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Direct lattice resolution in polydiacetylene single crystals

With the advent of modern electron microscopes the direct observation of structure in crystals of metals and ceramics by lattice imaging [1] is now becoming a relatively routine matter. The technique of using high resolution electron microscopy (HREM) to directly resolve lattice planes in crystals was first demonstrated in a classical series of papers by Menter [2, 3]. He showed that images could be obtained from thin crystals of copper and platinum phthalocyanines which contained fringes of the same separation as the lattice planes in these materials. A major drawback in extending the technique to other materials such as polymer crystals is that the crystals of organic materials invariably undergo radiation damage in the electron beam. The problem of beam damage is crucial in controlling the application of HREM to polymer crystals since it causes a rapid deterioration in the potential resolution [4]. Another problem that is encountered when studying polymers by electron microscopy is specimen preparation and the conventional techniques used include the precipitation of chain-folded lamellar crystals from dilute solution or microtoming or cleaving thin sections from bulk samples. Neither of these techniques are completely satisfactory as solution-grown crystals can only be observed in directions parallel to chain axis and microtoming or cleavage can introduce artefacts and cause damage to the crystals. Nevertheless, a careful and elegant study has been recently made by Dobb and co-workers [5, 6] upon the structure of fragments obtained from high-modulus aromatic fibres in which they were able to resolve lattice fringes as small as 0.43 nm from microcrystalline areas.

A significant step forward in the preparation of polymer crystals in morphologies suitable for study by electron microscopy was made with the use of solid-state polymerized polydiacetylene single crystals [7]. These materials developed about 10 years ago by Wegner and co-workers [8] are made by the polymerization of suitable substituted diacetylene monomer single crystals. Because the polymers are polymerized in the form of single crystals in the solid state the polymer single crystals can be 100% crystalline, of macroscopic dimensions and contain molecules in chain-extended conformations [7]. There is currently considerable interest in studies of the structure and properties of polydiacetylene crystals because of their interesting and unusual optical, electronic and mechanical properties. Many of these properties reflect the single-crystal nature of the polymers and it is the purpose of this communication to show briefly how the fundamental crystal lattice can be observed directly by HREM.

Recent studies by the authors and co-workers [7, 8, 10] have demonstrated the usefulness of transmission electron microscopy in studying the structure of polydiacetylene single crystals. Previous work has concentrated upon crystals of the p-toluene sulphonate derivative (pTS) [11]. It has been shown that these crystals contain stacking faults [10] and dislocations [12] and undergo twinning upon deformation [9]. Single crystals of pTS can be obtained in the form of thin (50 to 200 nm thick) foils which are relatively resistant to radiation damage in the electron beam. HREM has has been attempted with pTS but attempts to image the crystal lattice have met with only limited success. It is thought that this may be because either the crystals suffer from radiation damage at the high magnification (~ x 100 000)

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employed or the contrast from the lattice for the reflections chosen was too weak to produce satisfactory results.

This present report is concerned with HREM studies of another substituted diacetylene derivative, poly[1, 6-di)N-carbazolyl)-2, 4-hexadiyne], which will henceforth be referred to as pDCH [13, 14]. Fibrous monomer crystals were prepared by allowing a 4 x 10^{-3} M solution of the monomer in xylene to evaporate on a carbon film on a 200 mesh electron microscope grid. The crystals formed were up to 100 nm thick and several μm long. They were polymerized by heating at 175° C for ~20 h in an air oven [13]. The crystals were examined on the films in a JEOL 100 CX transmission electron microscope operated at 100 kV. The microscope was accurately aligned and the objective astigmatism corrected to ensure the highest resolution. The resolution was checked by obtaining lattice images from standards such as copper phthalocynanine (1.03 nm) and potassium chloroplatinate (0.563 nm). The images were obtained at a nominal magnification of 100 000 times which was checked with the standards. They were recorded on Kodak no-screen X-ray film which, because of its relatively large grain size, limited resolution at the magnification used to about 0.4 nm. However, the relatively high film speed enabled exposures to be obtained using an exposure time of 5.6 sec at a relatively low beam intensity. This is a considerable advantage for the study of beam-sensitive materials such as organic polymers.

