High resolution ^{13}C n.m.r. spectra of solid isotactic polypropylene

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The high-resolution ^{13}C n.m.r. spectra of three samples of solid isotactic polypropylene are reported. The spectra, obtained under conditions of proton dipolar-decoupling and fast magic-angle rotation and using cross-polarization, are of annealed and quenched samples of the α-crystalline form and of a sample of the β-crystalline form. Attention is drawn to the importance of knowing the proton relaxation characteristics in these experiments and some illustrative proton $T_{1\rho}$ data are given. The ^{13}C n.m.r. spectrum of the annealed sample of the α-crystalline form shows well-resolved splittings of the methyl and methylene resonances in a 2:1 intensity ratio. These splittings are interpreted in terms of the crystal structure of the α-form as suggested by X-ray diffraction. Quenching the α-form causes significant changes in the spectrum including a loss of resolution of the splittings obtained from the annealed sample. The β-form shows broad symmetrical resonances for the methyl and methylene carbons. The chemical shifts and other spectral features are discussed in the light of the proposed crystal structures and the effects likely to be produced by quenching.

Keywords Solids; polymers; polypropylene; structure; polymorphism; nuclear magnetic resonance

INTRODUCTION

In a previous communication concerning the high-resolution ^{13}C n.m.r. spectroscopy of solid polypropylene[1] it was indicated that a more detailed examination of the spectra of the solid isotactic form was in progress. This paper reports the results of this further investigation and concerns the dependence of the solid-state spectra on the history of the physical treatment of the sample and the relationship of these spectra to the structure of the crystalline regions of the materials.

EXPERIMENTAL

N.m.r. measurements

The high-resolution ^{13}C spectra were obtained using a purpose-built spectrometer which operates at 22.63 MHz for ^{13}C (90 MHz, ^{1}H). The usual spin-locked cross-polarization method was used for generating the ^{13}C signals[2]. Cross-polarization was generally carried out with r.f. field strengths of 40 kHz whilst the proton-dipolar decoupling field strength used was 60 kHz. Magic-angle sample rotation speeds of the order of 2 kHz were employed and were achieved using the device described elsewhere[3]. Some of the spectra reported here contain features whose chemical shift differences are of the order of 0.5 ppm and in order to observe such features reproducibly, it was found necessary to use decoupling fields of at least 60 kHz and to pay careful attention to setting the magic-angle and to shimming of the static field. To this end a rotor filled with water and spinning slowly at the magic-angle was used to adjust the field inhomogeneity. It is of some interest to note that the normal high-resolution shim coils used in electromagnets and defined on the assumption of y-axis spinning[4] are not entirely satisfactory for samples rotating in the xz plane at the magic angle.

The spectrometer frequencies were calibrated regularly using a static sample of liquid tetramethylsilane as a reference for both ^{1}H and ^{13}C. It is clearly impossible to avoid the problems of bulk-susceptibility shifts in the study of n.m.r. of solids as the use of external chemical shift references is the only means of calibration. For the samples investigated in this paper these effects are likely to be small as they were all the same chemical species and were all examined as rolled thin films in identical rotors. However, in general, care must be taken in making comparisons of chemical shifts from one sample to another.

In order to optimize the experimental conditions used in obtaining the ^{13}C spectra *via* cross-polarization it is our normal practice to determine the proton spin-lattice relaxation times in both laboratory and rotating frames. A detailed study of these relaxation processes for the polypropylene samples used in the work is under way but certain features are relevant to the interpretation of the ^{13}C spectra and so details of these measurements follow. These relaxation processes have been measured at a proton resonance frequency of 60 MHz using a home-built pulsed n.m.r. spectrometer. T_1 was measured using the 180–τ–90 pulse sequence whilst the $T_{1\rho}$ behaviour was investigated using the spin-locking sequence[5]. A spin-locking field strength of 1mT (10 gauss ≡ 40 kHz) was used which is the same as the r.f. field strength used for the cross-polarization experiments. Since the ^{1}H $T_{1\rho}$

