Molecular Deformation and Optomechanical Behavior of Glassy Diacetylene-Containing Segmented Block Copolyurethanes

Xiao Hu, John L. Stanford, Richard J. Day, and Robert J. Young*

Polymer Science and Technology Group, Materials Science Centre, University of Manchester and UMIST, Manchester M1 7HS, England

Received June 7, 1991

ABSTRACT: The mechanical and optomechanical behavior of glassy, diacetylene-containing, segmented copolyurethanes has been investigated. The polydiacetylene chains formed via solid-state cross-polymerization in the hard segment domains not only reinforce mechanically the copolymers at the molecular level but also confer on them optical properties similar to those of polydiacetylene single crystals. Resonance Raman spectroscopy is shown to be a powerful technique for structural characterization and as an optical strain probe for the study of copolymer deformation. During deformation, the C≡C triple bond stretching band in the Raman spectra of the diacetylene-containing copolymers was found to shift to lower wavenumbers by over -6 cm^{-1}/%, compared to -20 cm^{-1}/% for polydiacetylene single crystals. The relationship between the Raman band position and overall copolymer strain provides information about the molecular deformation of the polydiacetylene chains in the hard segment domains. Furthermore, it enables the strain in the copolymers to be measured by monitoring the Raman band position. The results clearly demonstrate, in these materials, the achievement of a unique combination of the optical properties of polydiacetylenes with the mechanical behavior and processibility of polyurethanes. These copolymers thus represent a new class of optically stress-strain sensitive, isotropic materials (optical strain sensors) which can be readily processed into and used in a variety of forms including fibers, films, bulk sheets, surface coatings, and composites.

Introduction

Previous studies have shown that the positions of bands in the Raman spectra of many oriented fibers shift substantially when the fibers are subjected to stress or strain. Such fibers include polydiacetylene single crystals,[1-5] aromatic polyamides,[6,7] poly(*p*-phenylenebenzobisthiazole),[8] gel-spun polyethylene,[9-11] and carbon fibers.[12,13] Polydiacetylene single crystals, in particular, give intense, well-defined resonance Raman spectra which exhibit the highest strain sensitivity, with C≡C triple-bond stretching bands shifting by as much as -20 cm^{-1} per 1% tensile strain. The mechanical deformation applied to these materials produces direct deformation of the covalent bonds in the macromolecular backbones, and the resulting changes in bond lengths and angles give rise to the shift in the vibrational frequency of a particular Raman band. This is related to the anharmonicity of the bond vibration.[2] Analysis of this phenomenon allows a unique study of the deformation in materials at the molecular level. In fact, Raman spectroscopy has been used successfully to measure stresses and strains in highly oriented fibers and to study in detail the micromechanics of fiber-reinforced composites. However, despite its success with highly oriented fibers and their composites, the use of Raman spectroscopy to study the deformation of less oriented polymers, such as conventional polyamides, polyesters, and polypropylenes, has produced relatively limited results. The values of the strain sensitivity of Raman bands reported for these materials[14,15] are disappointingly small (≈ 0.5 cm^{-1}/% strain). Hence, the use of Raman spectroscopy to measure the deformation in these materials is impractical.

The main objective of the present study was to develop novel alternative isotropic or pseudoisotropic, optically strain-sensitive materials with tailor-made mechanical properties. Ideally, these materials should produce well-defined Raman spectra with bands sufficiently sensitive to deformation. It is also desirable for such materials to be easily processed into various shapes and forms, such as films, coatings, fibers, and composite matrices. Such a combination of properties can be achieved in multiphase polymers by incorporating an optically strain-sensitive phase into a matrix either through copolymerization or through physical blending.

In this work, polydiacetylene chains were chosen as the strain-sensitive species and were formed in situ via thermally induced solid-state, topochemical cross-polymerization within the paracrystalline, diacetylene-containing copolyurethane hard-segment domains which were distributed uniformly throughout the continuous amorphous matrix. The preparation and systematic structural characterization of a wide range of diacetylene-containing copolymers have been described in a previous publication.[16] The polydiacetylene chains within the hard-segment domains act as optically active centers, which give the copolymers well-defined Raman spectra similar to those of the polydiacetylene single crystals. The question that arises is whether the Raman bands in these copolymers shift sufficiently upon deformation, as in highly oriented fibers, in order that values of stress and strain in the copolymers can be measured accurately using Raman spectroscopy. It is clear that the rates of the Raman band shift (in cm^{-1}/% strain) depend mainly on the efficiency of transfer of macroscopic deformation, applied to the copolymers, into molecular deformation of the polydiacetylene chains formed within the hard-segment domains. This in turn is controlled by the morphological structure of the copolymers and the mechanical properties of both the hard segments and the matrices. This paper describes the mechanical behavior of the copolymers with special emphasis on their unusual optomechanical behavior observed using resonance Raman spectroscopy.

Experimental Section

A. Materials. The glassy diacetylene-containing segmented block copolyurethanes were prepared via a one-shot bulk polymerization process[16] using starting materials of 4,4′-diphenylmethane diisocyanate (MDI), poly(propylene glycol) (PPG, $M_n \approx 400$), and 2,4-hexadiyne-1,6-diol (HDD). In some cases, a

---

* To whom all correspondence should be addressed.

