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Extended-chain polydiacetylene crystals

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The results of a preliminary study of the structure and morphology of a 100% crystalline polydiacetylene (pTS) have been presented. The crystals of the polymer have been prepared by solution crystallization of the monomer and subsequent thermal polymerization. They have been obtained in various morphological forms which include thin films, thin lamellae and fibrillar sections cleaved from macroscopic crystals. These various morphologies all have the polymer molecules in a chain-extended conformation and the polymer molecules lie in the plane of the thin crystals or sections. These morphologies are compared with the morphologies of conventional chain-folded semicrystalline polymers and they offer a unique opportunity to study new aspects of the structure and deformation of polymer crystals.

1. Introduction

Investigations of the structure and physical properties of crystalline polymers are often frustrated by difficulties in obtaining these materials in suitable morphologies. Conventional semi-crystalline polymers crystallized from the melt tend to be spherulitic and so are somewhat complicated systems to study. However several groups of workers have made considerable progress in understanding the structure mechanical behaviour of spherulitic polymers [1, 2]. About 20 years ago it was discovered that it was possible to obtain lamellar single crystals of polyethylene by precipitation from dilute solution [3]. Since that time it has been found that most other crystalline polymers can be obtained in the form of lamellar single crystals by solution crystallization.

The deformation of polymer single crystals has been studied by the deposition of the crystals on extensible substrates [4–6] such as mylar. Since the crystals normally have molecules in a chain-folded conformation and the molecular directions are usually approximately normal to the plane of the lamellar crystals, the only type of deformation that can be readily studied is that which takes place by shear or cleavage in directions perpendicular to the molecular chains [1, 5]. The morphology of, and chain orientation in, the lamellae severely limit the types of deformation that can be imposed upon the crystals.

It has been possible to observe the effects of other types of deformation upon polymer crystals by preparing bulk polycrystalline specimens having a single-crystal texture [1, 7, 8]. Considerable progress has been made in understanding the deformation mechanisms in polyethylene using this type of sample [1] but there is always the problem of following the deformation of the amorphous phase and understanding how it affects the deformation of the crystals.

An important step forward was made with the discovery that it was possible to prepare completely crystalline polymer crystals by the solid-state polymerization of certain diacetylene monomers. This work was started initially by Wegner and co-workers in Germany [9]. It has been extended at Allied Chemicals in the USA [10] and at Queen Mary College in London [11, 12]. Polydiacetylene single crystals can be obtained with dimensions of the order of centimetres. They offer a unique opportunity to study the deformation of macroscopic polymer crystals. It has been found recently that these crystals undergo deformation by means of a twinning process which causes the chain axes to rotate across the boundary of the twin [13, 14]. This type of deformation has been studied by both optical and scanning electron microscopy [12, 13]. However, the detailed mechanisms of this type of deformation can only be studied using transmission electron microscopy. This paper is con-

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cerned with the preparation of samples of a polydiacetylene with morphologies that are suitable for study using transmission electron microscopy. Such samples must be sufficiently thin that they are tranparent to electrons. Two main techniques have been used. One is the growth of thin monomer crystals from the evaporation of solvent from dilute solution and the subsequent thermal polymerization of these monomer crystals to produce polymer crystals with an identical morphology. The other method that has been employed is that of the cleavage of thin sections from the surface of macroscopic polymer crystals. It will be shown that both of these methods produce samples which are suitable for study in the transmission electron microscope. This paper is concerned with the structure of the various morphological forms that are produced and the details of the structure and deformation of these materials will be presented in subsequent publications.

2. Experimental details

The materials used in the present study were the monomer and polymer of 2,4-hexadiyne-1,6-diol *bis*(*p*-toluene sulphonate). The samples were supplied by Dr D. Bloor of the Physics Department, Queen Mary College. The polymer will be referred to in this presentation as pTS. It was prepared in its various morphological forms as outlined below.

It is known that the monomer of pTS is soluble in many common solvents. In particlular it has been found in this present study that small monomer crystals could be obtained by allowing dilute solutions in methanol, carbon tetrachloride or xylene to evaporate on carbon-coated electron microscope grids. The crystals formed by this method were generally irregularly sized and this method of specimen preparation for the electron microscope was not found to be particularly useful.

