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Solid state polymerization of bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol

Part 2 *Optical and scanning electron microscope observations*

D. BLOOR, L. KOSKI,* G. C. STEVENS
Department of Physics, Queen Mary College, University of London, UK

Optical and scanning electron microscopy have been used to assess the perfection of monomer and polymer crystals of bis-(*p*-toluene sulphonate) diacetylene. The degradation of polymer crystals and the morphology of polymer extracted from partially polymerized crystals have also been studied. The latter observations provide additional evidence that the polymerization is a homogeneous single phase transformation.

1. Introduction

Single crystals of many diacetylene monomers can be transformed into polymers by the action of heat, light or ionizing radiation. The arrangement of monomer and polymer molecules in crystals which polymerize is shown schematically in Fig. 1. The true nature of this solid state reaction has been established only recently [1]. Many diacetylenes, and in particular the bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol, polymerize to form large highly perfect polymer single crystals. Such polymerization is probably a homogeneous single phase transformation [2, 3]. In Part 1 [4] we have presented spectroscopic and X-ray diffraction evidence that this is the case for the bis-(*p*-toluene sulphonate) diacetylene. Additional optical and scanning electron microscope observations were made to obtain further support for this. The results of these observations are presented in Section 2. Information was also obtained about the degradation of polymer crystals, Section 3, and the perfection of monomer and polymer crystals, Section 4.

Details of sample preparation were given in Part 1. The monomer was prepared by the method due to Wegner [5]. Crystals of monomer were grown from acetone and methanol solutions and thermally polymerized in an argon atmosphere. Polymer was extracted from partially polymerized crystals by dissolving the unreacted monomer in acetone.

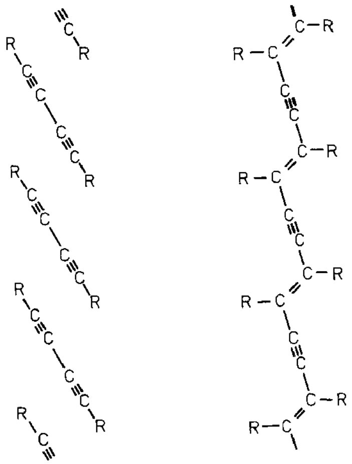

Figure 1 Left, arrangement of diacetylene monomer molecules necessary for solid state polymerization; right, diacetylene polymer chain.

2. Morphology of extracted polymer

X-ray diffraction and optical spectroscopy provide evidence for increasing crystallinity of the extracted polymer as the degree of conversion increases [4]. At low conversion levels the polymer chains are isolated in the monomer matrix and collapse on extraction to give an

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* Present address: Technical Research Centre of Finland, Helsinki, 18, Finland.

amorphous powder. As the amount of polymer increases some chains will occur as near neighbours so that some crystallinity is retained on extraction. Calculations based on random nucleation suggest that the bunching of the polymer chains is marked at conversion above 10%. This will favour a marked increase in crystallinity of the extracted polymer above 10% conversion. Since the rapid increase in polymerization rate of the bis-(*p*-toluene sulphonate) diacetylene above 10% conversion is due to the production of much longer polymer chains [4] we have a second reason for expecting greater crystallinity in this region.

These expectations are confirmed by microscopic observations. Fig. 2 shows optical micrographs of polymer extracts obtained from crystals polymerized at 70° C to conversions of 3.6, 9.3 and 22.5%. The results for extracts from crystals polymerized at 60 and 80° C to the same conversion levels are similar. The extract at 3.6% conversion is an amorphous powder with little sign of crystallinity, at 9.3% substantial alined regions appear and at 22.5% the sample is crystalline though still fibrous. SEM studies show the same morphologies, micrographs of extracts at 2.4, 11.7 and 96% conversion at 60° C are shown in Fig. 3. These show amorphous, layered and fibrous crystalline structures respectively. Even at 96% conversion there is evidence, at the highest magnifications, of traces of non-crystalline material. There is also evidence of regular crystallographic defects, these are discussed further in Section 4.

These observations clearly support the conclusion, reached in Part 1, that the bis-(*p*-toluene sulphonate) diacetylene undergoes a homogeneous single phase polymerization.

