The morphology of poly bis(p-toluene sulphonate) diacetylene crystals

Poly bis(*p*-toluene sulphonate)diacetylene is of considerable interest since it can be obtained in macroscopic single crystal form. It has, therefore, been the subject of numerous investigation, see for example [1]. In particular it has been possible to study, for the first time, the defects and deformation of a large polymer single crystal [2–7]. However, there are a number of different descriptions of the crystal morphology in the literature, some of which are incorrect.

The crystals of both polymer and monomer are monoclinic and, following crystallographic notation, the unit cell has symmetry $P2_1/c$ in the second setting [8]. This choice places the *b*-axis parallel to the polymer chains. For polymers it is usual to choose the *c*-axis in the polymer chain direction. This can be done by using a unit cell in the first setting. A convenient transformation is to rotate the $P2_1/c$ axis labels, so that $b \rightarrow c$, etc., and the new crystallographic indices can be obtained by rotation of the $P2_1/c$ indices, e.g. (1 0 2) in $P2_1/c$ becomes (2 1 0) [4, 7]. The new cell has symmetry $P2_1/a$, not $P2_1/b$ as stated previously, but does not follow crystallographic convention since $a > b$. The first setting cell with symmetry $P2_1/b$ has $a < b$ and the same *a*-axis as the $P2_1/c$ cell, hence (1 0 2) in $P2_1/c$ becomes (1 2 0) in $P2_1/b$. In the following discussion the $P2_1/c$ indices will be used and those for the alternative first setting cells given in Table I.

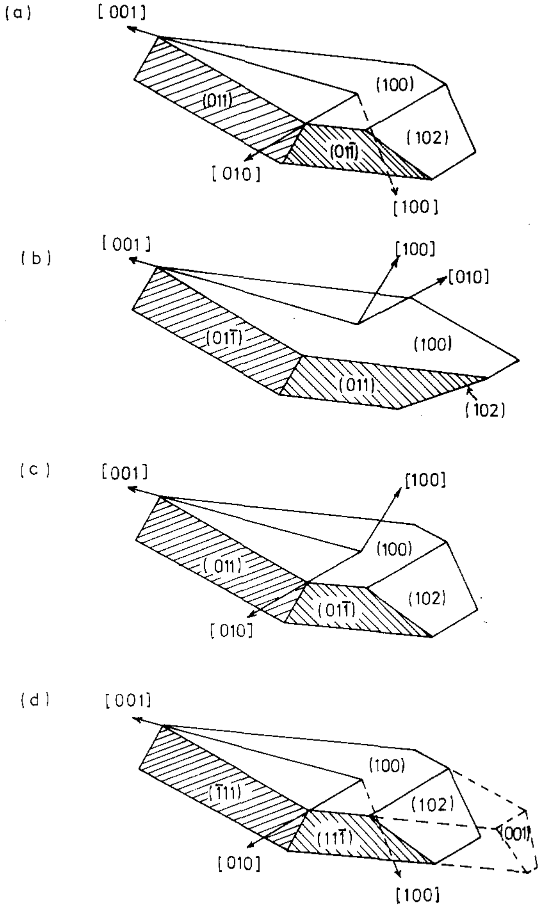

Figure 1 Morphologies of poly bis(*p*-toluene sulphonate) diacetylene crystals (a) after [2], (b) after [3], (c) after [1] and [6], and (d) after [4].

A number of different descriptions of the crystal morphology have been published, these are shown in Fig. 1. Fig. 1a shows the correct morphology, see Fig. 2, but with the choice of axes shown the shaded end facets are incorrectly indexed [2]. Fig. 1b [3] has a different choice

TABLE I Interfacial angles of poly bis(*p*-toluene sulphonate)diacetylene crystals determined by direct measurement and from the crystal structure data of [8].

