

# Electron microscopy of photo-oxidized polydiacetylene crystals

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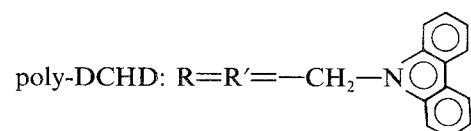
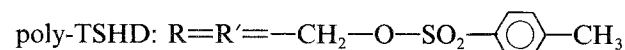
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The photo-oxidation of toluene sulphonate polydiacetylene single crystals has been studied by scanning and transmission electron microscopy. Submicron particles were observed as reaction products on the surfaces of crystals which had been exposed to 514 nm light from an argon ion laser. Electron diffraction showed that these particles were single crystals of *para*-toluene sulphonic acid. The appearance of the particles was correlated with the decrease in intensity of a Raman line associated with the presence of adsorbed oxygen on the crystal surface.

## 1. Introduction

Photo-oxidation of polymers is a subject of both scientific and commercial interest. There are very few instances, however, where the process is sufficiently simple for a detailed model to be developed [1]. The chromophore responsible for the initiation of the photo-oxidation may be the polymer itself, impurities included in processing or products of another photochemical process. The succeeding steps after the initial absorption of a photon can also be complex. An opportunity to study the photo-oxidation of a conjugated polymer in a very controlled manner is provided by single crystals of polydiacetylenes. The polymer chains are present in a crystal lattice of a high degree of perfection [2-4] with a relatively small number of impurities [5]. Although photo-oxidation of polydiacetylenes is a very special case it is possible that the results may have wider application.

Polydiacetylenes having the structure  $[RC-C\equiv C-CR']_n$  have been produced as macroscopic single crystals by the solid state polymerization of monomer crystals with a range of sidegroups R [6-8]. For light polarized parallel to the polymer chain the crystals have a metallic lustre. This is not due to conduction electrons, but to the intense absorption band at approximately 2 eV (620 nm) associated with transitions in the  $\pi$ -electron system on the backbone [9, 10]. The two polydiacetylenes which have been most extensively studied have sidegroups with the chemical formulae:



Crystals of the two polymers react very differently to being stored in air at room temperature with normal lighting conditions [11]. The poly-TSHD crystals

gradually discolour over a period of weeks and eventually turn black, while the poly-DCHD crystals retain their mirror-like reflectivity. Inspection of space-filling atomic models of the polymer chains based upon X-ray crystallographic data [12, 13] gives some indication as to the origin of this difference in behaviour. The sidegroups in poly-TSHD lie approximately in the plane of the backbone so that molecules like oxygen should have relatively easy access to the conjugated bonds within it. By contrast the bulky sidegroups of poly-DCHD stack at a large angle to the plane of the backbone and afford it much better protection. Once the surface of the poly-TSHD crystals has tarnished, further degradation of the crystals is very slow. The metallic lustre of crystals which are several years old can be readily restored by cleaving off a few micrometres of the surface.

Quantitative measurements of the adsorption of oxygen on poly-TSHD surfaces and their subsequent photo-oxidation have been made by resonance Raman (RR) spectroscopy [11, 14]. The intrinsic RR spectrum of poly-TSHD has four prominent lines at 952, 1203, 1485 and 2086  $cm^{-1}$  for all incident laser wavelengths in the visible. When oxygen was adsorbed on the surface, a new Raman line appeared at 1517  $cm^{-1}$ , of comparable intensity to the 1485  $cm^{-1}$  line, for incident laser photon energies within 0.1 eV of 2.4 eV (517 nm). The intensity of this extra Raman line was found to decrease approximately exponentially with the time of exposure to photo-oxidizing light. In addition, the 2.4 eV photon energy associated with the appearance of the 1517  $cm^{-1}$  line also corresponded with the threshold for photo-oxidation. Light of lower photon energy had no effect on the crystals until such high intensities were reached that thermal degradation of the surface occurred. It was concluded that the most likely mechanism for photo-oxidation involved the ene-reaction of singlet oxygen [15-17] in which the double bond is attacked and peroxide formed. A chemical test had showed that peroxide is present on

