

Far infra-red spectra (400—30 cm⁻¹) of isotactic polybut-1-ene in forms I and II

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Infra-red spectra of isotactic polybut-1-ene samples in crystalline modifications I (3_1 helix) and II (distorted 11_3 helix) have been obtained for samples of different crystallinity, at temperatures as low as 30K. The spectrum of form I is remarkably similar to that of isotactic polypropene (α form) and appears to characterize the 3_1 helical structure. The spectrum shows several features arising from the presence of lattice modes and the effects of crystal symmetry. In the case of form II the general spectral features are similar to those of form I, but it was not possible uniquely to characterize the different helical arrangement.

INTRODUCTION

Isotactic polybut-1-ene (IPB) exists in three crystalline modifications¹⁻³ of which forms I and II are the most well characterized. Form I is the most stable but form II can readily be obtained as a metastable modification. More stable samples of form II can be obtained when the IPB contains small amounts of certain copolymers (e.g. 4-methylpent-1-ene)⁴.

In both forms I and II the IPB chain is helical. For form I¹ the helix is of type 3_1 ; the rhombohedral unit cell contains six polymer chains, with $R\bar{3}c$ as the most likely space group⁵. In form II the helix is believed to be 11_3 (slightly distorted⁶) with the tetragonal unit cell ($P\bar{4}$) containing 4 polymer chains⁶⁻⁸.

Our studies of the α form of isotactic polypropene (α -IPP)⁹ identified far infra-red absorption bands characteristic of its 3_1 helical structure, and spectral features were observed arising from the arrangement of the polymer chains in the crystalline regions. It was therefore of some interest to determine whether the 3_1 helical structure of IPB form I could be similarly characterized, and also whether the spectra would allow distinction to be made between the structure of this form and form II.

EXPERIMENTAL

Samples of IPB form I

Highly isotactic polybut-1-ene powder was prepared for this study by ICI Plastics. Samples of form I (4.0 mm thick) were obtained by (a) moulding the starting material under pressure ('single-pressing'), followed by (b) subsequent remoulding without applied pressure ('double-pressing'); the conditions used were analogous to those applied to α -IPP⁹. The single-pressing is expected to result initially in form II which then transforms spontaneously into form I, whereas double-pressing should afford form I more

readily^{4,10}. However, up to ~5% form II may be present and remain in samples obtained from double-pressing, as determined by X-ray diffraction, and such samples were rejected. Samples used in this study were initially found to be between 51 and 62% crystalline by X-ray diffraction. The crystallinity was increased by annealing under oxygen-free nitrogen⁴. The sequence used in the present work was as follows: (i) heating up to 100°C at a rate of 30°C/h; (ii) heating to 115°C at a rate of 1°C/h; (iii) maintaining the temperature at 115°C for 2 h; (iv) cooling to ambient temperature at a rate of 6°C/h. The highest crystallinity so obtained was 68%, and all attempts to improve on this value [e.g. by increasing the time at stage (iii) by up to 30 h] were unsuccessful.

Sufficiently well-oriented samples for polarization measurements were obtained by single-pressing, rapid quenching of the melt in a bath at ~-78°C, subjecting the resultant material to slow hot-drawing in a tensile testing machine, heat-setting under tension at ~85°C for ~6 h, and finally cooling slowly to ambient temperature. The resulting samples were 1.4 mm thick and had been extended by ~300%.

Samples of IPB form II

Polybut-1-ene containing ~15 mol % of 3-methylpent-1-ene as copolymer was prepared by ICI Plastics. Specimens (4.0 and 6.0 mm thick) were obtained by hot-pressing the powdered substance using the method previously outlined for α -IPP⁹, and were found not to contain form I by X-ray diffraction. To increase the crystallinity, the samples were annealed under oxygen-free nitrogen according to the following sequence: (A) heating to 82°C at a rate of 20°C/h; (B) heating to 100°C at a rate of 1°C/h; (C) maintaining the temperature at 100°C for 1 h; (D) cooling to ambient temperature at a rate of 3°C/h. Since the X-ray diffractogram of the copolymer used is not fully characterized, crystallinity values can only be estimated approximately.