Planes $P2_1/c$ indices	Interplanar angles		First setting indices	
	Measured	Calculated	$P2_1/a$ $(a > b)$	$P2_1/b$ $(a < b)$
(1 0 0)–(1 0 2)	41.5 ± 0.3°	41.7°	(0 1 0)–(2 1 0)	(1 0 0)–(1 2 0)
(1 0 0)–(0 0 1)	61.6 ± 0.4°	61.9°	(0 1 0)–(1 0 0)	(1 0 0)–(0 1 0)
(1 0 0)–($\bar{1}$ 1 1)	(a) 101.0 ± 1.0° (b) 101.4 ± 0.2°	101.4°	(0 1 0)–(1 $\bar{1}$ 1)	(1 0 0)–($\bar{1}$ 1 1)
(1 0 0)–(1 1 $\bar{1}$)	(a) 78.4 ± 1.2° (b) 78.6 ± 0.3°	78.6°	(0 1 0)–($\bar{1}$ 1 1)	(1 0 0)–(1 $\bar{1}$ 1)
(1 0 0)–(0 1 1)		80.4°	(0 1 0)–(1 0 1)	(1 0 0)–(0 1 1)
(1 0 0)–(0 1 $\bar{1}$)		99.6°	(0 1 0)–($\bar{1}$ 0 1)	(1 0 0)–(0 $\bar{1}$ 1)

(a) Mean value for ten crystals with growth spirals on the end facets.
(b) Mean value for three crystals with flat end facets.

of axes, which correctly indexes the shaded end faces but gives a (1 0 2) facet orientation different from that observed. Fig. 1c [1, 6] retains the axes of Fig. 1b and the facet indices of Fig. 1a, which is clearly incorrect since the facet labelled (1 0 2) should be labelled $(1\,0\,\bar{2})$. Comparison with the crystal structure shows that $(1\,0\,\bar{2})$ is unlikely to be a growth or cleavage facet. A further alternative has been proposed [4] but the unit cell axes and facet indices were not illustrated. This choice is shown in Fig. 1d and has the same axes as Fig. 1a but with correctly indexed shaded end facets, i.e. (0 1 1) of Fig. 1a becomes $(\bar{1}\,1\,1)$, etc.

Experimental confirmation of the latter choice is made difficult by the occurrence of growth spirals on the end facets. These give rise to a 1° to 2° scatter in the interfacial angles measured with an optical goniometer. This is comparable with the difference in the orientations of (0 1 1) and $(\bar{1}\,1\,1)$ facets relative to the major (1 0 0) facet, see Table I. Measurements were, therefore, made on a number of samples. Average interfacial angles were obtained (a) for ten crystals with growth spirals on the end facets and (b) three crystals with perfectly flat end facets. The results are listed in Table I and show clearly that the choice of axes and indices of Fig. 1d is correct.

Table I also gives results for measurements on (1 0 2) and (0 0 1) growth facets, which occurred on a few crystals. Typical crystals with these facets are shown in Fig. 2. Although (0 0 1) facets have been noted before [4] cleavage has always been assumed to occur easily only on (1 0 0) and (1 0 2) planes. A number of cases of (0 0 1) cleavage were observed during this work and have also been seen during SEM studies of crystals compressed normally to the (1 0 0) facet [9].

Acknowledgements

This work was supported by a grant from the SRC. Mr D. J. Ando is thanked for preparing the bis(*p*-toluene sulphonate) monomer and members of the Department of Materials and the Polymer Group, Department of Physics, Queen Mary College are thanked for helpful discussions.

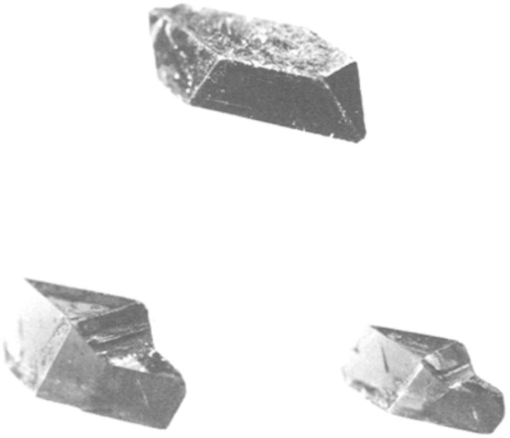

Figure 2 Crystals of bis(*p*-toluene sulphonate) diacetylene showing principal growth facets. At the top is a polymer crystal showing (1 0 0), $(\bar{1}\,1\,1)$, $(1\,1\,\bar{1})$ and (0 0 1) facets, cf. Fig. 1d, this crystal has a maximum dimension of about 1 cm along [0 0 1]. At the bottom are two monomer crystals with both (1 0 2) and (0 0 1) facets.

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Received 8 May
and accepted 20 June 1978.

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