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Deformation studies of thermotropic aromatic copolyesters using NIR Raman spectroscopy

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Abstract

Near infrared (NIR) Raman spectroscopy has been used to investigate the deformation behaviour of highly oriented fibres and tapes made from thermotropic aromatic copolyesters. It has been found that a number of Raman bands of thermotropic aromatic copolyesters show linear shifts towards lower wavenumbers with stress and strain following tensile deformation. The strain and stress dependencies of the 1600 cm^{-1} band due to stretching of the *p*-phenyl ring, have been studied in detail and discussed in relation to values reported for high-performance aromatic polymer fibres. The behaviour has been discussed in terms of the microstructure of the thermotropic aromatic copolyester materials compared with that of other highly-oriented aromatic polymer fibres. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic aromatic copolyesters; Near IR Raman spectroscopy; Deformation

1. Introduction

There has been considerable interest generated in the past 20 years in the synthesis and characterization of stiff, rod-like polymers, which usually contain rigid aromatic rings on the backbone of molecules. Their tendency to form nematic liquid crystalline phases in solution or in the melt provides an efficient means of achieving high degree of molecular alignment essential for making high stiffness materials. These stiff, rod-like molecules can be processed into high modulus fibres such as aramid, aromatic hetrocyclic rigid-rod PBT and PBO fibres from liquid crystalline solutions by using appropriate solvents (lyotropic type) [1]. Some molecules can also be processed directly from liquid crystalline melt using conventional methods such as melt-spinning, extrusion and injection-moulding, by reducing the transition temperatures through random copolymerisation of aromatic polyesters (thermotropic type) [2]. These thermotropic aromatic copolyesters not only possess easy processibility and dimensional stability, but also display excellent thermal and mechanical properties. This paper is concerned principally with thermotropic liquid crystalline polymers made from aromatic copolyesters.

Raman spectroscopy has been used successfully in the previous studies as a non-destructive technique to follow molecular deformation processes of high-performance polymer fibres such as aromatic hetrocyclic rigid-rod PBT [3] and PBO fibres [4], stiff-chain aromatic polyamide fibres such as Kevlar and Twaron [5–7], and conventional aromatic polyester fibres (PET) [8]. It has been shown that the position of the Raman band at around 1600 cm^{-1} due to vibrational mode of the aromatic rings, shifts almost linearly with stress or strain and the value of strain-induced band shift is controlled by the fibre modulus. However, the extension of the same technique (using dispersive Raman spectroscopy with a visible laser sources) to the thermotropic liquid crystalline polymers has been difficult due to strong fluorescence interference in the dispersive Raman spectrum. Most of the published work on thermotropic liquid crystalline polymers has been limited to the use of FT Raman spectroscopy [9,10]. The availability of near-infrared (NIR) diode laser for dispersive Raman spectroscopy has led to a dramatic improvement in the Raman spectra of fluorescent materials including thermotropic liquid crystalline polymers. This work demonstrates that it is possible to study thermotropic liquid crystalline polymers using a dispersive Raman system equipped with a near infrared laser source. It is shown that the deformation behaviour of highly oriented fibres and tapes of two different thermotropic copolyesters can be investigated in the manner similar to the previous work on the aromatic polymer fibres.

2. Experimental

Two different thermotropic liquid crystalline copolyesters

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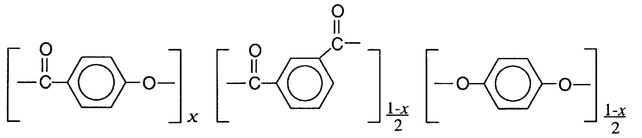
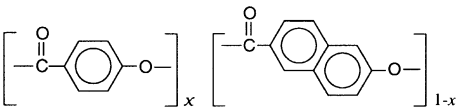
were used in the present study. One was prepared from random copolymerisation of *p*-hydroxybenzoic acid (HBA) with each of isophthalic acid (IA) and hydroquinone (HQ), and has the following chemical repeat unit



where x is the mole fraction of the monomer and is about 0.35. The copolyester was developed by ICI and was supplied in a tape form with a thickness of about 30 μm. The other copolyester was based on the random copolymerisation of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), which has the following chemical structure



where x is the mole fraction of monomer and is thought to be 0.73. The copolyester was developed and manufactured by the Celanese Research Company and supplied as melt-spun fibres. The diameter of individual fibres was determined using an optical microscope with an Image Analyser system to range between 21 and 25 μm. Assuming that the fibre cross-section is approximately circular, the fibre cross-sectional area can be determined from the fibre diameter for the calculation of stress.