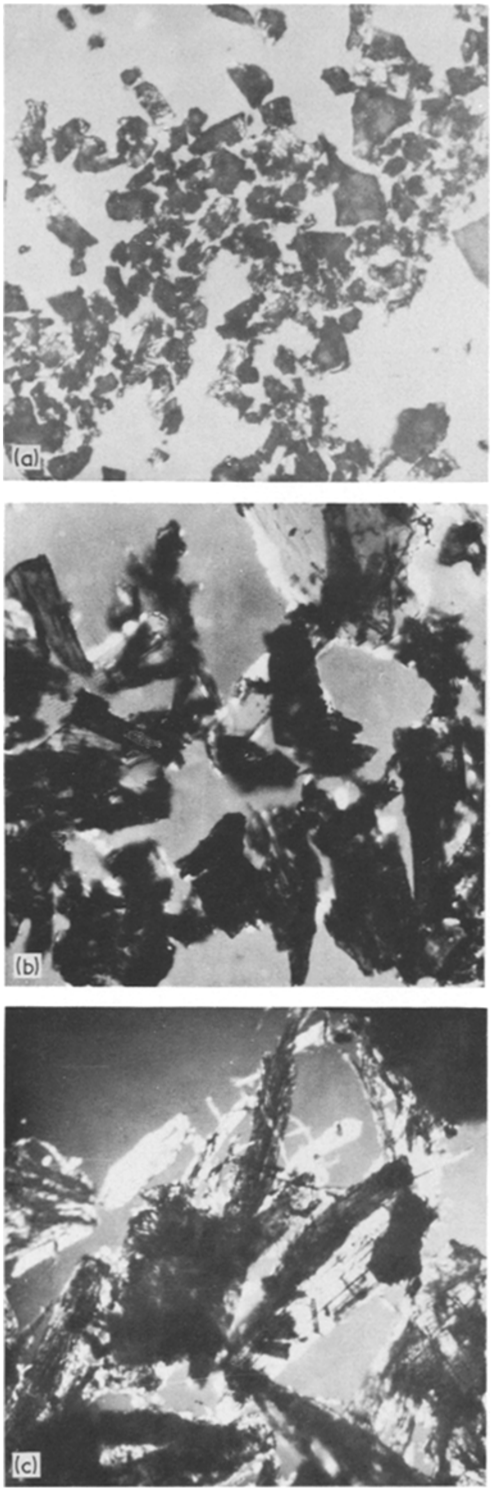


Figure 2 Optical micrographs of bis-(*p*-toluene sulphonate) diacetylene polymer extracted during polymerization in an inert atmosphere at 70° C: (a) extraction after 3.6% conversion, (b) extraction after 9.3% conversion and (c) extraction after 22.5% conversion. (a) and (b) about 1 mm square, (c) about 4 mm square.

3. Degradation of polymer crystals

Although the polymer produced by thermal polymerization at 60° C does not decompose when heated rapidly until 210° C prolonged heating causes decomposition at much lower temperatures [4, 5]. ESR and mass spectroscopy reveal a complex behaviour [6, 7]. Decomposition starts at about 110° C for samples polymerized at 60° C but immediately after polymerization at 70 and 80° C. Crystals heated to 140° C for 4 h and 150° C for 6 h in air were observed to be cracked along the easy cleavage directions of the polymer crystal. The exposed surfaces appeared fibrous and lost their metallic lustre.

