Strain measurement and deformation analysis in a diacetylene-containing urethane copolymer using Raman spectroscopy

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(Received 12 November 1992; revised 7 April 1993)

The opto-mechanical behaviour of a rigid diacetylene-containing segmented copolyurethane has been investigated in detail by using Raman spectroscopy. Experiments were carried out to determine the tensile and compressive strain dependence of the Raman frequency of the C≡C triple bond stretching mode in the copolymer. A similar initial strain-induced frequency shift of $4.7 \pm 0.5\ \mathrm{cm}^{-1}/\%$ strain was found in both tensile and compression tests. Angular strains were measured by obtaining the Raman spectra of the copolymer at different angles of the laser beam polarization with respect to the principal tensile axis, and it was found that the experimental results are in general agreement with classical elasticity theory, although they differ in detail. The molecular deformation of the polydiacetylene moieties in the copolymer has also been discussed.

(Keywords: opto-mechanical behaviour; diacetylene copolyurethane; Raman spectroscopy)

INTRODUCTION

The dependence of the molecular vibrational behaviour of polymers upon mechanical deformation has generated considerable interest from both experimental and theoretical viewpoints[1–6]. It is found that certain vibrational modes in the Raman spectra of some highly oriented polymers undergo substantial shifts in frequency when the polymers are subjected to tensile deformation[4–22]. These frequency shifts are due to the changes in the force constants of the chemical bonds resulting from the mechanical deformation of the molecules. It is possible to use these highly anisotropic polymers as optical strain gauges in the study of deformation micromechanics using a Raman microscope[7,8,11,19]. Such opto-mechanical behaviour, however, is much more difficult to follow in conventional isotropic polymers[3,23,24], as the frequency shifts of the Raman bands for these materials are usually very small and difficult to detect. The recent development[25–29] of diacetylene-containing copolymers has proved to be a breakthrough in producing isotropic polymers with significant strain-induced Raman band shifts similar to those of the highly oriented polymers. These copolymers have a unique combination of the optical properties of polydiacetylenes and the mechanical properties of polyurethanes. Moreover, the copolymers are processible and can be tailor-made to have the required optical and mechanical properties by controlling the chemistry of the system.

The peak position of the C≡C triple bond stretching mode of these diacetylene-containing copolymers has been found to be sensitive to an externally applied tensile stress and also to the resulting strain[25–29]. This sensitivity is usually expressed in terms of the wavenumber shift per unit tensile strain, i.e. $\mathrm{d}(\Delta\nu)/\mathrm{d}\varepsilon$. The strain dependence of the Raman band position depends upon the structure and morphology of the copolymers, and analysis of the opto-mechanical behaviour has revealed details of molecular deformation in the copolymers. The strains in these materials, in either the bulk or as coatings, can be measured using Raman spectroscopy and the elastically isotropic copolymers were shown to have potential as optical strain sensors[29]. Previous work has been concerned with the response of the Raman spectra to tensile stress and measurements of the resulting strains in the copolymers and it has only been performed during tensile deformation. In this paper, a more comprehensive study of the opto-mechanical behaviour of such a copolymer will be presented. The response of the Raman bands to stress has been examined during both tensile and compressive deformation. Furthermore, investigations have also been carried out concerning the measurement of molecular deformation in directions other than the principal stress axis and the results have been analysed using classical elasticity theory.

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0032-3861/94/010080-06

EXPERIMENTAL

Materials

The diacetylene-containing segmented copolyurethane used in this work was based on 4,4′-diphenylmethane diisocyanate (MDI), 2,4-hexadiyne-1,6-diol (HDD) and a polypropylene glycol with a number-average molar mass of about 400 g mol^{-1}. It was synthesized using a bulk one-shot procedure, with cross-polymerization of the diacetylene monomers being achieved by thermal treatment. Details of the synthesis and the structure/property relationships of the copolymers were described in previous publications[26,27]. The copolymer studied in this work contained 33 wt% of diacetylene-containing hard segments (HDD/MDI); it was formed at 60°C and cast into plaques prior to gelation. Thermal treatment was carried out at 100°C for 40 h. The material so obtained was rigid and deeply coloured with a Young's modulus of about 2.0 GPa[27]. Transmission electron microscopic analysis of microtomed ultrathin sections of the copolymer[26] was carried out by using a Philips 301 electron microscope, operating at 100 kV.