Raman spectra of both thermotropic copolyesters were obtained using Renishaw 1000 system and the 780 nm line of a 25 mW diode laser. The incident laser beam was focused on the sample to a ~2 μm diameter spot using a × 50 objective lens, with the polarisation direction parallel to the orientation direction of the tapes and fibre axis. A highly-sensitive Peltier-cooled charge coupled device (CCD) detector was used to collect the Raman spectra. The Raman spectra were curve-fitted using a Lorentzian function to determine the band positions.

The Raman deformation study on the liquid crystalline polyester tapes and fibres was carried out using a small straining rig, which fitted directly onto the microscope stage. The long strips ~1 mm wide were cut from the tapes (along the orientation direction) and then individual strips were fixed onto the block of the straining rig using aluminium foil tabs and cyanoacrylate adhesive. A gauge length of about 20 mm was used for both fibres and tapes and the samples were deformed in steps of about 0.05% by displacing the block using a micrometer attached to the straining rig. For the stressing experiment, the single fibres and strips from tapes were attached to the metal block as in the straining test with one end of the rig was connected to a load cell. When the sample was stretched, the load on the sample could be read from a digital load indicator to an accuracy of ±0.01 g.

3. Results and discussion

3.1. Raman spectra

It has been found in the past that it is virtually impossible to acquire Raman spectra from thermotropic liquid crystalline copolyesters using visible He–Ne laser source. The materials fluoresce so severely that the scattering produced saturates the detector even with the lowest laser intensity (99% filter) and shortest collection time (1 s). This may be due largely to the presence of small molecules and impurities inherited from the polymerisation stage, and probably some degradation of the materials during processing. In the present study well-defined and intense Raman spectra could be readily obtained from the two copolyesters, using the NIR diode laser. Raman spectra from both HBA/HNA fibres and HBA/IA/HQ tapes are presented in Fig. 1. The spectrum for the HBA/HNA fibre is very similar to that reported previously by Hendra et al. [10] on the identical copolyester

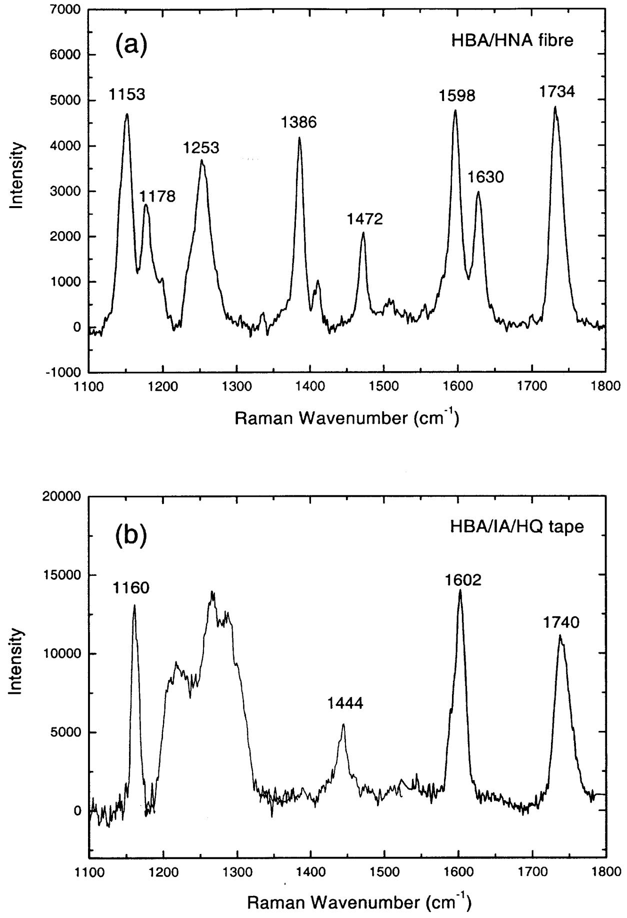


Fig. 1. Raman spectra of thermotropic copolyesters (a) HBA/HNA fibre and (b) HBA/IA/HQ tape, obtained between 1100 and 1800 cm^{-1}, using the 780 nm line of a diode laser.

