

# Raman spectroscopy of stressed high modulus poly(*p*-phenylene benzobisthiazole) fibres

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A Raman microscope has been used to investigate the deformation of high modulus poly(*p*-phenylene benzobisthiazole) (PBT) fibres. The structure of the fibres has been characterized using wide-angle X-ray diffraction and their mechanical properties have been determined using standard fibre tensile testing methods. It has been found that the as-spun fibres have a modulus of about 160 GPa and that this increased to about 240 GPa following heat treatment. This increase in modulus is accompanied by an improvement in structural order. Well-defined, intense Raman spectra can be obtained from individual fibres and three main bands at 1175, 1480 and 1600  $\text{cm}^{-1}$  have been identified. It has been found that all bands are strain sensitive with the 1480  $\text{cm}^{-1}$  band being the most sensitive, moving by  $-12.1 \pm 0.6 \text{ cm}^{-1}/\%$  strain for the heat-treated fibres. The reasons for the strain sensitivity of the Raman bands is discussed in relation to deformation of the bonds in the individual PBT molecules. The possibility of using the strain-induced band frequency shifts to follow the micromechanics of deformation in composites reinforced with PBT fibres is discussed.

(Keywords: Raman spectroscopy; poly(*p*-phenylene benzobisthiazole); mechanical properties; structure; molecular deformation)

## INTRODUCTION

Over recent years there have been important developments in the production of polymer fibres with high degrees of strength and stiffness<sup>1-10</sup>. These fibres are now finding use in engineering applications such as high performance composites<sup>11</sup>. Several different approaches have been used to obtain these high levels of mechanical performance. Efforts have been made to produce ultraorientation in flexible-backboned polymers with a high crystal modulus, such as polyethylene. This has been achieved by tensile drawing<sup>1,2</sup>, extrusion<sup>3,4</sup> and gel spinning<sup>5</sup>. High modulus polymer whisker single-crystal fibres can be produced from certain substituted poly(diacetylenes) by solid-state polymerization of single-crystal monomers<sup>6,7</sup>. High modulus fibres of aromatic polyamides such as poly(*p*-phenylene terephthalamide) (Kevlar) can be produced by the spinning of liquid crystalline polymer solutions<sup>8</sup>. The most impressive mechanical properties reported so far have been for fibres of heterocyclic rigid-rod polymers such as poly(*p*-phenylene benzobisthiazole) (PBT), again by spinning from liquid crystalline solutions. Such fibres have been reported to have moduli of the order of 110 GPa in the as-spun condition<sup>9</sup> but this can be increased to 300 GPa by heat treatment<sup>10</sup>. As these fibres also have high strength ( $\sim 2.5$  GPa) and good thermal and oxidative stability, they represent some of the strongest organic materials currently available. With their relatively low specific gravities ( $\sim 1.5$ ) they are obvious candidates for reinforcing fibres in composite for use in aerospace applications.

In our laboratory we have embarked upon a large programme of research concerned with the micro-

mechanics of the deformation of high modulus fibres and composites using Raman spectroscopy. It has been found that strong, well-defined Raman spectra are generally obtained from high modulus, highly oriented polymer fibres. Since when such polymers are deformed the bonds in the molecular backbone are strained and some of the frequencies of Raman-active bands decrease by an amount,  $\Delta\nu$ , dependent upon the band under consideration. The shifts in isotropic samples such as melt-crystallized polymers<sup>12</sup> are very small ( $\Delta\nu \sim 1 \text{ cm}^{-1}$  up to failure) since a high proportion of the deformation takes place through molecular uncoiling and sliding. However, for polymer single crystals stressed parallel to the molecular axis, the shifts can be considerable. Values of  $\Delta\nu$  in the order of  $-20 \text{ cm}^{-1}/\%$  strain have been reported<sup>13-15</sup> for the triple bond stretching band in substituted poly(diacetylenes). Shifts to a lower frequency of approximately  $5 \text{ cm}^{-1}/\%$  strain are found for the  $1610 \text{ cm}^{-1}$  band in Kevlar fibres<sup>16</sup>. However, the stress-induced shifts have been found to be somewhat smaller in lower modulus, less oriented aramid fibres since in this case the polymer chains experience less strain because of the difference in morphology<sup>17</sup>.

For many years, Wool and coworkers<sup>18-21</sup> have done considerable work on measuring stress induced frequency shifts in polymers such as oriented polypropylene, using infra-red spectroscopy. They found that the most stress-sensitive bands were those due to C-C stretching.

Although the infra-red technique has met with considerable success, it would appear that laser Raman microscopy offers significant advantages over infra-red for studies of the deformation of fibres. For example, the

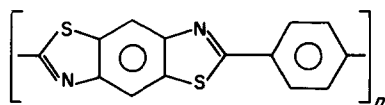
laser beam can be focused to a fine point ( $\sim 1\ \mu\text{m}$  in diameter) on either a single free-standing fibre or in a fibre in a resin allowing local changes in stress or strain to be studied. A considerable amount of the deformation in highly oriented polymer fibres takes place by stretching the backbone bonds, rather than in side groups. The backbone bond stretching modes such as C–C stretching tends to be Raman rather than infra-red active and so can be measured best using Raman spectroscopy<sup>21</sup>. In addition, many high modulus fibres have molecules with conjugated backbones. Resonance enhancement can take place, giving rise to extremely intense Raman scattering, by coupling certain vibrational modes with electronic transitions in the molecule. As well as leading to intense spectra with relatively low powers of incident laser beam, it allows the isolation of Raman bands of the chromophore, which gives rise to the electronic transition<sup>22</sup>.

This present study is concerned with the change in the Raman spectra of two forms of PBT, as-spun and heat-treated. The structure and tensile properties of the polymer are discussed first, then it is shown that the spectra can be obtained from single fibres that are very dependent upon stress and strain. The reason for this and the possible exploitation of the effect are then discussed.

## EXPERIMENTAL

### Materials and characterization

The PBT fibres used in this study were supplied by the Materials Laboratory of the Wright-Patterson Air Force Base, Ohio, USA, and were based on the molecule:



Two types of fibres were supplied. The first were straw-coloured 'as-spun' fibres prepared from a liquid crystalline solution in a concentrated acid. The second type were similar fibres which had also been heat treated at 625°C for 5 min and had a metallic copper colour.