0024-9297/92/2225-0684$03.00/0

second short-chain diol, dipropylene glycol (DPG), was also included. Two specifically designed series of copolymers were produced, one without DPG but with various HDD/MDI hard-segment contents (0–34% by weight) and the other using various amounts of DPG (0–5% by weight) at approximately constant hard-segment content (33% by weight). The copolymers were coded as P[*x*D*y*H] where *x* and *y* signify, respectively, the amounts of DPG and HDD used in preparation of the materials. Structure–property relationships in these copolymers were investigated using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and wide-angle X-ray diffraction (WAXD).[16] The copolymers were shown to be phase-separated, rigid materials at room temperature with T_g up to 98 °C (DMTA). Transmission electron microscope (TEM) micrographs showed clearly that the micron-sized, spherulitic, diacetylene-containing hard-segment domains were dispersed uniformly throughout the continuous poly(ether–urethane) matrices.[16]

B. Cross-Polymerization. Solid-state cross-polymerization of the copolymers was effected by thermal treatment of the samples at elevated temperatures. Thermal treatment conditions were optimized by monitoring the glass transition temperature (DSC) and the intensities in Raman scattering, as described in detail elsewhere.[16] The samples studied here were cross-polymerized using optimal conditions of 100 °C for 40 h. The initially soluble and light-colored, as-prepared copolymer precursors were transformed, after thermal treatment, into insoluble, infusible, and deeply colored materials. This transformation occurs by 1,4-addition polymerization of the diacetylene monomers within the paracrystalline hard-segment domains, giving rise to nonrandom cross-linking in the hard segments, and the resulting polydiacetylene chains confer on the copolymers unique optical properties. A schematic procedure of the cross-polymerization in the diacetylene-containing, MDI/HDD, hard segments is illustrated in Figure 1.

C. Mechanical Testing. Segmented copolyurethanes can be prepared so as to produce a variety of materials ranging from soft flexible elastomers to rigid, glassy thermoplastics or thermosets.[17] Similarly, the mechanical properties of the segmented, diacetylene-containing copolyurethanes investigated in the present study are controlled by chemical structure and the relative proportions of the reactants used to prepare the copolymers, as well as by the extent of cross-polymerization achieved subsequently in the hard-segment domains. The mechanical properties of the copolymers were determined using an Instron 1121 mechanical testing machine operated in the tensile mode. The cross-polymerized copolymers prepared in the form of sheets were machined into dumb-bell specimens with a nominal gauge length of 40 mm. The tensile tests were carried out at room temperature at a strain rate of 2.1×10^{-4} s^{-1}. The initial strains (<2.0%) were determined accurately using resistance strain gauges attached to the specimens, and the higher strains were calculated from crosshead displacements.

D. Analysis of the Strain Dependence of the Raman Band Position in the Diacetylene-Containing Copolymers. The Raman spectra of the copolymers were obtained using the 632.8-nm line of a 10-mW He/Ne laser (1 mW on the samples). A modified Nikon optical microscope with a 40× objective lens of 0.65 numerical aperture was used to focus the incident laser beam to a 2-μm spot on the specimen. The 180° back-scattered light was collected by the same objective lens and analyzed using a Spex 1403, 0.85-m double monochromator with 1800 grooves/cm gratings. A charge-coupled device, CCD (Wright Instruments), cooled with liquid nitrogen was employed to detect the Raman scattering with approximately 0.1-cm^{-1} resolution. The CCD has proved to be a low noise detector with high sensitivity and efficiency,[18] such that the typical scanning time in this work was 10 s for a window of 40 cm^{-1}. The strain dependence of the Raman band positions in the copolymers was determined by the deformation of the copolymers under the Raman microscope using a Polymer Laboratories miniature materials tester (MiniMat) with a 1000 N load cell operated in the tensile mode. This enabled the in situ measurement of the Raman spectra while the samples were being deformed or held at a constant stress or strain.

Bulk-polymerized copolymer samples were thermally cross-polymerized and machined into miniature dumb-bell specimens.

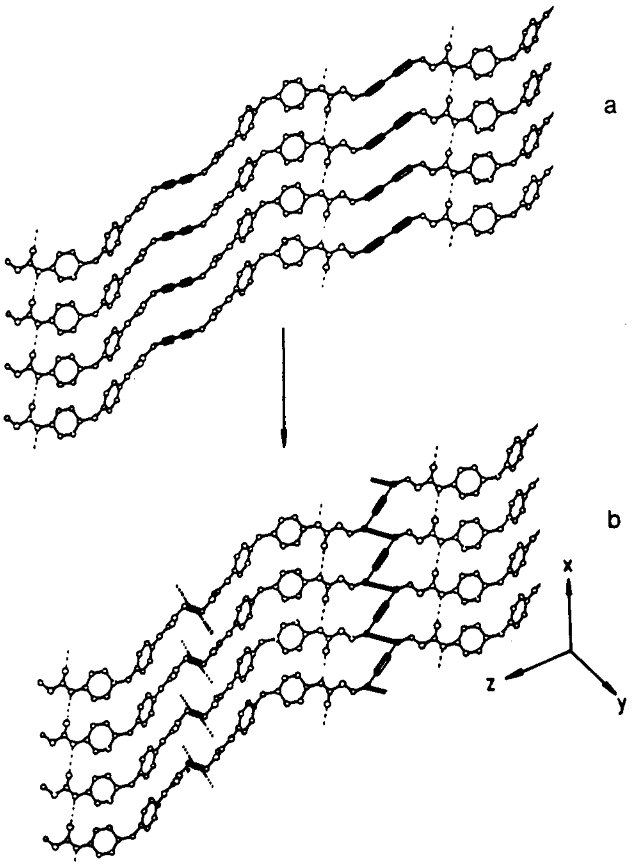

Figure 1. Schematic representation of the solid-state cross-polymerization within diacetylene-containing hard-segment domains. The idealized structures of MDI/HDD hard segments are shown (a) before and (b) after cross-polymerization. The direction of polyurethane chains is along the *z*-axis, and the directions of polydiacetylene backbones are along the *x*- and *y*-axes.

Specimens were also obtained by coating 10 wt % solutions of the as-prepared copolymer precursors in *N,N′*-dimethylacetamide (DMAc) onto various substrates including glass fibers, plastics, or metals and then allowing the cross-polymerization to occur in the thin coating layer (<0.1 mm) by heat treatment at 100 °C for 40 h after complete solvent evaporation.

Calibration of the relationship between the Raman peak positions for the copolymers and the externally applied strains was performed by stretching the samples stepwise under the Raman microscope and obtaining the Raman spectrum immediately after each step. The specimens were deformed at a speed of 1 mm/min with about 0.1% strain increment for every step. A resistance strain gauge, which monitored the strain to an accuracy of ±0.0014%, was attached to each sample with a special adhesive (Micro-measurements Group Inc., M-Bond 200). In the case of the coated glass fibers, a microstretching rig was employed to deform the single filaments. In all of the deformation studies in the Raman microscope, the incident laser beam was always polarized parallel to the tensile direction.

