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ABSORPTION AND ADSORPTION OF OXYGEN BY A POLYDIACETYLENE

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Crystals of the toluene sulfonate polydiacetylene have been prepared in an oxygen-free environment. Upon exposure to O_2, micro-crystals of the polymer were found to absorb an amount of gas equivalent to approximately two molecules per unit cell. Analysis of x-ray structural data suggested that the absorbed O_2 must reside on the surface or at crystalline defects. Adsorption of $^{16}O_2$ and $^{18}O_2$ on the surface of macro-crystals was monitored by the appearance of extra lines in the resonance Raman spectrum. Excitation profiles of the extra lines indicate that the presence of O_2 induced additional electronic transitions at 2.4 and 2.6 eV. The lower in energy has been tentatively identified as an electronic excitation on the perturbed backbone while the higher involves charge transfer between the backbone and the adsorbed O_2 molecule. Both types of excitation lead to photooxidation of the crystal surface.

Oxygen plays an important role in the electronic properties (1,2) of conjugated polymers as well as being an effective agent in their degradation (3). The large single crystals formed by the solid-state polymerization of certain diacetylenes provide a well defined system in which to study the effects of O_2. The resulting polydiacetylenes (PDA) have the backbone structure $\{CR-C{\equiv}C-CR\}_n$; the accessibility of the backbone to O_2 depends upon the shape and packing of the sidegroups R. The PDA derived from monomer crystals of the bis (p-toluene sulfonate) of 2,4-hexadiyne-1,6 diol (TS), which has the sidegroup R = $CH_2OSO_2C_6H_4CH_3$, is known to be sensitive to O_2. Crystals kept exposed to air in the light at room temperature over a period of weeks gradually lose their metallic lustre and turn black, although cleaving off the surface layer restores the metallic appearance.

The optical properties of freshly prepared PDA-TS crystals are dominated by an intense absorption band at approximately 2.0 eV which is due to a transition of the π-electron system of the PDA backbone which is largely excitonic in nature (4,5). Resonance Raman (RR) spectra at 300 K display only four lines of significant intensity; 2086 cm^{-1} and 1486 cm^{-1} associated with stretching modes of the triple and double bonds respectively, and 1203 cm^{-1} and 952 cm^{-1} associated with rotational motion about those bonds (6). A fifth line of weaker intensity at 1467 cm^{-1} is associated with a Fermi resonance between the 1486 cm^{-1} mode and the CH_2 scissors mode of the first molecular unit of the sidegroup (7).

Under certain conditions crystals of PDA-TS have been found to exhibit an extra Raman line at 1517 cm^{-1} for laser excitations in the region of 2.4 eV (8). The simultaneous occurrence of photodegradation and good correlation with data for other hydrocarbons led to the conclusion that a weak complex had been formed between O_2 molecules and the PDA backbone which had a charge transfer (CT) excitation at 2.39 eV. This paper presents the results of further investigations into the phenomenon.

ABSORPTION OF O_2 BY PDA-TS CRYSTALS

TS monomer was synthesised by the usual techniques (9). A mass of 0.407 g of the monomer was taken directly as precipitated from the final step of the chemical preparation and sealed into a glass vacuum system. The sample was in the form of a white powder consisting of micro-crystals with dimensions in the 10 to 100 μm range. After being held at a pressure of approximately 10^{-6} Torr for four days the monomer was thermally polymerized in situ. A one litre flask of O_2 at 760 Torr was then opened to the chamber containing the PDA-TS powder and the pressure instantaneously fell to 590 Torr as a result of the change in volume. Over a period of several days the pressure fell erratically to a stable value of 569 Torr. Mass spectrometric analysis of a sample of the gas in the vacuum system showed essentially pure O_2 so it was concluded that the 21 Torr drop in pressure was caused by absorption of O_2 by the PDA-TS powder. The amount absorbed was thus equivalent to 2.2 molecules of O_2 per unit cell of PDA-TS.

The large quantity of absorbed O_2 suggested that there might be a site within the unit cell for O_2 storage. Since TS monomer crystals prepared from both O_2-rich and O_2-free solvents were found to have essentially the same polymerization characteristics, it was known that such a site could not be located in the vicinity of the chemically reactive moiety of the monomer molecule. The search for a possible site was carried out by modification of standard crystallographic structure routines used for analysis of x-ray diffraction data. When atoms with standard van der Waals' radii were located on their appropriate sites within the PDA-TS unit cell it was found no site could be found for an O_2 molecule which did not involve considerable atomic overlap. The only possible conclusion was that the absorbed O_2 must be located largely at crystalline defects.

