The study of the physisorption of oxygen on polydiacetylene single crystals and monomolecular films by optical and resonance Raman spectroscopy

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(Received 6 August 1990; accepted 7 November 1990)

Optical and resonance Raman spectroscopy have been used to identify a structural phase transition that occurs when oxygen is adsorbed by polydiacetylene single crystals and monolayer Langmuir–Blodgett films. For specially prepared, initially oxygen-free, single crystals, the structural change was found to be reversible upon removal of the oxygen under vacuum. For the monolayer Langmuir–Blodgett films, it was not. Resonance Raman excitation profiles of two vibrational modes demonstrated that the dominant electronic transition in the polydiacetylene single crystals shifted from 1.98 to 2.24 eV as a result of oxygen adsorption.

(Keywords: Raman spectroscopy; polydiacetylene; Langmuir-Blodgett films; oxygen adsorption)

INTRODUCTION

Molecular oxygen plays an important role in the electronic properties of conjugated polymers as well as being an effective agent of their degradation. The study of the interaction between oxygen and the backbone of most conjugated polymers has been hindered, however, by the significant degree of structural and chemical heterogeneity in the materials thus far produced. By contrast the polydiacetylenes (PDAs) can be prepared as large single crystals or mono- and multilayer Langmuir–Blodgett (LB) films containing very low concentrations of structural and chemical defects[1]. Crystals and films of PDAs in which the packing of the side-groups does not restrict access of the conjugated backbone to molecular oxygen thus provide an attractive model system for the study of backbone–oxygen interaction.

The PDA conjugated backbone has the structure $[{=}CR{-}C{\equiv}C{-}CR'{=}]_n$, where the side-groups R and R′ may be the same or different. Both single crystals and LB films have been extensively studied by optical and resonance Raman spectroscopy, and the important electronic and vibrational excitations are well characterized. The optical properties of PDAs are dominated by an intense absorption band located at approximately 2 eV, which arises from a $\pi \rightarrow \pi^*$ electronic transition, plus a small number of associated vibrational sidebands[1–3]. The Raman spectra of the same vibrational modes exhibit intense resonant enhancement when the wavelength of the exciting laser lies within the optical absorption band[4,5]. Two vibrational modes at approximately 1500 and 2100 cm^{-1} contribute to all PDA Raman spectra; the former is associated with large amplitude of vibration at the double bond, while the latter corresponds to vibration of the triple bond. The number and frequency of other vibrational modes that contribute to the resonance Raman spectrum are determined by the nature of the side-groups[6].

Previous studies of the interaction of the PDA backbone with molecular oxygen have been carried out almost entirely with single crystals formed by the solid-state polymerization of the bis(*p*-toluenesulphonate) of 2,4-hexadiyne-1,6-diol (TS) monomer[7–10]. Two electronic transitions were identified as resulting from the formation of a molecular complex[8]. One at approximately 2.4 eV was tentatively identified with polymer that had been in some way perturbed by the formation of the complex. The second at 2.6 eV was attributed to a charge-transfer (CT) excitation involving the transfer of an electron from the PDA backbone to an associated oxygen molecule. It was also demonstrated that with appropriately prepared crystals the formation of the complex was reversible; the oxygen and its associated effects on the electronic structure could be removed by a vacuum of 10^{-3} Torr. Hence it was concluded that the oxygen was physisorbed onto the PDA backbone to form a weak charge-transfer complex of the type described in detail by Mulliken and Person[11].

Photochemical reaction of the oxygen with the PDA backbone was observed when TS polymer crystals were illuminated with light of wavelength shorter than 520 nm[8–10]. A model for the reaction has been proposed in which electronic excitation of the PDA backbone is followed by energy and spin exchange with the adsorbed oxygen. Singlet oxygen then can attack the double bond on the PDA backbone through the 'ene' reaction; the backbone is severed and *p*-toluenesulphonic acid produced from the side-groups[9,10].

This paper reports new measurements that yield a

Paper presented at Speciality Polymers '90, 8–10 August 1990, The Johns Hopkins University, Baltimore, MD, USA

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0032-3861/91/101761-09

considerably more detailed picture of the formation of the weak charge-transfer complex between the PDA backbone and the oxygen molecule. The resonance Raman excitation profile (EP) of the oxygen-induced electronic state at lower energy has been measured for both the double- and triple-bond vibrations. This provides a unique identification of that excitation with a perturbed polymer backbone. Further evidence to support this conclusion has come from studies of the dependence of the vibrational frequencies upon strain. An unsuccessful attempt was also made to study the molecular complex by ^{13}C solid-state nuclear magnetic resonance (s.s.n.m.r.).

A more detailed look at the nature of the backbone perturbation has been made possible by the study of monolayer LB films of a polydiacetylene. The polymerized films of 22,24-pentacosadynoic acid (ω-PCDA) had the PDA backbone on the surface opposite to the substrate with only a hydrogen as the external side-group. The ω-PCDA polymer films thus have the best possible surface-to-volume ratio for the study of oxygen adsorption.

EXPERIMENTAL

Specimen preparation

TS monomer was prepared in the standard way both in air and under oxygen-free conditions[8,12]. Prior to crystal growth, the monomer was carefully purified by several recrystallization cycles followed by a toluene wash if required. The dominant impurity in the monomer was coloured polymer; the purification process was carried on until the monomer was either in the form of a white powder or dissolved in a colourless solution. For oxygen-free material the purification process was carried out using degassed solvents under a nitrogen atmosphere.

Single crystals of TS monomer were grown over a period of 2 or 3 days by slow evaporation from a saturated solution of a 1:1 mixture of acetone and toluene. Crystallization was carried out under a controlled atmosphere in the dark to produce either oxygen-rich or oxygen-free crystals. Prior to polymerization the monomer crystals were cleaved into pieces about 0.5 mm thick. In addition the (010) surface of some samples was polished with a filter paper moistened with acetone. Polymerization was carried out by maintaining the crystals at 313 K for 3 days; for oxygen-free material this procedure was carried out under vacuum. Thin ribbons of crystal were prepared for the strain experiments by touching the surface of a crystal with adhesive tape near one edge. On withdrawing the tape, single-crystal fibres up to 8 mm long, 1 mm wide and a few micrometres thick could be cleaved off.

Two 1 g specimens of TS polymer in powder form were prepared for the ^{13}C s.s.n.m.r. experiments. One specimen was prepared under oxygen-free conditions and the other under oxygen-rich; Raman spectroscopy was used to confirm the disparity of oxygen content in the two specimens.