Results and Discussion

A. Stress/Strain Behavior of the Diacetylene-Containing Copolymers. Figure 2 illustrates the tensile stress/strain curves for the cross-polymerized diacetylene-containing copolyurethanes with various levels of HDD/MDI hard-segment content. The stress/strain curves for the copolymers formed using various amounts of the additional short-chain diol (DPG) are shown in Figure 3. The corresponding tensile data are tabulated in Tables I and II. The Young's modulus (*E*) was taken as the initial slope of the stress/strain curve, and the yield stress (σ_y), strain (ϵ_y), and fracture strain (ϵ_f) are also given. It can

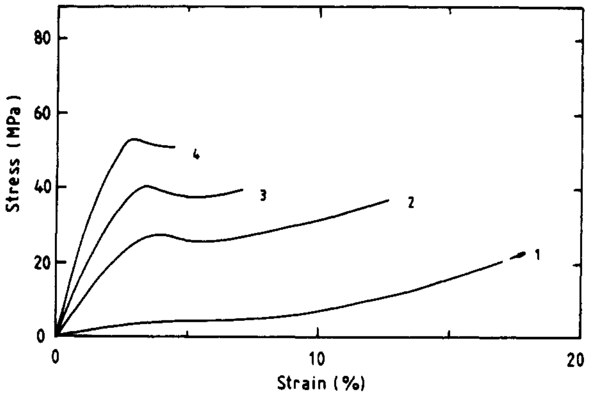

Figure 2. Stress/strain curves of the diacetylene-containing copolymers formed with various HDD contents: (1) 3.7% (P[0D5H]); (2) 5.7% (P[0D10H]); (3) 8.3% (P[0D15H]); (4) 10.4% (P[0D20H]).

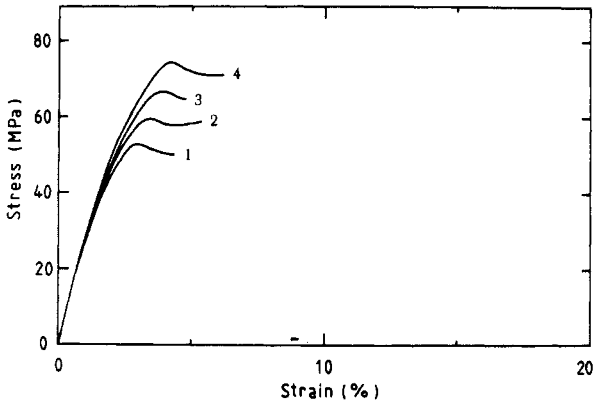

Figure 3. Stress/strain curves of the copolymers formed with various DPG contents: (1) 0% (P[0D20H]); (2) 1.94% (P[5D20H]); (3) 3.62% (P[10D20H]); (4) 5.08% (P[15D20H]).

Table I
Effect of HDD Content upon the Tensile Properties of the Copolymers

copolymer	w_{HDD} (%)	w_{HS} (%)	E (GPa)	σ_y (MPa)	ϵ_y (%)	ϵ_f (%)
P[0D0H]	0	0	0.005	*a*	*a*	450
P[0D5H]	3.7	12	0.12	*a*	*a*	27.5
P[9D10H]	5.7	19	0.93	24.3	3.9	12.2
P[0D15H]	8.3	27	1.54	39.9	3.5	7.3
P[0D20H]	10.4	34	1.66	51.2	3.0	4.5

[a] Yield point not observed.

Table II
Effect of DPG Content upon the Tensile Properties of the Copolymers

copolymer	w_{DPG} (%)	w_{HS} (%)	E (GPa)	σ_y (MPa)	ϵ_y (%)	ϵ_f (%)
P[0D20H]	0	34	1.66	51.2	3.0	4.5
P[5D20H]	1.94	33	1.70	58.7	3.4	5.3
P[10D20H]	3.62	32	1.78	62.6	3.9	4.8
P[15D20H]	5.08	32	1.72	66.9	4.3	6.7

be seen that Young's modulus (E) and yield stress (σ_y) increase steadily with increasing hard-segment content. This is mainly achieved through the increase in concentration of the diacetylene-containing phase which, after cross-polymerization, both acts as a rigid/strong polydiacetylene filler and provides chemical cross-links in the relatively ductile poly(ether–urethane) matrix and hence greatly enhances the rigidity of the copolymers. As a result, the fracture strain decreases drastically with increasing hard-segment phase content. An increase in yield stress is also found with an increase in the amount of DPG used in the preparation of the copolymers as shown in Figure 3. This may be explained as being due to the increase in the level of hydrogen bonding in the copolymers when the relatively long polyether chains of PPG400 are replaced by the shorter ones of DPG. However, a less significant change in Young's modulus is found for the copolymers formed using increasing amounts of DPG. This may appear to be somewhat anomalous since DPG/MDI units are stiffer than PPG400/MDI ones, and as the content of the former increases, an increase in the overall rigidity of the copolymers is expected. However, in the case of the diacetylene-containing copolyurethanes, the hardening effect of DPG/MDI units may be partially canceled out by changes in copolymer morphology. As reported previously,[16] the inclusion of a small amount of DPG was shown to cause severe disruption of the HDD/MDI hard-segment domains, which in turn causes a reduction in the number and size of the reinforcing polydiacetylene chains as well as a reduction in the chemical cross-links formed upon cross-polymerization.

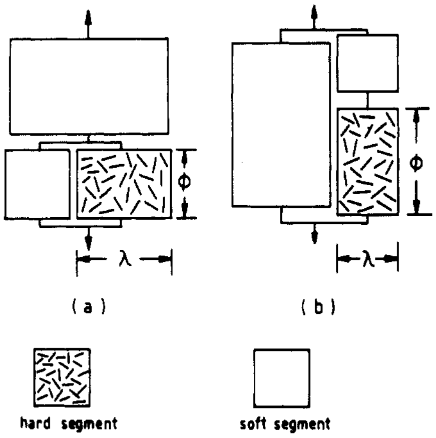

Figure 4. Schematics of the general forms of the Takayanagi model: (a) series-parallel; (b) parallel-series.

