JOURNAL OF MATERIALS SCIENCE 13 (1978) 62–71

Deformation mechanisms in polymer crystals

Part 2 *Twinning in macroscopic single crystals of bis(p-toluene sulphonate) diacetylene polymer*

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The deformation of polydiacetylene single crystals has been investigated by scanning electron microscopy. Three types of deformation twins have been identified. The twinning planes are (0 1 2), ($\bar{2}$ 1 2), and (2 1 2), types not previously reported in polymer crystals. Deformation features in polydiacetylene single crystals observed by other workers are interpreted in terms of these three twins. The possibility of similar types of twins occurring in other polymer crystals is discussed. The twins in the polydiacetylene single crystals and those found in other non-polymeric materials are compared.

1. Introduction

Deformation mechanisms in crystalline polymers have been studied extensively [1–19] and many of the features of the deformation of these materials are now understood. However, these investigations suffered from several difficulties. Macroscopic specimens of either oriented or isotropic polymer are usually polycrystalline [1] so that the interpretation of deformation may be rather ambiguous. This problem is in principle avoided by the use of polymer single crystals [21]. Until recently, these were usually very small. They have been typically, as in the case of polyethylene, lamellae of the order of a few hundred Å thick and a few μm across [21]. Their deformation can be studied only in the electron microscope [14–19] so although it is possible to measure strains in these crystals there is no way in which the stress required to activate particular deformation mechanisms can be determined. The recent synthesis of large polymer single crystals with which this series of papers is concerned appears to have overcome these difficulties [20]. The present paper is concerned with the deformation of cm sized crystals of the polymer based upon the bis (*p*-toluene sulphonate) ester of 2,4-hexadiyne-1, 6-diol. These diacetylene polymer crystals which have a high degree of perfection [22–26] are obtained by the solid state polymerization of monomer crystals. These crystals are potentially very useful for study of deformation mechanisms in crystalline polymers.

Features resulting from the deformation of these crystals have been reported recently. Schermann *et al.* [23] and Schultz [26] have observed apparent slip traces on facets of the polymer crystals and Bloor *et al.* [25] have observed stress-induced twins in deformed crystals. Attempts to explain these features in terms of various types of deformation mechanisms have not been able to give satisfactory explanations which are consistent with all the experimental observations. In this paper we show that many of the deformation features that have been

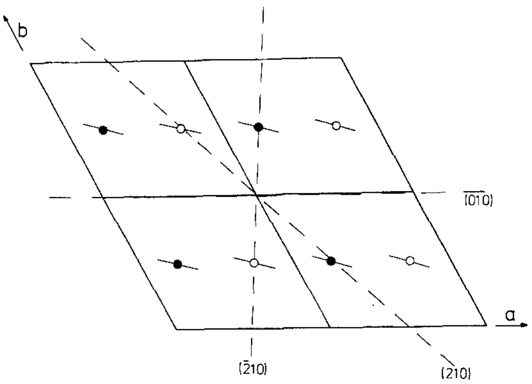

Figure 1 Projection of 4 unit cells of the polymer of bis (*p*-toluene sulphonate) diacetylene on the (0 0 1) plane. The points locate the centres of the polymer chains and the short line segments through them indicate the plane of the polymer backbone. The dashed lines are the twinning planes referred to in the text.

reported previously are due to twins. These twins are of the first kind [27, 28] with the twinning plane (K_1) and direction of the twinning shear (η_1) not parallel to the chain direction. The only twins previously observed in polymer crystals have been compound twins with K_1 and η_1 parallel to the chain direction [1, 7–9, 14, 16, 19].

2. Previous Investigations

2.1. Crystal structure of the diacetylene polymer

The crystal structure of the polymer of 2, 4-hexadiyne-1, 6-diol bis (*p*-toluene sulphonate) has been determined by Kobelt and Paulus [29] as being monoclinic ($P2_1/b$) with $a = 14.94$ Å, $b = 14.49$ Å and $c = 4.91$ Å and $\gamma = 118.1$ Å. The crystal structure was confirmed by Bloor *et al.* [24] who reindexed it such that the polymer chains were extended along the *c* direction as is conventional for polymer crystal structures and this convention will be used throughout the paper. A projection of 4 unit cells on (0 0 1) is given in Fig. 1. The two molecules in the unit cell are related to each other by a two-fold screw axis parallel to the chain direction. The three closest packed planes (0 1 0), ($\bar{2}$ 1 0) and (2 1 0) are drawn as dashed lines in the unit cells.

