

The far-infrared spectroscopy of some synthetic organic polymers.

STEPHENSON, David.

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A thesis entitled

THE FAR-INFRARED SPECTROSCOPY OF SOME SYNTHETIC ORGANIC POLYMERS

presented by .

DAVID STEPHENSON

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Dept. of Chemistry,
Sheffield City Polytechnic,
Pond Street,
Sheffield S1 1WB.

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Abstract

The Far-infrared Spectroscopy of Some Synthetic Organic Polymers by David Stephenson

Studies have been made on the far-infrared spectra of poly(vinyl chloride), polyethylene, poly(4-methyl-1-pentene), poly(1-pentene) forms I and II, and poly(ethylene terephthalate), the spectra of poly(1-pentene) forms I and II being reported for the first time. The essential purpose of these studies was to establish assignments more firmly than hitherto, and thus to relate the spectral features to such properties as chain conformation, configuration and crystallinity.

In the far-infrared spectrum of poly(vinyl chloride) the 185 cm^{-1} band has been assigned to a vibration of an interchain hydrogen bond in the chain fold regions, and it appears that the 64 cm^{-1} band is due to dipole-dipole interactions between adjacent chains. The frequency-temperature dependance of the 64 cm^{-1} band was studied as it appeared to show an unusual variation, but results were not conclusive. However in the case of the 72 cm^{-1} band in the spectrum of polyethylene two transitions were observed in the range 60 to 320 K which corresponded fairly well with previously reported transitions determined by other methods.

Correlation of bands through the series of poly(α -olefins) has enabled assignments of bands in the far-infrared spectra of poly(1-pentene) forms I and II and poly(4-methyl-1-pentene) to be made for the first time. Some of the bands in the far-infrared spectrum of poly(4-methyl-1-pentene) are split into two components, and this has been attributed to non-uniformity of its helical structure. Additionally, the study has led to a re-assessment of the previous assignments given to bands in the far-infrared spectrum of poly(1-butene) form I, and certain re-assignments have been made.

Finally, it has been possible to consolidate and extend assignments for the far-infrared spectrum of poly(ethylene terephthalate).

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List of abbreviations used in this thesis

PVC - poly(vinyl chloride)

U-C PVC - urea canal poly(vinyl chloride)

M-E PVC - Montedison fibre forming grade poly(vinyl chloride)

PE - polyethylene

T_g - glass transition temperature

PTFE - poly(tetrafluoroethylene)

PPr - polypropene

PBu-I - poly(1-butene) formI

PPe-I - poly(1-pentene) formI

PPe-II - poly(1-pentene) formII

P4MP - poly(4-methyl-1-pentene)

PET - poly(ethylene terephthalate)

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Chapter 1

Introduction

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1.1 Introduction

The mid-infrared spectra of a wide range of synthetic organic polymers have been recorded and catalogued (eg. 1 - 5). In this region of the spectrum there is relatively little vibrational coupling and consequently the molecule can reasonably be treated as several isolated units. Thus this part of the spectrum is ideal for identification of these relatively intractable materials, either by comparison with standard spectra or by identification of group frequencies.

Various polymers show changes in their mid-infrared spectra depending on the crystallinity and stereoregularity of the sample. The interchain interactions between adjacent chains may cause certain vibrational modes in the infrared spectrum of polymers to be split, the extent of the splitting being directly related to polymer crystallinity. This phenomena is known as correlation field splitting. The utility of this method, for determining crystallinity, is limited, because in centrosymmetric systems mutual exclusion occurs, making one component of the correlation splitting infrared-active and the other Raman-active. Thus, the magnitude of the resultant splitting is difficult to determine. Further the effect cannot occur in polymers which have only one chain per unit cell.

Configuration and conformation sensitive bands have also been used to determine crystallinity eg. C-Cl stretching bands in poly(vinyl chloride) (6), and bands due to trans and gauche conformers of the glycol segments in poly(ethylene terephthalate) (7,8). Such determinations, however, ignore the fact that a number of adjacent repeat units with suitable conformations and/or configuration are required for crystallisation and thus favourable structure for crystallisation, as determined by infrared spectroscopy, also occurs

in amorphous regions.

In the far-infrared region (10 to 450 cm^{-1}) the vibrational modes are mainly torsions and bending modes involving the whole repeat unit of the polymer. These vibrations being lower in energy than those that absorb in the mid-infrared region, are much more susceptible to changes in crystallinity and conformation. Below 100 cm^{-1} there are also, in the spectra of many polymers, bands believed to be due to interchain vibrations and hence they are very sensitive to changes in crystal structure and degree of crystallinity. These lattice bands, in crystalline polymers, can usually be identified since they are expected to move substantially to higher frequency on cooling the polymer. The lattice band in polyethylene at 72 cm^{-1} , for example, moves to 78 cm^{-1} on cooling the sample to 100 K (9); an intramolecular mode would be expected to increase its absorption frequency only by 1 to 2 cm^{-1} on such a temperature change.

The purpose of the present work was to relate the far-infrared spectra of various synthetic organic polymers to their bulk structure, by thermal treatment of the polymer samples, recording the spectra at different temperatures and utilising X-ray diffraction techniques. These techniques allow, with the aid of previous literature by other workers, the bands in the far-infrared spectra of the polymers studied to be assigned to specific vibrational modes.

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Chapter 2

The Far - infrared Spectrum of Poly(vinyl chloride)

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2.1 Introduction

Commercially, vinyl chloride is polymerised at a temperature between 45 °C and 72 °C, which produces a largely atactic amorphous polymer. At a lower polymerisation temperature, however, such as is used in the manufacture of Montedison fibre-forming grade poly (vinyl chloride) (PVC), a more stereoregular polymer with less chain branching is produced. These low temperature polymerisation conditions are also used for the preparation of experimental PVC samples (1-9), and because the initiators used in the reaction also act as chain terminators, a low molecular weight PVC is produced, which tends to crystallise more readily than higher molecular weight PVC of similar syndiotactic content. Almost completely syndiotactic PVC can be prepared by binding vinyl chloride in a urea canal complex and polymerising with high intensity γ -rays (10).

The degree of crystallinity, chain configuration and conformation are all important in determining the physical properties and processing characteristics of the polymer. Thus PVC has been extensively investigated by many techniques in order to gain information about its structure. X-ray scattering was the first technique used (11) and it was suggested that crystalline peaks present in the diffraction pattern were caused by syndiotactic sequences forming small crystalline regions within a largely amorphous polymer structure. X-ray diffraction is still the most widely used method for determining the crystallinity of PVC. The method of Weidinger and Hermans (12-14) is usually used for this determination; this assumes a two phase system of wholly ordered and wholly disordered material. However the work of Mamma and Nardi (15) has given clear indications of the presence of a phase of intermediate order, in the ab plane, and Guerrero and Keller (16) have suggested there may be two such intermediate phases. If this is

so, the X-ray background scattering^{er} measured is not a reliable indication of the incoherent scattering from the amorphous phase. Thus, a sample which is completely amorphous is really needed to obtain a correct crystallinity value by this method. A value of ca. 5% is obtained for the crystallinity of commercial PVC by this method (17). However, values as low as 0.5%, by small angle X-ray diffraction (18), and as high as 12% by density measurements (2), have been reported.

The infrared and Raman spectra of PVC in the carbon-chlorine stretching region ($600-710\text{ cm}^{-1}$) have been used to gain information about the tacticity of PVC. This method has also been used to determine the crystallinity of PVC, by ratioing the intensity of the band at ca. 640 cm^{-1} with the band at ca. 690 cm^{-1} (6,19,20,21). These bands are due to sequences in the chain structure of PVC which are believed to crystallise, and not to crystallise respectively. Thus they are not true crystallinity bands as defined by Zerbi et al. (22). Unlike the 720 and 730 cm^{-1} doublet in the spectrum of crystalline polyethylene they do not depend on a crystal lattice for their existence. A further drawback of this method is that account is not taken of syndiotactic sequences capable of crystallisation, which give rise to a band at 601 cm^{-1} (23). There is also a small peak at 647 cm^{-1} resolved graphically by Pohl and Hummel (24), which will give an incorrect value to the intensity of the 640 cm^{-1} band. More recently with the aid of computer curve fitting, the area of the 640 cm^{-1} and 601 cm^{-1} peaks have been combined to give a value for the crystallinity of PVC (25,26); however, the method does not give absolute values.

In Fig 2.1 a comparison between the spectrum of urea-canal PVC and that of a commercial sample is shown. The band at ca. 690 cm^{-1} which is prominent in atactic samples is due to long regular isotactic sequences and appears broad because of two underlying bands which are

believed to be due to short syndiotactic sequences. The spectrum of highly syndiotactic urea-canal PVC contains an absorption at ca. 601 cm^{-1} which is due to long syndiotactic sequences. This band shifts to higher frequency in less stereoregular commercial samples because of the increase in intensity of an underlying band at ca. 614 cm^{-1} which is due to short planar syndiotactic sequences. The band at ca. 640 cm^{-1} , due to long syndiotactic sequences, is relatively unchanged. More underlying bands have been revealed by computer curve fitting (26), and consequently the overall picture is complex, and thus there is great difficulty in obtaining meaningful configurational data by this method.

NMR spectroscopy has proved more useful recently in determining configurational parameters (27 - 29), but the solubility, especially of the more stereoregular PVC samples, is a limitation. The syndiotacticity of commercial PVC determined by this method is ca. 55% (27).

In the far-infrared region below 400 cm^{-1} , bands due to intermolecular vibrations and hence indicative of crystallinity occur. The far-infrared spectrum of PVC received considerable attention when this region of the spectrum became accessible; PVC (30-32) deuterated PVC (32,33) and model compounds (34-39) were studied. There have been two normal co-ordinate analyses carried out on syndiotactic PVC. The approach of Tasumi and Shimanouchi (32) was a single chain analysis and as such would not be expected to predict intermolecular modes. On the other hand Moore and Krimm (31) took into account possible interchain interactions. Both sets of results (for the region below 400 cm^{-1}) are summarised in Table 2.1. For the 3 intramolecular bands between 300 cm^{-1} and 400 cm^{-1} the analyses agree with the observed spectrum. However, the strong band at ca. 185 cm^{-1}

is not predicted by either model and consequently no credible assignment for it has been put forward. Furthermore, the band at 64 cm^{-1} has been assigned by Moore and Krimm (24) to the vibration of an intermolecular hydrogen bond, which has been brought into doubt by recent X-ray work (40,41). The present study seeks to resolve these deficiencies, in our understanding of the far-infrared spectrum.

2.2 Experimental

Samples

- (i) AS 7042: a commercial copolymer made by BP Chemicals of vinyl chloride/vinyl acetate containing 16% vinyl acetate.
 - (ii) Corvic (72 °C) a commercial polymer made by ICI using a polymerisation temperature of 72 °C.
 - (iii) Corvic (64 °C) a commercial polymer made by ICI using a polymerisation temperature of 64 °C.
 - (iv) M-E: a commercial polymer made by the Montecatini - Edison Company using a polymerisation temperature of -30 °C; it has a relative molecular mass, determined by viscometry, of 60 000.
 - (v) P75 TRO IME: an experimental polymer polymerised at 0 °C using t-butylmagnesium chloride (5). This sample was precipitated from the reaction mixture by adding methanol.
 - (vi) P74 TRO ITHF
 - (vii) P75 TRO ITHF
 - (viii) P78 TRO ITHF
- } experimental polymers polymerised as
} for P75 TRO IME, but these fractions were
} less soluble in tetrahydrofuran.
- (ix) U-C: an experimental polymer prepared in a urea-canal complex (10).

The samples are listed above in order of increasing potential crystallinity.

The samples were prepared for spectral measurements by three different methods. Methods (a) and (b) were used for samples (iv) to (ix), and method (c) for samples (i) to (iii).

- (a) Untreated cold pressed discs: prepared by pressing the PVC powder as supplied to form 13 mm diameter discs, between 0.1 mm and 0.2 mm thick depending on the sample and the region of the far-infrared spectrum to be covered.

- (b) Annealed discs: discs prepared as in method (a) were annealed at a temperature between 140 °C and 190 °C for between 30 mins. and 18 hours and slowly cooled from the annealing temperature at ca 1 °C per minute.
- (c) Cast films: Samples (i) (ii) and (iii) were supplied in the form of coarse powders and consequently could not be cold pressed successfully, but were sufficiently atactic to be readily soluble in tetrahydrofuran, thus enabling films to be cast. After most of the solvent was lost, the resulting films were dried under vacuum overnight.

A vacuum tight liquid cell with polyethylene windows modified as described by Goldstein and Willis (42) was used to record the spectrum of 2 - chlorobutane. An electrical heater and thermocouple was added to the liquid cell, and the polyethylene windows replaced by PTFE windows in order to record the spectrum of P75 TRO IME at 450 K.

2.3 Results

The X-ray diffraction patterns of selected samples are shown in Fig 2.2. The patterns are generally qualitatively similar, the differences being explicable in terms of the different syndiotacticities of the samples. The notable exception to this generalisation is that the highly syndiotactic U-C sample shows a smaller peak than would be expected for the 210 reflection at 25° and the 220 reflection at 40° . The change in the X-ray diffraction curves on annealing are shown for some of the samples in Figs 2.3a - 2.3d, and their crystallinity indices, calculated by the method of D'Amato and Strella (43), together with half peak height widths for sample U-C are in Table 2.2. As can be seen it is difficult to correlate changes in crystallinity index with changes in the diffraction patterns.

The far-infrared spectra from 40 to 230 cm^{-1} of the various samples are compared in Fig 2.4. The intensity of the band at 64 cm^{-1} is very similar in all but the samples of lowest crystallinity, viz. M-E and P75 TRO IME. On the other hand, the band at 185 cm^{-1} is very much sharper and stronger in the U-C sample than in other samples. A comparison of the spectra obtained on annealing the samples is shown for the 64 cm^{-1} and 88 cm^{-1} bands in Figs 2.5a - 2.5d, and for the 185 cm^{-1} band in Figs. 2.6a - 2.6j. All the bands observed are tabulated along with their relative intensities in Table 2.3. A comparison between the 64 cm^{-1} and 88 cm^{-1} band at room temperature (ca. 300 K) and ca. 30 K for three of the samples are shown in Figs 2.7a - 2.7d. It can be seen from these Figures and Table 2.3 that the shift in position of the band at 64 cm^{-1} , on cooling, is very marked in the highly syndiotactic U-C sample but not in the other samples and in this sample it also shifts far more than 88 cm^{-1} band. In Fig 2.8a and 2.8b the spectrum from 80 cm^{-1} to 440 cm^{-1}

of the vinyl chloride/vinyl acetate copolymer is compared with a commercial PVC sample. All the bands, except the band at 64 cm^{-1} which was not observed in either spectrum, are much weaker and broader in the copolymer especially the two bands above 400 cm^{-1} which are believed to be due to isotactic structure. The spectrum of P75 TRO IME at 450 K is shown in Fig 2.9 from 50 to 100 cm^{-1} , the 64 cm^{-1} and 88 cm^{-1} bands still being present.

The spectrum of 2-chlorobutane from 100 cm^{-1} to 450 cm^{-1} is shown in Figs 2.10a and 2.10b.

2.4 Discussion and Assignment

The absorptions in the far-infrared spectrum of PVC have been largely explained by normal co-ordinate analysis. Thus the bands at 88, 312, 348 and 358 cm^{-1} have been predicted and assigned by two independent groups of workers (31,32). However, the origins of the two bands at 64 cm^{-1} and 185 cm^{-1} present more of a problem.

The band at 64 cm^{-1} is not predicted for an isolated chain (32), but was predicted by Moore and Krimm (31), when they took into account interchain interactions. In Fig 2.4 it may be seen that the band at 64 cm^{-1} in PVC becomes more intense as the syndiotacticity, and hence the crystallinity, of the sample is increased. Furthermore, shifts to a higher wavenumber occur on cooling the most crystalline U-C sample (Fig 2.7a), suggestive of a lattice mode; the 64 cm^{-1} band in the other samples (Figs 2.7b to 2.7d) does not change in frequency to anything like the same extent on cooling, thus

discounting the possibility that the frequency shift is due to the occupation of excited vibrational energy levels at room temperature (hot bands). Thus the PVC samples, other than U-C, must be insufficiently syndiotactic to allow contraction of the crystal lattice on cooling. The evidence therefore suggests that this band is due to interchain vibrations. There is, furthermore, evidence to suggest that the band could be due to a specific hydrogen bonded interaction.

The evidence upon which the hydrogen bond assignment was based was experiments on model compounds, viz. secondary chloroalkanes, by Warrier and Krimm (12). These authors showed that these compounds also have a band at ca. 64 cm^{-1} which disappears in the gas phase and on dilution, indicating that the absorption is caused by interactions between adjacent molecules in the liquid secondary chloroalkanes.

Additionally experiments carried out on deuterated secondary chloroalkanes (35) showed that the 64 cm^{-1} band was shifted by an amount predicted assuming interchain hydrogen bonding. Also Conte et al. (41) calculated that hydrogen bonds could be formed in the chain fold regions, and suggested that the 64 cm^{-1} band could be a manifestation of this.

However, if this were the case the short chain PVC samples, which would be expected to contain fewer chain folds, would have a less intense 64 cm^{-1} absorption than would the long chain U-C sample. Examination of Fig 2.3 shows that this is not so. The shape and intensity of the 64 cm^{-1} band in sample U-C is very similar to that for P74 TRO ITHF and P75 TRO ITHF. Furthermore, X-ray work carried out by Wilks et al. (40) and more recently by Conte et al. (41) showed that in the crystalline regions of PVC (away from chain folds) the separation between hydrogen and chlorine atoms was ca. 4.7 \AA which is substantially greater than van der Waals' contact distance of ca. 4.1 \AA . Thus suggesting that although the 64 cm^{-1} band may be due to an interchain interaction, it cannot be attributed to hydrogen bonding.

The 185 cm^{-1} band is not predicted by either the single chain analysis of Tasumi and Shimanouchi (32) or by Moore and Krimm (31) who took into account possible interchain interactions. The band has previously been assigned to less prevalent conformations (36,37,39). The present work is not compatible with this interpretation as the band becomes sharper and more intense with the more stereoregular PVC samples (Fig 2.3). It must therefore be due to some part of the structure of PVC which is present in quite large concentrations and is not allowed for in the two normal co-ordinate analyses. Normal co-ordinate analyses are carried out assuming ideal crystals containing polymer chains of infinite length; thus folding of the

polymer chains is ignored. So the 185 cm^{-1} band could be due to interactions in chain fold regions. This is further implicated by the fact that in Fig 2.3 the 185 cm^{-1} band is more intense in the long chain U-C sample, which probably contains a greater concentration of chain folds (c f. the 64 cm^{-1} band in Fig 2.3). Additionally Conte et al. (41) calculated that there could be favourable interchain interactions in chain fold regions, the calculated interchain distances being short enough to allow hydrogen bonding.

2.5 Conclusions

The most plausible assignment for the 185 cm^{-1} band in syndiotactic PVC is that it is due to the vibration of an interchain hydrogen bond in the chain fold regions. The band at 64 cm^{-1} is probably due to dipole-dipole interactions between adjacent chains.

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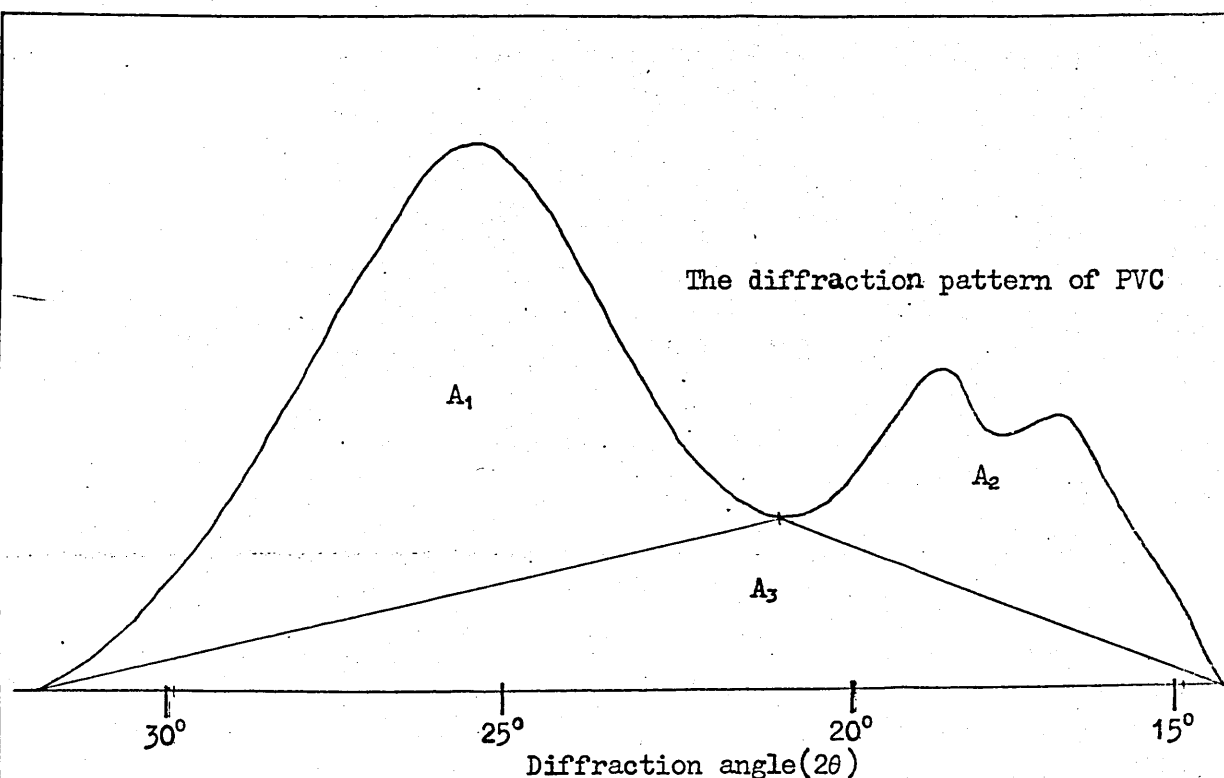
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Table 2.1

Summary of normal coordinate analyses performed on syndiotactic PVC
(Data are in cm^{-1})

Moore and Krimm [2]			Tasumi and Shimamouchi [1]		
Calculated	Observed	Assignment (PED) ¹	Calculated	Observed	Assignment (PED) ¹
29	--	C-Cl...H bend(97)	--	--	
64	67	Torsion(32)C-Cl...H bend(29)	54	--	Internal rotation(95)
90	89	Torsion(79)	117	--	Internal rotation(81)
--	180	Less prevalent conformations	--	180	Internal rotation and lattice vibration
321	315	C-C-Cl bend(48)	310	312	C-Cl bend(63)
330	345	C-C-Cl bend(86)	347	340	C-Cl bend(79)
376	358	C-C-Cl bend(47)	349	364	C-Cl bend(57)

¹ PED: Potential energy distribution (in percent).



$$\text{Crystallinity index} = \frac{\text{Area } A_1 + \text{Area } A_2}{\text{Area } A_1 + \text{Area } A_2 + \text{Area } A_3}$$

Table 2.2

Tabulation of the crystallinity index of variously treated samples of PVC

Sample	Urea-canal	P75 TRO	ITHF P74 TRO	ITHF P75 TRO	IME
Untreated cold pressed disc	83	67	57	55	
Disc annealed at 140°C for 1 hour	84	76	80	55	
Annealed at 140 °C for 6 hours	84	67	76	58	
Annealed at 140 °C for 31 hours	91	67	66	58	

Tabulation of half peak height band widths for urea-canal PVC

Band position(2θ)	18°	25°	31°	40°
Untreated cold pressed disc	3.0°	3.0°	2.8°	3.7°
Disc annealed at 140°C for 1 hour	2.8°	2.8°	2.3°	2.7°
Annealed at 140 °C for 6 hours	2.8°	2.6°	1.9°	2.7°
Annealed at 140 °C for 31 hours	2.8°	2.6°	2.2°	2.8°

Table 2.3

Bands observed in the far-infrared spectra of various PVC samples.

Sample1 untreated cold pressed disc.

Sample2 :sample1 annealed for 1 hour at 140 °C } Cooled from 140 °C at

Sample3 :sample2 annealed for 17 hours at 140 °C } 1° per minute

Figures give band positions in wavenumbers(cm^{-1})

Spectra recorded at 30 K

Spectra recorded at 300 K

Sample1	Sample2	Sample3	Sample1	Sample2	Sample3
Urea-canal PVC					
72		71	—	64	65
90		90	88	88	88
191		193	185	188	181
314		315	314	315	315
344		344	344	344	345
358		359	359	359	361
P74 TRO ITHF					
68	67	65	—	63	63
88	87	88	—	88	87
181	—	—	—	—	—
190	190	190	—	190	187
312	310	312	—	311	312
347	—	—	—	348	347
361	361	361	—	361	359
P75 TRO ITHF					
	67	68	66	63	
	88	86	85	87	
	195	188	188	189	185
	310	311	311	312	310
	345	344	—	—	
	358	361	359	358	
P75 TRO ILE					
66	61	—	—	63	67
88	88	83	—	85	85
—	162	151	160	—	—
—	—	—	—	178	179
180	185	179	181	183	187
310	309	310	314	310	310
344	339	—	343	344	342
360	363	361	361	361	362
—	—	—	366	366	367
Montedison fibre forming grade					
68	62	—	—	62	63
88	88	—	—	88	85
167	—	—	—	—	—
179	184	—	181	181	181
—	193	—	—	186	186
312	311	—	313	312	312
—	—	—	—	349	347
361	358	—	363	361	361
373	—	—	—	381	—
—	—	—	430	—	—

Fig 2.1

A comparison between the mid-infrared spectra of U-C PVC and a commercial sample.

Urea-canai PVC
Commercial PVC

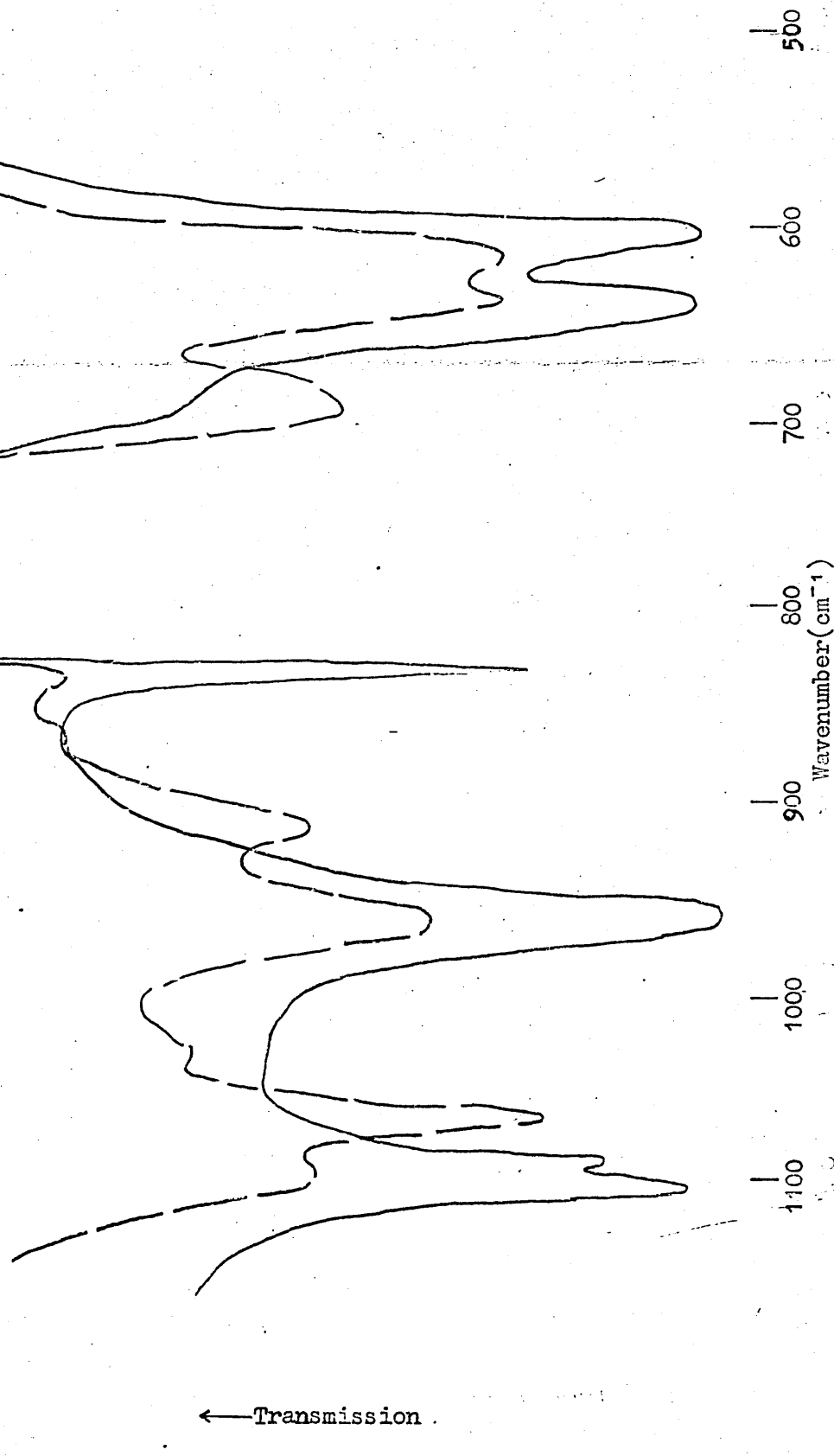


Fig 2.2
The X-ray diffraction patterns of various samples of PVC.
(all samples in cold pressed disc form)

————— P74 TRO ITHF
 ————— P75 TRO ITHF
 - - - - - P75 TRO IME
 + + + + + M-E
 U-C
 - · - · - P78 TRO ITHF
 + + + + + ICI 'Corvic'

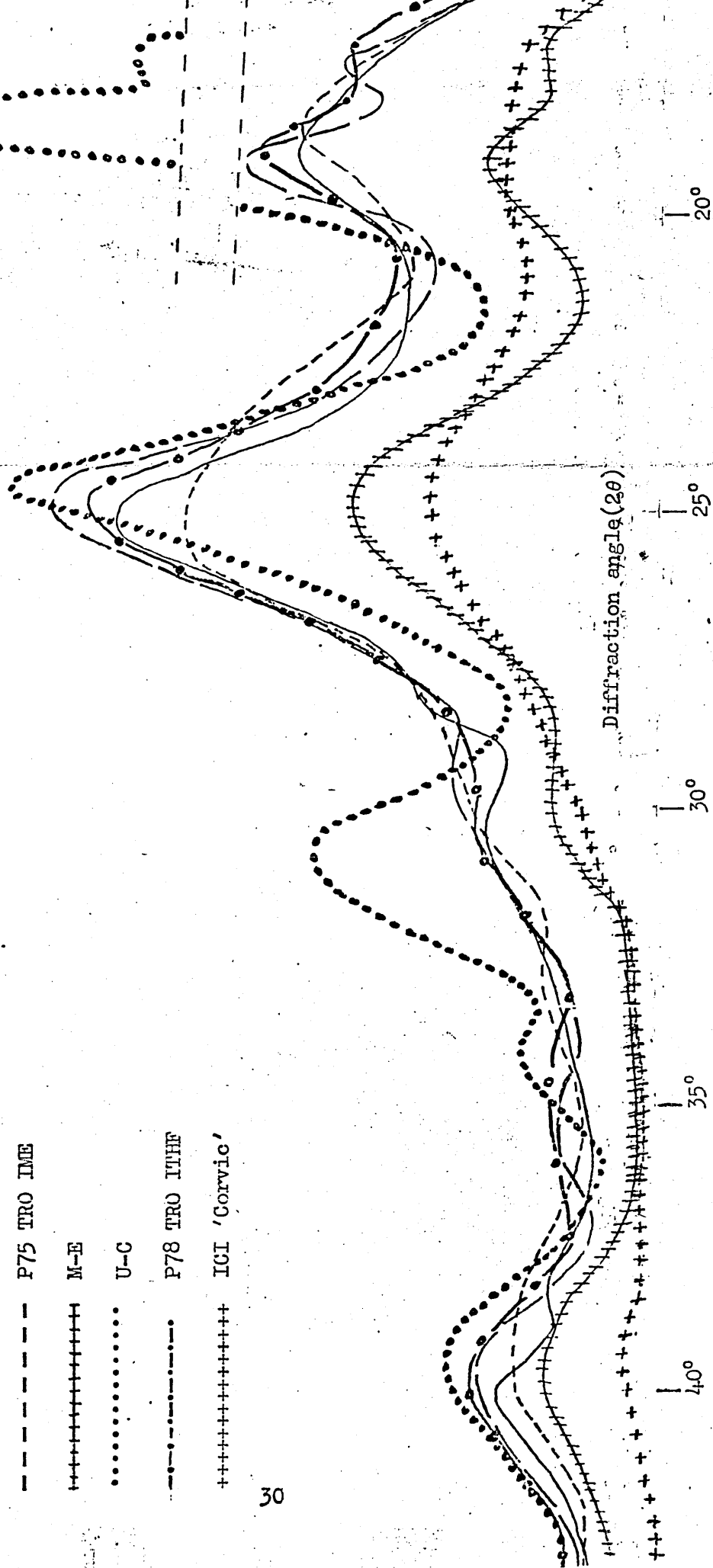


Fig 2.3a The X-ray diffraction patterns of annealed PVC samples.