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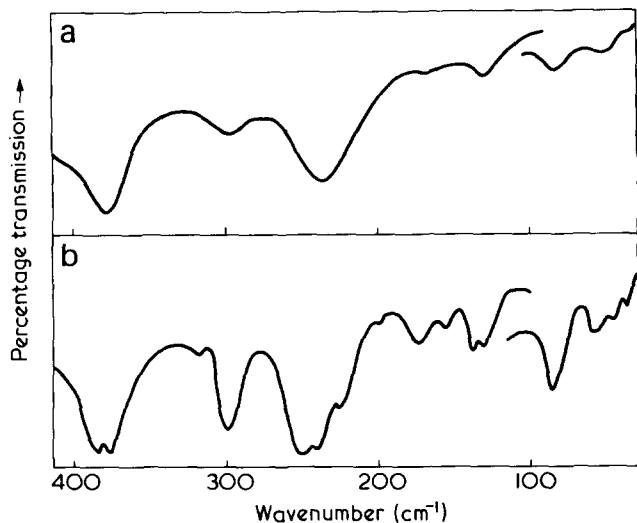


Figure 1 Far infra-red spectra of IPB form I at (a) $\sim 300\text{K}$; (b) $\sim 30\text{K}$. Sample thickness was 4 mm, with X-ray-determined crystallinity of 68%

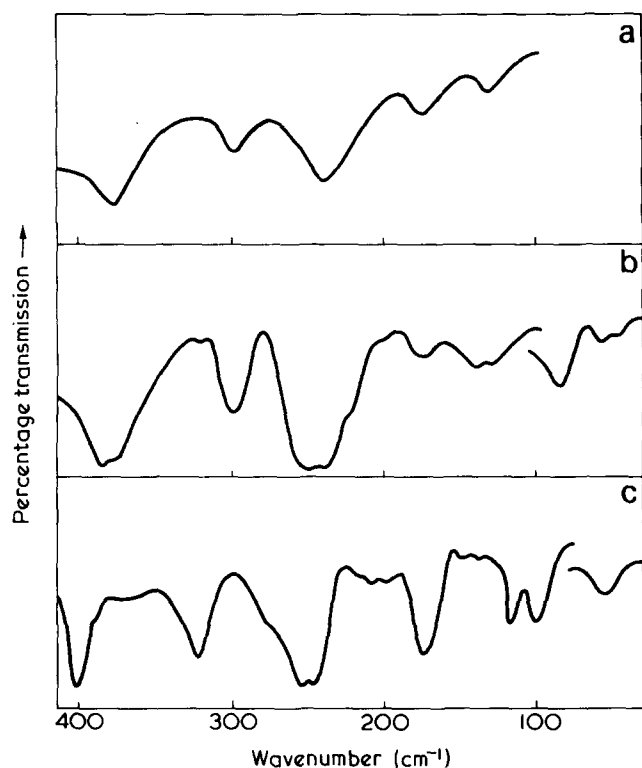


Figure 2 Far infra-red spectra at $\sim 100\text{K}$ of IPB form I and $\alpha\text{-IPP}$. (a) IPB form I, 4 mm thickness, 55–60% crystalline; (b) IPB form I, 4 mm thickness, 68% crystalline; (c) $\alpha\text{-IPP}$, 3.2 mm thickness, 70% crystalline

The final samples of form II obtained are thus believed to be only 45–50% crystalline, and no significant improvement was found even when the time at stage (C) was increased to 48 h.