Analysis of deformation using Raman spectroscopy

Raman spectra of the copolymer were recorded using a Raman microscope system which is based on a SPEX 1403 double monochromator with a modified Nikon optical microscope attachment. A charge-coupled device (CCD), cooled with liquid nitrogen, was employed for the signal detection and a 15 mW Helium/Neon laser (wavelength 632.8 nm) was used as the excitation source. A (× 40) objective lens with a numerical aperture of 0.65 was used and the laser was focused on to a spot of 2 μm in diameter on the sample. The scattered light was collected using a 180° back-scattering geometry with the same objective lens and then focused on the entrance slit (0.40 mm wide) of the spectrometer. In the present study, a 10 s scanning time was used to obtain a spectrum with a spectral window of about 40 cm^{-1}. Three scans were necessary to obtain the C≡C stretching mode band but since the scattering was very intense this did not lead to any significant error. The spectra were curve-fitted into a Gaussian profile on a quadratic background using a non-linear least squares fitting routine based on the Levenberg–Marquardt algorithm. A ± 5 cm^{-1} resolution was usually achieved for the determination of the absolute values of Raman frequency. The strain-induced frequency shift, however, could be measured to an accuracy of better than ± 0.5 cm^{-1}.

The strain dependence of the frequency of the C≡C triple bond stretching mode was determined *in situ*. Deformation was applied to the copolymer specimens under the Raman microscope by using a Minimat miniature materials tester (Polymer Laboratories). The specimens were deformed, either in tension or in compression, in steps of about 0.05% strain, and Raman spectra of the C≡C stretching mode were then obtained at various strain levels. Dumb-bell-shaped specimens with dimensions of 2.5 x 10 x 40 mm in the gauge length region were used in the tensile experiments, while in compression tests, rectangular-shaped specimens with dimensions of 4 x 6 x 12 mm, were deformed in a compression cage fitted on the Minimat. The externally applied deformation was measured using a resistance strain gauge attached to each specimen. The Raman band of the C≡C stretching mode was used as the diagnostic band throughout the deformation study, and the laser was always polarized parallel to the principal stress axis, except in the case of angular strain measurement, which is described as follows.

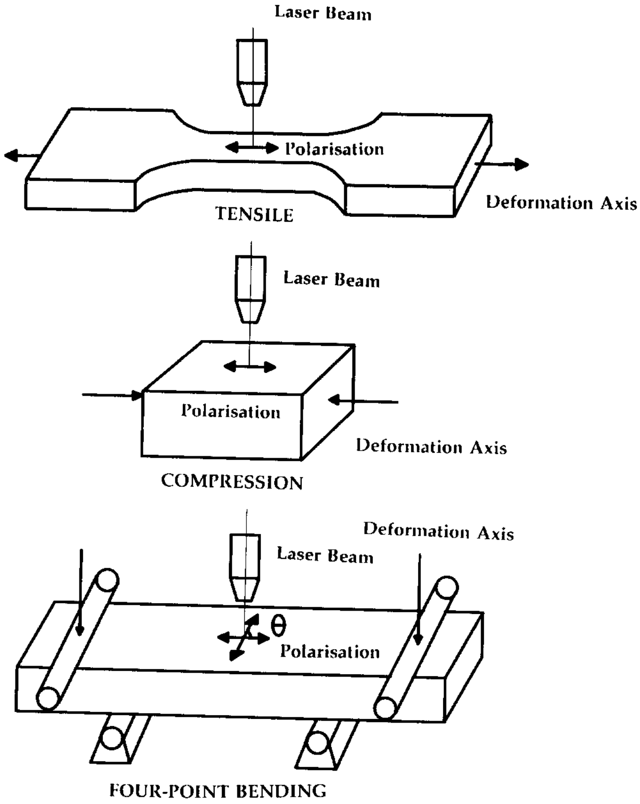

Figure 1 Schematic representation of the geometric arrangements used for Raman deformation measurements in tensile, compression and four-point bending tests