Wide-angle X-ray scattering (WAXS) patterns were obtained from both types of fibres using a flat-plate transmission geometry and Ni-filtered  $\text{CuK}\alpha$  radiation. This enabled the level of molecular orientation in the two types of fibres to be compared.

Individual fibres were examined in a scanning electron microscope (Jeol JSM35A). They were cleaned with solvent and then rendered conductive by sputter coating with a thin layer of gold. The fibres were viewed in different directions to both examine their perfection and also to determine their dimensions for the calculation of stresses. The magnification of the microscope was calibrated prior to these measurements.

### Mechanical testing

Individual PBT fibres were mounted across holes on paper cards using a slow setting, cold-curing, epoxy resin adhesive. Once the adhesive had set the pieces of card were mounted between fibre testing grips in a model 1121 Instron and the card edges were cut. Data for stress-strain curves were collected using an HP85 computer and also on chart paper. Load ranges of between 2 and 5 N were employed using a 5 N capacity load cell. The gauge

length of the single fibre specimens was about 50 mm and the fibre strain was determined from the crosshead displacement. A crosshead speed of  $1\ \text{mm min}^{-1}$  was used making an initial strain rate of  $3.3 \times 10^{-4}\ \text{s}^{-1}$ . At least 10 samples of each type of fibre were employed. All tests were carried out at  $23 \pm 1^\circ\text{C}$  and a relative humidity of  $50 \pm 5\%$ .

### Raman microscopy

Raman spectra were obtained from individual PBT fibres using a Raman microscope system. This is based upon a SPEX 1403 double monochromator connected to a modified Nikon optical microscope. Spectra were obtained at a resolution of the order of  $\pm 5\ \text{cm}^{-1}$  using the 632.8 nm line of a 10 mW He/Ne laser. A  $\times 40$  objective lens with a numerical aperture of 0.65 was used and this gave a  $2\ \mu\text{m}$  spot when focused (although the objective lens was generally defocused to reduce the possibility of damage through excessive heating). The laser beam was always polarized parallel to the fibre axis for all measurements.

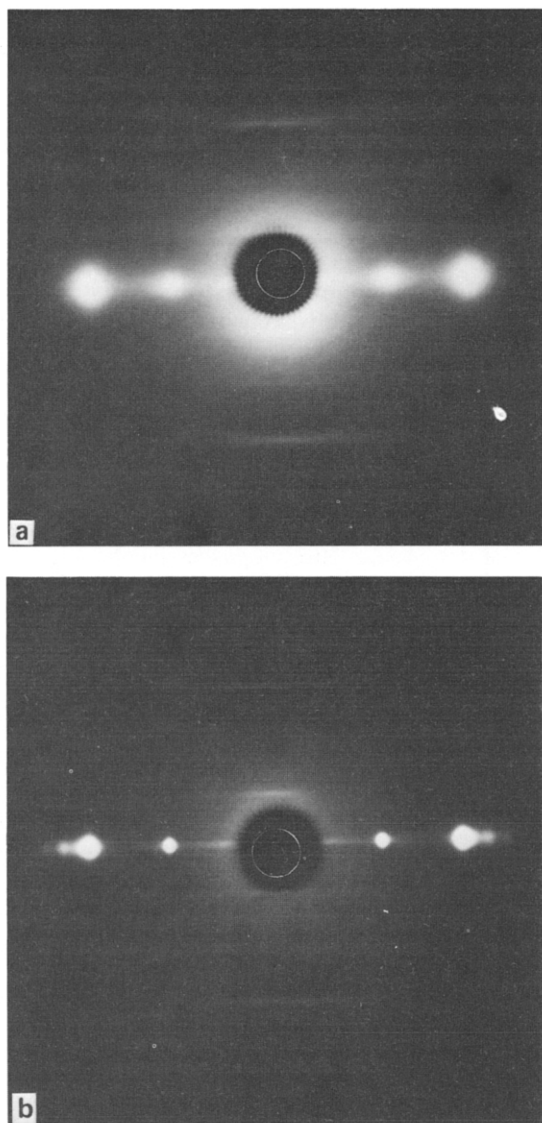
Spectra were obtained from fibres during deformation in a small straining rig which fitted directly onto the microscope stage. Individual fibres were fixed between aluminium foil tabs which were placed onto the aluminium blocks of the straining rig using a cyanoacrylate adhesive, giving a gauge length of about 10 mm, which was measured accurately using the light microscope. The fibres were deformed by displacing the blocks using a micrometer attachment which could be read to  $\pm 0.005\ \text{mm}$ . This allowed a precision of the order of  $\pm 0.05\%$  for strain measurement. Raman spectra were obtained during deformation by scanning strong individual peaks between loading steps of 0.1% strain. Since it took about 15 min to scan a peak this corresponded to an effective strain rate of the order of  $1 \times 10^{-6}\ \text{s}^{-1}$ .

## RESULTS AND DISCUSSION

### Structure

The WAXS patterns for the as-spun and heat-treated fibres are shown in Figure 1. The as-spun fibre has a pattern consisting of diffuse equatorial peaks (Figure 1a). The heat-treated fibres have sharper equatorial peaks and better defined layer lines (Figure 1b), indicating an improvement in structural order. These WAXS patterns are similar to those found by previous workers on PBT tapes<sup>23,24</sup>. It is thought that the heat treatment increases the conjugation length in the polymer by improving the planarity of the molecule. This leads to the colour change in the material following heat treatment resulting in a better defined molecular structure and improved orientation. From diffraction evidence similar to that in Figure 1, Odell *et al.*<sup>24</sup> concluded that PBT polymer is only two-dimensionally crystalline, with the polymer chains packing parallel to each other but lacking register in the longitudinal direction.

Figure 2 shows scanning electron micrographs of individual as-spun and heat-treated PBT fibres. Considerable variation in fibre diameter was found and the diameters of both types of fibres ranged typically between 10 and  $14\ \mu\text{m}$ . A mean value of  $12 \pm 1\ \mu\text{m}$  was found for both the as-spun fibres and the heat-treated ones. Measurements were made at several points on the



**Figure 1** Wide-angle X-ray scattering patterns for bundles of PBT fibres. (a) As-spun; (b) heat-treated

deformed fibres so that accurate values of fibre diameter could be obtained for the calculation of stresses. Striations parallel to the fibre axis were found on some fibres but in general they were seen to be relatively defect-free and of uniform appearance.

