

Infra-red and Raman spectra of poly(*m*-methylene terephthalate) polymers

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A detailed comparison of the infra-red and Raman spectra of poly(trimethylene terephthalate) (3GT), poly(tetramethylene terephthalate) (4GT) and poly(ethylene terephthalate) (2GT) is reported. Particular attention has been given to the changes in the spectra which occur on crystallization. Additionally, the spectra of oriented 4GT samples have been examined under applied stress, because this produces a change in the structure of the crystalline regions. It is shown that the differences between the spectra of these polymers can be satisfactorily accounted for by changes in the conformation of the molecular chains involving both *trans/gauche* isomerism in the glycol sequence and the planarity of the terephthalate residue.

INTRODUCTION

In the last few years, an extensive research programme on the structure and properties of poly(*m*-methylene terephthalate) polymers has been underway in our laboratories. Previous publications describing this research have been primarily concerned with changes in the molecular conformations under stress^{1,2}, using X-ray diffraction and Raman spectroscopy, and the consequent interpretation of the mechanical behaviour³, particularly the tensile stress-strain behaviour and recovery from strain.

As part of the research programme, a detailed analysis has been carried out of the infra-red and Raman spectra of poly(trimethylene terephthalate) (3GT) and poly(tetramethylene terephthalate) (4GT) in conjunction with a re-examination of the spectra of poly(ethylene terephthalate) (2GT) and some key related model compounds. Although a comprehensive discussion has already been presented recently⁴ it seems appropriate to summarize the principal findings in a short publication which is more generally available.

The most striking feature of the recent investigation has been the observation that a reversible crystal transformation occurs on stretching oriented 4GT at room temperature. The changes in unit cell dimensions¹, in conjunction with the spectroscopic data² and more detailed crystallographic studies⁵, are consistent with the molecular chain conformation changing with extension to a fully extended chain in which the glycol residue has an all-*trans* sequence. In the unstressed state, the glycol residue takes a crumpled form with a *gauche-trans-gauche* sequence. At the same time, it seems likely that there may be changes in the terephthalate residue with regard to the orientation of the phenylene/carbonyl bonds and the planarity of this residue as a whole⁵.

These considerations of the molecular conformation of 4GT link directly with much earlier discussions of the interpretation of the infra-red spectrum of 2GT. It had been observed that there were considerable differences between the infra-red spectra of extruded and quenched 2GT (the amorphous state) and polymer which has subsequently been drawn or heat crystallized. It was proposed by one of us that the major differences were not due to crystallinity differences *per se* but to rotational isomerism in the ethylene glycol residue^{6,7}. In particular, bands at 1470, 1340, 975

and 845 cm⁻¹ were assigned to vibrations of the *trans* ethylene glycol conformation and bands at 1450, 1370, 1040 and 898 cm⁻¹ to vibrations of the *gauche* conformation. The structure of the crystalline regions of 2GT shows only the *trans* glycol conformations. The amorphous regions on the other hand, could contain both *trans* and *gauche* glycol conformations, the exact proportions depending on the treatment of the polymer.

An alternative interpretation for the changes in the infra-red spectrum due to orientation and crystallization was proposed by Liang and Krimm⁸, who suggested that all the differences could be accounted for by changes in the symmetry and resonance characteristics of the substituted benzenoid ring framework. At this stage the discussion was much advanced by the examination of deuterated polymers⁷⁻⁹ and model compounds, of which the most important was the cyclic trimer of ethylene terephthalate, cyclic tris-ethylene terephthalate¹⁰. The latter compound showed the absorptions assigned to the *gauche* conformations only, the corresponding *trans* absorptions being absent. Molecular models of the cyclic trimer, together with crystallographic and optical data showed that it is very likely that the glycol linkages are in the *gauche* conformation, but that the molecule is approximately planar with the carbonyl groups in the *cis* position with respect to the benzene ring as distinct from *trans* as in crystalline 2GT. This suggested that the conformational changes occurring involve the phenylene/carbonyl bond in addition to the glycol residue^{9,11}. Concurrent with these developments Krimm made a re-appraisal of his band assignments and concluded that in several cases crystallinity-sensitive bands which had been assigned to vibration of the terephthalate residue might be better assigned to vibrations of the glycol residue¹². Similar conclusions had also been made by other workers, including Daniels and Kitson¹³, and Miyake¹⁴.

In the present paper the infra-red and Raman spectra of 3GT and 4GT are presented and compared with those of 2GT. In all cases the spectra of both amorphous and annealed semicrystalline polymer were available. Band assignments are attempted taking into account the previous investigations, and two recent short communications on 2GT by Boerio and coworkers^{15,16}, which appeared when our own studies were nearing completion.

EXPERIMENTAL

Spectra

Raman spectra of the polyesters were recorded in the region 200–1800 cm^{-1} using a Coderg Pho double grating spectrometer. The excitation source was a Coherent Radiation Argon ion laser producing about 10 mW at 4880 Å wavelength.

The infra-red spectra of the isotropic samples were obtained using a Grubb Parsons double beam spectrometer, type S3A employing a prism monochromator. For the oriented samples a Grubb Parsons Spectromajor was used and a polarizer enabled the collection of dichroic data. The frequency range covered by the infra-red spectra was about 600–1800 cm^{-1} .

Materials

Samples used in this study were prepared in various ways in order to meet the demands of the spectroscopic methods employed.

The Raman technique may be applied to a wide range of sample geometries. Considering the isotropic spectra, good results were obtained from melt-extruded-then-quenched polymer chips (amorphous) which were later annealed for several hours at the appropriate crystallization temperature and rerun.

Depolarization measurements were carried out using the amorphous samples only. The annealed samples were opaque and consequently scrambled the input polarization.

A different method of preparation had to be adopted for the isotropic infra-red samples. To avoid the problem of over-absorption (which would certainly have occurred with the polymer chips) a very fine powder of each polymer was prepared. This was done by dissolving the chip in dichloroacetic acid and rapidly precipitating it by aqueous dilution. WAXR photographs of the washed and dried powders revealed them to be of low crystallinity. Potassium bromide discs were then made containing 2 mg of powder per 500 mg of KBr. After the amorphous spectra had been obtained the discs were annealed as described earlier and rerun. That annealing of the powder produced an increase in crystallinity was also confirmed by WAXR.

Oriented samples

Measurements of both infra-red and Raman spectra under an applied deformation were performed on thin (30 μm) drawn ($\lambda = 5$) 4GT tape which had previously been annealed. The sample was mounted in a small extensometer and subjected to either zero or 15% strain.