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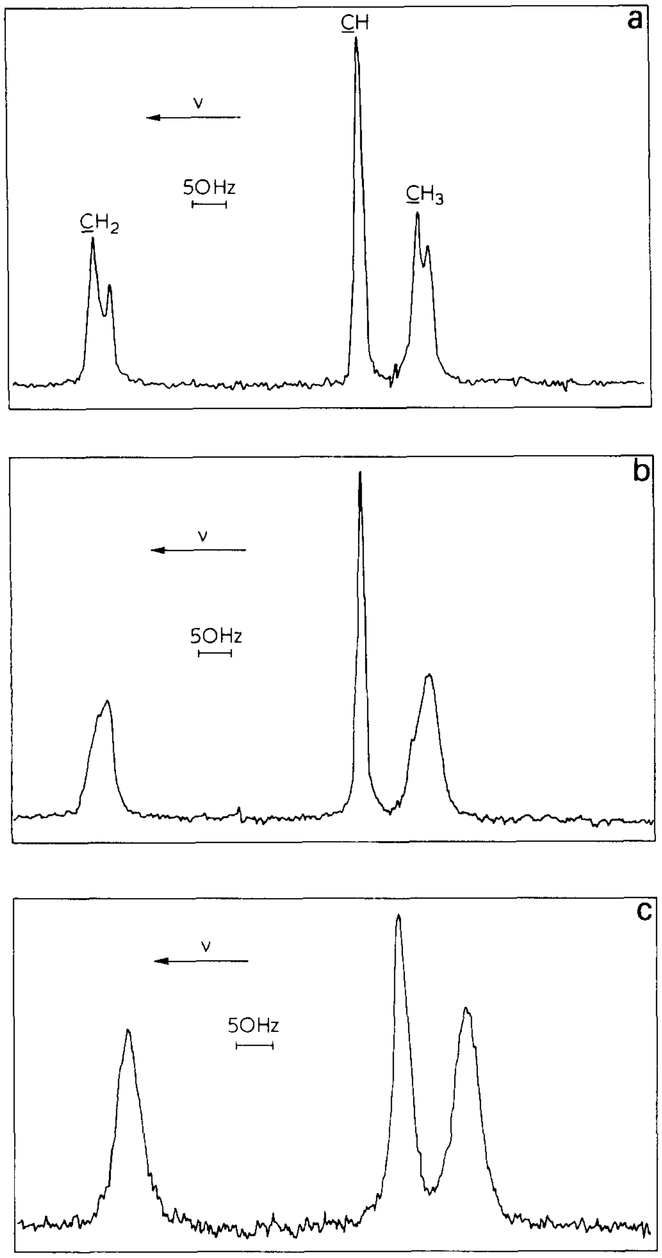

Figure 1 ^{13}C high-resolution n.m.r. spectra of various forms of solid isotactic polypropylene. The spectra were obtained as described in the experimental section with a cross-polarization contact time of 5 ms, a recycle time of 3 s and are the result of 4000 transients recorded with quadrature detection, a dwell time of 500 μs, an acquisition time of 256 ms and a filter bandwidth of 500 Hz. (a) The annealed α-form; (b) the quenched α-form and (c) the β-form

behaviour in these materials is dominated by low-frequency motions, the difference in spectrometer operating frequency for the relaxation and cross-polarization measurements (60 MHz and 90 MHz respectively) is unlikely to be significant.

Sample preparation

The polymer used in this investigation was a commercially available grade of polypropylene, manufactured by ICI Ltd., having a melt-flow index of 20. It had an isotactic content in excess of 97% as determined by proton magnetic resonance in solution from the racemic diad concentration[6]. For all samples the polymer was initially fabricated as a thin film in order to facilitate rapid quenching and other procedures required to prepare the desired samples.

Three samples were prepared as follows: (i) an annealed sample of the α form, obtained by maintaining the film at a temperature of 433K for 60 min; (ii) a quenched sample of the α form obtained by rapidly cooling from the melt (at a temperature higher than 503K) by immersion in ice/water followed by rapid reheating to 373K and subsequent cooling to ambient temperature to remove any of the smectic form, and (iii) a sample of the β form, obtained by rapid cooling from a melt temperature between 463K and 503K to a temperature between 373K and 393K. The final samples, in the form of thin films, were rolled into tight cylindrical rolls and inserted into 5 mm o.d. glass or machined Macor rotors. Typical sample weights were of the order of 50 mg. All measurements were made at ambient probe temperature.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C n.m.r. spectra of the three samples investigated and gives the exact experimental conditions under which they were obtained. The major features of these spectra which are of note are (i) the observation for the annealed α form of well-resolved splittings of the resonance absorptions in the spectral regions associated with the methyl and methylene carbons; (ii) the reduced resolution of such splittings and the change in the intensity distributions in these regions for the quenched α form; (iii) the symmetrical lineshapes for these resonance absorptions in the β form, and (iv) the relative chemical shifts of solution and solid samples.