2.1. Crystallization on the surface of water

A standard method of obtaining organic molecular crystals for electron microscopy is by the evaporation of the solvent from a dilute solution of the species on the surface of water. For this to occur the solvent must be volatile, immiscible with, and less dense than, water. Xylene is a solvent which has these properties and has been used with anthracene crystals for example [15].

A 1×10^{-2} M solution of TS monomer was made and filtered to remove any traces of polymer (insoluble in xylene) that may have been present. It was then allowed to cool to room temperature and a few drops of the solution were then put onto the surface of distilled water and the solvent allowed to evaporate. Two days later the resulting film which floated on the water surface was collected on 200 mesh EM grids.

2.2. Crystallization on mylar

In order to look at the deformation of lamellar polymer crystals it is necessary to deposit the crystals onto an extensible substrate. Several drops of the solution of TS monomer in xylene (Section 2.1) were deposited upon 25 μm thick mylar and allowed to dry. The monomer crystals which remained after the xylene evaporated were annealed on the mylar film in an air-oven at 60° C for approximately 70 h to complete the polymerization [11]. The formation of polymer crystals was manifested by the change in appearance of the initially colourless film. After annealing it became purple when viewed in transmitted light and had a gold metallic lustre in reflected light. The films were lightly shadowed with gold palladium and were extracted from the mylar using 25% aqueous polyacrylic acid solution [5]. They were then carbon-coated and the polyacrylic acid was dissolved away in distilled water leaving the polymer crystals adhering to a carbon film floating on the water surface. This was then collected on grids for examination in the electron microscope.

2.3. Cleavage of macroscopic crystals

In order to complete the morphological study of pTS, thin cleaved sections obtained from macroscopic crystals, also supplied by Dr Bloor, were examined. The crystals have been described in detail elsewhere [11, 12] and can have dimensions of the order of centimetres. Thin sections are readily pulled from the (0 1 0) face of the crystals using adhesive tape. In general the sections produced by the initial cleavage were rather thick and it was necessary to repeatedly cleave the sections, in order to obtain thin sections which were transparent in the electron beam. The sections were seperated from the adhesive tape by soaking them in trichloroethylene. This solvent dissolved the adhesive gum and the sections which floated off in the solvent were collected on 200 mesh EM grids.

2.4. Electron microscopy

The electron microscope used was a JEOL JEM-7 operated at 100 kV. The crystals were somewhat beam-sensitive [16] at room temperature (22° C). In order to minimize beam damage the crystals were viewed at relatively low magnifications and low beam intensity. Using this technique it was found that significant beam damage, as monitored by the loss of a diffraction pattern or the disappearance of bend contours in the bright-field image, did not occur until at least 10 to 15 sec had elapsed.

3. Results and discussion

The micrographs presented in this paper represent a preliminary study of the morphology of pTS. A more detailed study of the structure and deformation of the various morphologies will be presented in later publications. In each of the three morphologies shown in this present paper the molecules in the crystals are in a completely chain-extended conformation. The plane of the thin crystals in each case corresponds to (0 1 0) with the molecular direction [0 0 1] lying in this plane. This is an orientation which is completely different from that normally encountered in lamellar single crystals of conventional semicrystalline polymers [3–6] where the molecules are normally folded with the chain direction approximately perpendicular to the lamella surface [5].

3.1. Crystals grown on water

Thin monomer crystals were grown on the surface of water at room temperature by the evaporation of dilute xylene solution. They were in the form of thin films which had a slight pink coloration which was indicative of the presence of a small amount of polymer. When examined in the electron microscope the film was seen to contain many bend contours. As soon as it was exposed to the electron beam the contours were seen to move around rapidly. It was assumed that the electron beam was initiating polymerization which is known to be exothermic and the heat evolved was causing distortion of the thin film. After a few seconds the bend contours ceased to move and remained for about 1 min at normal viewing intensity after which time they disappeared indicating that beam damage was becoming significant. All of the micrographs shown here are of the polymerized film.

A typical area of polymer film is shown in Fig. 1a. The doubly exposed 5 μm square is the area selected for the selected-area diffraction pattern (SADP) in Fig. 1b. A striking feature of the bright-field micrograph is the presence of a high density of bend (extinction) contours. These are due to the film not being absolutely flat and the processes which lead to their formation have been described elsewhere [15, 17]. Jones and Williams [15] have recently shown that the way that bend contours are displaced or distorted by crystal defects can be used to analyse the defects in the crystal. This is particularly useful in beam-sensitive materials where time is not available for specimen tilting or detailed diffraction analysis. This technique has been called "real space crystallography" [15]. It can be seen in Fig. 1a that there is considerable interaction between crystal defects and the bend contours in certain areas of the micrograph.