B. Modulus Modeling: Takayanagi Model. The elastic properties of multiphase polymer blends, copolymers, and composites can be predicted[19–21] by several theories in terms of the elastic properties and relative proportions of each constituent phase. As indicated previously, the copolymers studied are essentially composites in which the polydiacetylene-containing hard segments reinforce the ductile poly(ether–urethane) matrices. Since the hard segments in the copolymers have a similar chemical structure, as shown in Figure 1, it is reasonable to assume that they have similar properties, particularly, a similar Young's modulus. It should be possible to determine the effective hard-segment modulus (E_{HS}) using composite theories since the moduli of the unreinforced soft segments and the reinforced copolymer composites can be obtained experimentally and the hard-segment contents are known for all materials. In the present study, an analysis has been carried out using the Takayanagi models,[21] which have two general forms, namely series-parallel and parallel-series as illustrated in Figure 4. It is known[16] that the poly(ether–urethane) is the continuous matrix phase; hence, the relevant equations for the copolymer composite modulus (E_C) are

$$\frac{1}{E_C} = \frac{1-\phi}{E_M} + \frac{\phi}{\lambda E_{HS} + (1-\lambda)E_M} \tag{1}$$

for the series-parallel model and

$$E_C = \left[\frac{(1-\phi+\phi\lambda)E_{HS} + \phi(1-\lambda)E_M}{(1-\phi)E_{HS} + \phi E_M}\right]E_M \tag{2}$$

for the parallel-series model, where E_M is the matrix

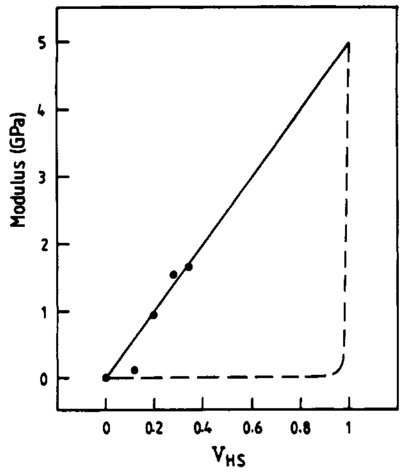

Figure 5. Plot of copolymer modulus versus hard-segment volume fraction showing that the moduli of the copolymers with higher hard-segment contents agree well with the Takayanagi model when ϕ is equal to 1.0 (parallel model): full circles, experimental data; solid line, parallel model; dashed line, series model.

modulus and ϕ and λ are the volume fractions of the hard segments parallel and perpendicular with respect to the tensile axis. Thus, the volume fraction of the hard segments (V_{HS}) is given by

$$V_{HS} = \phi\lambda \qquad (3)$$

and is approximately equal to the weight fraction of the hard segments (W_{HS}), assuming similar densities for the HDD/MDI and PPG400/MDI phases.

Figure 5 is a plot of the modulus E_C as a function of volume fraction of hard segment (V_{HS}), and the results show that the moduli of the three copolymers with higher hard-segment contents are in reasonable agreement with the predictions of Takayanagi model when ϕ equals to unity and when a hard-segment modulus of 5 GPa is chosen. A value of unity for ϕ reduces the Takayanagi model to the simple parallel case. The copolymer with the lowest diacetylene-containing hard-segment content (P[0D5H]) can also be fitted to the Takayanagi models by the selection of suitable ϕ values, which are found to be equal to 0.9660 for the series-parallel model and 0.9957 for the parallel-series model. This may be attributed to the morphological differences between copolymer P[0D5H] and the other copolymers since this copolymer contains only a very small amount of HDD/MDI hard segments and has a microstructure significantly different from the other copolymers as described previously.[16]

The conclusion is that the theoretical modeling of the tensile moduli of the copolymers gives the prediction of the modulus of the diacetylene-containing (MDI/HDD) hard segments as 5 GPa, and it is worth considering if this is a reasonable estimate. The modulus of MDI/EG (ethylene glycol) polyurethane hard segments is about 3 GPa.[22] Therefore, it is not unreasonable to assume that the uncross-polymerized MDI/HDD hard segments would also have a modulus of at least 3 GPa. Nevertheless, after cross-polymerization, the hard segments may be envisaged as molecular composites, with the polydiacetylene chains formed in situ acting as the reinforcement at the molecular level. Figure 1 implies that the cross-polymerized hard segments have a three-dimensional network structure and in reality the hard segments are only paracrystalline. Therefore, the hard segments can be treated mechanically as three-dimensional randomly distributed fiber-reinforced composites. In this case, the "fibers" are the extended polydiacetylene molecular chains. Hence, according to the rule of mixtures under a uniform-strain condition[23]

$$E_{HS} = \eta_0\eta_1E_1V_1 + E_2(1 - V_1) \qquad (4)$$

where E_{HS}, E_1, and E_2 are the moduli of the cross-polymerized hard segments, the polydiacetylene chains, and the hard segments without reinforcement, respectively. V_1 is the volume fraction of the polydiacetylene backbones in the hard segments, which is estimated to be 0.133 from the stoichiometry of the reaction assuming 100% conversion for the solid-state cross-polymerization. η_0 is an orientation efficiency factor of the high-modulus polydiacetylene chains in the hard segments, equal to 0.2 for three-dimensional random distribution.[23] η_1 is a length correction factor, which is taken as unity since the polydiacetylene backbones should have high aspect ratio.[23] Young's moduli of polydiacetylene single crystals are typically 40–60 GPa in the chain direction, and the theoretical modulus of a polydiacetylene backbone without side groups is about 250 GPa.[4] Hence, a value of 9.25 GPa is calculated for the modulus of the hard segments using eq 4. This value is somewhat higher than 5 GPa, which was estimated from mechanical measurements. However, this is not unexpected given the possible imperfection of hard-segment crystallization and hence less than 100% conversion of the solid-state cross-polymerization.