Evidence for the nature of the defects responsible for such a large take up of O_2 comes from cleaving single crystals known to contain O_2 under ultra-high vacuum (UHV) conditions and analysing the released gases by mass spectrometry. The results for both TS monomer and polymer crystals were approximately the same. Of the gas molecules given off by cleaving on (100) planes, approximately 80% were acetone, 15% O_2, 4% p-toluene sulfonic acid, and 1% other atmospheric gases. These results suggest that under normal crystal growth conditions the O_2 enters the crystal in association with the solvent and that the defects responsible for inclusion are likely to be planar. Transmission electron microscopy has shown that PDA-TS crystals contain substantial numbers of stacking faults on at least seven different crystallographic planes (10). Sample geometry restrictions in the electron microscope prevented investigation of stacking faults on the (100) plane but, since that is the plane of easiest cleavage in the crystals, they are almost certainly present on that plane as well. It is not known whether the acetone and O_2 enter the crystal simultaneously with the formation of the stacking faults or diffuse into the monomer crystal at a later stage along existing stacking faults. Multiple cleaving of a number of crystals on the (100) plane by adhesive tape usually removed nearly parallel sheets of polymer of roughly 10 μm thickness. It is possible that this thickness is associated with the typical spacing between stacking faults in PDA-TS crystals.

ADSORPTION OF O_2 ONTO THE CRYSTAL SURFACE

Macroscopic O_2-free crystals of TS monomer have been prepared by slow evaporation under inert atmosphere from acetone solution (11). Dissolved O_2 had been removed from the acetone by bubbling nitrogen or argon through it for four hours prior to dissolving the TS monomer. The monomer was recrystallized three times and then selected crystals were polymerized for 72 hours at 333 K under a vacuum of 10^{-5} to 10^{-6} Torr. Crystals prepared in this manner displayed no Raman lines other than those due to the pure polymer, provided they were stored under refrigeration and were then held in a vacuum lower than 10^{-5} Torr for three hours before spectra were

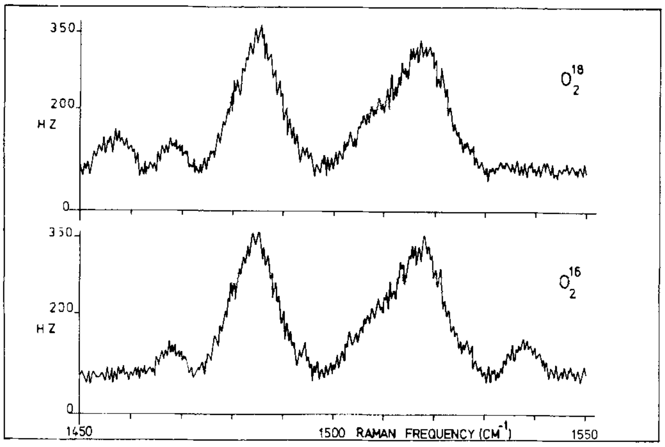

FIGURE 1 Raman spectra for PDA-TS crystals exposed to $^{16}O_2$ and $^{18}O_2$ at 295 K for an incident laser photon energy of 2.60 eV.

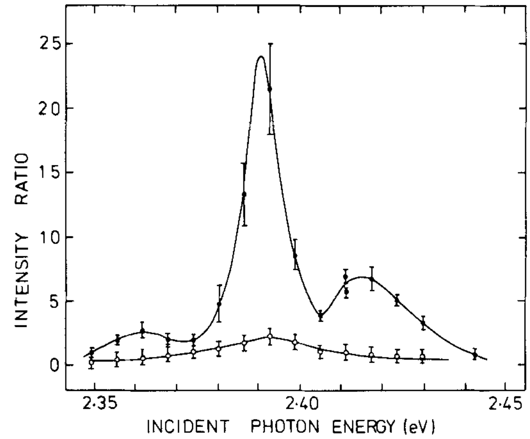

FIGURE 2 Excitation profiles of the 1517 cm^{-1} Raman line at 295 K (open circles) and 4 K (full circles).

recorded. When O_2 was allowed into the vacuum system the adsorption of the O_2 onto the PDA-TS crystal surface was detected by the appearance of two extra lines in the RR spectrum for incident laser photon energies in the range 2.3 to 2.7 eV. Typical spectra are shown in Fig. 1 for adsorption of both $^{16}O_2$ and $^{18}O_2$. The intensity of the lines saturated in two to three hours; the lines disappeared on a similar time scale if the vacuum was restored. The O_2-induced Raman line at 1517 cm^{-1} is isotope independent while the second line appears at 1538 cm^{-1} for $^{16}O_2$ and 1455 cm^{-1} for $^{18}O_2$.

