Vibrational spectroscopic study of structural changes in isotactic polypropylene below the melting point

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Some 30°C below the melting point in annealed samples of highly crystalline polypropylene, considerable changes occur in the coefficient of linear expansion and in a wide variety of temperature derivatives of spectroscopic features. It is shown that these changes are athermal and therefore are not attributable to premelting as has been suggested in the past.

INTRODUCTION

The mid-infra-red spectrum of isotactic polypropylene (IPP) has been studied in detail by several workers[1-4] and there is general agreement on the various assignments. The spectrum is devoid of features that can be classified as 'crystallinity bands', that is vibrations which arise from correlation splitting resulting from a three-dimensionally ordered structure[2]. Only the far-infra-red spectrum appears to contain features specific to intermolecular vibrations[5].

However, there are a number of bands in the infra-red spectrum of IPP that are dependent on the conformations of the individual chains. These are commonly designated 'regularity' bands[2] and result from vibrations of those sections of the chain which have the 3_1 helical structure. Regularity bands should therefore disappear on sample melting, when all but the shortest helices are thought to be destroyed. On this basis, the regularity bands in the IPP spectrum occur at 809, 841, 900 and 1220 cm^{-1}, together with the one at 998 cm^{-1} which weakens considerably in the melt. Although the band at 973 cm^{-1} has part of its origin in the helical structures it also contains a component specific for chains in disordered regions having an irregular conformation[6].

Studies on propylene–ethylene and propylene–deuteropropylene copolymers covering a range of compositions have shown that these regularity bands only appear for minimum helical sequence lengths. Kishin and Rishina[7] studied a range of propylene–perdeuteropropylene copolymers and concluded that the minimum n value for the appearance of the 841 cm^{-1} band lies in the range 10–14, whereas the value for the 998 cm^{-1} band is 10 or 11. They also found a value of 4 for the 973 cm^{-1} band, which is not specific for regularity.

Miyamoto and Inagaki[8] prepared polymers containing short helical IPP segments by the thermal degradation of conventional IPP, followed by hydrogenation to eliminate the unsaturated end groups also formed. They found that the 998 cm^{-1} band is still present when the sequence length falls to 10 units. Finally, Kobayashi et al.[9] also examined random propylene–deuteropropylene copolymers, using 1,1,2-trideuteropropylene as the comonomer. They concluded that only the 841 and 998 cm^{-1} bands remain for sequence lengths as short as 10, the other regularity bands having disappeared. These various results are in sensible concordance. They show that as n is increased, the first band to appear is at 998 cm^{-1}, for an n value within the range 5–10, followed by the one at 841 cm^{-1}, for $n \sim 13$. The remainder of the regularity bands are associated with longer sequences, for which n is at least 15.

Zichy[10] has obtained evidence relating to minimum sequence lengths by a different approach. She followed the band intensity changes that occur when IPP specimens are uniaxially stretched to various draw ratios in the range 2 to 7.3. She concluded that the minimum sequence length necessary for the appearance of a particular regularity band increases in the order 1256, 900, 998, 841, 809 and 1220 cm^{-1}, a finding that is in reasonable agreement with the results of the copolymer studies noted above. In that the regularity bands disappear in the molten phase, or weaken very considerably in the case of the one at 998 cm^{-1}, it is of interest to measure their intensity as a function of temperature, particularly in the region approaching the melting range. It may then be possible to discern difference behaviours for the various regularity bands, which, in view of their association with different helical sequence lengths, could provide information on structural changes below the melting point. The results of such a study are now reported.

EXPERIMENTAL

Two samples, supplied by the Petrochemicals and Plastics Division of ICI, were used for the study. Both had isotactic contents of 98%, determined by ^{13}C n.m.r. spectroscopy, and both contained 1.1% of material soluble in boiling n-heptane during a 48 h extraction period. They were prepared for infra-red spectroscopy examination by hot pressing into thin films at 185°C. The films so obtained were either allowed to cool slowly to ambient temperature, or quenched in ice–water and then annealed at 160°C for 10 min.

Samples of widely differing thermal history were prepared by the following methods. Sample A was quenched from 230°C into ice–water, to produce the smectic form, in which the polymer chains have the usual 3_1 helical structure but there is disorder in the packing of the chains[11]. However, the helical content is approximately 70%[12]. Sample B was also quenched in ice–water from 230°C, but was then heated to 100°C and allowed to cool to ambient temperature, giving a material of relatively low crystallinity. Sample C was pressed at 220°C, cooled, then reheated to 160°C and cooled slowly back to ambient temperature, to give a material of rather greater crystallinity. The crystallinities of these samples, deduced from their densities, were A non-crystalline, B 50% and C 69%.