2.2. Observation of possible slip traces

Schermann *et al.* [23] looked in some detail at the deformation of both the monomer and polymer crystals of the bis (*p*-toluene sulphonate) diacetylene. They observed etch pits on the monomer crystal (0 1 0) facet and interpreted these in terms of dislocations. Although they were unable to find any suitable solvent for etching the polymers features were observed in crystallographic directions on the (2 1 0) polymer crystal cleavage facet. They found these features in the [$\bar{1}$ 2 0], [1 2 2], [1 $\bar{2}$ 2] and [0 0 1] directions (Table I). An attempt was made to explain these as conventional slip traces giving rise to steps on the crystal surface. Using this model, in the (2 1 0) face of the polymer crystal the [$\bar{1}$ 2 0] trace must be due to (0 0 1) [0 1 0] slip and the [$\bar{1}$ 2 2] and [1 $\bar{2}$ 2] traces due to (0 1 1) [1 0 0] slips. Both of these slip systems involve a shear across the molecules and the breaking of the strong covalent bonds which is a highly unlikely process [1]. Although such slip systems are possible and observed in the monomer crystals Schermann *et al.* [23] also concluded that such processes would be unlikely to occur in the polymer. Thus the features observed in the polymer crystals are unlikely to be slip traces. Schultz [26] came to the same conclusion about these features on (2 1 0) and suggested in addition that the [0 0 1] traces he observed on (0 1 0) could be due to $(hk0)$ $[k\bar{h}0]$ transverse slip which would be possible in a polymer crystal.

2.3. Observation of stress twins

Bloor, Koski and Stevens [25] examined crystals of the diacetylene polymer both optically and also in the scanning electron microscope. They looked in detail at the (0 1 0) facet and found deformation features in the [1 0 0] and [1 0 1] directions (Table I). These features were not steps as would be expected for slip traces but had a finite width (~ 1 μm) so Bloor *et al.* [25] described them as stress twins. In a later publication Bloor and Cottle [30] examined in detail one crystal which in cooling down to liquid

TABLE 1 Crystallography of deformation features observed in previous work on polydiacetylene single crystals

Face	Trace of boundary of feature	Workers
(2 1 0)	[$\bar{1}$ 2 0]	[23]
(2 1 0)	[$\bar{1}$ 2 2]	[23]
(2 1 0)	[1 $\bar{2}$ 2]	[23]
(2 1 0)	[0 0 1]	[23]
(0 1 0)	[1 0 0]	[25], [30]
(0 1 0)	[1 0 1]	[25]

helium temperature had developed a large stress twin 0.2 mm wide across the whole of the crystal. The deviation of the molecular chains across the boundary of this feature was reported as 21.7 ± 0.1°. The stress twin was interpreted as being due to a stress induced phase change which would give a new crystal structure with a reduced value of b, an increased value of γ but a constant value of c. Resonance Raman spectra showed no difference in the major features between 800 and 2500 cm^{-1} for the deformed and undeformed areas [30]. In this spectral region Resonant Raman spectra are far more sensitive to backbone than sidegroup structure [30]. Thus the assumed phase change was explained as one in which the backbone structure remained constant but that of the side groups was modified in an undetected manner.

3. Experimental

3.1. Specimen preparation

The bis (*p*-toluene sulphonate) diacetylene polymer crystals were prepared as described elsewhere [24]. It was found that almost any kind of mechanical deformation could induce twinning in these crystals. The twinned crystals were carefully cleaved along (2 1 0) and mounted onto stubs for examination in a scanning electron microscope (JEOL, JSM-50A). In general two specimens were prepared from each crystal, one with the (0 1 0) crystal face parallel to the surface of the stub and the other with the (0 1 0) face perpendicular to the surface so that twins could observed on the different faces. The crystals were coated with a thin film of gold so that their surfaces would be conductive in the microscope. The particularly large twin described previously by Bloor and Cottle [30] was also examined.

3.2. Raman scattering

More detailed resonant Raman spectra were obtained from the crystal containing the large twin described in Section 2.3. The incident dye laser beam (15850 cm^{-1}) of 10 mW intensity was focused first on the twin and then on the undeformed crystal. The high reflectance of the crystal at this incident light frequency enabled the laser beam to be precisely located on the twin by observation of the specularly reflected beam. The spectra were recorded at 2 cm^{-1} resolution using a double monochromator and photon counting system with the crystal in a cryostat at 80 K. The backscattering geometry was used with the incident laser beam striking the crystal face, parallel to the twins at an angle of 20°. The axis of the collection optics for the scattered light was normal to the crystal face.

4. Results

4.1. Raman scattering

Bloor and Cottle [30] investigated the room temperature resonant Raman spectra of the stress twin and undeformed crystal for frequency shifts from 800 to 2500 cm^{-1}. No significant differences in these spectra were observed. In the present experiments the crystal was cooled to 80 K so that low frequency Raman Spectra in the region 20 to 300 cm^{-1} could be recorded. Such low frequency vibrations of the polymer backbone would be expected to have a large component of interchain motion and hence be very sensitive to sidegroup conformation. Fig. 2 shows that the spectrum