Fig. 4 shows scanning electron micrographs of

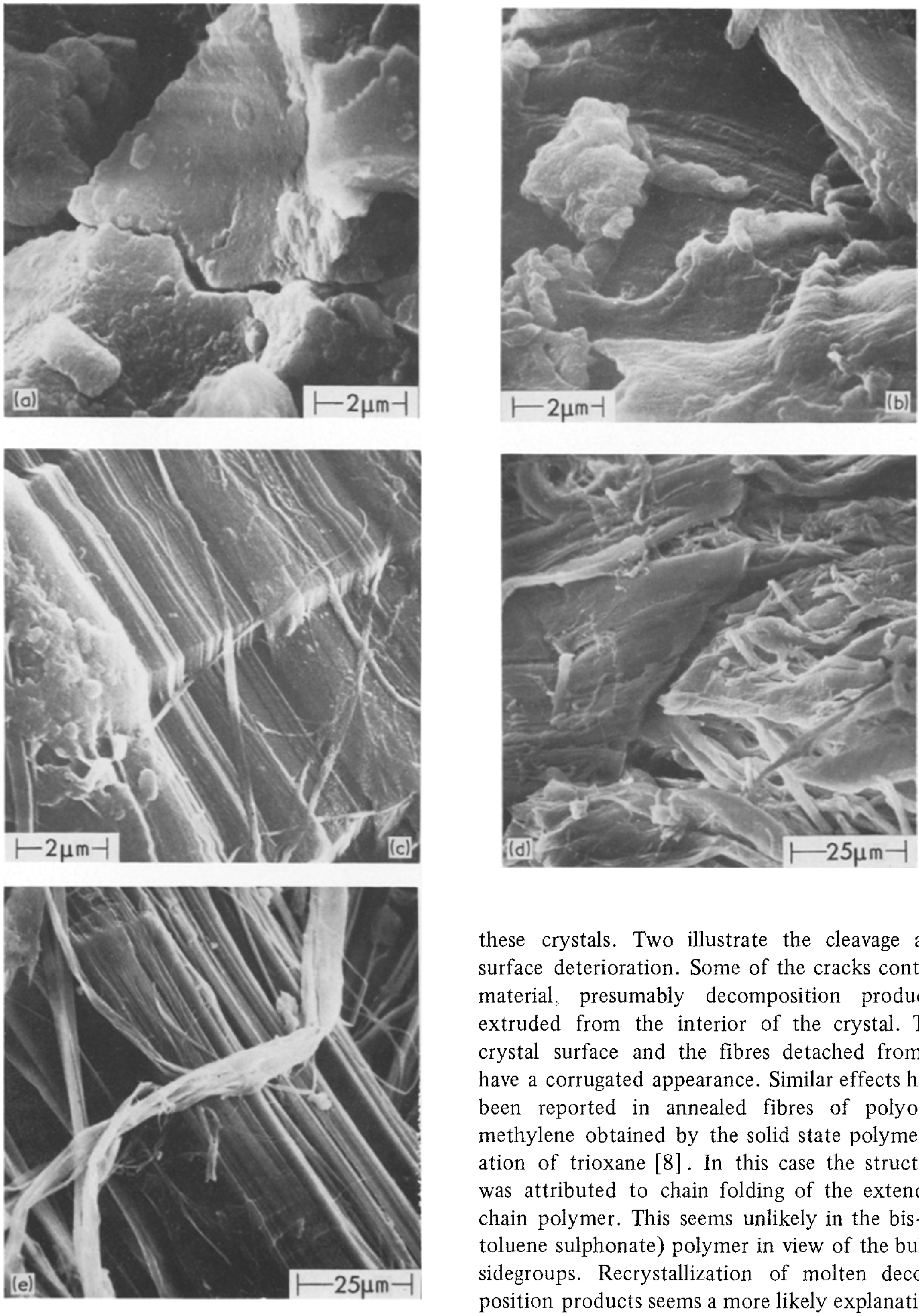


Figure 3 Scanning electron micrographs of extracted polymer, polymerization at 60° C in an inert atmosphere. (a), (b) and (c) extraction after 2.4, 11.7 and 96% conversion, high magnification; (d) and (e) extraction after 11.7 and 96% conversion, low magnification.

these crystals. Two illustrate the cleavage and surface deterioration. Some of the cracks contain material, presumably decomposition products, extruded from the interior of the crystal. The crystal surface and the fibres detached from it have a corrugated appearance. Similar effects have been reported in annealed fibres of polyoxymethylene obtained by the solid state polymerization of trioxane [8]. In this case the structure was attributed to chain folding of the extended chain polymer. This seems unlikely in the bis-(*p*-toluene sulphonate) polymer in view of the bulky sidegroups. Recrystallization of molten decomposition products seems a more likely explanation. There is additional evidence for this in the occurrence of solidified droplets and poorly formed crystals on the cleavage faces produced during heating. These are clearly visible on the right-hand side of Fig. 4b. The surfaces of crystals