The infra-red spectra were measured between ambient temperature and 160°C at $2 cm^{-1}$ resolution over the range 700–1800 cm^{-1}, using a Nicolet MX-1 FTIR spectrometer and a variable-temperature cell. The absence of bands at 1715 cm^{-1} (C=O) and 1640 cm^{-1} (C=C) is indicative of insignificant amounts of degradation products[13] consequent upon the pressing and annealing operations. Although it would have been preferable to measure band areas as a function of temperature, to allow for possible changes in band half-widths, the considerable overlap that occurs between some of the bands examined precludes this approach in most cases. Hence, peak absorbances, measured from suitable baselines, were obtained for the majority of the bands.

Raman spectra were run on a Coderg T800 Raman spectrometer at temperatures between ambient and 160°C. The 514.5 nm line from an argon ion laser was used for excitation, with 100 mW of power at the sample. A fixed spectral range could be selected with a computerized iterative scanning facility, to obtain spectra with good signal-to-noise ratios over time periods that minimized the degradation at higher temperatures. The samples were examined as small cylinders, moulded at 185°C and then allowed to cool to ambient temperature.

Measurements of linear dimension as a function of temperature were made over the temperature range 60 to 160°C using rectangular specimens with rounded ends, moulded at 185°C and allowed to cool to ambient temperature. Marks were made, approximately 4 cm apart, on the long direction of the specimens. Each sample was placed in an oven, on a PTFE-coated surface to reduce friction, and the length was determined by measuring between the marked points with a travelling microscope. The temperature was monitored with a thermocouple in contact with the specimen. At the beginning of each series of measurements, the sample was annealed for 20 min at 160°C. Its length was determined at this ceiling temperature, and then at a series of temperatures decreasing by steps of approximately

5°C down to 60°C. The cycle was then repeated in the direction of increasing temperature.

The ^1H decoupled ^{13}C spectra obtained from polymer as a solid at room temperature through to the melt were run on a JEOL FX-100 spectrometer fitted with a heated sample accessory capable of maintaining (to 1°C) any selected temperature in the range ambient to 180°C. A 9 μs pulse width was used, with a 1 s interval between pulses. Each scan comprised 8000 data points and the accumulation of 100 scans provided a satisfactory signal-to-noise ratio.

RESULTS

Infra-red spectroscopy

The results of the measurements have been evaluated in terms of plots of peak absorbance as a function of temperature for the regularity bands at 809, 841, 900, 998, 1168 and 1220 cm^{-1} and also, for comparison, for the non-regularity bands at 973 and 1256 cm^{-1}. *Figure 1* shows the plots for the bands at 900, 973 and 1220 cm^{-1}, and these are typical of the results as a whole. In the case of the two regularity bands there is a linear decrease of absorbance with increasing temperature, to about 130°C, beyond which the absorbance decreases much more rapidly. In contrast, there is a linear decrease of absorbance with increasing temperature over the whole range studied in the case of the non-regularity band at 973 cm^{-1}. These two types of behaviour are found for all the bands belonging to the respective categories. To investigate reversibility, the spectra were recorded as the
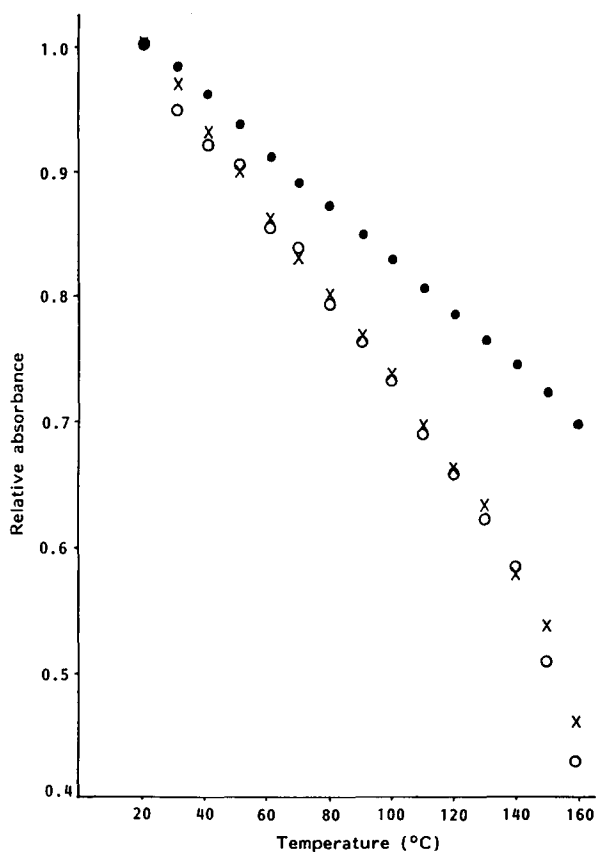