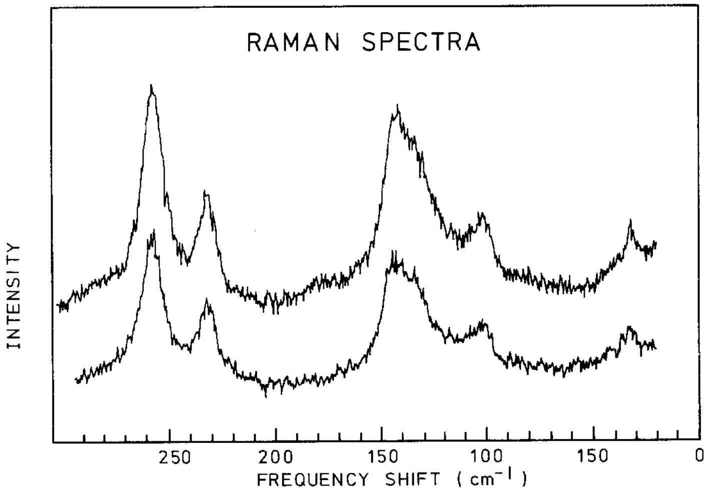

Figure 2 Resonant Raman spectra at 80 K from the twinned region (lower curve) and undeformed region (upper curve) of the polydiacetylene crystal previously investigated at room temperature by Bloor and Cottle [30].

from the undeformed crystal (upper curve) is the same as that from the large twin (lower curve) in all essential features. The intensity of the latter spectrum was about 20% lower since the diameter of the focal spot of the indicent laser beam on the crystal was about 10% greater than the width of the twin. The strong similarity between the two spectra is very good evidence that the crystalline structures in the large twin and undeformed region are identical. Since there is no significant broadening of spectral features in going from the undeformed region to the twin then it would also appear that there is no additional residual strain.

4.2. Observation of twins

The deformed polydiacetylene crystals were examined in the scanning electron microscope and three types of twin observed. They differed in the angles which the traces of their twinning planes made to [0 0 1] on the two crystal faces, (0 1 0) and (2 1 0). From the directions of these traces it was possible to determine the twinning plane (K_1) and twinning direction (η_1) and hence the elements of the twin (K_1, η_1, K_2, η_2) could be deduced [27]. The three types of twin are designated by their twinning planes which were (0 1 2), ($\overline{2}$ 1 2), and (2 1 2). The elements of the twins and the shears involved are listed in Table II. They are all twins of the first kind (type 1) since K_1 and η_2 are rational and η_1 is not [28]. In the electron micrographs two viewing directions have been used. Both are perpendicular to the chain direction [0 0 1] which is vertical in all the micrographs shown. The viewing directions are illustrated schematically in Fig. 3.

TABLE II Elements of twins found in polydiacetylene single crystals. Each type has η_1 irrational and the indices of the closest rational direction are given.

K_1	η_1	K_2	η_2	s
0 1 2	$\sim\overline{10}, \overline{22}, 11$	0 1 0	0 0 1	0.384
$\overline{2}$ 1 2	$\sim 33, \overline{2}, 34$	$\overline{2}$ 1 0	0 0 1	0.658
2 1 2	$\sim\overline{22}, \overline{18}, 31$	2 1 0	0 0 1	0.986

4.2.1. (0 1 2) twin

The most common twin in the polydiacetylene single crystals was found to be the (0 1 2) type. Scanning electron micrographs of some of these twins are shown in Fig. 4. The large twin described previously by Bloor and Cottle [30] was re-examined and found to be of the (0 1 2) type as illustrated in Fig. 4. In Fig. 4a the viewing direction is 90° to (0 1 0) while the sloping, rougher (2 1 0) cleavage plane is seen obliquely at the left. The (0 1 2) twin can be seen as a bright band about 100 μm wide across the two planes. It can be seen that the trace of the twinning plane is at 90° to [0 0 1] on the (0 1 0) plane but not perpendicular to [0 0 1] on (2 1 0). The same twin is shown in Fig. 4b with the viewing direction parallel to (0 1 0) and perpendicular to [0 0 1] at an angle of about 48° to the normal to (2 1 0). The striations are caused by the crystal fibres being

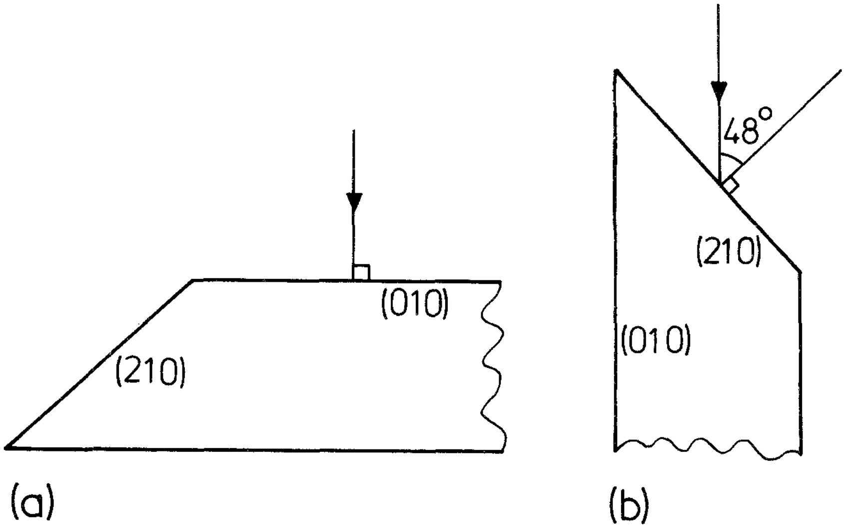

Figure 3 Viewing directions for polydiacetylene crystals in the scanning electron microscope; (a) normal to the (0 1 0) plane and (b) parallel to the (0 1 0) plane at an angle of 48° to the normal of the (2 1 0) plane.