Physical measurements

Far infra-red spectra in the $400\text{--}30\text{ cm}^{-1}$ region, including polarization measurements, were obtained as described previously⁹. Spectra were computed to a resolution of 4 cm^{-1} ; our best estimate of the noise level was $\pm 2\%$ transmission. For low temperature measurements a CTi Cryodyne model 20 closed-cycle helium cryostat was used,

enabling temperatures as low as 20K to be achieved at the cold station, with the sample estimated to be colder than 30K. X-ray diffraction measurements were carried out on a Philips PW 1010 diffractometer (by kind permission of Dr E. Gillam, City of London Polytechnic).

RESULTS

The spectra typically obtained are illustrated in Figures 1–4, and a summary of the wavenumber data is given in Table 1. As is most clearly seen in the case of form I, the spectra show the same marked improvement in quality (intensification and sharpening of bands) as the crystallinity of the samples is increased (Figure 2) as was previously found for $\alpha\text{-IPP}$ ⁹. The effect of cooling the specimens was even more clearly seen in the present study (Figure 1) because it was possible to achieve even lower temperatures ($\sim 30\text{K}$ rather than $\sim 100\text{K}$). The most notable feature of the spectra of form I is the close similarity in general form and in crystallinity/temperature effects compared with $\alpha\text{-IPP}$ (Figure 2). This point is considered further in the Discussion section.

While the effect of copolymerization was to yield exceptionally stable samples of IPB form II, crystallization was inhibited (see Experimental section). As a consequence of this only the strongest bands can be discerned from the spectra, even at $\sim 30\text{K}$.

DISCUSSION

Previous infra-red measurements¹¹ on IPB (form I or II) were restricted to the wavenumber region greater than

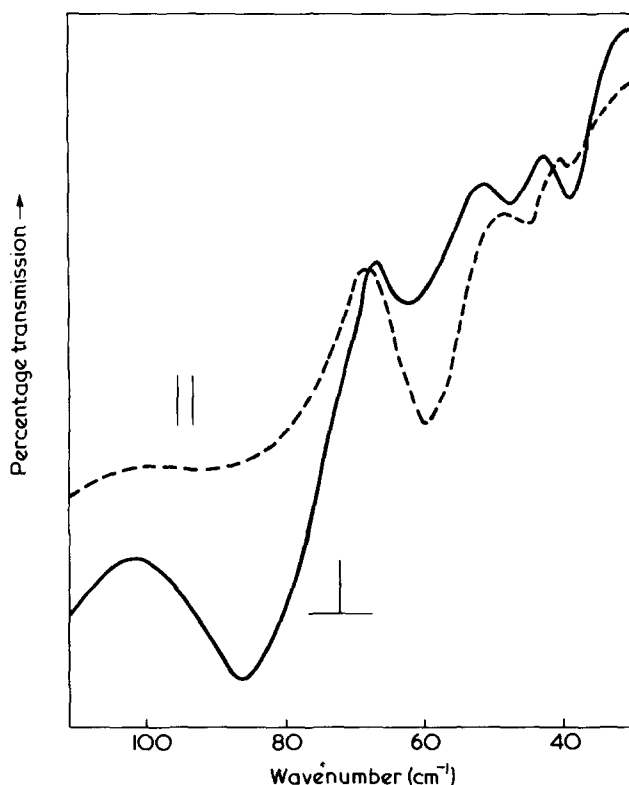


Figure 3 Polarized far infra-red spectra of oriented IPB form I at $\sim 100\text{K}$. Sample thickness was approx. 4.5 mm overall (obtained by layering 3 samples). Symbols || and \perp correspond respectively to the electric vector of the radiation parallel and perpendicular to the direction in which the sample had been drawn