Figure 1 Temperature dependence of the infra-red bands near (×) 900, (●) 973 and (○) 1220 cm^{-1} in isotactic polypropylene

Table 1 Transition temperatures and temperature coefficients of absorbance determined from various bands in the infra-red spectrum of isotactic polypropylene

Band position (cm^{-1})	Transition temperature, T_t (°C)	$\left(\dfrac{dA}{dT}\right)_{T<T_t}$	$\left(\dfrac{dA}{dT}\right)_{T>T_t}$	Difference in slope
809	137±2	−0.0022	−0.0061	−0.0039
841	138±2	−0.0031	−0.0076	−0.0045
900	133±3	−0.0033	−0.0066	−0.0033
973	–		−0.0027	–
998	136±2	−0.0038	−0.0064	−0.0026
1168	137±2	−0.0027	−0.0056	−0.0029
1220	139±3	−0.0034	−0.0082	−0.0048
1256	136±2	−0.0024	−0.0059	−0.0035

temperature was cycled between 100 and 155°C twice. Cooling and heating data were similar and repeated on the second cycle.

It is possible to interpret the absorbance–temperature plots in rather more detail, by two approaches. The first is to determine the temperature at which the deviation from linearity commences; this temperature may well represent the point at which a helix of a particular length begins to shorten as the result of thermally induced perturbations and it may therefore be regarded as a transition temperature. It is not particularly easy to judge the point at which non-linearity occurs, but an apparent transition temperature, which proves very useful for comparative purposes, may be determined readily by ascertaining the temperature value at which the straight line drawn through the absorbance values over the linear region intersects with the best straight line through the absorbance values above this temperature value. It is clear that this approach will yield apparent transition temperatures marginally higher than the true values; nevertheless, this semiempirical approach has proved convenient and reproducible. The values so obtained for the various regularity bands are given in *Table 1*.

The second approach to the more detailed interpretation of the absorbance–temperature plots is to determine the fractional change of absorbance between the apparent transition temperature and the ceiling temperature of 160°C. Given that the decrease in the absorbance above the transition temperature is the consequence of the destruction of helices of a particular length, the fractional change in absorbance should relate directly to the concentration of those that have disappeared. Temperature coefficients of absorbance below and above the transition temperature have been obtained, from the absorbance–temperature plots, and are given in *Table 1*. In contrast to the transition temperature values, where the differences do not exceed the estimated experimental errors, the temperature coefficients of absorbance, both below and above the transition temperature, show a spread of some 50%. The results for the two polypropylene samples did not differ significantly, as is also the case between extracted and non-extracted materials, and between quench cooled and slowly cooled samples. Although samples A, B and C, with differing thermal histories, showed some differences in their spectra at ambient temperature that are indicative of a greater relative content of short helices in the poorly crystalline sample A, they behaved similarly when examined at elevated temperatures.

Raman spectroscopy

Although the quality of the Raman spectra obtained was not particularly good, because of background fluorescence which was only partially eliminated by 'burning out', the results are useful because they confirm those obtained by infra-red spectroscopy. This is particularly the case with the strongest peaks, those at 812, 844, 1001 and 1222 cm^{-1}, where there is a marked change of slope in the intensity *versus* T plot at a transition temperature of about 135°C. The change in intensity as a function of temperature follows a similar order to that already noted in the case of the infra-red bands, being greatest for the Raman bands at 1001, 901 and 1222 cm^{-1}.