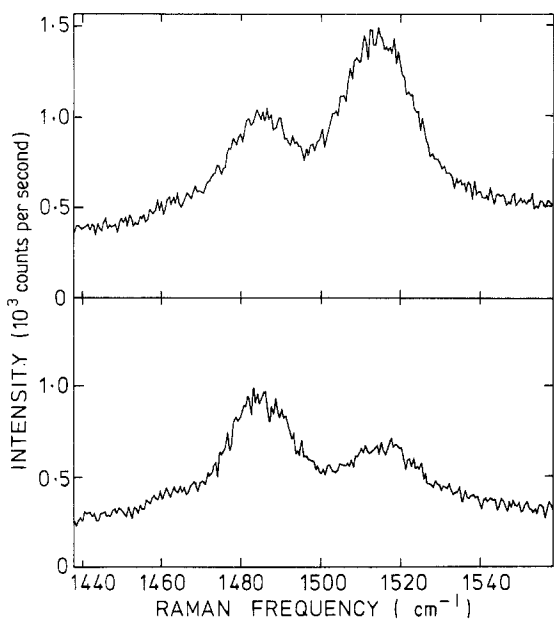


Figure 1 Resonance Raman spectra of a poly-TSHD crystal. The upper trace was obtained from a fresh (100) surface; the lower from the same spot after 8 min exposure to the 6 mW 514 nm laser beam. The spectra were recorded with a 0.5 mW 514 nm laser beam at a resolution of  $5\text{ cm}^{-1}$ .

freshly photo-oxidized surfaces. It was suggested that the singlet oxygen was produced by energy and spin exchange with the poly-TSHD backbone in its 2.4 eV excited state.

In the present experiment single crystals of poly-TSHD have been studied by scanning (SEM) and transmission (TEM) electron microscopy to investigate the nature of the damage to the surface caused by photo-oxidation. The reaction products found on the surface have also been studied by electron diffraction.

## 2. Experimental details

Monomer single crystals of millimetre dimensions were prepared for the SEM measurement by slow evaporation from acetone solution [5]. Crystals sufficiently thin ( $\sim 100\text{ nm}$ ) for the TEM were prepared by allowing a few drops of  $10^{-2}\text{ M}$  monomer in xylene solution to evaporate on the surface of water [2]. The crystals were then collected on a 400 mesh copper microscope grid. Both types of sample were converted from monomer to polymer by annealing for 72 h at 333 K in air. The polymer crystals for the SEM were cleaved to give fresh (100) faces.

The presence of adsorbed oxygen was monitored by RR spectroscopy using the 514 nm line of an argon ion laser with  $180^\circ$  backscattering geometry [14]. The 0.5 mW beam was brought to an approximately  $200\text{ }\mu\text{m}$  diameter focus; this intensity was sufficiently low that no detectable photo-oxidation occurred during the 2 min it took to scan a Raman spectrum. Photo-oxidation was induced by increasing the power in the beam to 6 mW for 1 min between successive Raman spectra.

The SEM images were produced using a JEOL JSM 35CF scanning electron microscope. The samples were mounted on a copper alloy disc and vacuum coated with gold prior to observation. The TEM and electron diffraction studies were carried out in a JEOL