- Untreated cold pressed disc
- - - Annealed for 1 hour at 140 °C
- +++++ Annealed for 6 hours at 140 °C
- - - - - Annealed for 31 hours at 140 °C

The X-ray diffraction patterns of sample U-C

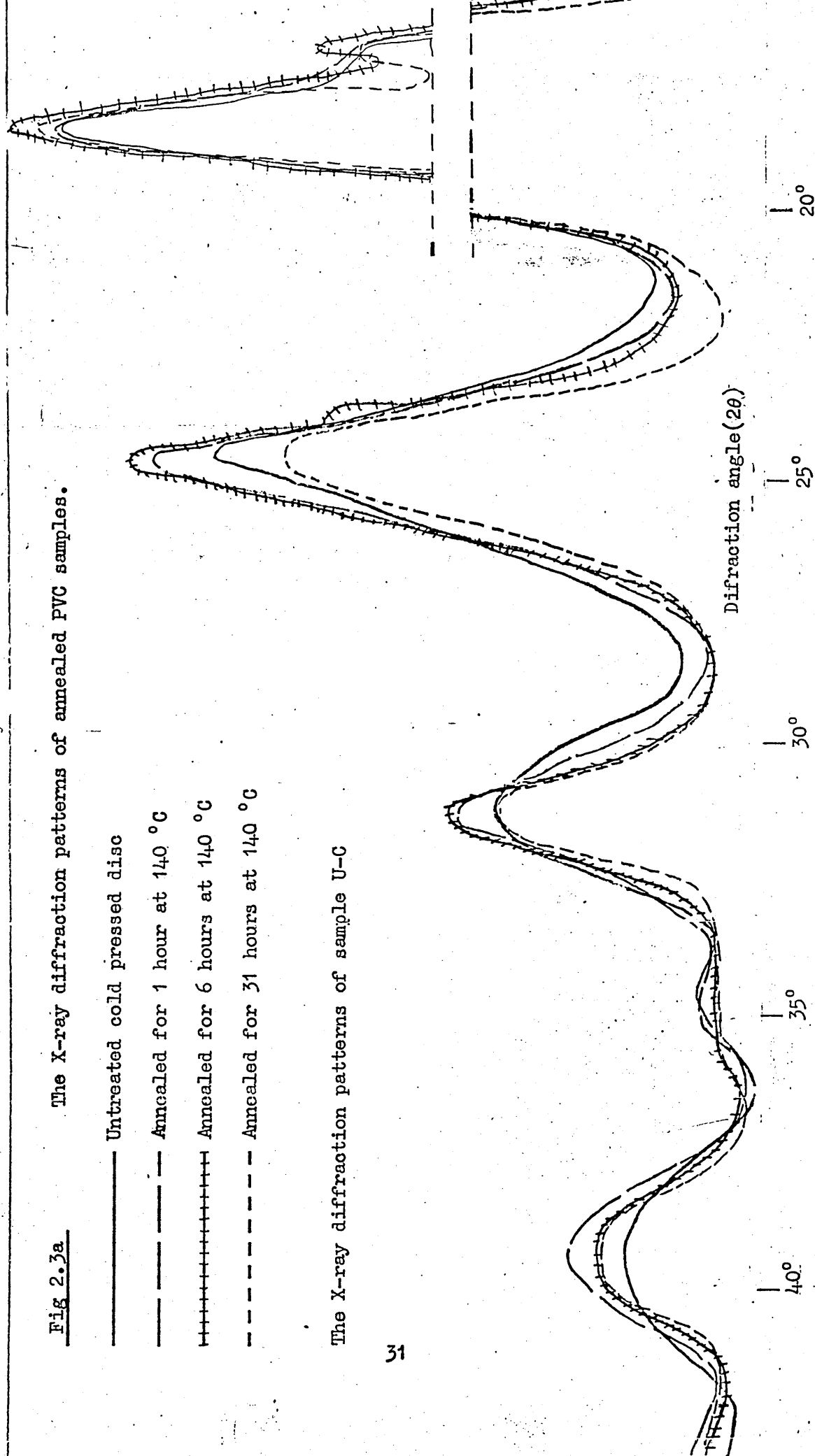


Fig 2.3b

X-ray diffraction patterns of sample P75 THO ITHF

(Sample treated as for U-G fig 2.3a)

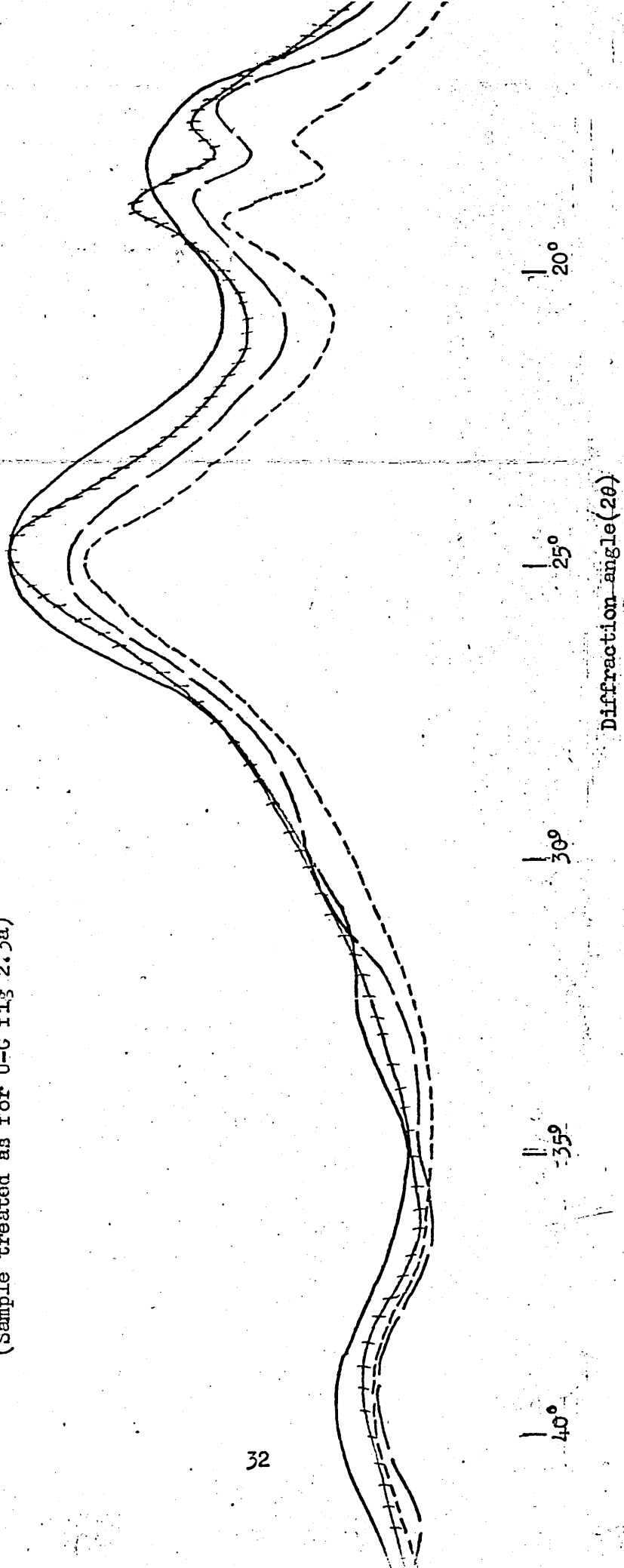


Fig 2.3c

X-ray diffraction patterns of sample P74 TRO ITHF
(Sample treated as for U-C Fig 2.3a)

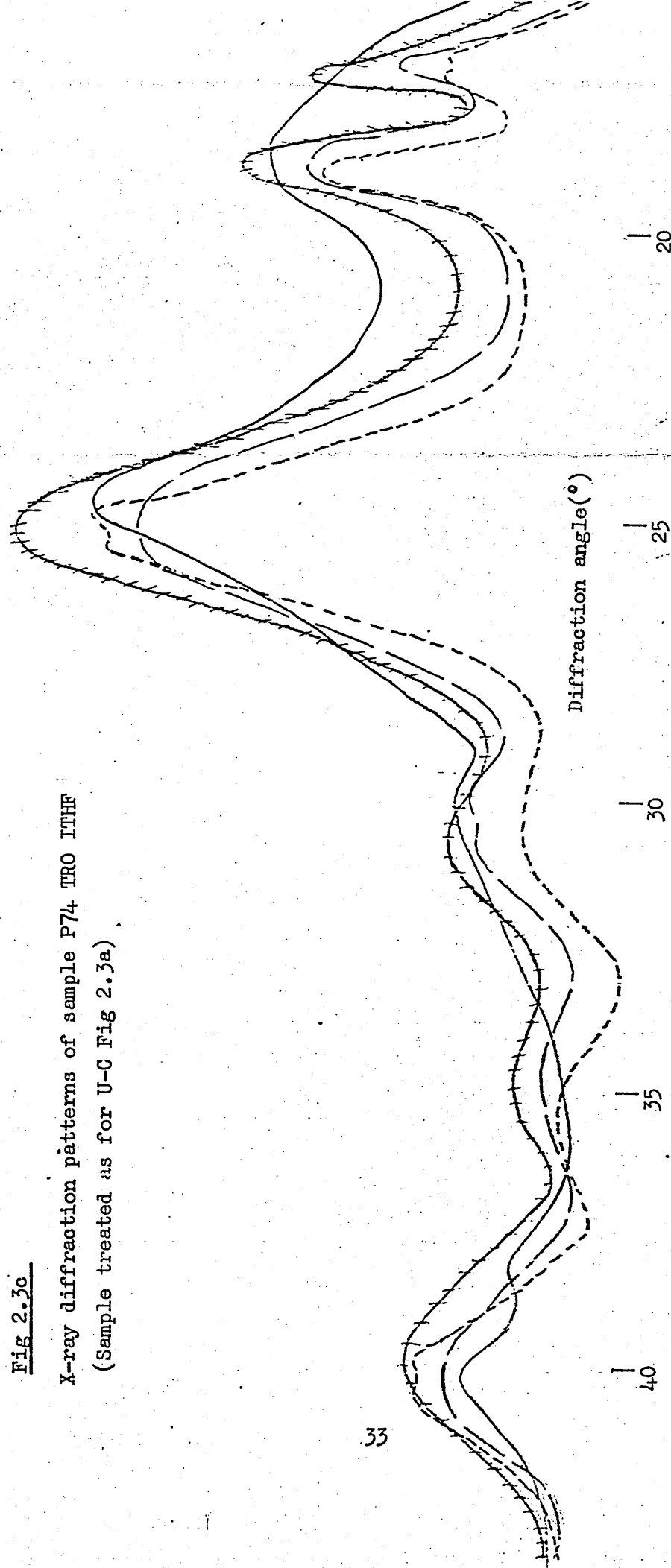


Fig 2.3d

X-ray diffraction patterns of sample P75 TRO ITHF
(Sample treated as for U-C Fig 2.3a)

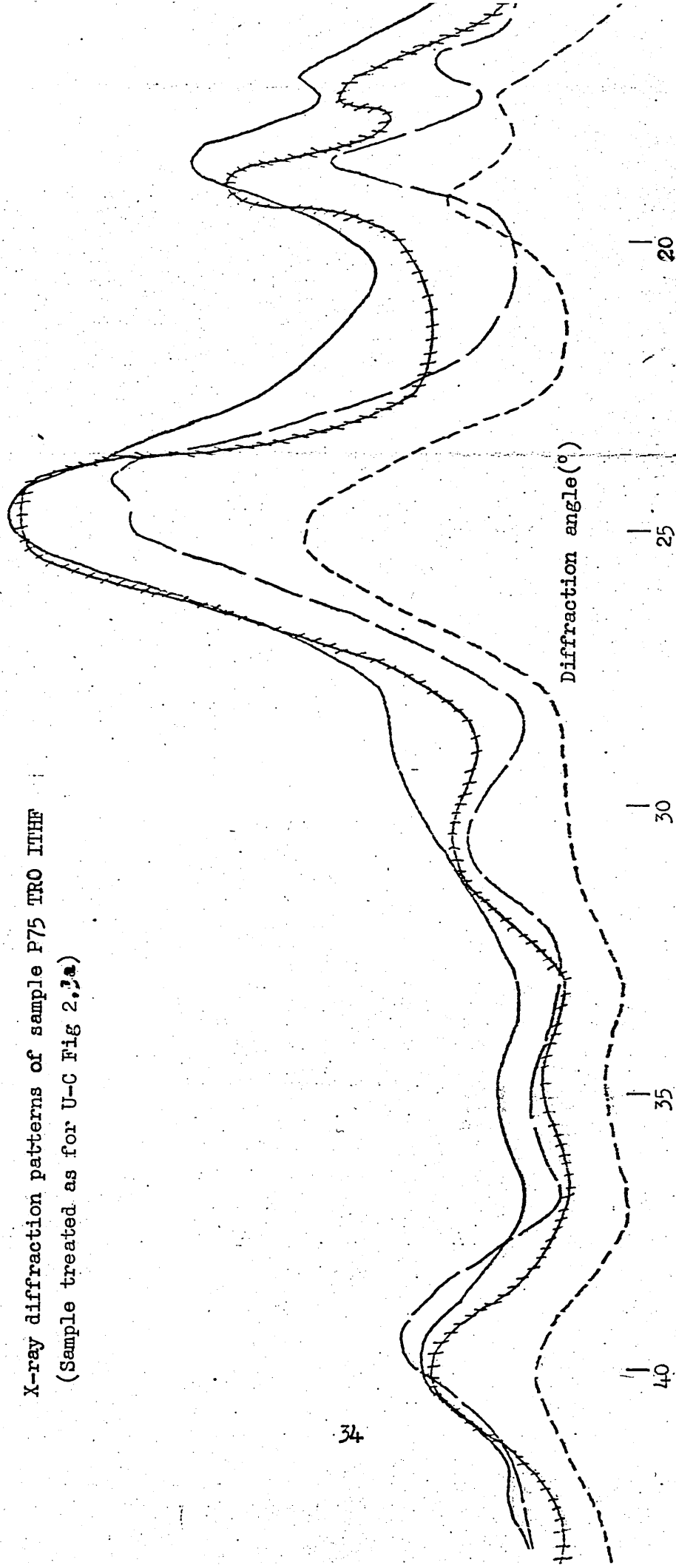


Fig 2.4

The far-infrared spectra (40-100 cm^{-1} and 160-230 cm^{-1}) of various samples of PVC.

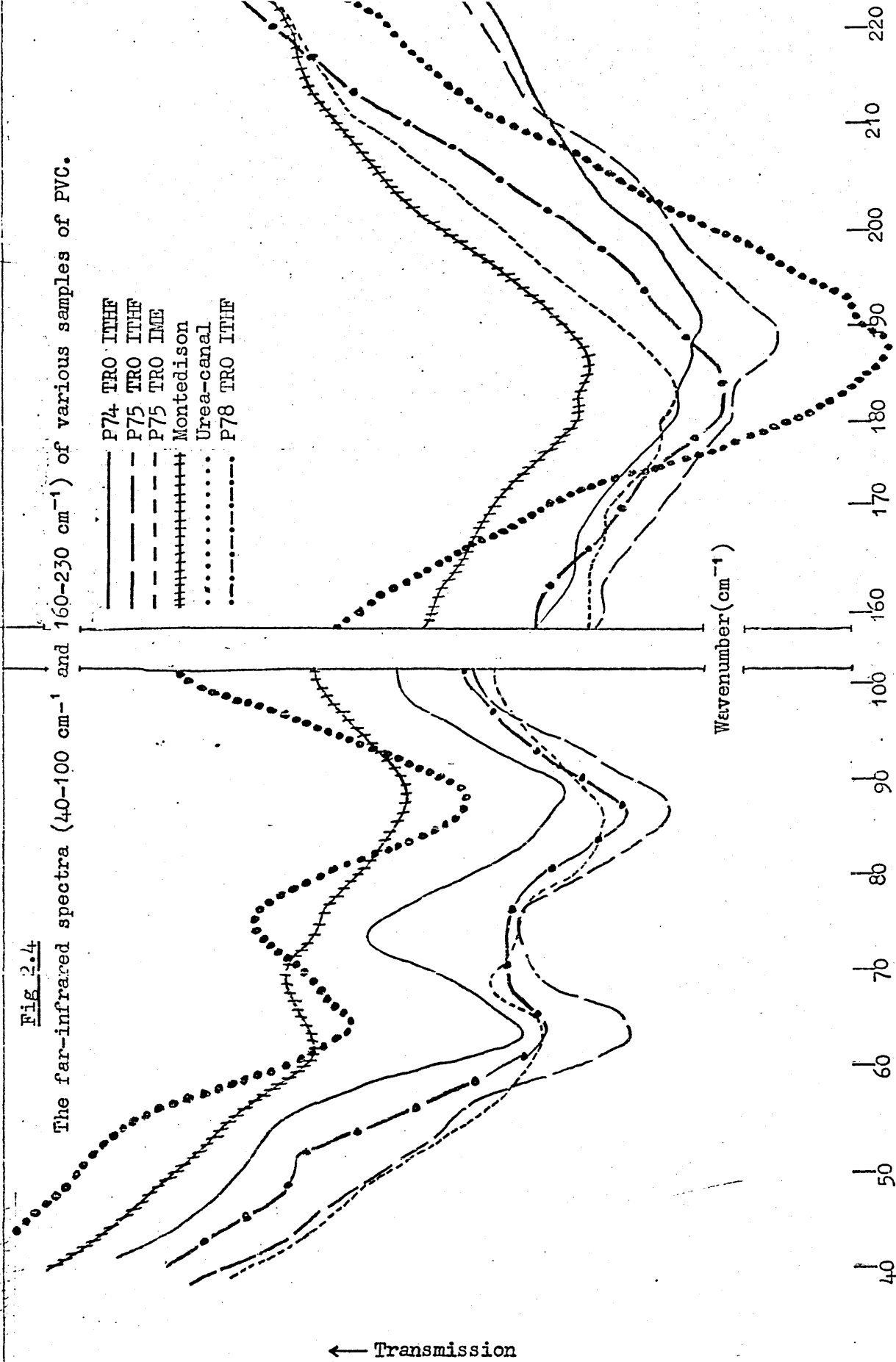


Fig 2.5a

The far-infrared spectrum of P74 TRO LTHF

The transmittance of the ca. 88 cm^{-1} band has been adjusted to the same value in all four spectra. In order to show any changes in the ca. 64 cm^{-1} lattice band.

- Untreated cold pressed disc
- - - Annealed for 1 hour at 140°C
- +++++ Annealed for 6 hours at 140°C
- - - Annealed for 31 hours at 140°C

Samples cooled to ambient temperature at $1^\circ\text{C}/\text{min}$.

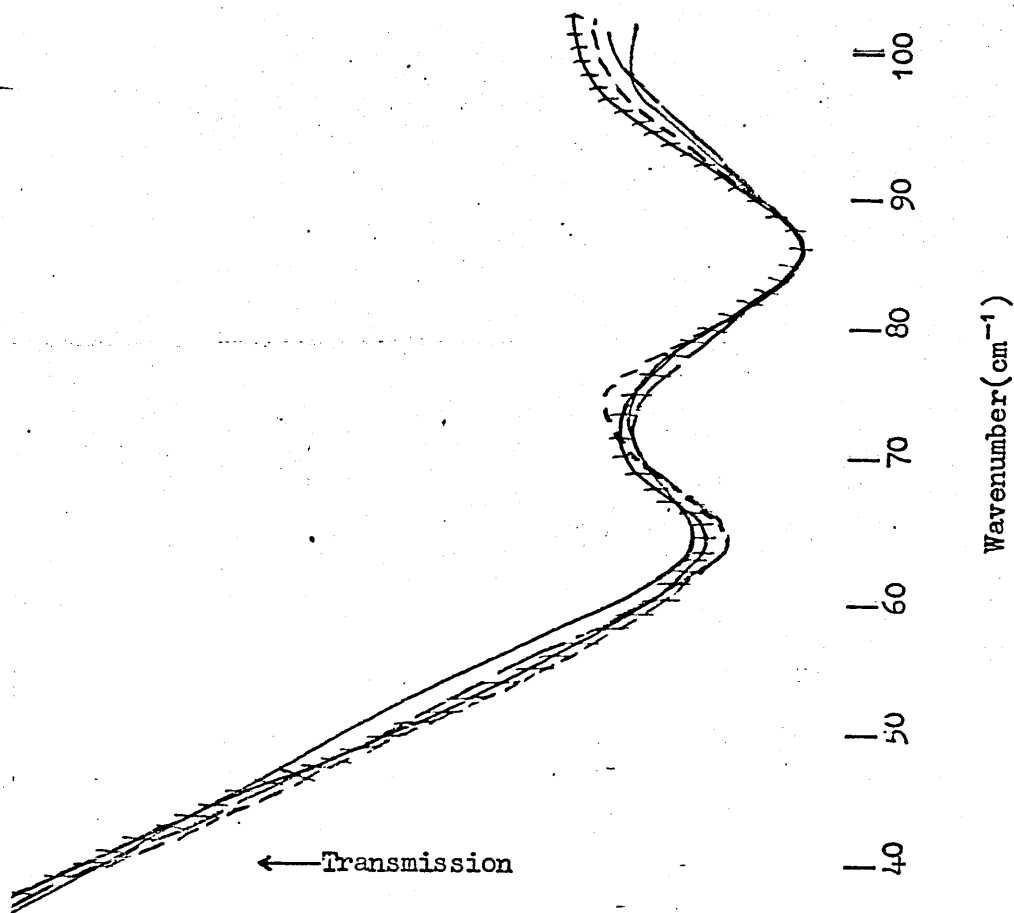


Fig 2.5b

The far-infrared spectrum of P75 TRO ITHF
(treated as described in fig 2.5a)

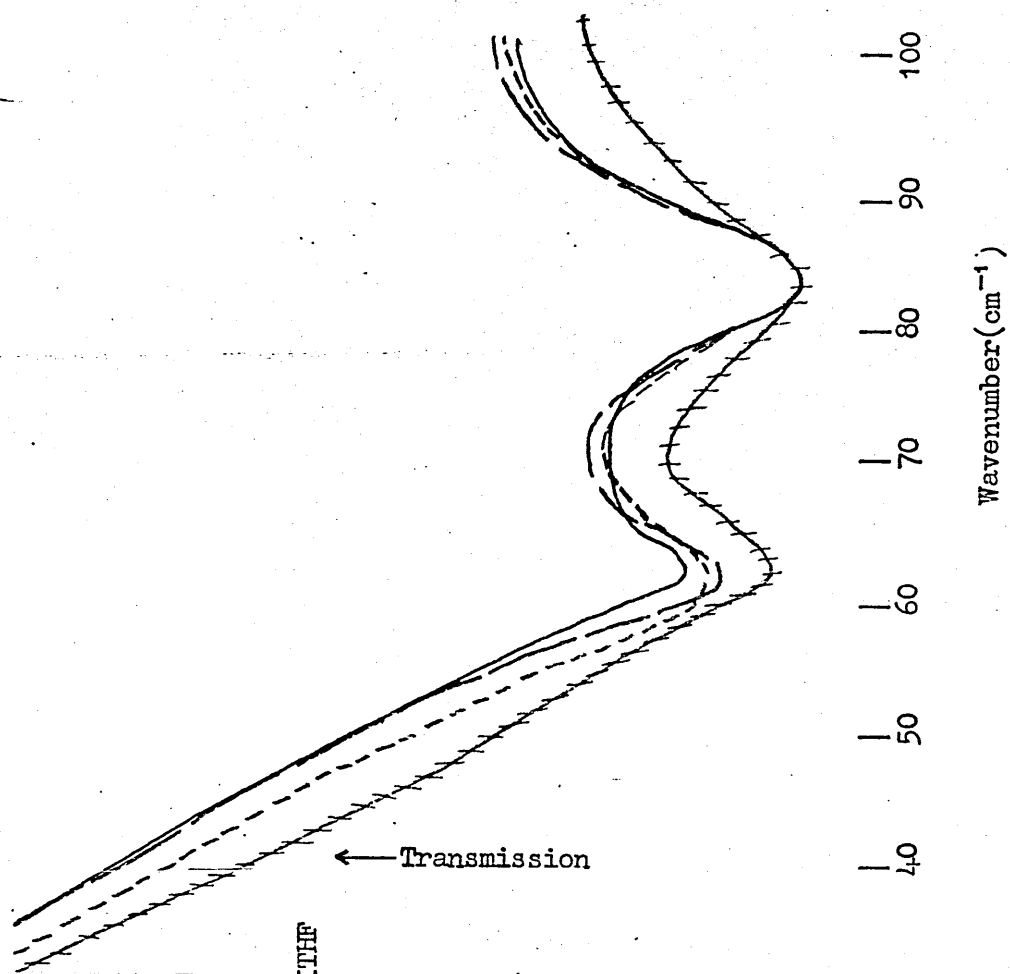


Fig 2.50

The far-infrared spectrum of P75 TRO ITHF
(treated as described in fig 2.5a)

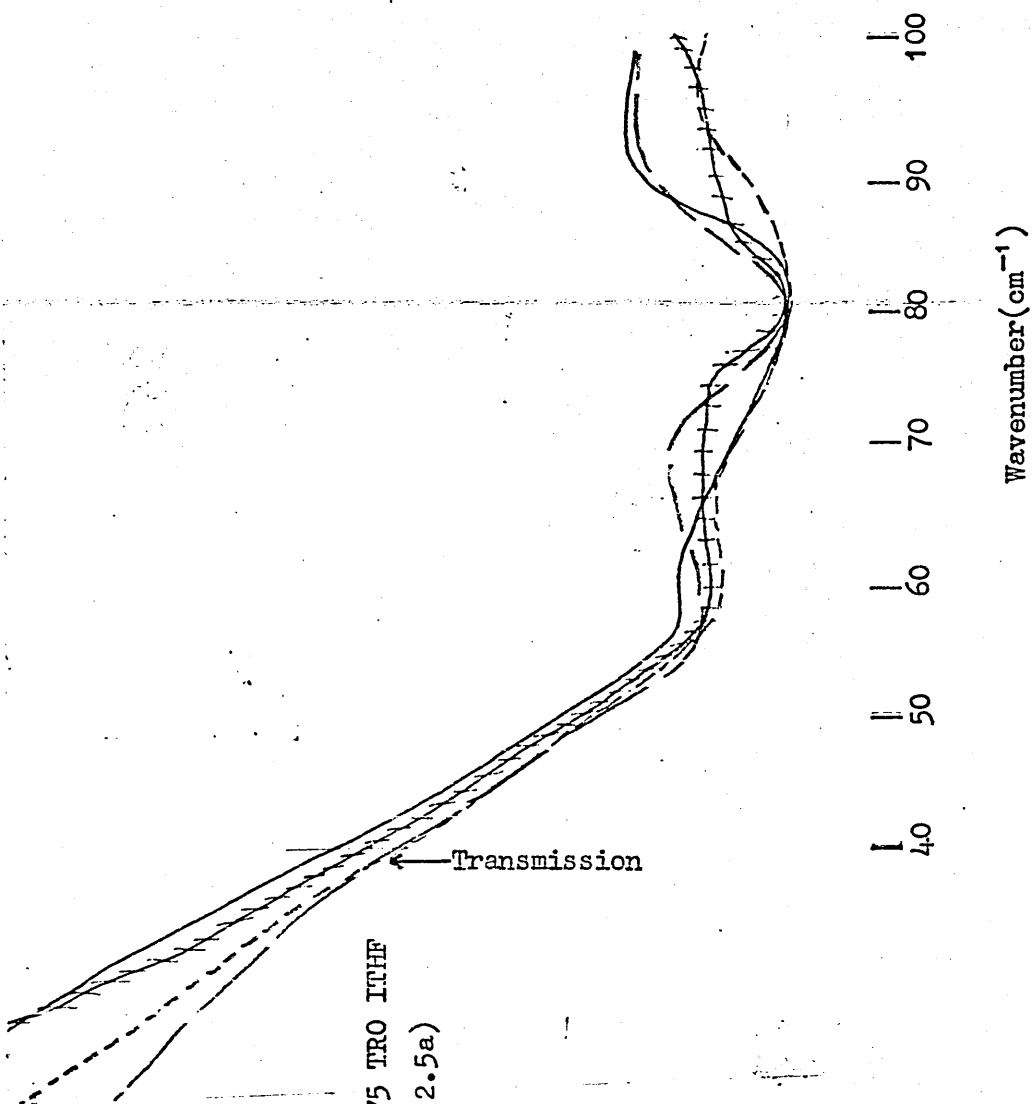
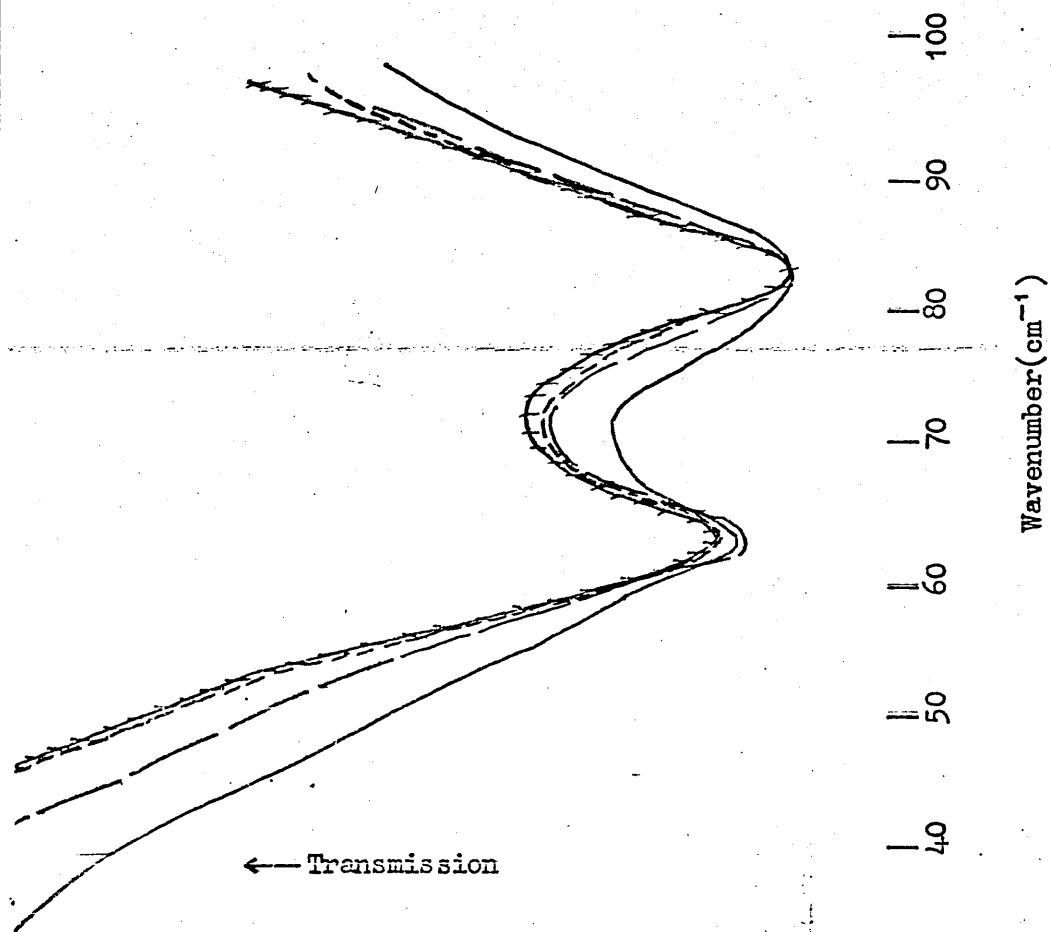