Linear dimensions

The linear dimension as a function of temperature is shown in *Figure 2*. It is proportional to temperature over the range 65 to 130°C; above this latter temperature, the linear dimension increases more rapidly as a function of temperature. Because of the curvature of this plot above
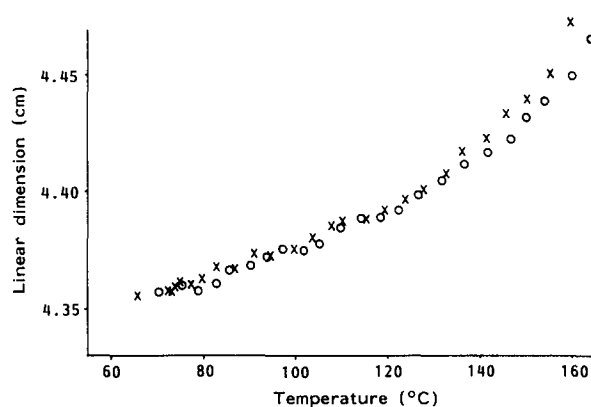
Figure 2 The variation of linear dimensions with temperature in isotactic polypropylene: (×) decreasing temperature; (○) increasing temperature
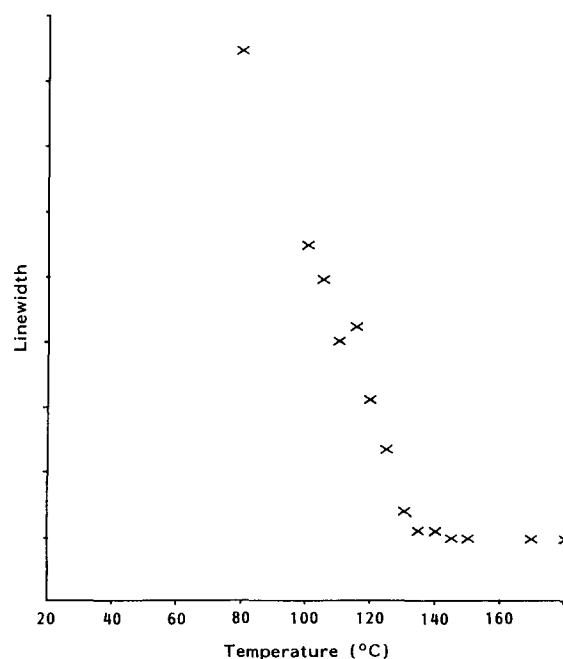
Figure 3 Temperature dependence of the methyl signal bandwidth in the n.m.r. spectrum of isotactic polypropylene

130°C, it is difficult to extrapolate with any degree of precision to determine a transition temperature, but the value will lie in the range 130±5°C.

N.m.r. spectroscopy

At ambient temperature the signal from the relatively mobile material that is present consists of a single broad, weak peak. When the temperature is increased to 50°C this signal splits into three components, specific for the carbon atoms of the methine, methylene and methyl groups. As the temperature was increased further, the resolution improved, a consequence of the decreasing widths of the peaks with increasing temperature. The band half-widths were measured as a function of temperature over the range 80–180°C. The results for the methyl carbon signal, given in *Figure 3*, show that the half-width decreases linearly with increasing temperature to 136°C, where there is a very pronounced break point, beyond which there is no further decrease with increasing temperature. The results for the methine and methylene carbon atoms are very similar.

DISCUSSION

The results from the four types of measurements show unequivocally that a structural change occurs at about 135°C, some 20°C below the melting point determined by differential scanning calorimetry. Two of the types of measurements undertaken, the linear dimension and the solid-state n.m.r. spectrum, measure changes on a macroscale. The former reflects the increase in volume and decrease in density as a function of thermal expansion, together with any phase or structural changes that may occur. The markedly greater decrease in density above 135°C is indicative of a change other than thermal expansion, which suffices to account for the decrease up to 135°C. This more rapid increase in volume above the transition temperature is suggestive of an increase in concentration of disordered phase, but this cannot be the result of a melting phenomenon 20°C below the melting point. The reversibility and repeatability on cycling the temperature, described above, confirm that the process is not annealing.

Disordering, in the form of an increase in the concentration of more mobile material, is also indicated by the abrupt change in the n.m.r. line width at 135°C. Unlike the density, it does not change with temperature above the transition temperature and it may be surmised that such changes as have occurred have imparted a considerable degree of mobility to individual chains.