It should be noted that the hard-segment modulus predicted by the Takayanagi model is the average modulus since the copolymers are macroscopically isotropic and the hard segments are randomly oriented. When the copolymers are deformed, stress and strain are transferred to the hard segments from the continuous poly(ether–urethane) matrix. The localized hard-segment deformation in relation to the overall deformation of the copolymers is mainly controlled by the relative moduli of and the degree of adhesion between the two phases. However, the fact that the three copolymers fit well in the parallel model implies that the average strain in the hard segments is similar to the overall strain on the specimens for these copolymers during deformation. This is very significant since it will be shown that a key point of this work was to achieve maximum stress transfer into the diacetylene-containing, hard-segment phase. It will be demonstrated that Raman spectroscopy provides a unique method to examine the details of the localized deformation at molecular level. A further discussion of the molecular deformation of the polydiacetylene species in the hard segments will be presented later in conjunction with the results from Raman spectroscopy measurements.

C. Strain Dependence of Raman Bands in the Diacetylene-Containing Copolyurethanes. The cross-polymerized diacetylene-containing copolymers were shown in a previous paper to have well-defined Raman spectra.[16] Figure 6 illustrates a typical resonance Raman spectrum of the diacetylene-containing copolymer P[0D20H]. The intensities in Raman spectra are closely related to the concentration of the diacetylene units in the copolymers, to the conditions for cross-polymerization, and also to the morphological structures of the copolymers.[16] It is well-known[2-4] that the intensities of Raman spectra of the polydiacetylene single crystals are dependent upon the direction of the polarization of the incident laser beam in respect to the chain axis. Intense spectra are only obtained when the laser is polarized parallel to the chain axis, while only very weak signals can be obtained when the laser polarization is perpendicular to the chain direction. This demonstrates the high degree of optical anisotropy of the single crystals. In contrast, the diacetylene-containing

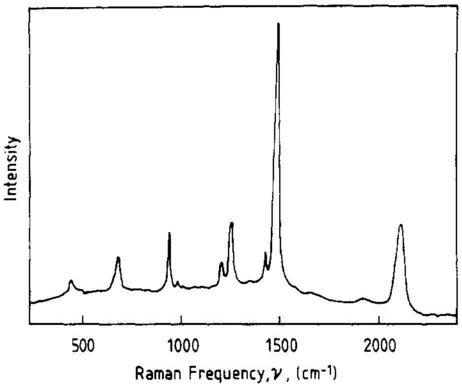

Figure 6. Raman spectrum of the cross-polymerized diacetylene-containing copolyurethane P[0D20H].

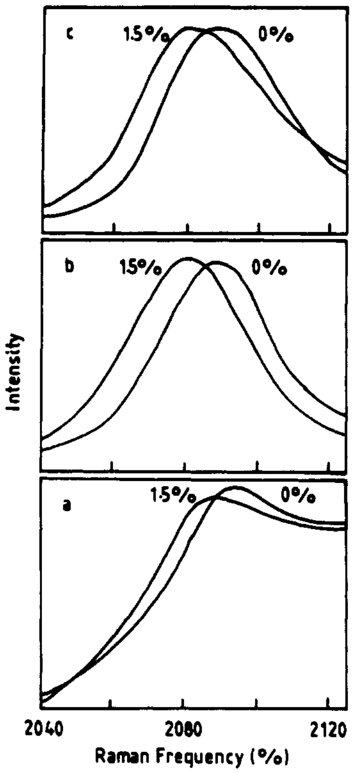

Figure 7. Raman spectra for the C≡C triple-bond stretching band of the copolymers before and after tensile deformation: (a) P[0D15H]; (b) P[0D20H]; (c) P[5D20H]. Values of strain are also indicated.

copolymers are optically isotropic and the Raman signals are independent of the direction of the laser polarization since the polydiacetylene molecules are randomly oriented in the hard-segment domains throughout the copolymers. Since the C≡C triple-bond stretching band in the spectra of polydiacetylene single crystals is known to possess the highest strain sensitivity,[5] the 2090-cm^{-1} C≡C stretching band in the diacetylene-containing copolymers was selected as the diagnostic band to monitor strain in the present study. No attempt has been made to measure the strain sensitivity of the C=C double-bond stretching bands or of the other vibrational bands in the copolymers since they were known[5] to have much lower strain sensitivities.

It was found that the C≡C triple-bond stretching bands in the copolymers shifted to a lower wavenumber coupled with a gradual band broadening when the copolymers were subjected to tensile strain, as shown in Figure 7 for some typical samples. The shifts in the band position clearly indicate that the overall mechanical deformation in the copolymers is translated directly into deformation of the polydiacetylene molecules formed in the hard-segment domains, and the band broadening suggests that there is a distribution of strain levels between the individual polydiacetylene chains.

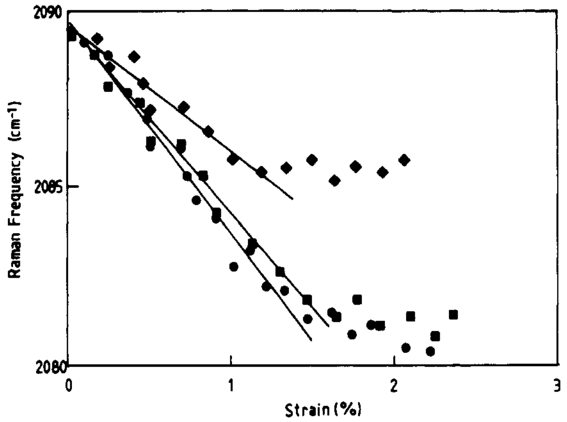

Figure 8. Strain dependence of the Raman band position (ν) for the C≡C triple-bond stretching mode in the copolymers: (◆) P[0D15H]; (●) P[0D20H]; (■) P[5D20H].