The ω-PCDA monomer was prepared using a modification of an earlier procedure[13]. After several recrystallization cycles the final purification was carried out by high-pressure liquid chromatography (h.p.l.c.) in the chloroform solvent used for spreading the films on the Langmuir trough. The chemical preparation was only 0.2% efficient so that after the final purification step we had less than 10 mg of material with which to work.

The subphase of the Lauda trough was water drawn from a Millipore system with $CdCl_2$ added to a concentration of 10^{-3} M. It was found necessary to maintain a pH of approximately 6.5 using NaOH, but film stability appeared to be relatively insensitive to temperature. A 10^{-3} M solution of ω-PCDA in h.p.l.c.-grade chloroform was spread at the air/water interface using a microsyringe. The films were stable and exhibited collapse pressures in excess of 35 mN m^{-1}.

The substrates for the LB films were Spectrasil-grade B quartz prepared using standard cleaning procedures. The hydrophilic slides were immersed in the subphase prior to spreading of the Langmuir film; deposition of the monolayers occurred upon withdrawal of the slides. The films were transferred at a surface pressure of approximately 20 mN m^{-1} at a typical speed of 20 μm s^{-1}. The films were polymerized under a nitrogen atmosphere by exposure to 254 nm light from a low-pressure Hg lamp. Polymerization was carried out in a spectrophotometer so that the development of the polymer could be monitored.

Solid-state nuclear magnetic resonance

Spectra were obtained with a Bruker MSL-300 instrument operating at 74.5 MHz for ^{13}C detection. Cross-polarization and magic angle spinning were used, and the samples were contained in 7 mm diameter rotors in double air-bearing probes. The magic angle spinning rates were in the region 4.3–4.8 kHz and the TOSS technique was used to simplify the spectra by elimination of the spinning side-bands. Single contact cross-polarization with flip-back was used and the ^1H decoupling field was 70 kHz. Chemical shifts were referenced to external tetramethylsilane via the secondary standard adamantane.

Optical spectroscopy

Optical absorption measurements were carried out using a Perkin–Elmer 555 spectrophotometer. For the low-temperature measurements the specimens were located in an Oxford Instruments continuous flow cryostat.

Raman spectroscopy

Raman spectra were excited using the fixed wavelengths of a Spectra Physics argon laser and a Coherent krypton laser. A continuous range of laser wavelengths in the region 535–569 nm was provided by a Coherent dye laser with coumarin 6 dye dissolved in ethylene glycol (plus a few drops of the triplet quencher cyclooctatetraene) as the lasing medium. The laser intensity was kept below 1 mW throughout the experiments and only used to illuminate the specimens while collecting data. The possibility of damage to the specimens was reduced further by using a line focus for the laser beam.

The Raman scattered radiation was collected in the 180° back-scatter mode using an *f*/1.2 camera lens. The radiation was dispersed by a Spex 1401 double monochromator with 1200 lines/mm diffraction gratings used in the scanning mode when the detector was a cooled RCA 34031A photomultiplier with photon-counting electronics. The majority of spectra were recorded, however, using an EEV P8603 charge-coupled device

(CCD) installed in a Wright Instruments cryogenically cooled camera as the detector[14]; in this case the monochromator was used as a variable-bandpass filter with the exit slit removed. The dispersion across the CCD was 200–300 cm^{-1}, depending upon the incident laser wavelength. The data from the 386×570 two-dimensional array of 22 μm square pixels were analysed with the aid of an IBM AT-compatible computer. The reductions in laser intensity and exposure time made possible by the use of the CCD camera were essential for successful measurements on the photosensitive PDA samples. In some cases it proved possible to obtain resonance Raman spectra from a monolayer LB film with only 10 μW of incident laser power.

RESULTS AND DISCUSSION

Single-crystal measurements

Oxygen-induced Raman bands. Figures 1a and *1b* illustrate typical Raman spectra in the vicinity of 1500 and 2100 cm^{-1} taken from the (010) surface of a TS PDA single crystal at 300 K with 514.5 and 501 nm laser excitation, respectively. The bands at 1465, 1483 and 2086 cm^{-1} are associated with the unperturbed polymer, while those at 1515 and 2115 cm^{-1} have been induced by oxygen adsorption. The association of the latter Raman bands with oxygen is demonstrated in *Figures 2a* and *2b*, where the decay of these bands as a function of

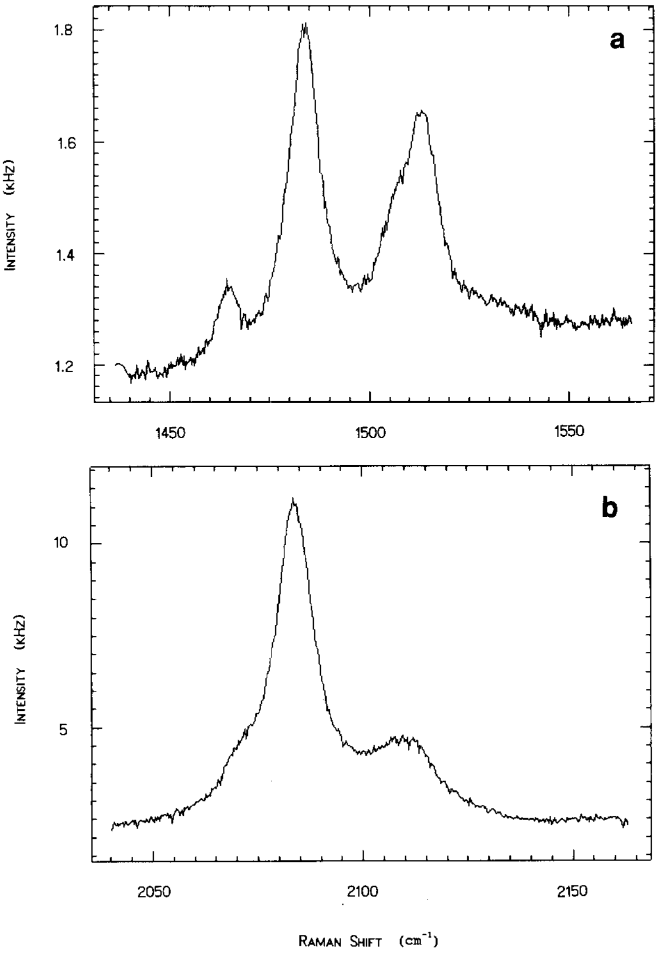

Figure 1 Raman spectra of a TS PDA single crystal: (a) 514.5 nm laser excitation in the region of the frequency of the 'double-bond' vibration; (b) 501 nm laser excitation in the region of the 'triple-bond' vibration

