Letters

Rolling textures and a martensitic transformation in polyoxymethylene

In a recent paper Preedy and Wheeler [1] studied the rolling texture of polyoxymethylene by X-ray pole figure techniques. The observed textures were interpreted in terms of a stress-induced martensitic transformation of the hexagonal phase to an orthorhombic phase. The lattice parameters of the orthorhombic phase used in the interpretation of the textures were those reported by Carazzolo and Mammi [2] to be $a = 4.77$ Å, $b = 7.65$ Å and $c = 17.80$ Å. However, as stated by Preedy and Wheeler [1] this structure was not stress-induced but was obtained by the use of a particular polymerization process which resulted in the dimension of the c-axis of the orthorhombic cell being different from that reported for the hexagonal phase which has the lattice parameters [3, 4] $a = 4.46$ Å and $c = 17.3$ Å. A change in the dimensions of the repeat distance along the chain axis would not be expected to arise in a martensitic transformation involving the transverse displacement of chains.

There must, therefore, be some doubt as to the validity of assigning the lattice parameters determined by Carazzolo and Mammi [2] to the transformation in the observed rolling textures of polyoxymethylene. The precision of the X-ray techniques used in the study of textures in bulk semi-crystalline polymers is such that small differences in lattice parameters from those referred to above would not be detected. Chang *et al.* [5] in a more recent study of the texture of rolled polyoxymethylene have stated that the evidence for the orthohombic phase is inconclusive because the Bragg angles for the hexagonal $(10\bar{1}0)$ and orthorhombic (110) and (020) are so close to each other that their poles cannot be resolved.

Stress-induced martensitic transformations which have been recorded in X-ray studies of deformed bulk polyethylene [6] have also been identified in electron microscopy and electron diffraction studies [7] of deformed polyethylene single crystals. The latter technique provides a more precise way of studying the crystallography of the transformation processes and has recently been used to study the operative intra-lamellar deformation processes in polyoxymethylene [8]. This letter reports on the first results of the investigation which shows that a stress-induced martensitic transformation is operative in the deformation of single crystals of polyoxymethylene and is probably the transformation reported to feature in the rolling texture of polyoxymethylene [1].

Single crystals of polyoxymethylene were prepared from a solution of dimethyl phthalate and deposited on a Mylar substrate. The Mylar was strained by 15% uniaxially and the crystals were stripped from the substrate and examined with a transmission electron microscope in a way described previously [7]. The electron diffraction patterns obtained from the deformed single crystals showed in some cases some reflections in addition to those expected from the hexagonal phase. The additional reflections could be indexed as reflections from the (110) and (020) planes of an orthorhombic crystal structure. The (200) reflection was not observed and confirms the structure factor calculations of Carazzolo and Mammi who showed that $I_{110}/I_{200} \simeq 0.02$. The intensity of the orthorhombic reflections were weak relative to the reflections from the hexagonal phase and were observed more frequently when a liquid nitrogen cooled specimen stage was used. Orthorhombic reflections have not been reported previously in similar studies of polyoxymethylene [9]. This may be due to the effect of localized electron beam heating in the electron microscope and to heating of the specimen during carbon or metal coating, both of which could cause the reversion of the orthorhombic to the hexagonal phase. This reversion has been reported to occur in bulk polyoxymethylene at approximately 333 K.

An example of an electron diffraction pattern of the type obtained from a deformed single crystal of polyoxymethylene is shown in Fig. 1a. Two orthorhombic [001] diffraction patterns as well as the [0001] hexagonal pattern are present. A tracing of the diffraction pattern is shown in Fig. 1b where open and filled triangles are used to represent the reflections which occur in the two separate orthorhombic patterns. Fig. 1c and d show the relative orientation of the orthorhombic and hexagonal phases represented in Fig. 1a.