In searching for conformational changes in the spectra it is important to recognize effects which may be due simply to changes in overall orientation as the strain is applied. In the case of the Raman spectra I_{33} was compared with I_{11} (or I_{22}). I_{33} is the Raman intensity arising from a vibrational mode when the input and output polarization directions are parallel to each other and also to the 3-axis (chosen to be the draw direction) of the sample. I_{11} (or I_{22}) is the intensity when the input and output polarizations are parallel to each other and to the 1 (or 2)-axis in the sample. This is any direction normal to the draw direction for fibre symmetry.

In a highly oriented sample I_{33} and I_{11} (or I_{22}) are associated with extremes of the polarizability tensor components. Therefore, if a major intensity change occurs in both I_{33} and I_{11} spectra and in the same sense then it is safe to as-

sume that the change is not simply due to changes in orientation.

The I_{33} spectra were obtained by mounting the sample with its draw direction vertical. For the I_{11} spectra the draw direction was horizontal and at approximately 50° to the beam direction (to avoid reflection of the main beam into the spectrometer). In both cases the input and output polarization directions were vertical.

Orientation effects in the infra-red experiment were determined by recording both parallel and perpendicular spectra. The polymer spectra are shown in Figures 1–6. In Figures 7 and 8 are given the Raman and infra-red spectra of cyclic tris-ethylene terephthalate for comparison.

DISCUSSION

General considerations, including molecular symmetry and conformational changes

As a prelude to making the band assignments it seems appropriate to discuss some key points regarding the molecular symmetry of the three polymers starting with 2GT. Following the approach of much previous work, including that in the PhD thesis already referred to⁴, it is assumed that the band assignments can be made on the basis of an

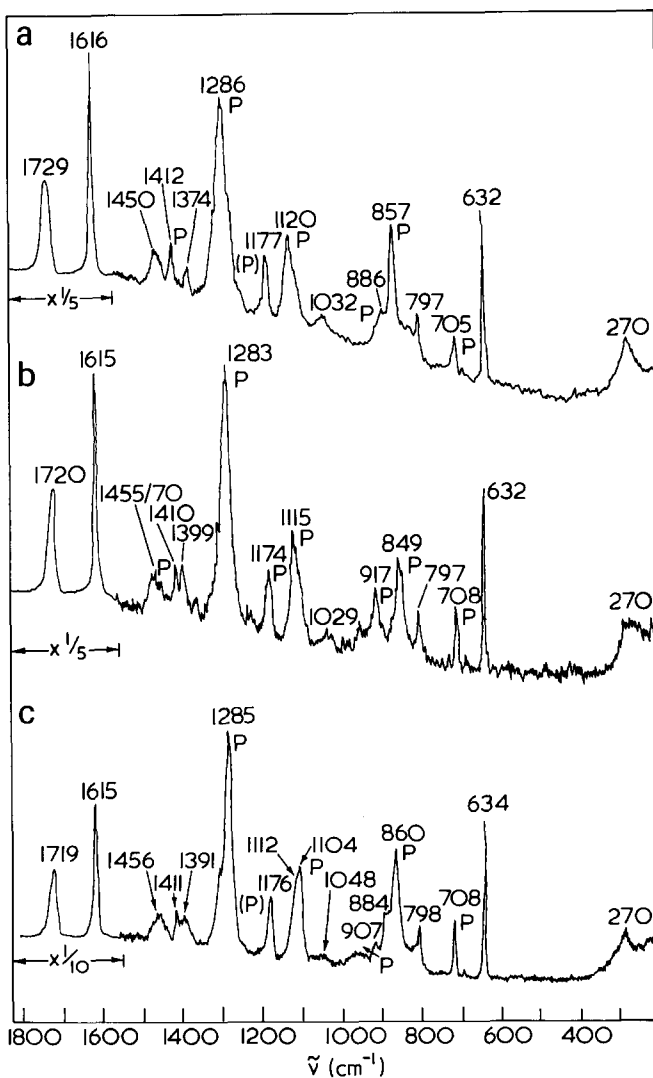


Figure 1 Raman spectra of amorphous isotropic (a) 2GT; (b) 3GT and (c) 4GT

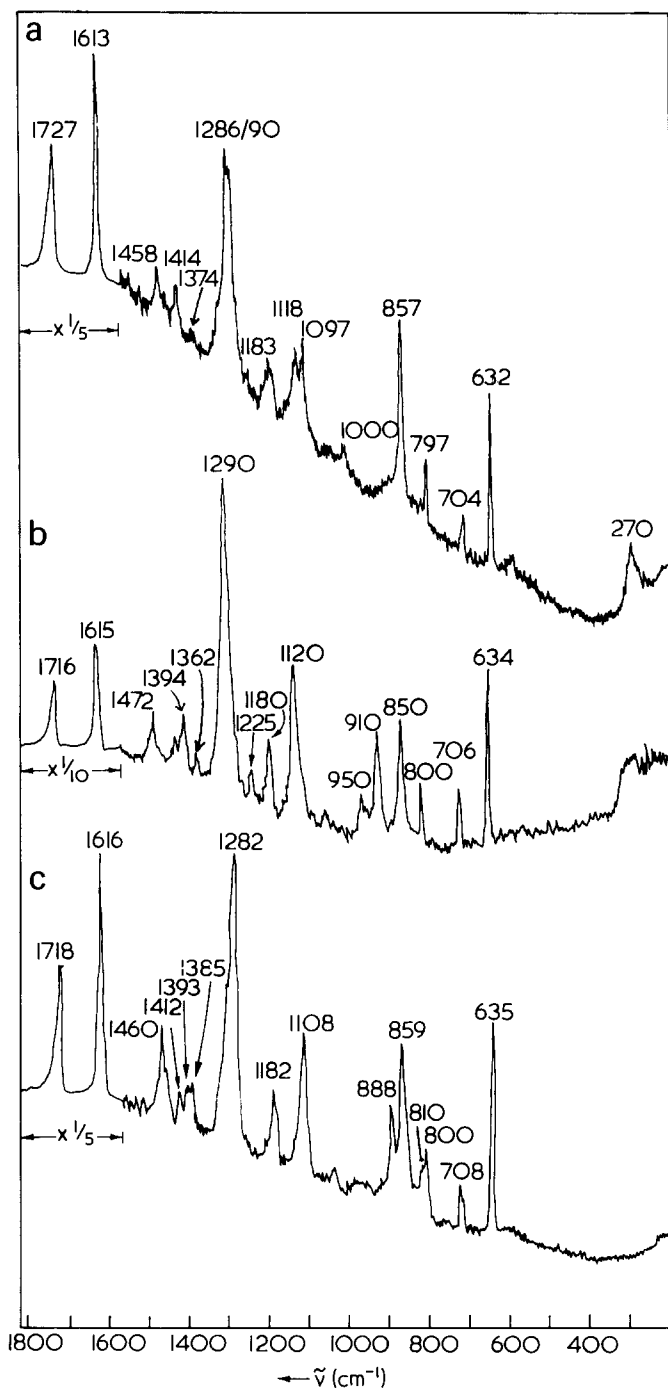
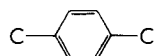


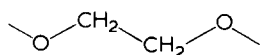
Figure 2 Raman spectra of annealed isotropic (a) 2GT; (b) 3GT and (c) 4GT

isolated chain molecule. Moreover, it is further assumed that the vibrational modes for a chain can be separated into those associated with the *para*-disubstituted benzene ring and those associated with the glycol residue.