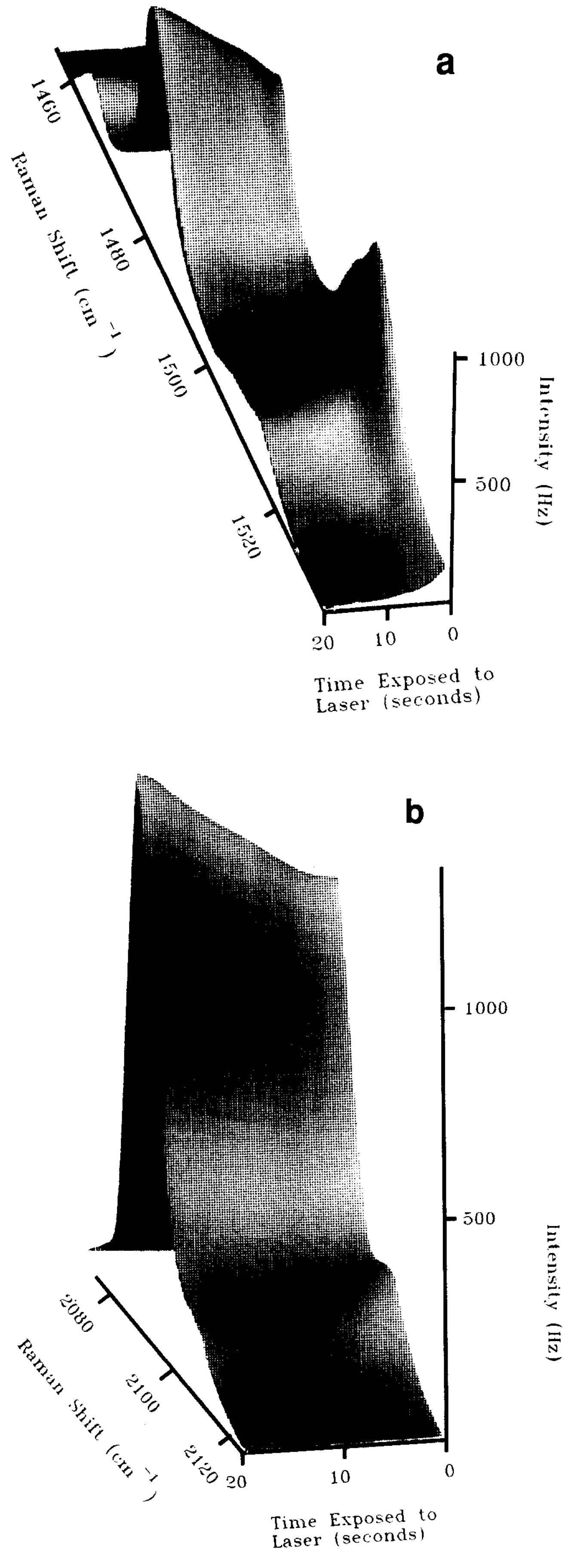

Figure 2 Time dependence of the Raman spectra in *Figure 1* showing the decay of the Raman bands at 1515 and 2115 cm^{-1} induced by adsorption of O_2: (a) 514.5 nm laser excitation in the region of the frequency of the 'double-bond' vibration; (b) 501 nm laser excitation in the region of the 'triple-bond' vibration

the exposure time to the laser is shown. The increase in intensity of the Raman bands of the unperturbed TS PDA is thought to arise from the conversion of the highly absorbing perturbed material to relatively transparent photooxidation products[10]. The simultaneous presence of Raman bands at approximately 1500 and 2100 cm^{-1} is a very strong indicator of the presence of the PDA backbone. The fact that these bands are shifted to higher frequency suggests that oxygen adsorption has perturbed the backbone structure, and presumably the crystal structure, of those segments of PDA chains which have been affected. The shift in the Raman bands also suggests that the energy of the electronic excitation for the perturbed PDA should be shifted to higher energy[4].

For crystals prepared under oxygen-free conditions and subsequently polished, the oxygen-induced Raman bands shown in *Figure 1* could be removed by placing the crystals under a vacuum of 10^{-3} Torr for 1 h. Exposure to atmospheric oxygen caused the bands to reappear reversibly, in agreement with an earlier study[8]. By contrast, the Raman bands at 1515 and 2115 cm^{-1} could only be removed by the process of photooxidation from crystals that had not been prepared under oxygen-free conditions. This is an indication that much of the adsorbed oxygen generally does not lie at exposed surface positions from which it can be easily removed.

Strain dependences of the Raman bands. Uniaxial strain measurements were carried out on a number of TS PDA single-crystal fibres. The fibres were glued to the jaws of a micrometer as described previously[15] and stretched elastically in the chain direction by as much as 5%. Raman spectra were taken with the 501 nm laser line so that the triple-bond Raman bands of both perturbed and unperturbed material were present as, for example, in *Figure 1b*. The frequencies of both were found to shift to lower frequency at approximately 20 cm^{-1}/% with increasing uniaxial strain. By way of illustration, a succession of exposures as a function of increasing and decreasing strain were made on a few rows of pixels on the CCD detector; after each exposure the image was shifted down the detector so a fresh exposure could be made. The resulting image on the CCD detector shown in *Figure 3* has strain along the horizontal axis and Raman shift along the vertical. The band intensities vary with strain since the electronic structure of the PDA backbone and the conditions for resonance Raman scattering are also strain-dependent. The CCD image shows the effect of strain with considerably greater clarity than the associated Raman spectra.

The approximate equality of the strain dependences of the Raman bands clearly demonstrates that the perturbed and unperturbed material are in intimate physical contact. Adsorption of the oxygen onto exposed PDA backbones does not cause the polymer to separate from the underlying unexposed material. This strong coupling provides the necessary driving mechanism required for the perturbed material to return to the unperturbed state after removal of the adsorbed oxygen as previously reported[9].