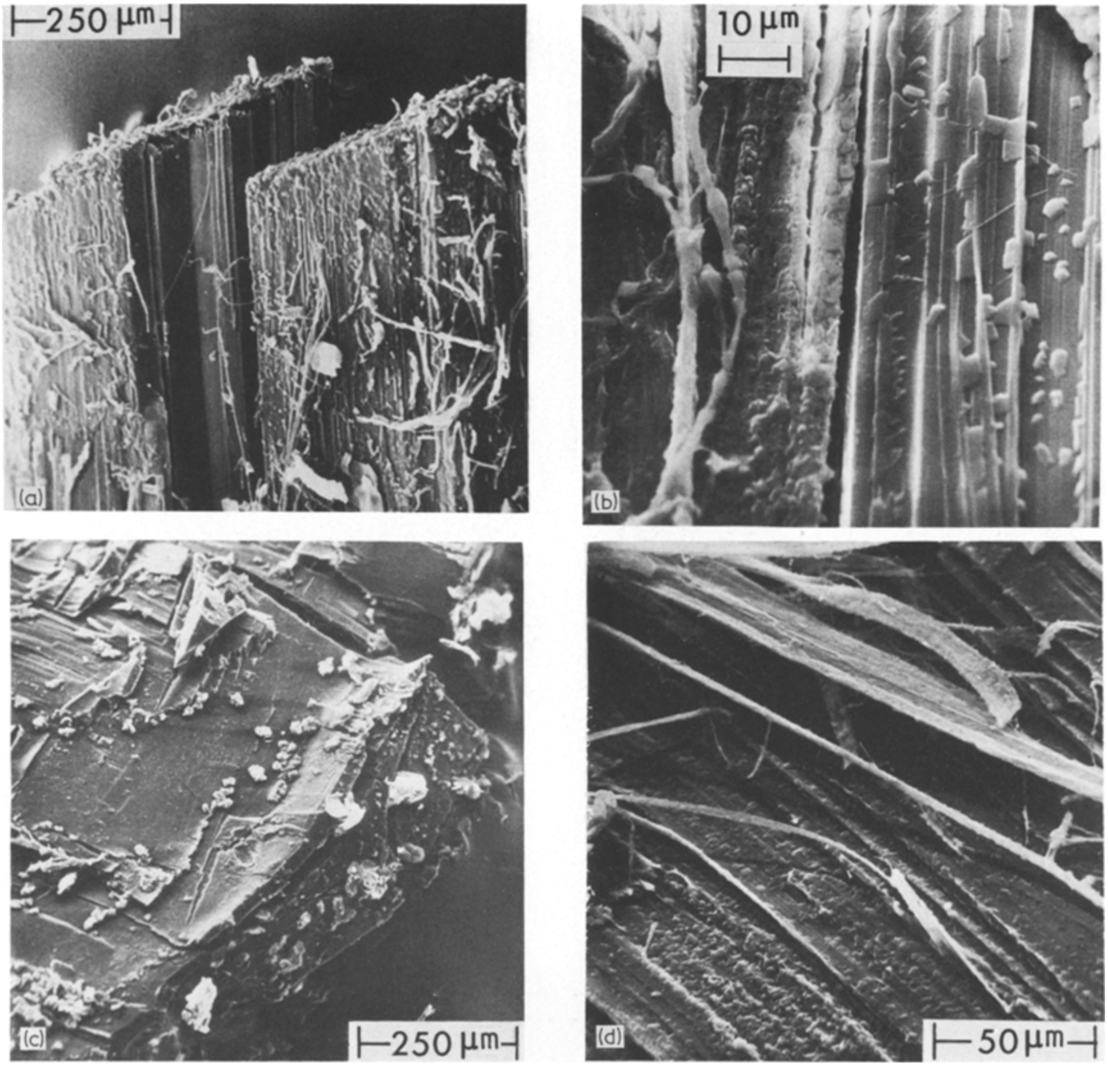


Figure 4 Scanning electron micrographs of polymer crystals heated in air: (a) and (b) sample heated to 140° C for 4 h; (c) and (d) sample heated at 150° C for 6 h.

in polycrystalline samples are often covered with much smaller crystals. These have well formed facets and are clearly of different origin than the features in Fig. 4b, which we attribute to decomposition products.

The microscope observations provide a direct confirmation of the occurrence of polymer decomposition well below 210° C.