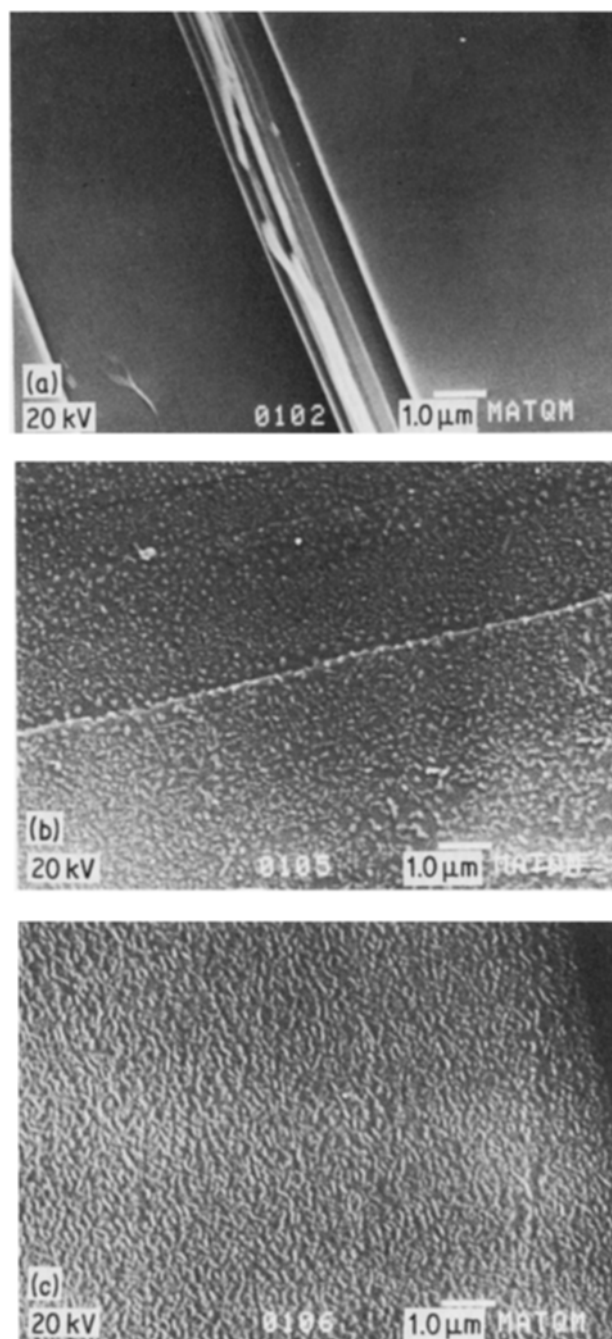


Figure 2 SEM of Poly-TSHD crystals (a) before exposure to the 6 mW 514 nm laser beam, (b) after 2 min exposure and (c) after 8 min exposure.

100CX electron microscope operated at 100 kV. In order to minimize beam damage the crystals were viewed at relatively low magnification and low beam intensity.

## 3. Results

Fig. 1 shows the Raman spectrum covering the region of the  $1485$  and  $1517\text{ cm}^{-1}$  lines prior to and after 8 min accumulated exposure to the 6 mW laser beam. The appearance of the crystal surface within the area of the focal spot before and after such exposure is shown in Fig. 2. The freshly cleaved crystal surface is smooth at this magnification except for cleavage steps and a few fibres which were pulled out during the cleaving process. After 2 min exposure the surface is densely covered with particles of  $0.1$  to  $0.2\text{ }\mu\text{m}$  dimension. After 8 min the density of particles is so high