The lattice parameters of the orthorhombic phase were calculated from measurements on six electron diffraction patterns. In calculating the

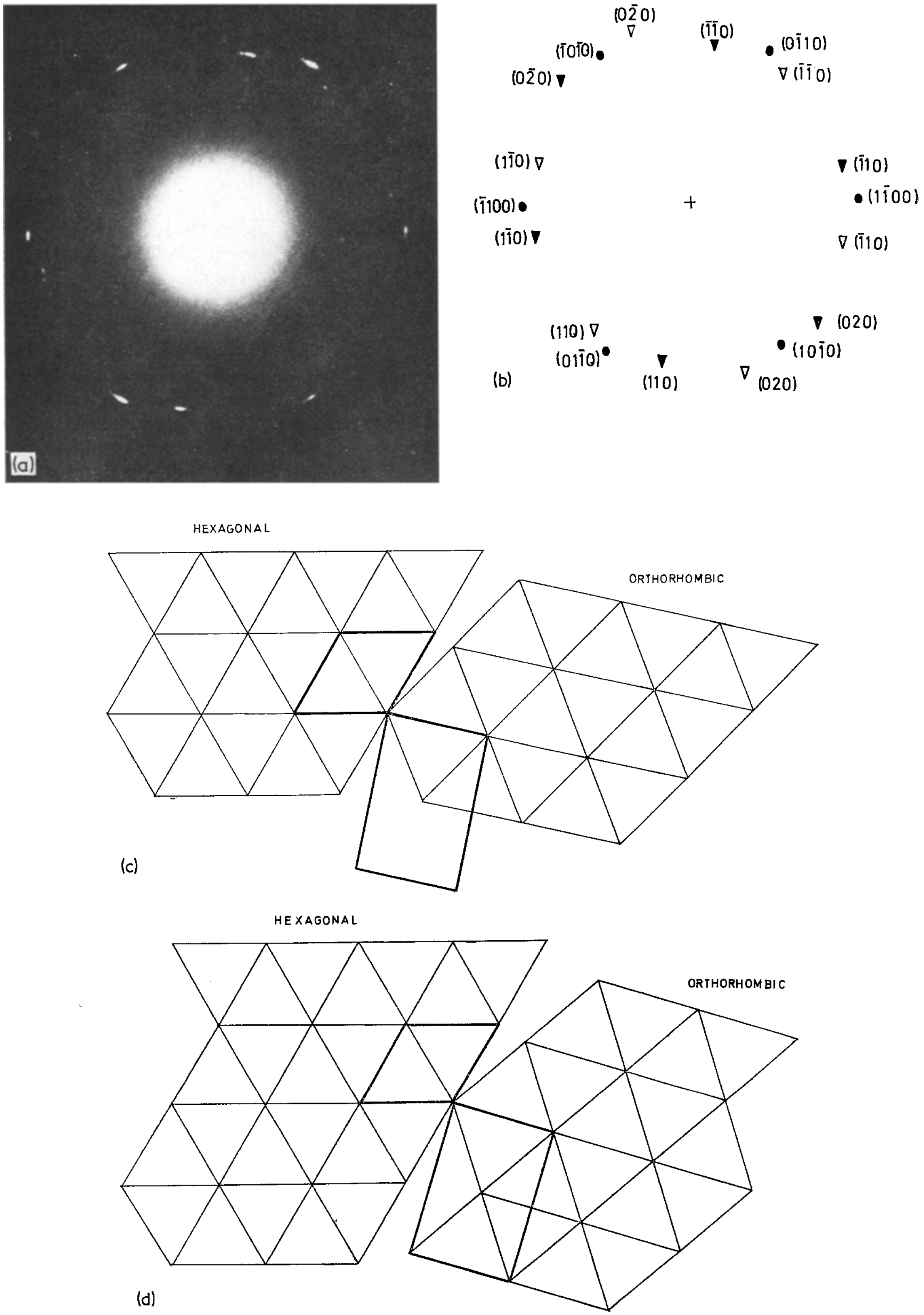
(a)
$(0\bar{2}0)$ ∇
$(\bar{1}\bar{1}0)$ ▼
$(\bar{1}0\bar{1}0)$ ●
● $(0\bar{1}10)$
$(0\bar{2}0)$ ▼
∇ $(\bar{1}\bar{1}0)$
$(1\bar{1}0)$ ∇
▼ $(\bar{1}10)$
$(\bar{1}100)$ ●
+
● $(1\bar{1}00)$
$(1\bar{1}0)$ ▼
∇ $(\bar{1}10)$
▼ (020)
(110) ∇
● $(10\bar{1}0)$
$(01\bar{1}0)$ ●
▼ (110)
∇ (020)
(b)
HEXAGONAL
ORTHORHOMBIC
(c)
HEXAGONAL
ORTHORHOMBIC
(d)