4. Defects in monomer and polymer crystals

The bis-(*p*-toluene sulphonate) diacetylene polymer is monoclinic with symmetry $P2_1/b$ [9]. The monomer has the same symmetry but slightly different unit cell dimensions [4]. Slowly grown crystals have $(0\,1\,0)$, $(1\,\bar{1}\,1)$ and $(\bar{1}\,1\,1)$ facets. As the growth rate increases the crystals become extended in the *c*-direction and truncated in the *a*-direction. When the *c*-axis extension is small the additional facets are not planar, as shown in Fig. 5. The mean orientation of these irregular facets is close to $(1\,\bar{1}\,0)$. Small $(2\,1\,0)$ and $(1\,0\,0)$ facets appear on the irregular facet on the larger crystals. The *c*-axis extension can become very pronounced, under these conditions the lateral facets are comcomposed of numerous high index facets distributed around the $(5\,\bar{4}\,0)$ plane. Twin features are rare, but twinning on the $(0\,1\,0)$ plane was observed in one crystal terminated by a $(2\,\bar{1}\,0)$ facet. The monomer crystals cleave easily on $(0\,1\,0)$, $(2\,1\,0)$ and $(0\,0\,1)$ planes.

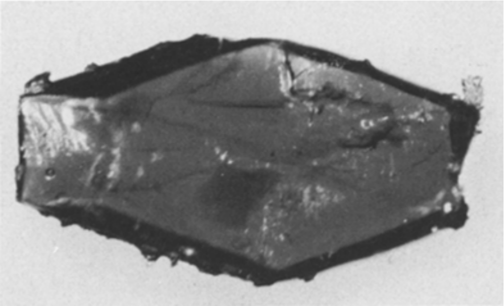
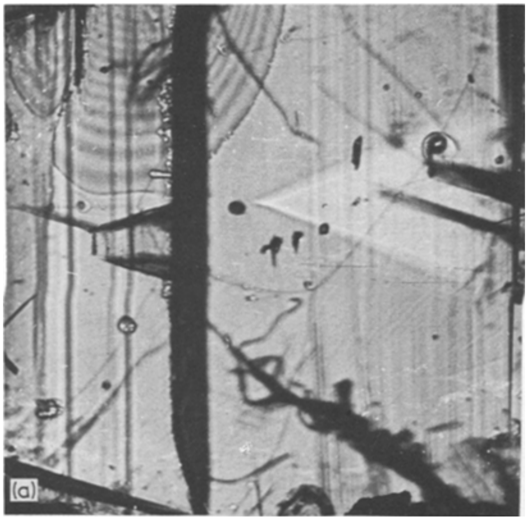


Figure 5 Monomer crystal with *c*-axis extension showing the irregular terminal facets. Light polarized parallel to the *c*-axis reveals the boundary of the irregular facet during growth, these features are not visible in light polarized perpendicular to *c*. Maximum dimension of the crystal is about 5 mm.

The irregular facets observed on many crystals will incorporate impurities which would be rejected at a crystallographic facet. This inclusion can be detected in partially and fully polymerized samples view in light polarized parallel to the polymer chains. At the absorption edge the refractive index for this polarization rises to a large value. If the orientation of the polymer chains is affected by defects in the crystal there will be a large change in the refractive index. When the crystal is illuminated with a collimated light beam these variations will produce marked intensity variations in the transmitted light. This effect is shown in Figs. 5 and 6 for partially and fully polymerized crystals. The regions bounded by the irregular facets during growth can be seen clearly as well as growth horizons due to fluctuations in impurity concentration. These regions must have a high dislocation density but the polymer crystal shows clean cleavage on (0 1 0) and (2 1 0) planes. The fact that lattice strains do not have a marked effect on the polymerization is to be expected since the initially formed polymer can produce a drastic compression of the monomer along the *c*-axis, far larger than any variation produced by impurities.