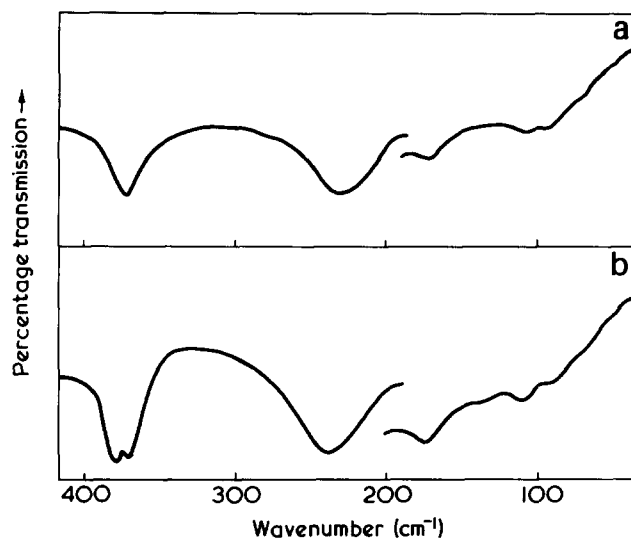


Figure 4 Far infra-red spectra of IPB form II containing 15 mol % of 3-methylpent-1-ene copolymer at (a) $\sim 300\text{K}$; (b) $\sim 30\text{K}$. Sample thickness was 6 mm, with X-ray-determined crystallinity of 45–50%

300 cm^{-1} and are of little assistance in the present study, although the Raman spectrum has been reported¹² down to 200 cm^{-1} . Normal coordinate analyses have been published, but are either limited to wavenumbers above 800 cm^{-1} (form I only, *A* and *E* modes)¹³ or deal exclusively with *A* modes¹². Moreover, no formal assignment of the calculated values to the predicted normal modes was made (but potential energies quoted)¹². The approach adopted in the present work was thus analogous to that used for $\alpha\text{-IPP}$ ⁹, with comparisons drawn from the results of that study.

For the 3_1 helical structure of form I, an approximate representation of the spectrum can be obtained under the C_3 line group, predicting 34 *A* and 35 *E* modes for an isolated chain, all infra-red and Raman active. In the case of form II (approximately an 11_3 helix) there are more atoms in the repeat unit of the chain, but a C_{11} line group analysis¹⁴ predicts the same number of infra-red-active modes (34 *A* + 35 *E*₁) for isolated chains in the two forms (see Appendix).

The most remarkable feature of the results obtained is the degree of similarity between the spectra of IPB form I and $\alpha\text{-IPP}$ (Figure 2). This quite clearly shows the value of far infra-red spectroscopy in the characterization of the backbone arrangement of organic polymers, since isolated chains of the two compounds in question differ only in the nature of their pendant groups. Unfortunately, it is not possible to state how characteristic the spectra are of the 3_1 helical structure of polyalk-1-enes, because the data for IPB form II (distorted 11_3 helix) were of insufficiently high quality. However it is noteworthy that the *A* mode calculations¹² indicate that wavenumber differences below 400 cm^{-1} between corresponding modes in forms I and II of IPB should be less than 7% (say, $\sim 10\text{ cm}^{-1}$), and indeed the recognizable bands in the spectrum of form II may be correlated with those of form I.

Such differences as are observed between $\alpha\text{-IPP}$ and IPB form I are expected to arise at least in part from differences in crystalline packing arrangements, and since both lattice modes and the effects of crystal symmetry were noted in our study of $\alpha\text{-IPP}$ ⁹, it was of interest to compare with data on IPB.

In the region below 90 cm^{-1} $\alpha\text{-IPP}$ showed one infra-red

band (55 cm^{-1} at $\sim 100\text{K}$), the behaviour of which in samples of differing crystallinity and with varying temperature led to assignment as a lattice (interchain) mode⁹. In the present work we find that IPB form I exhibits three features (resolved bands at 86 and 53 cm^{-1} , and a weak shoulder at 33 cm^{-1}) in this region at $\sim 300\text{K}$. The 53 cm^{-1} (broad) band splits into two components below $\sim 100\text{K}$ (58 and 46 cm^{-1}), and shoulder at 33 cm^{-1} intensifies and shifts to 36 cm^{-1} at $\sim 30\text{K}$. We interpret these results as follows:

(1) the 86 cm^{-1} band, being unshifted on cooling the sample and showing only a 'normal' intensification at low temperatures, is assigned as an internal mode of the chains, and because of its perpendicular dichroism (Figure 3) is attributed *E* symmetry (see Appendix);