Fig 2.5a

The far-infrared spectrum of sample U-C
(Treated as described in fig 2.5a)



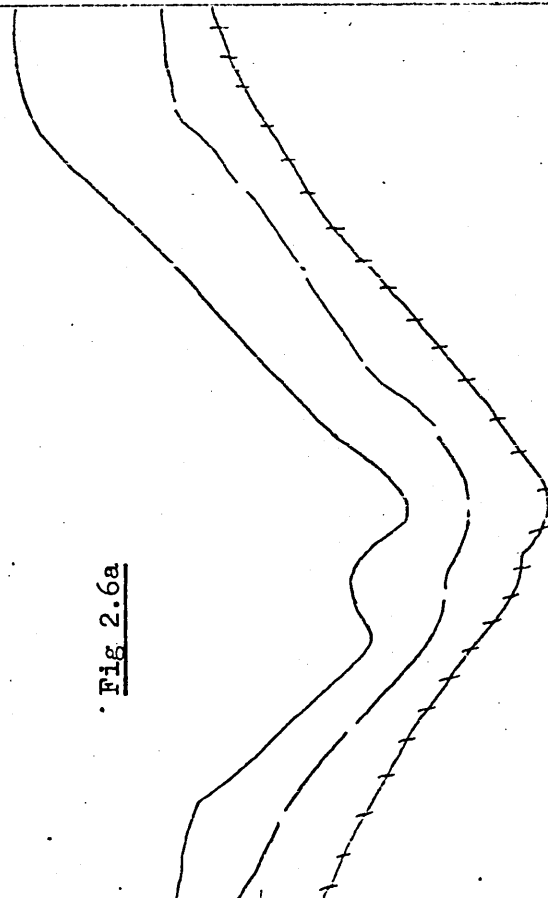
— Untreated cold pressed disc

--- Untreated cold pressed disc annealed at 140 °C for 1 hour

+++++ The above sample annealed at 140 °C for 17 hours

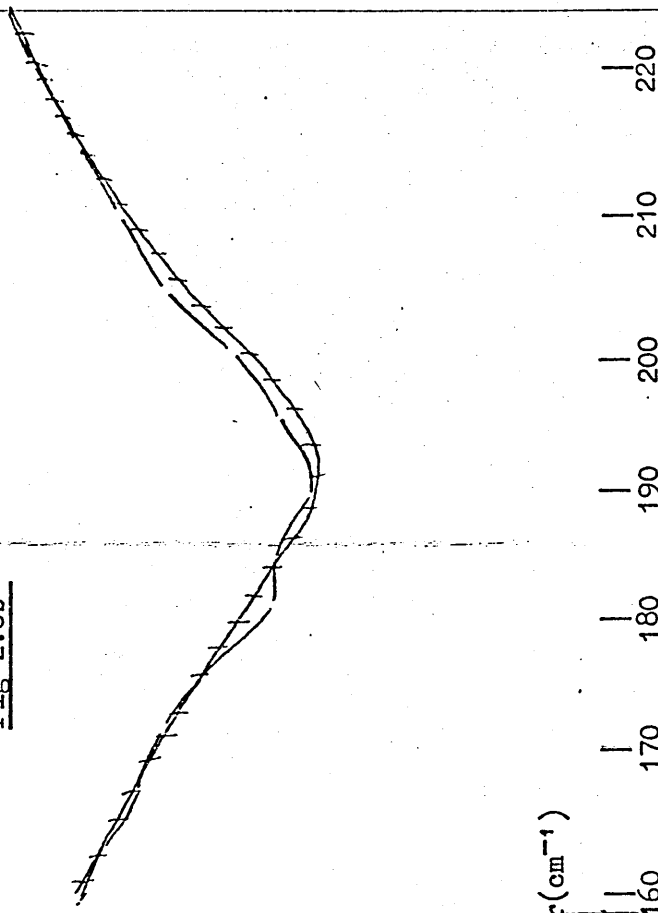
The far-infrared spectra (160-230 cm^{-1}) of sample P74 TRO ITHF

Fig 2.6a

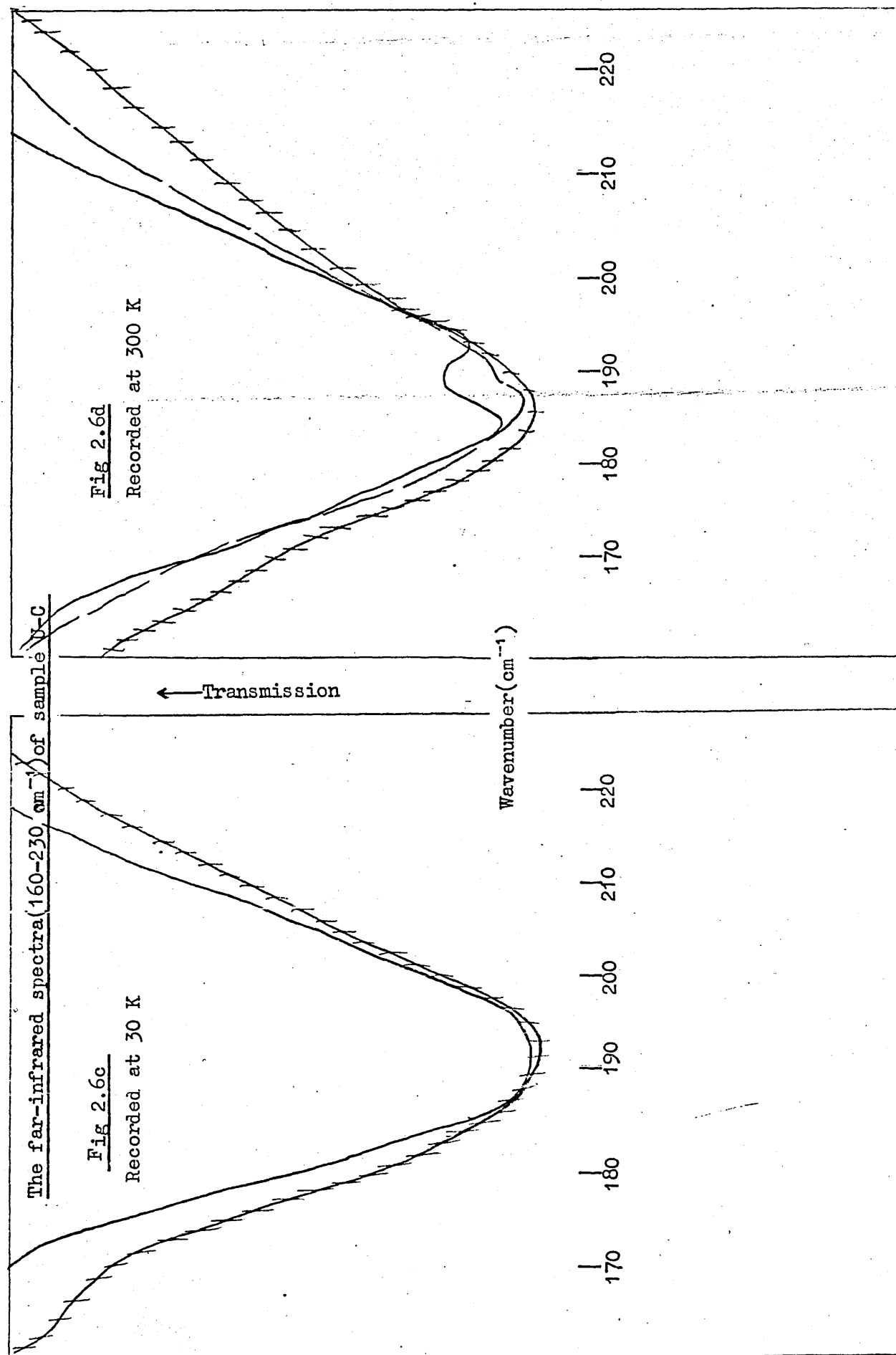


↑ Transmission

Fig 2.6b



Wavenumber(cm^{-1})



The far-infrared spectra (160-230 cm^{-1}) of sample P75 TRO ITHF
(samples prepared as in fig 2.6a.)

Fig 2.6e
Recorded at 30 K

← Transmission

Wavenumber (cm^{-1})

170 180 190 200 210 220

Fig 2.6f
Recorded at 300 K

170 180 190 200 210 220

The far-infrared spectra (160-220 cm^{-1}) of sample P75 TROIME
(samples prepared as in fig 2.6a)

Fig 2.6g

Recorded at 30 K

← Transmission

Wavenumber (cm^{-1})

160 170 180 190 200 210 220

Fig 2.6h

Recorded at 300 K

160 170 180 190 200 210 220

The far-infrared spectra (160-230 cm^{-1}) of sample M-E
(samples prepared as in fig 2.6a)

Fig 2.6i
Recorded at 30°K

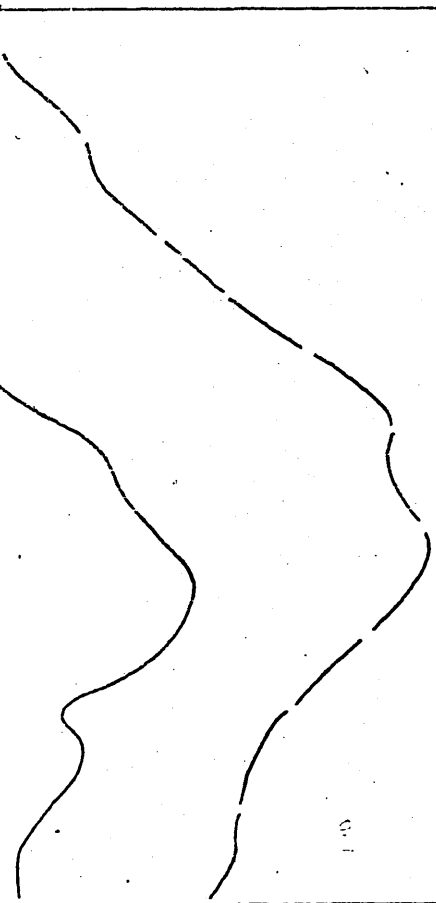
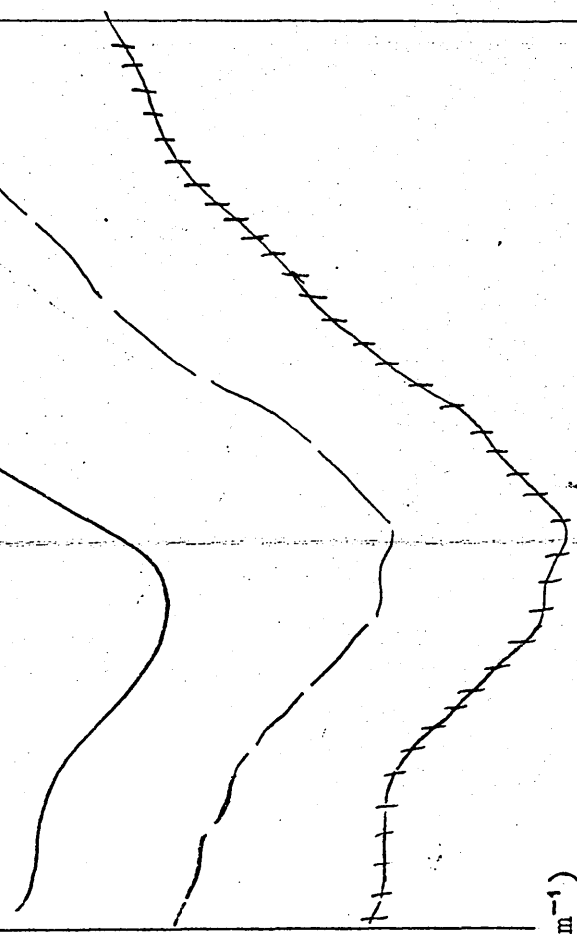


Fig 2.6j
Recorded at 300 K



Wavenumber(cm^{-1})

↑ Transmission

Fig 2.7a

The far-infrared spectrum of sample U-C
recorded at 30 K and 300 K

(Cold pressed disc annealed for 1 hour at 140 °C)

← Transmission

— Spectrum recorded at ca. 30 K

- - - Spectrum recorded at ca. 300 K

Wavenumber(cm^{-1})

100

90

80

70

60

50

40

Fig 2.7b

The far-infrared spectrum of sample
P74 TR0 ITHF recorded at 30 K and 300 K

(Cold pressed disc annealed for 1 hour at 140 °C)

← Transmission

— Spectrum recorded at ca. 30 K

- - - Spectrum recorded at ca. 300 K

Wavenumber(cm^{-1})

40 50 60 70 80 90 100

Fig 2.70

The far-infrared spectrum of sample
P75 TRO ITHF recorded at 30 K and 300 K

(Cold pressed disc annealed for 1 hour at 140 °C)

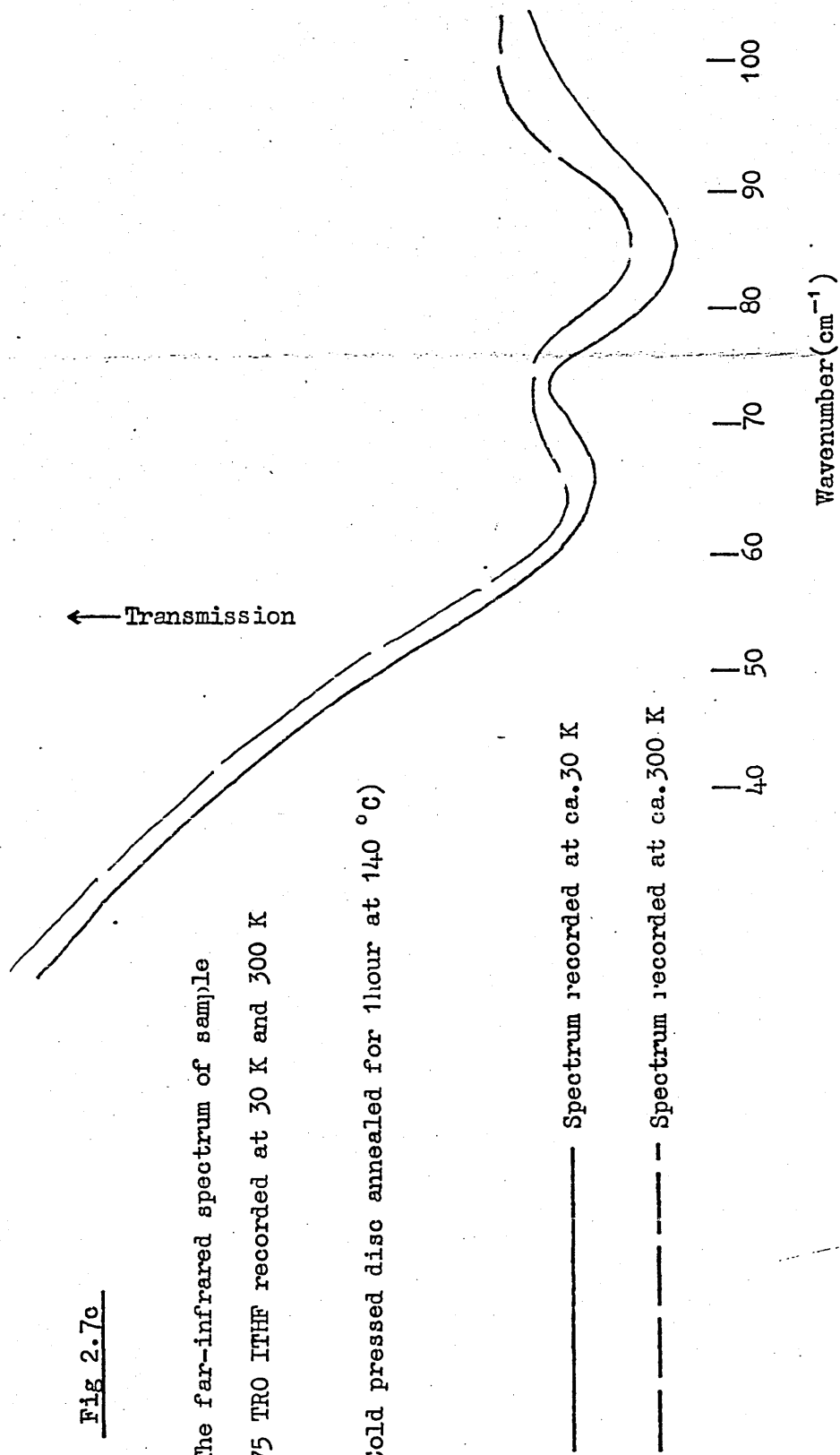


Fig 2.7d

The far-infrared spectrum of sample P75 TRO ITHF
recorded at 30 K and 300 K

(Cold pressed disc annealed for 1 hour at 140 °C)

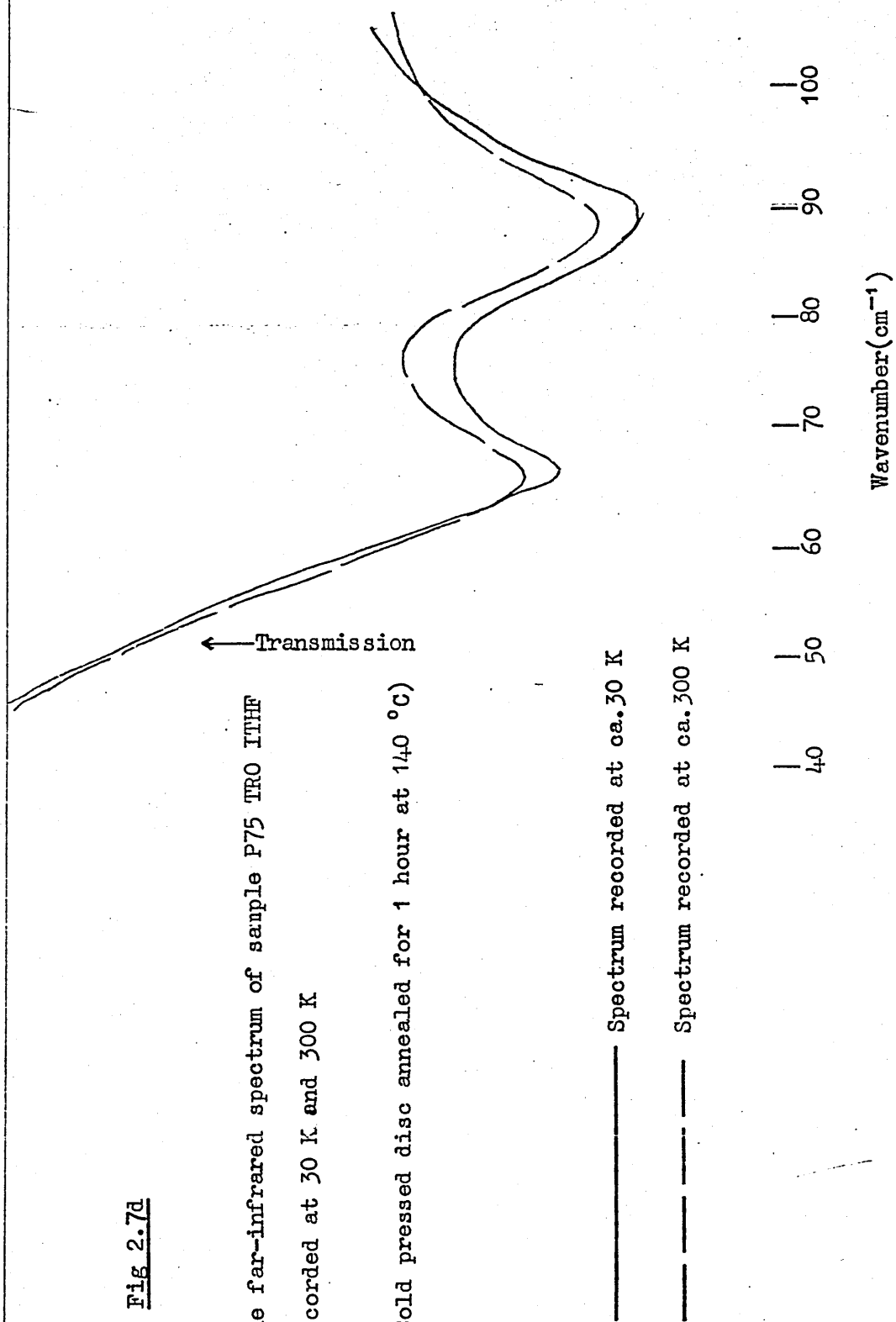


Fig 2.8a

----- PVC (commercial sample polymerised at 64 °C)

———— VC/VA (a copolymer of vinyl chloride and vinyl acetate with 16% vinyl acetate).

← Transmission

90 100 110 120 130 140 150 160 170 180 190

Wavenumber (cm⁻¹)

Fig 2.8b

----- PVC (commercial sample polymerised at 64 °C)

———— VC/VA (a copolymer of vinyl chloride and vinyl acetate with 16% vinyl acetate).

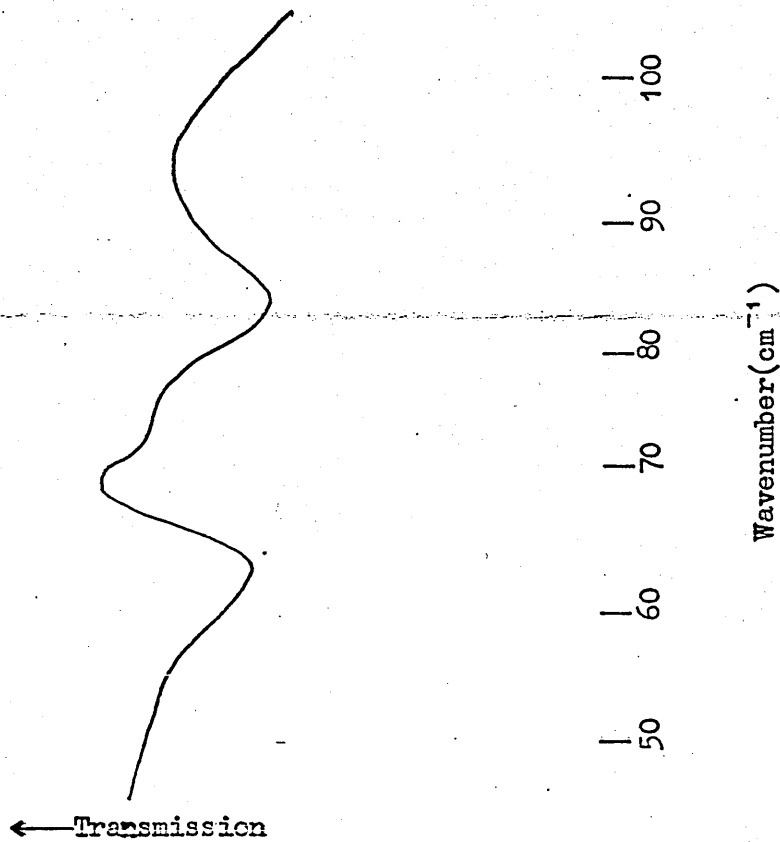
← Transmission

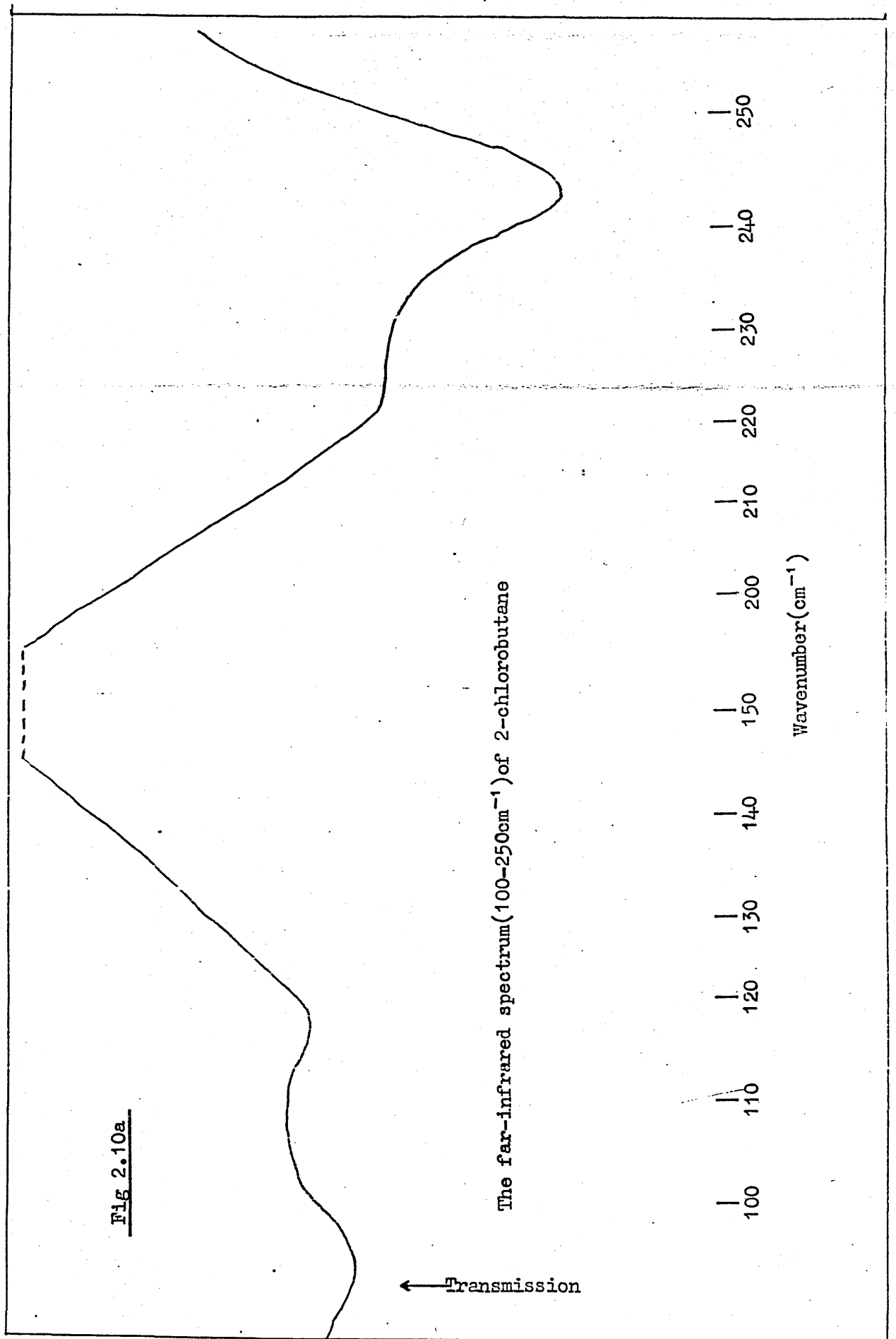
Wavenumber (cm⁻¹)

320 330 340 350 360 370 380 390 400 410 420 430

Fig 2.9

The spectrum of PVC sample P75 TRO LME
at ca. 450 K (sample heated in a liquid
cell containing PTFE windows)





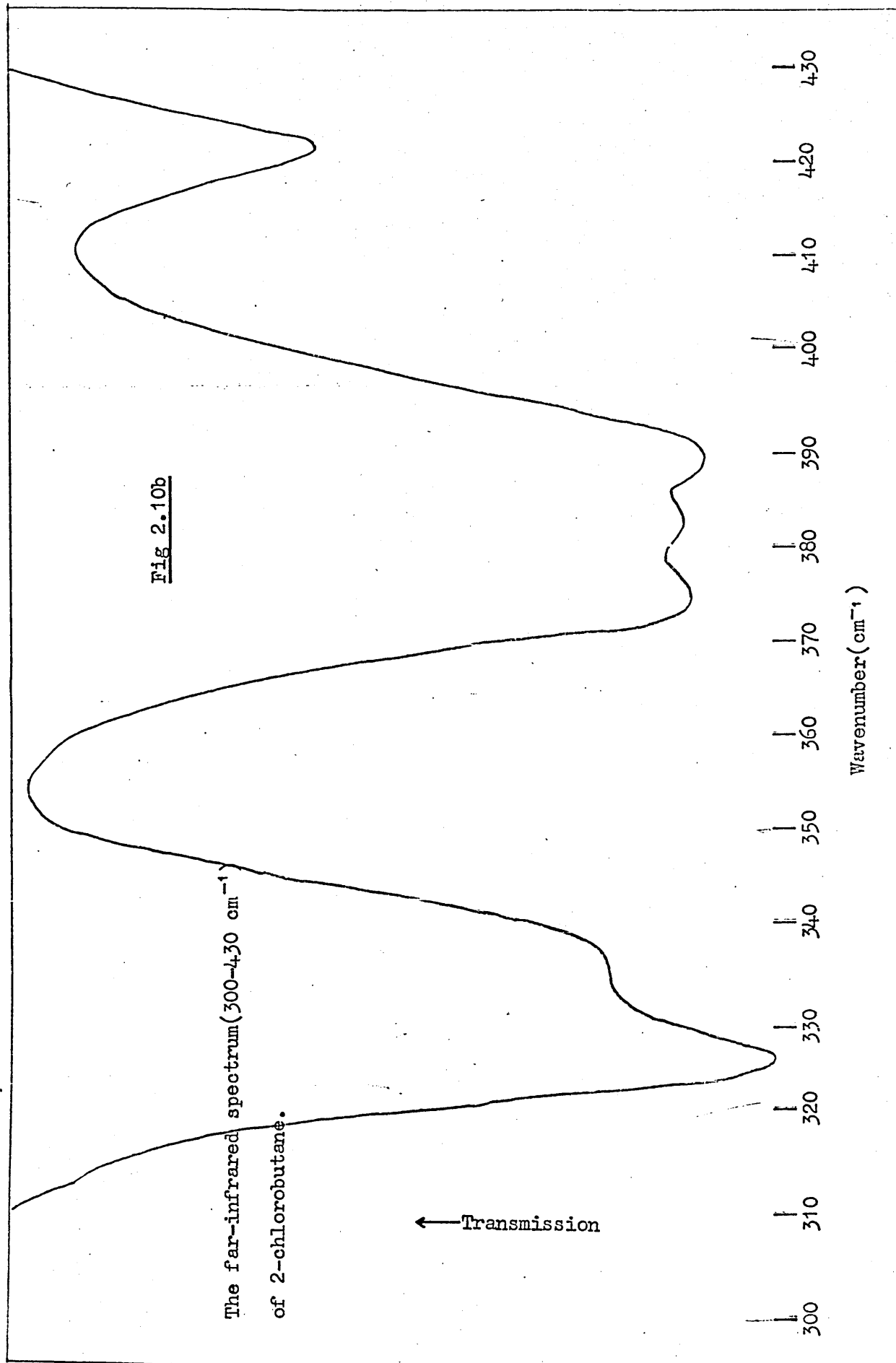


Fig 2.10b

Chapter 3

The Frequency - temperature Dependence of the Vibrational Lattice Bands in Polyethylene and Poly(vinyl chloride)

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3.1 Introduction

At low frequency in the far-infrared spectrum many bands appear broad at room temperature, because at ca. 300 K there is sufficient thermal energy to populate vibrational energy levels higher than the ground level, $\bar{\nu} \approx kT/hc$ (where $\bar{\nu}$ is the wavenumber of the band, k is the Boltzmann constant, T is the temperature in Kelvin, h is Planck's constant and c is the velocity of light). As the higher energy levels are closer together this gives rise to lower frequency transitions which broaden, and shift the band to lower wavenumber at room temperature as compared with lower temperatures. Lowering the temperature reduces the 'hot band' contribution with sharpening of the observed band and an increase in wavenumber of the apparent absorption maximum. However, lattice bands shift much more than would be expected by this mechanism, due to contraction of the crystal lattice on cooling producing an increase in the effective force constant of intermolecular vibrational modes. Thus a substantial shift to higher frequency of lattice bands occurs on lowering the sample temperature.