Table 1 summarizes the chemical shifts of the main peaks in the solid and solution state spectra.

Before discussing the features outlined above, it is worth considering the influence the experimental techniques used may have on the spectra. Of particular importance is the fact that many polymers are heterogeneous[7]. In the case of polypropylene, for example it is generally accepted that it consists structurally of organized or crystalline regions separated by regions which are less dense and less organized, usually referred to as amorphous. The relative dimensions of these regions may be altered by various physical treatments. From the point of view of ^{13}C n.m.r. spectra, in which the signal is generated by polarization transfer from protons, this structural heterogeneity may have a significant effect. For example, the proton magnetic resonance spectrum of the annealed sample of α-isotactic polypropylene at room temperature consists of a broad line, which accounts for the major part of the intensity, and a narrow line which is no more than 10% of the intensity. Investigation of the relaxation of the spin-locked proton magnetization of this sample revealed a decay which required a minimum of

Table 1 The observed ^{13}C chemical shifts (ppm from external TMS; relative shifts accurate to ±0.1 ppm) of the principal features in the n.m.r. spectra of various solid samples of polypropylene

Sample	CH_2	CH	CH_3
α-Crystalline	45.2 44.2	26.8	22.6 22.1
α-Quenched	44.2	26.8	22.1
β-Crystalline	45.0	27.1	22.9

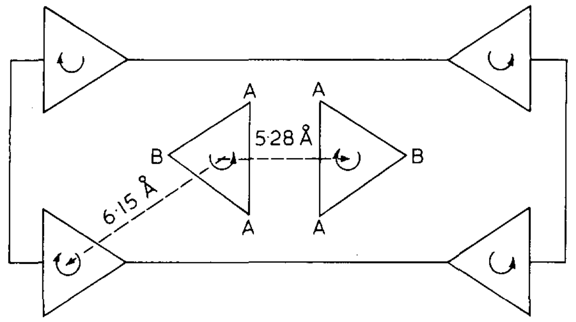

Figure 2 Structure of the α-form of solid isotactic polypropylene as determined by X-ray diffraction[8,9]. The figure shows a projection perpendicular to the molecular axis. The triangles represent the isotactic polypropylene molecules which have a 3 : 1 helical conformation. The arrows represent the handedness of each helix. The labels A and B identify the inequivalent sites discussed in the text which, because the CH—CH_2 bond is almost parallel with the *c*-axis[8], are applicable to all three types of carbon site, i.e. methyl, methine and methylene. It should be noted that the structure consists of paired helices of opposite handedness with their centre-to-centre separation of 5.28 Å substantially less than the separation from other helices

three exponential processes for its description. Treated as a three-component decay, the relative intensities and relaxation times were 48% with $T_{1\rho} = 108$ ms; 25% with $T_{1\rho} = 15$ ms and 27% with $T_{1\rho} = 0.83$ ms. In addition it was shown that the narrow line in the spectrum was associated with the fastest $T_{1\rho}$ process, although clearly not accounting for all of it. The proton spin-lattice relaxation, however, was found to be indistinguishable from a single exponential process ($T_1 \simeq 700$ ms). These observations are consistent with a heterogeneous structure which, in its simplest form, can be considered to have three different environments in which the molecular motions, and, hence, relaxation times, differ. These different environments must have dimensions which are in the right range to allow spin-diffusion to average the T_1's but not the (shorter) $T_{1\rho}$ values[7]. This type of behaviour is well recognized but its implications for cross-polarization have not been given much attention. In the case of the annealed sample we find that to a good approximation we are only generating ^{13}C n.m.r. signal intensity from those carbons associated with the two longer proton $T_{1\rho}$'s and the broader parts of the proton spectrum. This is almost certainly some fraction of the more crystalline part of the material since efficient cross-polarization requires a strong, near-static dipolar coupling between ^{13}C and ^{1}H spins which is most likely to exist in the more rigid crystalline regions. These in turn would be expected to give the broadest ^{1}H spectrum which, we have shown, is associated with the longer $T_{1\rho}$ components. To illustrate the subtle effects which can arise, we mention the fact that the quenched sample of the α-form shows somewhat different proton $T_{1\rho}$ behaviour and we are presently investigating the quantitative aspects of this problem and its relevance to cross-polarization.