Table III
Strain Sensitivity of the Frequency of the C≡C Triple-Bond Stretching Band in the Diacetylene-Containing Copolymers

copolymer	W_{HDD} (%)	W_{HS} (%)	$\Delta\nu/\Delta\epsilon$[a] (cm^{-1}/%)
P[0D0H]	0	0	*b*
P[0D5H]	3.7	12	*b*
P[0D10H]	5.7	19	*c*
P[0D15H]	8.3	27	3.8 ± 1.0
P[0D20H]	10.4	34	6.2 ± 0.4
P[5D20H]	10.2	33	5.3 ± 0.4
P[10D20H]	9.9	32	*c*
P[15D20H]	9.7	32	*b*
single crystals			20 ± 0.5[d]

[a] Δν and Δε are the Raman band shift and the overall strain in the copolymers. [b] No detectable Raman signals. [c] Very weak Raman signal unsuitable for strain measurements. [d] Value obtained when the laser was polarized parallel to the fiber axis (direction of deformation).[2-4]

Figure 8 illustrates the relationship between the Raman peak position (ν) and the overall copolymer strain (ε) for three of the diacetylene-containing copolymers. A linear relationship is found to about 1.5% strain in copolymers P[0D20H] and P[5D20H] but only to 1% strain for P[0D15H]. The deviation from the linearity at higher strain is attributed to plastic deformation occurring in the continuous ductile matrix. Table III lists the strain sensitivities of the band position for the C≡C triple-bond stretching mode for the different copolymers. The values are given in reciprocal centimeters shifted per 1% mechanical strain (Δν/Δε), which are calculated from the initial linear part of the plots shown in Figure 8. These data demonstrate clearly that the optomechanical behavior of the copolymers is readily modified through careful control of copolymer composition, thermal treatment, and morphology.

High values of Δν/Δε of the order of ∼6 cm^{-1}/% were obtained for the diacetylene-containing copolymers with spectra which are sufficiently well-defined for Raman strain measurement. Although the shifts in the copolymers are considerably smaller than those obtained in polydiacetylene single crystals, it is still possible to measure the deformations in the copolymers to an accuracy of 0.1% strain with a spatial resolution of 2 μm, under the present conditions, through monitoring of the Raman band positions once the correlation between the Raman band frequency and the applied strain has been established (Table III). The stress- or strain-induced Raman frequency shifts for the cross-polymerized diacetylene-containing copolymers also give unique insight into the micromechanics of the deformation of the hard segments in relation to the overall deformation in the materials.

Raman spectroscopy is being used as an optical stress or strain probe to monitor the deformation of the polydiacetylene chains which are formed in situ and are randomly distributed within the hard-segment domains.[16] The study of single-crystal polydiacetylenes using Raman spectroscopy[4,5] has demonstrated that when such single crystals are deformed along the chain direction, the position of $C\equiv C$ triple-bond stretching band shifts by about -20 cm^{-1}/% strain regardless of the crystal modulus, which is essentially controlled by the size and shape of the substituent groups. Strong Raman scattering is only observed when the direction of the laser polarization is parallel to the axis of the polydiacetylene molecules, that is, parallel to the fiber axis. This implies that, in the diacetylene-containing copolymers studied in this present work, the Raman scattering comes principally from the polydiacetylene species in the hard segments which are oriented parallel to the polarization direction of the laser beam, which coincides with the tensile axis used in the deformation experiments. Consequently, the strain-induced shifts in Raman frequency ($\Delta\nu/\Delta\epsilon$) are obtained mainly from the deformation of the polydiacetylene chains aligned parallel to the tensile axis. This means that the Raman spectroscopy essentially probes only the deformation of the molecular chains in this particular orientation.

As discussed previously, the parallel model predicts that the average strain in the hard segments is similar to the overall strain in the copolymer samples of P[0D10H], P[0D15H], and P[0D20H] during deformation. However, Raman measurements give values for the rates of frequency shift ($\Delta\nu/\Delta\epsilon$) of -3.8 cm^{-1}/% for P[0D15H] and -6.2 cm^{-1}/% for P[OD20H]. These values are much smaller than the value of $\Delta\nu/\Delta\epsilon$ obtained for the polydiacetylene single crystals. A simple explanation is that the polydiacetylene chains are randomly distributed within the hard-segment domains in the copolymers. Although it is reasonable to assume that the average strain in the hard segments is similar to the overall strain in the samples, the actual strain in an individual elastically anisotropic hard segment will depend upon the relative orientation of the polydiacetylene chain direction with respect to the tensile axis. This anisotropy leads to the hard segments with polydiacetylene chains parallel to the axis being subjected to lower strains than those in the transverse direction. Since it is found that the uniform strain situation cannot be applied to the hard segments, the hard-segment modulus predicted by the Takayanagi model is consequently only about half the value obtained from eq 4. It is therefore expected that the strain-induced Raman band shifts in the copolyurethanes would be no more that half those for the single-crystal analogues. The further shortfall of the strain sensitivity of the Raman bands in the copolymers may be attributed to the slight plastic deformation in the relatively soft matrices and also to the partial depolarization of the laser beam caused by reflection from mirrors in the optical path, which leads to scattering from off-axis polydiacetylene moieties. In addition, it may also be due to change of resonance conditions in polydiacetylene chains in the copolymers after deformation. Detailed study on the excitation profile of these materials is necessary to quantify this effect, and this is beyond the scope of the present paper.

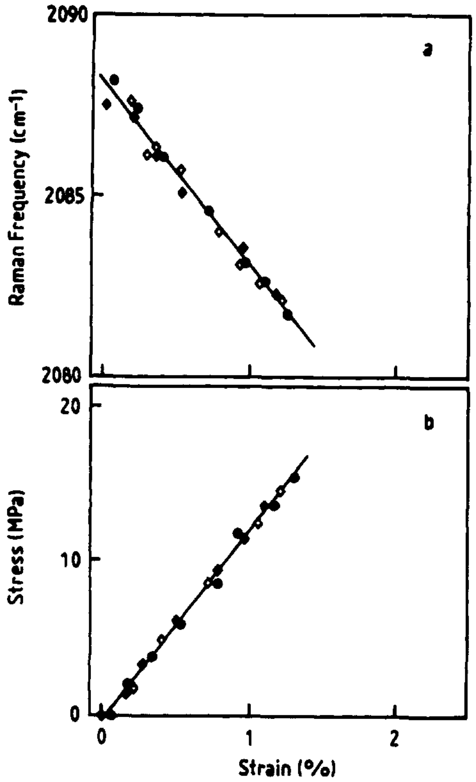

Figure 9. (a) Plot of Raman frequency (ν) versus strain (ϵ) in copolymer P[5D20H] during cyclic loading at relatively low strain level. (b) Corresponding stress/strain curve. Key: (●) loading; (●) unloading; (◇) reloading.