The vibrational spectroscopic results provide information that is microstructural in character, because the various bands studied are specific for helical units of differing lengths. It is clearly apposite to look for a possible correlation between the temperature coefficients of absorbance and the minimum sequence lengths, as established by previous workers, necessary for the appearance of the various regularity bands. However, in so doing, it is necessary to take into account the change of absorbance with temperature below the transition temperature.

The variation of absorbance with temperature in the vibrational spectra of various molecules which are incapable of undergoing conformational changes is well established. There is a linear decrease of band intensity with increasing temperature but the magnitude of this effect varies quite appreciably for the various vibrational modes of a given molecule, and for different molecules[13–17]. For example, whereas the temperature coefficient approximates to zero in the case of the 1213 cm^{-1} (v_4) band of chloroform over the temperature range 170–300 K for a solution in carbon disulphide, similar measurements[17] on the 1087 cm^{-1} (v_{22}) band of acetone gave a temperature coefficient of absorbance of −0.00397.

If the reasonable assumption is made that the observed changes in the intensities of the various isotactic polypropylene bands below the transition temperature are simply a manifestation of this generally occurring temperature coefficient, the magnitudes of the effect for the various bands studied, ranging from −0.0022 to −0.0038, are of the anticipated level. In the absence of microstructural changes this temperature coefficient would be operative up to the melting point, as is indeed the case for the 973 cm^{-1} band, which has a coefficient of −0.0027 up to 165°C. Hence, in order to establish the change consequent upon the disordering processes that occur above the transition temperature it is necessary to calculate the difference in the temperature coefficient above and below the transition temperature. Values for this difference are given in *Table 1*.

When these difference values are arranged in increasing order of magnitude the bands to which they relate fall in the order 998, 1168, 900, 1256, 809, 841 and 1220 cm^{-1}. This sequence may be compared with the one obtained by Zichy[10] from her deformation studies 1256, 900, 998, 841, 809 and 1220 cm^{-1}. Bearing in mind that the experimental errors in both studies are such that there could be an inversion among pairs or triplets in the sequences and leaving aside the present result for the 1168 and 1256 cm^{-1} bands (the former not examined by Zichy), there is a definite correspondence between the two sequences. Those bands specific for the shorter helical sequences, namely 998 and 900 cm^{-1}, have smaller differences in temperature coefficients of absorbance above the transition temperature than do those at 809, 841 and 1220 cm^{-1}. It therefore follows that between the transition temperature and the melting point, the concentration of longer helices decreases more rapidly than that of their shorter counterparts. This result is not unexpected in view of the fact that the very short helices, for which the 973 cm^{-1} band is specific, persist in the melt and the somewhat longer ones, characterized by the band at 998 cm^{-1}, do not wholly disappear.

Nevertheless, these results do show unexpected features. The onset of disordering of all the helical structures responsible for the regularity bands at a well defined temperature some 20°C below the lowest temperature at which melting commences poses an interpretational problem, as does the sudden increase in molecular mobility at the transition temperature, which remains unchanged up to the melting point as indicated by the solid-state n.m.r. line widths. This problem is compounded by the absence of a detectable change in the d.s.c. trace in the vicinity of the transition temperature. This latter result has two possible explanations. The first is that the energy changes involved in whatever disordering processes occur between the transition and melting temperatures are too small to be detected. It is difficult to prove or disprove this hypothesis in the

absence of knowledge of the nature of these disordering processes. Alternatively, the explanation may lie in the rate at which disordering occurs. The infra-red measurements involved a stepwise increase in the temperature, with a period of some minutes for temperature equilibration at each level before the spectrum was recorded. Conversely, the temperature changes continuously, and at a much faster rate, during the d.s.c. measurements, and if the structural disordering is a relatively slow process it could escape detection. This would suggest that d.s.c. measurements should be made at a low heating rate. However, it was found that heating rates of less than $5°C min^{-1}$ gave such small peaks during the melting process that the measurements proved unreliable.

Finally, the results of the infra-red measurements on the $1256 cm^{-1}$ band merit comment, for two reasons that may prove to be related. This band has not, hitherto, been regarded as a regularity band. However, the fact that it shows the onset of a more rapid loss of intensity at a temperature identical with those for the regularity bands suggests that a disordering process is occurring. If this disordering is other than the shortening of 3_1 helices it is not surprising that the temperature coefficient of absorbance does not fit into the otherwise reasonable correlation with helix length, as deduced from studies on drawn specimens, found for the regularity bands.

ACKNOWLEDGEMENTS

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