system using the FT Raman spectroscopy. It can be seen from Fig. 1(a) that there are about eight principal Raman bands observed between 1100 and 1800 cm^{-1}. These bands appear at approximately 1153, 1178, 1253, 1386, 1472, 1598, 1630 and 1734 cm^{-1}, respectively. Similar Raman bands at around 1160, 1602 and 1740 cm^{-1} have also been seen in the spectrum of HBA/IA/HQ tapes. This suggests that these bands may have the same band assignments, considering that both copolyesters consist of the same monomer HBA. Although it is not possible to assign most of the bands to their corresponding molecular vibration modes due to lack of Raman studies on the model materials and theoretical calculations. It is likely that the 1600 cm^{-1} band is due mainly to stretching of the *p*-phenyl ring and the 1730 cm^{-1} band is apparently attributed to stretching of the carbonyl group (C=O), using the analogy of similarly-assigned bands in aromatic polyester (PET) fibres [8]. The exact position of the 1600 and 1730 cm^{-1} bands is different in two copolyesters as shown in Fig. 1, due to the differences in the chemical environment of these bands and the different microstructure of the materials.

The effect of deformation on the whole Raman spectrum of HBA/HNA fibre is shown in Fig. 2. It can be seen that most of the bands in the region from 1100 to 1800 cm^{-1} shift significantly towards lower wavenumbers under a tensile stress of 1.9 GPa. The effect of stress and strain on the Raman band position for each band has been investigated and it is found that the band shifts appear to be linear functions of stress and strain. Table 1 demonstrates clearly that different Raman bands have different stress dependences, due to inherently differences in the band shift rates and local stress distributions on different bonds of the molecular chain. The 1730 cm^{-1} band for the carbonyl side group is the least sensitive to the tensile deformation on the fibre, as shown by the small stress-induced band shift in Table 1. The 1253, 1600 and 1630 cm^{-1} bands, associated with stretching of the backbone on the molecule chains appear to be the most stress-sensitive bands, showing largest band shifts. The behaviour of the HBA/HNA fibres should be contrasted with that of HBA/IA/HQ tapes that showed only relatively small band shifts during tensile deformation, since only 0.2 GPa could be applied to the tape before failure took place.

Table 1
Raman band position and corresponding stress and strain dependencies for the highly oriented fibres of HBA/HNA copolyester, and estimated fibre modulus

Band position ν (cm^{-1})	Strain dependence $d\Delta\nu/d\epsilon$ (cm^{-1}/%)	Stress dependence $d\Delta\nu/d\sigma$ (cm^{-1}/GPa)	Modulus[a] (GPa)
1734	−1.2 ± 0.2	−1.4 ± 0.2	86
1630	−4.1 ± 0.2	−4.6 ± 0.2	89
1598	−3.3 ± 0.2	−3.9 ± 0.2	85
1472	−1.8 ± 0.2	−2.1 ± 0.2	86
1386	−2.7 ± 0.2	−3.0 ± 0.2	90
1253	−5.5 ± 0.4	−6.2 ± 0.2	89
1178	−2.4 ± 0.3	−2.8 ± 0.2	86
1153	−2.3 ± 0.5	−2.5 ± 0.4	92

[a] $E = \frac{d\Delta\nu/d\epsilon}{d\Delta\nu/d\sigma}$

This present study is concerned primarily with the 1600 cm^{-1} band due to stretching of the *p*-phenyl ring, because this band appears in all the aromatic polymer fibres [7]. In the following sections, the deformation process in both of the thermotropic aromatic copolyesters will be studied in detail using this ~1600 cm^{-1} band and the results will be compared to the behaviour of the aromatic polymer fibres investigated previously [3–8].

3.2. The effect of tensile deformation on the 1600 cm^{-1} band

Fig. 3 shows the spectra for the HBA/HNA fibres in the range of 1575–1650 cm^{1} exhibiting the 1598 cm^{-1} band both undeformed and at a tensile strain of 2.0% prior to fibre failure. It can be seen from the figure that the 1598 cm^{-1} band is very sensitive to deformation and the tensile strain results in a substantial band shift towards lower wavenumber. The position of the 1598 cm^{-1} band

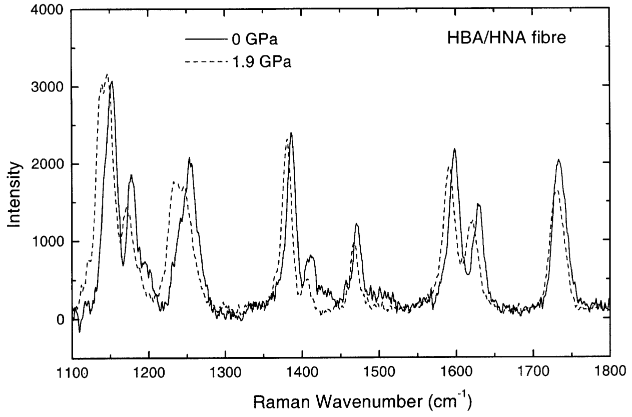


Fig. 2. Raman spectra for the HBA/HNA fibres, obtained in the region between 1100 and 1800 cm^{-1}, subjected to a tensile stress of 1.9 GPa.