Repeating the adsorption experiments in the presence of N_2 and/or H_2O vapor had no effect on the RR spectra. The intensity of laser light on the sample had to be kept very low or photooxidation occurred; for most of the RR spectra an unfocused laser beam of about 1 mW intensity was used. Similar spectra have been recorded from the (102) and (001) crystal facets (12) which are parallel to the polymer chain. No evidence for O_2 has been observed on the (011) facet which makes an angle of 80.4° with the polymer chain direction. Crystals grown from benzene, toluene, hexane, and cyclohexane from which the dissolved O_2 had not been removed also exhibit RR spectra indicating the presence of adsorbed O_2. Exposing O_2-free crystals to the pure gases N_2, H_2O, CO, CO_2, NO or NO_2 induced no extra lines in the PDA-TS Raman spectrum. By contrast, exposure to I_2 produced weak Raman lines at 165, 214 and 1580 cm^{-1} for laser excitation centred at 2.57 eV.

The excitation profile (EP) was measured for each of the O_2-induced Raman lines for incident laser photon energies in the range 2.3 to 2.7 eV using the techniques previously described (13). In that research the RR cross section for the 1486 cm^{-1} line of the pure polymer had been found to be nearly constant over the range so the intensity of that line has been used as an internal standard in the present experiments. Thus in the EPs shown in Figs. 2, 3 and 4 the intensities of the O_2-induced Raman lines have been ratioed to that of the 1486 cm^{-1} line. Figure 2 is the EP of the 1517 cm^{-1} line in the vicinity of 2.4 eV. The approximately symmetric profile at 295 K develops structure at 4 K; this is probably associated with the structural phase transition of PDA-TS which occurs at approximately 195 K (14). In addition the intensity ratio at 2.39 eV increases by more than a factor of 10 on cooling from 295 K to 4 K. The EP of the 1517 cm^{-1} line is plotted in Fig. 3 in the vicinity of 2.6 eV at 295 K for $^{16}O_2$ and $^{18}O_2$ and at 4 K for $^{16}O_2$. The intensity is considerably lower than at 2.4 eV and only increases by about a factor of four on cooling from 295 K to 4 K but again structure develops in the profile. The EP of the 1517 cm^{-1}

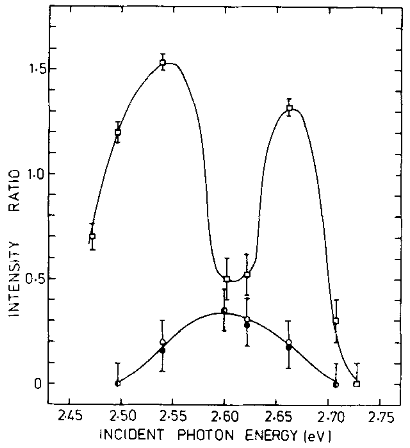

FIGURE 3 Excitation profiles of the 1517 cm^{-1} Raman line for $^{16}O_2$ (open circles) and $^{18}O_2$ (full circles) at 295 K and $^{16}O_2$ (squares) at 4 K.

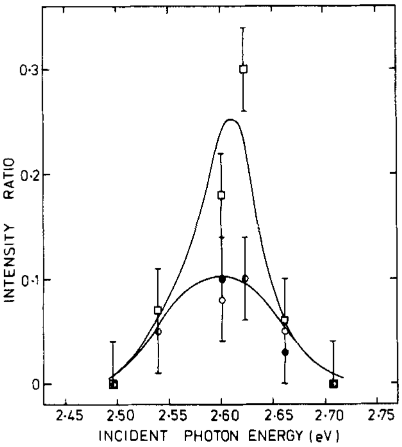

FIGURE 4 Excitation profiles of the 1538 cm^{-1} Raman line for $^{16}O_2$ at 295 K (open circles) and 4 K (squares) and the 1455 cm^{-1} Raman line for $^{18}O_2$ at 295 K (full circles).

line is virtually identical for adsorption of both $^{16}O_2$ and $^{18}O_2$. The EPs of the 1538 cm^{-1} line for adsorbed $^{16}O_2$ at 295 K and 4 K and the 1455 cm^{-1} line for adsorbed $^{18}O_2$ at 295 K are shown in Fig. 4. At 295 K the EPs for the 1455 cm^{-1} line of $^{18}O_2$ and the 1538 cm^{-1} line of $^{16}O_2$ are essentially the same. Upon cooling to 4 K the profile for the 1538 cm^{-1} line does not appear to develop structure and only increases in intensity by approximately a factor of three. At 4 K the frequencies of the two Raman lines of $^{16}O_2$ are 1524 cm^{-1} and 1541 cm^{-1}.