The α- and β-crystalline forms

Isotactic polypropylene is known to adopt a helical conformation in the solid with three monomer units per turn (i.e. a 3:1 helix). The various crystalline modifications of polypropylene have been extensively studied[8,9], and *Figure 2* indicates the present view of the arrangement of the helical molecules in the crystalline region of the α form. The view shown is a projection along the helix axis with the corners of the triangles representing the positions of the methyl groups in the 3:1 helix. The circular arrows indicate the handedness of the individual helices. The probability of both left- and right-handed helices being present is real and indeed it is considered that in the α-form the most likely structure contains left and right handed pairs in close proximity as indicated in *Figure 2*. It is considered that these pairs of helices are able to form a closer association because of the ability of left and right handed 'screws' to enmesh. It is evident in this structure that two distinct environments for the monomer unit exist as a result of this interaction between helices of opposite handedness and these are identified in *Figure 2* by the labels A and B. Each corner of the triangles representing the helical polypropylene chains in *Figure 2* can be equated in symmetry terms to the positions of all three carbon atoms of a monomer unit[8] and thus we would expect all three ^{13}C resonance lines to be split into two lines with relative intensities 2:1. As can be seen from *Figure 1a* the spectrum of the annealed sample of the α-isotactic form shows resolved splittings for the methyl and methylene carbons. In addition, careful investigation of the methine carbon resonance indicates the presence of an asymmetric lineshape consistent with the existence of an unresolved splitting of the order of 3 Hz with an intensity distribution in the same sense as those seen for the resonances of the methyl and methylene carbons. Since the form and origin of the lineshapes for the component lines in each spectral region is not known, it is not possible to make an unambiguous deconvolution of the bands to obtain accurate relative areas for the individual lines. However, the appearance of the methylene band, for example, is not inconsistent with a 2:1 intensity distribution, assuming the individual linewidths to be similar. In addition, when the spectra were obtained as a function of contact time, it was found that although the methyl, methine and methylene bands cross-polarized at different rates, as would be expected[10], the intensities within a given band cross-polarized at the same rate. This indicates a similar local environment for the two lines which therefore cannot be assigned individually to amorphous and crystalline components. We therefore assign the lines to the inequivalent sites in the crystal structure, as discussed above. These splittings, all of the order of 1 ppm or less, should be compared with the large splitting of 8.7 ppm we reported for the methylene carbon ^{13}C resonance in syndiotactic polypropylene[1]. In that case the splitting was identified as arising from two inequivalent sites for the methylene carbon intrinsic to the conformation adopted by this form of polypropylene, and its magnitude was explained in terms of a 3-bond intramolecular effect (the γ-effect). The smaller size of the spectral splittings observed for α-isotactic polypropylene is consistent with their being intermolecular in origin as suggested above. *Figure 2* shows that the centre-to-centre distance of the enmeshed pairs of helical chains is 5.28 Å compared with the corresponding smallest distance of 6.15 Å between helices in different pairs. These splittings are thus further examples of crystallographic inequivalences in solid-state n.m.r. spectroscopy[11]. The fact that the methyl and methylene splittings are of similar magnitude whereas that of the methine is an order of magnitude smaller presumably arises from the fact that

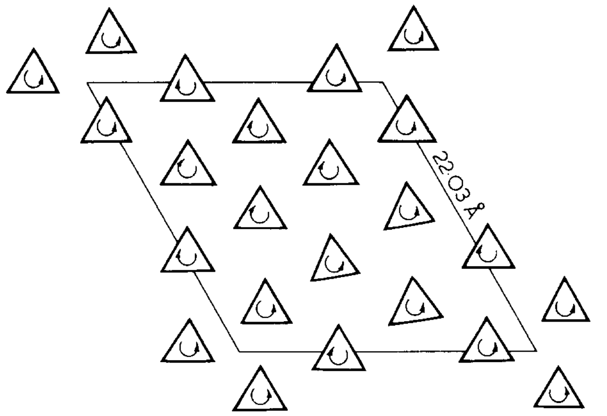

Figure 3 Structure of the β-form of isotactic polypropylene as proposed from X-ray diffraction[9]. The conventions used are as for *Figure 2*. Note the absence of any pairing of helical chains of opposite handedness and the rotation of the three molecules in the bottom right of the unit cell with respect to the others

this carbon is shielded from intermolecular effects by its methyl substitution. In solution state ^{13}C n.m.r. it is well known that tacticity effects on the methine resonance of polypropylene are much smaller than those observed for the other carbons[12].