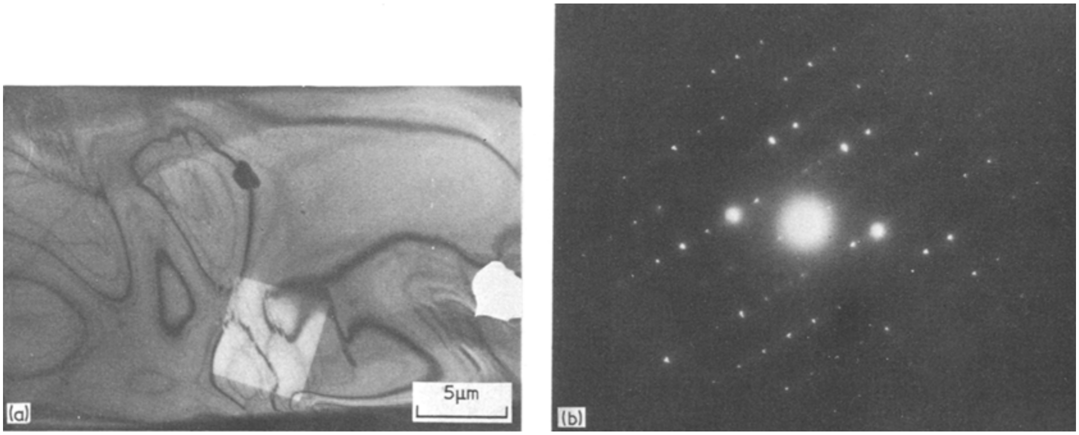

Figure 1 Thin single-crystal film of pTS prepared by evaporation of a solution of monomer in xylene on the surface of water. (a) Area of film showing bend contours and defects. (b) SADP from doubly exposed area in (a) showing that the chain direction is in the plane of the film.

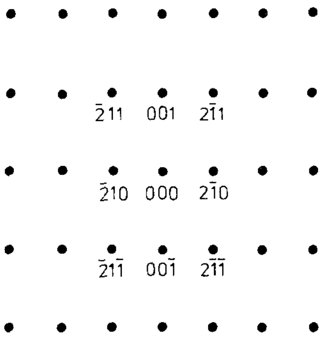

Figure 2 Schematic diagram of reciprocal lattice section of pTS for a beam direction of [1 2 0].

It is not possible at this stage to identify the particular defects but they could be dislocations or microtwins [15].

The SADP shown in Fig. 1b is from a relatively large area which contains defects. The SADP shows an approximately single-crystal orientation but there is evidence of doubling of the individual spots and some extra spots are present. In the macroscopic single crystals of pTS the large face is known to be (0 1 0) [12]. The crystal structure of pTS has been determined by Kobelt and Paulus [18] as monoclinic ($P2_1/b$) with a = 14.94 Å, b = 14.49 Å and c = 4.91 Å and γ = 118.1 Å. [1 2 0] is approximately perpendicular to (0 1 0) and so a projection of the reciprocal lattice of pTS along [1 2 0] is shown in Fig. 2. It was found that the principal reflections in the SADP in Fig. 1b corresponded to those in the lattice in Fig. 2 showing that the thin films crystallized on water, the plane of the film is probably (0 1 0). However, the bends in the film and the presence of defects tend to make the diffraction pattern rather complicated.

Fig. 3a and b show further examples of the film grown on the surface of water and polymerized in the electron beam. The areas shown in these two micrographs are near the edges of the films and again show bend contours but the areas appear to be more perfect with less evidence of the interaction between crystal defects and the bend contours. Analysis of defects in the pTS films using real-space crystallography [15] will be presented in a later publication.