A high resolution micrograph of a pDCH crystal is shown in Fig. 1 along with a diffraction pattern from the same crystal. The micrograph was obtained using an objective aperture which excluded all reflections other than the two indicated on the diffraction pattern. The spacing of the planes corresponding to these reflections was measured to be 1.22 ± 0.03 nm. The crystal structure of pDCH has been reported [14] as being monoclinic, $P2_1/a$ with $a = 1.740$ nm, $b = 1.287$ nm, $c = 0.491$ nm and $\gamma = 108.3°$, when indexed (unconventionally) with the chain direction as c. The reflections used to obtain the lattice image were on a zone axis perpendicular to the chain direction and hence were of the $(hk0)$-type. The only lattice planes with spacings of the order of 1.2 nm in pDCH and (0 1 0) and $(1\,\bar{1}\,0)$ with spacings of 1.22 and 1.17 nm, respectively, and so it was thought that the measured reflections corresponded most closely to those expected from (0 1 0). Since the fringes seen in the micrograph in Fig. 1 were found to be parallel to the edge of the crystal fibre and hence also parallel to the chain direction it was assumed that they were also from $(hk0)$-type planes. The spacings of the fringes were measured using the 1.03 nm fringes from the $(2\,0\,\bar{1})$ planes in copper phthalocyanine crystals as a calibration standard [2]. The spacing in the pDCH crystals was found to be 1.2 ± 0.1 nm. This

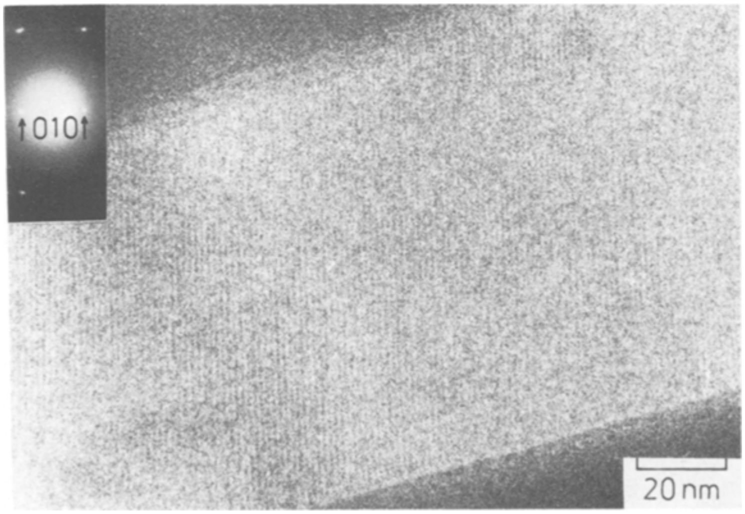

Figure 1 High resolution electron micrograph of lattice fringes in pDCH single crystals. The reflections used to obtain the periodic image are indicated in the diffraction pattern (inset). The chain direction c is vertical in both the micrograph and the diffraction pattern.

is in excellent agreement with the spacing of the reflections measured from the diffraction pattern and so it can be assumed that the (010) lattice planes have been successfully imaged in pDCH single crystals.

It is worth considering the reasons why direct lattice resolution is possible in pDCH crystals. The main reason appears to be that pDCH is very resistant to beam damage. Although quantitative measurements have not yet been made it is thought that they are a factor of two or three times more resistant than pTS and they appear to have approximately the same stability as the copper phthalocynanine standards. Also, the fibrous crystals have a roughly hexagonal cross-section and so they tend to lie on the substrate in a variety of orientations. Inspection of the crystal structure of pDCH in the paper of Enkelmann *et al.* [14] shows that when the crystal is viewed along the *a*-axis (unconventionally indexed) the (0 1 0) planes appear as widely-spaced stacks of molecules. The presence of these stacks in this orientation probably helps to obtain a good periodic image [1]. In pTS the crystals tend to adopt a lamellar habit [7] with a surface normal of approximately [120]. In this orientation the stacks of molecules are off-set from each other.

It is clear that the ability to obtain lattice images from polydiacetylene single crystals should enable considerable progress to be made in the understanding of the structure and properties of polymer crystals. In particular it is intended to use the technique to study the structure of defects such as dislocations, stacking faults, grain boundaries and twins in these materials.

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High strength microcrystalline alloys prepared by devitrification of metallic glass

Metallic glasses (amorphous metals) are conveniently prepared by rapid quenching from the melt of certain glass-forming alloys [1–3]. This requires quench rates of the order of 10^5 to 10^6 °C sec^{-1} or higher. Such quench rates are obtained by depositing molten metal in a thin layer onto a heat extracting member, such as a block of copper. Known methods for doing this include splat quenching, hammer-and-anvil quenching, as well as the melt-spin procedures. However, in all of these procedures, the quenched glassy metal product must have at least one small dimension, usually less than 0.1 mm thick. Glassy metals obtained by the melt-quench procedure, therefore, are limited to powders, thin wires and thin filaments such as

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