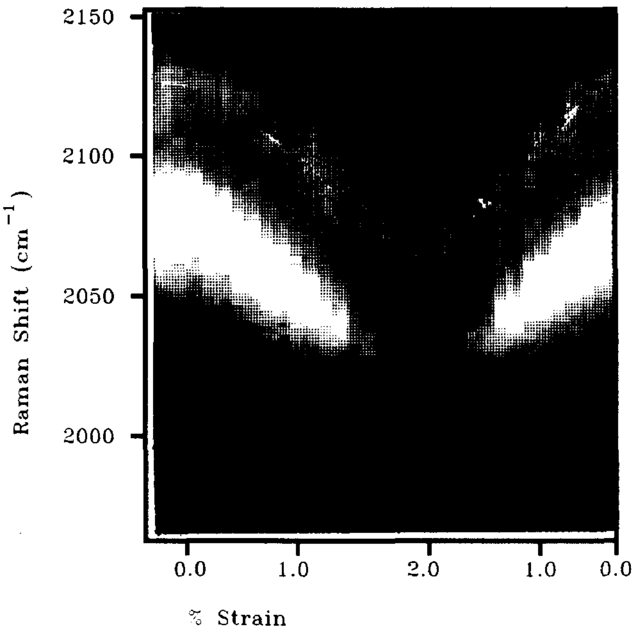

Figure 3 Photographic image taken with the CCD detector showing the variation of the frequencies of the 2086 and 2115 cm^{-1} Raman bands with strain. Spectra were recorded at one edge of the CCD detector for a particular strain value and then shifted along the detector electronically so that a new spectrum at a different strain could be recorded

Resonance Raman excitation profiles. Theoretical analysis of the excitation profile (EP) of vibrational modes in PDAs has been based upon the assumption of separability of the electronic and vibrational wavefunctions in the Franck–Condon approximation. The key quantities in the model are the overlap integrals between the harmonic oscillator wavefunctions in the ground and excited states. These are usually expressed in terms of the dimensionless vibronic coupling parameter z, which is directly proportional to the displacement that occurs along the normal mode coordinate between the ground and excited electronic states. When overtones and combination bands are included, the algebraic expressions for the EP are very complicated. Most of the physics, however, can be seen from the following expression, which only includes the lowest-order terms. For a single electronic excitation of energy E_0, the resonance Raman cross-section, to which the EP is proportional, for the ith vibrational mode is given by:

$$S_i(E_L)=k\left(\frac{z_i^2}{(E_0-E_L)^2+\gamma^2}+\frac{z_i^2(1-z_i^2)^2}{(E_0-hF_i-E_L)^2+\gamma^2}\right) \qquad (1)$$

where the value of k is independent of the laser photon energy E_L, aside from containing a factor of $(E_L E_S^3)$, where E_S is the photon energy of the scattered radiation. The frequency of the ith vibrational mode in the electronic excited state is F_i and γ is the full width of the Lorentzian lineshape at its half-maximum value. Thus the two important maxima in the EP of the ith vibrational mode are expected to occur at E_0, the energy of the pure electronic transition, and E_0+hF_i, while the relative heights of the two maxima are determined by z_i.

For TS PDA crystals unaffected by oxygen adsorption, the value of E_0 was found to be 2.98 eV, equal to that determined by optical spectroscopy within experimental uncertainty[3]. In the analysis it was necessary to take into account the fact that much of the Raman scattered light came from polymer chains lying within the bulk of the crystal. The raw data needed to be corrected for the effects of adsorption and reflection of both the incident laser beam and the Raman scattered radiation[5].

In the present experiments the integrated intensities of

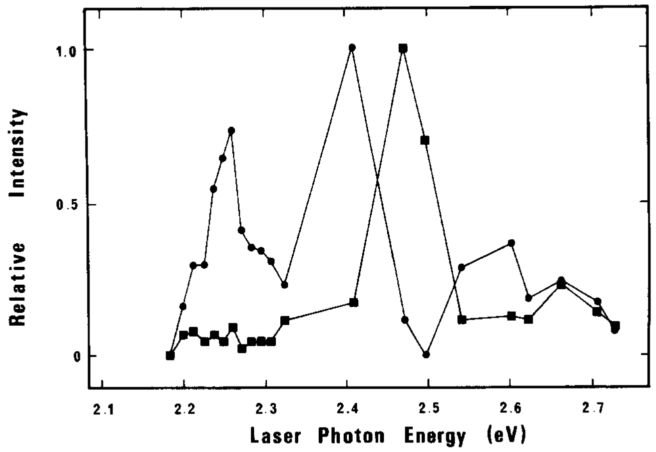

Figure 4 Integrated intensities of the 1515 cm^{-1} (circles) and 2115 cm^{-1} (squares) oxygen-induced Raman bands as a function of the photon energy of the exciting laser. The experimental uncertainty on all the data points is ±0.05

the 1515 and 2115 cm^{-1} Raman bands induced by oxygen adsorption in TS PDA single crystals were measured at 20 different laser wavelengths. The raw data, which are shown in *Figure 4*, at first presented a difficult problem. It had been assumed that the polymer chains affected by oxygen lay on the surface of the crystal; in this situation it would be unnecessary to make absorption and reflection corrections. The intensity data in *Figure 4*, however, do not show clearly the two maxima expected in the EP of a PDA. The same corrections were then applied to the intensity data as had been applied to the data for unperturbed crystals. The results, together with data for the 1515 cm^{-1} Raman band obtained in earlier experiments, are presented in *Figure 5*. The uncertainty in these results is high, as much as 50% between 2.1 and 2.3 eV and 5% at higher energies, because the absorption corrections were large and the intensities of the Raman bands over much of the range were very low. The laser intensity had been deliberately kept very low in order to avoid the effects of irreversible intensity changes arising from photooxidation.

The full curves in *Figure 5* have been calculated using equation (1) with higher-order terms included; this is the same model as was successfully used to interpret the EP of TS PDA crystals that were not affected by oxygen[5]. The parameters E_0, $\nu_e(1555\ \mathrm{cm}^{-1})$, $\nu_e(2115\ \mathrm{cm}^{-1})$ and z were obtained by fitting the model to both EPs simultaneously. The values of these parameters for TS PDA with adsorbed oxygen are compared with those for the unperturbed material in *Table 1*.

The EPs for both vibrational modes in *Figure 5* show the double maximum characteristic of a PDA; as expected, the lower-energy maxima are coincident while those at higher energy are not, since they refer to vibrational modes of different frequency. The quality of the fit between the model and the experimental data strongly suggests that it was necessary to correct the raw data for the effects of absorption and reflection. If this is true then the inescapable conclusion is that much of the perturbed material must lie below the surface of the polymer crystal. As the oxygen molecule is known to be too large for inclusion in the unit cell, then the adsorption of the PDA backbone must take place at defects such as microcracks[8].