Angular strain measurement in the copolymer was carried out in order to analyse the molecular deformation of the polydiacetylenes in the copolymer along various directions with respect to the principal stress axis. This was done by deforming strips of the copolymer (2.5 x 10 x 55 mm) to certain strain levels using an in-house constructed four-point bending rig and varying the angle, θ, between the direction of the laser beam polarization and the principal stress axis. The four-point bending rig was employed because it was more compact than the Minimat and could be rotated around (by 90°) on the microscope stage. In this work, tests were carried out at three different levels of axial strain, determined by using a resistance strain gauge, while at each strain level the angle, θ, was varied from -10 to 120° and the Raman spectra of the C≡C stretching mode were recorded at intervals of 5°. *Figure 1* illustrates the geometries of the specimens used in tensile, compression and four-point bending tests.

RESULTS AND DISCUSSION

Structure of copolymers

Transmission electron microscopy confirmed the two-phase structure of the copolymer. The spherulitic aggregates of the HDD/MDI hard segments were dispersed uniformly in the poly(ether–urethane) matrix phase, as shown in *Figure 2*. The polydiacetylene chains that formed in the hard segment aggregates caused

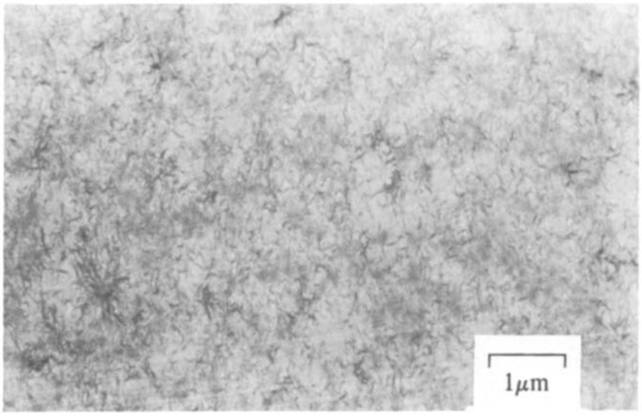

Figure 2 Transmission electron micrograph of a microtomed section of a sample of the diacetylene-containing urethane copolymer, obtained without staining

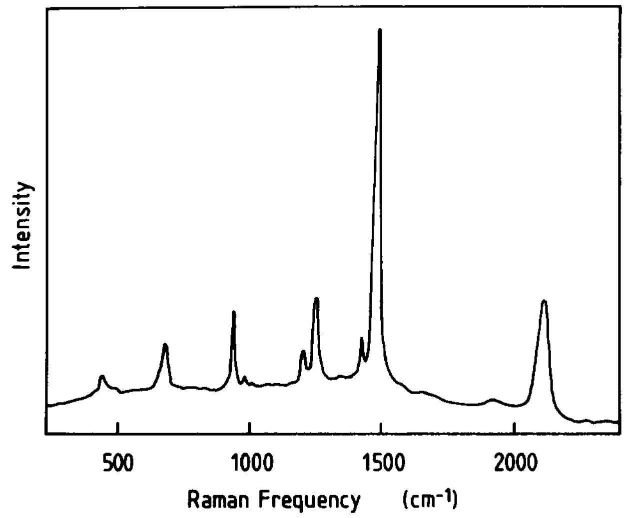

Figure 3 Raman spectrum in the region 300–2400 cm^{-1} for the diacetylene-containing urethane copolymer

chemical crosslinking in the copolymer and acted as a mechanical reinforcement at the molecular level[26,27]. They also become optically active moieties which give the copolymer a strong resonance Raman spectrum (shown in *Figure 3*), which resembles those obtained for polydiacetylene single crystals[5–7].

Analysis of tensile and compressive deformation using Raman microscopy

The full Raman spectrum in the range 300–2400 cm^{-1} for the diacetylene-containing copolymer is shown in *Figure 3*, and shows Raman bands which are characteristic of all polydiacetylene crystals[5–8]. The resonance Raman effect[5] enhances the intensity of scattering from the polydiacetylene species to such an extent that any scattering from the poly(ether–urethane) phase is swamped. *Figure 4* shows the Raman band for the C≡C triple bond stretching mode of the copolymer in the region of 2090 cm^{-1}, both before and after tensile and compressive deformation. A significant shift to lower frequencies is observed when the copolymer is subjected to tensile deformation, as was found previously[27,29]. On the other hand, it is also important to note that the Raman band shifts to higher frequencies under axial compressive deformation. Some broadening of the Raman band with straining (both in tension and in compression) can also be seen in *Figure 4*, indicating that the deformation of the polydiacetylene moieties at the molecular level in the copolymer is not necessarily uniform.

