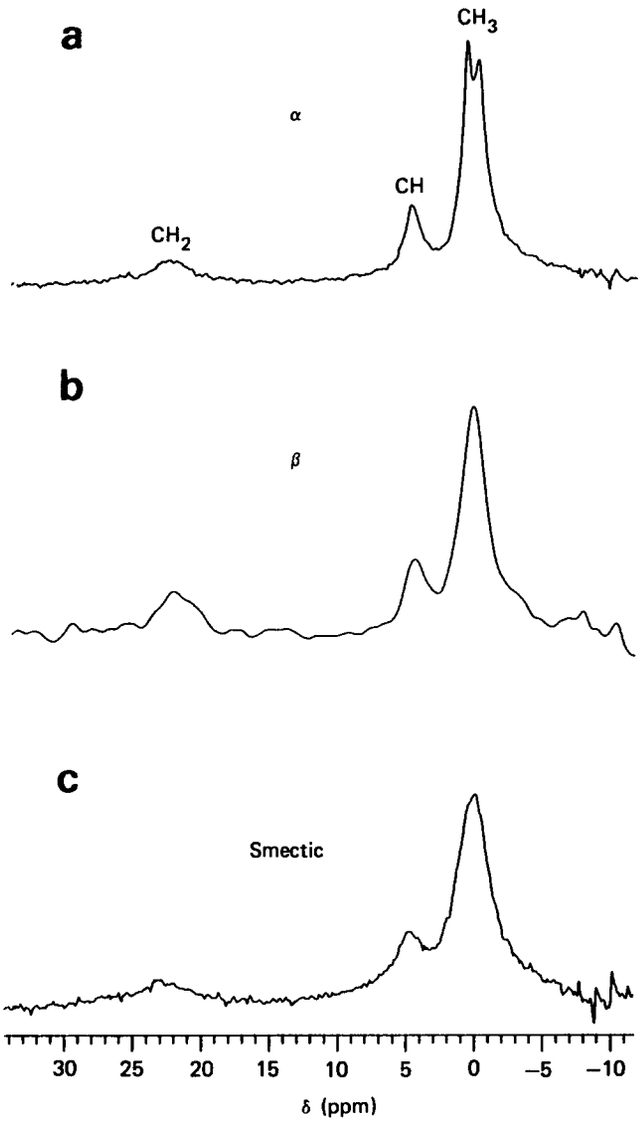


**Figure 4** MAS/DD spectra of i-PP in (a) α-form, (b) β-form and (c) smectic form. Spectra were recorded at ambient temperature with no reference employed

**Table 2** $^{13}C$ n.m.r. chemical shifts (ppm)[a] for i-PP in the solid state

| i-PP | $CH_2$ | CH | $CH_3$ |
|---|---|---|---|
| α-form | 0, 1.07 | 0.20 | 0, 0.88 |
| β-form | 0.37 | 0.02 | 0.27 |
| smectic form | 0.47 | 0 | 0.08 |

[a] $^{13}C$ n.m.r. chemical shifts observed at ambient temperature and referenced to the most upfield resonance of each carbon type

site resonances to those observed in their β-form i-PP. We were unable to obtain β-form i-PP following their preparation method, a finding confirmed by X-ray diffraction. The difficulties in obtaining pure β-form i-PP exclusively via thermal treatment is noted in the literature[2,19,26,27]. Instead special nucleating agents[28,29] or unidirectional crystallization[19] are employed. Consequently, Bunn *et al.*[14] may not have studied i-PP in the pure β-form.

$^{13}C$ n.m.r. chemical shifts recorded for the smectic form of i-PP are nearly coincident with those found for the β-form. This finding suggests that the local packing of $3_1$ i-PP helices in the smectic form closely resembles that found in the β-form.

Having concluded that the local packing of chains is similar in the β- and smectic forms of i-PP, based on their observed $^{13}C$ chemical shifts, let us look at the spin-lattice

**Table 3** $^{13}C$ $T_1$ relaxation times for solid i-PP at ambient temperature

| | $T_1$ (s) | | |
|---|---|---|---|
| i-PP | CH | $CH_2$ | $CH_3$ |
| α-form | 37[a] | 52[a] | 0.32[a], 0.80[a], 0.48[b] |
| β-form | 29[a] | 34[a] | 0.75[a], 0.44[b] |
| smectic form | 22[a] | 33[a] | 0.75[a], 0.51[b] |
| solution[c] | 0.40[b] | 0.20[b] | 0.75[b] |