In the spirit of these assumptions the vibrational modes of the



part of the chain will be considered as separable from those of the



part of the chain. This bypasses initially the role of the car-

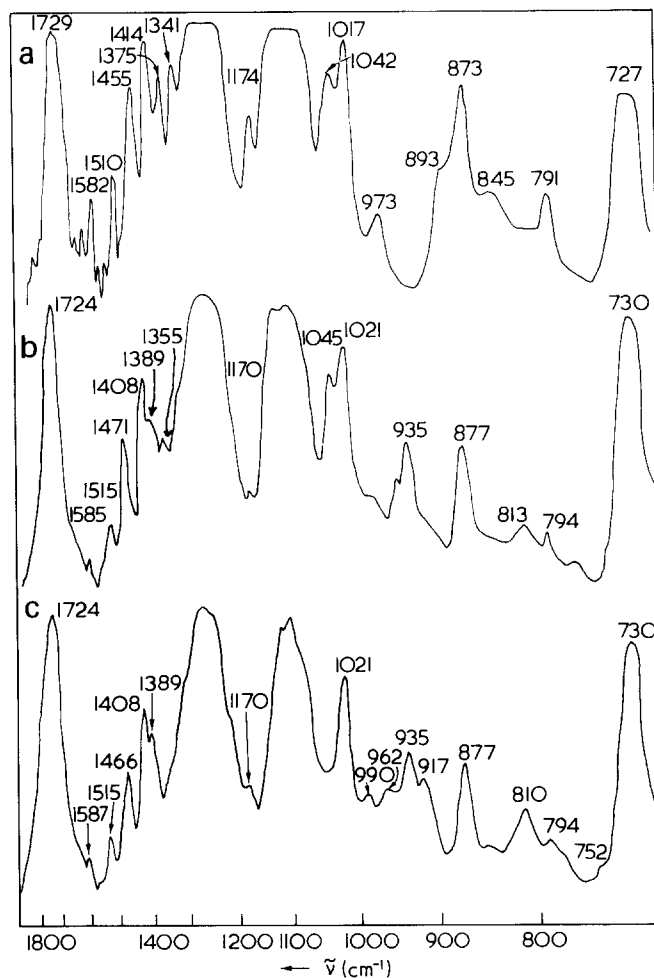


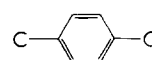
Figure 3 The infra-red spectra of amorphous isotropic (a) 2GT; (b) 3GT and (c) 4GT

bonyl groups, both in affecting the benzenoid group vibrations and vibrations which are associated in this simplified scheme with the glycol residue. Clearly this simple approach will not be entirely satisfactory but it will give a good starting point for the analysis of the spectra.

Consider first the benzenoid group. This is assumed to behave as any *p*-disubstituted benzene ring in which there is identical substitution. As such it belongs to the molecular point group V_h which has the following character table of symmetry species¹⁷:

V_h	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	
A_g	1	1	1	1	1	1	1	1	$\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z, σ_{xy}
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y, σ_{zy}
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x, σ_{yx}
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x

The



group is centro-symmetric, which means that the mutual exclusion rule applies, i.e. a symmetry mode cannot be both Raman and infra-red active, although it may be inactive in

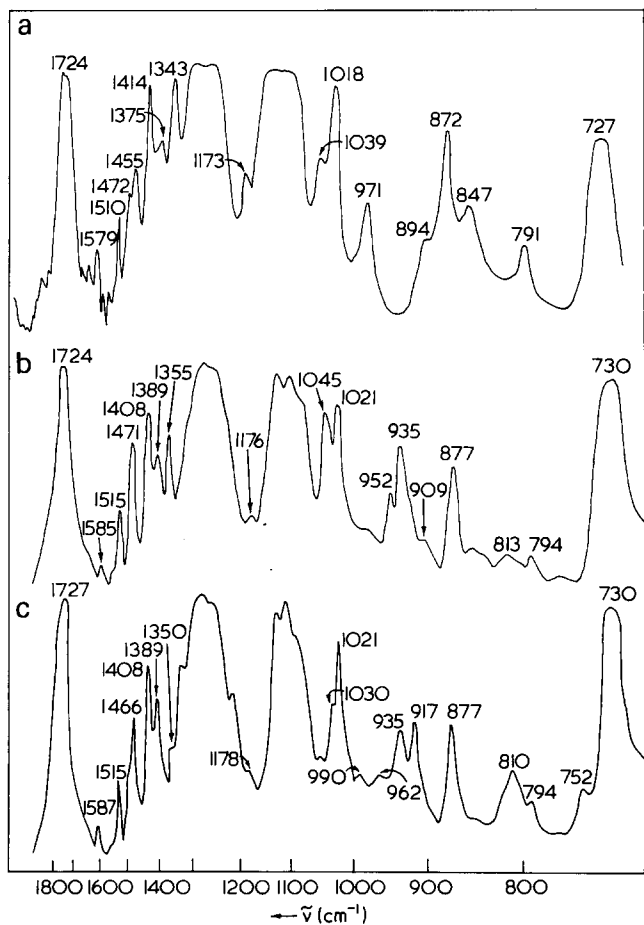


Figure 4 The infra-red spectra of annealed isotropic (a) 2GT; (b) 3GT and (c) 4GT

both. In the V_h point group the A_u species is the only totally inactive one. The A_g vibrations are Raman active and polarized, all B_g vibrations are Raman active and depolarized and B_u vibrations are infra-red active and may have either perpendicular or parallel dichroism with respect to the main symmetry axis (the 1-4 direction).

The above considerations are only true for a planar and centro-symmetric system. The substituent groups in the benzene ring are carbonyl groups and it therefore does seem likely that the whole terephthalate residue is stabilized by conjugation. This means that the internal vibrations of the benzene ring will be affected by changes in the terephthalate residue as a whole. In the crystalline regions of 2GT the terephthalate residue is planar with the carbonyl groups in the *trans* configuration. The infra-red spectrum of 2GT does show some bands which can be assigned to Raman active modes (e.g. 1174 cm^{-1}) which would be infra-red inactive for a centro-symmetric system. These are more intense in the spectrum of amorphous PET and the cyclic trimer, which is consistent with rotations of the carbonyl group away from the symmetrical *trans* configuration. In 3GT and 4GT such effects may well be of importance in the assignments for the crystalline material. For example, it is believed that the 3GT crystal structure shows appreciable rotations of the carbonyl groups away from the planar *trans* configuration for steric reasons.