The EP of a vibrational mode observed in RR spectroscopy is determined primarily by two factors, the transition diple moment (M) of the relevant electronic excitation and the displacement (D) along the normal coordinate of the vibrational mode which occurs in the transition from the ground to the excited state (15). The shape and linewidth of the EP should be similar to that of the absorption coefficient while the total cross section is proportional to M^2D^2. In the present experiments the EPs shown in Figs. 2, 3 and 4 suggest that two distinct electronic transitions are induced by the adsorption of O_2 on the surface of PDA-TS crystals. At 295 K transition I is centred at 2.39 eV and has a f.w.h.m. of approximately 0.02 eV, a width similar to that of the dominant 1.98 eV transition of PDA-TS crystals (4), while transition II at 2.60 eV has a f.w.h.m. of 0.1 eV. Since, in addition to having the same width, transition I is insensitive to the O_2 isotope adsorbed it seems likely that transition I is localized on the PDA-TS backbone. There are at least two possible explanations for the origin of transition I. In the first, O_2 adsorption effects a change in the structure of the polymer backbone and shifts the allowed transition from 1.98 eV to 2.39 eV. The locally altered force constants would also shift the Raman active vibrational mode frequency from 1485 cm^{-1} to 1517 cm^{-1}. The second possibility arises from the breaking of the inversion symmetry of the polymer chain by the adsorption of O_2. The usually forbidden transitions of the type $A_g \rightarrow A_g^*$ become allowed and there is experimental (16) and theoretical (17) evidence that the lowest of these transitions occur in the vicinity of 2.4 eV in PDAs. In this case the 1517 cm^{-1} Raman line would have B_u rather than A_g symmetry. The lattice vibrational model which has successfully modelled the A_g modes has also predicted a B_u mode of roughly that frequency (6,18).

We have attempted to observe transitions I and II directly by monitoring the change in the reflectivity of the (100) crystal surface during the adsorption of O_2. There appeared to be a nearly uniform decrease in reflectivity over the whole spectral range by a few percent with a slight alteration of structure in the vicinity of 2.4 eV. It is too early, however, to draw any definite conclusions other than the obvious one that the values of M for transitions I and II are very much smaller than that of the 1.98 eV transition.

The EPs in Figs. 3 and 4 show that the product M^2D^2 is smaller for transition II than transition I; it is not possible at this stage to say which of M or D makes the greater contribution to the decrease. The Raman line at 1517 cm^{-1} associated with transition II appears to originate from the same vibrational mode as the 1517 cm^{-1} line associated with transition I, since the frequencies are the same within experimental uncertainty and both insensitive to isotopic substitution. Thus in both transitions the 1517 cm^{-1} Raman line must arise from a vibrational mode of the PDA-TS backbone. In contrast the other vibrational mode associated with transition II has a value of 1538 cm^{-1} for $^{16}O_2$ and 1455 cm^{-1} for $^{18}O_2$. Since the frequency ratio is very nearly equal to the square root of the isotropic mass ratio we conclude that this vibrational mode corresponds to the oscillation of the two oxygen atoms about the center of mass of the O_2 molecule. In the gas phase O_2 has a vibrational frequency of 1555 cm^{-1} so there appears to be a decrease in frequency of 17 cm^{-1} upon adsorption. Thus transition II is associated with vibrational modes on both the PDA-TS backbone and the adsorbed O_2 molecule. This strongly suggests that transition II is a CT excitation in which an electron is transferred from the PDA chain to the O_2 molecule (19). Extrapolation of the work of Chien (20) on O_2 adsorbed to a wide variety of hydrocarbons (see Fig. 3 of Ref. 8) suggested that a CT excitation for O_2 adsorbed on a PDA would be expected in the 2 - 3 eV range (8). The identification in that paper of transition I as the CT excitation appears to be incorrect; in the light of the present work we conclude that transition II at 2.60 eV is the expected CT excitation. The limited results for adsorbed I_2 are also what might be expected from a type II transition. There have been a number of studies of CT excitations arising from the interaction of I_2 with various hydrocarbons (19).