Dislocation etch pits on the (0 1 0) facet are elongated and aline along [0 0 1] as reported by



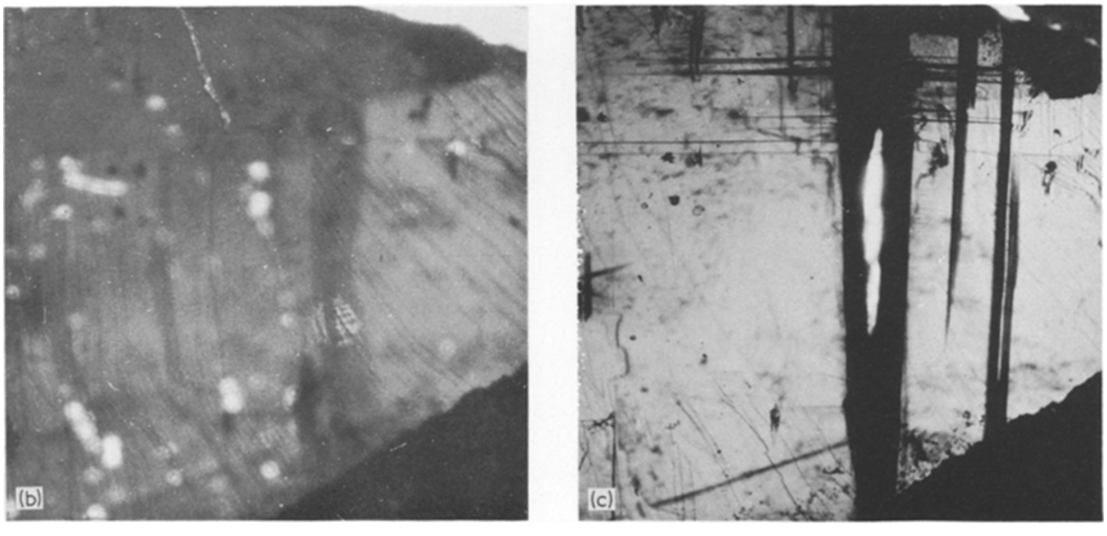


Figure 6 Polymer crystals showing defects under the irregular growth facet. (a) V-shaped areas of strain propagating to the right, *c*-axis vertical; (b) growth horizons due to impurity inclusion; (c) as (b) showing clean cleavage on (2 1 0), horizontal features are stress twins. Light polarized parallel to the *c*-axis in (a) and (b), unpolarized in (c). Micrographs are of regions about 2 mm square.

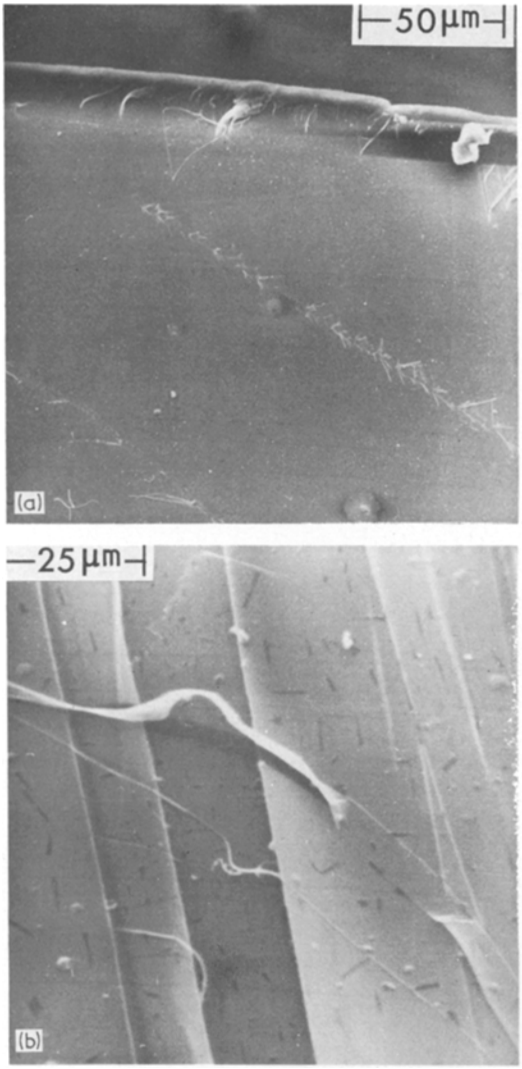


Figure 7 Scanning electron micrographs of clean and imperfect cleavage on (0 1 0) plane of polymer crystals. (a) clean cleavage with fibres pulled out along [0 0 1] at the edge, the broken fibres lie along [2 0 5] and terminate in a faint feature along [1 0 0]. (b) imperfect cleavage face covered with thin fibres.