From experience with 2GT, it seems likely that in all these polymers the changes in the infra-red and Raman spectra due to changes in the glycol residue with crystallization and orientation, are likely to be much more striking

than those due to changes in the terephthalate residue. In the crystalline regions of 2GT the glycol residue takes the extended planar *trans* conformation. This has the point group C_{2h} , and the corresponding character table is:

C_{2h}	E	$C_2(z)$	$\sigma_h(xy)$	i	
A_g	1	1	1	1	R_z
A_u	1	1	-1	-1	T_z
B_g	1	-1	-1	1	R_x, R_y
B_u	1	-1	1	-1	T_x, T_y

Again the mutual exclusion rule is valuable. A_g modes are Raman active and polarized, B_g modes are Raman active

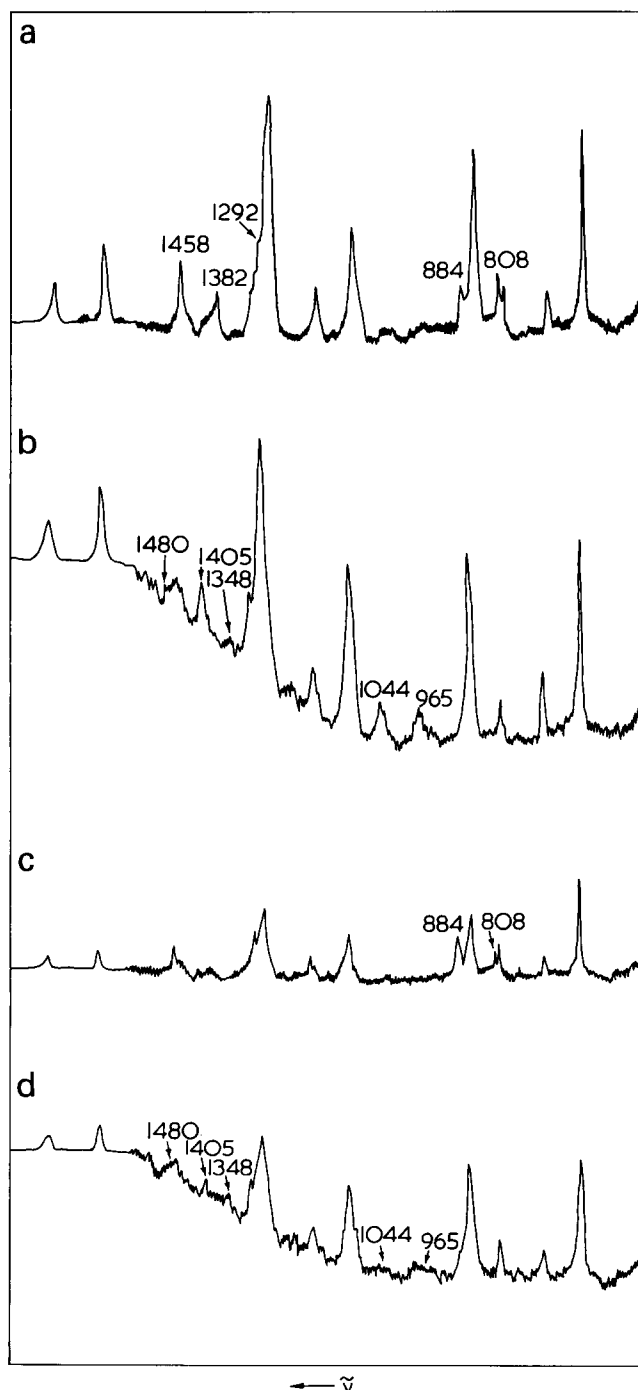


Figure 5 Comparative Raman spectra of oriented 4GT tape: (a) and (c) zero strain; (b) and (d) 15% strain. (a), (b) l_{33} ; (c), (d) $l_{11} (= l_{22})$

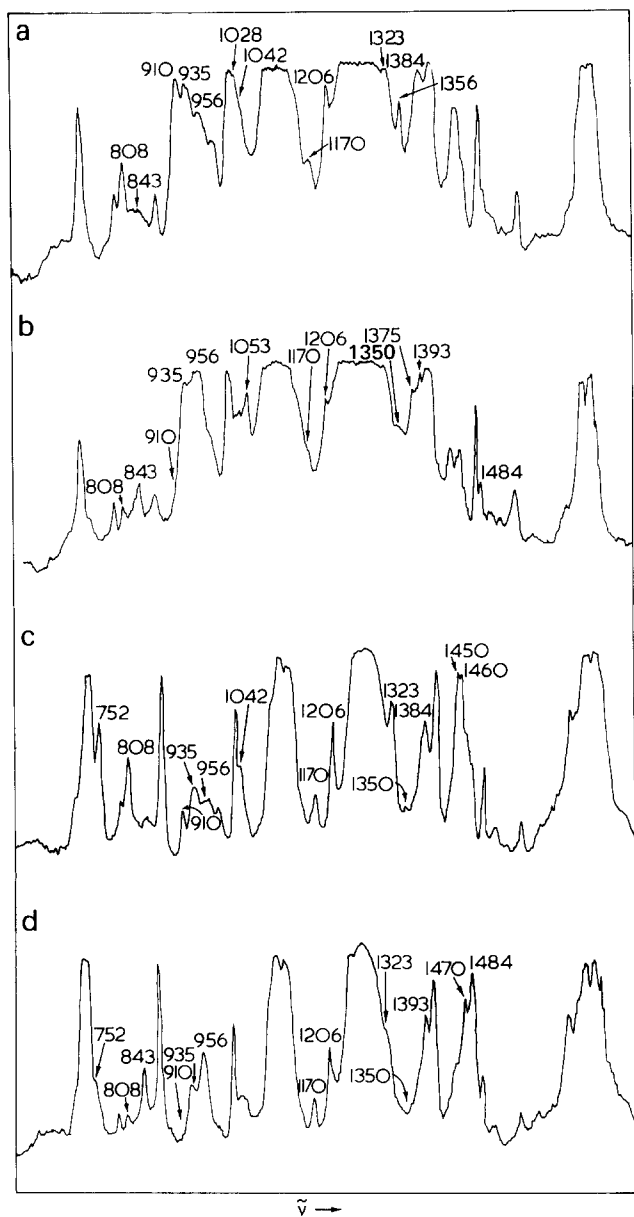


Figure 6 Comparative infra-red spectra of oriented 4GT tape: (a) and (c) zero strain; (b) and (d) 15% strain. (a), (b) \parallel r polarization; (c), (d) \perp r polarization