Figure 5 illustrates the correlations between the Raman frequency of the C≡C stretching mode, Δν, in the copolymer upon the overall strain (up to ±1%). An approximately linear relationship is found in both

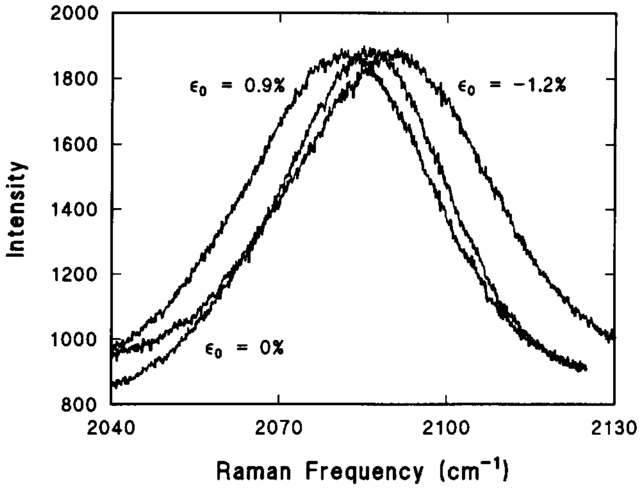

Figure 4 Variation of the position of the 2090 cm^{-1} Raman band for a sample of the diacetylene-containing urethane copolymer, undeformed and subject to tensile (positive) and compressive (negative) deformation

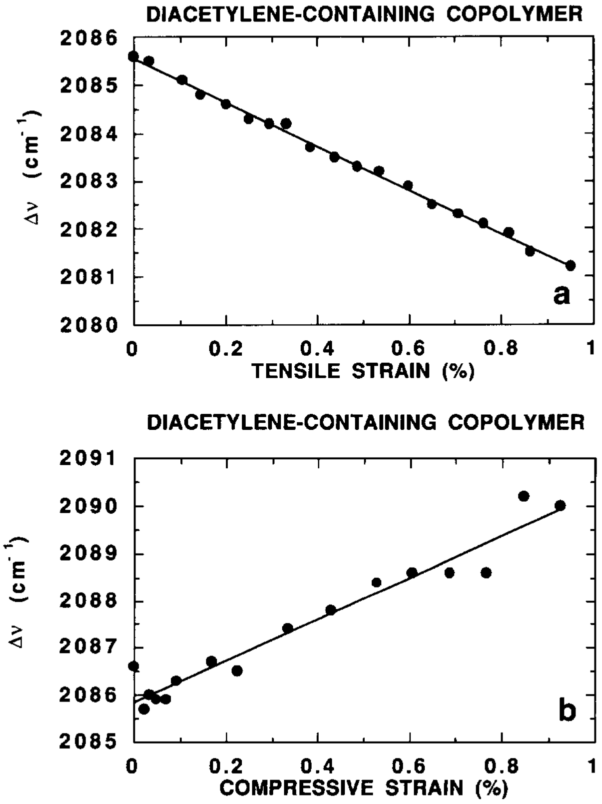

Figure 5 Dependence of the peak position of the C≡C stretching mode Raman band for the diacetylene-containing urethane copolymer upon: (a) tensile strain and (b) compressive strain

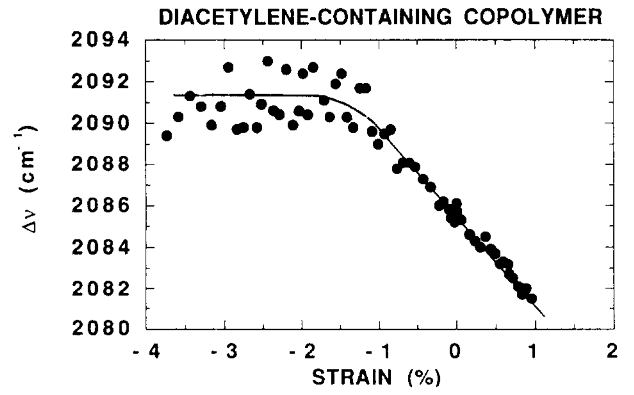

Figure 6 Dependence of the peak position of the $\mathrm{C{\equiv}C}$ stretching mode Raman band upon strain, both tensile (positive) and compressive (negative), for the diacetylene-containing urethane copolymer