[a] Measured with CP using the pulse method of Torchia[20]
[b] Measured by inversion–recovery[21] without CP
[c] Measured in solution at 46°C by Randall[22] using the inversion–recovery method[21]

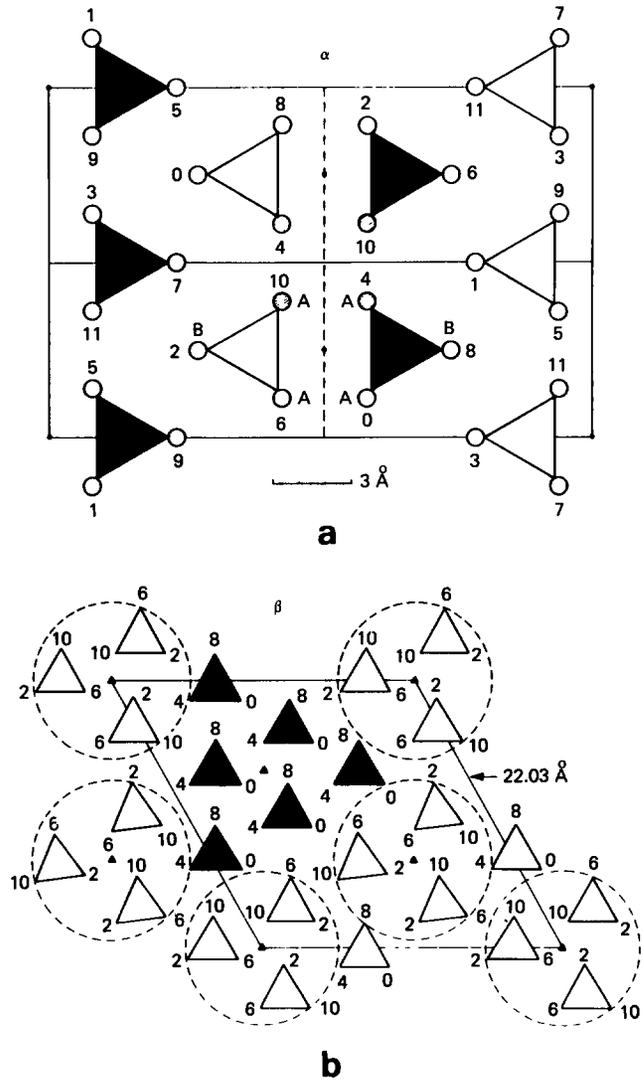


**Figure 5** Crystal structures of (a) α-form[1] and (b) β-form[2] of i-PP. Full (RH) and open (LH) triangles indicate $3_1$ helical i-PP chains of different handedness. A and B label the inequivalent sites discussed in the text, and are applicable to all three carbon types, because the $CH–CH_2$ bond is nearly parallel with the *c*-axis. Numerals at the triangle vertices indicate heights of methyl groups above a plane perpendicular to the *c*-axis in twelfths of *c*. The circles at the triangle vertices in (a) correspond to methyl carbons, and the cross-hatched and stippled pairs of circles correspond to the enmeshed A site methyls

relaxation time ($T_1$) behaviour of the carbon nuclei in the three polymorphs of i-PP. The $T_1$ relaxation times of the crystalline carbons were obtained while cross-polarizing using the Torchia[20] pulse sequence. Smectic-form i-PP $T_1$ values (see *Table 3*) are very similar to those measured for the $\beta$-form crystals, while the $\alpha$-form $T_1$ values appear unique. The $T_1$ values reported previously for $\alpha$-form i-PP by Fleming *et al.*[12] are in good agreement with the values shown in *Table 3*.

The $T_1$ values obtained by the inversion–recovery method[21] are dominated by the relaxation of the amorphous carbons and are obtained without CP. As expected from the spectra obtained without CP (see *Figure 4*) only the $T_1$ of the methyl carbons are obtained by this method, and, within experimental error, they are the same for all three i-PP polymorphs. In addition, the $T_1$ values measured for the methyl carbons in the crystals and in solution are similar to the amorphous methyl spin–lattice relaxation times. Clearly the spin–lattice relaxation times of methyl carbons are dominated by their internal rotations and not by the segmental motions of the i-PP chains.

The two methyl resonances observed in the CPMAS spectrum of $\alpha$-form i-PP (see *Figure 3a*) relax at different rates with $T_1 = 0.43$ and 0.80 s for the downfield and upfield peaks, respectively. Having identified these resonances with the A and B packing sites in the $\alpha$-form crystalline lattice (see *Figure 5a*), it is worth mentioning that both the $\beta$- and smectic form crystalline methyls have $T_1 = 0.75$ s in agreement with the $T_1$ of the $\alpha$-form, B site methyl carbons. This observation supports the conclusion, obtained previously from a comparison of $^{13}C$ chemical shifts, that the interhelical separation of chains is similar for the B sites in $\alpha$-form crystals and in the $\beta$- and smectic-form i-PP crystals.