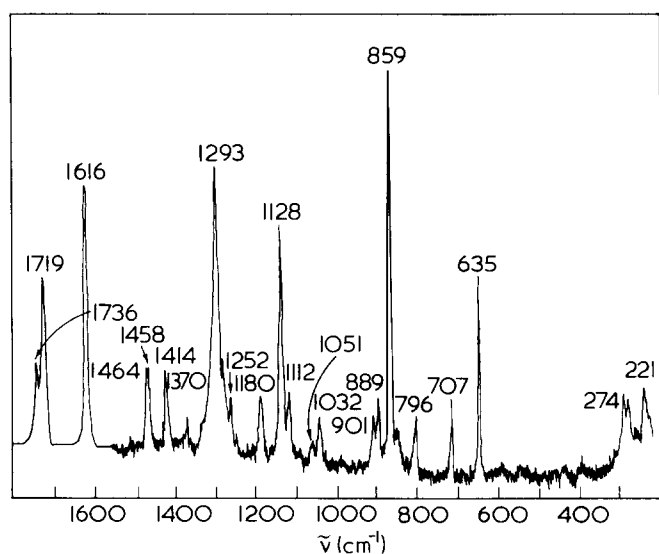


Figure 7 The Raman spectrum of cyclic tris-ethylene terephthalate

and depolarized, whilst the A_u and B_u are infra-red active. This holds only for the *trans* conformation; rotational isomerism which leads to the *gauche* conformation produces a non-centro-symmetric glycol residue and a new set of vibrational modes. These are characteristic of *gauche* conformations in the amorphous regions of the polymer, but also appear in the crystalline cyclic trimer.

In 3GT and 4GT, the possibility of different conformations of the glycol residue is also important, but there are considerable differences in detail. Structural considerations suggest that in 3GT the molecular chain in the crystalline regions is severely contracted compared with the fully extended all *trans* glycol conformation. It has indeed been concluded that the glycol residue in the crystalline regions consists of *gauche* sequences only, so that in this polymer any *trans* sequences must be associated with the amorphous regions, an exactly contrary situation to 2GT.

In 4GT the position is complicated by the fact that there is one stable crystal form for zero stress conditions at room temperature, but an overall extension of an oriented sample to about 15% gives a new crystal form in which the molecular chain is fully extended with an all *trans* glycol residue. The zero stress crystal form, on the other hand, is approximately *gauche-trans-gauche* in the glycol residue which retains its centro-symmetric symmetry. The change in crystal form produces dramatic changes in the infra-red and Raman spectra, which have already been used to monitor the transformation².

Raman spectra

The most striking point about the Raman spectra of the three polymers is their very obvious similarity. This gives considerable support to the assumption that the band assignments can be made on the basis of separating vibrational

modes of the common $\text{C}-\text{C}$ group from those

of the very different glycol residues. Table 1 lists the most prominent Raman bands in the spectra of these polymers, together with the suggested vibrational assignments. It can be seen that the majority of bands are common to all three materials, and these are readily assigned to benzene ring and carbon-oxygen vibrations. Prominent amongst these are the benzene ring modes ~ 1616 , 1410 , 1170 , 857 and 632 cm^{-1} , and the C=O stretching vibration $\sim 1720 \text{ cm}^{-1}$.

Of rather more interest are the regions where there are notable differences between the three polymers. Considering first of all the 3GT spectra in Figure 1, there are at least

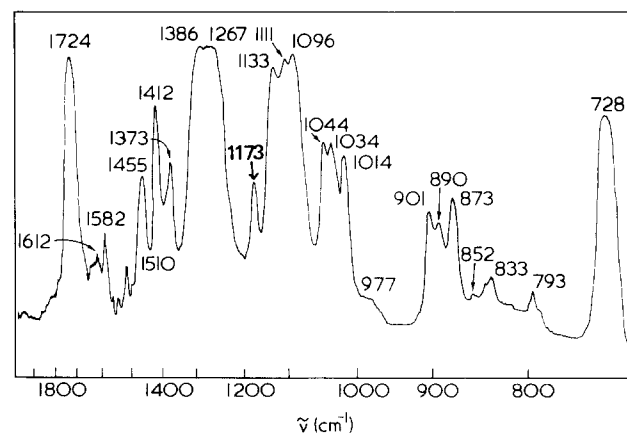


Figure 8 The infra-red spectrum of cyclic tris-ethylene terephthalate

Table 1 Raman band assignments

Amorphous 2GT (cm ⁻¹)	Annealed 2GT (cm ⁻¹)	Amorphous 3GT (cm ⁻¹)	Annealed 3GT (cm ⁻¹)	Amorphous 4GT (cm ⁻¹)	Annealed 4GT (cm ⁻¹)	Assignment
1729	1727	1720	1716	1719	1718	A _g C=O stretch
1616	1613	1615	1615	1615	1616	Ring A _g C—C stretch
~1450	1458	1455–1470	1472	1456	1460	Glycol C—H deformations
1412	1414	1410 ?	V. weak	1411	1412	Ring B _{2u} C—C stretch
1374	1374	1360 ?	1362 ?	—	—	A _g CH ₂ wagging
~1286	~1286–1290	~1283	~1290	1285	~1282	†1 (A _g) + 2(A _g) + 3(B _{3g})
1177	1183	1174	1180	1176	1182	Ring A _g CH in-plane bend
1120*	1118/1097	1115	1120	1112/1104	1108	†3(B _{2u}) or 4(A _g)
1032	~1000	1029	—	~1048 ?	Could be v.w.	Glycol A _g C—C stretch ?
886	—	—	—	884 (w)	888	Glycol A _u CH ₂ rocking
857	857	849	850	860	859	Ring A _g C—C breathing
797	797	797	800	798	800	Ring B _{1g} CH out of plane
705	704	704	706	708	708	Ring B _{2g} C—C—C out of plane bend
632	632	632	634	634	635	Ring B _{3g} C—C—C in plane bend
~270	~270	~270	~270	<270	<270 ?	†5 (A _g) + 6(B _{2g})

† 1 = Ring—carbonyl stretch; 2 = O—C— stretch; 3 = ring CH in-plane bend; 4 = C—O stretch; 5 = ring C—C—C in plane; 6 = ring C—C out of plane.

* Splits on annealing

two regions in which marked departures from 2GT are observed. Both of these regions, moreover, demonstrate sensitivity to crystallization.