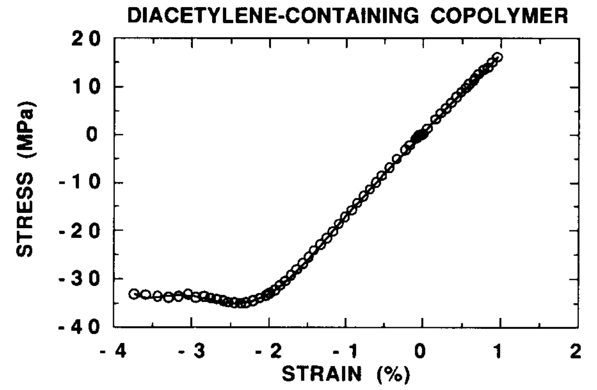

Figure 7 Tensile compressive stress–strain curve for the diacetylene-containing urethane copolymer

the tensile and compression experiments up to this strain level. A linear least squares fitting of the data shows that the rate of the Raman frequency shift with strain in compression, $[d(\Delta\nu)/d\varepsilon]_{\mathrm{COMP}}$, is similar to that in tension, $[d(\Delta\nu)/d\varepsilon]_{\mathrm{TENS}}$, being equal to 4.5 ± 0.6 and $4.8 \pm 0.4\,\mathrm{cm}^{-1}/\%$ respectively. This implies that the macroscopic deformation of the copolymer is transferred directly into molecular deformations of the polydiacetylene chains in the hard segment aggregates. This strain dependence of the Raman frequency also enables elastic strain to be measured in the copolymer by using Raman spectroscopy for any general state of stress or strain[29].

Figure 6 is a combined plot of Raman frequency $\Delta\nu$ *versus* strain ε in the range -4% to 1% (where the negative sign indicates an axial compression). The corresponding stress–strain (σ–ε) curve, measured simultaneously by using the Minimat, is presented in *Figure 7*. The sample fractured in tension without yielding at approximately 1% strain, but in compression the material behaved in a more ductile manner and underwent plastic deformation in a similar manner to other glassy polymers[30]. Similar formulations of the same material have been reported[27] to have tensile fracture strains of up to approximately 3%. In compression, a deviation from linearity in the $\Delta\nu$–ε curve (see *Figure 6*) was observed at $>1\%$ compressive strain. This is thought to be due predominantly to the plastic deformation occurring in the poly(ether–urethane) phase. It can also be seen that a large scatter of the data develops after the onset of plastic deformation. This is due to the deformation mechanisms of the copolymer in compression where it was found by using optical microscopy that shear bands[30] formed after compressive yielding, giving rise to considerable strain heterogeneity and the consequent scatter in the Raman data which are obtained only from $\approx 2\,\mu\mathrm{m}$ regions of the copolymer.

The $\Delta\nu$–ε curve in *Figure 6* is essentially a molecular stress/strain curve for the glassy copolymer and this can be compared with the macroscopic σ–ε curve of *Figure 7*. It can be seen that the two curves essentially mirror each other and yield takes place at a similar strain in the two cases, but with the Raman data showing significant local variations of strain, due to the formation of shear bands making the yield point more difficult to define.