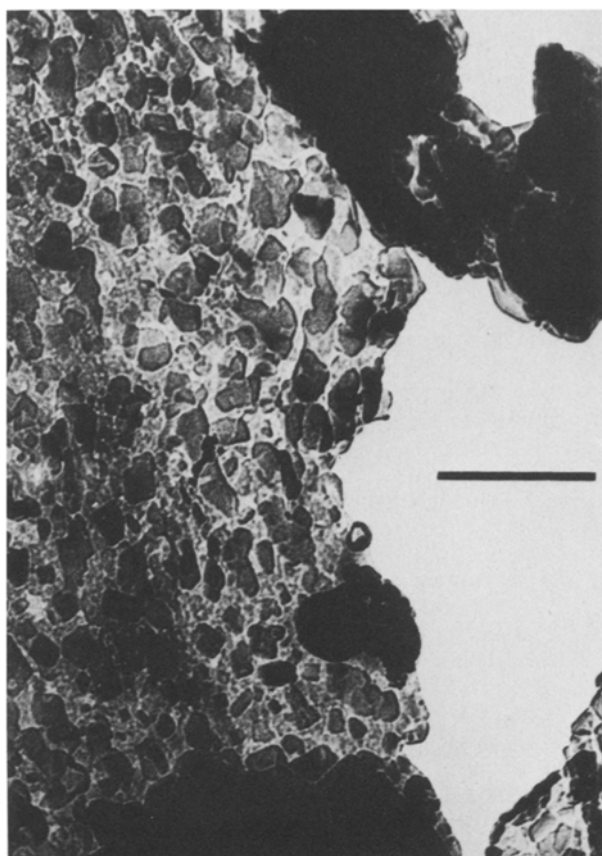


Figure 3 TEM of a photo-oxidized poly-TSHD crystal. The bar is 2  $\mu\text{m}$  long.

that almost no smooth areas remain on the crystal surface.

The thin crystal in the TEM image shown in Fig. 3 had an exposure similar to that in Fig. 2c. Again the

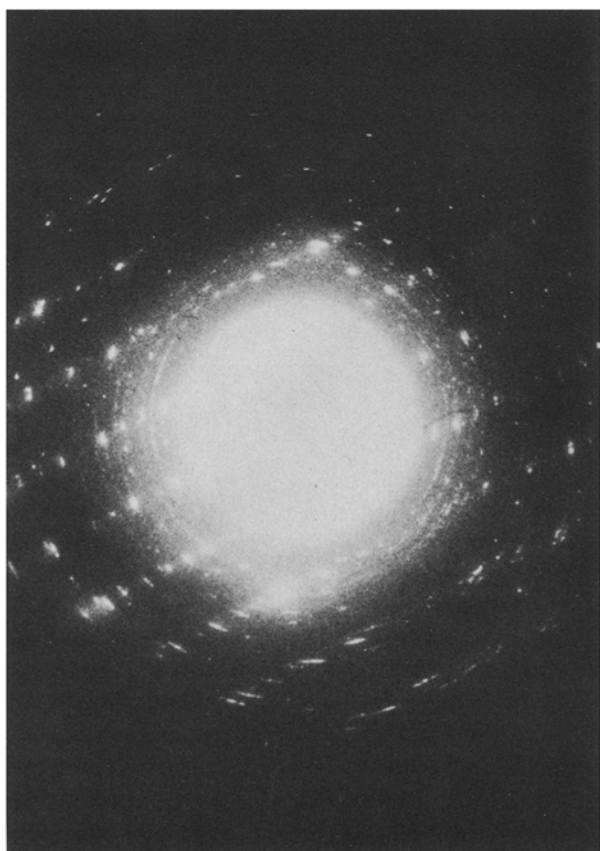


Figure 4 Electron diffraction pattern of the crystal in Fig. 3.

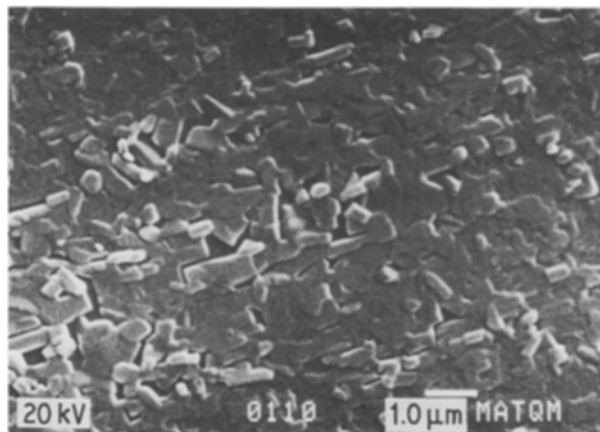


Figure 5 SEM of a poly-TSHD crystal which had been left on a shelf in air for over 3 years.