The first region is around 800–950 cm⁻¹. The polarized band at 886 cm⁻¹ in the spectrum of amorphous 2GT is replaced in amorphous 3GT by a more intense and complex band at about 917 cm⁻¹, which is also polarized. On annealing 3GT, this band intensifies, its frequency falling to 910 cm⁻¹ and a second band appears at about 950 cm⁻¹. The 2GT band, on the other hand, disappears on annealing and has therefore been assigned to a vibration of a *gauche* conformation of the glycol residue. The precise assignment is given in Table 1. It is reasonable to assign the bands at 910 and 950 cm⁻¹ in 3GT to vibrations of the crystalline glycol residue in this polymer. This is clearly consistent with their increase in intensity on annealing. Moreover the crystalline glycol residue in 3GT is non-centro-symmetric and modes of vibration will be both Raman and infra-red active. It is therefore reasonable to find two bands at 910 and 950 cm⁻¹ rather than one in 2GT. In support of this hypothesis it is to be noted that exactly analogous behaviour is observed in the infra-red spectra of amorphous and annealed 3GT. There are two infra-red bands, ~910 and 950 cm⁻¹, which intensify markedly on annealing.

The second region in which differences occur is around 1400 cm⁻¹. In 2GT a single band is seen at 1412 cm⁻¹ which does not appear to be very sensitive to changes in crystallinity. In 3GT there are two bands; one at 1392 cm⁻¹ which is not greatly affected by annealing, and a band at 1410 cm⁻¹ whose intensity is markedly reduced. This band in 2GT is assigned to a benzene ring C—C stretching mode, and it is unlikely to be a glycol residue band since it is unaffected by glycol deuteration. It is an infra-red active mode only for molecules possessing a centre of symmetry, and this is consistent with its being a weak band in the Raman spectrum of 2GT. The situation is complicated by the fact that bands associated with vibrations of the glycol residue are also to be expected in this region. In 2GT, bands at 1458 and 1374 cm⁻¹ are both assigned to methylene CH deformations. Invoking the same arguments as were adopted for the 910 and 950 cm⁻¹ bands, it would be expected that the non-centro-symmetric nature of the glycol residue in crystalline 3GT will lead to vibrational modes being observed in both Raman and infra-red spectra. It is there-

fore possible that the 1410/1394 doublet in 3GT is predominantly associated with the glycol residue, with some underlying band due to a benzene ring mode. Consistent with this view, bands are observed in the infra-red spectra of 3GT at both frequencies, and the low frequency band (1389 cm⁻¹ in the infra-red spectrum) is significantly enhanced by annealing.

There is a third region in which differences are to be observed between the spectra of 2GT and 3GT. This is around 1100–1200 cm⁻¹. Most strikingly, a band in 2GT at 1120 cm⁻¹ (assigned to an aromatic C—H in plane bending mode) splits on annealing into bands at 1118 cm⁻¹ and 1097 cm⁻¹, respectively. A significant result in this respect is the very close similarity between the amorphous 2GT and that of the cyclic trimer. It appears that the 1097 cm⁻¹ band is to be associated with the planar molecule of the crystalline regions and it has been assigned to an A_g C—O stretching mode. This assignment is confirmed by the reduction in intensity of this band in the infra-red spectrum of 2GT on crystallization. It is notable that the 3GT Raman spectra show only a band at ~1120 cm⁻¹, with perhaps a small shift to higher frequency on annealing. This result is consistent with the view that the terephthalate residue is never planar in 3GT, irrespective of whether the molecular chain is in a crystalline environment or not.

The Raman spectrum of 4GT can be discussed along very similar lines to that of 3GT. Again, many of the benzene ring and carbon—oxygen vibrational modes are straightforward to identify by analogy with 2GT, and these are given in Table 1. Furthermore, the major differences between the spectrum of 4GT and the other polymers is confined to the same three regions. There is however a major complication due to the transformation occurring in the crystal structure when an oriented sample is stretched. This means that it is also desirable to take into consideration the comparison of spectra from oriented samples at zero strain, and at about 15% strain, where most of the crystalline regions have changed to their new form. As indicated in the Introduction, crystallographic studies⁵ indicate that the glycol residue in the unstrained state is close to *gauche-trans-gauche* and changes to the all *trans* sequence on straining. In both cases the crystal structures which have been proposed show a centro-symmetric structure for the glycol residue. The proposed structures also show significant non-planarity in the

Table 2 I.r. band assignments

Amorphous 2GT (cm ⁻¹)	Annealed 2GT (cm ⁻¹)	Amorphous 3GT (cm ⁻¹)	Annealed 3GT (cm ⁻¹)	Amorphous 4GT (cm ⁻¹)	Annealed 4GT (cm ⁻¹)	Assignment
1724	1724	1724	1724	1727	1727	B _U C=O stretch
1582	1579	1585	1585	1587	1587	Ring B _{3g} C-C stretch
1510	1510	1515	1515	1515	1515	Ring B _{1U} C-C stretch
1455*	1472/1455	1471	1471	1466	1466	†1(A _g) + 1(B _U)
1414	1414	1408 (?)	1408	1408	1408	Ring B _{2U} C-C stretch
1375	1375	1389 (?)	1389 (?)	1389	1389	A _g CH ₂ wag
1341	1343	1355	1355	—	1350	B _U CH ₂ wag
1240–1290	1240–1290	1240–1290	1240–1290	1240–1290	Several bands appear	†2(B _U) + 3(B _g) + 3(A _U) + 4(B _{1U}) + 5(B _{2U})
1174	1173	1170 (V.w.)	1176 (w)	1170 (w)	1178 (w)	Ring A _g CH in plane bend
1124	1124	1124	1124	1124	1124	Ring B _{2U} CH in plane bend
1096	1096	1104	1104	1104	1104	B _U C-O stretch
1042	1039	1045	1045	—	1030	Glycol A _g C-C stretch
1017	1018	1021	1021	1021	1021	Ring B _{2U} CH in plane bend
973	971	?	?	990–962	990–962 ?	Vibration of <i>trans</i> glycol segments ^a
893–5	894	—	909 (?)	—	—	A _U CH ₂ Rocking
873	872	877	877	877	877	†6(B _{3U}) and/or 7(B _U) ?
845	847	—	May be present	May be present	?	?
791	791	794	794	794	794	Ring B _{2g} CH out of plane (C ₆ libration)
727	727	730	730	730	730	†8(B _{2U}) and/or 6(B _{3U}) ?

† 1 = CH₂ bend; 2 = O-C stretch; 3 = CH₂ twist; 4 = C-C stretch; 5 = ring C-C-C stretch (Kekule); 6 = ring CH out of plane; 7 = C-O-C deformation; 8 = ring C-C in plane bend

* Splits on annealing

^a Grime and Ward

terephthalate residue, due to rotations of the carbonyl groups from the plane of the benzene ring.