Figure 1

Figure 1 (a) Electron diffraction pattern obtained from a deformed single crystal of polyoxymethylene. (b) Tracing of the electron diffraction pattern shown in (a). The reflections from the hexagonal and the two orthorhombic phases are represented by filled circles and open and filled triangles respectively. (c) and (d) are schematic diagrams of the hexagonal and orthorhombic lattices showing the orientation relationships between the two phases as represented by the electron diffraction pattern in (a). The unit cells are indicated by bold lines.

lattice parameters of the orthorhombic phase the previously reported lattice parameters of the hexagonal phase were used, $a = 4.46$ Å, and it was assumed that the lattice parameter c remains invariant under the transformation at $c = 17.3$ Å.

The lattice parameters of the orthorhombic phase were calculated from the measurements of electron diffraction patterns of deformed polyoxymethylene single crystals to be $a = 4.96 \pm 0.03$ Å and $b = 7.44 \pm 0.04$ Å. Within experimental error these parameters are indistinguishable from those of polyethylene. No polyethylene was present, however, during the preparation of the crystals, and in such a case the familiar diamond shaped polyethylene crystals would have been detected. The orientation relationships observed are also quite different from those observed by Takahashi [10] in the polyethylene single crystals grown eptaxially on polyoxymethylene single crystals.

Many electron diffraction patterns of the type shown in Fig. 1a were recorded and show that a hexagonal to orthorhombic phase transformation in polyoxymethylene is operative under the conditions of test described. It is, therefore, possible that the same transformation process could be operative in cold-rolled polyoxymethylene as postulated by Preedy and Wheeler [1].

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References

1. J. E. PREEDY and E. J. WHEELER, *Nature, Phys. Sci.* **236** (1972) 60.
2. G. A. CARAZZOLO and M. MAMMI, *J. Polymer Sci.* **A1** (1963) 965.
3. H. TADOKORO, T. YASUMOTO, S. MURAHASHI and I. NITTA, *ibid* **44** (1960) 266.
4. E. H. ANDREWS and G. E. MARTIN, *J. Mater. Sci.* **8** (1973) 1315.
5. E. P. CHANG, R. W. GRAY and N. G. MCCRUM, *ibid* **8** (1973) 397.
6. T. SETO, T. HARA and K. TANAKA, *Jap. J. Appl. Phys.* **7** (1968) 31.
7. P. S. ALLAN, E. B. CRELLIN and M. BEVIS, *Phil. Mag.* **27** (1973) 127.
8. N. HARRIS and M. BEVIS, to be published.
9. K. J. O'LEARY and P. H. GEIL, *J. Macromol. Sci. Phys. B* **2** (1968) 261.
10. T. TAKAHASI, in "Encylcopaedia of Polymer Science and Technology" (Interscience Publishers, New York, 1968) Vol. 9, p. 239.

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The change in deviation parameter on crossing a phase or twin boundary

It is well known that diffraction contrast in the electron image of a crystal is sensitively dependent upon the exact orientation relative to the electron beam [1]. When a phase or twin boundary is present in the field of view, oriented nearly parallel to the beam, a difference in diffraction conditions pertains on either side of the boundary, and corresponding differences in contrast occur. Examples have been discussed recently in papers dealing with molecular crystals [2, 3]. In both studies there are regions of interest in which significant departure from a Bragg orientation is present on either side of a boundary. In the "real space crystallography" analysis of Jones and Williams, they assume that their films have a constant curvature over the field of view and estimate local orientations at