Angular strain measurement using Raman spectroscopy

Measurements were made of the dependence of the Raman frequency, $\Delta\nu$, upon the angle, θ, between the direction of polarization of the laser beam and the tensile deformation axis of the samples. *Figure 8* shows plots of the Raman frequency, $\Delta\nu$, of the copolymer *versus* the angle, θ, at three different strain levels (0.4, 0.7 and 0.9%). In the undeformed state, the Raman frequency $\Delta\nu$ is independent of the θ, confirming that the material is structurally isotropic. Once the copolymer is deformed, however, the Raman frequency is strongly dependent upon θ. This means that the molecular deformation in the polydiacetylene chains is strongly related to the direction of the laser beam polarization with respect to the principal stress axis. In this case, $\Delta\nu$ increases as the angle θ increases over the range from 0 to 90° for all of the three strain levels that were tested, indicating a decreasing level of tensile strain with an increase in θ. The copolymer may be considered to be essentially a molecular composite with the polydiacetylene molecules acting as the 'fibres' which reinforce the hard segment aggregates which are randomly dispersed in the poly(ether–urethane) matrix phase. Since the Raman scattering comes predominantly from the polydiacetylene molecules which are oriented parallel to the direction of polarization of the laser beam, the Raman frequency, $\Delta\nu$ (measured at an angle θ) essentially measures only the deformation of

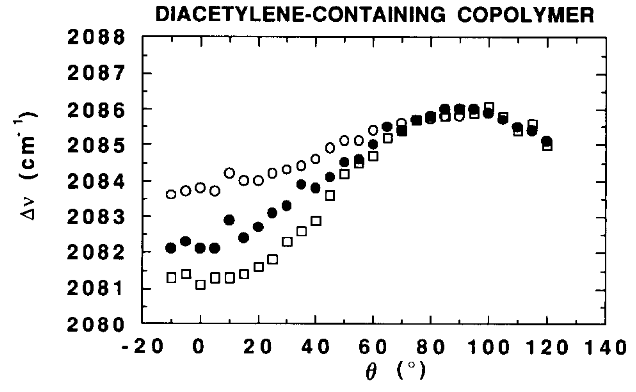

Figure 8 Dependence upon the angle θ of the peak position of the $\mathrm{C{\equiv}C}$ stretching mode Raman band for the diacetylene-containing urethane copolymer, measured at three different levels of tensile strain: ○, 0.4%; ●, 0.7%; and □, 0.9%

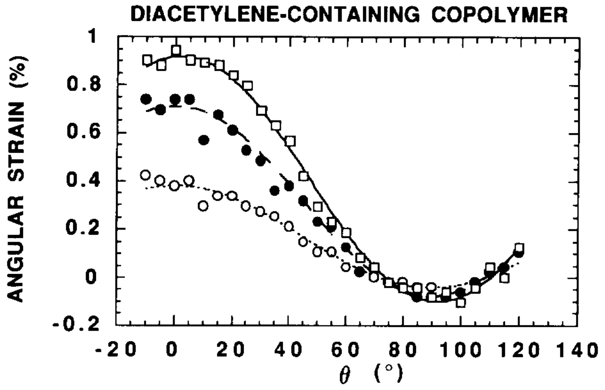

Figure 9 Variation of the derived values of the angular strain as a function of the angle θ for the diacetylene-containing urethane copolymer. The lines are derived from equation (1) by using a value of Poisson's ratio, ν, of 0.11: ○, 0.4%; ●, 0.7%; and □, 0.9%

the polydiacetylene chains oriented in that particular direction in the copolymer.

It was shown in *Figure 6* that Raman spectroscopy can be used for measurement of both the tensile and compressive strain since the Raman frequency of the C≡C stretching mode of the copolymer had a similar strain dependence in both tension and compression. Hence the $\Delta\nu$ values measured at various angles in *Figure 8* can be converted into strain values, ε_θ, by using the average value of the elastic tensile and compressive strain dependence of the Raman frequency, which is 4.7 cm^{-1}/% strain for this material (see *Figure 5*). These Raman-measured strain values are plotted in *Figure 9* as a function of the angle θ. The tensile strain decreases with increasing angle (over the range from 0 to 90°) and eventually becomes compressive at angles greater than 70° due to the transverse Poisson's contraction.

Data analysis was also carried out using classical elasticity theory[31] for isotropic elastic materials (see Appendix); this has shown that the angular strain, ε_θ, should be related to the axial strain through the following equation:

$$\varepsilon_\theta=\varepsilon_0(\cos^2\theta-\nu\sin^2\theta) \quad (1)$$

where ε_0 is the principal strain ($\theta=0$) and ν is the Poisson's ratio of the material.