3.2. Crystals grown on mylar

A typical micrograph of pTS crystals grown on mylar is given in Fig. 4a. The crystals had been polymerized and stripped off the mylar and backed with carbon as described in Section 2.2. The crystals in Fig. 4a are then lying on a carbon film. The doubly exposed square is the area taken for the SADP in Fig. 4b. The crystals can be seen to be in the form of irregularly shaped lamellae with some straight edges. As with the crystals grown on the surface of water, the lamellae can be seen to contain bend contours and in some cases defects are seen to interact with the bend contours. The diffraction pattern is again from rather a large selected area and so the spots are doubled because the crystals appear to be slightly split. However, the principal reflections correspond again to the schematic pattern in Fig. 2 indicating that the beam direction is approximately [1 2 0] and the plane of the lamellae is (0 1 0). In Fig. 4b there are extra spots between the main ones on the first and second order layer lines. This could be due to either double diffraction [15] or to variations in specimen orientation due to bends [17] within the film. However,

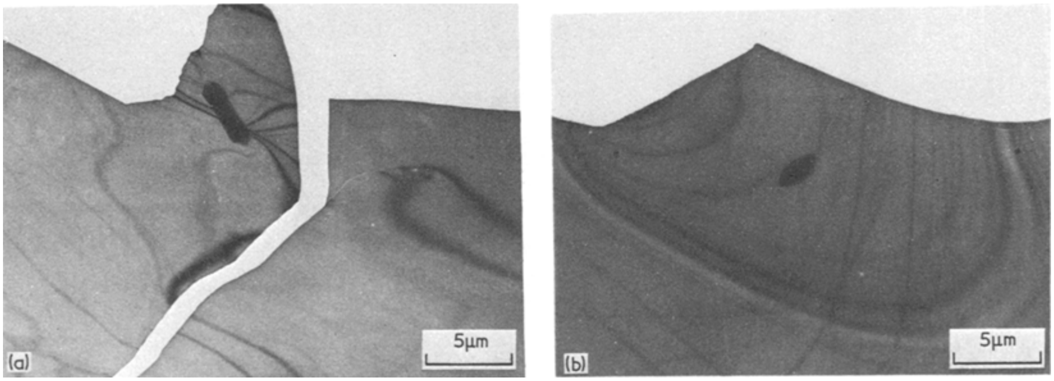

Figure 3 Thin films of pTS similar to the one in Fig. 1. (a) Area near an edge containing a crack. (b) Relatively defect-free area at edge of film.

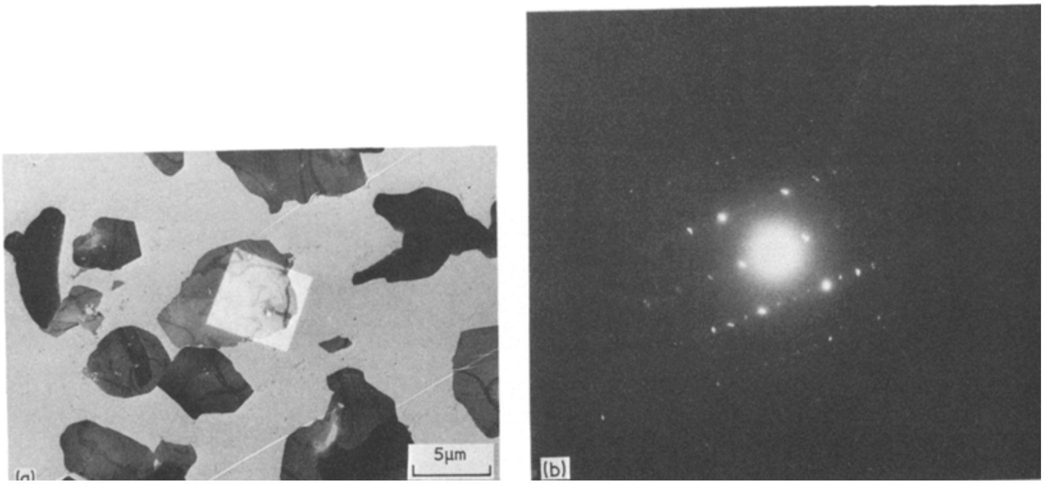

Figure 4 Lamellar single crystals of pTS grown by the evaporation of monomer solution on the surface of mylar. (a) Crystals on a carbon film after removal from the mylar using polyacrylic acid. (b) SADP from doubly exposed area in (a) indicating that the chain direction is in the plane of the lamellae.

an important conclusion that can be drawn from the diffraction pattern is that the chain direction of the polymer molecules lies in the plane of the lamellae. This must be contrasted with observations of solution-crystallized lamellar polymer crystals where the molecules are normally folded with the chain direction approximately perpendicular to the lamellar surfaces. The new morphology found in pTS means that we have an orientation which enables us to view polymer single crystals in directions perpendicular to the molecules. In conventional polymer crystals in the form of lamellae, viewing is restricted to directions parallel to the molecules. It should facilitate the examination of defects in polymer crystals and help to provide a new insight into the structure and deformation of polymer crystals.