(2) the feature observed at 46 cm^{-1} appears to have been resolved out of the broad 53 cm^{-1} band on cooling, and so is also believed (showing no discernible temperature dependence) to be an internal mode;

(3) the 58 cm^{-1} band thus appears to have its origin at lower wavenumbers at $\sim 300\text{K}$ ($\sim 53\text{ cm}^{-1}$), and since such a shift is characteristic of lattice modes of organic polymers such as polyethene, polyoxymethene, poly(tetrafluoroethene) and $\alpha\text{-IPP}$ (48 cm^{-1} at $\sim 300\text{K}$ shifting to 55 cm^{-1} at $\sim 100\text{K}$)⁹, we confidently assign this band to a lattice mode. The observed parallel dichroism indicates that it is of *A*₁ symmetry and hence is either the single rotational lattice mode or one of the two translational lattice modes predicted (see Appendix);

(4) the very noticeable enhancement in intensity of the 33 cm^{-1} shoulder, and its shift to higher frequency on cooling, is also indicative of assignment as a lattice mode. It exhibits perpendicular dichroism and must thus be an *E* translational or rotational mode (see Appendix).

We are therefore able, with some confidence, to attribute differences in the spectra of $\alpha\text{-IPP}$ and IPB form I at the lower wavenumbers to different crystalline arrangements of chains of the same helical conformation.

For the higher wavenumber part of the spectra, it is again necessary to consider the effects of the crystal lattice

Table 1 Summary of observed far infra-red bands ($400\text{--}30\text{ cm}^{-1}$) in the spectra of IPB forms I and II (data in cm^{-1})

	Form I*			Form II [‡]	
	$\sim 300\text{K}$	$\sim 100\text{K}$	$\sim 30\text{K}$	$\sim 300\text{K}$	$\sim 30\text{K}$
380	{ 385 375 320	{ 385 375 320	Correlation splitting of <i>E</i> line group mode	375	{ 380 372
300	300	300			
240	{ 250 238 225 200 175	{ 250 238 225 200 175	Correlation splitting of <i>E</i> line group mode	230	235
	158	158		170	175
130	134	{ 136 128	Correlation splitting of <i>E</i> line group mode	108	110
86	86	86		\perp (<i>E</i>) internal mode	95
53	{ 55 46	{ 58 46	Internal mode		
33		36		\perp (<i>E</i>) lattice mode	

* *A* line group modes are calculated at 347, 259, 212, 187, 114, and 64 cm^{-1} (ref 12);

[†] except where indicated the dichroism was too weak to be determined with confidence;

[‡] containing 15 mol % of 3-methylpent-1-ene copolymer

in understanding the observed spectral features of form I. Thus the splitting of the 130 cm^{-1} band into a doublet (136 and 128 cm^{-1}) at low temperatures and in samples of high crystallinity very closely resembles the appearance and behaviour of the 100 cm^{-1} feature of α -IPP (113 and 98 cm^{-1} at $\sim 100\text{K}$)⁹. Accordingly, we propose an analogous band assignment (E) and invoke the same origin for the splitting, viz a crystal field effect. In the present case, however, it is possible to distinguish between static (site symmetry) and dynamic (correlation) effects, because the site group is the same as the line group (C_3) so that site group splitting cannot occur (see Appendix). Thus we deduce that the observed splitting of the band at 130 cm^{-1} arises from a correlation field effect.

In a similar manner it is possible to attribute splitting of the ~ 380 and $\sim 240\text{ cm}^{-1}$ bands of form I samples of higher crystallinity (into doublets, respectively at 385 , 375 cm^{-1} and 250 , 238 cm^{-1}) to correlation field effects. The region around 240 – 250 cm^{-1} is particularly similar to that for α -IPP⁹. It is also interesting to note that the 375 cm^{-1} band in IPB form II also shows splitting (380 and 372 cm^{-1}) at low temperatures.