The results summarized in *Table 1* also clearly show that the TS PDA that has been perturbed by oxygen absorption has a different physical structure from the unperturbed material. The energy of the electronic transition has been shifted from 1.98 to 2.24 eV; the double- and triple-bond vibrational frequencies in the ground state have increased by 32 and 29 cm^{-1}, respectively. The changes in ν_e are considerably larger than expected, similar to an earlier result with PDA LB films, and may result from a difficulty in the corrections for absorption and reflection. For example the correction

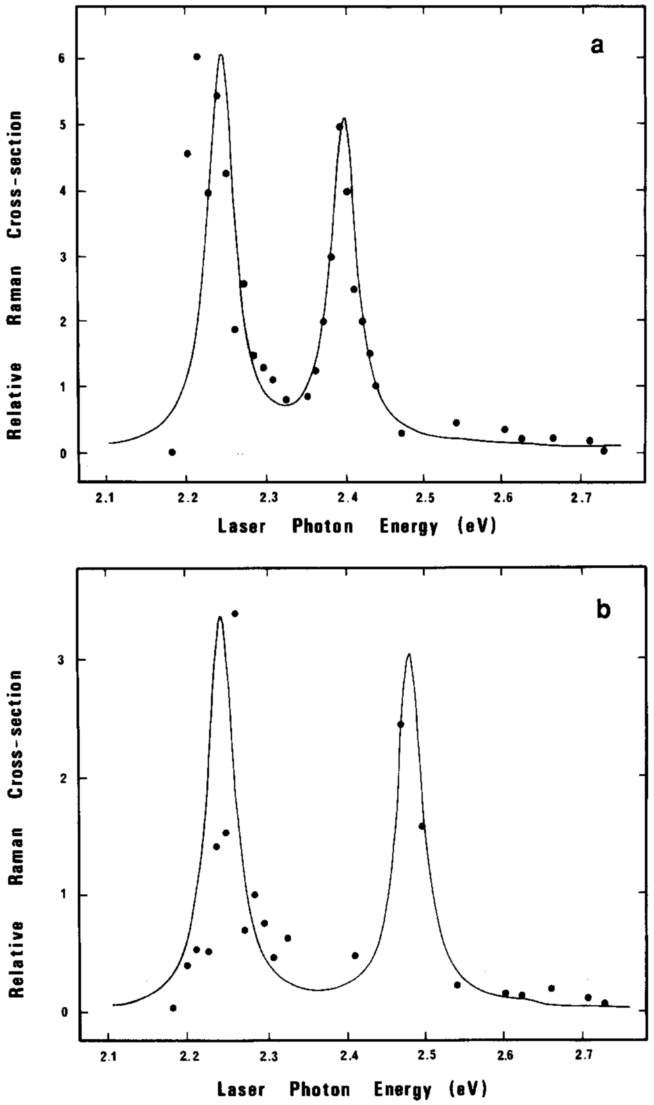

Figure 5 Excitation profiles for the oxygen-induced Raman bands: (a) 1515 cm^{-1} band; (b) 2115 cm^{-1} band. The experimental uncertainty on the data points is approximately ±50% between 2.1 and 2.3 eV and ±5% at higher energies. The full curves result from simultaneous least-squares fits to the two sets of data using the standard model

Table 1 Values of the electronic excitation energy E_0, ground-state vibrational frequency f, excited-state vibrational frequency F, and vibronic coupling parameter z, for single crystals of TS PDA and TS PDA perturbed by oxygen adsorption

	E_0 (eV)	f (cm^{-1})	F (cm^{-1})	z
TS PDA	1.98	1483	1420	0.55
		2086	2040	0.40
TS PDA perturbed	2.24	1515	1250	0.30
		2115	1780	0.22

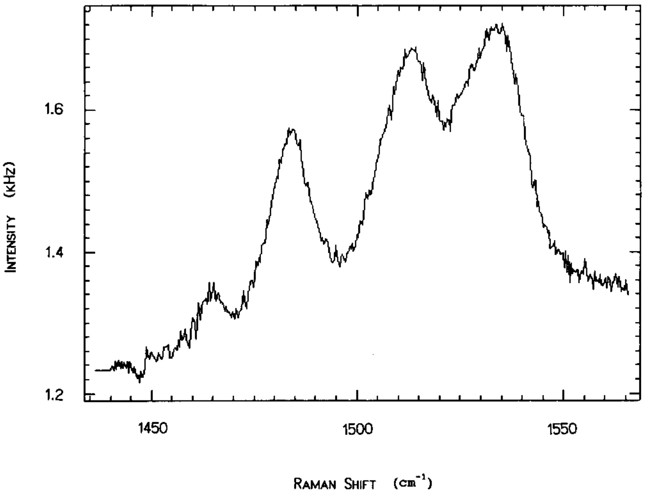

Figure 6 Raman spectrum of a rough region of the same TS PDA single crystal as in *Figure 1a*, under otherwise identical experimental conditions

factor should in principle include the effects of the perturbed as well as the unperturbed material.

Charge-transfer excitation. Figure 6 is a Raman spectrum taken under identical conditions, on the same crystal, as that in *Figure 1a*; the latter spectrum, however, was taken from a smooth area of the crystal while the spectrum in *Figure 6* was recorded from a rough area. The Raman band at 1535 cm^{-1} has previously been associated with a charge-transfer excitation involving electron motion from the PDA to an adsorbed oxygen molecule. The EP for this Raman band was found to have a single maximum at an excitation energy of 2.62 eV[8]. The frequency is just 20 cm^{-1} lower than that for an isolated oxygen molecule; no corresponding Raman band has been found at a frequency appropriate to a triple-bond vibration, thus suggesting that the 1535 cm^{-1} band is not attributable to a PDA structure. The frequency of this Raman band was also found[8] to exhibit an isotopic shift when $^{18}O_2$ was substituted for $^{16}O_2$. Thus we have concluded that the 1535 cm^{-1} Raman band arises from molecular vibrations of O_2 resonantly enhanced by the charge-transfer excitation from the perturbed PDA backbone to the adsorbed O_2 molecule responsible for the perturbation of the structure. The variability of the ratio of the intensity of the Raman band arising from the perturbed PDA to that associated directly with the adsorbed oxygen molecule suggests that the volume of perturbed material is greater than that to which oxygen is directly adsorbed.