#### Mechanical testing

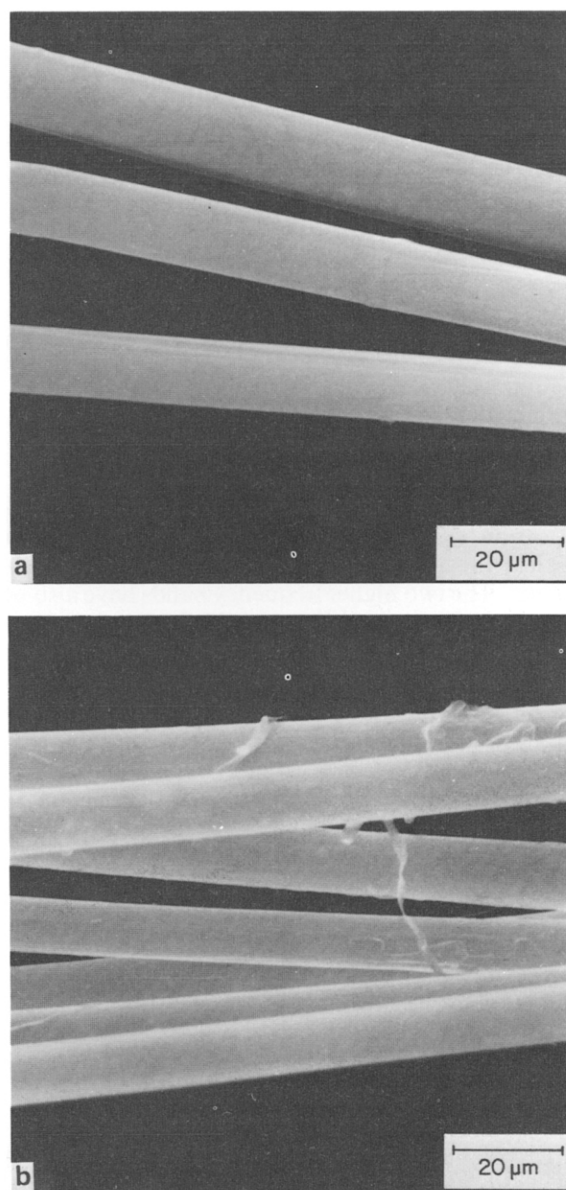
Stress-strain curves for individual as-spun and heat-treated PBT fibres are shown in *Figure 3*. Mean values of Young's modulus, fracture stress and elongation to failure obtained from five sets of specimens are given in *Table 1*. The curve for the as-spun fibre (*Figure 3a*) shows a pronounced deviation from linearity at a strain of about 1.0%, whereas the curve for the heat-treated fibre is approximately linear up to fracture (*Figure 3b*). Similar behaviour has been found by other workers<sup>9</sup> for PBT. *Figure 4* shows cyclic stress-strain curves for the two types of fibre where the stress has been removed at a strain of about 1.5% and then immediately reapplied. It can be seen that the as-spun fibre shows a pronounced degree of permanent plastic deformation (*Figure 4a*) whereas the heat-treated fibre only exhibits a small amount of hysteresis (*Figure 4b*). Clearly, the as-spun is capable of

undergoing yield. However, the fact that the stress-strain curve on reloading has approximately the same slope as for the original loading implies that this plastic deformation does not lead to an improvement in modulus through better orientation as with, for example, aramid fibres<sup>25</sup>. The plastic deformation must take place through a mechanism such as molecular translation in the stressing direction. In contrast, the higher modulus heat-treated fibre with improved structural order does not appear to yield.

#### Raman microscopy

Raman spectra could be readily obtained from different positions on the PBT fibres using relatively low powers of laser radiation. Typical spectra from deformed and undeformed, as-spun and heat-treated fibres are shown in *Figure 5*. The spectra consisted of a few well-defined intense peaks on a strong fluorescent background.

It can be seen from *Figure 5* that three principal bands are found in the Raman spectra of PBT fibres between 1100 and 1700  $\text{cm}^{-1}$ . These are located at approximately



**Figure 2** Scanning electron micrographs of coated PBT fibres. (a) As-spun; (b) heat treated

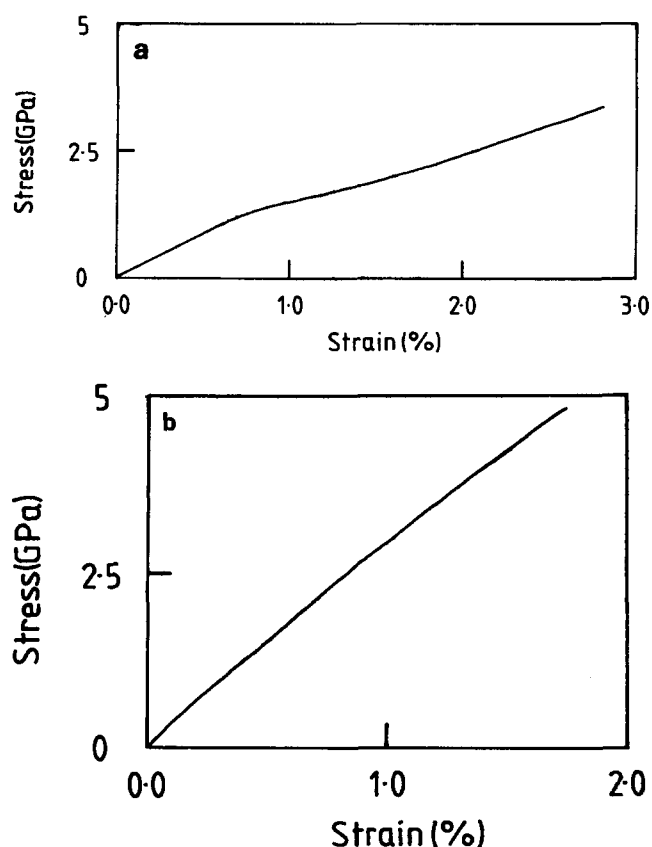


Figure 3 Stress-strain curves for individual PBT fibres. (a) As-spun; (b) heat treated