It was also found that the strain-induced Raman band shifts in the copolymer samples were reversible. A cyclic loading–unloading experiment was specially designed to investigate this reversibility using Raman spectroscopy. In this test, bulk (3-mm-thick) tensile samples of copolymer P[5D20H] were strained stepwise under the Raman microscope to certain strain levels and then unloaded gradually. They were strained again after the complete unloading. It was found that the Raman band position shifted to lower wavenumber upon tensile straining and then shifted back to higher wavenumber when the stress and strain were released. Figures 9 and 10 illustrate the relationships between the Raman frequency (wavenumber) and the applied strain in cyclic loading tests up to different strain levels. The corresponding stress/strain relations are also displayed for comparison. When the strain level is about 1.0%, the copolymer demonstrates complete elastic behavior, the strain-induced Raman band shift is completely reversible, and the corresponding stress/strain curve shows no sign of plastic deformation or yielding (Figure 9). It appears that both the soft- and hard-segment phases behave elastically at this strain level. When the strain level exceeds 1.5%, as seen in Figure 10, residual strain was observed in the specimens after unloading. This is due mainly to plastic deformation. However, the strain-induced Raman band shift still displays some reversibility even at the higher strain level. Figure 11 is a plot of Raman frequency versus stress during the cyclic loading–unloading test, obtained by combining the data from parts a and b of Figure 10. The fact that all the points fall on a single line indicates that stress rather than strain determines the optical sensitivity of the copolymers.

The diacetylene-containing copolymers, prior to cross-polymerization, were shown to be soluble and to display thermoplastic features, so that they can be easily processed

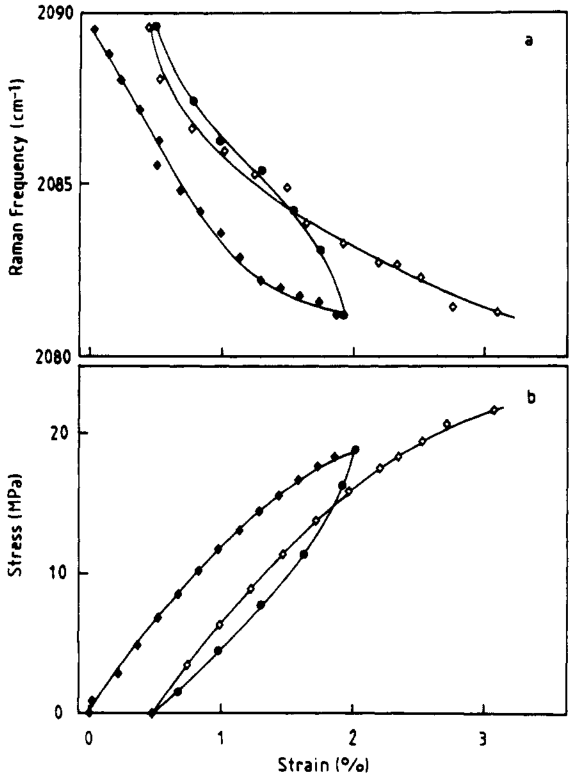

Figure 10. (a) Plot of Raman frequency (ν) versus strain (ϵ) in copolymer P[5D20H] during cyclic loading at a higher strain level. (b) Corresponding stress/strain curve. Key: (◆) loading; (●) unloading; (◇) reloading.

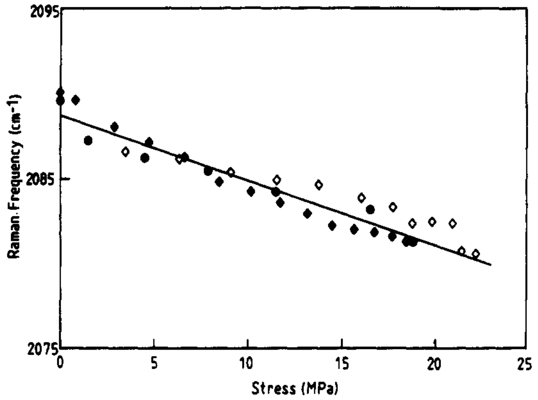

Figure 11. Plot of Raman frequency (ν) versus stress in copolymer P[5D20H] during cyclic loading using the data from Figure 10: (◆) loading; (●) unloading; (◇) reloading.

as other linear polymers. In the present work, a 10% solution of copolymer P[5D20H] in DMAc was coated onto the surfaces of various substrates including a polymer strip (a highly cross-linked conventional polyurethane), an aluminium sheet, and a single filament of glass fiber (25 μm in diameter). After solvent evaporation and subsequent cross-polymerization, the coated specimens were stretched under the Raman microscope and the strains in the substrates were followed from the change of Raman peak positions in the coatings. The strains in the polyurethane and aluminum substrates were determined using resistance strain gauges and those in the glass fibers by the crosshead displacement in a micrometer-controlled straining rig. Figure 12 is a plot of the Raman band frequency of the copolymer coating versus strain using a glass fiber substrate. It can be seen that the linear relationship between the Raman frequency and the strain holds up to the strain level of 2%, compared with 1.5% for the copolymer P[5D20H] in the bulk form (Figure 8).

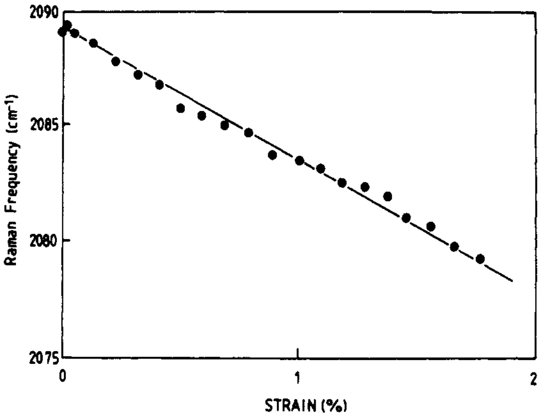

Figure 12. Plot of the Raman frequency (ν) in the copolymer coating against the tensile strain (ϵ) using a glass fiber substrate.