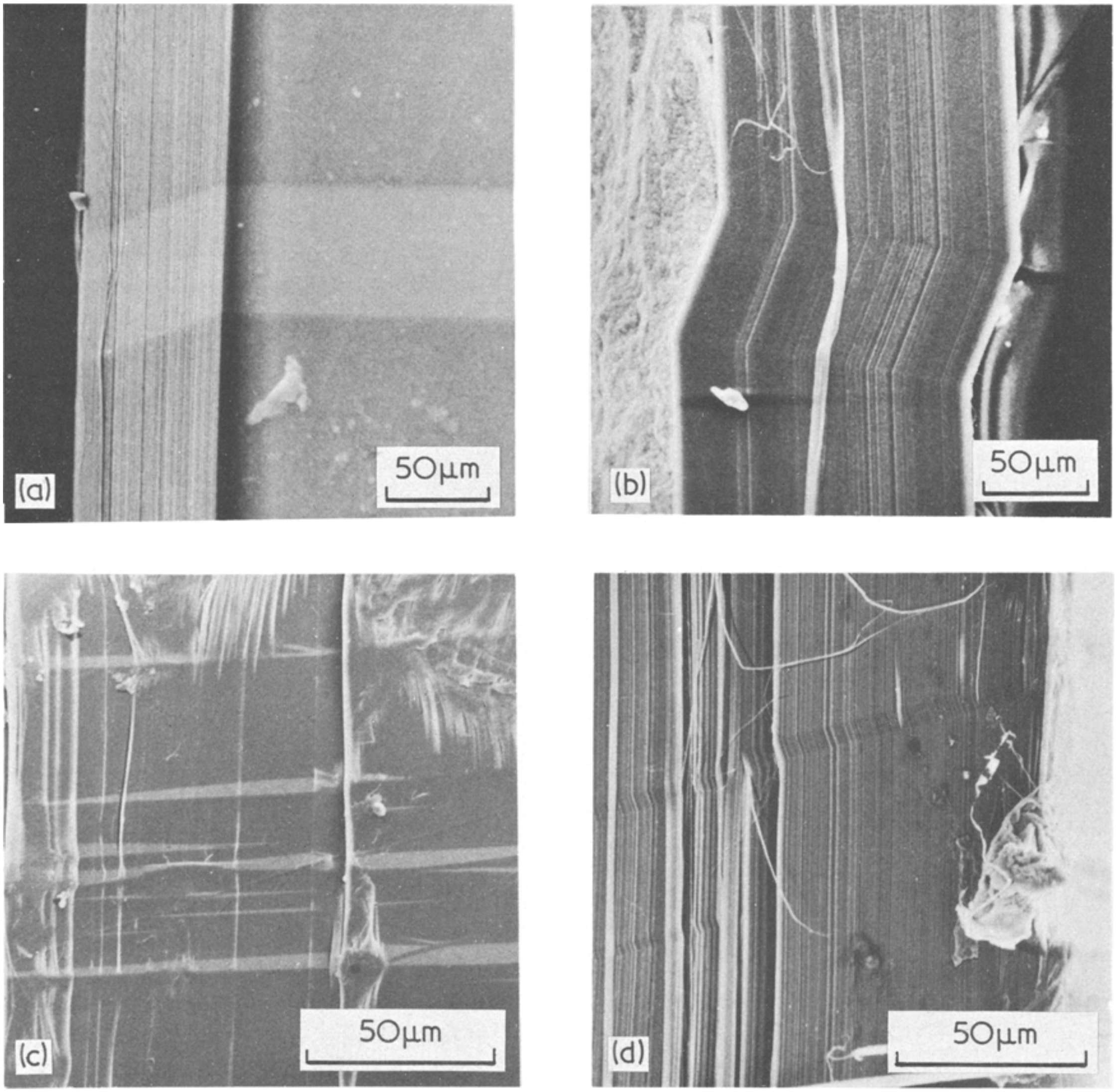

Figure 4 Scanning electron micrograph illustrating the (0 1 2) type of twin. The viewing direction in (a) and (c) is normal to the (0 1 0) plane as in Fig. 3a. while that in (b) and (d) is parallel to the (0 1 0) plane as in Fig. 3b.

pulled off during cleavage and are useful in that they define the direction of the molecular chains ([0 0 1]).The direction of the molecules changes by 22 ± 1° across the boundary plane when viewed in this orientation which is consistent with the more accurate measurement of 21.7 ± 0.1° by Bloor and Cottle [30]. However, the K_1 twinning plane is not perpendicular to [0 0 1] as they assumed but is at 79 ± 1° to [0 0 1] when viewed parallel to [1 0 0]. This is in fact the $[1\bar{2}1]$ direction. Thus the K_1 plane, which gives a trace of [1 0 0] on (0 1 0) and $[1\bar{2}1]$ on (2 1 0), is (0 1 2).