Table 1 Mechanical property data for the PBT fibres (mean of at least five tests)

Property	As-spun	Heat treated
Young's modulus (GPa)	$190 \pm 20$	$250 \pm 25$
Tensile strength (GPa)	$3.0 \pm 0.2$	$4.0 \pm 0.2$
Strain to failure (%)	$2.6 \pm 0.4$	$1.6 \pm 0.3$

1175, 1480 and  $1600\text{ cm}^{-1}$  with the  $1480\text{ cm}^{-1}$  band being the most intense for an excitation wavelength of 632.8 nm. The two higher frequency bands have also been reported by Shen *et al.*<sup>26</sup> for solid PBT using Raman spectroscopy and are also obtained in the infra-red spectra of PBT film<sup>27</sup>. The  $1480\text{ cm}^{-1}$  band was tentatively assigned to a stretching mode of the heterocyclic ring and the  $1600\text{ cm}^{-1}$  band was thought to be due to stretching of the phenyl rings but may also contain contributions from other vibrations<sup>28</sup>. The  $1175\text{ cm}^{-1}$  band, which has not been reported in PBT solutions or solid PBT pellets<sup>26</sup>, may be due to stretching of the C-C link between the aromatic rings, or possibly residual acid<sup>27</sup>.

It can be seen from Figure 5 that the spectra for both the as-spun PBT and the heat-treated material change with deformation. Certain peaks shift to lower frequency and peak intensities also change. Detailed changes in the spectra are described below.

#### Effect of deformation on the Raman spectra

Figure 6 shows the spectra for the two types of PBT fibre in the  $1400\text{--}1500\text{ cm}^{-1}$  region in the undeformed state and following deformation of the fibres to 2% strain. It can be seen that there is a significant change in the

$1480\text{ cm}^{-1}$  band for both fibres with the peak position shifting by almost  $-30\text{ cm}^{-1}$  for the high-modulus heat-treated fibre. It can also be seen that there is also some broadening of the peak during deformation.

The effect of deformation upon the  $1480\text{ cm}^{-1}$  peak can be seen in more detail in Figures 7 and 8. The change in peak position with strain is shown in Figure 7a for the as-spun fibre. It can be seen that there is a linear shift in Raman frequency up to a strain of about 1% and then there is no further shift, even when the strain is increased in excess of 3%. It is highly likely that the discontinuity is due to yielding in the as-spun fibres since the stress-strain curve of the fibre shows a yield point at a strain of about 1% (Figures 3a and 4a) although different strain rates

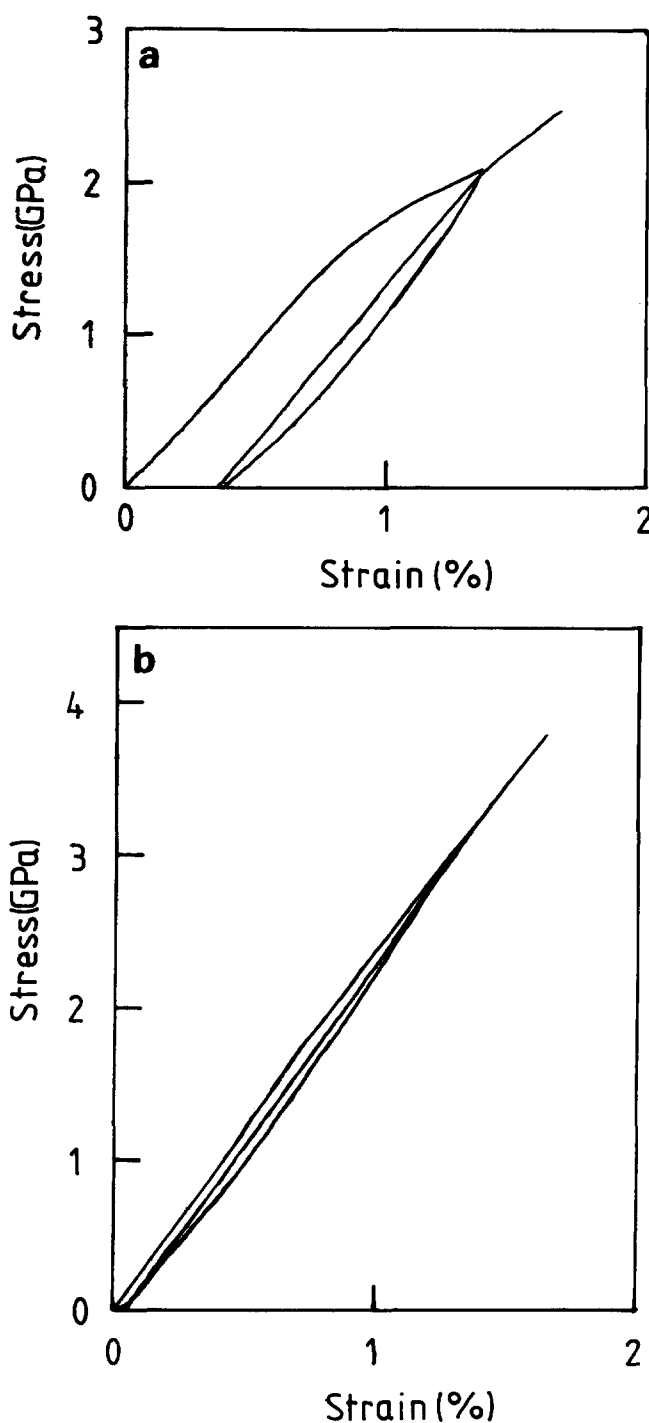
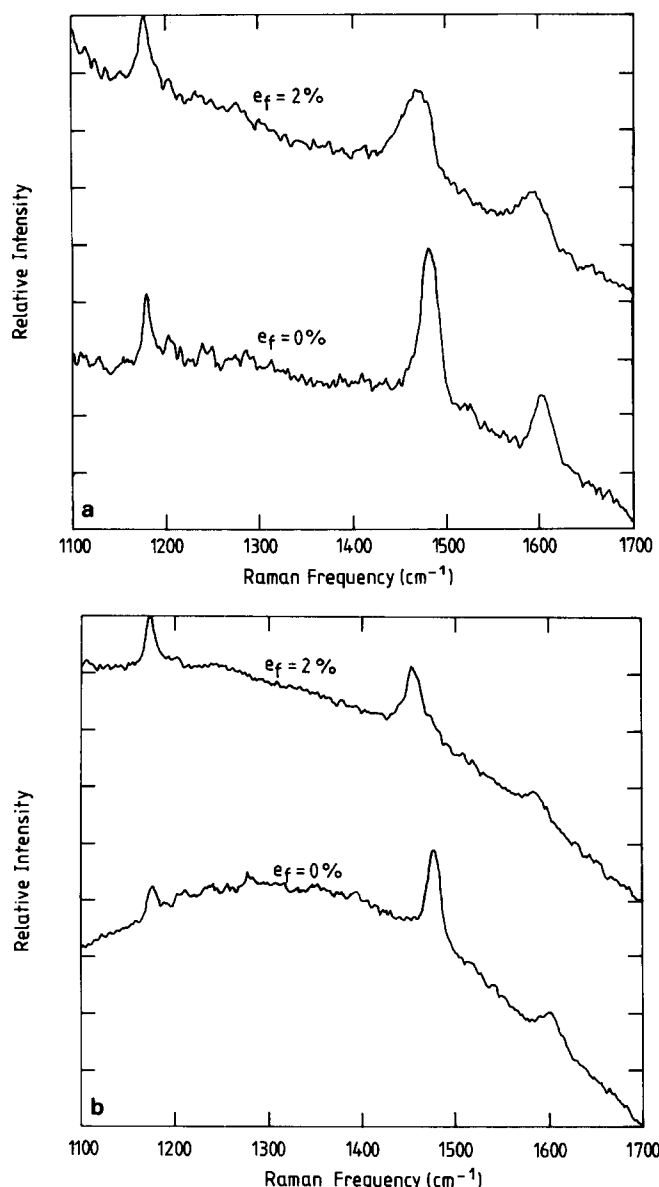