The β form of isotactic polypropylene is also considered to consist of helices with the same 3:1 character as in the α-form. However X-ray diffraction studies indicate that it differs in the way the helices are packed together in the crystalline regions. *Figure 3* illustrates the proposed structure of the β-form as deduced from X-ray studies[9]. As can be seen, the proposed structure indicates the presence of left- and right-handed helices arranged in groups of the same handedness. This arrangement does not allow the close approach of pairs of helices as found in the structure of the α-form. It is to be expected, therefore, that interchain interactions may well be less in the β form, and this probably accounts for the absence of any resolvable splittings in the spectrum of this form. The structure shown in *Figure 3* implies the existence of inequivalent sites but, because of the relatively large centre-to-centre separation of the helices in this structure, any splittings arising from such effects would be expected to be small. It is perhaps significant however that the methyl carbon resonance is broader than the methylene or methine resonances in the spectrum of the β form, which would be expected if a number of unresolved splittings existed since the methyl groups, being on the outside of the helices, would be the most affected by neighbouring chains which are not capable of enmeshing as in the α form.

Quenched α form

The spectrum of this sample differed considerably from that of the annealed sample. The main changes observed were (i) a shift in the frequencies of the maximum peak intensities in the methyl and methylene regions to coincide with those of the lower intensity lines in these regions for the annealed sample and (ii) an apparent lowering of resolution in that the splittings, whilst still discernible, only appear as shoulders. As noted above, the proton $T_{1\rho}$ behaviour shows some differences from that of the annealed sample. The relaxation is still three-component but the proportions and particularly the relaxation times of the components are different. Simple quantitative considerations show that it is not possible to explain the changes in the ^{13}C spectra by assuming that somehow the spectrum of the amorphous region has now been added by comparison with that of the annealed sample. On this basis it is clear that there has been a transfer of resonance intensity to the chemical shift characteristic of the outer, less perturbed, methyl/methylene environments of *Figure 2*. X-ray diffraction data on quenched polypropylene show broader reflections and intensity changes in comparison with annealed samples but confirm that it is still basically in the α-form. The usual interpretation of these X-ray observations is to suggest a wider range of positions for the helical molecules in the unit cell and/or that the crystal size and perfection is much reduced. Since the n.m.r. data indicate that the environment of the methyl and methylene groups is less distinct, indeed that the resonance frequency favoured is that assigned to the outer position in the 'enmeshed' pair of helices, it is considered that these pairs of helices are more separated in the quenched state to give a more open structure. Whether this may be thought of in terms of trapped defects in the structure, e.g. helices which are translated with respect to each other or similar effects, is not easily decided.

Chemical shift differences

In addition to the obvious differences between the α and β forms of polypropylene referred to, close examination of the comparative chemical shift values reveals interesting differences. Again, because of the external referencing procedures one must exercise caution in making comparisons but there are clearly significant relative differences as the figures in *Table 1* show. For example, the methyl resonance in the β form is close to or slightly to high frequency of the methyl line of relative intensity 2 in the α-form whilst the methylene resonance falls between the two in the α-form. These small differences could arise from a number of effects. Firstly, the exact distances between the chains are different in the two structures, which could lead to small shift differences. Secondly, it is possible that the proximity of the internal methyl groups in the enmeshed pairs causes distortion which could also lead to small chemical shift differences. Calculations performed on the measured X-ray data for the α form[13] show that there are probably two minor changes in the positioning of the internal methyl groups due to the way in which helices traverse the unit cell as discussed by Wunderlich[14]. In principle then, it is possible that there is a further, unresolved splitting on the higher intensity methyl resonance of the α-form.

CONCLUSIONS

The information obtained from the ^{13}C high-resolution spectrum of solid isotactic polypropylene demonstrates the potential of this method for the investigation of the details of molecular structure in the solid state. Not only may intramolecular effects be seen in terms of chemical shifts but intermolecular effects also clearly give rise to subtle changes in both signal intensities and chemical shifts. Thus, it has been demonstrated that different morphologies give rise to recognizably different spectra, enabling the n.m.r. technique to distinguish between the α and β crystalline forms of isotactic polypropylene.

Changes in the packing of molecules, which arise when less perfect crystals are formed, for example in quenched samples, can be detected, and the concept of more open helical pairs in the quenched form has been proposed to explain these changes whilst the unit cell configuration is still retained.

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