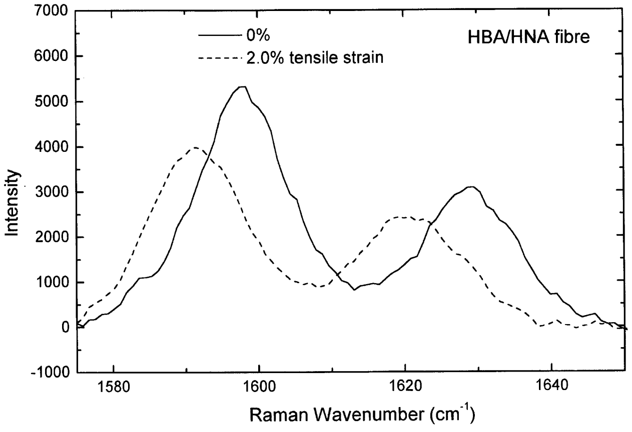


Fig. 3. Raman spectra of the 1600 cm^{-1} band for the HBA/HNA fibres, obtained at 0 and 2.0% tensile strain, respectively.

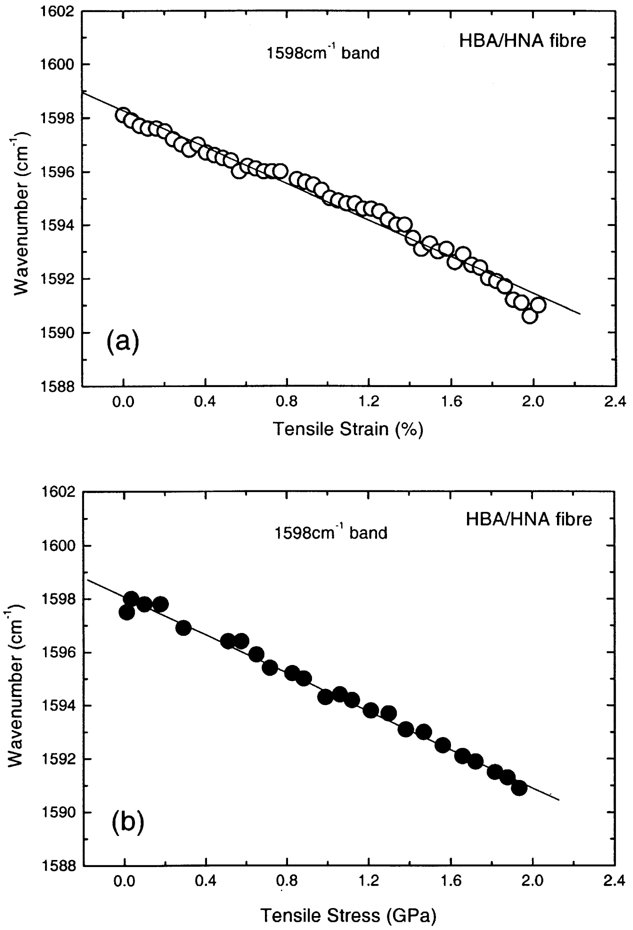


Fig. 4. The dependence of the position of the 1600cm^{-1} band for the HBA/HNA fibres upon (a) tensile strain, (b) tensile stress.

as a function of tensile strain for the HBA/HNA fibres is shown in Fig. 4(a). The response of band shift to the tensile strain appears to be linear up to fibre failure and the slope of the line in the figure is found to be around −3.3 ± 0.2 cm^{-1}/% strain. The dependence of the position of the 1598 cm^{-1} band upon stress for the HBA/HNA fibres is shown in Fig. 4(b). It is found that the band position also shows a linear downshift with stress and the value of stress-induced band shift from the slope of the line is −3.9 ± 0.2 cm^{-1}/GPa.

