Technique for determining unit-cell constants of polyhydroxyvalerate using electron diffraction

Polyhydroxyvalerate (PHV) is a naturally occurring bacterial polyester which has been isolated by Wallen and co-workers [1, 2]. The crystal structure of synthetic racemic PHV has been investigated [3]. Recent investigations have shown that the unit-cell constants of naturally-occurring PHV are the same as those of synthetic racemic PHV [4]. The more recent investigation has also included limited confirmation of base plane dimensions obtained by electron diffraction. In this paper, a technique is presented whereby three-dimensional electron diffraction data can be obtained. This technique involves precise eucentric tilting about a crystallographic axis. Results of analysis of PHV using this technique are presented here.

Single crystals of PHV were supplied by Dr R. H. Marchessault of this centre. This polymer had been partially fractionated by the following method. The sample had been purified by dissolving once in boiling ethanol (0.05%) followed by crystallization at room temperature for 24 h. The polymer was re-crystallized again in the same manner except that the crystallization was allowed to take place at 65° C for 24 h. The precipitate was then collected by filtration. The resultant PHV single crystals were then suspended in methanol. Electron microscope grids were prepared by placing a drop of this suspension on carbon coated grids and allowing the solvent to evaporate.

Observation of these grids in a Philips EM400 HMG electron microscope revealed the presence of well-formed single crystals as shown in Fig. 1. It is interesting to note the mosaic-like structure of these crystals. The exact method of formation of this mosaic structure is not yet understood. Electron diffraction was obtained from these

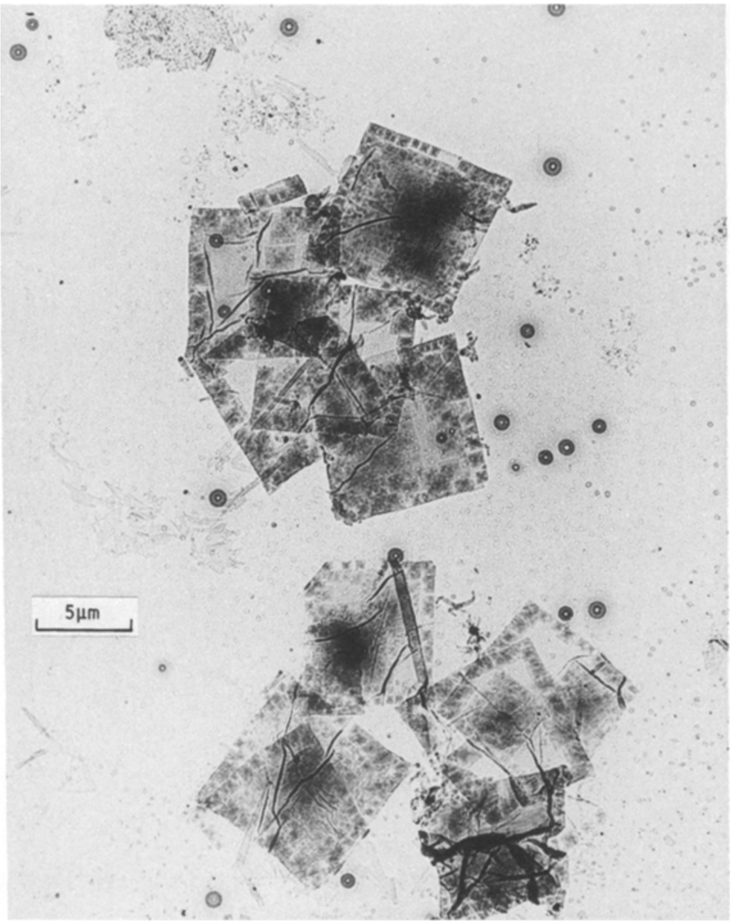

Figure 1 Transmission electron micrograph of PHV single crystals.

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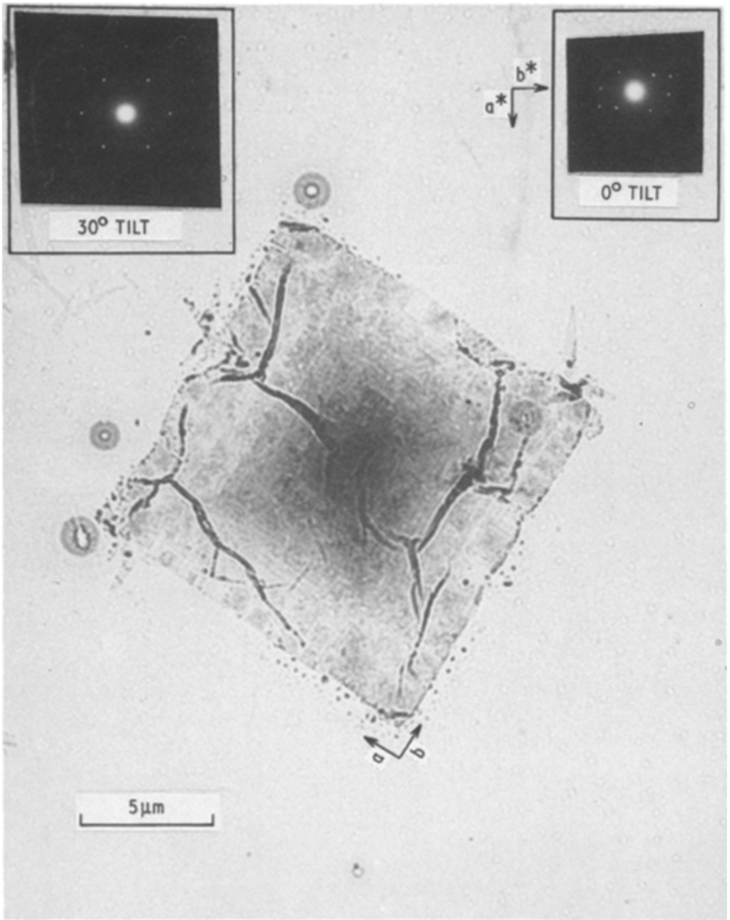