3.2 Experimental

Samples

High density polyethylene sample PE1: unknown origin.

High density polyethylene sample PE2: unknown origin.

High density polyethylene sample EE 3:BP Chemicals Rigidex 50 blend 9175.

Urea-canal PVC.

All three PE samples were in the form of hot-pressed sheets 3 to 4 mm thick. Urea-canal PVC in the form of a coarse powder was either used untreated or cooled using liquid nitrogen, to make it brittle, and ground in a ball mill, in order to homogenise and break up the larger particles in the sample, before being cold pressed into discs as described in Chapter 2. Polyethylene was recrystallised from the melt by heating sample discs to 160 °C for 4 hours and cooling to ambient temperature at 1 °C per minute. PVC discs were annealed at 150 °C or 180 °C for between 1 and 17 hours, and cooled to ambient temperature at 1 °C per minute.

The sample temperature during the spectral measurements was controlled with a Cryodyne and measured with a thermocouple attached to the cold head. This was calibrated by placing the cold head in various slush baths; the graph, after calibration, of slush bath temperature versus thermocouple reading is shown in Fig 3.1. The thermocouple reading was compared with another thermocouple, similarly calibrated, placed within a PE disc, and thus a correction graph from measured cold head temperature to true sample temperature could be plotted (Fig 3.2). A possible inaccuracy of this method is that the sample thermocouple could be conducting heat into the sample making the sample temperature erroneously high. However, spectra obtained with the thermocouple embeded in the sample corresponded well with those from equivalent samples without a thermocouple within them.

The energy throughput was cut down by the presence of the thermocouple when sealed in the samples, so this procedure was not used routinely.

On reaching the required temperature, the samples were allowed 15 minutes to attain a steady temperature before spectral measurements were carried out. An accuracy of ± 2 K was expected for the temperature measurements, and the theoretical spectral resolution was 2.5 cm^{-1} which allowed band positions to be measured to an estimated precision of $\pm 0.5 \text{ cm}^{-1}$. The measurement of the position of band centre was achieved from the computer readout of the Fourier transformed interferogram, which consisted of a spectrum made up of a series of points spaced at 2.5 cm^{-1} intervals, by assuming the band centre corresponded to the centre of a parabola passing through three points adjacent to the band centre. The centre of the parabola was calculated from the co-ordinates of these three points using a computer programme (given in Appendix I, at the end of this thesis).

3.3 The 72 cm⁻¹ Lattice Band in Polyethylene

3.3.1 Introduction

There have been many temperature transitions reported for PE, most of which have been attributed to the glass transition temperature (T_g). Values from 140 K to 340 K have been reported for T_g (1), and other transitions are claimed as low as 108 K by torsion pendulum (2) and as high as 370 K by torsion braid analysis (3). The wide variation in the reported data has been the basis of several reviews. Davis and Eby (1) concluded that $T_g = 231 \pm 9$ K, whereas Boyer (4) concluded $T_g = 195 \pm 10$ K, and more recently Beatty and Karasz (5) concluded $T_g = 145$ K.

As T_g is the temperature at which the interactions between adjacent chains in the amorphous regions are overcome by thermal energy (effectively the melting point of the amorphous phase), it is not surprising that in a largely crystalline polymer such as PE T_g should be difficult to detect. Several methods are available to determine T_g , for example changes in specific volume with temperature, but because discontinuities in the variation are only small, T_g is very difficult to locate (5). Even heat capacity measurements (5) give rise to great difficulty in locating amorphous transitions in PE. To overcome the problem of high crystallinity, copolymers of different compositions have been used and T_g measurements extrapolated back to pure PE (6,7). However a small concentration of copolymer could adversely affect the structure of PE making the extrapolation non-linear at very low concentrations of the copolymer material (4,8). Recently (5,8) ultra high molecular weight PE which can be made reasonably amorphous has become available, but still the value of T_g in PE is far from being settled. However the balance of evidence is in favour of a value around 145 K.

3.3.2 Far-infrared Measurements

The far-infrared spectrum of PE contains a lattice band at 72 cm^{-1} . Its observed frequency is in good agreement with calculations by Tasumi and Shimanouchi(9), and Tasumi and Krimm (10). Its shift in frequency with temperature has been noted previously by Krimm and Bank (11) who obtained a linear plot of band position against temperature of the form $\bar{\nu} = 80.7 - 0.0323 T$, and by Frank et al. (12) who obtained a $\bar{\nu}/T$ plot which shows a change in gradient at 243 K.

3.3.3 Results

The graphs of band position against temperature for the three untreated PE samples are shown in Figs 3.3, 3.4 and 3.5. The graphs for sample PE1 and PE2 that have been recrystallised from the melt by cooling at 1°C per minute from 160°C are shown in Figs 3.6 and 3.7, respectively. The observed transitions are tabulated in Table 3.1. There are two observed temperature transitions in the various samples in the range 60 - 320 K: between 120 K and 160 K and between 225 K and 305 K.

3.3.4 Discussion and Conclusions

(a) Transition Temperatures

The results obtained show a dependence on sample pre-treatment. Two effects are noted on recrystallisation: the transitions move to lower temperature and the transitions become broader and less prominent.

The transitions are found at lower temperatures because on increasing the crystallinity, by recrystallisation from the melt, the most favourable interactions in the amorphous phase are converted to crystalline material. Thus after heat treatment is complete a greater proportion of weaker amorphous interactions are left to be

broken at the transition temperature and consequently the transition takes place at lower temperature. This effect is seen most clearly on annealing sample PE1 (Figs 3.3 and 3.6).

An increase in crystallinity also leads to a broadening of the transitions; this is most noticeable on comparing Fig 3.3 (PE1 untreated) and Fig 3.6 (PE1 recrystallised). The effect may be attributed to a decrease in the amount of amorphous material which make any transitions due to the amorphous phase weaker.

Thus, it can be seen that the temperatures at which transitions occur in PE are dependent on the crystallinity of the sample. This would explain why a wide range of values have been reported for T_g and other transitions in PE.

(b) Origin of the transitions

In the present work, two temperature transitions have been identified from the temperature shift of the ca. 72 cm^{-1} lattice band in PE. The transition in the various samples between 120 K and 165 K corresponds reasonably well with a previously reported transition at ca. 145 K (1,4,5). The other transition occurring between 225 K and 305 K probably corresponds to the transition previously reported at 240 K (1,4,5).

Boyer (4) concluded that the 145 K transition is a γ chain relaxation, whereas Beatty and Karasz(5) considered that the transition was the glass transition temperature. γ chain relaxations are thought (4) to involve between 4 and 7 adjacent chain atoms which begin to vibrate and twist. Such transitions only usually occur in branched polymers (5); high density PE however has a low concentration of chain branches. For example, sample PE3 has a branching level, estimated as methyl groups, not exceeding one per thousand carbon atoms. At such a low branching level γ chain relaxations would not

be expected to occur, and certainly would not be detectable by the measurements of the present work. Thus the transition observed in the samples between 120 K and 165 K is probably the glass transition temperature.

Davis and Eby (1) concluded that the transition at ca. 240 K was the glass transition temperature and Boyer (4) that it was a transition involving loose loops and tie molecules. It had however been noticed in previous experiments (14) that the temperature at which this transition occurs is not reproducible. It was thus suggested by Sakaguchi et al. (15) that the transition was caused by a melting phenomenon associated with thermodynamically unstable crystals; such melting, they postulated, should occur between 220 K and 270 K depending on the thermal history of the sample. This postulation is in fair agreement with the present work insofar as the transition has been found to occur between 225 K and 305 K in the various samples studied.

The evidence therefore suggests that the transition occurring between 120 K and 165 K is the glass transition temperature and the transition occurring between 225 K and 305 K is due to the fusion of thermodynamically unstable crystals.

3.4 The 64 cm^{-1} Lattice Band in PVC

3.4.1. Introduction

The lattice band in U-C PVC, at ca. 64 cm^{-1} , shifts by some 8 cm^{-1} on cooling from 320 K to 60 K. The glass transition temperature is easily determined for commercial PVC samples as they are largely amorphous, the value obtained being ca. 360 K (16-20). However, the properties of PVC at low temperature, unlike PE, have not been extensively studied and no transitions below T_g have been reported.

3.4.2 Results

The variations of band position with temperature for two different discs of untreated U-C PVC are shown in Figs 3.8 and 3.9. Figs 3.10 and 3.11 relate to a disc annealed for 1 hour at 180°C and for 17 hours at 150°C , respectively (both being cooled from the annealing temperature at 1°C per minute). Figs. 3.12 and 3.13 relate to discs formed from U-C PVC which was ground to a fine powder before the discs were pressed.

3.4.3 Discussion and Conclusions

From Figs 3.8 to 3.13 it can be seen that unlike the results for PE the PVC data do not show a consistent pattern. Moreover, even positions for the same sample studied at the same temperature are not reproducible (cf. Figs 3.8 and 3.9). There are a number of possible explanations of why this happens.

- (a) The PVC discs used are ca. 30 times thinner than the PE discs used and consequently may not allow uniform conduction of heat from the centre of the disc to the sample holder.
- (b) U-C PVC could be structurally susceptible to temperature changes and cycles, and thus the order in which the data points are collected and the number of cooling cycles undergone by the sample could affect the position at which the ca. 64 cm^{-1} lattice band appears in the spectrum.

(c) Fig 3.15 shows the spectrum of U-C PVC from which the background spectrum of the instrument has not been subtracted. The spectrum shows a strong band due to PE, from which the detector lens is constructed, which masks the 64 cm^{-1} band of the PVC sample at room temperature. Thus particularly at the high temperatures studied, even though the spectrum obtained using a sample was ratioed against a 'background spectrum', errors in locating the 64 cm^{-1} band of PVC are likely to result. This would be further influenced by the broadness of the band in comparison to that of PE (see Fig 3.14). These, and possibly other reasons, could explain why the PE results were reproducible whereas the PVC results were not. It is however difficult to decide which, if any, was the major cause of the inconsistent PVC results.

3.5 References

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Table 3.1

Tabulation of temperature transitions observed in polyethylene
from far-infrared measurements.

Sample	Transition 1 (K)	Transition 2 (K)
Untreated PE1	135	270
PE1 (recrystallised)	120	<u>ca.</u> 225
Untreated PE2	165	305
PE2 (recrystallised)	160	290
Untreated PE3	120	305

Fig 3.1

Thermocouple calibration using constant temperature baths

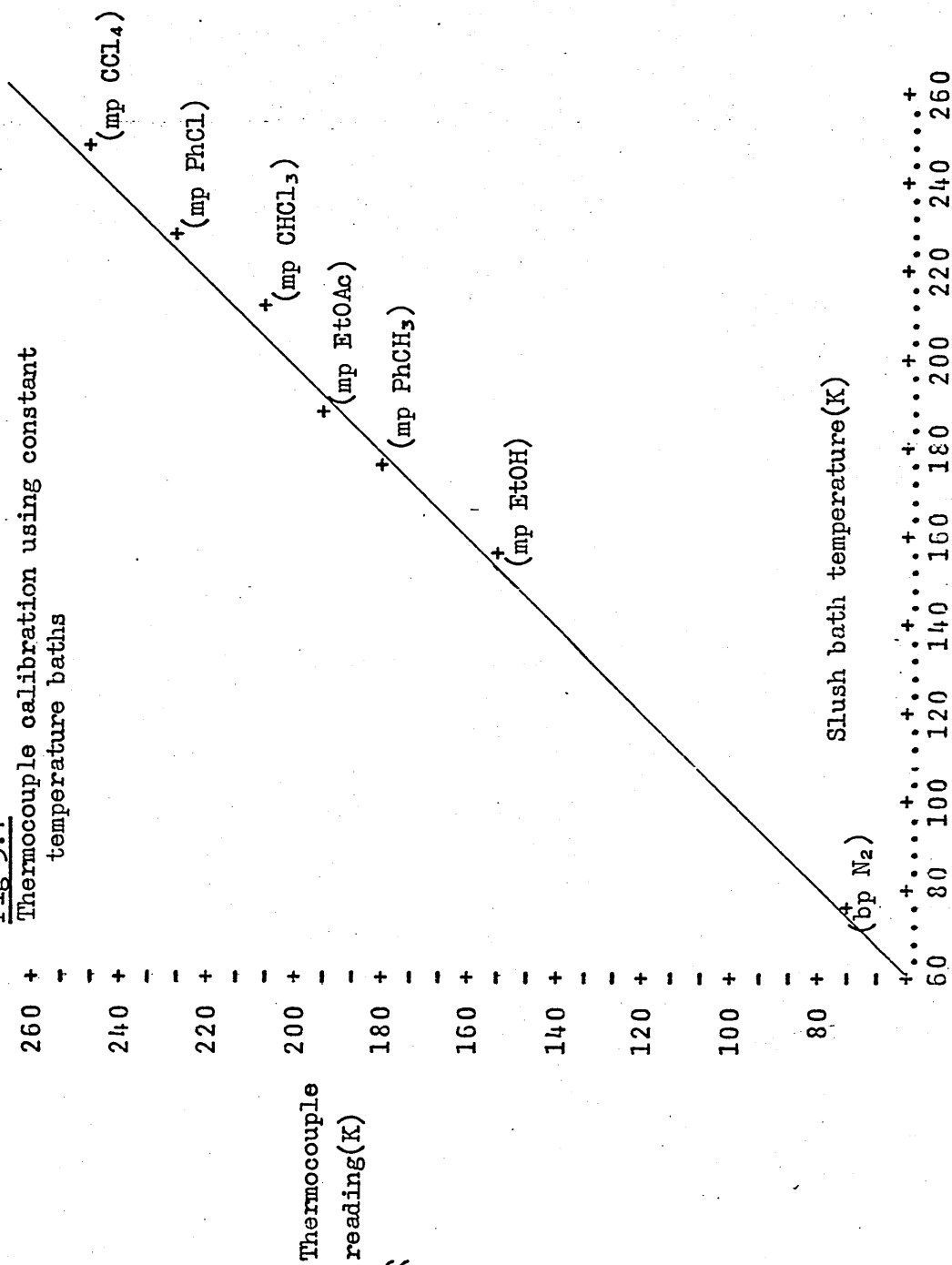
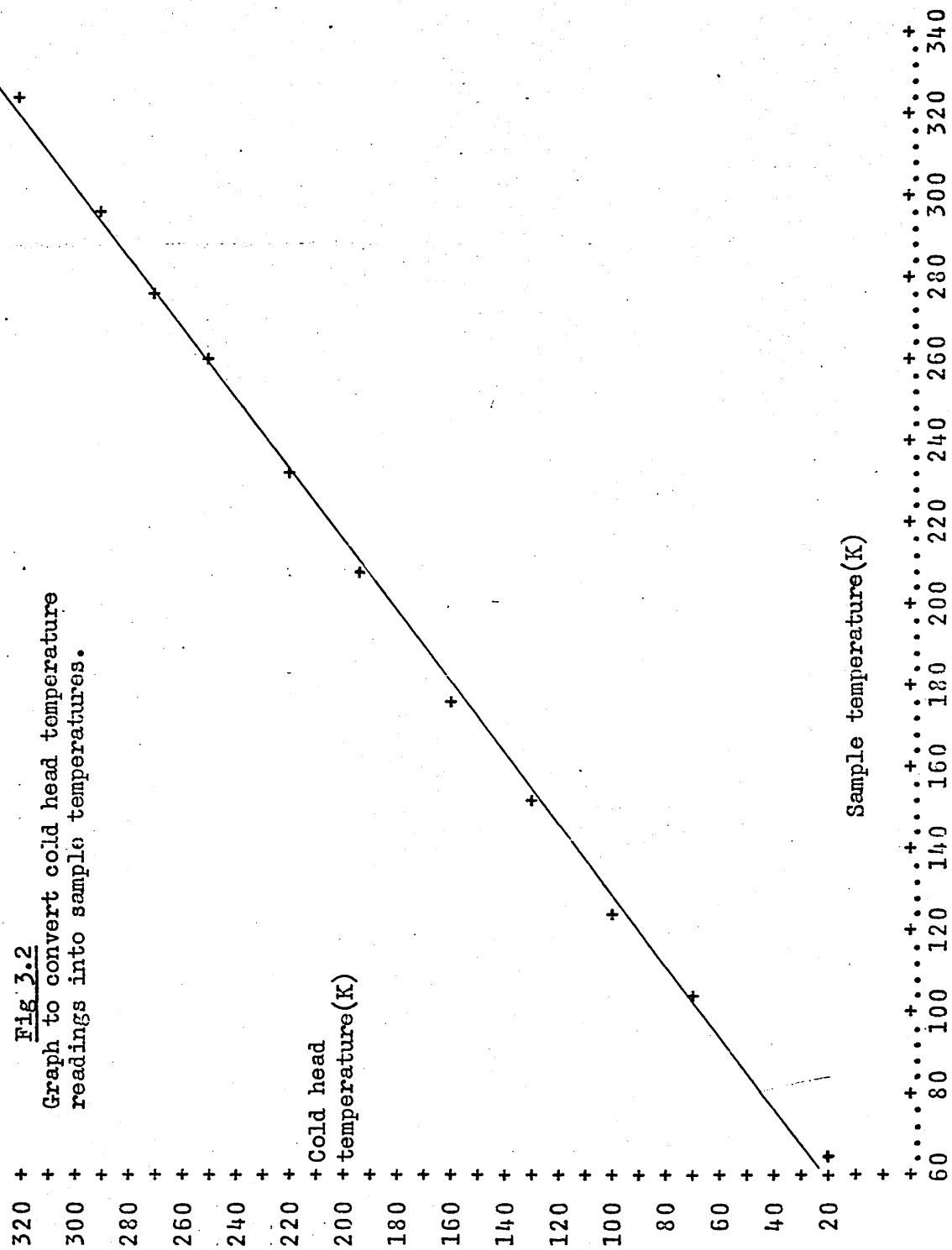


Fig 3.2

Graph to convert cold head temperature readings into sample temperatures.



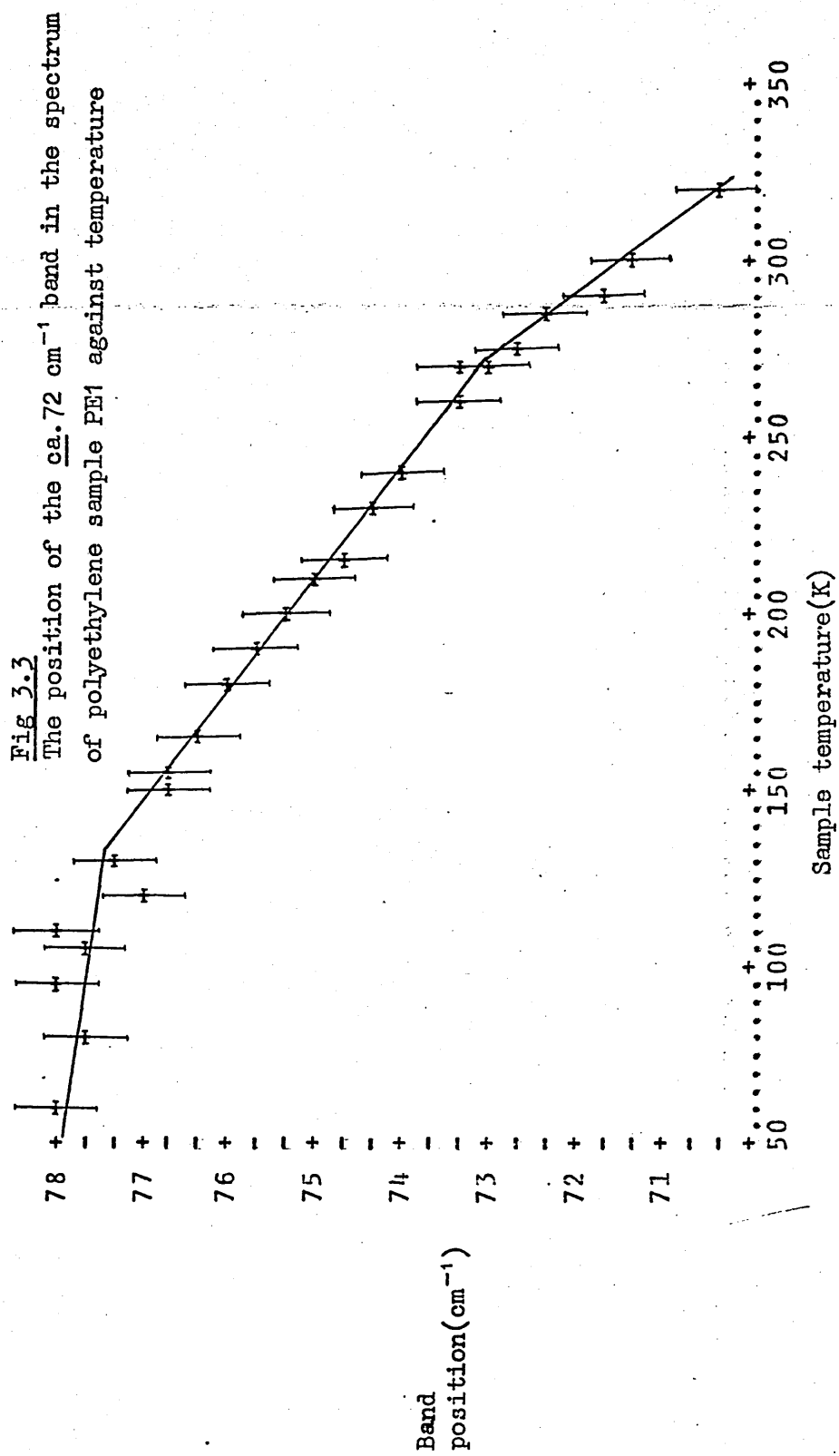
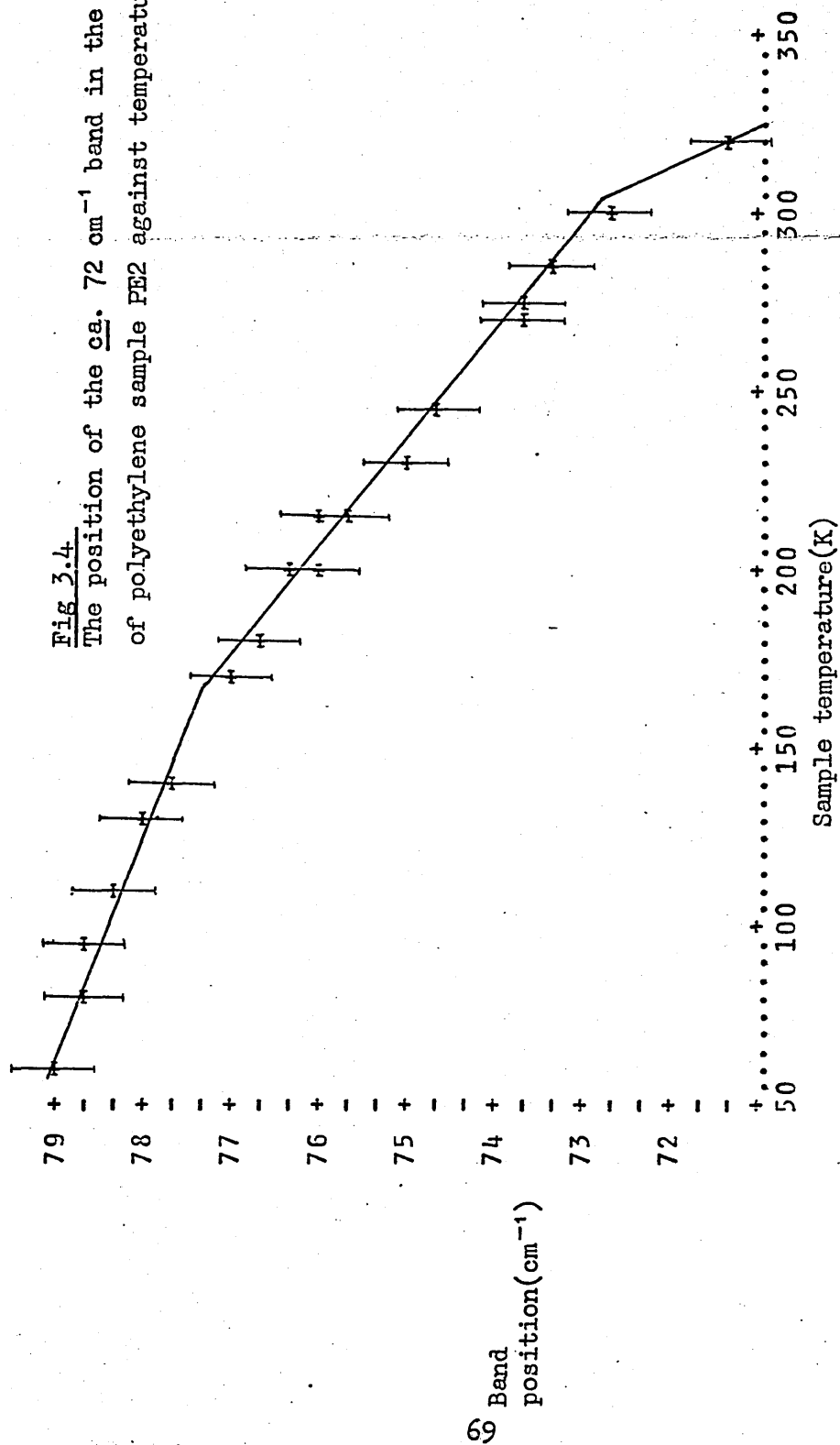


Fig 3.4

The position of the ca. 72 cm^{-1} band in the spectrum of polyethylene sample PE2 against temperature.