Fig. 5 presents the spectra for the HBA/IA/HQ tapes in the range of 1580–1630 cm^{-1}, with the 1602 cm^{-1} band both undeformed and at a tensile strain of 1.4%, at which point the sample tended to fibrillate along the orientation direction. It is shown that the 1602 cm^{-1} band also shifts towards lower wavenumber under tensile deformation. The dependence of the position of the 1602 cm^{-1} band upon tensile strain for the HBA/IA/HQ tapes can be observed from Fig. 6(a). The band shift is found to be linearly proportional to the strain, with the value of strain-induced band shift of about −1.0 ± 0.4 cm^{-1}/% strain. The position of the 1602 cm^{-1} band as a function of tensile stress for the HBA/IA/HQ tapes is shown in Fig. 6(b). The band shift again shows a linear decrease with stress and the stress-induced band shift from slope of the line is −4.1 ± 0.6 cm^{-1}/GPa. This indicates that there is still significant axial molecular stressing during deformation of HBA/IA/HQ tapes, although only a small shift of ~1 cm^{-1} is observed up to failure.

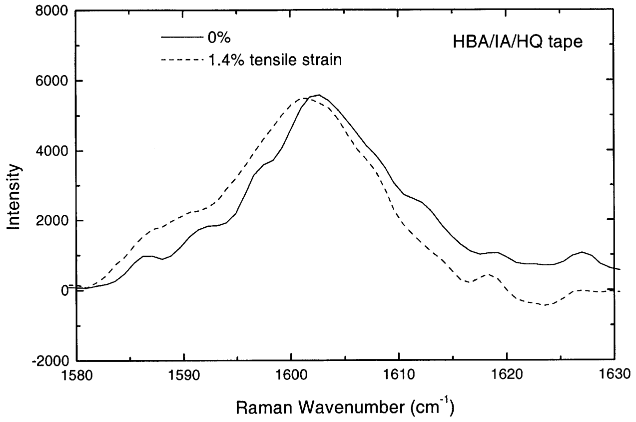


Fig. 5. Raman spectra of the 1602 cm^{-1} band for the HBA/IA/HQ tapes obtained at 0 and 1.4% tensile strain, respectively.

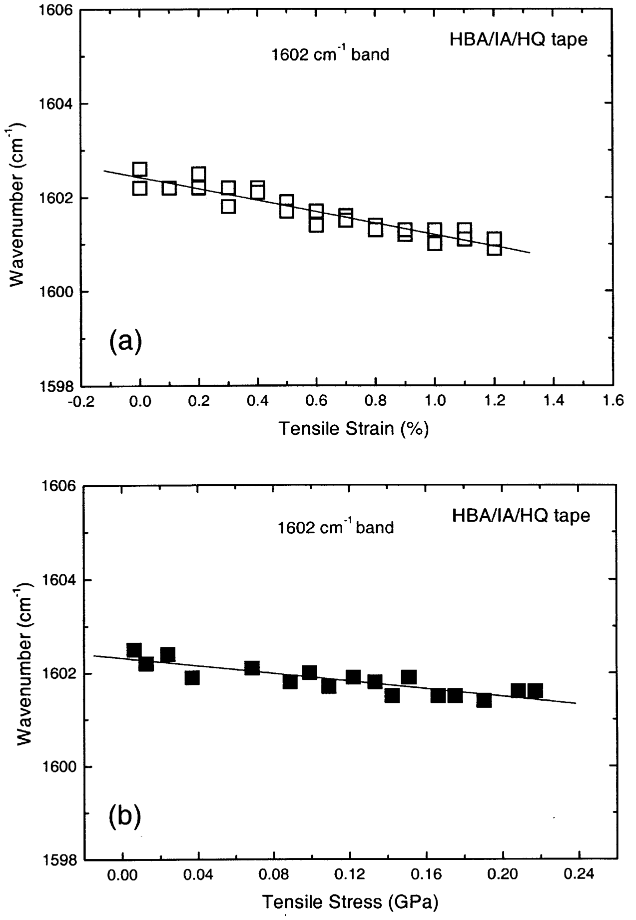


Fig. 6. The dependence of the position of the 1602 cm^{-1} band for the HBA/IA/HQ tapes upon (a) tensile strain, (b) tensile stress.

An unusual aspect of the deformation in these thermotropic copolyesters is that the band shapes remain, to a first approximation, unchanged with applied stress or strain (see Figs. 3 and 5). This behaviour is rather different from that reported for other aromatic polymer fibres such as aramid and PET fibres, for which most of the bands broaden significantly with stress or strain [7]. Such broadening has been interpreted in terms of local distributions of stress on the molecules in the fibres. It appears, therefore, that there may be a more uniform stress distribution on the molecular chains in the thermotropic polyester fibres during tensile deformation, although an explanation for this in terms of fibre microstructure remains unclear. This is an area that could benefit from further investigation as it may give a further insight into the mechanisms of molecular deformation in polymer fibres.