The (0 1 2) twin is illustrated schematically in Fig. 5. Since the angle of deviation of the (0 1 0) planes is 21.7° (Fig. 4b), covalent bonds must not be broken and the crystal structure must remain the same during the twinning the K_2 plane must be (0 1 0) and η_2 must then be [0 0 1]. η_1 lies in (0 1 2) and is perpendicular to [1 0 0]. This direction is in fact irrational and approximates to $[\overline{10}, \overline{22}, 11]$. The full elements of the (0 1 2) twin are given in Table II. The twinning shear is calculated from the relation [28]

$$s = 2 \tan \phi \qquad (1)$$

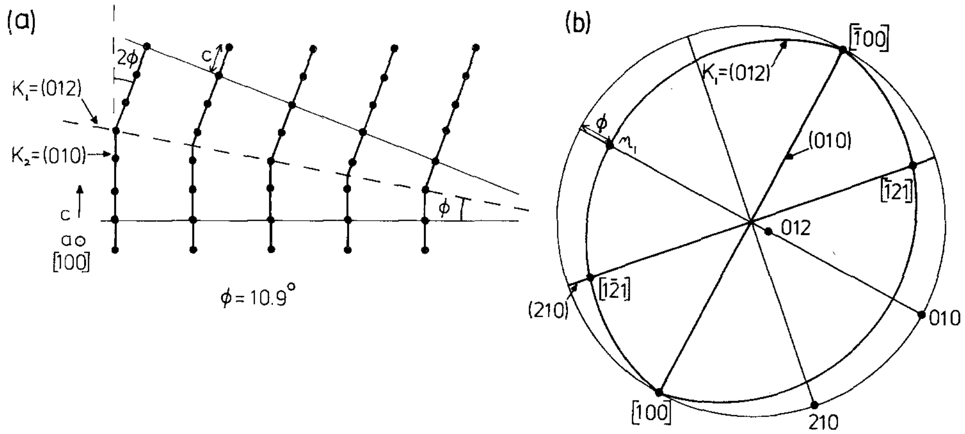

Figure 5 Schematic illustration of the (0 1 2) type of direction. (a) Polymer chains viewed parallel to the [1 0 0] twinning plane and direction. (b) Stereogram showing the twinning plane and direction.