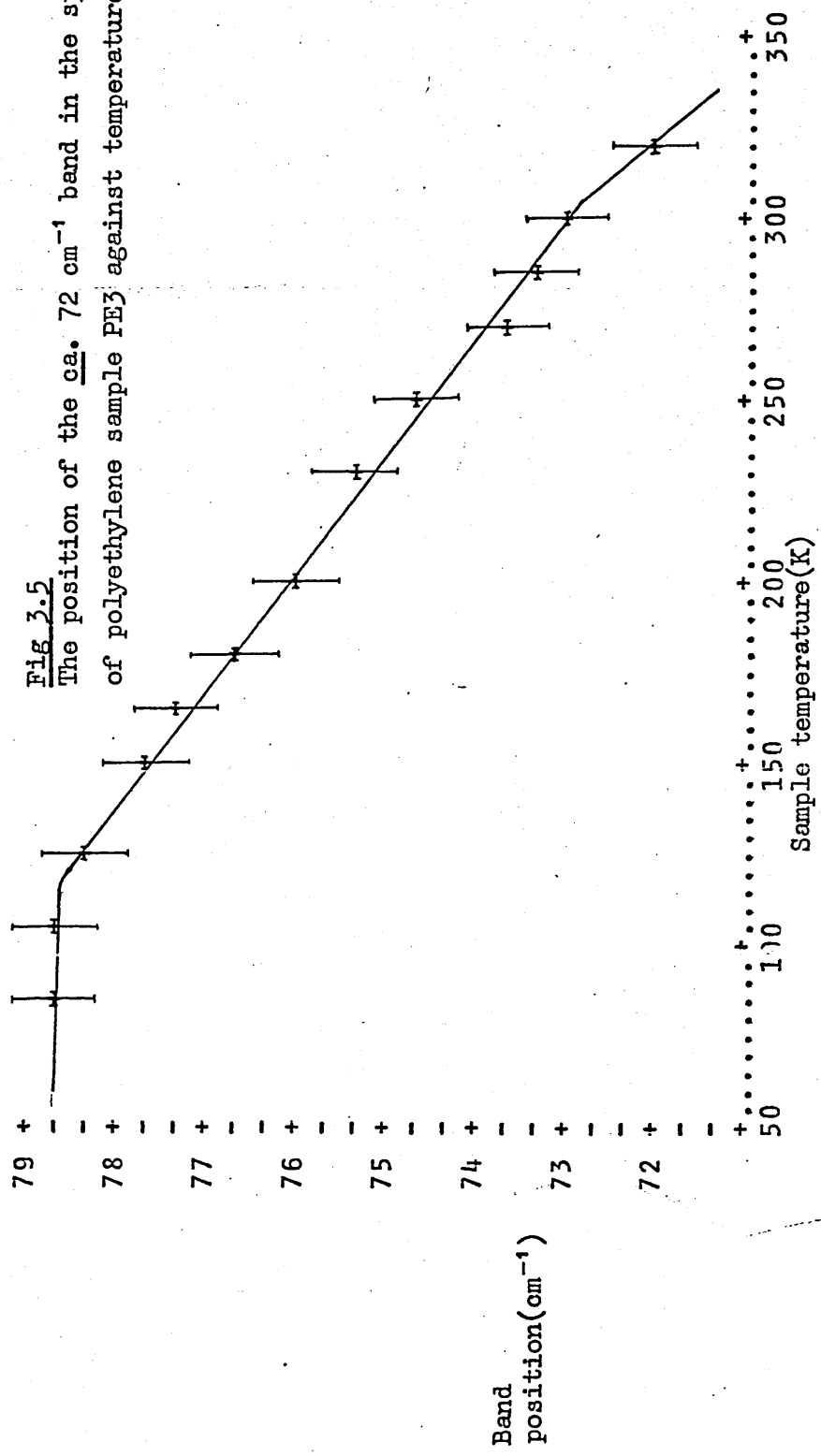
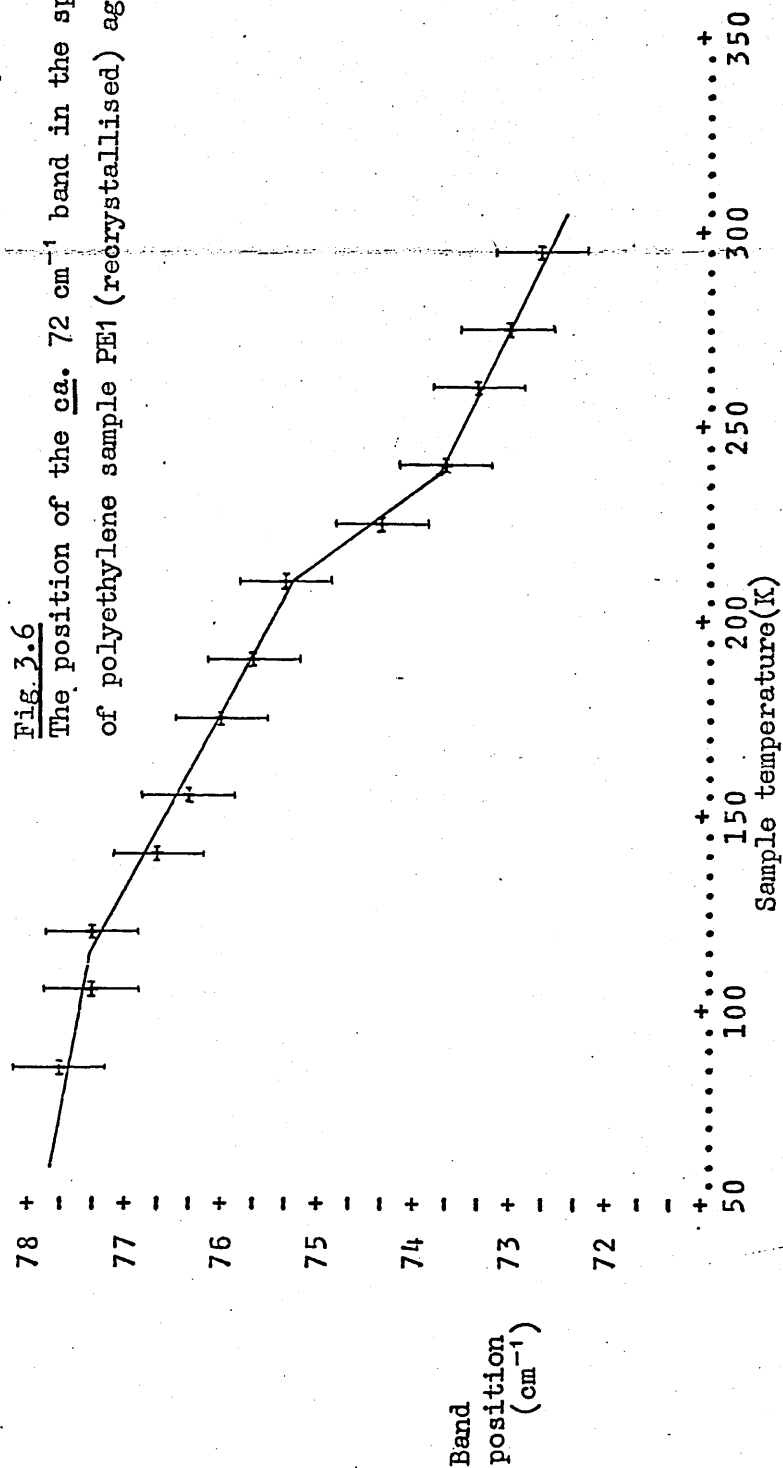
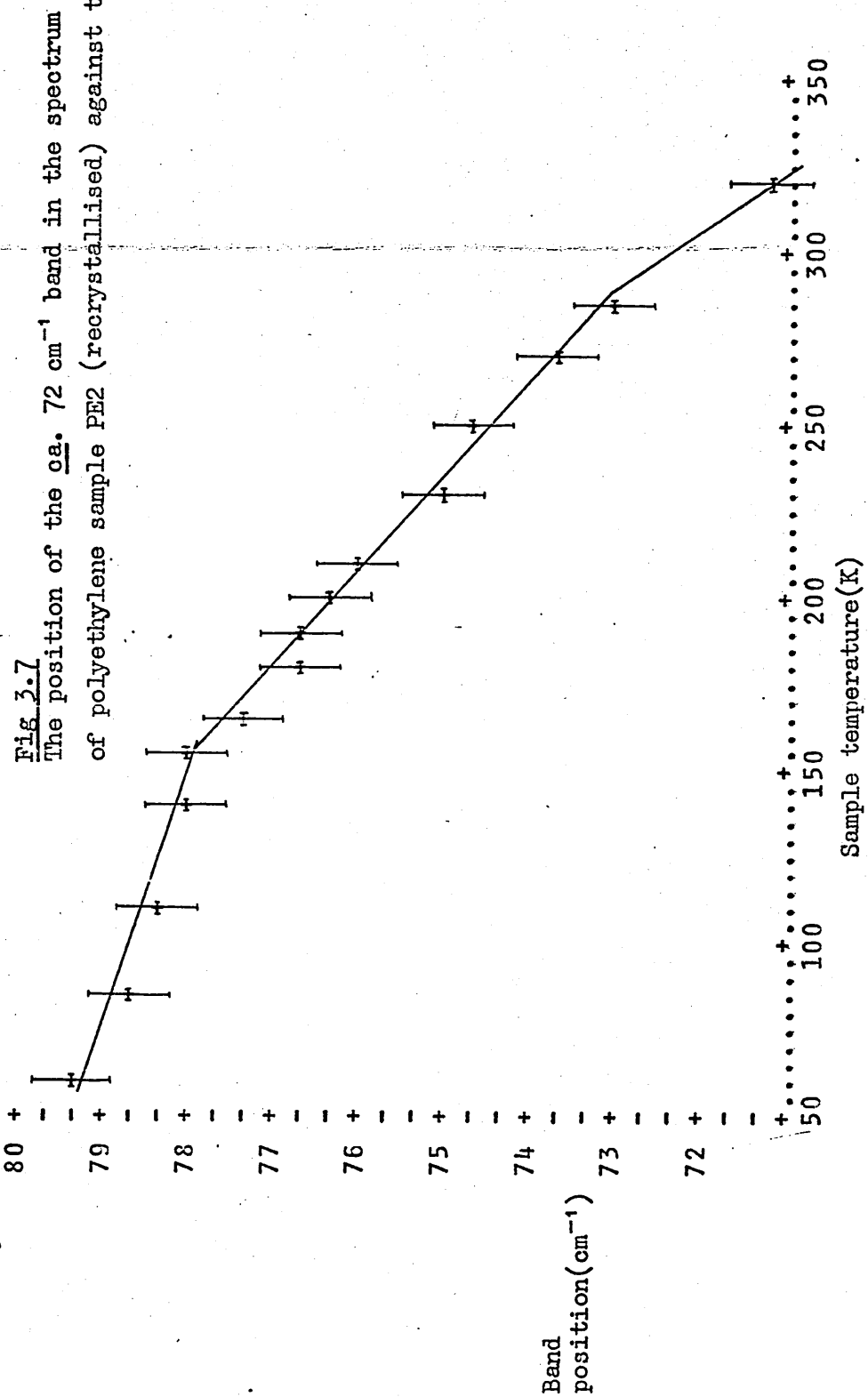
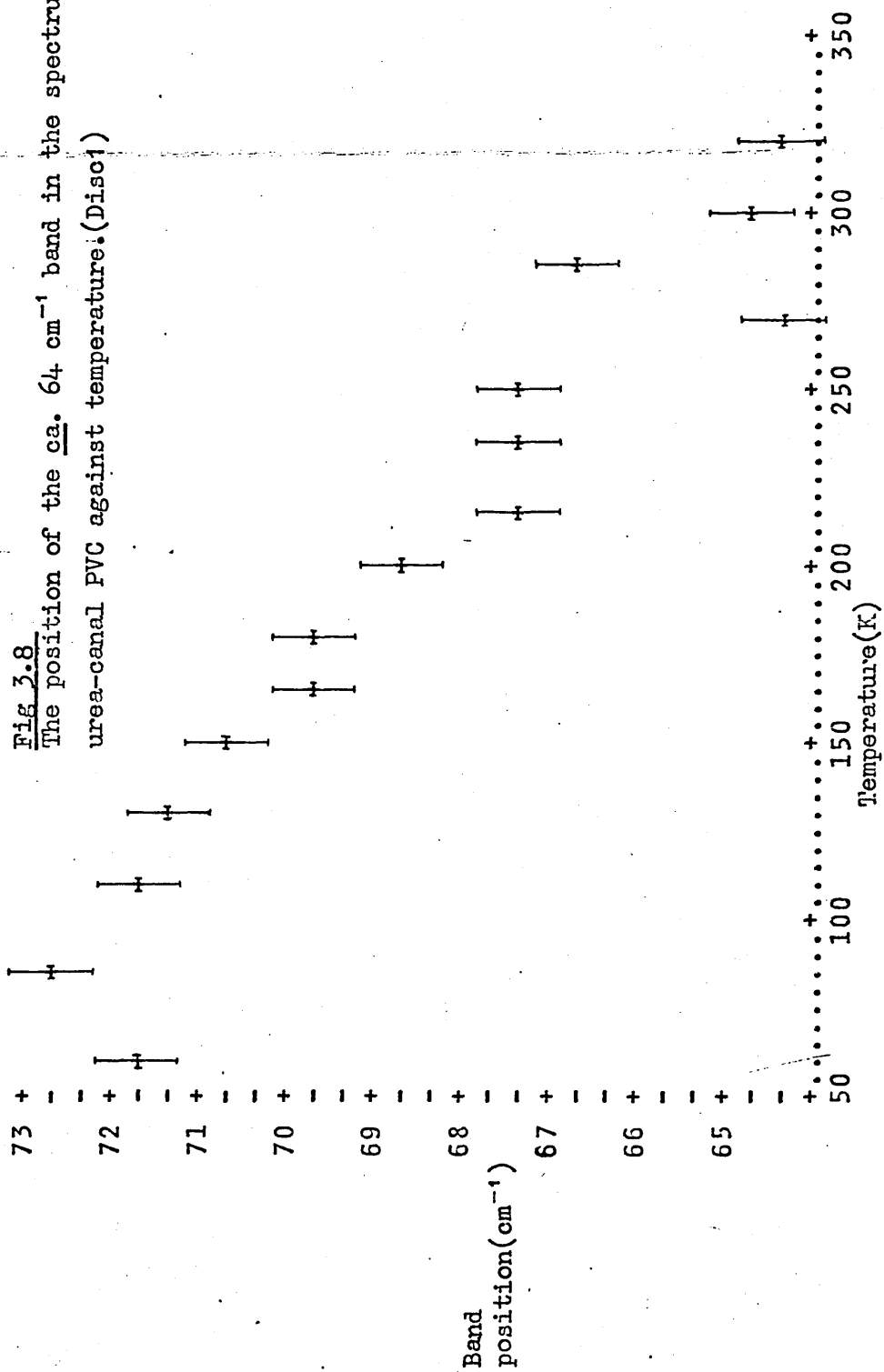


Fig.3.6
The position of the ca. 72 cm^{-1} band in the spectrum
of polyethylene sample PE1 (recrystallised) against temperature .







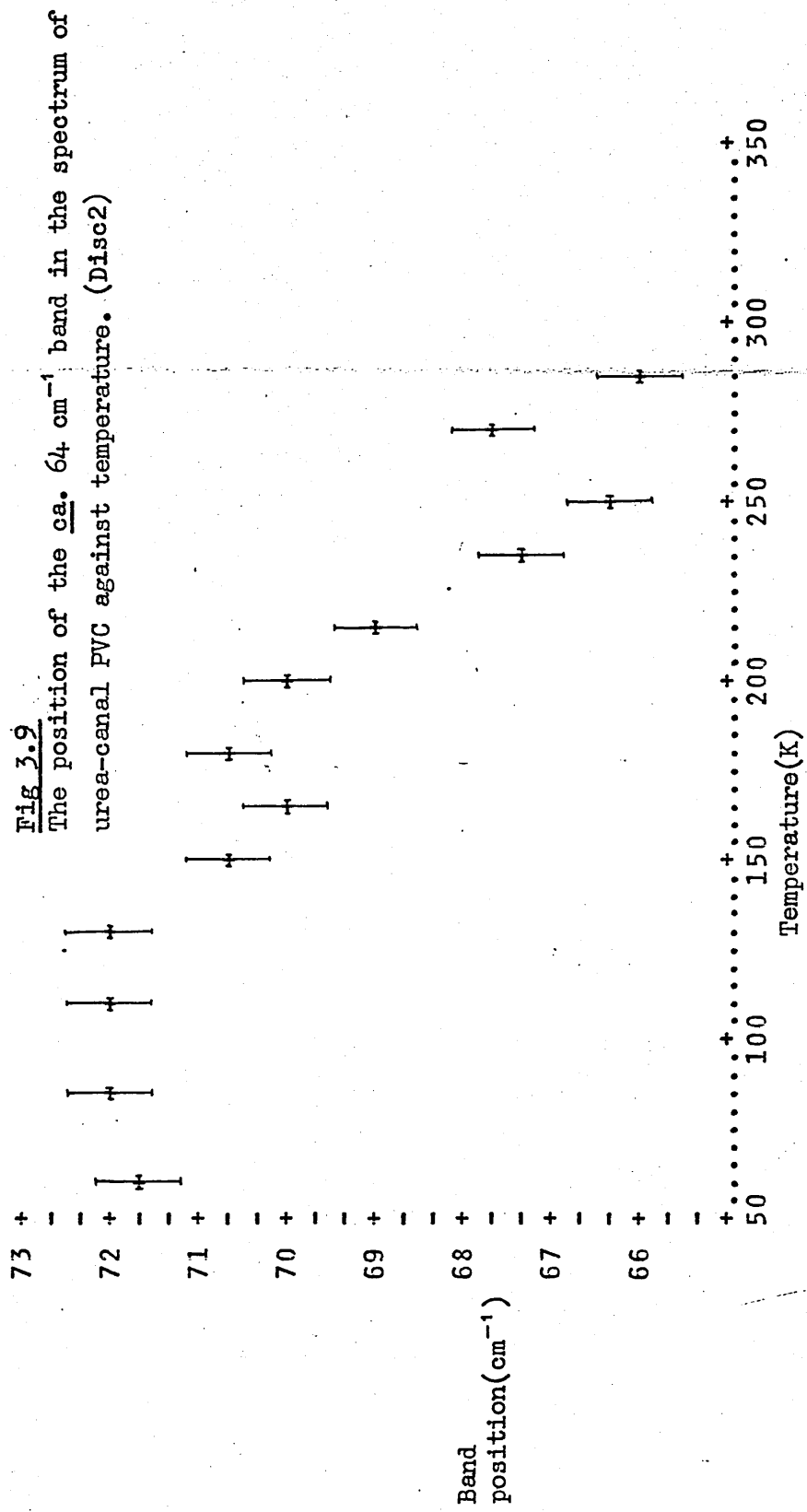
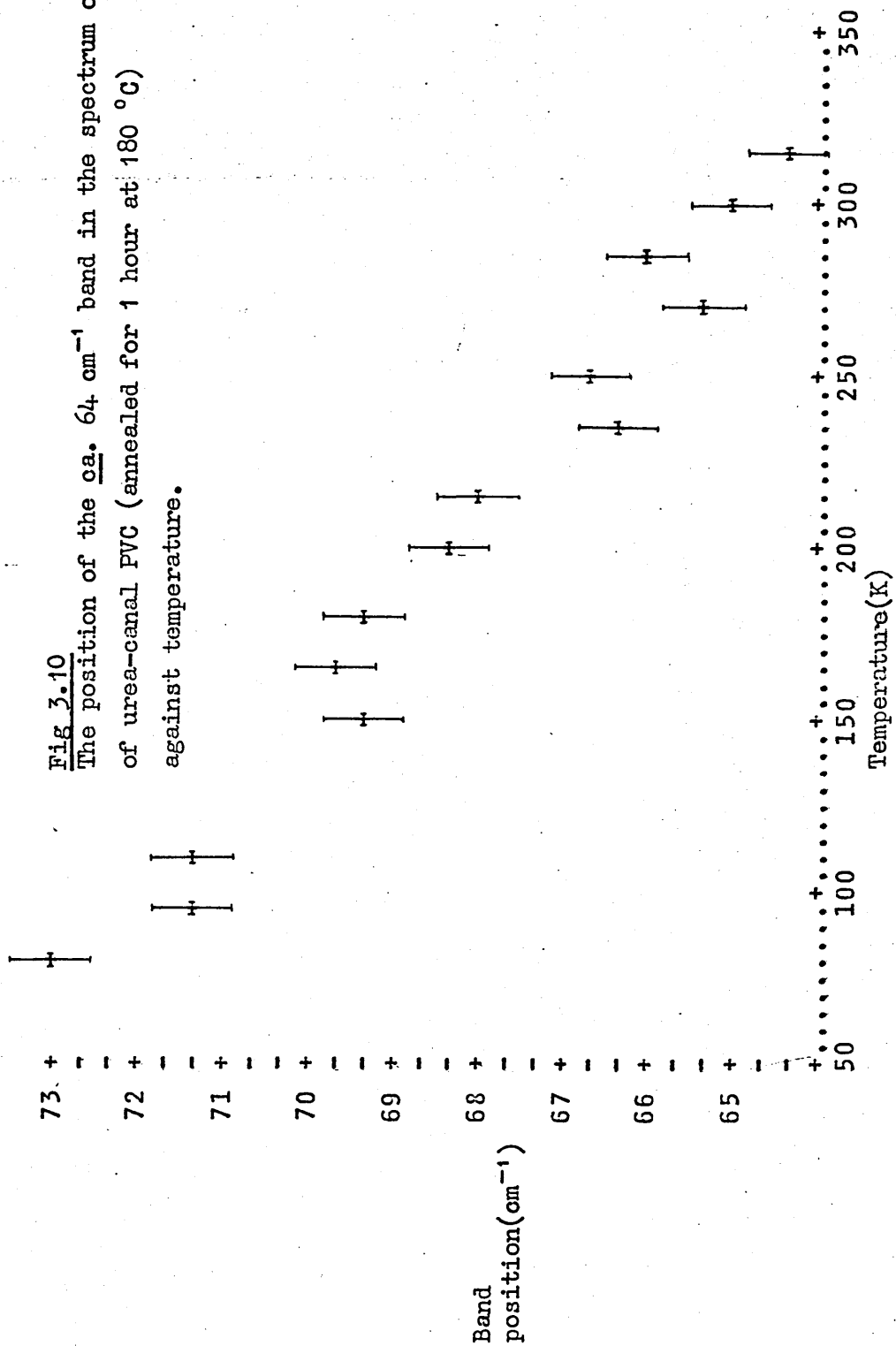


Fig 3.10
The position of the ca. 64 cm^{-1} band in the spectrum of
of urea-canal PVC (annealed for 1 hour at 180°C)
against temperature.



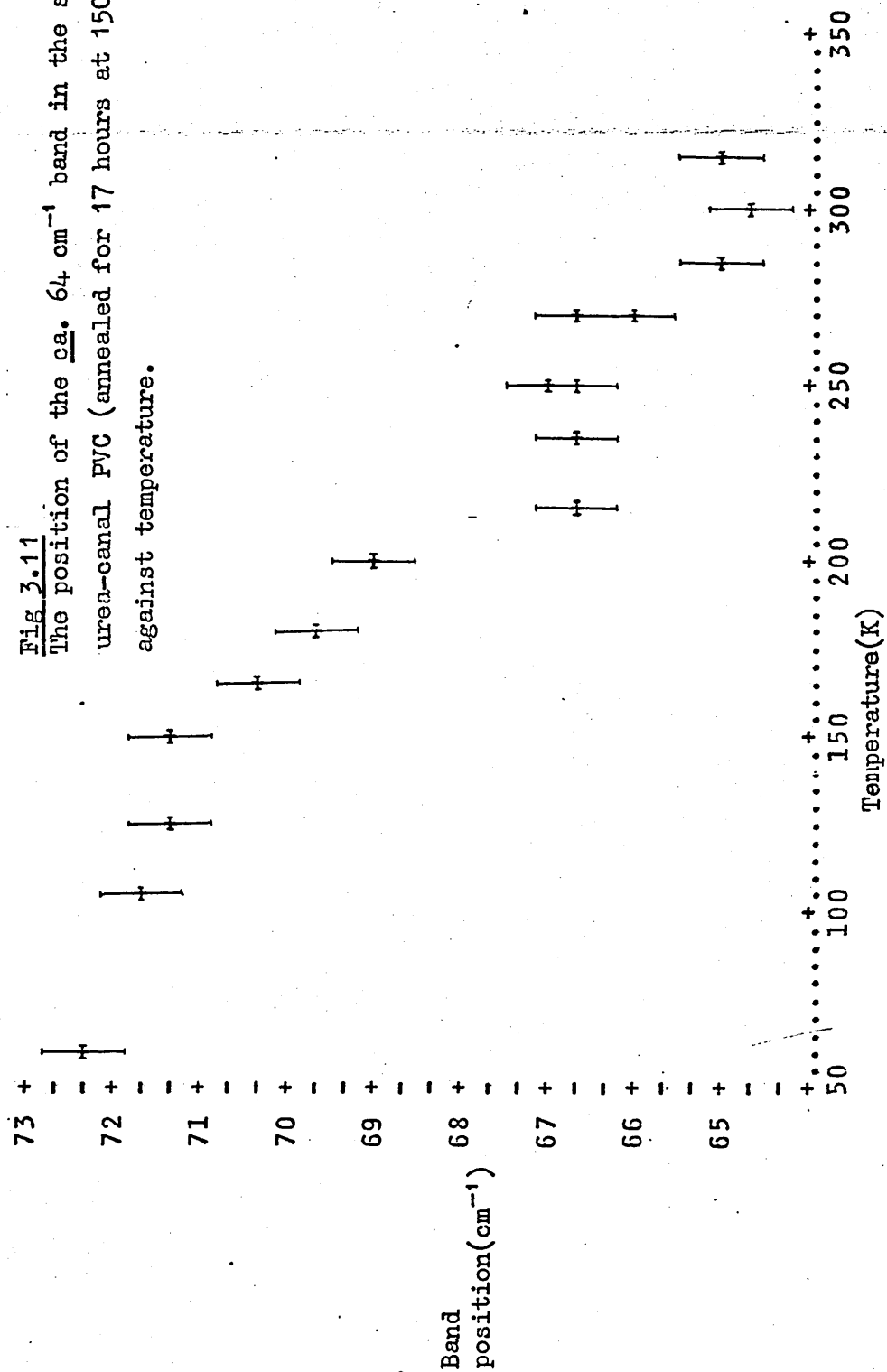
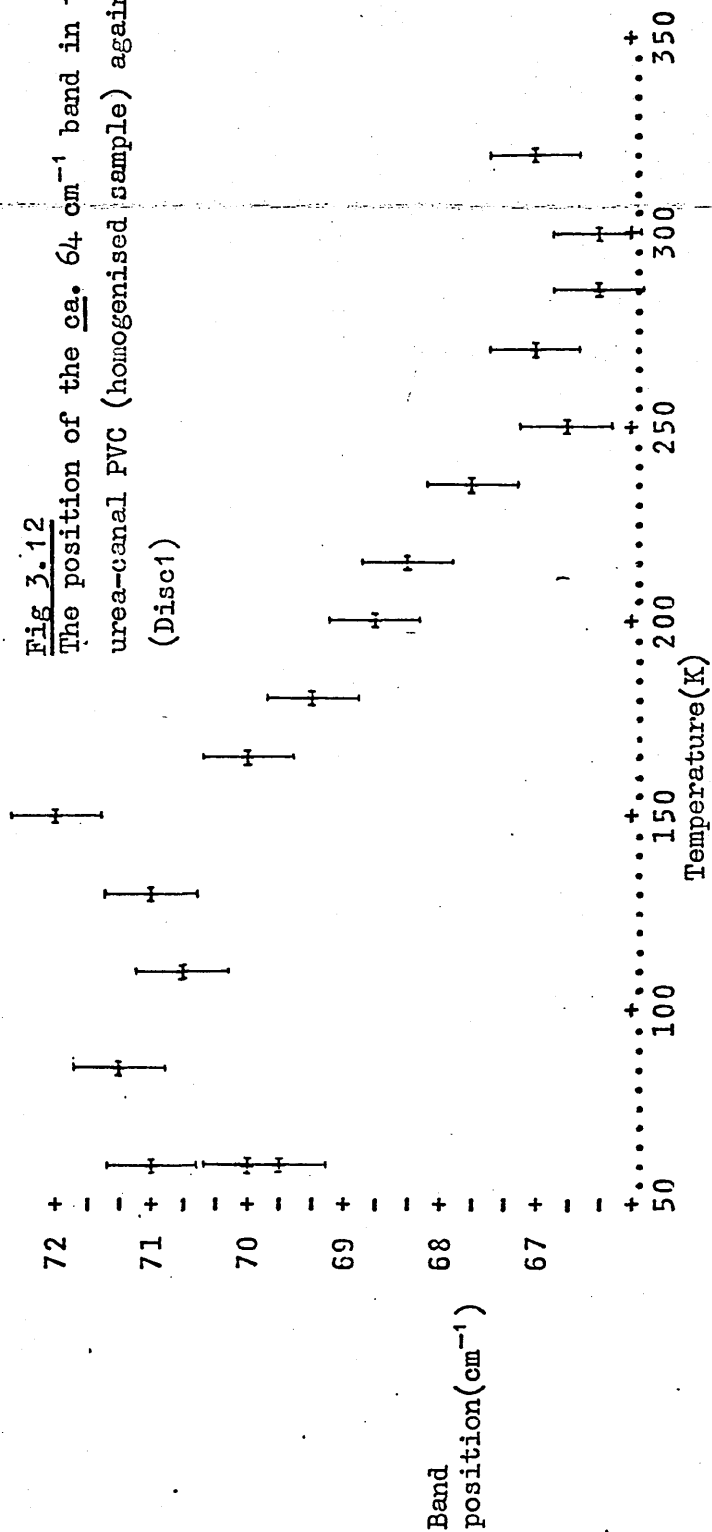


Fig 3.12
The position of the ca. 64 cm^{-1} band in the spectrum of
urea-canal PVC (homogenised sample) against temperature.
(Disc1)



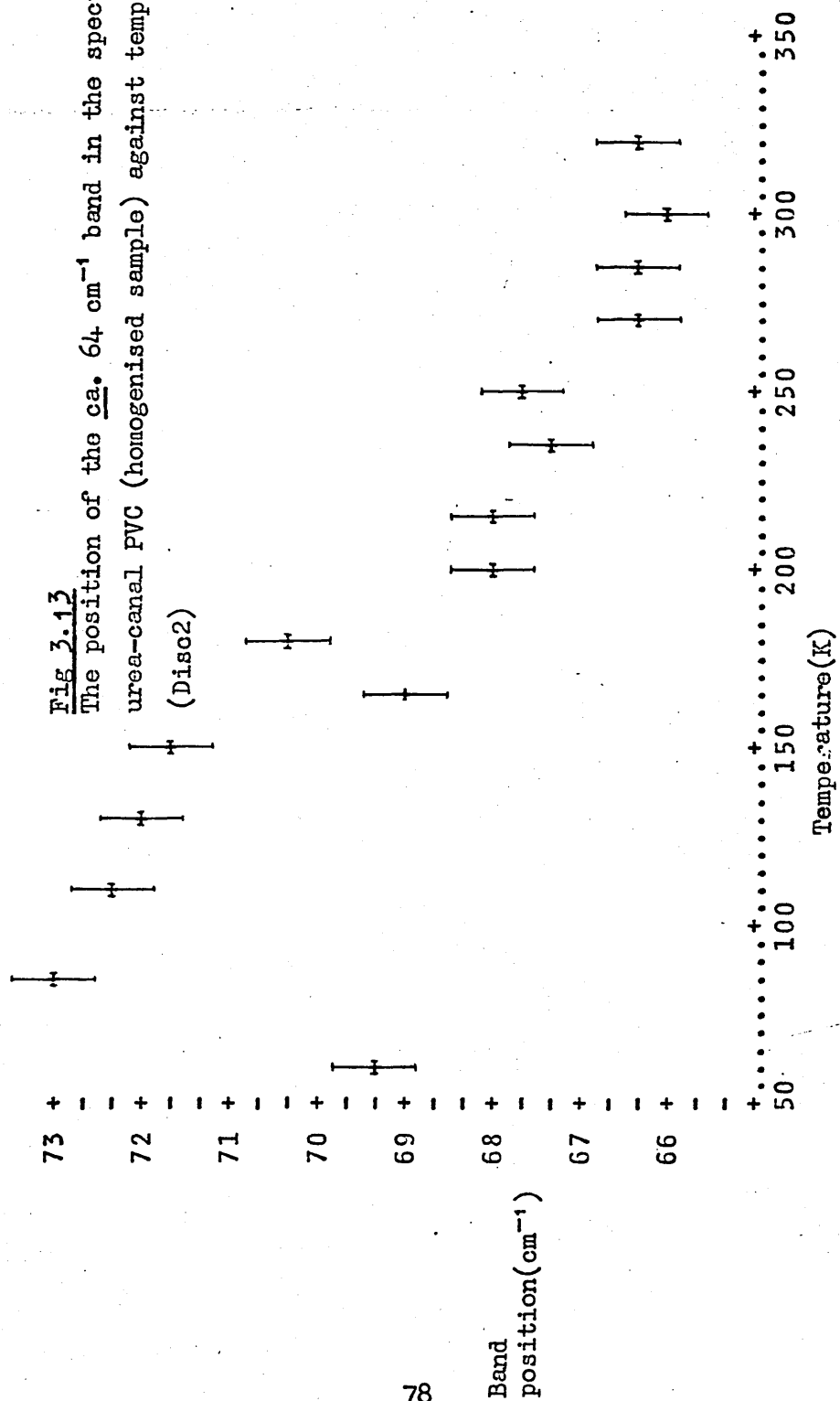


Fig 3.14

The far-infrared spectra of U-C PVC and polyethylene sample PE1.