As in 3GT, first consider the region around 700–900 cm⁻¹. All 4GT samples show bands at 632, 708, 800 and 859 cm⁻¹ which are common to 2GT, 3GT and 4GT. Annealed 4GT and the oriented sample of 4GT at zero strain show bands at 808 and 884 cm⁻¹ which are completely absent in the spectrum of the strained sample. It is therefore clear that they are associated with the *gauche-trans-gauche* glycol residue in the unstrained crystal. It is to be noted that a band is present at a similar frequency (886 cm⁻¹) in amorphous 2GT, which disappears on annealing. This band has been assigned to a C-H rocking mode of the *gauche* glycol residue in 2GT. It is therefore very reasonable to assign the two bands in 4GT to C-H rocking vibrations. On stretching, two new bands appear at 1044 and 965 cm⁻¹ which can be assigned to Raman active C-H rocking modes of the all *trans* sequence. This will be discussed in more detail later, when the infra-red spectrum of 4GT is considered.

Marked changes are also observed in the region around 1400 cm⁻¹. Bands at 1458 and 1382 cm⁻¹ in the oriented polymer at zero strain, show dramatic decreases in intensity as the polymer is strained, and new bands appear at 1405 and 1348 cm⁻¹. The spectra are clearly complicated by overlapping bands, but it is reasonable to assign these to underlying benzene ring vibrations, and the bands which change to C-H bending and wagging modes of the glycol residues for the two crystal forms.

Finally there is the region ~1100 cm⁻¹, where bands appear in 2GT and 3GT which appear to relate to the planarity of the terephthalate residue. It is interesting to note that all spectra of 4GT show a single band at 1108 cm⁻¹. This frequency is between the 1097 cm⁻¹ for the planar form of 2GT, and 1120 cm⁻¹ which appeared to be common to amorphous 2GT and crystalline 3GT. It is concluded that this intermediate result for 4GT is consistent with the crystallographic evidence which shows a non-planar terephthalate residue for both crystal forms.

Table 3 Stress-sensitive i.r. bands of drawn 4GT

$\nu(\pm 3 \text{ cm}^{-1})$	Dichroism (π or σ)	Effect of strain (\uparrow or \downarrow)	Possible assignment
1484	σ	\uparrow	X CH ₂ bend, Phase II ^a
1470	σ	\uparrow	X CH ₂ bend, Phase II
1460	σ	\downarrow	X CH ₂ bend, Phase I ^a
1450	σ	\downarrow	X CH ₂ bend, Phase I
1393	π (?)	\uparrow	X CH ₂ wagging, Phase II
1384	π	\downarrow	X CH ₂ wagging, Phase I
1375	π	\uparrow (?)	CH ₂ wagging (A or Phase II)
1350	π	\downarrow	X CH ₂ wagging, Phase I
1323	π (?)	\downarrow	Twisting modes of Phase I and A
1206	—	\downarrow (Slight)	
1170	—	\downarrow (Slight)	
1053	π	\uparrow	X C-C stretch, Phase II
1042	π	\downarrow	X C-C stretch, Phase I
1028	π	\downarrow	
956	π	\uparrow	X CH ₂ rocking, Phase II*
910	π	\downarrow	X CH ₂ rocking, Phase I*
843	σ (?)	\uparrow	X CH ₂ rocking, Phase II
808	—	\downarrow	A CH ₂ rocking
752	σ	\downarrow	X CH ₂ rocking, Phase I

^a X, denotes crystalline; A, amorphous. Phase I is *GTG* form; Phase II is *TTT* form

* The dichroism of this band is not consistent with its assignment

Infra-red spectra

As with the Raman spectra, the first point which is apparent about the infra-red spectra of these three polymers is their great similarity. Again, many of the benzene ring and carbon oxygen vibrations can be assigned. These include the C=O stretching vibration ~1720 cm⁻¹ and benzene ring modes ~1582, 1510, 1410, 1020 and 875 cm⁻¹ (see Table 2). It is notable that the intense band ~1730 cm⁻¹, assigned to C=O stretching, which is a single band in all the Raman spectra, appears as a doublet in the infra-red spectrum of drawn 4GT, and as a complex group of bands in that of drawn 3GT (not shown for reasons of space). This

can be attributed to the non-planar nature of the terephthalate residue in 3GT and 4GT. The absence of any apparent splitting of this band in the infra-red spectra of the isotropic polymers may be, in part, due to the rather low resolving power of the S3A prism spectrometer on which they were obtained.

As in the case of the Raman spectra, it is convenient to discuss the three regions ~ 900 , 1400 and 1100 cm^{-1} where differences are apparent between the spectra of the three polymers. Starting with 3GT, the 900 cm^{-1} region shows a considerable number of bands which do not appear in 2GT. For the crystalline regions of 3GT, three C-H rocking modes can be expected, which because of the non-centro-symmetric glycol residue, can all be both infra-red and Raman active. Indeed, three bands are observed, ~ 952 , 909 and 850 cm^{-1} , which are very appreciably increased in intensity on annealing, and are therefore assigned to C-H rocking modes of the crystalline 3GT. As discussed above, bands which increase in intensity on annealing are observed in the Raman spectrum at 950 and 910 cm^{-1} and as there is an intense benzene ring mode vibration at 850 cm^{-1} in the Raman spectrum this could obscure a band due to a C-H rocking mode. The 3GT infra-red spectrum also shows bands at 935 and 813 cm^{-1} which are present in both the amorphous and the annealed samples. It is likely that these bands are associated with C-H rocking vibrations of the glycol residue in the amorphous regions. In this respect it is interesting to note that there is a similar band at 935 cm^{-1} in the infra-red spectrum of 4GT, which is also present in both unannealed and annealed spectra. A possible assignment would be the C-H rocking mode of a *trans-trans* CH₂ sequence, which does occur in the crystalline regions of either 3GT or 4GT, but cannot occur at all in 2GT, where there is no band at 935 cm^{-1} .

The second region where striking changes occur on crystallization is $\sim 1400 \text{ cm}^{-1}$, with a large increase in the intensity of bands at 1389 and 1355 cm^{-1} assigned to C-H wagging modes and a band at 1471 cm^{-1} assigned to a C-H bending vibration. All these bands are present in the Raman spectrum of annealed 3GT, which is consistent with the absence of a centre of symmetry.

3GT shows an infra-red band at 1045 cm^{-1} which is considered to be analogous to the band at 1042 cm^{-1} in 2GT, which has been assigned to an A_g C-C stretching mode of a *gauche* conformation by many workers. This band in 3GT intensifies on annealing, consistent with the structural knowledge of 3GT, which suggests an all *gauche* sequence in the crystalline regions.