Figure 2 Transmission electron micrograph of PHV single crystals with superimposed electron diffraction patterns obtained under tilted and normal conditions.

crystals under weak beam conditions (120 kV, 40 nm spot size, 20 μm condensor aperture) since the crystals were extremely electron beam sensitive. Diffractograms obtained with the electron beam normal to the crystal surface confirmed the $h\,k\,0$ data of Morikawa *et al.* [4]. In addition, diffraction was obtained from crystals under titled conditions. In this case, the amount of tilt was 30°. Diffraction from tilted specimens is relatively simple with the Philips 400 HMG because the specimen tilt is eucentric about the electron axis. The procedure used to obtain diffraction patterns from these samples was to first ensure that the specimen height was adjusted to fulfill the conditions for eucentric tilting. The specimen stage could then be rotated and tilted simultaneously until a symmetrical diffraction pattern was observed, as shown in Fig. 2.

From this tilted diffractogram, eleven unique reflections were observable. These reflections have generalized $h\,k\,l$ values and the measured d-spacings agree well with those calculated from the previously proposed unit-cell [3]. The orthorhombic unit-cell dimensions are: $a = 0.932$ nm, $b = 1.002$ nm and $c = 0.556$ nm. Observed systematic absences are in agreement with the proposed $P_{2_1, 2_1, 2_1}$ space group. Observed d-spacings from the electron diffractogram are compared with the calculated d-spacing of the proposed unit-cell in Table I. The excellent agreement of the calculated d-spacings with the d-spacings measured from the tilted diffractogram substantiate the unit-cell β-axis dimension obtained by other workers [3, 4].

We believe that this is the first published evidence of electron diffraction using specimen tilting to substantiate the fibre repeat of polymer single crystals. These results suggest that further, more sophisticated, analysis using specimen tilting be performed on polymers.

TABLE I Comparison of calculated *d*-spacings [4] with those observed from electron diffraction

hkl	$d_{calc.}$ (nm)	$d_{obs.}$ (nm)
0 1 0	1.002	–*
1 0 0	9.932	–*
1 1 0	0.683	0.686 (8)
0 2 0	0.501	0.501 (7)
2 0 0	0.466	0.470 (7)
1 2 0	0.441	0.441 (7)
2 1 0	0.423	0.428 (6)
2 1 0	0.423	0.422† (6)
0 2 1	0.372	0.372† (5)
2 2 0	0.341	0.345 (4)
0 3 0	0.334	–*
1 3 0	0.315	0.319 (4)
3 0 0	0.311	–*
3 1 0	0.297	0.302 (4)
3 1 0	0.297	0.299† (3)
2 3 0	0.272	0.273 (3)
3 2 0	0.264	0.268 (3)
0 4 0	0.251	0.252 (2)
2 3 1	0.244	0.247† (2)
1 4 0	0.242	0.243 (2)
3 2 1	0.239	0.237† (2)
1 4 1	0.222	0.222† (2)
1 3 2	0.208	0.208† (2)
1 5 0	0.196	0.195 (1)
0 4 2	0.186	0.186† (1)
2 5 1, 5 2 0	0.175	0.175† (1)
2 4 2	0.173	0.173† (1)
0 3 3	0.162	0.162† (1)

*Unobserved.
†Observed in tilted diffractograms.
Numbers in parentheses are the estimated errors in the last decimal place.

Acknowledgement

The authors are indebted to Dr R. H. Marchessault for providing the sample and the stimulus to undertake this investigation.

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*Received 17 April
and accepted 30 June 1980*

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Electrical conductivity of zinc phosphide thin films

Optical and electrical properties of GaP and similar phosphides belonging to III–V compounds have been thoroughly investigated and some of these materials are already being used for commercial purposes in opto-electronic devices [1–3]. Similar studies on the phosphides of zinc and cadmium, of the $A^{II}B^{V}$ type, are limited. Recent investigations on the physical and chemical properties of these phosphides indicate that they may also be useful in semiconductor devices [4–6]. Very recently, the potential use of Zn_3P_2 in terrestrial solar cells has been stressed by Möller *et al.* [7]. Continuing efforts to find new materials are very important to the progress of the electronic industries. Some aspects of polycrystalline Zn_3P_2 have also been studied by us, for example, energy storage properties and electrical conductivity. The Zn_3P_2 was prepared in our laboratory using commercially available chemicals [8, 9]. Luminescence and conductivity have been attributed to the formation of complexes such as Zn–O and Zn–P. In this note the results of further investigations on electrical conductivity, measured in the temperature range 130 to 550 K, of thin films of Zn_3P_2 deposited on glass substrates under vacuum by an evaporation technique, are reported and discussed.

Zinc phosphide powders, used in the vacuum deposition of thin films, were essentially prepared by the two methods described in an earlier paper

0022–2461/81/020547–03$02.30/0