(Both recorded at ca.60 K)

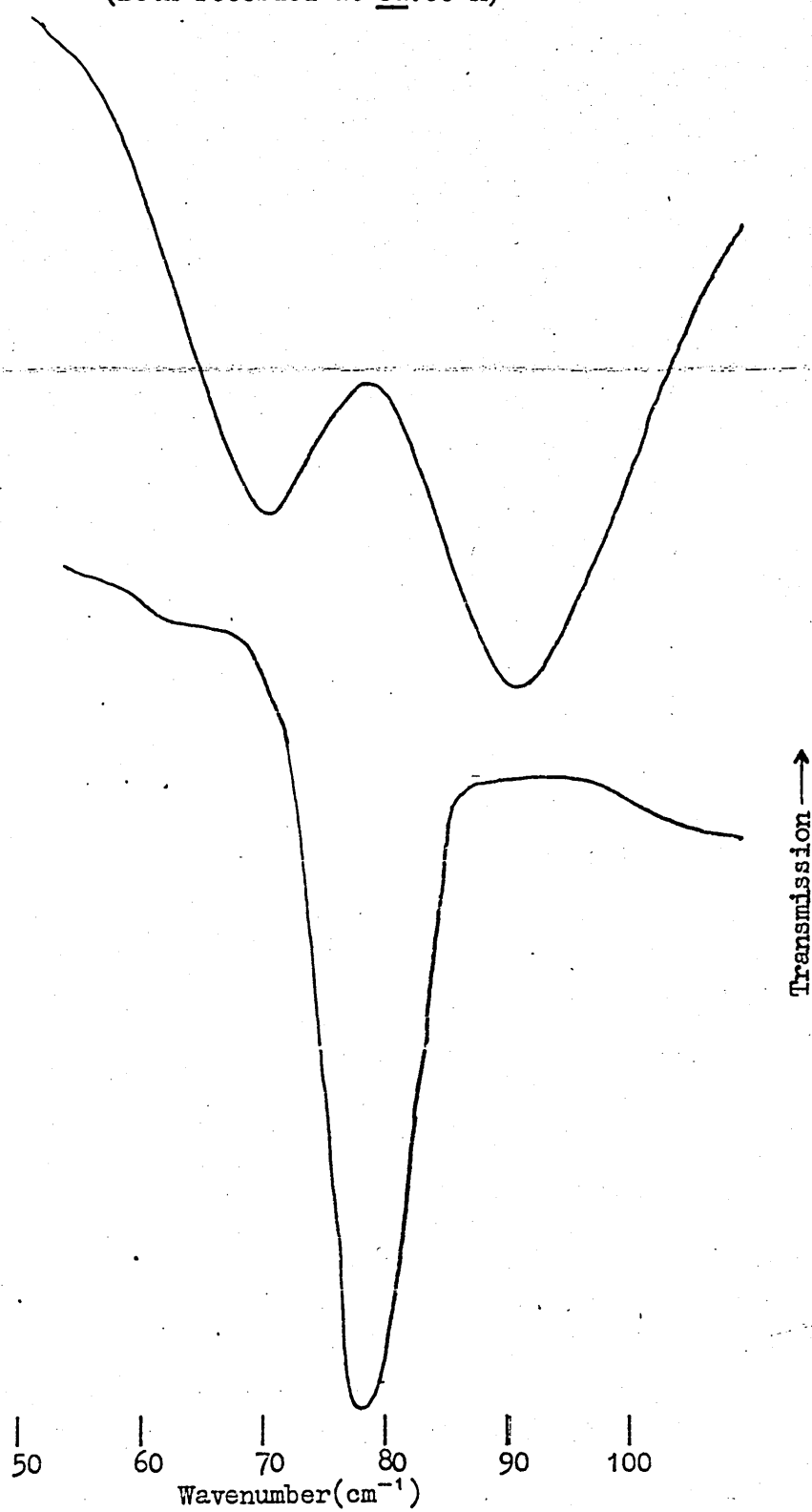
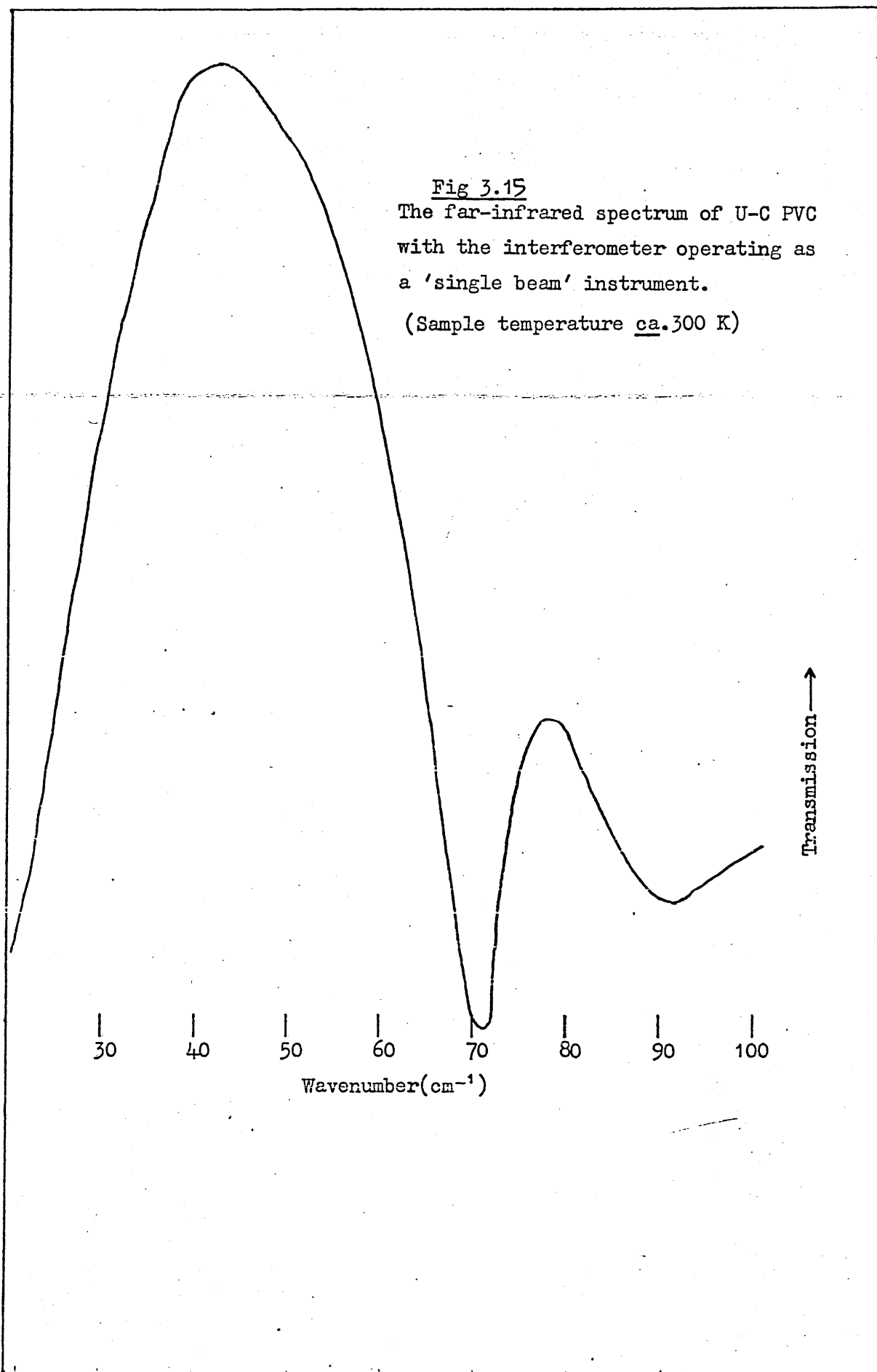


Fig 3.15

The far-infrared spectrum of U-C PVC
with the interferometer operating as
a 'single beam' instrument.

(Sample temperature ca.300 K)



Chapter 4

The Far-infrared Spectra of Isotactic Poly(1-pentene) and Isotactic Poly(4-methyl-1-pentene)

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4.1. Introduction

Only the first member of the series of poly(α -olefins), polyethylene, is able to take up a planar zigzag chain structure (equivalent to a 2_1 helix). Polypropene is constrained by steric hindrance, between side chains, to take up a 3_1 helix (three repeat units in each turn of the polymer chain). Some poly(α -olefins) exhibit more than one helical form such as poly(1-butene), which forms 3_1 and 11_3 helix structures, the helix adopted being dependent on thermal treatment.

Because the backbone of all poly(α -olefins) is essentially the same, there is expected to be some correlation between their far-infrared spectra, particularly for bands due to vibrations localised within the main chain. Such correlation has been noticed between polypropene and poly(1-butene) (1). Also, calculations of the shift in frequency of bands in the far-infrared spectrum on changing the helical structure have been performed on poly(1-butene) (2). The objective of the present study is to determine whether these similarities extend to the far-infrared spectra of poly(1-pentene) and poly(4-methyl-1-pentene).

4.2 Poly(1-pentene)

4.2.1 Introduction

Poly(1-pentene) was first synthesised by Natta and Corradini (3). It can be produced in three basic crystalline modifications. Form II is produced when the polymer is pressed at ca. 120 °C (4) or by quenching from the melt with ice-water and annealing at room temperature (5). Form II is converted to form I by annealing at between 78 °C and 87 °C for ca. 24 hours (4,5) or at 68 °C for 314 hours (6). Crystalline modification III is obtained from dilute solutions of amyl acetate (ca. 0.08% by weight) (7) using the self-seeding method of crystal growth described by Blundell et al. (8). Slight differences in structure found within forms I and II have been labelled Ia, Ib, IIa and IIb (9).

X-ray studies on modification I revealed an orthogonal unit cell, the chains adopting a 3_1 helix (9). Form II was shown to have a monoclinic unit cell (9), but whereas the helix structure was believed by Turner-Jones and Aizlewood (9) to be 4_1 , Decroix et al. (10) suggested it was a 5_1 helix. Decroix et al. argued that the repeat distance of the polymer chains was too large for a 4_1 helix. However, poly(1-butene) form III has an even larger repeat distance and has been shown to adopt a 4_1 structure (11). Thus it seems most likely that poly(1-pentene) form II consists of 4_1 helices. Form III is believed to adopt a 7_2 arrangement (7) as X-ray parameters are compatible with those for poly(4-methyl-1-pentene) (12) and poly(1-hexene) (13) which have been shown to have the 7_2 structure.

4.2.2 Experimental

(a) Preparation of Poly(1-pentene)

Reagents

- (i) 1-Pentene puriss.
- (ii) Diethylaluminium chloride, 25% in hexane.
- (iii) Titanium trichloride, 77%; aluminium trichloride 23%.
- (iv) n-Heptane.

Procedure

Poly(1-pentene) was prepared using a Zeigler-Natta type catalyst prepared from diethylaluminium chloride and titanium trichloride. The diethylaluminium chloride was supplied as a solution/suspension in hexane. The titanium trichloride was also made into a suspension by transferring approximately 3 g into 100 cm³ of dry n-heptane, the procedure being performed in a glove box flushed with dry nitrogen. The reaction was carried out in a 250 cm³ round-bottomed flask fitted with thermometer, stirrer, CO₂/acetone condenser, nitrogen input tube, and a suba seal. Heptane (100 cm³) was added to the reaction flask and the apparatus flushed for 30 minutes with nitrogen. Through the suba seal, using a syringe, 22 cm³ of diethylaluminium chloride in hexane was added followed by 20 cm³ of the titanium trichloride suspension with vigorous stirring. After about 15 minutes, when the catalyst had formed, 10.0 g (15.5 cm³) of 1-pentene was added, and the reaction mixture heated to between 50 °C and 70 °C for 3 hours. After this period ethanol was added to quench the catalyst and the resulting mixture extracted first with dilute hydrochloric acid, then with water. The heptane fraction, containing dissolved poly(1-pentene), was retained and dried with anhydrous sodium sulphate, and the heptane removed on a rotary evaporator. Residual solvent was

removed by placing the polymer under vacuum for 24 hours. A yield of 15% was obtained.

(b) Preparation of the Polymer for Spectral Measurements.

The polymer was cooled using liquid nitrogen to below its glass transition temperature, in order to make the sample brittle, and while at this temperature was ground in a ball mill to a fine powder. The powdered polymer thus produced was hot pressed at ca. 90 °C into a 13 mm disc ca. 3 mm thick. The polymer was found to be substantially more optically dense in the mid-infrared as compared with the far-infrared spectral region. In view of this small slices were cut off the main disc and used to record the mid-infrared spectra. By

comparison with the spectra of forms I and II recorded by Gabbay and Stivala (14), the nature of the crystalline form present could be determined. Heating the disc to ca. 130 °C was used to change the polymer to form II. Heating the polymer disc at between 78 °C and 79 °C for 22 hours, followed by slow cooling (78 °C to 70 °C at 6 ° hour⁻¹, 70 °C to 50 °C at 18 ° hour⁻¹, and 50 °C to 20 °C at 24 ° hour⁻¹) changed to polymer to crystalline form I.

The spectra obtained were essentially the same as those of a small sample kindly supplied by Dr. S. M. Gabbay.

4.2.3. Results.

The far-infrared spectra of poly(1-pentene) forms I and II are shown in Figs. 4.1 and 4.2 respectively. For comparison with these, the spectra of polypropene, poly(1-butene) and poly(4-methyl-1-pentene) are shown in Figs 4.3, 4.4 and 4.5 respectively. The absorptions in the far-infrared spectrum of poly(1-pentene) are also tabulated in Table 4.1, together with the absorptions for the α , β and γ forms of polypropene and for forms I and II of poly(1-butene). The assignments of the bands observed in the far-infrared spectrum of poly(1-pentene) forms I and II are tabulated in Tables 4.2 and 4.3 respectively.

4.3 Poly(4-methyl-1-pentene)

4.3.1. Introduction

Poly(4-methyl-1-pentene) (PlMP) was first prepared by Natta et al. (15). Its crystal structure was determined by Frank et al. (12) using X-ray and electron diffraction techniques. The 7_2 helix proposed was confirmed by Litt (16), using X-ray diffraction. However Litt observed a faint 001 reflection from drawn fibres of PlMP, which should not be present in the X-ray diffraction pattern of a perfect 7_2 helix. Thus, Litt proposed that steric hindrance between adjacent side chains caused the helix to distort slightly. From the unit cell dimensions it was also found that the crystalline regions of the polymer are less dense than the amorphous regions (17).

The mid-infrared spectrum of PlMP has been recorded and assigned by Gabbay and Stivala (18). In the far-infrared spectral region, PlMP has been found to be (at thicknesses up to ca. 2 mm) highly transmissive and consequently it is used as a window material in the far-infrared region (19,20). PlMP is a particularly useful window material below 100 cm^{-1} as in this region polyethylene, the usual window material, has a strong band at ca. 73 cm^{-1} (see Chapter 3). Additionally, PlMP may be used as a cell window material when heating of the samples under study is desired above the softening point of polyethylene (up to ca. 160°C).

4.3.2 Experimental

Samples

- (i) PlMP-1 : hot pressed sheet 3.2 mm thick of unknown origin.
- (ii) PlMP-2 : hot pressed sheet 1.9 mm thick polymerised by Mitsui and Company, and supplied by Yarsley Technical Centre.

In order to get sufficient absorption in the far-infrared regions, 2 thicknesses of the PlMP-1 sheet were used, and for the PlMP-2 sheet

3 thicknesses were required. To avoid interference fringes caused by partial internal reflection at air/sample interfaces, nujol oil was placed between the layers of sample.

4.3.3 Results

The effect of annealing on the diffraction patterns of P4MP-1 and P4MP-2 are shown in Figs 4.6 and 4.7 respectively. Because of the low initial crystallinity of P4MP-1 (evident from the broadness of the peaks in the X-ray diffraction pattern) its diffraction pattern changes considerably on annealing. After a long period of annealing, (ca. 18 hours) the diffraction pattern of P4MP-1 begins to resemble that of untreated P4MP-2 indicating that sample P4MP-2, before any annealing, has a significant crystallinity. Consequently annealing has little effect on the diffraction pattern of P4MP-2 (Fig 4.7). The effect of annealing on the far-infrared spectra of P4MP-1 and P4MP-2 are shown in Figs 4.8 and 4.9 respectively, both samples show essentially the same spectral features. On annealing sample P4MP-1, the broad band at ca. 240 cm^{-1} is resolved into 3 component bands, and the other bands sharpen considerably. In the far-infrared spectrum of sample P4MP-2 the bands are seen to sharpen on annealing, the ca. 240 cm^{-1} band being resolved into 3 components after only 20 minutes of annealing; further annealing has little effect on the spectrum.

The far-infrared spectrum of annealed P4MP-2 is shown in Fig 4.5. For comparison with this the spectra of polypropene, poly(1-butene) and poly(1-pentene) forms I and II are shown in Figs 4.3, 4.4, 4.1 and 4.2 respectively. The absorption bands of P4MP in the far-infrared spectrum are tabulated together with the absorptions of other poly(α -olefins) in Table 4.1, while assignments are tabulated in Table 4.3.

4.4 Discussion and Assignments

(a) The 3_1 helices

In the far-infrared spectra of poly(α -olefins) (below 400 cm^{-1}) most of the bands observed are believed to be due to vibrations of the polymer backbone and thus the far-infrared spectra of poly(α -olefins) that adopt 3_1 helices would be expected to show similarities. Comparing Figs 4.1, 4.3 and 4.4 certain bands can be seen to occur in all these spectra, at roughly the same frequencies. In Table 4.1 the similar bands are grouped together across the range of poly(α -olefins) studied. Since the last assignment of the far-infrared spectrum of poly(1-butene) form I (PBu-I) (1,23) a more comprehensive vibrational analysis has been carried out by Holland-Moritz and Sausen (21), predicting unlike the previous analysis (2) E chain modes. Thus in order to assign the far-infrared spectrum of poly(1-pentene) form I (PPe-I), by extrapolation from polypropene (PPr), it has been necessary to re-affirm and re-assign some bands in the far-infrared spectrum of PBu-I. These assignments are set out in Table 4.2, together with vibrational analysis data (22) and bands observed in the far-infrared spectrum of PPe-I.

Unlike PBu-I and PPr, the spectrum of PPe-I contains no absorptions below 100 cm^{-1} . This is attributed to the sample having a low crystallinity, making any bands at this low frequency too weak and broad to be observed.

PPe-I and PBu-I show a very similar doublet between 120 cm^{-1} and 140 cm^{-1} and a similar pair of bands is also observed in PPr, occurring at 98 cm^{-1} and 113 cm^{-1} . These features have been assigned to an E chain mode calculated at 121 cm^{-1} for PBu-I (21) and at 114 cm^{-1} for PPe-I (22), the band being split by correlation field effects. For both PBu-I and PPe-I the band has been calculated (21,22)

to be due to a part torsion, part CH_2CHCH_2 bend.

The band predicted at 167 cm^{-1} and 207 cm^{-1} for PPe-I (22) and 193 cm^{-1} for PBu-I are assumed to be too weak to be observed.

A band is observed at 173 cm^{-1} in the far-infrared spectrum of PPr, at 187 cm^{-1} in PBu-I, and at 180 cm^{-1} in PPe-I. The band in the spectrum of PBu-I is reported to have parallel dichromism (1) and has been previously assigned (1) to the A mode predicted at 187 cm^{-1} (2). This is in good agreement with the more recent calculations of Holland-Moritz and Sausen (21) who predict a band with a similar potential energy distribution at 192 cm^{-1} . The band at 180 cm^{-1} in the spectrum of PPe-I is thus assigned to the corresponding A mode calculated at 210 cm^{-1} by Holland-Moritz et al. (22). For both PBu-I and PPe-I the band has been calculated (2,21,22) to be a torsional mode.

A band in the far-infrared spectrum of PPe-I is observed at 221 cm^{-1} which seems to correspond to the weak band observed at 210 cm^{-1} (1) in PPr and the weak shoulder at 225 cm^{-1} in PBu-I. In the spectrum of PPr this band has previously been assigned to an E chain mode (1), and thus the corresponding band at 221 cm^{-1} in PPe-I is assigned to an E mode calculated (22) to occur at 216 cm^{-1} and be due to a torsional vibration.

The next feature in the far-infrared spectrum of PPe-I is a band at 237 cm^{-1} which corresponds to the doublet at 238 cm^{-1} and 250 cm^{-1} in PBu-I and at 245 cm^{-1} and 250 cm^{-1} in PPr. In PPr the bands have been shown to have parallel dichroism (1,24) and consequently has been assigned to a correlation split A mode (1). Thus the doublet in the spectrum of PBu-I is assigned to a correlation split A mode calculated by Cornell and Koenig (2) at 270 cm^{-1} and by Holland-Moritz and Sausen (21) at 259 cm^{-1} . The corresponding band in

PPe-I at 237 cm^{-1} is unsplit, probably because of the low crystallinity of the sample does not allow resolution of the components; like the similar bands in PPr and PBu-I, it is also assigned to an A mode, calculated (22) to be a $\text{CH}_2\text{CHRCH}_2$ bend at 261 cm^{-1} .

The next band observed in the far-infrared spectrum of PPe-I is at 283 cm^{-1} . A similar band appears some 20 cm^{-1} higher in the spectrum of PBu-I at 300 cm^{-1} and about 20 cm^{-1} higher than that in the spectrum of PPr. In PPr the band is assigned to an E mode (1) as it shows perpendicular dichroism (1,24). The band at 300 cm^{-1} in the spectrum of PBu-I is consequently also assigned to an E mode, calculated at a frequency of 361 cm^{-1} (21). Similarly, the corresponding band at 283 cm^{-1} in the spectrum of PPe-I is assigned to an E mode predicted at 281 cm^{-1} (22). In both PBu-I and PPe-I the band is believed to be due partly to a $\text{CH}_2\text{CHRCH}_2$ bend and partly a bend of the side chain (21,22), which explains the shift in frequency observed on moving from PPr to PBu-I to PPe-I.

The next observed band in the spectrum of PPe-I is at 306 cm^{-1} and this is assigned to the A mode predicted at 288 cm^{-1} (22), this is again believed to be due to part $\text{CH}_2\text{CHRCH}_2$ bend, part side chain bend. Thus, the weak band at 320 cm^{-1} in the spectrum of PBu-I (1), which is not predicted, is probably analogous to this as the shift (14 cm^{-1}) that occurs from PBu-I to PPe-I is of the order that would be expected for a band partly due to side chain vibration.

A band at 344 cm^{-1} is observed in the far-infrared spectrum of PPe-I which is not observed in PBu-I yet is observed in poly (α -olefins) with the same length side chains eg. PPe-II and P4MP, see Table 4.1. This suggests that this band is probably due to a side chain vibration. Thus, it is assigned to the predicted E mode at 390 cm^{-1} (22), which is calculated to be partly due to side chain bending (22).

The final band in the far-infrared spectrum of PPe-I (below 400 cm^{-1}) is at 373 cm^{-1} and is similar to the doublet at 375 cm^{-1} and 385 cm^{-1} in the spectrum of PBu-I, and to the single band in the spectrum of PPr at 400 cm^{-1} . In case of PBu-I the doublet centred on 380 cm^{-1} has previously been assigned to an E mode. A more likely assignment however is to the A mode predicted by Cornell and Koenig at 347 cm^{-1} (2) and by Holland-Moritz and Sausen at 363 cm^{-1} (21), as the corresponding band in PPr has been shown to have parallel dichroism (1,24), characteristic of an A mode. Thus, the 373 cm^{-1} band in the spectrum of PPe-I is also assigned to an A mode predicted at 418 cm^{-1} and believed to be due to a $\text{CH}_2\text{CHRCH}_2$ bend (22).

(b) Poly(1-pentene) Form II (PPe-II) and Poly(4-methyl-1-pentene) (P4MP).

There have been no vibrational analyses carried out on either PPe-II or P4MP. However, even though P4MP crystallises in a 7_2 helical structure and PPe-II in a 4_1 helical structure, the spectra of these polymers should show some similarities to the 3_1 helices discussed on the previous section. This is explained by the similarities in the C_n line groups (particularly the symmetries that are infrared-active) which these polymer belong to. For PBu, Cornell and Koenig (2) calculated the expected shift of the A modes if PBu helix was changed from 3_1 to 7_2 to 4_1 . These calculated values agree well with the observed data for PPe structures. Comparing PPe-I with PPe-II in Table 4.1, it is seen that band number 4 moves 17 cm^{-1} to lower wavenumber on changing from a 3_1 to a 4_1 helix. Cornell and Koenig (2) calculated the similar change for PBu to be 15 cm^{-1} . Similarly, fair agreement is obtained on comparing band 7 which is seen 17 cm^{-1} lower in PPe-II than in PPe-I, a shift which may be

compared with that calculated for P₃ helices (29 cm^{-1}). Finally, band 11 increased in wavenumber by 25 cm^{-1} on passing from PPe-I to PPe-II, the calculated value for P₃ helices being an increase of 20 cm^{-1} .

By comparison of the spectra of the various samples (Figs 4.1 to 4.5) it is possible to correlate the remaining bands observed in the far-infrared spectrum of PPe-II with bands observed in the spectra of 3_1 helix polymers (Table 4.1), and thus indicate likely assignment of these bands (Table 4.3).

The far-infrared spectrum of P₄MP has been similarly assigned in Table 4.3. The major difference between the spectra of PPe-II and P₄MP is the apparent splitting of bands 7,8 and 11 in P₄MP. The cause of the splitting is attributed to the non-uniformity of the 7_2 helix in P₄MP, previously identified by X-ray diffraction techniques (16).

4.5 Conclusions

A more complete assignment of the spectrum of PBU-I below 400 cm^{-1} has been proposed (Table 4.2) together with, for the first time, assignments of bands observed in the far-infrared spectrum of PPe-I. Similarities between the far-infrared spectra of poly(α -olefins) which contain 3_1 helices have been demonstrated to extend to PPe-I. It has also been demonstrated that the far-infrared spectra of PPe-II and PLMP, which have 4_1 and 7_2 helical structures respectively, can be correlated with the more extensively studied 3_1 helical structure polymers, on the basis of expected band shifts on changing the helix pitch. Additionally, in the spectrum of PLMP below 400 cm^{-1} three bands are split, each into two components; this effect has been attributed to non-uniformity of the helical structure. However, detailed assignments of PLMP and PPe-II will have to await the availability of normal co-ordinate analyses.

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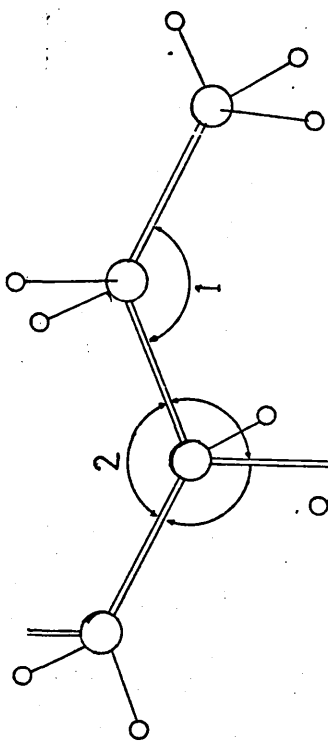
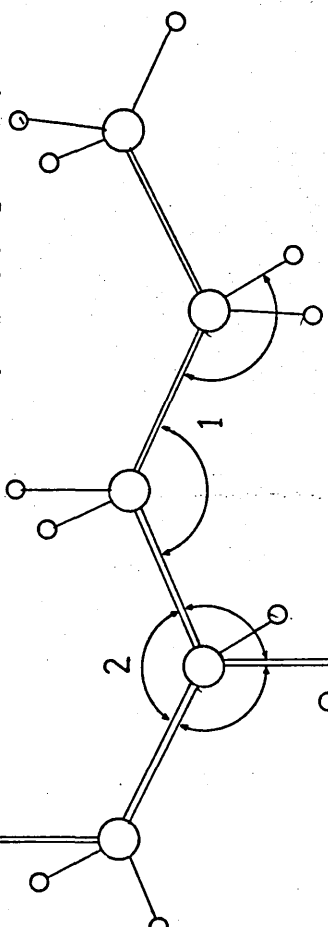
Table 4.1 The far-infrared spectra of some poly(α -olefins).

Band positions in cm^{-1} ; figures in brackets refer to weak bands.

Band number	Polypropylene*			Poly(1-butene)*		Poly(1-pentene)		Poly(4-methyl-1-pentene)
	Form α 3 helix 1	Form β 3 helix 1	Form γ 3 helix 1	Form I 3 helix 1	Form II 11 helix 3	Form I 3 helix 1	Form II 4 helix 1	
1				86				
2	{ 98 (113)	{ 98 (113)	{ (98) (113)	{ 128 (136)	{ 100 (138)	{ (124) (135)		7 helix 2 (88)
3	{ (135) (145)			(158)	(155)		(122)	144
4	173	(170)	(170)	175	180	180	163	
5	(198)			(200)				
6	(210)			(225)		221		232
7	{ 245 (255)	250	250	{ 238 (250)	240	237	220	{ 251 (259)
8	321	321	321	300		283	311	{ 283 (300)
9				(320)		(306)		(328)
10						344	333	358
11	400	400	400	{ 375 (385)	{ 370 (380)	373	398	{ 389 (396)

* Data obtained from reference 1.

Table 4.2 The calculated and observed far-infrared bands for poly(1-butene) form I and poly(1-pentene) form I.

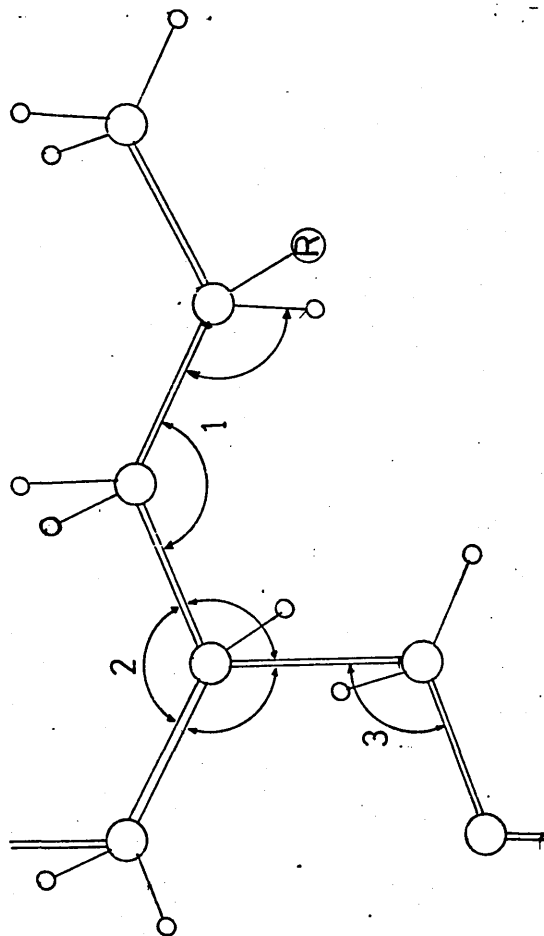
		Poly(1-butene)		Poly(1-pentene)				
		Observed	Calculated [21]	Observed	Calculated [2]	Observed	Calculated [22]	
		cm ⁻¹	PED*	cm ⁻¹	PED*	cm ⁻¹	PED*	
		121	2(4.3%), τ (24%), 3(20%)	124	---	114	τ (4.2%), 2(31%)	
		128	---	135	---	131	τ (3.7%), 3(28%)	
		136	---	---	---	167	1(50%), 3(21%)	
		158	---	---	---	207	τ (6.4%)	
		---	---	---	---	210	τ (9.3%)	
		193	τ (7.3%)	---	---	---	---	
		192	τ (6.1%)	180	---	---	---	
		229	1(3.4%), 2(2.8%), τ (20%)	---	---	216	τ (50%), 1(2.1%)	
		239	2(3.5%)	---	---	261	2(5.3%)	
		270	2(4.9%)	237	---	281	1(3.7%), 2(2.3%)	
		361	2(30%), 1(2.9%)	283	---	288	2(2.4%), 1(2.4%)	
		---	---	306	---	390	1(2.8%), 2(2.5%)	
		---	---	344	---	418	2(4.1%), 1(30%)	
		363	2(4.8%)	373	---	---	---	
		375	---	---	---	---	---	
		385	---	---	---	---	---	

* Potential energy distribution

τ = torsion 1, 2 and 3 = bends

Table 4.3 Bands observed in the far-infrared spectra of poly(1-pentene) form II and poly(4-methyl-1-pentene) together with their assignments.