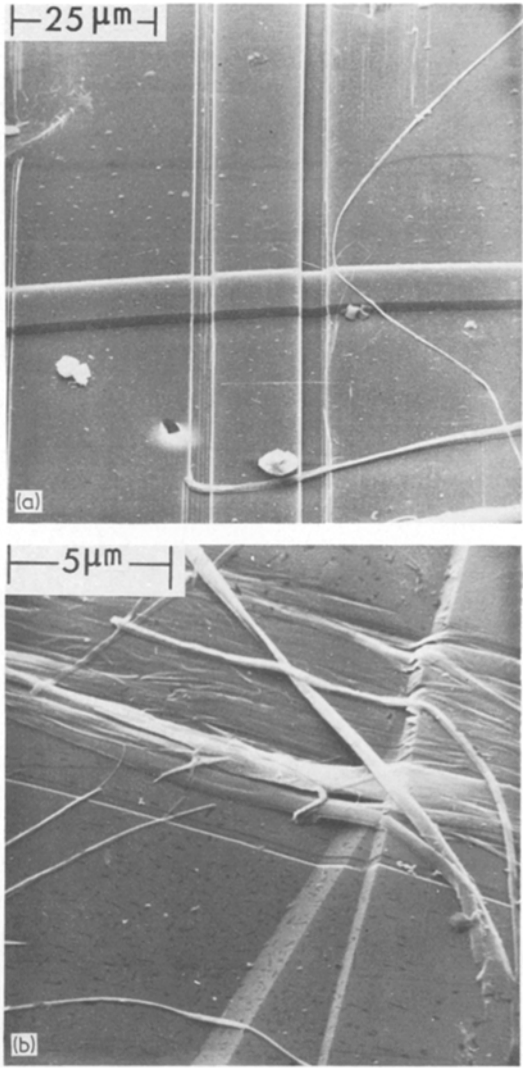


Figure 8 Scanning electron micrographs of stress twins on a (0 1 0) cleavage face. (a) the twin runs in the [1 0 0] direction and is displaced nearly normal to the surface, fibres are pulled out along [0 0 1]. (b) features alined along [1 0 0] and [1 0 1] merge in a strained region with broken fibres.

Schermann *et al.* [10]. They also report alinement along [1 0 0] and [1 0 5]. In addition we observe alinement along [1 0 1] and [1 0 2]. Crystals grown and polymerized between glass slides show cleavage along [1 0 2]. Schermann *et al.* have identified two slip systems in the monomer, (2 1 0) [0 0 1] and (0 0 1) [1 0 0]. Identification of other systems requires a more thorough investigation of etch pit distributions on other facets.

Evidence for another alinement of defects is shown in Fig. 7a. This is a scanning electron micrograph of a polymer (0 1 0) cleavage plane of high quality. Fibres pulled out at the edge of the crystal define the *c*-direction. Two lines of short broken fibres run across the facet and terminate in a faint feature lined along [1 0 0]. Sample tilting can be corrected for using the [0 0 1] and [1 0 0] directions. The defects are, thus, found to aline along a direction between [1 0 2] and [1 0 3], close to [2 0 5]. Similar alinement has been observed in the optical microscope.

Cleavage faces are often covered with an array of fibres adhering to the surface. These are extremely thin and flexible as shown in Fig. 7b.

They result from charging of surfaces on cleavage which attracts fibres back to the surface if the cleavage is not perfectly clean. Such fibres will have a marked effect on reflection spectra since they form a randomly orientated, birefringent, transmitting layer on the sample. Care must be taken to ensure that clean cleavage surfaces are used for such measurements.

On some (0 1 0) cleavage faces of polymer crystals features running in the [1 0 0] [1 0 1] and $[\bar{1}\,0\,1]$ can be seen, see Fig. 6. In the SEM these are seen to be steps in the crystal surface similar to those seen on extracted fibres, Fig. 2. In general there is no sign of cleavage at these steps (Fig. 8a), except where the polymer appears to be strained (Fig. 8b). These features can be produced by stressing the crystal and anneal out over a period of a few months at room temperature. The displacement of the crystal is normal to the (0 1 0) facet, since the cleavage features left by fibres travel across the steps undeviated (Fig. 8a). The [1 2 0] direction is at about 88° away from the (0 1 0) facet and is the most likely direction of displacement. The polymer chains propagate across the steps, this and the annealing behaviour suggests that they are deformation twins since the energy required to break polymer chain bonds is too great to allow slip across the chain direction.