Figure 4 Cyclic stress-strain curves for individual PBT fibres. (a) As-spun; (b) heat treated



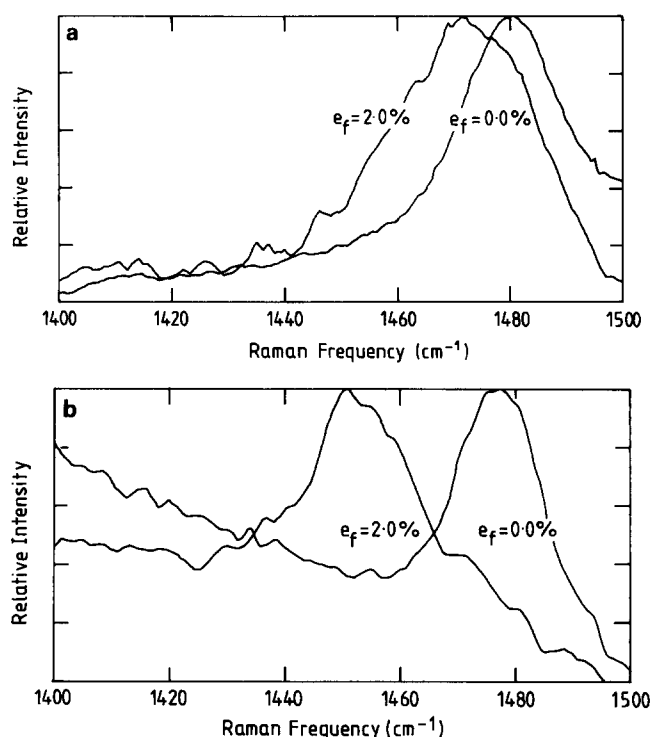
**Figure 5** Raman spectra in the range 1100–1700  $\text{cm}^{-1}$  for individual PBT fibres obtained at fibre strains ( $e_f$ ) of 0% and 2%. (a) As-spun; (b) heat treated

were used for the two types of test. This is further confirmed by examination of Figure 8a, which shows the effect of strain cycling upon the peak shifts in the as-spun fibres. The fibre was strained to 2% strain, relaxed and then strained to failure. It can be seen that there is a permanent plastic deformation of about 1% since the Raman peak frequency returns to its undeformed value ( $\sim 1480 \text{ cm}^{-1}$ ) whilst there is still a fibre strain of 1.0%. Since the Raman technique follows the molecular strain directly, this demonstrates that it is an extremely powerful tool for observing molecular processes involved in the deformation and yield of polymer fibres.

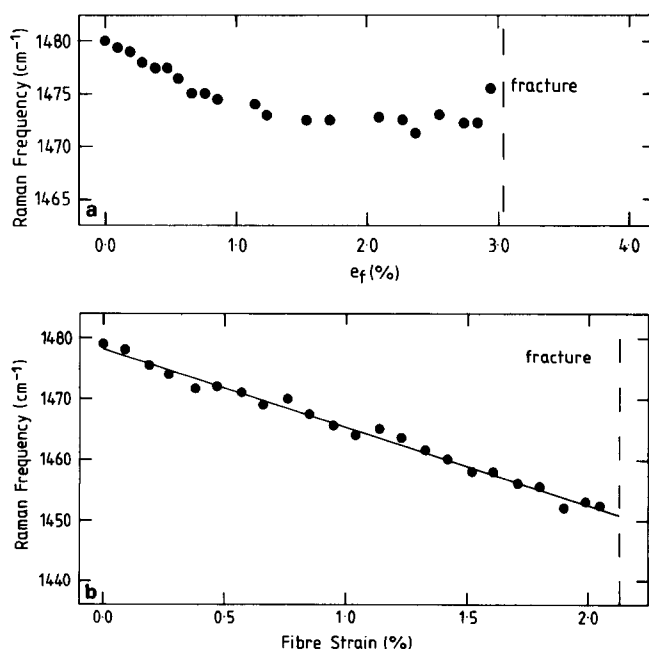
It was shown in Figures 3 and 4 that the deformation of the heat-treated higher modulus PBT fibres is more elastic than the as-spun ones and that they do not undergo yield. This is confirmed in Figure 7b, where it can be seen that there is a linear decrease in the Raman frequency of the peak with increasing fibre strain up to fracture, which occurred at about 2.1% strain. Figure 8b shows that there is some hysteresis, however, in the deformation of the heat-treated fibres. In this case, a fibre

was deformed to a strain of 1.6%, relaxed and then reloaded up to failure. It can be seen that there is a small offset strain of about 0.2% and that the curve for reloading has a slightly higher slope than that for the original straining cycle but shows no gross yielding.