3.3. The effect of microstructure on the band shifts

It has been demonstrated [6,7,11] that the effect of microstructure upon the mechanical behaviour of highly oriented polymer fibres or tapes can be interpreted in terms of an aggregate model. The highly oriented fibre or tape can be assumed as an aggregate of a series of anisotropic units with a uniform orientation distribution, which are subjected to a uniform stress throughout the aggregate along the orientation axis. Then the macroscopic modulus can be simply expressed by the following equation [11]

$$\frac{1}{E} = \frac{1}{E_c} + \frac{\langle \sin^2\theta \rangle}{G} \tag{1}$$

where E the macroscopic Young's modulus, E_c the average chain modulus, G the shear modulus and $\langle \sin^2\theta \rangle$ the mean value of orientation over the chains in the units about orientation axis. This indicates that tensile deformation in highly-oriented fibres and tapes takes place by a combination of crystal stretching (first term) and crystal rotation (second term). The Raman band shift is a clear indication of the levels of axial stressing on the molecular chains hence the Raman band shift reflects only chain stretching. The Raman band shift should, therefore, correlate directly with stress rather than overall strain, which can be dominated by chain rotation. It has been found that the strain-induced shift of the $\sim$1600 cm^{-1} Raman band is around 3.3 cm^{-1}/% strain for the HBA/HNA fibres with a modulus of 65 GPa, compared to only $\sim$1.0 cm^{-1}/% strain for the HBA/IA/HQ tapes with a modulus of 15 GPa. The reason why the strain-induced band shift increases with fibre modulus can be easily explained by the above equation. It is evident that the molecular chains are subjected to higher stresses in the higher modulus materials than those in the lower modulus ones, at the same level of strain. Thus a higher level of chain stretching, i.e. a larger band shift would be expected in the higher modulus material. It also explains that the difference between the macroscopic Young's modulus of highly oriented fibres and tapes arises from the degree of molecular orientation. When molecular chain alignment is imperfect, the application of tensile stress can generate a shear stress parallel to the chain axis. Because the shear modulus is very low, such a small shear stress can result in considerable contribution to the overall strain and, thus, a significant reduction in macroscopic modulus. The X-ray diffraction patterns from both HBA/HNA fibres and HBA/IA/HQ tapes confirm that the molecular orientation in the HBA/HNA fibres is much higher than that in the HBA/IA/HQ tapes [12].

The results in Figs. 4 and 6 show that the stress-induced band shift of the $\sim$1600 cm^{-1} band has the same value of approximately -4.0 cm^{-1}/GPa for both HBA/HNA fibres and HBA/IA/HQ tapes made of thermotropic aromatic copolyesters. This value is also similar to that observed by Yeh and Young [7] for a number of aromatic polymer fibres including rigid-rod PBT and PBO fibres, aramid to PET fibres. Previous studies [13,14] have shown that thermotropic random copolyesters are mainly two-dimensionally crystalline with the molecular chains packing parallel to each other but lack register in the longitudinal chain direction. The molecular packing and ordering of these thermotropic copolyesters are distinctly different from those of crystalline polymer fibres such as aramids. Nevertheless it appears that for all the aromatic polymers the stresses experienced by the stretching mode of *p*-phenyl ring on the molecular chains are the same under the same macroscopic stress, regardless of differences in the chemical structure, modulus, and morphology (crystalline or liquid crystalline)—a consequence of the series aggregate model [11].

Since the stress-induced band shift for the $\sim$1600 cm^{-1} band due to stretching of the *p*-phenyl ring, is a constant for all the aromatic polymer fibres and tapes, it can be expressed as follows,

$$\frac{\mathrm{d}\Delta\nu}{\mathrm{d}\sigma} = \alpha \tag{2}$$

where α is about -4.0 cm^{-1}/GPa. The strain-induced band shift can be described as

$$\frac{\mathrm{d}\Delta\nu}{\mathrm{d}\epsilon} = \frac{\mathrm{d}\Delta\nu}{\mathrm{d}\sigma} \times \frac{\mathrm{d}\sigma}{\mathrm{d}\epsilon} \tag{3}$$