A low temperature study of the time evolution of transitions I and II provides evidence that there are two different sites for O_2 adsorption on the crystal surface. Figure 5 shows the approach to saturation for the 1517 cm^{-1} Raman line for laser excitation in the transition I band compared with that for the 1517 cm^{-1} and 1538 cm^{-1} lines for laser excitation in the transition II band. In this experiment the initially O_2-free crystal was held in a vacuum of approximately 10^{-6} Torr for two days at 295 K, cooled to 120 K, exposed to O_2, and then cooled to 4 K in approximately 15 minutes. The intensity of

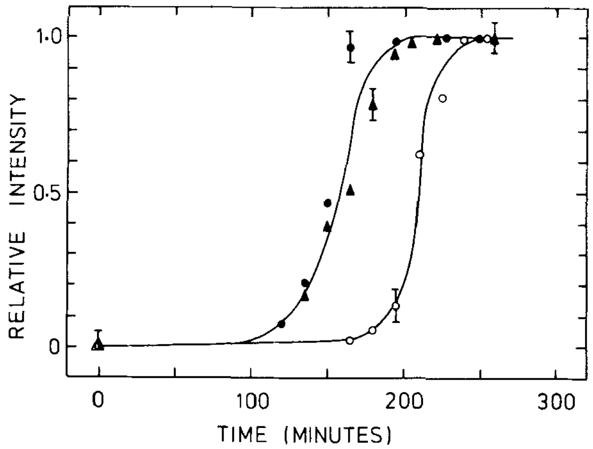

FIGURE 5 Intensities of the 1517 cm^{-1} and 1538 cm^{-1} Raman lines relative to their saturation values at 4 K as a function of the time elapsed since exposure of the crystal to O_2. Open and full circles are for the 1517 cm^{-1} line with laser excitations of 2.41 eV and 2.60 eV respectively. Triangles are for the 1538 cm^{-1} line with a laser excitation of 2.60 eV.

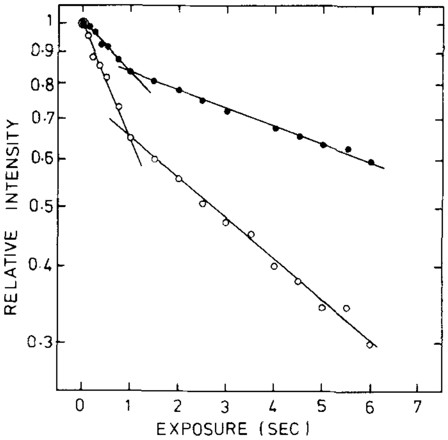

FIGURE 6 Intensity of the 1517 cm^{-1} Raman line relative to its initial value as a function of the duration of exposure to incident laser radiation at 2.41 eV (open circles) and 2.60 eV (full circles).

the Raman line associated with transition I saturated some 50 minutes later than that of the two lines associated with transition II. At 295 K the saturation times of the two transitions are similar and a few minutes shorter than that of transition II at 4 K.

Photooxidation of the crystal surface was observed when illuminated with laser light of too great intensity. The *resulting darkening of the surface was accompanied by a* simultaneous decrease in the intensity of the O_2-induced Raman lines with little effect on the intensity of the 1486 cm^{-1} line of the polymer. This is further evidence that adsorption of O_2 is limited to the outermost surface layers of the crystal. Figure 6 shows the relative decrease in the intensity of the 1517 cm^{-1} line from its maximum value as a function of exposure to uniform laser radiation of intensity 0.3 W/mm^2 in the vicinity of transitions I and II. The exposure was controlled with an electronic shutter. Radiation of the same intensity at laser photon energies of 1.91 and 2.18 eV produced no detectable photooxidation. For both transitions there appears to be a two stage process of photooxidation with excitation into the band of transition I causing photooxidation at roughly twice the rate as excitation into the band of transition II. This is further evidence that transitions I and II are different in character.

In summary we have found that O_2 is adsorbed onto the surface of PDA-TS crystals; bulk absorption only occurs at crystal defects believed to be primarily stacking faults. The *adsorbed* O_2 *induces electronic transitions* at 1.39 eV and 2.60 eV which have been detected by RR spectroscopy. The excitation which is lower in energy is localized on the perturbed polymer backbone while that which is higher involves a CT excitation from the polymer to the adsorbed O_2.

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