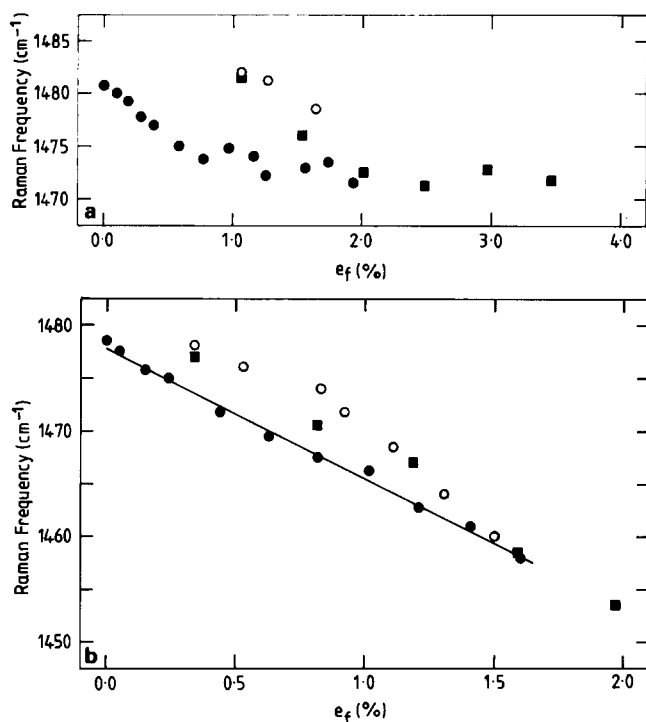
The broadening of the  $1480 \text{ cm}^{-1}$  Raman band with strain is shown in Figure 9 for the two types of fibre. In this case, the position of the leading (L) and trailing (T) edges of the peaks, defined by approximating the band to a triangle and taking the positions of the half-height of the triangle, are plotted as a function of strain. It can be seen



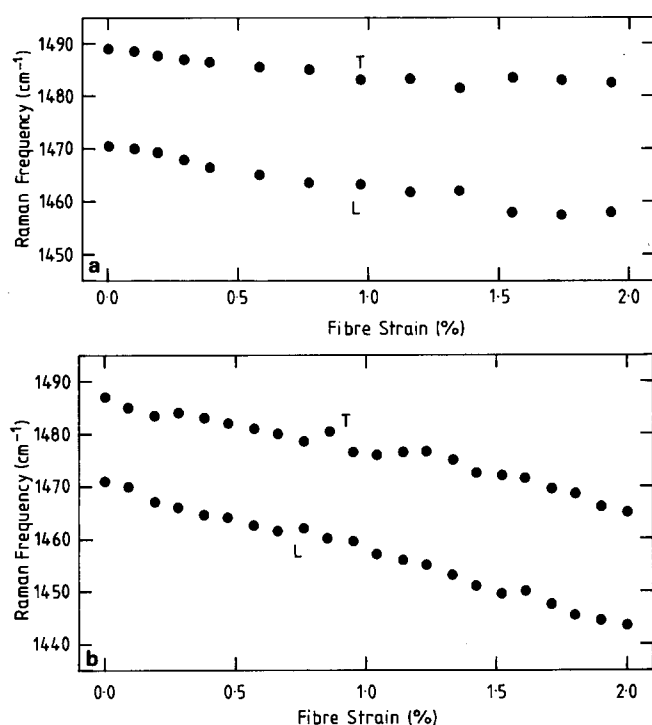
**Figure 6** Raman spectra in the region of the  $1480 \text{ cm}^{-1}$  band for a PBT fibre obtained at fibre strains ( $e_f$ ) of 0% and 2% showing the peak shift. (a) As-spun; (b) heat treated



**Figure 7** Variation of the position of the  $1480 \text{ cm}^{-1}$  peak with fibre strain for PBT fibres. (a) As-spun; (b) heat treated



**Figure 8** Variation of the position of the  $1480\text{ cm}^{-1}$  peak with fibre strain for PBT fibres subjected to cyclic loading. ●, First loading; ○, first unloading; ■, second loading. (a) As-spun; (b) heat treated

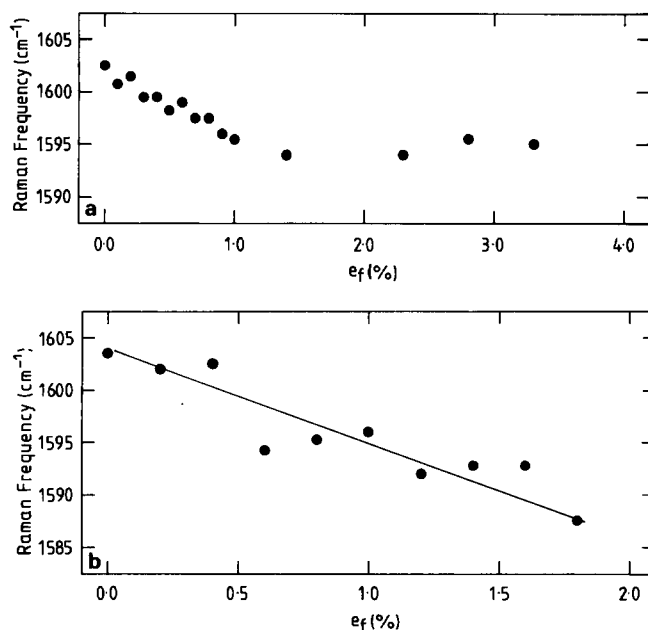


**Figure 9** Variation of the positions of the leading (L) and trailing (T) edges of  $1480\text{ cm}^{-1}$  peak with strain for PBT fibres. (a) As-spun; (b) heat treated