Although this equation describes the general form of the relationship in *Figure 9* there was only poor agreement between the experimental data and theory when a Poisson's ratio of 0.39 for the copolymer (measured using resistance strain gauges) was used. The experimental data were found, however, to be in very good agreement with the theory when a Poisson's ratio of 0.11 was used. The apparent difference in this ratio may be due to the copolymer having a phase-separated structure. The macroscopic Poisson's ratio is a reflection of the deformation of the two-phase material, whereas the Raman technique follows only the deformation of the diacetylene-containing hard segments. It appears that during the transverse Poisson's contraction of the material, the hard segments are subjected to a lower strain than the low-modulus matrix, meaning that the apparent Poisson's ratio measured by using Raman spectroscopy is less than that measured macroscopically (determined by resistance strain gauges).

CONCLUSIONS

The strain dependence of the C≡C triple bond stretching mode of the diacetylene-containing copolymer has been established for both tensile and compressive deformation. The Raman band shifts to a lower frequency when the copolymer is subjected to tensile deformation and shifts to a higher frequency when the material is deformed in compression. The levels of frequency shift per unit strain were virtually the same in tension and in compression at small strain levels ($<1\%$). Using Raman spectroscopy it has also been possible to measure the strain in the deformed copolymer as a function of the angle between the tensile axis and the direction of polarization of the laser beam. The experimentally determined angular strain data were found to be in good agreement with those calculated using classical elasticity theory.

ACKNOWLEDGEMENTS

The work was supported by a research grant from the SERC. One of the authors (RJY) is grateful to the Royal Society for support in the form of a Wolfson Research Professorship.

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APPENDIX

Elasticity analysis

Raman spectrocopy measurements have been made of the dependence of the strain in the diacetylene-containing copolymer upon the angle of the laser beam polarization with respect to the tensile axis. The problem involves the deformation of the infinitesimally small unit in the material that is probed by the laser beam, with the latter polarized at an angle θ to the stress axis (as shown in *Figure A1*). The strain in the x-direction in the unit, at an angle θ to the principal stress axis, may be measured by Raman spectroscopy by utilizing the polarization of the laser beam.

Since the copolymer absorbs the light strongly at the frequency of the laser that is used, the laser beam is only probing the deformation of the surface of the material. There cannot be any stress perpendicular to the free surface[30] and hence it is essentially a plane stress problem in the $(x-y)$ plane, as shown in *Figure A1*. It must also be assumed that the material is elastically isotropic and that the deformation is linear elastic.

The stress in the x-direction in the unit is given by[31]

$$\sigma_x = \sigma \cos^2 \theta \tag{A1}$$

and the corresponding stress in the y-direction is given by[31]

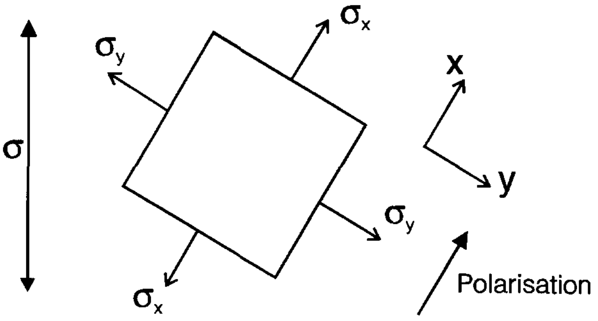

Figure A1 Schematic illustration of the deformation of an infinitesimally small element in a material where the direction of polarization of the laser beam is at an angle (θ) to the tensile axis

$$\sigma_y = \sigma \sin^2 \theta \tag{A2}$$

while the strain in the x-direction in the unit, ε_x is given by[31]

$$\varepsilon_x = \frac{1}{E}(\sigma_x - \nu\sigma_y) \tag{A3}$$

where ν is the Poisson's ratio of the material and E is its Young's modulus. Combining equations (A1)–(A3) gives

$$\varepsilon_x = \frac{\sigma}{E}(\cos^2 \theta - \nu \sin^2 \theta) \tag{A4}$$

Hence, if ε_0 $(=\sigma/E)$ is the axial strain, as measured by the strain gauge aligned parallel to the tensile axis, then

$$\varepsilon_x = \varepsilon_0(\cos^2 \theta - \nu \sin^2 \theta) \tag{A5}$$

This gives the relationship between the axial strain and the strain measured at an angle θ to the tensile axis.