Table 4 Stress-sensitive Raman bands of drawn 4GT

$\nu(\pm 3 \text{ cm}^{-1})$	Effect of strain (\uparrow or \downarrow)	Possible assignment
1480	\uparrow	X CH ₂ bend, Phase II ?
1458	\downarrow	X CH ₂ bend, Phase I
1405	\uparrow	X CH ₂ wagging, Phase II or CH ₂ bend, Phase II
1382	\downarrow	X CH ₂ wagging, Phase I
1348	\uparrow	X CH ₂ wagging, Phase II or X CH ₂ twisting, Phase II ?
1292	\downarrow (?)	X CH ₂ twisting, Phase I ?
1044	\uparrow	X CH ₂ rocking + C-C stretch, Phase II
965	\uparrow	X CH ₂ rocking, Phase II
884	\downarrow	X CH ₂ rocking, Phase I
808	\downarrow	X CH ₂ rocking, Phase I

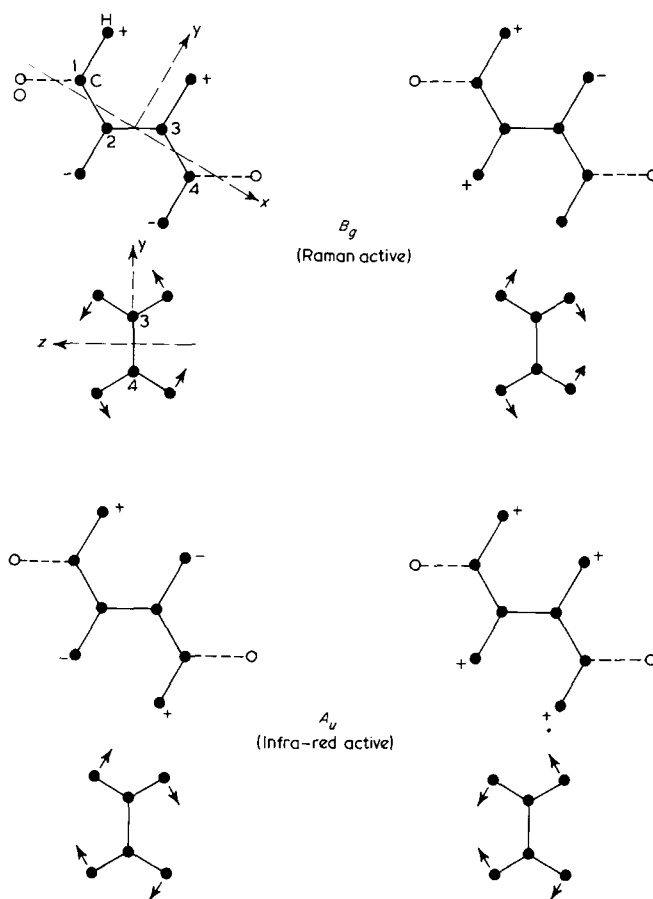


Figure 9 Schematic representation of CH₂ rocking modes in the all *trans* glycol sequence of 4GT: +, denotes motion out of the plane of the paper; -, denotes motion into the plane of the paper

A final point of interest in the infra-red spectrum of 3GT is the surprisingly large intensity of bands at 1616 and 632 cm^{-1} , which are associated with the Raman spectra only in 2GT and 4GT. These bands are the benzene ring mode vibrations 8(a) and 1, respectively¹⁷, and for a centro-symmetric structure i.e. V_h point group would be Raman active only. This comparatively large intensity in the infra-red spectra is further confirmation for the non-centro-symmetric nature of the terephthalate residue in 3GT.

In considering the 4GT infra-red spectrum, we will again start with the 900 cm^{-1} region and a detailed consideration of the C-H rocking modes. Both crystal forms of 4GT are centro-symmetric, and it is convenient to consider first the rocking modes of the all *trans* extended form shown in Figure 9. This illustrates the four C-H rocking modes, two of which are Raman active and two infra-red active. Similar considerations apply to the *gauche-trans-gauche* zero stress crystal form. The key spectra are now those showing the oriented samples of 4GT at zero strain and $\sim 15\%$ strain (Figure 6). Infra-red bands at 917 and 752 cm^{-1} , which are greatly enhanced by annealing (compare with Figures 3 and 4), disappear completely on stretching and new bands appear at 962 and 840 cm^{-1} . The comparable changes in the Raman spectra are the disappearance of bands at 888 and 810 cm^{-1} and the appearance of new bands at 1044 and 965 cm^{-1} . We therefore assign the bands at 917 , 752 cm^{-1} to C-H rocking modes of the *gauche-trans-gauche* sequence and those at 962 and 840 cm^{-1} to the all *trans* sequence.

These assignments do not cover the intense band at 810 cm^{-1} which is not significantly affected by annealing, but

disappears completely on stretching. This band can therefore be associated with the non-crystalline regions of the polymer, and a possible assignment would be to a C-H rocking mode of a *gauche-gauche* CH₂ sequence, which does not occur in either of the two crystal forms. This band will be of particular interest with regard to mechanical properties, as it can be used to monitor changes in the non-crystalline regions when the polymer is stressed. There is also the band at 935 cm⁻¹, which we have discussed above in respect of 3GT, and has tentatively been assigned to the C-H rocking vibration of a *trans-trans* CH₂ sequence. This band is unaffected by annealing and also does not change its intensity markedly on stretching which is at least consistent, if it is associated with an extended *trans-trans* sequence.

As with the Raman spectra, the infra-red spectra of 4GT also show very appreciable changes in the region around 1400 cm⁻¹. Annealing intensifies bands near 1350, 1383 and 1450/60 cm⁻¹. These are also present in the spectrum of the oriented polymer under zero stress and are assigned to C-H bending and wagging modes of the *gauche-trans-gauche* crystal sequence. When the polymer is under strain these bands are replaced by bands ~ 1375, 1393, 1470 and 1484 cm⁻¹, which are therefore assigned to the bending and wagging modes of the all *trans* crystal unit.

The 1100 cm⁻¹ region does not show any significant variation, but there are further marked changes around 1000 cm⁻¹. A band which is intensified by annealing, but disappears on stretching, occurs near 1030 cm⁻¹. By analogy to amorphous 2GT and annealed 3GT, it is assumed that this band can be assigned to an A_g C-C stretching mode of a *gauche* sequence in the crystal. A new band is seen at 1053 cm⁻¹ which could be due to the corresponding vibration for an all *trans* sequence.

CONCLUSIONS

- (1) Many bands in the infra-red and Raman spectra of 2GT, 3GT and 4GT can be readily assigned to internal modes of vibration of the para-disubstituted benzene ring and are common to all three polymers.
- (2) The differences between the spectra of the three polymers can be separated into two aspects.

(a) Rotational isomerism in the glycol residues, either due to changes on crystallization or, in oriented samples of 4GT, to a change in crystal structure under stress.

(b) Differences in the degree of planarity of the terephthalate residue, due to rotation of the carbonyl groups about the carbonyl-phenylene bond.

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