Solid-state n.m.r. The ^{13}C s.s.n.m.r. spectra of oxygen-free TS PDA powder and a similar oxygen-rich sample are compared in *Figure 7*. The bands were readily identified with those predicted from a knowledge of the crystallographic structure of TS PDA. The spectra are identical within the noise of the measurement even though the samples had a very favourable surface-to-volume ratio. Thus it was not possible to learn anything about changes in bonding that occur when oxygen adsorbs onto the polymer backbone. From these data the volume of perturbed material has been estimated to be less than 2% of the total.

Studies of monolayer Langmuir–Blodgett films

The freshly polymerized monolayer LB films of ω-PCDA PDA had the faint blue appearance common to carefully prepared PDA LB films[16,17]; this is known as the 'blue' phase. The optical absorption spectrum of a typical ω-PCDA PDA film, covering both sides of the quartz slide, is shown in *Figure 8a*. The value of optical density of approximately 0.005 per layer is also typical for PDA LB films[17]. When exposed to solvents such as methanol or heated above 60°C, the ω-PCDA films underwent the phase change expected of PDA LB films[17]. The colour of the films changed to the pale pink colour typical of the 'red' phase; the optical absorption spectrum of a typical red film is shown in *Figure 8b*. There is still a trace of the main absorption peak of the blue phase at 650 nm but the dominant absorption occurs at 530 nm.

The ω-PCDA polymer films differed in one important respect from those of earlier studies. The blue-to-red phase transition was found to occur in films that were stored in the dark at ambient conditions within a few days. This is in contrast to 12,8-PCDA polymer films, which have remained in the blue phase even after storage for several years in ambient conditions in our laboratory. It appears that the alkane side-groups on the 12,8-PCDA molecules are sufficiently closely packed to prevent

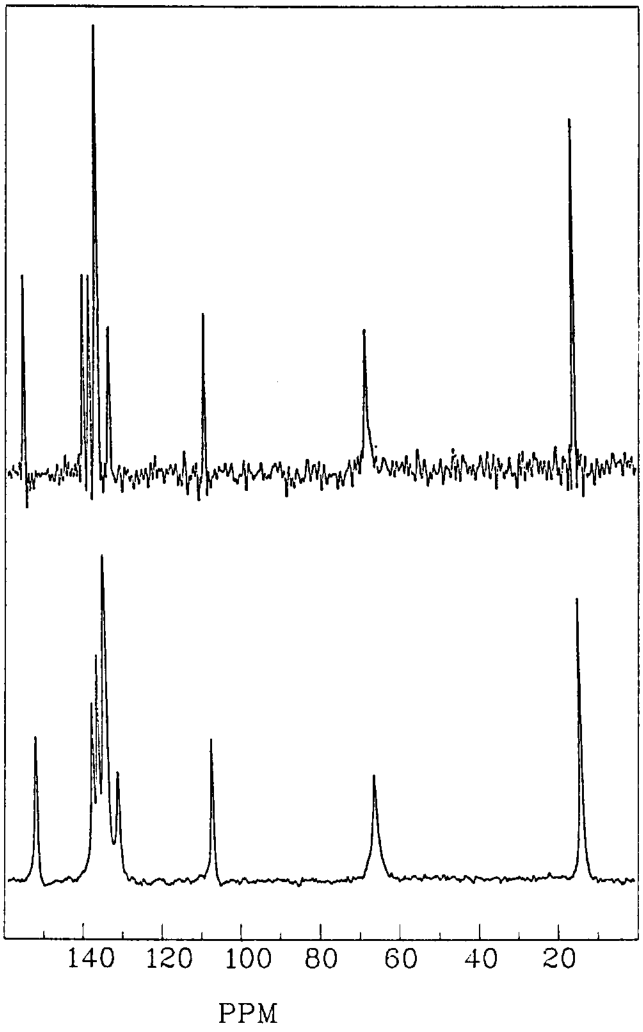

Figure 7 Solid-state n.m.r. spectra for oxygen-rich (upper) and oxygen-free (lower) polycrystalline TS PDA specimens

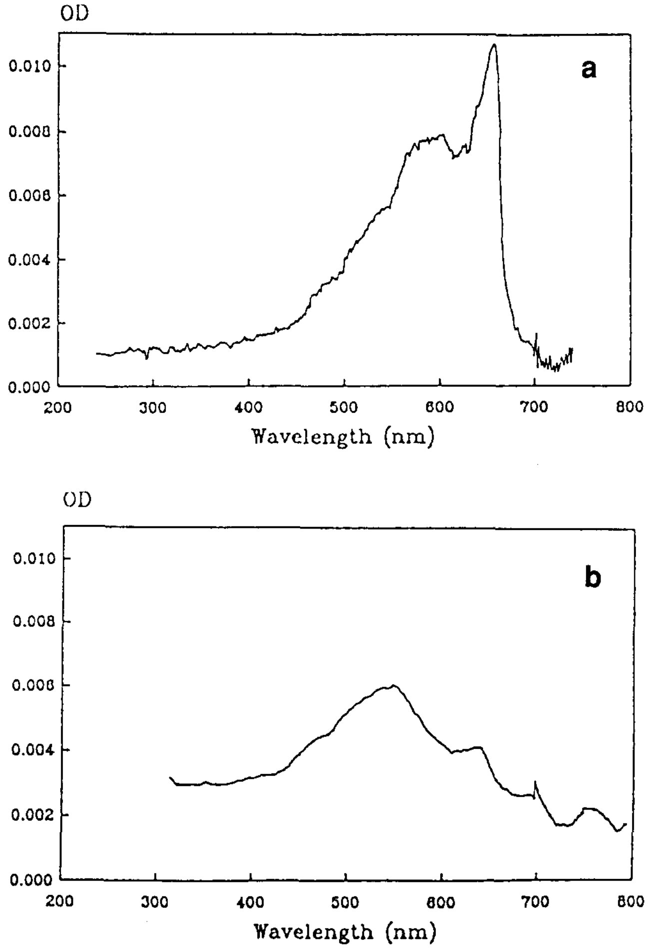

Figure 8 Optical absorption spectra of a monolayer film of ω-PCDA PDA: (a) 'blue' phase; (b) 'red' phase. The film covered both sides of the microscope slide

adsorption of oxygen onto the PDA backbone in LB films with a low defect density. Furthermore, the phase change was found to occur, at a somewhat slower rate, for ω-PCDA polymer films kept in the dark at 253 K. The instability of these films made from a material that only existed in very small quantities presented considerable experimental difficulties.