Table IV
Strain Sensitivity of the Raman Frequency of the C≡C Stretching Band in the Copolymer P[5D20H] Coated on Different Substrates (Behavior Linear to ≈2% Strain)

substrate	$\Delta\nu/\Delta\epsilon$ (cm^{-1}/%)
polyurethane	5.5 ± 0.4
glass fiber	5.7 ± 0.4
aluminum	5.5 ± 0.4

This is probably due to the differences in the history of the sample preparation between the bulk and coating materials and the constraint of the substrates. Similar results were obtained in the samples with the aluminum or plastic substrates. Table IV shows that the rate of the Raman band shift is about −5.5 cm^{-1}/% and essentially constant for all three types of substrates. This value is also similar to that obtained from the bulk copolymer (see Table III). The results from these coating studies therefore demonstrate that glassy, diacetylene-containing copolymers, such as those developed in this work, can be used as accurate optical strain-sensitive coatings on a variety of substrates.

Conclusions and Summary

Detailed studies have been carried out on the mechanical and optomechanical behavior of the diacetylene-containing copolymers. The polydiacetylene chains formed in the hard-segment domains give the copolymers unique optical properties similar to those of the polydiacetylene single-crystal analogues. In particular, well-defined resonance Raman spectra have been obtained from some of the copolymer samples. Above all, the C≡C triple-bond stretching bands in the copolymers were found to shift to lower wavenumbers by more than −6 cm^{-1}/%, compared with −20 cm^{-1}/% for the polydiacetylene single crystals. Nevertheless, the unusual optomechanical behavior of these copolymers enables the evaluation of deformation in the copolymers by monitoring Raman band positions. The strain in the copolymers can be measured to a high accuracy of about 0.1% with a spatial resolution of 2 μm using the Raman microscope.

The advantage of the diacetylene-containing copolymers is the combination of the optical properties of polydiacetylenes and the mechanical properties and processibility of polyurethanes. Hence, in multiphase copolymer systems, the drawback of the brittleness and intractability of the polydiacetylene single crystals has been overcome and the unique optical strain sensitivity has been satisfactorily retained. Unlike the single crystals, the copolymers, prior to cross-polymerization, are soluble and can be easily processed into various shapes and forms to produce strain-sensitive films, coatings, and composite matrices. Obviously, the successful combination of the properties of two different phases within a copolymer system has produced a new class of materials with properties unachievable by either of the components in isolation. There is considerable potential for these types of isotropic, multiphase materials in applications as novel optical strain sensors.[24]

Acknowledgment. This work was supported by a research grant from the SERC.

References and Notes

(1) Mitra, V. K.; Risen, W. M., Jr.; Baughman, R. H. *J. Chem. Phys.* **1977**, *66*, 2731.
(2) Batchelder, D. N.; Bloor, D. *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 569.
(3) Galiotis, C.; Young, R. J.; Batchelder, D. N. *J. Polym. Sci.: Polym. Phys. Ed.* **1983**, *21*, 2483.
(4) Young, R. J. In *Developments in Oriented Polymers-2*; Ward, I. M., Ed.; Elsevier: London, 1987; p1.
(5) Wu, G.; Tashiro, K.; Kobayashi, M. *Macromolecules* **1989**, *22*, 188.
(6) Galiotis, C.; Robinson, I. M.; Young, R. J.; Smith, B. J. E.; Batchelder, D. N. *Polym. Commun.* **1985**, *26*, 354.
(7) Van Der Zwaag, S.; Notholt, M. G.; Young, R. J.; Galiotis, C.; Robinson, I. M.; Batchelder, D. N. *Polym. Commun.* **1987**, *28*, 276.
(8) Day, R. J.; Robinson, I. M.; Zakikhani, M.; Young, R. J. *Polymer* **1987**, *28*, 1833.
(9) Tashiro, K.; Wu, G.; Kobayashi, M. *Polymer* **1988**, *29*, 1768.
(10) Prasad, K.; Grubb, D. T. *J. Polym. Sci.: Polym. Phys. Ed.* **1989**, *27*, 381.
(11) Kip, B. J.; Van Eijk, M. C. P.; Meier, R. J. *J. Polym. Sci.: Polym. Phys. Ed.* **1991**, *29*, 99.
(12) Robinson, I. M.; Zakikhani, M.; Day, R. J.; Young, R. J.; Galiotis, C. J. *Mater. Sci. Lett.* **1987**, *6*, 1212.
(13) Young, R. J.; Day, R. J. *Br. Polym. J.* **1989**, *21*, 17.
(14) Evans, R. A.; Hallam, H. E. *Polym. Lett.* **1976**, *17*, 839.
(15) Fina, L. J.; Bower, D. I.; Ward, I. M. *Polymer* **1988**, *29*, 2147.
(16) Hu, X.; Stanford, J. L.; Day, R. J.; Young, R. J. *Macromolecules*, in press.
(17) Hepburn, C. *Polyurethane Elastomers*; Applied Science: London, 1982.
(18) Batchelder, D. N. *Eur. Spectrosc. News* **1988**, *80*, 28.
(19) Takayanagi, M.; Imada, K.; Kajiyama, T. J. *Polym. Sci.* **1966**, *C15*, 263.
(20) Dickie, R. A. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1, p 353.
(21) Ward, I. M. *Mechanical Properties of Solid Polymers*; Wiley: Chichester, 1983; p 298.
(22) Lyne, J.; Stanford, J. L.; Still, R. H. Unpublished results.
(23) Hull, D. *An Introduction to Composite Materials*; Cambridge University Press: Cambridge, 1981.
(24) Hu, X.; Day, R. J.; Stanford, J. L.; Young, R. J. PCT Application No. PCT/GB 91/00118.

Registry No. HDD/MDI/PPG (block copolymer), 136128-77-3; HDD/MDI/PPG/DPG (block copolymer), 137125-42-9.