It is interesting that the $\alpha$-form methyl carbons associated with the A and B packing sites exhibit $T_1$ relaxation times different by almost a factor of 2. The B site methyls are rotating twice as fast as the enmeshed methyl carbons at the A sites, because they are apparently on the fast side of the $T_1$ minimum[12].

The results of our solid-state $^{13}C$ n.m.r. studies of the three polymorphs of i-PP are consistent with several known structural features of the $\alpha$- and $\beta$-form crystals and permit us to infer the local chain packing structure in the smectic form. Both the $^{13}C$ chemical shifts and spin–lattice relaxation times observed for the smectic-form carbons indicate that the packing of their $3_1$ helices is similar (at least on a very local scale) to the packing of i-PP chains in the $\beta$-form crystals.

This conclusion is consistent with the proposal of Gailey and Ralston[6] who suggested that smectic-form i-PP is composed of small (50–100 Å) hexagonal or $\beta$-form crystals. Suggestions that the smectic form is composed of monoclinic, or $\alpha$-form, microcrystals made by Bodor *et al.*[7], or a smectic form packing characterized locally by a core of $\alpha$ structure surrounded by chains in a pseudohexagonal arrangement made by Corradini *et al.*[8], are not consistent with the results of our $^{13}C$ n.m.r. study. Also the suggestion made by Miller[9] and Zannetti *et al.*[10] that $\alpha$-form paracrystallinity (distortions of the monoclinic lattice with loss of long-range order) characterizes the structure of smectic-form i-PP is not supported by our results.

As noted earlier, our smectic-form sample of i-PP did not exhibit a melting endotherm. Instead, a small exotherm was observed (see *Figure 2c*), indicating recrystallization to the $\alpha$-form, which subsequently melted. Unlike the transformation of $\beta$-form to $\alpha$-form crystals which proceeds via the molten state[2,27], the conversion of smectic to $\alpha$-form crystals is a solid–solid transition in agreement with the results of Zannetti *et al.*[10,30]

Our $^{13}C$ n.m.r. results, both chemical shifts and $T_1$ values, indicate similar local packings of $3_1$ helical chains in the smectic and $\beta$-form crystals. If the $3_1$ helices in the smectic-form crystals are packed in groups of the same handedness (see *Figure 5b*) as has been suggested[2] for the $\beta$-form crystals, then how can transformation to the $\alpha$-form crystals, where helices of opposite handedness are packed together (see *Figure 5a*), proceed without passing through the melt as is observed in the $\beta$ to $\alpha$ transition?

Zannetti *et al.*[10,30] suggest an unwinding and rewinding of $3_1$ helical portions of the smectic-form chains which result in an intramolecular mechanism for the smectic to $\alpha$ transition. We suggest an alternative explanation which also seems consistent with the $^{13}C$ n.m.r. results. Suppose the chains in smectic-form i-PP are packed with $3_1$ helices of the opposite handedness together as in the $\alpha$-form crystals, but without the enmeshing of methyl groups as in the A sites of the $\alpha$-crystals (see *Figure 5a*). Instead all the local packing arrangements in the smectic form might be characterized by interhelical distances comparable to the $\alpha$-form B sites, which our $^{13}C$ n.m.r. studies indicate to be the case also for the $\beta$-form helices.

In this model the transformation of smectic to $\alpha$-form would only require modest rotations and translations about and along the $3_1$ helical axes. This would be a predominantly intramolecular transformation, as suggested by Zannetti *et al.*[10,30], but would not require the unwinding and rewinding of portions of the $3_1$ helices, which we find difficult to envision.

We believe that our report on the study of the local structural environments in the three crystalline modifications of i-PP by $^{13}C$ n.m.r. has demonstrated the utility of this approach. CPMAS $^{13}C$ n.m.r. investigations of solid polymers appear to be uniquely suited to the study of their structures and dynamics.

## ACKNOWLEDGEMENTS

We are grateful to A. J. Lovinger for providing a sample of $\beta$-form i-PP, to F. C. Schilling for helpful discussions and characterization of the Profax i-PP by solution $^{13}C$ n.m.r. and to P. A. Mirau for programming the Torchia $T_1$ pulse sequence on our spectrometer.

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