The Raman spectra of the monolayer ω-PCDA PDA films were found to be very similar to those observed for 12,8-PCDA PDA films[18]. Thus it was decided to concentrate efforts on those Raman bands which were characteristic of all PDA backbones, the modes with large amplitude of vibration at the double and triple bonds. *Figure 9* shows the Raman bands at 300 K in the blue phase excited with 647 nm radiation and *Figure 10* shows those in the red phase excited with 514.5 nm radiation. There was little sign of Raman photoselection when exciting radiation of other wavelengths was used[4]; in all films there were no more than the two sets of well defined Raman bands. The spectra are noisy, as very low laser powers, less than 100 μW with a line focus, were used to excite them. The spectra in *Figure 10* suggest that there is some residual blue-phase material present in the red film; because of the changes in conditions of resonance it is difficult to assess accurately how much remains.

To overcome the relative instability of the blue-phase monolayers, resonance Raman experiments were carried out at 77 K. *Figure 11a* shows the Raman spectrum in the region of the double-bond vibration excited with 10 mW of incident 647 nm radiation in a line focus. In spite of the comparatively high power level, the film was stable under these conditions of irradiation. By contrast *Figure 11b* shows a spectrum taken under identical conditions immediately after liquid oxygen was condensed into the cell over a period of 5 min. The integrated intensity of the double-bond Raman band has shrunk by more than a factor of 2 while the band has shifted to higher frequency with the width approximately doubled. The dramatic changes in the spectra suggest that the presence of oxygen can induce the blue-to-red phase transition even when the monolayer film is held at 77 K. On a longer timescale this conclusion was confirmed by taking optical absorption spectra. At the time when the spectrum in *Figure 11b* was recorded, the residual blue phase was clearly in a very stressed condition. The frequency shift of the band maximum from 1455 to 1464 cm^{-1} suggests a compressive elastic strain in the blue material of approximately 0.6%, if a strain dependence similar to TS PDA is assumed[15]. The increased breadth most likely arises from a significant strain distribution within the film.

Finally the intensity of the 1525 cm^{-1} Raman band for the double-bond vibration of a monolayer film in the red phase at 300 K was measured as a function of time, first under vacuum and then in an oxygen atmosphere. The intensity of the 514.5 nm laser beam used to excite the spectra was increased to a point where photo-

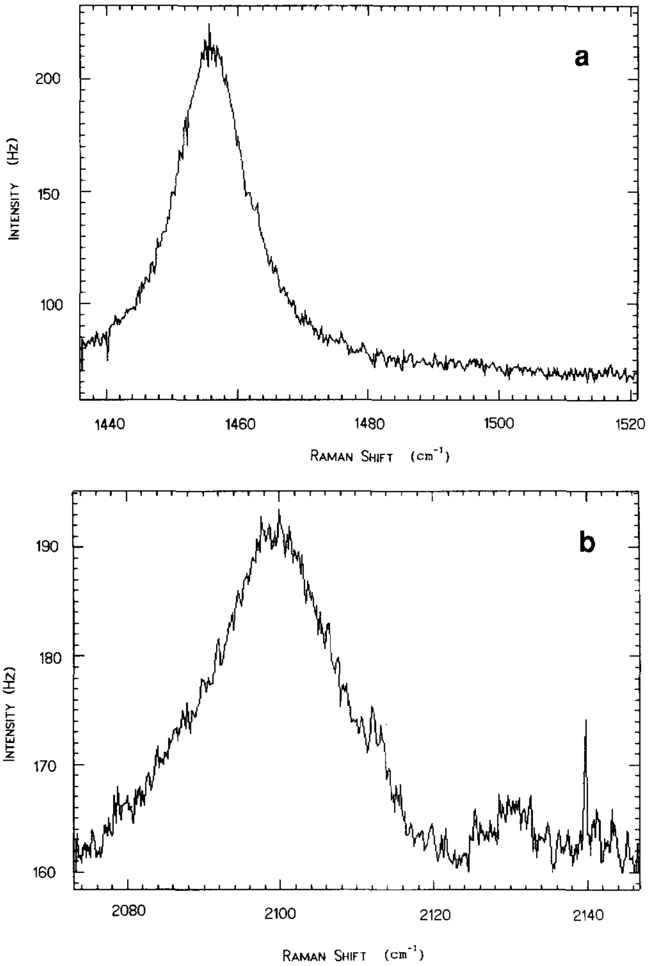

Figure 9 Raman spectra of a monolayer film of ω-PCDA PDA in the 'blue' phase excited with 647 nm laser radiation: (a) 'double-bond' vibration; (b) 'triple-bond' vibration

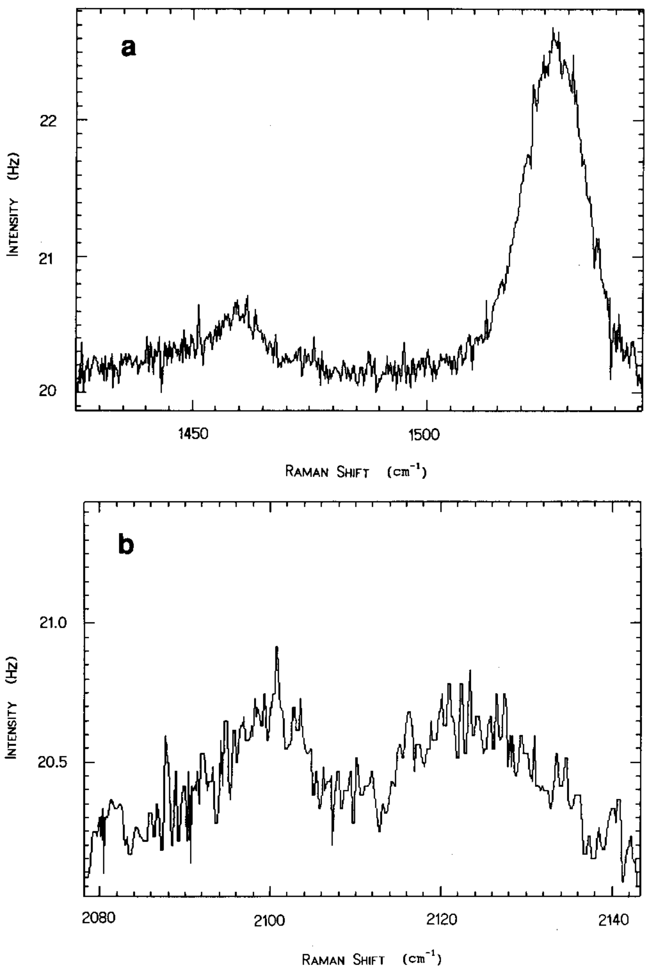

Figure 10 Raman spectra of a monolayer film of ω-PCDA PDA in the 'red' phase excited with 514.5 nm laser radiation: (a) 'double-bond' vibration; (b) 'triple-bond' vibration