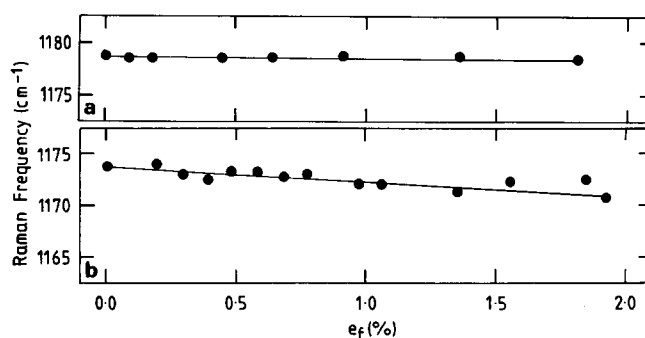
that there is a gradual broadening of the band with strain for both types of fibre. In the case of the as-spun fibre, *Figure 9a*, there is a change in slope at about 1% strain for both the leading and the trailing edges. However, even after yield the band undergoes significant further broadening indicating an increasing range of molecular strain in the fibres during the plastic deformation. *Figure 9b* shows the broadening of the  $1480\text{ cm}^{-1}$  band for the

heat treated fibre. In this case there is a gradual broadening of the band up to failure. There is clearly a range of stress on individual molecules and the broadening of the peak is an indication of perhaps some overstressed (and perhaps understressed) bonds. Similar behaviour has been reported by Wool and coworkers<sup>18-20</sup> from their infra-red studies on polypropylene fibres, although it bears little structural similarity to PBT. This is clearly an area worthy of further study.

Although most of the investigation has concentrated upon strain induced frequency shifts for the strongest, most well-defined  $1480\text{ cm}^{-1}$  band, shifts were also found for the two other main peaks. *Figure 10* shows the dependence of the position of the  $1600\text{ cm}^{-1}$  peak upon applied strain for the two types of PBT fibres. In the case of the as-spun fibre, there is a linear decrease in frequency with strain up to the yield point at about 1.0% strain and then no change in frequency with further straining (*Figure 10a*). This behaviour is very similar to that of the  $1480\text{ cm}^{-1}$  band for this fibre shown in *Figure 7a*. The dependence of the position of the  $1600\text{ cm}^{-1}$  peak for the heat treated fibres is shown in *Figure 10b*. Although there was considerable scatter in the data due to the difficulty in defining the peak position, it can be seen that there is an approximately linear decrease in the peak position with



**Figure 10** Variation of the position of the  $1600\text{ cm}^{-1}$  peak with fibre strain for PBT fibres. (a) As-spun; (b) heat treated



**Figure 11** Variation of the position of the  $1175\text{ cm}^{-1}$  peak with fibre strain for PBT fibres. (a) As-spun; (b) heat treated

**Table 2** Peak positions ( $\bar{\nu}$ ) and strain sensitivity ( $\Delta\bar{\nu}$ ) of the main Raman bands in PBT fibres. The tentative assignments are also indicated

Band	As-spun		Heat treated		Tentative assignment
	$\bar{\nu}$ ( $\text{cm}^{-1}$ )	$\Delta\bar{\nu}$ ( $\text{cm}^{-1}/\%$ strain)	$\bar{\nu}$ ( $\text{cm}^{-1}$ )	$\Delta\bar{\nu}$ ( $\text{cm}^{-1}/\%$ strain)	
$1175\text{ cm}^{-1}$	$1175 \pm 2$	$0 \pm 1$	$1174 \pm 2$	$-1.3 \pm 0.5$	C-C stretching
$1480\text{ cm}^{-1}$	$1480 \pm 2$	$-8.3 \pm 1.0$	$1477 \pm 2$	$-12.1 \pm 0.6$	Stretching of heterocyclic rings
$1600\text{ cm}^{-1}$	$1602 \pm 2$	$-6 \pm 1$	$1603 \pm 2$	$-8 \pm 1$	Stretching of phenyl ring

applied strain. Again, the behaviour is similar to that of the  $1480\text{ cm}^{-1}$  peak shown in Figure 7.

In contrast to the behaviour of the other two main bands, it was found that the position of the  $1175\text{ cm}^{-1}$  band was relatively insensitive to the level of applied strain, as can be seen from Figure 11. It was difficult to determine the change in frequency for the as-spun fibre but a small decrease in frequency of the  $1175\text{ cm}^{-1}$  band is found for the heat-treated fibre (Figure 11b).

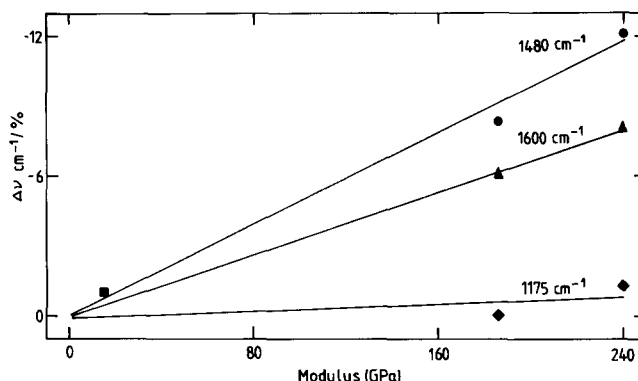
It is clear that the sensitivity of the particular bands to strain depends upon both the structure of the fibres and the type of band. This is discussed further below.

## STRAIN SENSITIVITY OF RAMAN BANDS

### Effect of structure

The sensitivity of the different bands to strain in the two types of PBT fibre examined is summarized in Table 2. It can be seen that the frequency shifts for each band are always higher for the high modulus heat treated fibres than for the lower modulus as-spun fibres. This is clearly an indication that, in the higher modulus fibres, the molecular bonds are subjected to higher stresses at a given level of strain than for the lower modulus fibres. The frequency shifts for the three bands in the two types of PBT fibre are plotted against fibre modulus in Figure 12. The lines have been plotted from  $\Delta\nu = 0$  at  $E = 0$ , as it is assumed that there can be no frequency shift for a zero modulus fibre. Although there are only limited data available, it can be seen that there is a linear increase in the rate of frequency shift with increasing fibre modulus. Stress induced frequency shifts have been reported by Shen and Hsu<sup>27</sup> in the infra-red spectra of PBT films with moduli of 15–22 GPa. Shifts of the order of  $1\text{ cm}^{-1}$  were found for a number of bands at an applied strain level of about 1%. The shift of the  $1480\text{ cm}^{-1}$  infra-red band for the low modulus PBT film of Shen and Hsu is also plotted in Figure 12 and it can be seen that it falls on the same line as the Raman data for this present study, indicating the generality of the effect.