$\mathrm{d}\sigma/\mathrm{d}\epsilon$ equals the macroscopic Young's modulus E, and $(\mathrm{d}\Delta\nu/\mathrm{d}\epsilon)$ can, therefore, be rewritten as

$$\frac{\mathrm{d}\Delta\nu}{\mathrm{d}\epsilon} = \alpha \times E \tag{4}$$

Hence the value of strain-induced band shift is proportional to the macroscopic Young's modulus for the aromatic polymer fibres and tapes. This behaviour has been examined and confirmed by a series of aramid, PBO, and PET fibres with different modulus [7]. This allows us to determine the macroscopic Young's modulus of an aromatic polymer directly from the strain-induced band shift of the $\sim$1600 cm^{-1} band. The tensile moduli estimated from strain-induced band shifts are about 85 GPa for the HBA/HNA copolyester fibres and 25 GPa for the HBA/IA/HQ copolyester tapes, which both are significantly higher than the Young's modulus values of 65 GPa [14] and 15 GPa [12,15] measured for the HBA/HNA fibres and HBA/IA/HQ tapes. The errors from measurements of cross-sectional area and linear fitting for determining the Young's modulus and the strain-induced band shift are less than 10%, and can not account for such large differences in the modulus. What needs to be explained, therefore is why the modulus estimated from the strain-induced band shifts by Raman is different from macroscopic Young's modulus determined from mechanical testing.

This discrepancy in the fibre modulus indicates that a skin–core effect may be present in the thermotropic copolyester fibres. Similar behaviour has also been observed in the aramid fibres [6]. Since the penetration depth of the laser beam is less than 2 μm into the fibre surface, it is clear that the Raman measurements are concerned only with deformation of the fibre skin rather than the whole fibre. The Young's modulus measured from mechanical testing is a property of the whole fibre, while the modulus deduced from the strain-induced band shifts reflects only the modulus in the skin region of the fibre. This value can be the same as the measured Young's modulus only when the fibres have a uniform structure. The result of higher modulus in the skin region indicates that the fibre structure is not uniform and there might be variation of orientation across the fibre cross-section. Jaffe and Sawyer [16] observed the skin–core difference, with a more highly oriented skin than core on extruded rod made from identical HBA/HNA copolyesters. It would be interesting to correlate the Raman data with the orientation measurements from SAD patterns using transmission electron microscopy or micro X-ray techniques. This will be the subject of a further investigation.

The skin–core difference or variation in orientation may also present in the HBA/IA/HQ tapes since the strain-induced band shifts were measured mainly from the strips cut from edge of the 5 mm wide tape. Variation in molecular orientation with positions in the HBA/IA/HQ moulding sections has been observed from micro X-ray diffractions [15]. Since Raman microscopy can detect signal from an area of only 2 μm in diameter, the changes in Raman band positions, at the same level of overall strain, could be mapped out to show the local stress distribution in the tapes. Fig. 7 shows the shifts in the position of the 1602 cm^{-1} band as a function of strain on the tape, obtained at the centre and the edge of the tape, respectively. It can be seen that the strain-induced band shifts are significantly larger at the edge of the tape, with the value up to -1.4 cm^{-1}/% strain, compared to only about -0.6 cm^{-1}/% strain at the centre of the tape. Since the strain-induced band shift is proportional to the Young's modulus [Eq. (4)], this indicates that the modulus is higher at the edge of the tape than that at the centre of the tape. The response of band shift to the same level of strain, i.e. local stress distribution, at various positions from centre to the edge of the tape is shown in Fig. 8. Using the relationship described in Eq. (4), the variation of modulus with the position from centre to the edge of the tape is estimated from the strain induced band shifts (in Fig. 8), and is shown in Fig. 9.

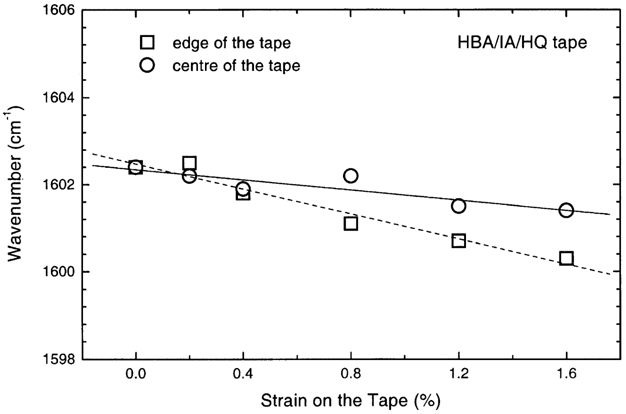


Fig. 7. The position of the 1602 cm^{-1} band as a function of strain on the tape, observed at centre and edge of the HBA/IA/HQ tape, respectively.