particles typically have a 0.1 to 0.2  $\mu\text{m}$  transverse dimension. The selected-area electron diffraction pattern for this region of the crystal is shown in Fig. 4. The regular array of spots is just that expected for diffraction by a single crystal of poly-TSHD [2]. The diffraction rings at the centre of the pattern which are not present with freshly prepared crystals must arise from the particles on the surface which appear during photo-oxidation. Thus the particles on the surface are likely to be single crystals, or at least polycrystalline. The diameters of the diffraction rings give lattice spacing which are essentially identical to *para*-toluene sulphonic acid (PTSA) with the chemical formula  $\text{HOSO}_2\text{C}_6\text{H}_4\text{CH}_3$ . This was established by X-ray diffraction of PTSA powder using a Debye-Scherrer camera. This identification of PTSA as the photo-oxidation product was confirmed by washing the samples with water in which PTSA is highly soluble and analysing the resultant solution by high-pressure liquid chromatography.

An SEM image of a poly-TSHD crystal surface which has been “naturally” photo-oxidized by being left on a shelf in air for over 3 years is shown in Fig. 5. The particles on the surface are significantly larger, 0.2 to 1  $\mu\text{m}$ , than those on rapidly photo-oxidized crystals. The tendency of the crystals to be faceted suggests that they are likely to be single crystals.

#### 4. Discussion

The most significant result of these experiments is the positive identification of PTSA as a reaction product of the photo-oxidation of poly-TSHD. This is one of the end products of the series of chemical reactions initiated by the absorption of a photon by the polymer backbone in the presence of oxygen. The two steps leading to the production of PTSA would appear to be the breaking of the C–O bond in the sidegroup followed by abstraction of one of the H atoms of the  $\text{CH}_2$  unit. A suggestion for the complete reaction scheme of the photo-oxidation process will be presented in a later paper [17]. The other chief reaction products are expected to be volatile.

The SEM images of the photo-oxidized crystals in Figs. 2 and 5 suggest that the observed darkening of the crystals during photo-oxidation arises from the

presence on the crystal surface of particles which are in linear dimensions approximately equal to the wavelengths of visible light. In a reflectivity experiment much of the incident light would be scattered out of the specularly reflected beam. Thus although the underlying intact polymer must still be highly reflecting and the PTSA crystals transparent at visible wavelengths, the crystal will appear dark instead of metallic. Some of the colour change could also be due to short segments of polymer chain formed at intermediate stages of the photo-oxidation process. Thus far there has been no clear indication of such oligomers in the optical or Raman spectra.

The continuity of the photoreaction product on the surface of the heavily photo-oxidized crystals in Figs. 2 and 5 explains the passivation of the surface to further oxidation and the disappearance of the  $1517\text{ cm}^{-1}$  Raman line. Once the oxygen adsorbed on the surface is used up, the largely complete coverage of the surface by PTSA crystals prevents further oxygen from reaching the underlying polymer. The larger PTSA crystals on the surface of the slowly photo-oxidized crystal indicate that the PTSA molecule has mobility on the poly-TSHD crystal surface. Although the equilibrium vapour pressure of PTSA has not yet been determined, it is sufficiently large to give the compound a distinctive odour. The melting point of PTSA is  $105^\circ\text{C}$  so significant surface mobility could be expected. The vapour pressure was not so high that there was any appreciable loss of material in the vacuum of the TEM during the exposures required to obtain Figs. 3 and 4.

## 5. Conclusions

One of the end products of the photo-oxidation of the surface of single crystals of the polydiacetylene poly-TSHD is *para*-toluene sulphonic acid. The compound results from the breaking off of the sidegroup at the C–O bond and the formation of the acid. The reaction product condenses into submicron crystalline particles on the photo-oxidation surface. The completion of the surface coverage prevents further oxidation of the underlying polymer.

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