Similar features have been reported by Schermann *et al.* [10] on polymer (2 1 0) cleavage faces alined along $[\bar{1}\,2\,0]$, $[1\,\bar{2}\,2]$ and $[\bar{1}\,2\,2]$ directions. These are undoubtedly the traces of the deformation twins on the (2 1 0) facet. The orientation of these features in the bulk of the crystal can be observed by optical transmission microscopy. Fig. 9 shows stress twins on an (0 1 0) face in reflection and transmission. The [0 0 1] features are extended on (0 0 1) and the $[\bar{1}\,0\,1]$ feature on an inclined plane, the (3 2 2) and $(3\,2\,\bar{2})$ planes have the desired traces on (2 1 0). Alternative planes in the latter case are $(2\,\bar{1}\,2)$ and $(\bar{2}\,1\,2)$ but these lie almost edge on to the (0 1 0) face. The polymer chains are alined along [1 2 0] with their nearest neighbours in adjacent (0 1 0) planes, while the plane of the polymer chain is about 70° away from [1 2 0] so that the sidegroups will not hinder bending of the chain. This is the most likely direction of displacement for (0 0 1) twins, and $(2\,\bar{1}\,2)$ and $(\bar{2}\,1\,2)$ twins if they occur, similar arguments favour [1 2 4] and $[1\,2\,\bar{4}]$ displacements on the (3 2 2) and $(3\,2\,\bar{2})$ planes. The structure in the deformed regions must differ from that in the undeformed crystal since these displacements cannot produce true twins. The polymer chains must be more closely packed in the deformed regions which will require re-arrangement of the sidegroups.

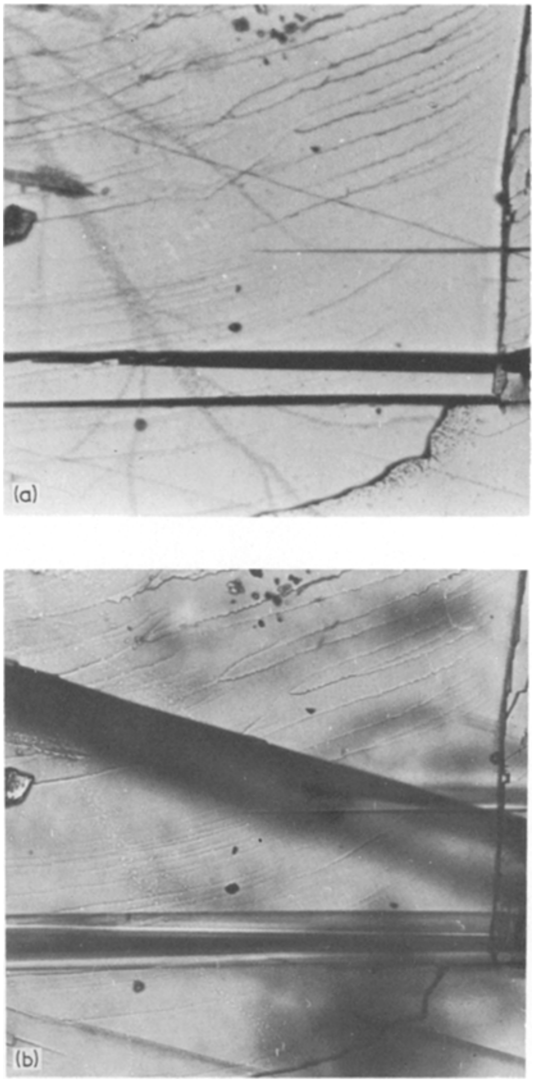


Figure 9 Optical micrographs of stress twins observed (a) in reflection and (b) in transmission. Features alined along [1 0 0] and $[\bar{1}\,0\,1]$ are visible in reflection. In transmission these are seen to lie in (0 0 1) and an inclined plane, possibly (3 2 2), respectively. The micrographs show a region about 0.2 mm square.

Likely mechanisms of deformation twinning have been identified and can be interpreted qualitatively in terms of the crystal structure. Further work is necessary to determine the nature of the molecular re-arrangement in the deformed regions.

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