Further examples of the lamellar single crystals of pTS are shown in Fig. 5. The crystals in these micrographs are somewhat larger (up to 25 μm across) and the detail of the bend contour patterns can be seen clearly.

Some preliminary studies have been carried out on the deformation of these crystals when deposited on the mylar substrate. They have been found to undergo cleavage and chain axis rotation twinning [14]. Details of these studies of deformation and the structure of the lamellar crystals will follow in a later publication.

3.3. Cleaved sections from macroscopic crystals

Macroscopic polymer crystals of pTS are shown in Fig. 6. These crystals are of the order of centi-

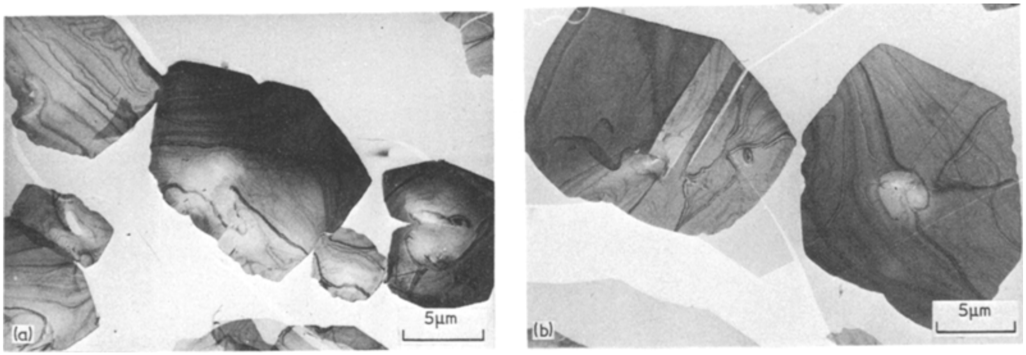

Figure 5 Lamellar single crystals of pTS showing bend contours. (a) Crystals of different sizes. (b) Relatively large crystals showing a pseudo-hexagonal morphology.

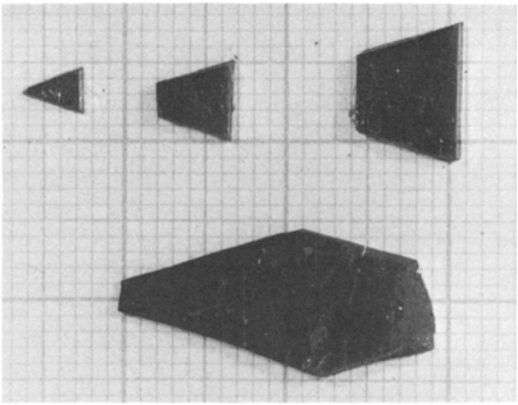

Figure 6 Macroscopic single crystals of pTS (supplied by Dr D. Bloor). The lines on the graph paper have a spacing of 1 mm.

metres in size and their deformation behaviour has been discussed in detail in previous publications [13, 14]. In order to study the internal structure of the crystals, thin sections were taken as described in Section 2.3. A bright-field micrograph of a section is shown in Fig. 7a. The doubly-exposed square again corresponds to the area taken for the SADP in Fig. 7b. It can be seen that the crystals tend to fibrillate when they are cleaved. In the microscope they are also found to be prone to charging which can make detailed analysis of their structure rather difficult.

The SADP in Fig. 7b is again similar to the reciprocal lattice section in Fig. 2 and it indicates that the molecular chains are oriented along the fibre axis in the cleaved crystals.

The cleaved sections of pTS may be compared with similar cleaved sections of a macroscopic polymer crystal, $(SN)_x$ [19, 20]. There has been considerable interest expressed recently in this material because of its superconducting properties [21]. The study of cleaved sections is facilitated in $(SN)_x$ because it is also a metallic conductor at room temperature and charging problems are reduced. However, $(SN)_x$ is found to have a microstructure in which unusual and interesting contrast effects have been seen [19, 20]. On the other hand, the microstructure of cleaved pTS appears to be more uniform than that of $(SN)_x$ but small areas can be seen in which there are fine striae running perpendicular to the chain axis as is found in $(SN)_x$ [20].