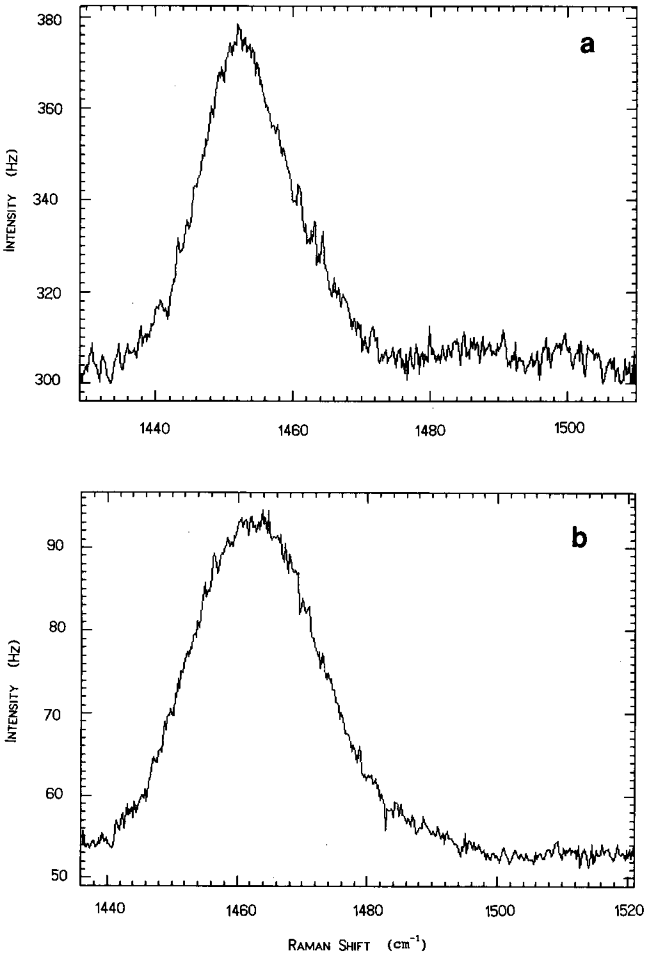

Figure 11 Raman spectra of a monolayer film of ω-PCDA PDA in the region of the 'double-bond' vibration, excited with 647 nm laser radiation: (a) film in the 'blue' phase; (b) film after conversion to the 'red' phase

oxidation would be relatively rapid. The results in *Figure 12* show that before the admission of oxygen the integrated intensity of the band was relatively stable. With the admission of oxygen, however, the integrated intensity fell rapidly, dropping to 40% of the initial value within 4 min. Two conclusions may be drawn from this result. First, a vacuum of 10^{-3} Torr is sufficient to remove the adsorbed oxygen from the red film; when oxygen is readsorbed then the expected photooxidation occurs upon irradiation with a 514.5 nm laser beam. Second, the absence of photooxidation before oxygen is readsorbed suggests that a monolayer film is stable in the red phase, even without the presence of oxygen. This is in contrast to the single crystals of TS PDA, where it was found that, under certain conditions, the phase transition was reversible. This result is not unexpected for the monolayer films of ω-PCDA PDA, as the blue-to-red phase transition is irreversible in LB films of a number of PDA materials[17]. Both the reversibility of the transition in TS PDA and the irreversibility in ω-PCDA PDA must be largely determined by side-group packing and interactions.

CONCLUSIONS

The adsorption of oxygen to form a weak charge-transfer complex with the polydiacetylene backbone has been demonstrated in single crystals and monolayer LB

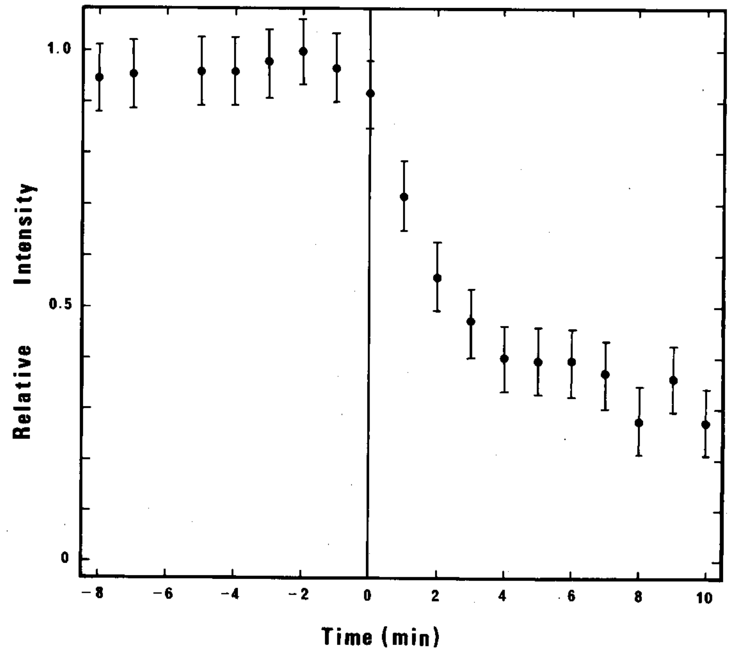

Figure 12 Integrated intensity of the 1525 cm^{-1} Raman band of a monolayer film of ω-PCDA PDA as a function of time. The film was held under a vacuum of approximately 10^{-4} Torr before oxygen was admitted at atmospheric pressure at time 0. The Raman spectra were excited by a 514.5 nm laser beam

films. The adsorption induces a structural phase transition in both the single crystals and the LB monolayers; the dominant electronic transition was found by resonance Raman specgroscopy to be at 2.24 eV in the single crystals, 0.26 eV higher than in the unperturbed crystal. The phase transition has been found to be reversible in single crystals but irreversible in the monomolecular films.

ACKNOWLEDGEMENTS

We acknowledge the support of the Science and Engineering Research Council for this research and for the studentship of BJES. The s.s.n.m.r. was carried out at the University of London Intercollegiate Research Service at RHBNC. We are grateful to Mr Simon Bedford for the synthesis of the ω-PCDA monomer.

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