Similar behaviour has been found recently for aramid fibres with different levels of modulus<sup>17</sup>. The behaviour is entirely reasonable since high modulus fibres such as aramids and PBT have high values of stiffness because they contain well-aligned rigid-rod molecules. The different values of modulus due to a variety of heat treatments reflect different degrees of molecular alignment in such fibres. The fibres with better aligned molecules have the highest levels of modulus because more stress is being taken directly by the covalent bonds in the molecular backbone. This is then reflected in the magnitude of the strain induced frequency shifts that would be expected. Hence, when the technique is being used to study the deformation of individual fibres or their behaviour in composites<sup>29</sup>, it will be even more sensitive and accurate with higher modulus fibres.



**Figure 12** Variation of the strain induced peak frequency shift with fibre modulus for the three main bands in PBT. ●,  $1480\text{ cm}^{-1}$  band; ▲,  $1600\text{ cm}^{-1}$  band; ◆,  $1175\text{ cm}^{-1}$  band; ■,  $1480\text{ cm}^{-1}$  band (from i.r. data in Ref. 27)

### Sensitivity of different Raman bands

Table 2 demonstrates clearly that for a particular type of fibre the frequencies of the Raman-active bands have different dependencies upon strain. In principle, it should be possible to gain some insight into the way in which the stress and strain are distributed between different bonds along the molecular backbone in PBT. However, before this can be done it would be necessary to know the inherent strain sensitivity of the different bands. The strain sensitivity reflects the anharmonicity of the potential functions between the atoms in the bonds. Theoretical calculations of the inherent shifts for a polymer molecule are hindered by the lack of information upon these potential functions. Further theoretical work upon this problem is currently being undertaken.

## CONCLUSIONS

It has been found that Raman microscopy is a powerful technique for the investigation of the deformation of PBT fibres at the molecular level. As well as gaining an important insight into response of the fibre molecules to strain it is clear that the Raman technique can be applied generally to the study of the deformation of high modulus polymer fibres and composites. The investigation is currently being extended to other types of high modulus fibres and to the study of the micromechanics of their deformation in composites.

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# REFERENCES

- 1 Capaccio, G. and Ward, I. M. *J. Mater. Sci.* 1975, **15**, 219
- 2 Capaccio, G., Gibson, G. and Ward, I. M. in 'Ultra-High Modulus Polymers' (Eds A. Ciferri and I. M. Ward), Applied Science, London, 1979, p. 1
- 3 Zachariades, A. E., Mead, W. T. and Porter, R. S. in 'Ultra-High Modulus Polymers' (Eds A. Ciferri and I. M. Ward), Applied Science, London, 1979, p. 77
- 4 Mead, W. T., Desper, C. R. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 859
- 5 Lemstra, P. J. in 'Developments in Oriented Polymers: 2' (Ed. I. M. Ward), Applied Science, London, 1987
- 6 Baughman, R. H., Gleiter, H. and Sendfeld, N. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 1871
- 7 Galiotis, C. and Young, R. J. *Polymer* 1983, **24**, 1023
- 8 Schaefgen, J. R. in 'Strength and Stiffness of Polymers' (Eds A. E. Zachariades and R. S. Porter), Marcel Dekker, New York, 1983, p. 327
- 9 Allen, S. R., Filippov, A. G., Farris, R. J. and Thomas, E. L. in 'Strength and Stiffness of Polymers' (Eds A. E. Zachariades and R. S. Porter), Marcel Dekker, New York, 1983, p. 357
- 10 Allen, S. R., Farris, R. J. and Thomas, E. L. *J. Mater. Sci.* 1985, **20**, 2727
- 11 Greenwood, J. H. and Rose, P. G. *J. Mater. Sci.* 1974, **9**, 1809
- 12 Evans, R. A. and Hallam, H. E. *Polymer* 1976, **17**, 838
- 13 Mitra, V. K., Risen, W. M. and Baughman, R. H. *J. Chem. Phys.* 1977, **66**, 2731
- 14 Galiotis, C., Young, R. J. and Batchelder, D. N. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 2483
- 15 Batchelder, D. N. and Bloor, D. J. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 569
- 16 Galiotis, C., Robinson, I. M., Young, R. J., Smith, B. J. E. and Batchelder, D. N. *Polymer* 1985, **26** (Commun), 354
- 17 van der Zwaag, S., Northolt, M. G., Young, R. J., Galiotis, C., Robinson, I. M. and Batchelder, D. N. *Polym. Commun.* in press
- 18 Wool, R. P. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 1795
- 19 Wool, R. P. and Boyd, R. H. *J. Appl. Phys.* 1980, **51**, 5116
- 20 Bretzlaff, R. S. and Wool, R. P. *J. Appl. Phys.* 1981, **52**, 5964
- 21 Wool, R. P., Bretzlaff, R. S., Li, B. Y., Wang, C. H. and Boyd, R. H. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1039
- 22 Batchelder, D. N. and Bloor, D. in 'Advances in Infrared and Raman Spectroscopy' (Eds R. J. Clark and R. E. Hester), Wiley-Heyden, London, 1984, Vol. 2
- 23 Minter, J. R., Shimanwa, K. and Thomas, E. L. *J. Mater. Sci.* 1981, **16**, 3303
- 24 Odell, J. A., Keller, A., Atkins, E. D. T. and Miles, M. J. *J. Mater. Sci.* 1981, **16**, 3309
- 25 Northolt, M. G. *Polymer* 1980, **21**, 1199
- 26 Shen, D. Y., Venkatesh, G. M., Burchell, D. J., Shu, P. H. C. and Hsu, S. L. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 509
- 27 Shen, D. Y. and Hsu, S. L. *Polymer* 1982, **23**, 969
- 28 Venkatesh, G. M., Shen, D. Y. and Hsu, S. L. *J. Polymer Sci., Polym. Phys. Edn* 1981, **19**, 1475
- 29 Galiotis, C., Young, R. J., Yeung, P. H. J. and Batchelder, D. N. *J. Mater. Sci.* 1984, **19**, 3640