CONCLUSIONS

The present study, particularly when taken with previous work, has shown that far infra-red absorption spectra in the 400 – 30 cm^{-1} region of polyalkenes are rich in features characteristic of the hydrocarbon backbone structure. The very close resemblance between the spectra of α -IPP and IPB form I, which contain the same (3_1) helical $[-\text{CH}_2\text{CH}<]_n$ structure, is a vivid illustration of this. The resemblance extends not only to band positions and relative intensities, but also to the splitting, shifting and intensification of bands as the crystallinity of the samples is increased and/or the temperature is lowered. These latter effects, which arise from crystal field phenomena and the behaviour of lattice vibrational modes, clearly demonstrate the sensitivity of the far infra-red spectra not only to chain structure but also to the crystalline packing of the chains relative to one another.

The work has also demonstrated further the importance of crystallinity in determining the quality of far infra-red spectra. Thus only the general features of the spectrum of IPB form II could be discerned because samples of only moderate crystallinity were obtained. However, the spectrum was notable in that the gross features were similar to those of IPB form I, but not sufficiently well defined to determine whether or not the different chain conformation (distorted 11_3 helix) could be characterized separately to the 3_1 helical structure.

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APPENDIX

Vibrational analyses

The 3_1 helical structure of IPB form I belongs to the C_3 line group, and a simple line group vibrational analysis for an isolated chain based on the isomorphous point group C_3 shows that the $104(3N - 4)$ normal modes reduce as $34A + 35E$ in which the A modes show parallel dichroism and the E modes show perpendicular dichroism in infra-red absorption. The space group is $R\bar{3}c$, but when carrying out the unit cell analysis it is appropriate to assume that randomization of the screw sense (left- and right-handed) and direction ('up' or 'down' with respect to the C - C_2H_5 direction) will not influence the lattice modes since each individual chain must be specifically oriented. Thus randomization of orientation from one cell to the next is immaterial, and consequently the appropriate space group is the idealized one, $R3c$. This is analogous to the approach adopted for α -IPP⁹. A unit cell (factor group) analysis¹⁵ thus results

Table 2 Unit cell group analysis for IPB form I*

C_{3v}	T'	T_A	T	R	n_L	Activity
A_1	3	1	2	1	3	Infra-red and Raman
A_2	3	0	3	1	4	Inactive
E	6	1	5	2	7	Infra-red and Raman

*Based on $R3c$ space group, isomorphous point group C_{3v} , six polymer chains per primitive cell; T' = total number of translational degrees of freedom; T_A = number of acoustic modes; T = number of optical translatory lattice modes ($= T' - T_A$); R = number of rotational lattice modes; n_L = total number of optical lattice modes ($= T + R$)

Table 3 Correlation between chain line group, chain site group and unit cell group of IPB form I*

Line group (C_3)	Site group (C_3)	Unit cell group (C_{3v})
A	(6) A	$3A_1$ $3A_2$
E	(6) E	$6E$

*Based on space group $R3c$ (six chains passing through the primitive cell)

as in *Table 2*. Each chain is on a C_3 line group symmetry site, with six chains passing through the unit cell (isomorphous point group C_{3v}). The correlation between the line group, site group and unit cell (factor) group is given in *Table 3*. It is seen that the doubly degenerate (E) modes of the chain retain their degeneracy in the crystal. It may be assumed that dichroism of line group modes will be unaffected by crystal packing⁹, so that all A modes should

exhibit parallel dichroism and all E modes perpendicular dichroism.

For form II, the 11_3 helical structure is of line group symmetry C_{11} , so that the $392 (3N - 4)$ modes of the isolated chain are $34A + 35E_1 + 36E_2 + 36E_3 + 36E_4 + 36E_5$ (the A and E_1 modes only being infra-red active). The four chains passing through the $P\bar{4}$ unit cell are on general (C_1) sites so that $A \rightarrow A$ and $E_1 \rightarrow 2A$ under the site group.