Observed bands cm ⁻¹ Poly(1-pentene) Form II	Observed bands cm ⁻¹ Poly(4-methyl- 1-pentene)	Assignment	Sym
—	88	Lattice	
{124 135}	122	$\tau + 2$	E
180	163	Φ	A
—	232	$\tau + 1$	E
220	{251 259}	2	A
311	{283 300}	∇	E
333	358	$1 + 2$	E
398	{389 396}	$2 + 1$	A
		∇	



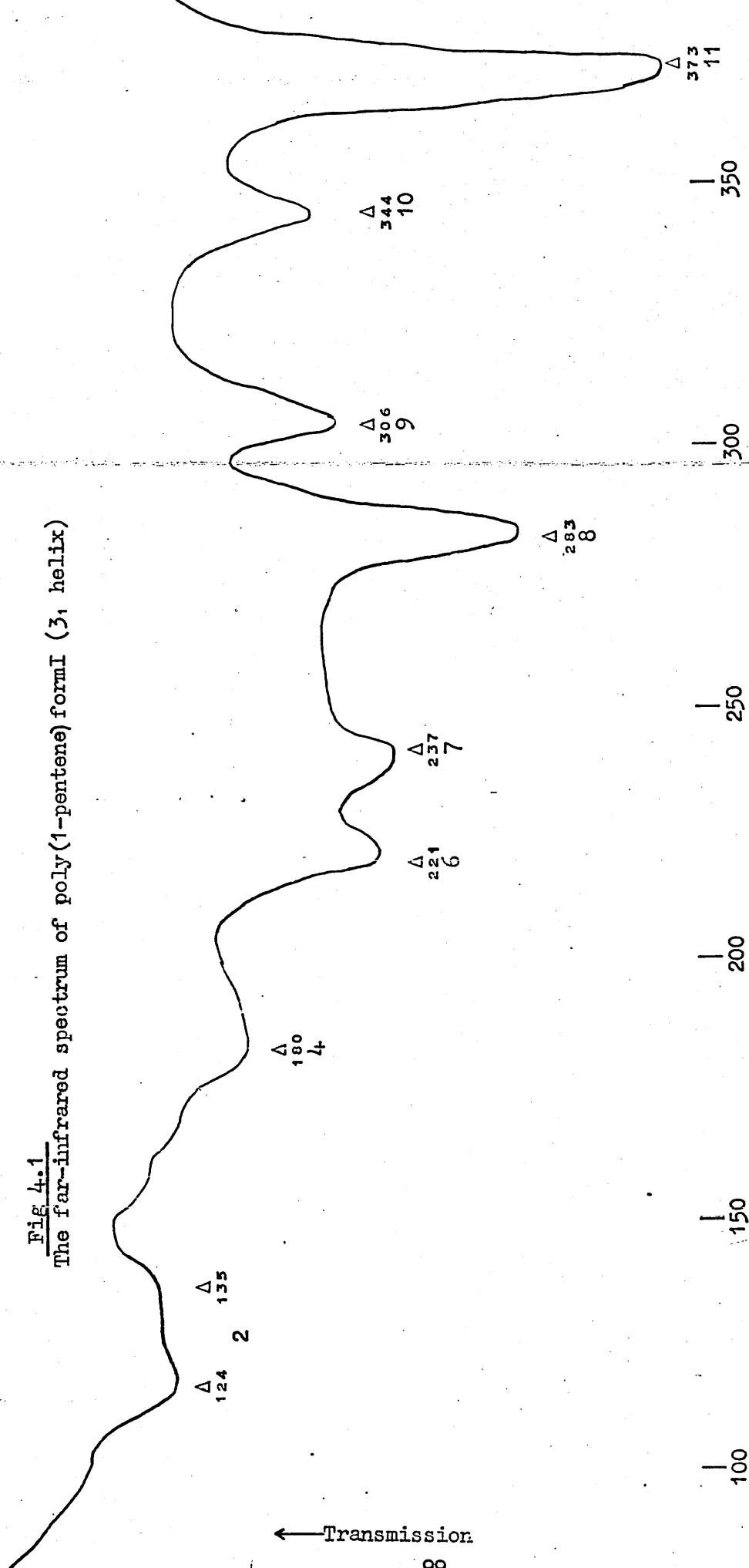
R = hydrogen for poly(1-pentene)

R = methyl for poly 4-methyl-1-pentene

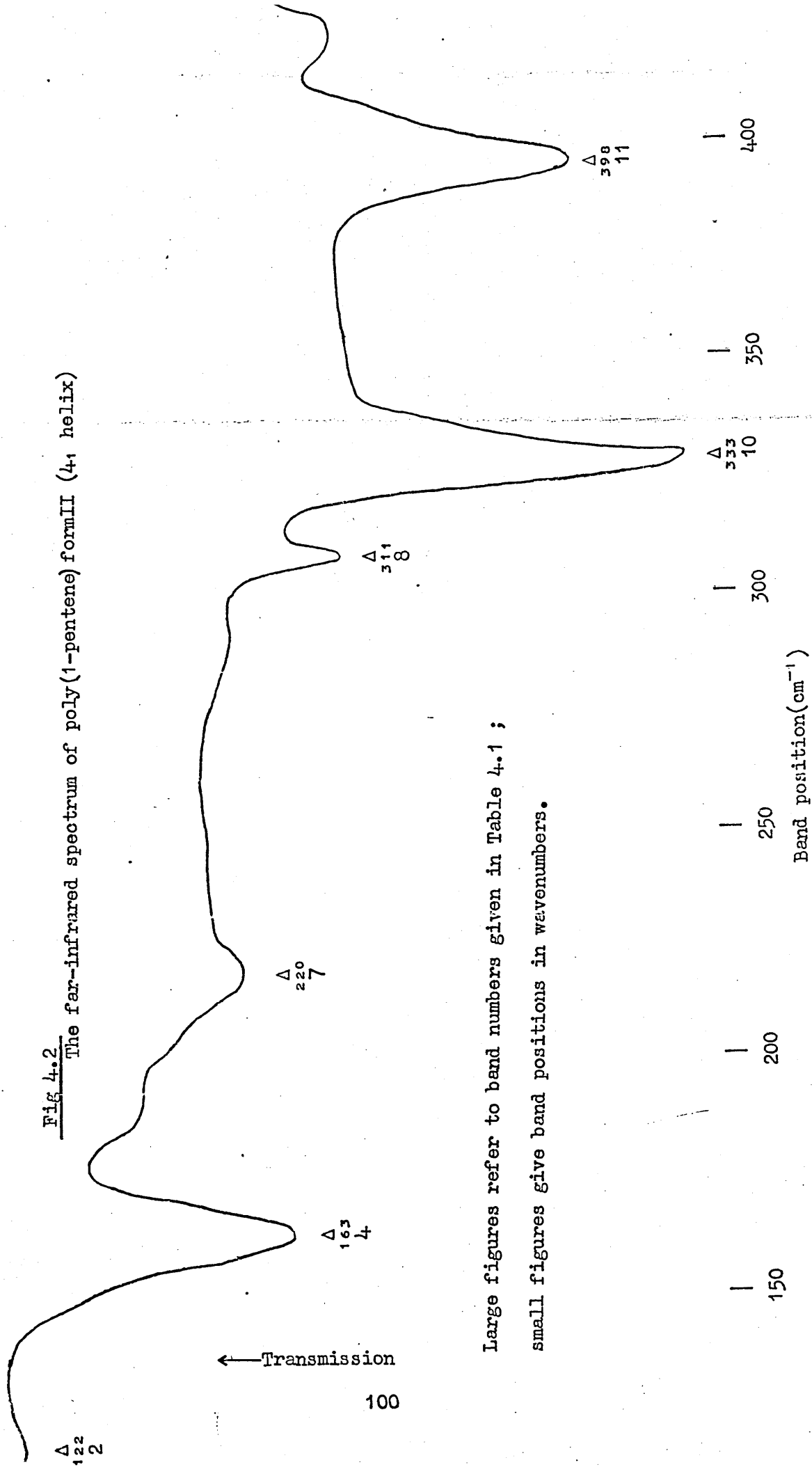
.1, 2 and 3 are bending modes ∇ indicates band split due to the non-uniform helix of poly(4-methyl-1-pentene)

τ is a torsional mode Φ indicates band split due to correlation field effects

Fig 4.1
The far-infrared spectrum of poly(1-pentene) form I (3, helix)

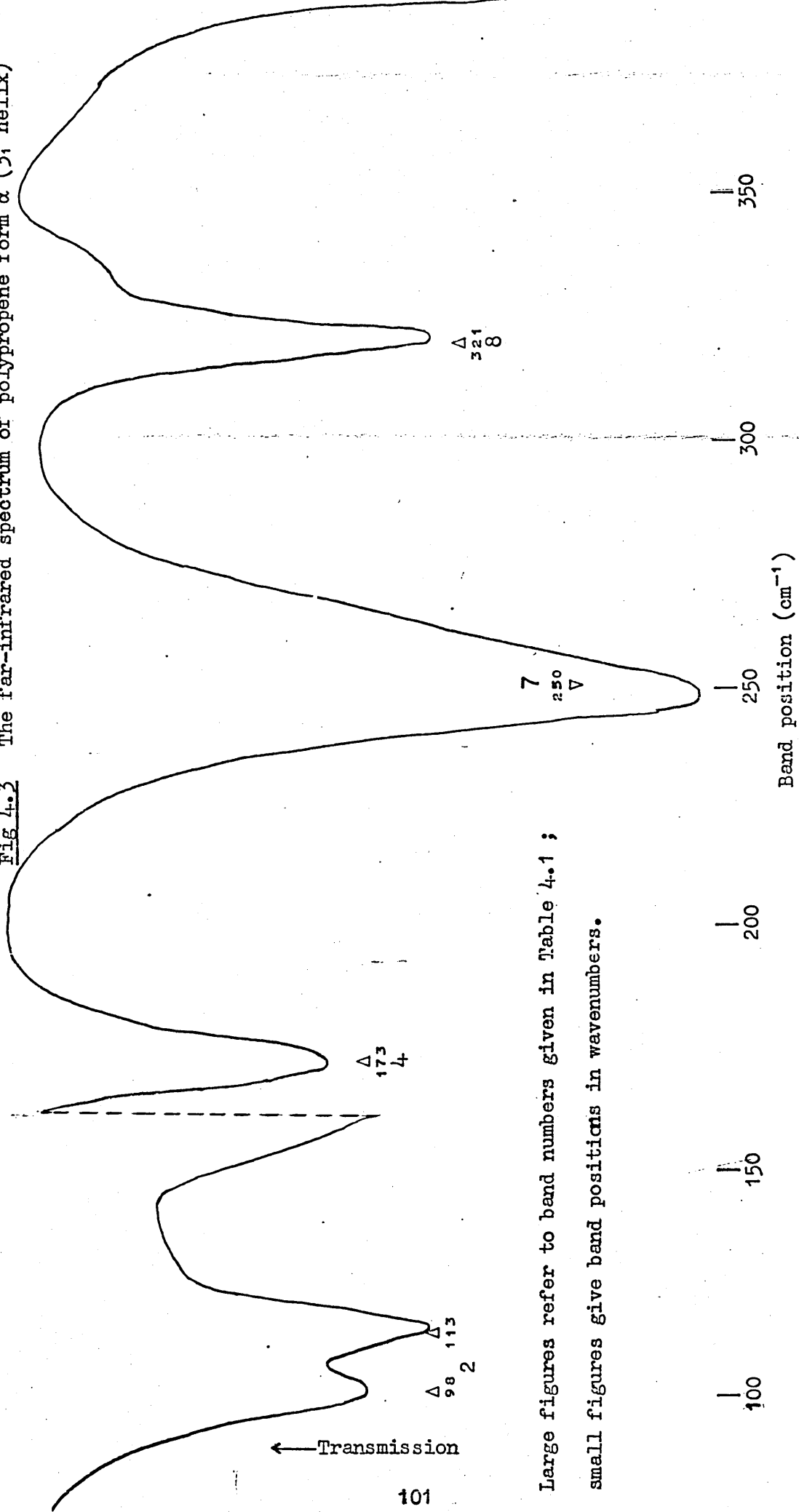


Large figures refer to band numbers given in Table 4.1 ; small figures give the band position in wavenumbers.



Large figures refer to band numbers given in Table 4.1 ;
small figures give band positions in wavenumbers.

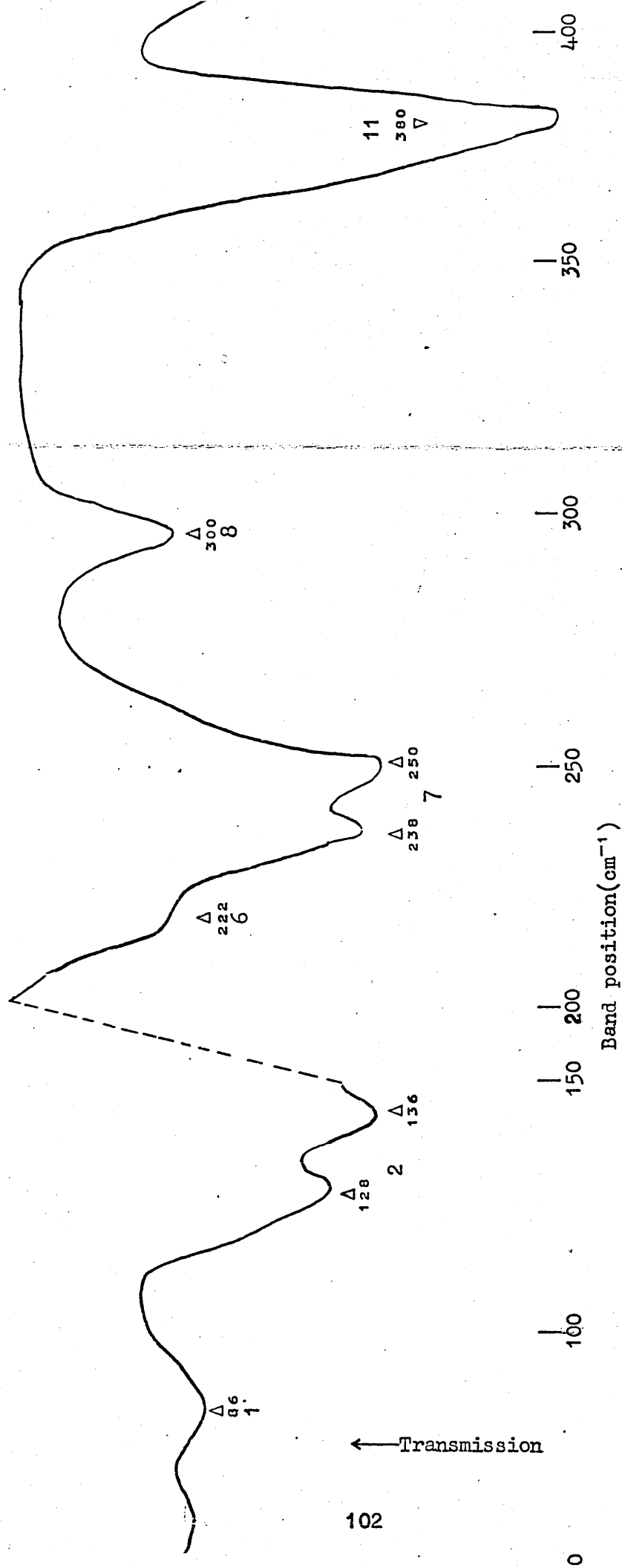
Fig 4.3 The far-infrared spectrum of polypropene form α (3, helix)



Large figures refer to band numbers given in Table 4.1 ;

small figures give band positions in wavenumbers.

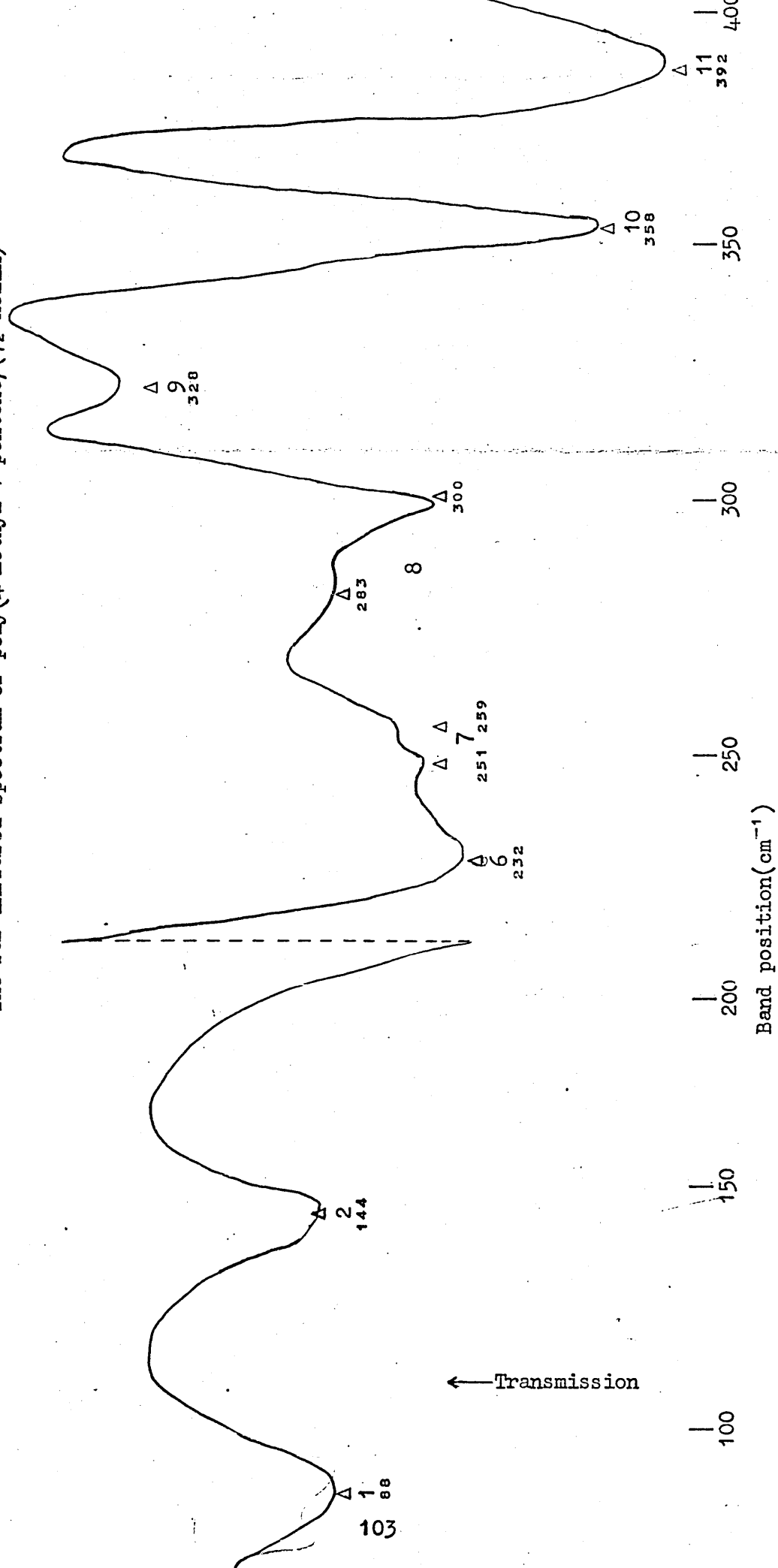
Fig 4.4 The far-infrared spectrum of poly(1-butene) form I (3, helix)



Large figures refer to band numbers given in Table 4.1 ; small figures give band positions in wavenumbers.

Fig 4.5

The far-infrared spectrum of poly(4-methyl-1-pentene) (7₂ helix)



Large figures refer to band numbers given in Table 4.1 ; small figures give the band position in wavenumbers

Fig 4.6

The X-ray diffraction patterns of variously treated samples of P4MP 1.

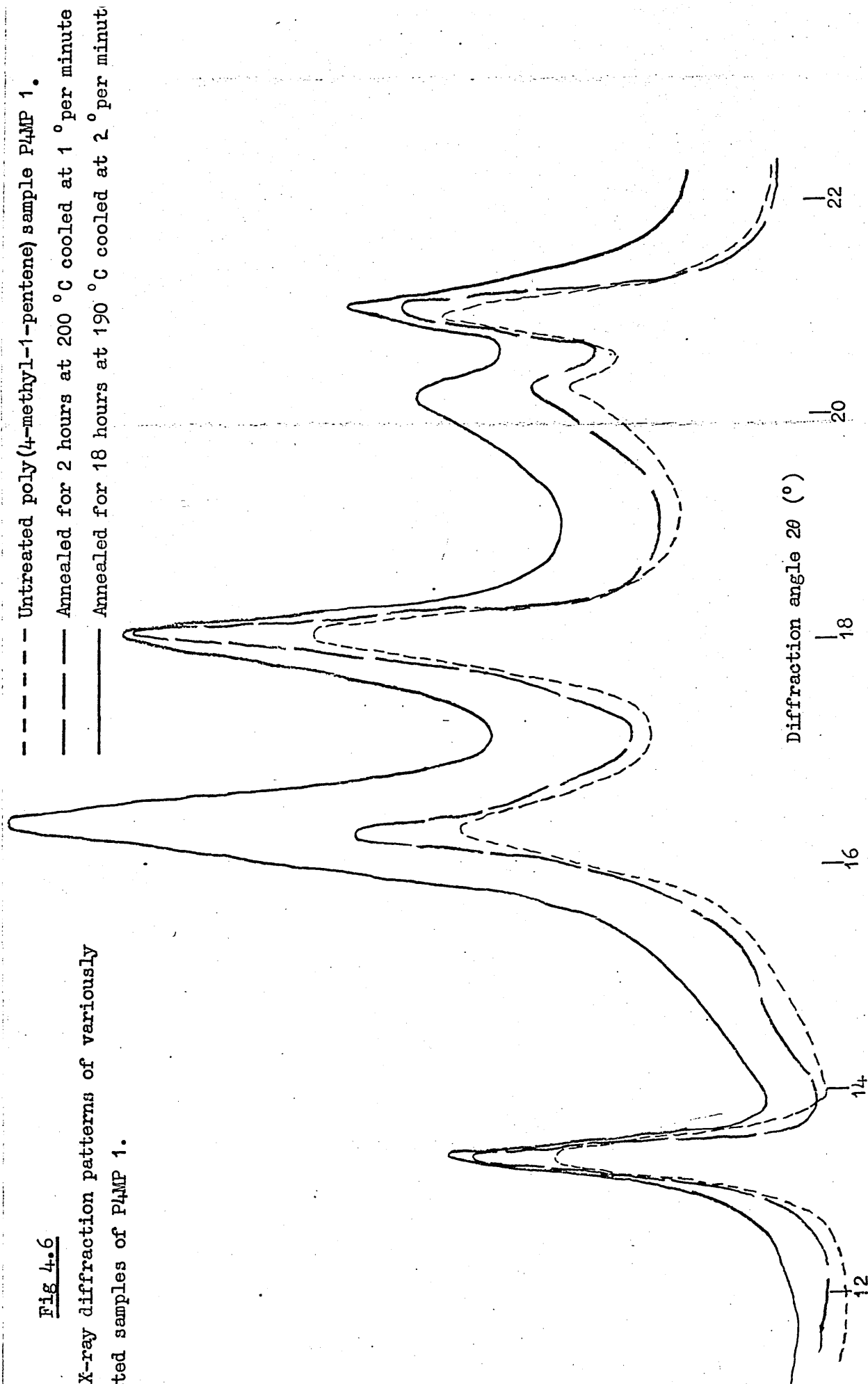


Fig 4.7

The X-ray diffraction patterns of variously treated samples of P4MP 2.

--- Untreated poly(4-methyl-1-pentene) sample P4MP 2.
--- Annealed for 30 minutes at 190 °C cooled at 2 °/minute.
— Annealed for 18 hours at 190 °C cooled at 2 °/minute.

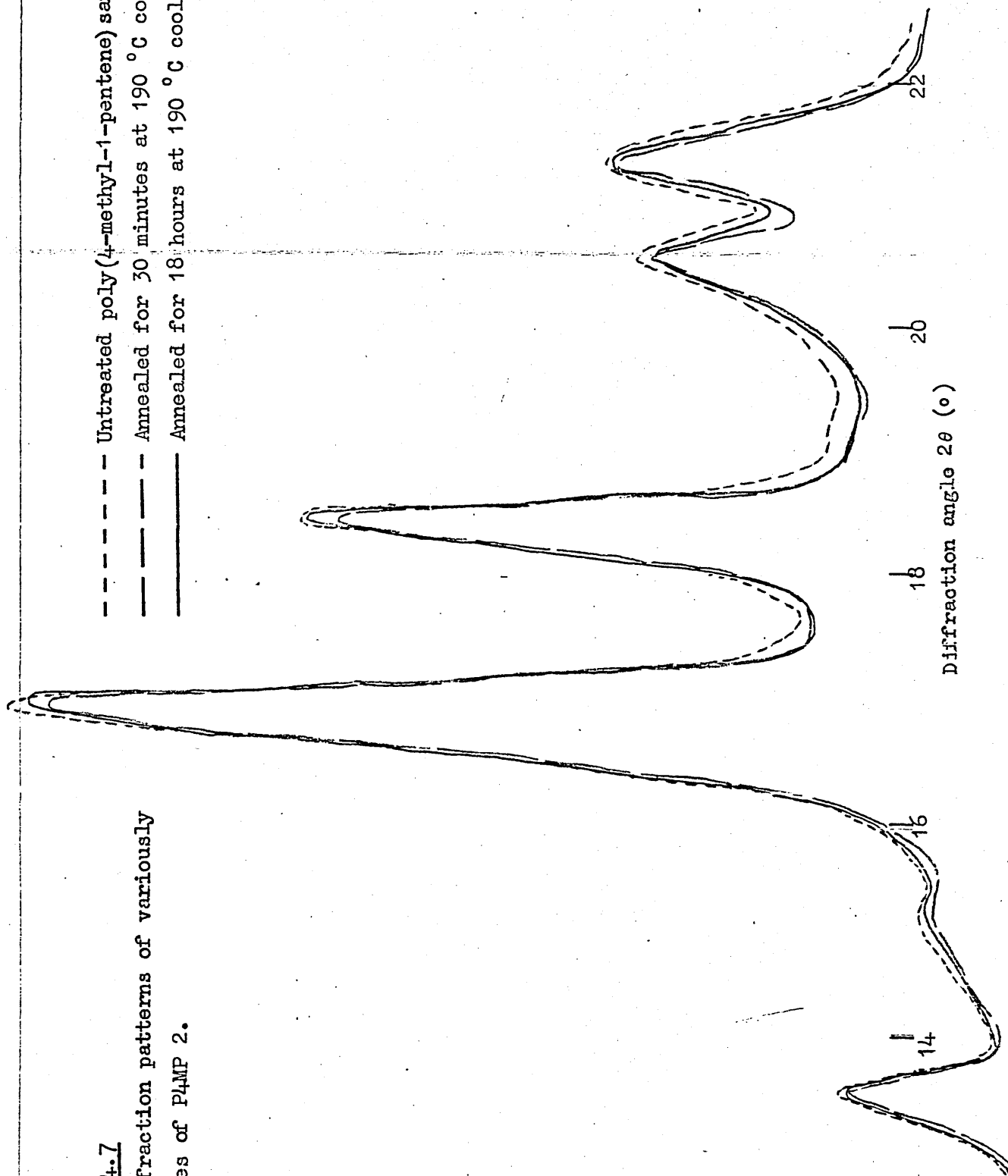


Fig 4.8 The far-infrared spectra of variously treated poly(4-methyl-1-pentene)(sample P4MP-1)
Untreated poly(4-methyl-1-pentene) sample P4MP 1.

Annealed for 2 hours at 200 °C cooled at 1 ° per minute.