Another important feature that can be found in the cleaved pTS crystals is twinning. Fig. 8 shows an area of crystal containing a relatively large twin about 1 μm thick and 4 μm long. The boundary of this twin makes an angle of about 72° to the chain axis in the (0 1 0) plane. This means that the trace of the boundary is a ⟨1 0 1⟩ direction. Similar traces have been found in macroscopic pTS crystals after deformation [13, 14] and have been shown to be due to chain-axis rotation twins with a K_1 twinning plane of $(2\bar{1}2)$ [14]. It is not certain at what stage the twin in Fig. 8 had been formed. The crystals used for cleavage were previously undeformed but deformation could have been induced by handling the crystals during sectioning. It seems more likely that the twin formed after cleaving

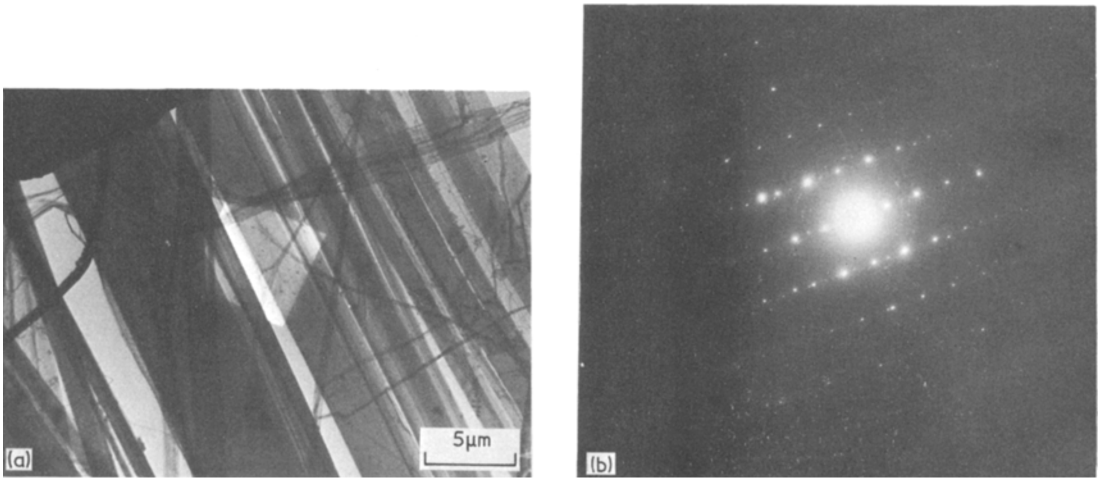

Figure 7 Cleaved fibrillar section of a macroscopic pTS crystal. (a) Typical area. (b) SADP from doubly exposed area in (a) showing that chain direction is parallel to the fibril axis.

Figure 8 Cleaved fibrillar section of macroscopic pTS crystal showing a twin and unusual contrast features in its vicinity.

because the twin is relatively short and is restricted to a single fibril.

The twins in pTS sections may be compared with kink bands found in similar thin sections of $(SN)_x$ that have been reported recently [20]. The kink bands have a large range of kink angles rather than the few well-defined angles that are found for the twins in pTS. In both cases the molecules bend across the kink or twin boundary. It appears that the fibrous nature and the large number of defects in the structure of $(SN)_x$ may allow the formation of kinks to take place with a large variation in kink angle. Since pTS has a more perfect structure, twins with coherent boundaries, rather than kinks, are found.

A detailed investigation into the structure and deformation of macroscopic pTS crystals using transmission electron microscopy is taking place at the moment and the results of this investigation will be reported at a later date.

4. Conclusions

It has been shown that it is possible to obtain thin extended-chain crystals of a polydiacetylene (pTS) which are suitable for studies in the transmission electron microscope. In the present paper preliminary investigations are reported on the structure of three particular morphological forms. They are

(i) crystals grown from solution on the surface of water, (thin films);

(ii) crystals grown from solution on mylar (thin lamellae); and

(iii) cleaved sections from macroscopic polymer single crystals (fibrils).

In each case the chain direction has been shown by selected-area electron diffraction to be in the plane of the crystal film. Some preliminary results of the structure and deformation of the various forms have been presented. More detailed results will be presented in subsequent publications.

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