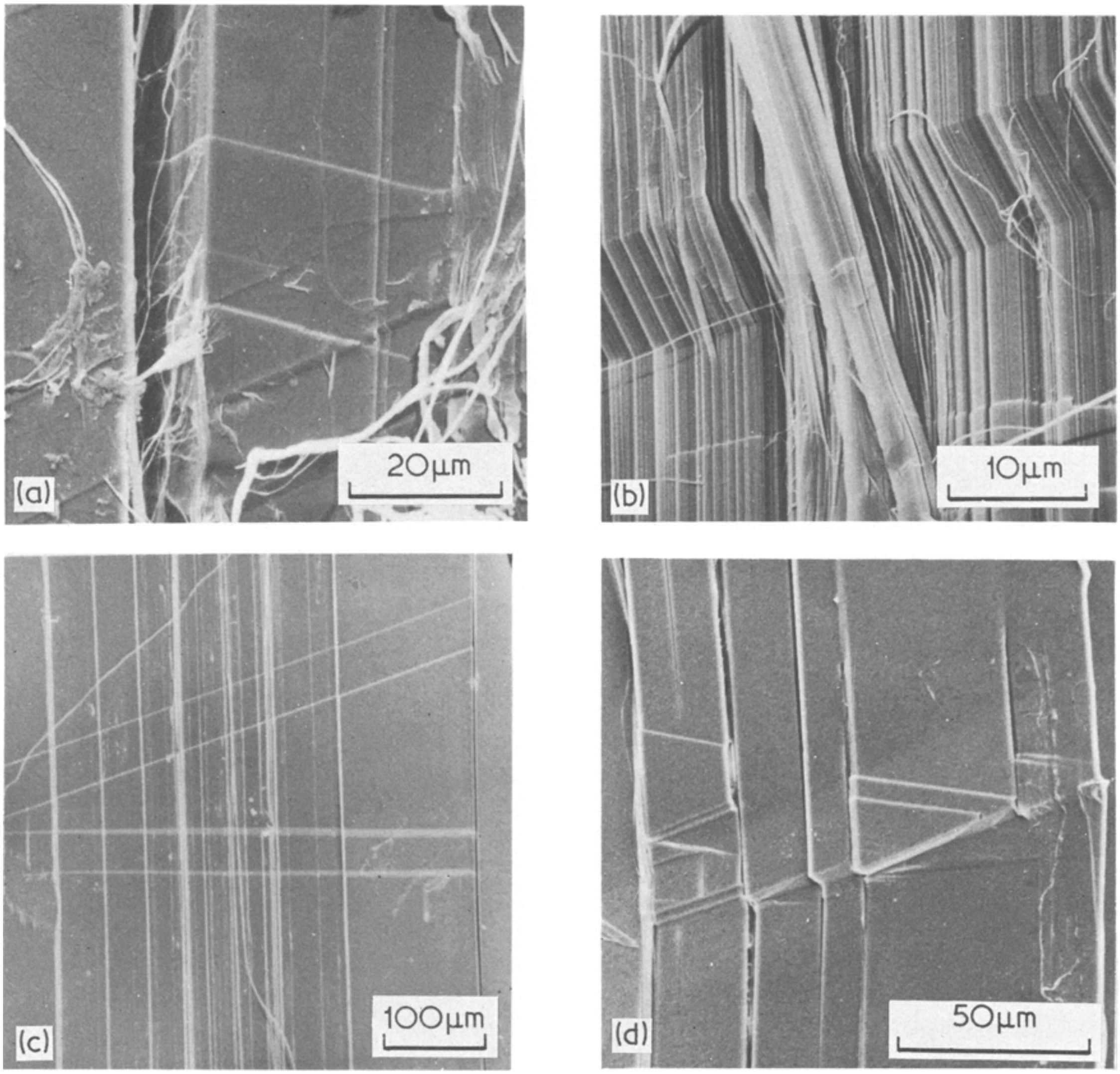

Figure 6 Scanning electron micrographs illustrating the $(\bar{2}1\,2)$ type of twin. The viewing direction in (a), (c) and (d) is normal to the (0 1 0) plane and that in (b) is parallel to the (0 1 0) plane.

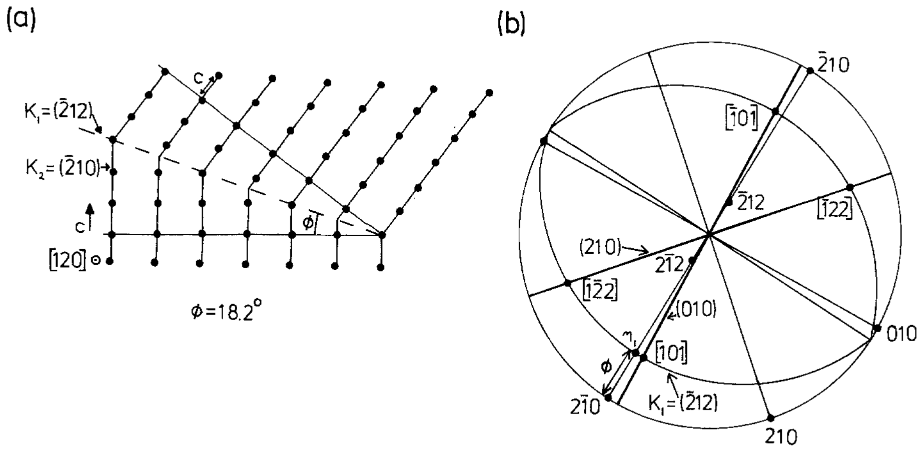

Figure 7 Schematic illustration of the $(\bar{2}\,1\,2)$ type of twin. (a) Polymer chains viewed parallel to the [1 2 0] direction. (b) Stereogram showing the twinning process.

where ϕ, the angle between η_2 and the normal to K_1, is shown in Fig. 5a A stereogram illustrating the (0 1 2) twinning plane (K_1) is given in Fig. 5b.

Other examples of the (0 1 2) twin are also shown in Fig. 4. The group of small twins on the (0 1 0) face in Fig. 4c terminate in the crystal and have the characteristic lenticular shape seen in other materials [27, 28]. Fig. 4d shows a pair of smaller (0 1 2) twins on the (2 1 0) face of another crystal.

4.2.2. $(\bar{2}\,1\,2)$ twin

Many examples of the $(\bar{2}\,1\,2)$ type of twin were also found in deformed crystals. They were generally narrower than (0 1 2) twins as shown in Fig. 6. An (0 1 0) face of a crystal containing $(\bar{2}\,1\,2)$ twins is shown in Fig. 6a. There is a large crack in the centre of the (0 1 0) face and the (2 1 0) cleavage plane can be seen clearly in the crack. The traces of a pair of narrow $(\bar{2}\,1\,2)$ twins can be seen as [1 0 1] on the (0 1 0) face and $[1\,\bar{2}\,2]$ on the (2 1 0) face so that the twinning plane must be $(\bar{2}\,1\,2)$. Fig. 6b shows a (2 1 0) face containing a relatively large $(\bar{2}\,1\,2)$ twin. The deviation of the molecules is about 40° in this projection and the trace of the boundary plane is $[1\,\bar{2}\,2]$. Fig. 6c shows an (0 1 0) plane with a pair of $(\bar{2}\,1\,2)$ twins in [1 0 1] along with a pair (0 1 2) twins in [1 0 0]. This micrograph clearly demonstrates the difference between the two types of twins. Fig. 6d shows a number of $(\bar{2}\,1\,2)$ twins on the (0 1 0) face of a bent crystal. Twins are in both the [1 0 1] and $[1\,0\,\bar{1}]$ directions and tend to be in pairs.