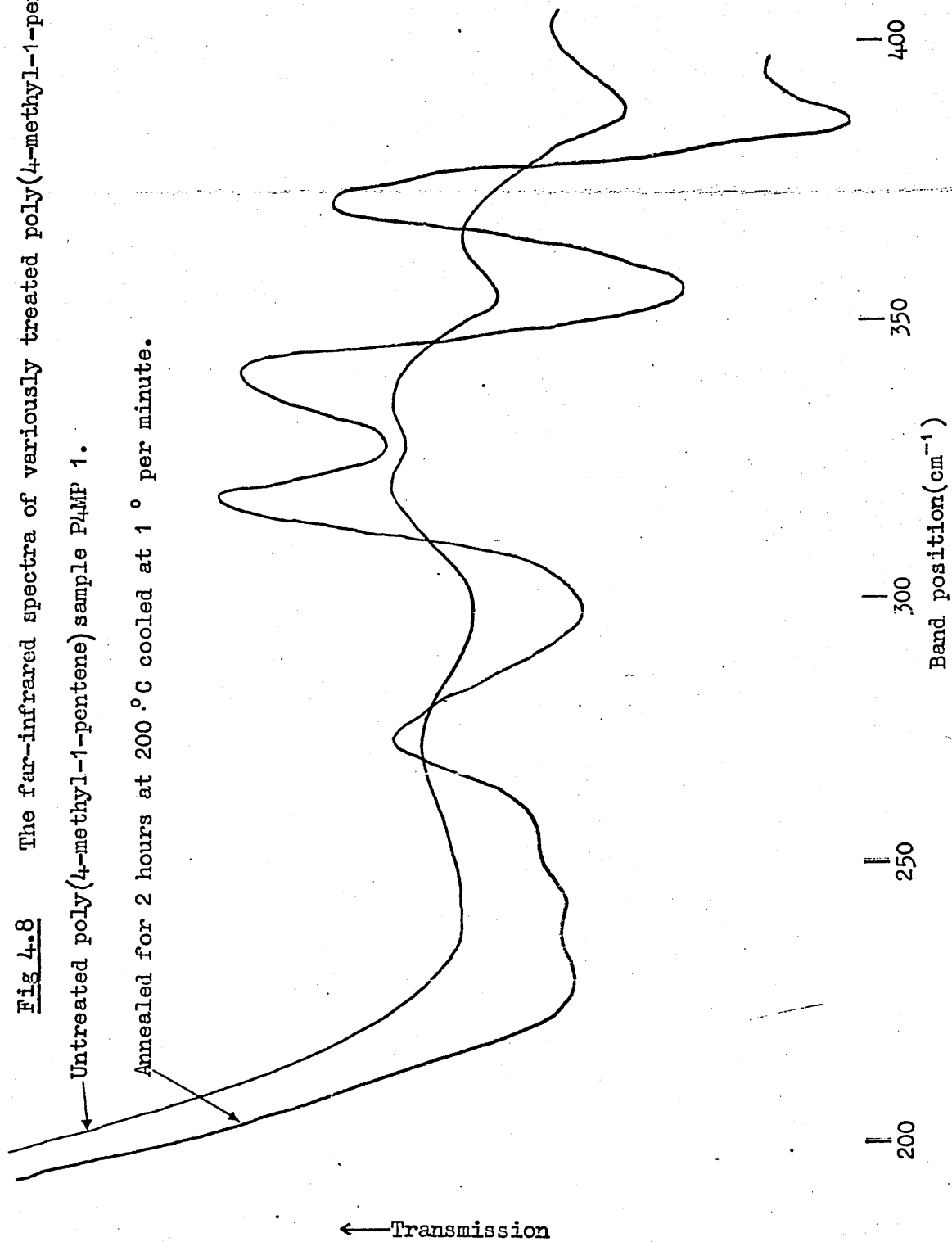
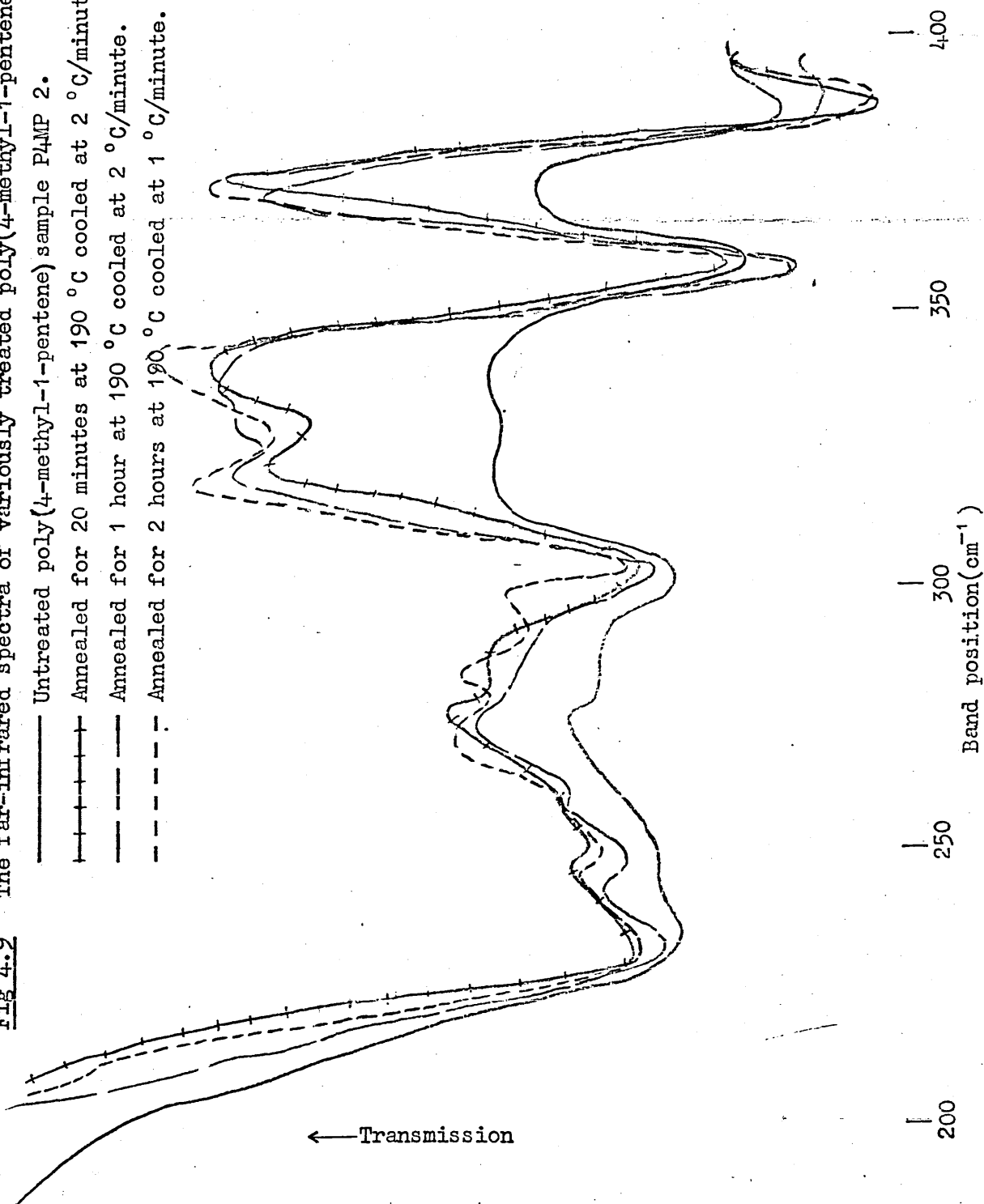


Fig 4.2 The far-infrared spectra of variously treated poly(4-methyl-1-pentene)(sample P4MP-2)

- Untreated poly(4-methyl-1-pentene) sample P4MP 2.
- - - - - Annealed for 20 minutes at 190 °C cooled at 2 °C/minute.
- - - - - Annealed for 1 hour at 190 °C cooled at 2 °C/minute.
- - - - - Annealed for 2 hours at 190 °C cooled at 1 °C/minute.



Chapter 5

The Far-infrared Spectrum of Poly(ethylene terephthalate) (PET).

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5.1 Introduction

Poly(ethylene terephthalate) (PET) is one of the few polymers which can be produced in either a substantially amorphous or a highly crystalline state at room temperature by various heat treatments of the sample. The infrared and far-infrared spectra of PET in these two extreme conditions were found to be quite different and certain bands were assigned to either crystalline or amorphous structure (1). The changes in structure causing this dramatic spectral change on crystallisation were attributed by early workers either to trans-gauche isomerism in the ethylene glycol segments of the molecule (2), or to changes in the resonance characteristics of the substituted benzenoid part of the molecule (this being non-planar in amorphous structure) (3). However, crystallisation is now thought to be more complex, involving the whole molecule and not merely changes in conformation about specific bonds (4,5). Four vibrational analyses have been carried out on crystalline PET (5-8) all of which failed through some weakness of the method adequately to predict the far-infrared spectrum of PET below 150 cm^{-1} .

The present study seeks to confirm previously reported far-infrared spectral data (8,9), and to rationalise and consolidate the various interpretations which have been put forward.

5.2 Experimental

Samples:

- (i) Crystalline PET.
- (ii) Amorphous PET.
- (iii) Ethylene terephthalate tetramer.

Samples (i) and (ii) were in the form of hot pressed sheets ca. 0.1 mm thick. Sample (iii) was in the form of a cold-pressed disc pressed from 20 mg of powdered tetramer. Sample (i) was annealed at 220 °C for 17 hours, and then cooled at a rate of 1 °C per minute, but this had little effect on its spectrum.

5.3 Results

The far-infrared spectrum of crystalline PET recorded at ca. 60 K is shown in Fig 5.1 for the region below 150 cm^{-1} ; eight bands are clearly discernable. The spectrum changes little on raising the temperature to ca. 300 K; the bands broaden slightly and shift to lower wavenumber by 1 to 2 cm^{-1} . The small shift in position observed is attributable to occupation of excited vibrational energy levels at room temperature (hot bands). Lattice bands in crystalline polymers usually shift by ca. 8 cm^{-1} during a similar temperature change due to changes in lattice dimensions.

Fig 5.2 shows the far-infrared spectrum of an amorphous PET sample. As can be seen, the spectrum is totally different from that of crystalline PET. The three bands observed below 250 cm^{-1} are broad and are not at the same position as the bands in the spectrum of crystalline PET (Fig 5.1).

Figs 5.3a and 5.3b shows the far-infrared spectrum of a linear tetramer of ethylene terephthalate; the bands observed are roughly the same as those in the spectrum of crystalline PET (Fig 5.1) except below 90 cm^{-1} where no bands were observed for the linear tetramer.

Tabulated in Table 5.1 are the bands observed in the far-infrared spectrum of PET (below 200 cm^{-1}), together with previously reported spectra, and possible band assignments.

5.4 Discussion and Conclusions

Four vibrational analyses have been carried out on crystalline PET (5-8). Boitsov and Gotlib (6) and Danz et al. (7) used only very approximate models and force fields, and considered only in-plane vibrations. Thus, the results they obtained are limited in their usefulness. Manley and Williams (8), in order to get a higher symmetry point group for PET than the C_i determined by X-ray work (10), divided the repeat unit into two parts for convenience. Thus vibrations involving the whole repeat unit, such as absorb in the far-infrared spectrum, may not be predicted using this method. Additionally, Manley and Williams (8) stated that the point group of the $\text{COC}_6\text{H}_4\text{CO}$ part of the molecule was D_{2h} , which is quite clearly erroneous. Their results therefore are of no value in assigning the bands in the far-infrared spectrum of PET. Boerio et al. (5) paid little attention to low frequency out-of-plane torsions because of the difficulty in calculating the force field for these modes. The three bands predicted by Boerio et al. (5) below 200 cm^{-1} , at 135 , 80 and 54 cm^{-1} , have been assigned to the bands observed at 139 , 63 , and 49 cm^{-1} respectively (Table 5.1). The band predicted at 141 cm^{-1} (5) is either too weak to be observed or masked by the strong band at 139 cm^{-1} .

A possible assignment of some of the low frequency vibrations in PET has been put forward by Frank et al. (11,12). They suggested that rotations, which usually absorb at low frequencies, are shifted in PET to higher frequencies by coupling between groups in adjacent chains, the coupling being due mainly to the anisotropic polarisability of the benzene ring and the dipole moment of the carbonyl group. The coupling is said to produce a torsional wave at right angles to the chain axis. The main evidence for this kind of mechanism is

analogy with the band at ca. 100 cm^{-1} in benzene, which is broad for the liquid phase but sharpens considerably and moves to higher frequency for the solid. It would, however, be expected that bands influenced by such a mechanism in crystalline PET would shift to higher frequency on lowering the sample temperature, because the chains would pack closer together thereby increasing interchain coupling. None of the bands in crystalline PET, however, show such an effect. It must therefore be concluded that if this interpretation is valid there is little increase in the packing density on cooling PET.

Using the most reliable normal co-ordinate analysis (5) and the concept of 'coupled rotations' (12) it is possible to assign several of the far-infrared bands of PET (Table 5.1). There remain, however, several problems, discussed below.

The bands at 19 and 34 cm^{-1} resemble interference fringes (Fig 5.1), but as they have been observed at the same frequency in samples of differing thickness, and their observation corresponds well with previously reported data (9), this explanation of their origin has been discounted. The bands were not predicted by Boerio et al. (5), consequently they have been left unassigned.

The broad bands at 46 , 117 and 185 cm^{-1} which are only observed in amorphous PET could be 'liquid lattice bands' (13). The far-infrared spectrum of polyethylene shows an underlying continuum which increases in intensity as sample amorphosity increases; this has been attributed (13) to a 'smeared-out liquid lattice band'. Calculations (14) performed on classical liquids treated in a similar manner to solids except that in the liquid the vibrating units have no fixed rest position suggest there is some structural correlation between molecules, the correlation increasing with viscosity. As the

structure of the amorphous phase of polymers resembles a viscous liquid, absorptions due to vibrations of a liquid lattice should be present in their far-infrared spectra. In polyethylene the interactions will be non-specific, giving rise to a blanket far-infrared absorption, but in the case of PET polar groups along the chain will tend to favour more specific interactions. This is thought to explain the three broad bands observed in the far-infrared spectrum of amorphous PET (Table 5.1).

The intensity of the band at 139 cm^{-1} shows an extraordinary dependence on crystallinity, closely resembling the behaviour of the 78 and 104 cm^{-1} bands. However, Frank *et al.* (12) could not associate it with the same origin as the latter pair of bands, and thus proposed that the band was due to an out-of-plane mode of the $(\text{CH}_2)_2$ groups. It has also been proposed (15) that the 139 cm^{-1} band could be due to vibrations in chain fold regions. However, this seems unlikely as the far-infrared spectrum of a linear tetramer of ethylene terephthalate (Figs 5.3a and 5.3b), which is expected to contain no chain folds, has an analogous absorption band at ca. 140 cm^{-1} . Boerio *et al.* (5) concluded that the 139 cm^{-1} band corresponds to the mode they calculated at 135 cm^{-1} : a bend of Ph-C and $\text{CH}_2\text{CH}_2\text{O}$ parts of the molecule. This assignment seems plausible as the parts of the molecule on which the vibration is centred are expected to be altered on crystallisation (4,5), explaining the marked dependence of the intensity of this band on sample crystallinity. The invariance of the band position with temperature mitigates against assignment as a lattice mode. Thus the evidence seems to be in favour of Boerio's assignment (5) for the 139 cm^{-1} band. This and other assignments for bands in the far-infrared spectrum of PET (below 200 cm^{-1}) are tabulated in Table 5.1.

5.5 References

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Table 5.1

The far-infrared absorptions of poly(ethylene terephthalate), below 250 cm^{-1} .

This study	Ref.9	Ref.8	Calculated frequency(cm^{-1})*,
Observed(cm^{-1})	Observed(cm^{-1})	Observed(cm^{-1})	Assignment, source reference*
19	24	--	
34	37	36	
--	(42)	46	'Liquid lattice band'
49	54	58	54 A(49%), B(32%) [5].
63	--	68	80 C(29%), D(27%), E(17%) [5].
78	85	--	82 Coupled rotation [12].
104	100	95	105 Coupled rotation [12].
--	(117)	117	'Liquid lattice band'
139	138	138	135 F(46%), G(30%) [5].
(185)	(188)	190	'Liquid lattice band'

Figures in brackets refer to bands observed only in substantially amorphous samples

A= -O-C- torsion ; B= Ph-C torsion ; C= ring torsion ;

D= Ph-C out of plane bend ; E= Ph-H out of plane bend ;

F= Ph-C bend ; G= $\text{CH}_2\text{-CH}_2\text{-O}$ bend .

*If applicable

Fig 5.1

The far-infrared spectrum of crystalline PET annealed at 220 °C for 17 hours.

Spectrum recorded at ca. 60 K.

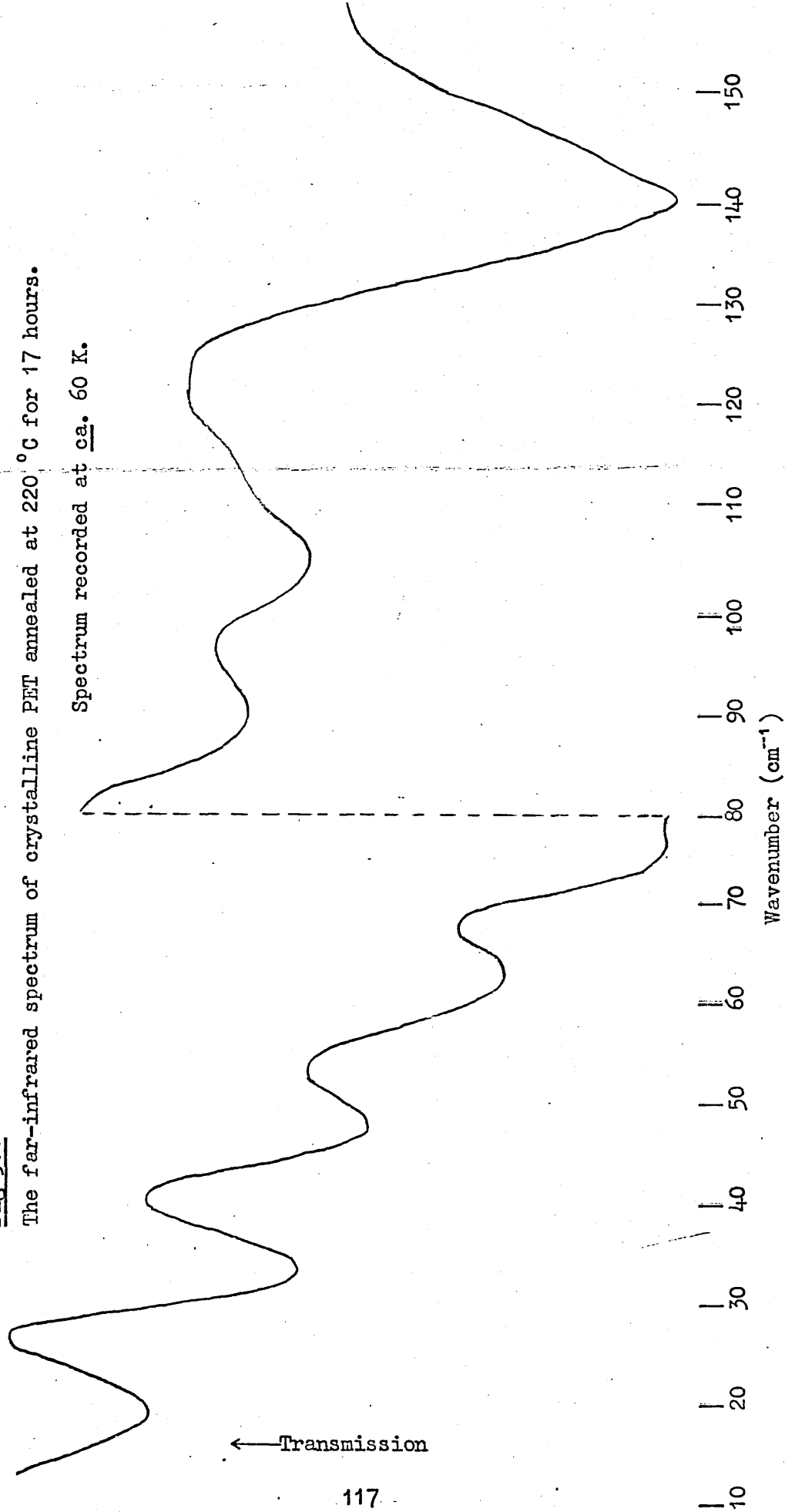


Fig 5.2

The far-infrared spectrum of amorphous PET
(untreated sample) spectrum recorded at ca. 60 K.

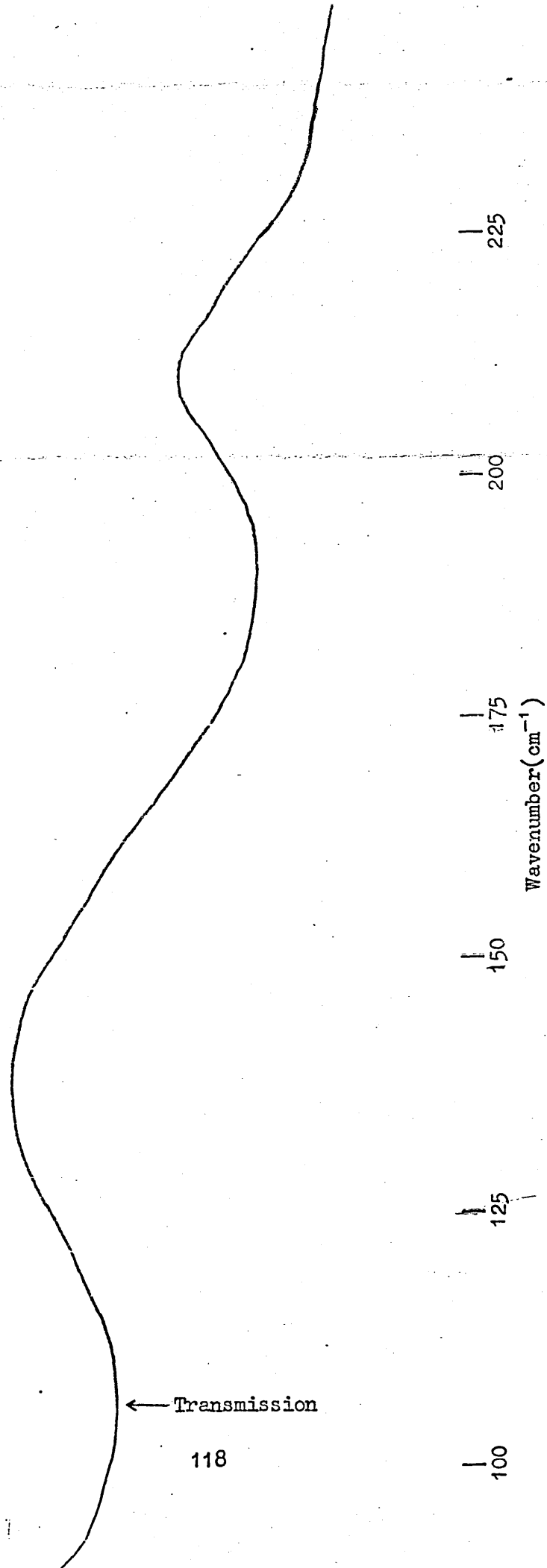


Fig 5.3a

The far-infrared spectrum of linear tetramer ethylene terephthalate (100 to 250 cm^{-1})

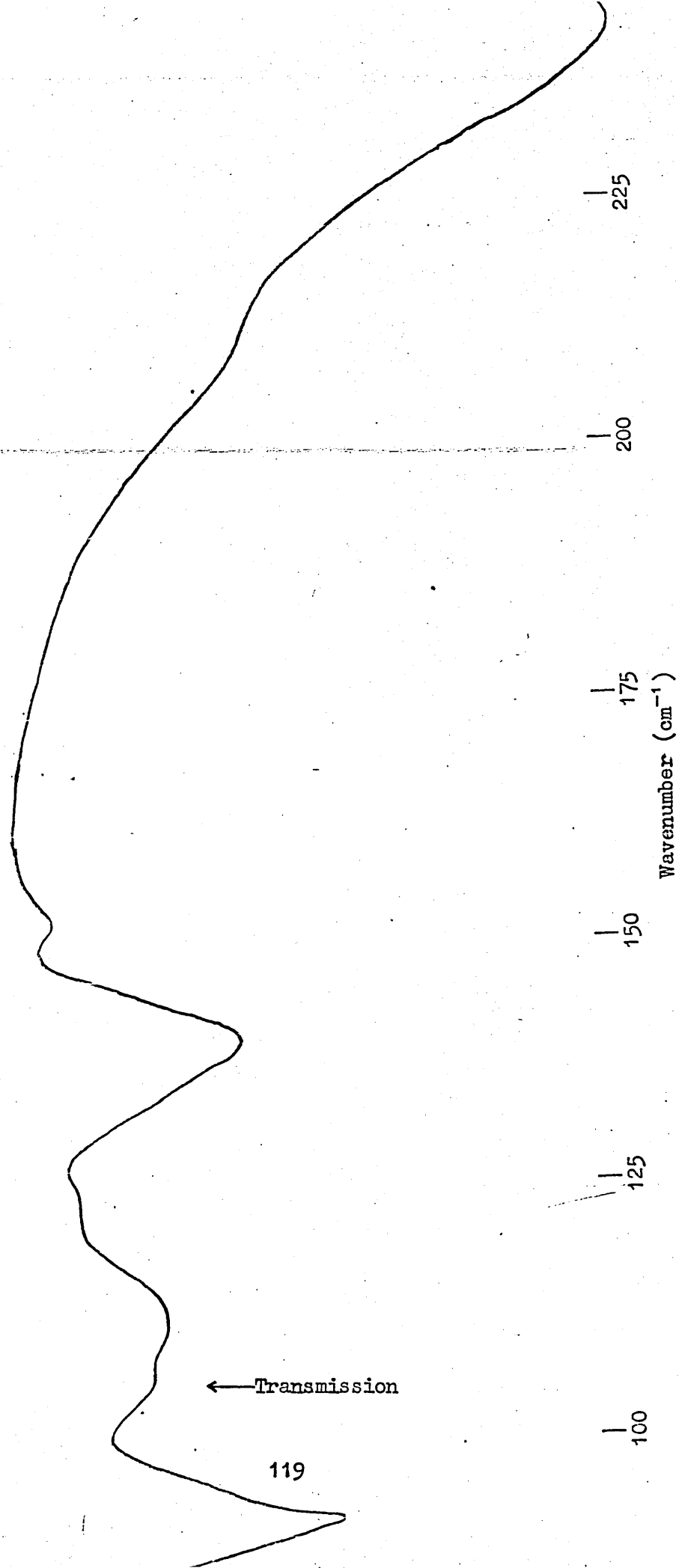
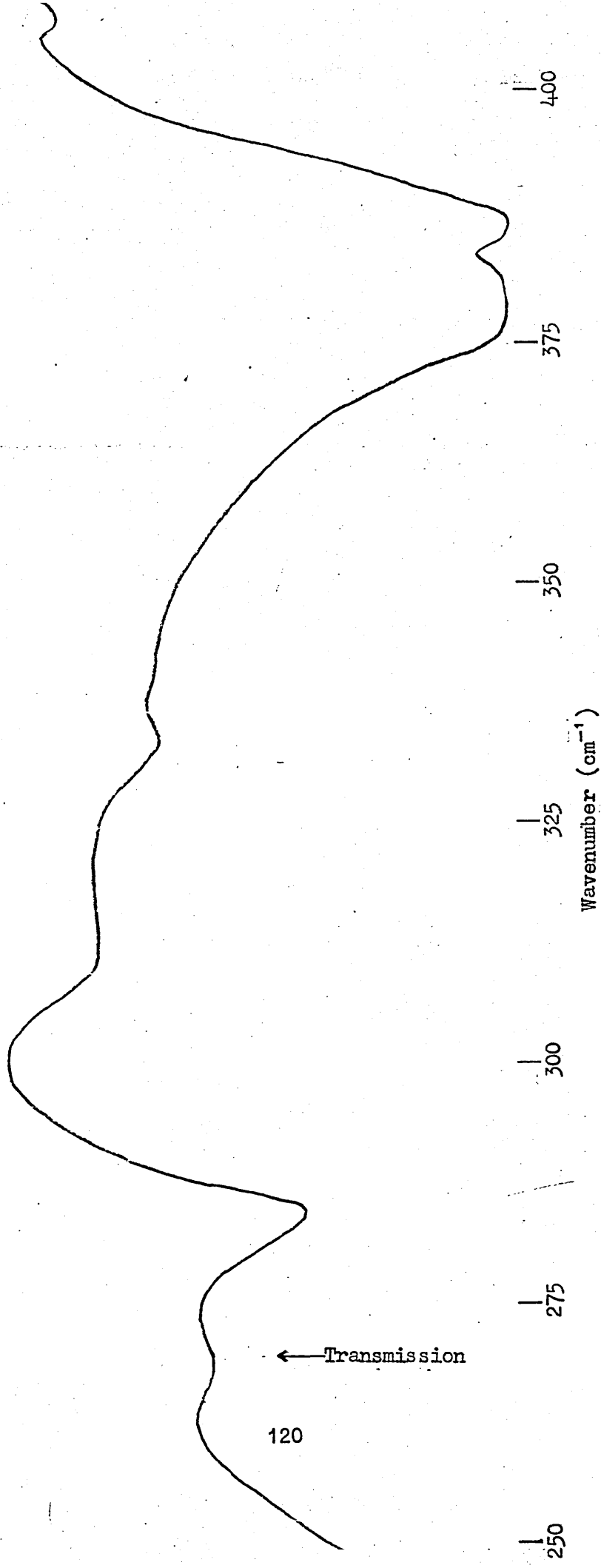


Fig 5.3b

The far-infrared spectrum of linear tetramer ethylene terephthalate (250 to 400 cm^{-1})



Chapter 6

Experimental

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6.1 Far-infrared Spectroscopy

Far-infrared spectra were recorded using a Beckmann RIIC FS-720 Fourier transform spectrometer. A sampling interval of $8\text{ }\mu\text{m}$ was used for all the interferograms; 512 points on each interferogram were recorded on paper tape giving a resolution of $\text{ca. } 2.5\text{ cm}^{-1}$ and allowing a band width of $\text{ca. } 450\text{ cm}^{-1}$. Two different beam splitters were utilised in the recording of the spectra: $6\text{ }\mu\text{m}$ thick poly(ethylene terephthalate) for the frequency range 40 to 450 cm^{-1} , and $25\text{ }\mu\text{m}$ thick poly(ethylene-terephthalate), with quartz filtering, for the range 10 to 400 cm^{-1} . Fourier transformation (1) was carried out on this data, stored on paper tape, using a programme (2) executed on an IBM 1130 computer. The position of sharp absorptions on the resulting spectra, determined using the computer programme given in Appendix I, are considered accurate to $\pm 0.5\text{ cm}^{-1}$. The sample temperature was controlled using a Cryogenic Technology model 20 cryodyne. For accurate sample temperature determination the cryodyne thermocouple was calibrated as described in Section 3.2 which gave the sample temperature accurate to $\pm 2\text{ K}$. To test spectral reproducibility, particularly in samples containing weak, broad absorptions, the spectrum of each sample was recorded at least five times.

6.2 X-ray Diffraction Instrumentation

X-ray diffraction measurements were made using a Phillips 1130/00/60 generator fitted with an Advanced Metals Research 3-202 diffractometer. Copper K_{α} radiation (wavelength 1.542 Å) was used for all the X-ray diffraction work.

6.3 References

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Academic Press, New York, 1972.
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Appendix I Computer programme to find the position of band centres.

```
/LOAD VSBASIC
010REM PROGRAMME TO FIND BAND CENTRES KNOWING THREE POINTS
020REM (I1,V1) (I2,V2) (I3,V3)
030REM WHERE I IS INTENSITY AND V FREQUENCY OF THE POINT IN CM-1
040PRINT"ENTER TEMPERATURE"
050INPUTT
060IFT=0THEN230
070PRINT"ENTER POINTS I1,V1,I2,V2,I3,V3"
080INPUTI1,V1,I2,V2,I3,V3
090A=I1-I2
100B=I1-I3
110C=V1-V2
120D=V1-V3
130E=V1**2-V2**2
140F=V1**2-V3**2
150G=-1*(((A/E)-(B/F))*((E/C)-(F/D)))
160H=2*(((C/E)-(D/F))*((A/C)-(B/D)))
170J=G/H
180PRINT USING190,"AT A TEMPERATURE OF",T,"K"
190FORM SKIP3,X10,C,POS31,PIC(Z##),POS35,C,SKIP
200PRINT USING210,"THE BAND POSITION IS",J,"CM-1"
210FORM X9,C,POS31,PIC(Z##,H),POS37,C,SKIP3
220GOTO40
230END
```

Details of Programme of Postgraduate Study

The author has:

- a) Attended a course of six lectures entitled Chemical Applications of Group Theory given by Dr M. Goldstein.
- b) Attended a course of six lectures entitled The Polymer Molecule given by Dr G.C. Corfield.
- c) Attended meetings of the Infrared and Raman Discussion Group at Kings College London, Kodak (Harrow), and ICI (Welwyn Garden City).
- d) Completed the following reading study programme
 - i) Introductory Group Theory for Chemists, G. Davidson, Elsevier, 1971.
 - ii) Chemical Infrared Fourier Transform Spectroscopy, P.R. Griffiths, Wiley, 1975.
 - iii) Vibrational Spectroscopy of Solids, P.M.A. Sherwood, C.U.P., 1972.
 - iv) Laser Raman Spectroscopy, T.R. Gilson and P.J. Hendra, Wiley, 1970.
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 - vi) Structural Studies of Macromolecules by Spectroscopic Methods, K.J. Ivin (Ed.), Wiley, 1976; Chapters 3-7 and 10.
 - vii) Laboratory Methods in Infrared Spectroscopy, R.G.J. Miller and B.C. Stace (Eds.), Heyden, Second Edn., 1972; Chapters 4, 5, 7, 9, 16 and 17.
 - viii) Polymer Spectroscopy, D.O. Hummel (Ed.), Verlag Chemie, 1974.
 - ix) Structure of Crystalline Polymers, H. Tadokoro, Wiley, 1979.