It has been shown [6,11] that the correlation between degree of molecular orientation and macroscopic modulus can be described quantitatively by an aggregate model under the assumption of uniform stress [as Eq. (1)]. However, this is only the case when the fibres have a uniform structure. The variation of modulus shown in Fig. 9 indicates that the microstructure of the tape is not uniform. Therefore the mechanical modelling by Blundell et al. [15] is used here to explain the mechanical behaviour of the tape. It is first assumed that the whole tape consists of parallel-aligned layers, each layer containing the units with the uniform average orientation, all which are under the assumption of uniform stress. Then the whole tape is considered as a laminate of layers under the assumption of uniform strain.

Thus, the average modulus from the tape can be estimated

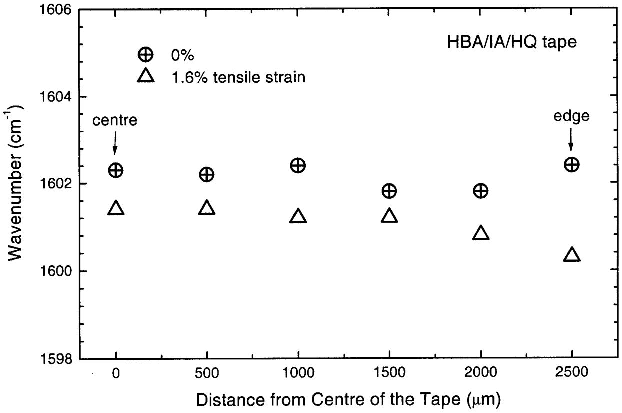


Fig. 8. The position of the 1602 cm^{-1} band as a function of distance from centre to the edge of the tape, with the tape at 0 and 1.6% tensile strain.

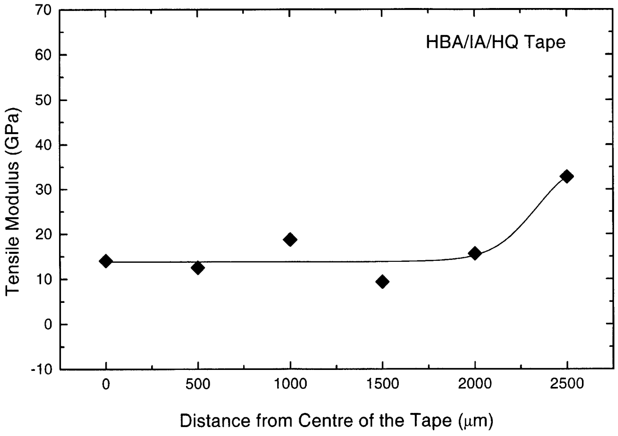


Fig. 9. The variation of modulus (derived from Fig. 8) with distance from centre to the edge of the tape.

from the following relationship

$$E = \frac{\int_0^{w_0} E(w)\,\mathrm{d}w}{\int_0^{w_0} \mathrm{d}w} \qquad (5)$$

where w_0 is half the width of the tape (~2500 μm) from centre to the edge of the tape assuming the tape having central symmetry, $E(w)$ is the variation of modulus with the distance from centre to the edge of the tape as shown in Fig. 9. The predicted modulus for the tape is about 16 GPa, which is in excellent agreement with the experimental value of 15 GPa.

4. Conclusions

This present study shows that well-defined intense Raman spectra could be obtained from highly oriented fibres and tapes made from thermotropic aromatic copolyesters using the 780 nm line of NIR diode laser source. It has been found that the ~1600 cm^{-1} band due to stretching of the *p*-phenyl ring, shifts linearly with both stress and strain for the HBA/HNA fibres and HBA/IA/HQ tapes. The results also show that the strain-induced band shift increases with modulus, with a value of around $-3.3\ \mathrm{cm}^{-1}/\%$ strain for the high modulus fibres (65 GPa), but only about $-1.0\ \mathrm{cm}^{-1}/\%$ strain for the low modulus tapes (~15 GPa). The stress-induced band shifts, however, are found to be the same for both thermotropic copolyester fibre and tape, having the value of approximately $-4.0\ \mathrm{cm}^{-1}/\mathrm{GPa}$. Most importantly this study shows that the presence of skin–core structure due to variation in orientation in both thermotropic aromatic copolyester fibres and tapes, could be detected readily through the use of Raman microscopy.

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