The $(\bar{2}\,1\,2)$ twin is illustrated schematically in Fig. 7. A projection of the crystal structure viewed parallel to [1 2 0] is given in Fig. 7a. Assuming that the same conditions as for the (0 1 2) twinning hold, the K_2 plane in this case must be $(\bar{2}\,1\,0)$ and η_2 must be [0 0 1]. η_1 lies in $(\bar{2}\,1\,2)$ and is perpendiculay to [1 2 0]. This means that it is irrational and approximately equal to $[33, \bar{2}, 34]$. The full elements of the twin are given in Table II. Using Equation 1 the twinning shear is 0.658. A stereogram illustrating the $(\bar{2}\,1\,2)$ twinning plane is given in Fig. 7b.

4.2.3. (2 1 2) twin

This type of twin was less common that the others and was more difficult to identify. It was originally postulated from features seen on the (2 1 0) face as shown in Fig. 8. These twins are the narrowest of three types observed and need higher magnifications to be clearly resolved. Segments of the twins are perpendicular to [0 0 1] on (2 1 0) but the twins tend to be on different levels on consecutive (0 1 0) planes causing steps along the twin. This effect is sometimes found in twins of other materials [27] and is probably caused by the tendency of the crystals to cleave on (0 1 0). It is possible to characterize the twin from $[1\,\bar{2}\,0]$ trace of the twinning plane on (2 1 0) and the 46° deviation of the molecules across the twin boundary in the (2 1 0) face viewed parallel to [1 0 0]. Both of these observations and comparison with the other types of twins lead to the suggestion that the twinning

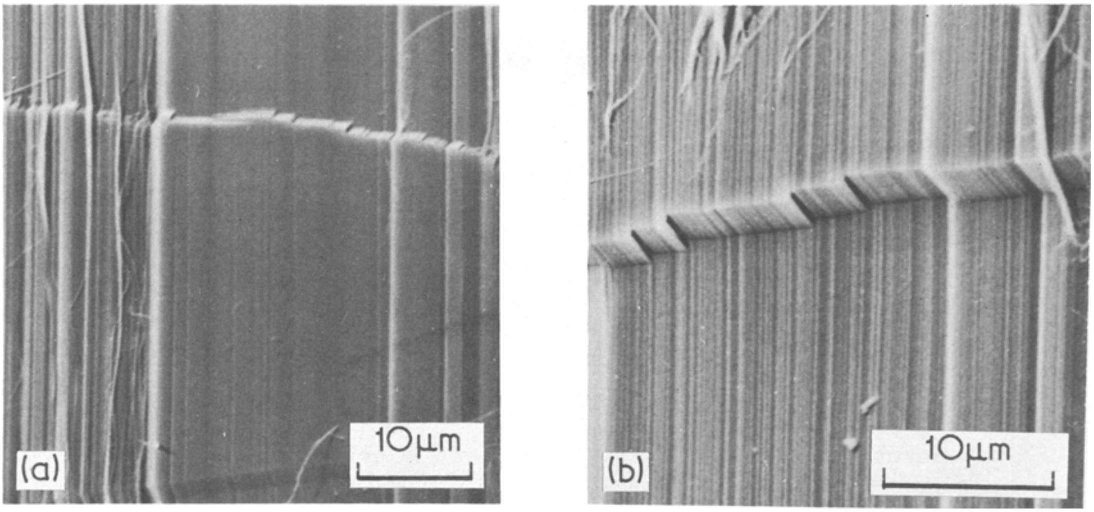

Figure 8 Scanning electron micrographs illustrating the (2 1 2) type of twin. The viewing direction in both micrographs is parallel to the (0 1 0) plane.

plane in this case is (2 1 2). Like the ($\bar{2}$1 2) twin this (2 1 2) twin has a trace of [$\bar{1}$0 1] on (0 1 0) so that the two types of twins can only be confidently distinguished from their traces on (2 1 0).

The (2 1 2) twin is illustrated schematically in Fig. 9. A projection of the crystal structure parallel to [1 $\bar{2}$ 0] is given in Fig. 9a. Assuming that the same conditions as for (0 1 2) and ($\bar{2}$1 2) twins hold then K_2 must be (2 1 0) and η_2 must be [0 0 1]. η_1 lies in (2 1 2) and is perpendicular to [1 $\bar{2}$0]. Because of the low symmetry it is irrational and approximately equal to [$\overline{22}$, $\overline{18}$, 31]. The elements of the twin are listed in Table II. The twinning shear can be calculated from Equation 1 and is 0.986. A stereogram containing the (2 1 2) twinning plane is given in Fig. 9b.

5. Discussion

The twins in the polydiacetylene single crystals, were first thought to be kink bands, similar to those first found by Orowan [31] in single crystal of hexagonal metals and more recently found in oriented semi-crystalline polymers such as nylon [32], polyethylene [33–36] and polypropylene [37, 38]. In fact it is possible to make such an interpretation. For example the (0 1 2) twin can be thought of as being a kink band due to one

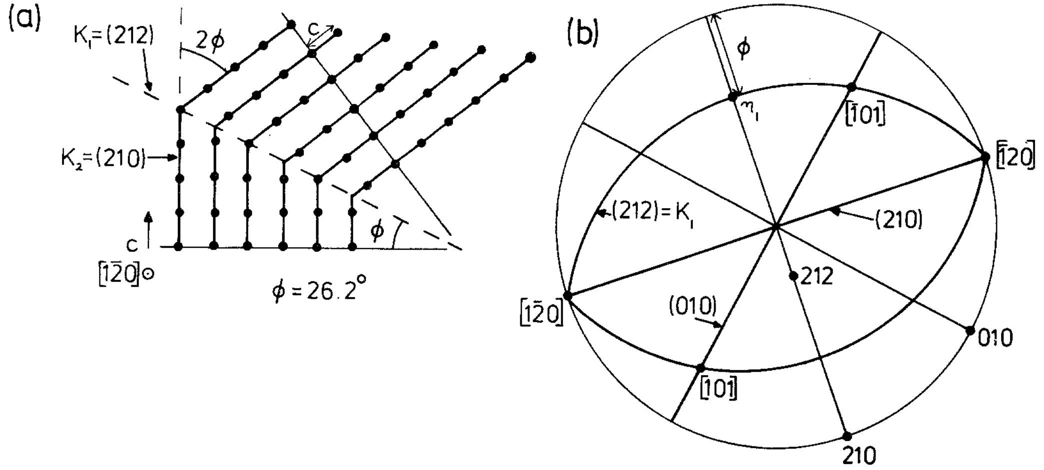

Figure 9 Schematic illustration of the (2 1 2) type of twin. (a) Polymer chains viewed parallel to the [1 $\bar{2}$ 0] direction. (b) Stereogram showing the twinning process.

unit of [0 0 1] chain direction slip taking place on every (0 1 0) plane. However, this type of deformation leads to a boundary between the deformed and undeformed areas which is coherent [28] and with the crystal structure on one side of the boundary plane being a mirror image of the crystal structure on the other side. This means that material either side of the boundary plane has a more specialized relationship than is required for a kink and hence the features are twins. It is possible for the twinning to take place because within the deformed areas the crystal structure can be retained by displacements of c on consecutive K_2 planes. Thus it is not necessary to break the strong covalent bonds along the polymer backbone to twin the structure. For each of the twins with K_1 planes of (0 1 2), $(\bar{2}12)$ and (2 1 2) the K_2 planes are all close-packed planes, namely (0 1 0), (2 1 0) and (2 1 0) respectively (Table II).

At this stage it is possible to make some comments upon the similarity between twinning in the polydiacetylene single crystals and twinning in non-polymeric materials. The twins which terminate within a crystal taper to a point, as shown in Fig. 4c, appear to be similar to twins observed in other materials [27, 28]. If the atomic structure of the twins are also similar then there must be an array of dislocations at the taper and hence the interface must be incoherent [28]. Many examples of twins terminating at cracks within crystals were found (eg. Fig. 6d). In other materials high stresses at the tips of twins have been known to nucleate cracks [28] but in the polydiacetylene crystals there is not yet experimental evidence of such a correlation.

The type of twins described in this paper have not been reported before in polymer crystals and Bevis and Crellin [8] have considered such modes to be unlikely in polyethylene. However, there is nothing special about the crystal structure of the polydiacetylenes and no fundamental reason why such twins should not occur in other crystalline polymers. A likely candidate in polyethylene would be twins with K_1 planes of the {1 1 2} type. Twinning in orthorhombic uranium [39] has been used to predict the tupe of twins in polyethylene crystals [7]. The main type of twins predicted and observed were compound twins of the {3 1 0} and {1 1 0} type. Both of these twins involve shears in planes parallel to the molecules and the possibility of finding twins involving twinning shears which bent the molecules was not considered. However, in uranium (1 1 2) twins are found [28] and work is currently in progress to see if similar twins occur in polyethylene.

With the identification of these twins it is now possible to resolve the problems encountered with the observation of apparent slip traces in Section 2. It is clear that these traces are really narrow twins. The directions of these traces correspond to the traces of the K_1 planes of the three of twins described in Section 4 and listed in Table II.

6. Conclusions

A new type of deformation twinning in polymer crystals has been identified in large polydiacetylene single crystals with a high degree of perfection. The K_1 twinning planes are not parallel to the polymer molecules and three distinct types of twin have been identified. They have twinning planes of (0 1 2), $(\bar{2}12)$ and (2 1 2) involving twinning shears of 0.384, 0.658 and 0.986 respectively. Previously observed deformation features in polydiacetylene single crystals have been shown to be twins with the K_1 planes given above.

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Received 27 April and accepted 12 May 1977.