# A single crystal of polyethylene crystallized under high pressure

**S. Miyashita, T. Asahi, H. Miyaji and K. Asai**
*Department of Physics, Faculty of Science, Kyoto University, Kyoto, 606, Japan*
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A single crystal of polyethylene about 2 μm thick has for the first time been obtained through high pressure crystallization and studied by X-ray diffraction and scanning electron microscopy. A band of a few μm thickness observed on the fractured surface of high pressure crystallized polyethylene is identified as a single crystal at least several tens of μm wide. Furthermore, a bulk composed of several bands stacked approximately parallel gives hexagonal symmetry in an X-ray oscillation photograph, the oscillation axis being parallel to the end surface of the bands. On the basis of these observations, it is concluded that a thick single crystal in the hexagonal phase splits into several bands on the transition from the hexagonal to the orthorhombic phase; $\langle 110 \rangle$ or $\langle 010 \rangle$ of each band in the orthorhombic phase corresponds to one of three possible *a*-axes in the hexagonal phase.

**(Keywords: polyethylene; single crystal; melt crystallization; high pressure; hexagonal phase)**

## INTRODUCTION

Since Wunderlich *et al.*[1] discovered band structures on the fractured surface of polyethylene, melt-crystallized under high pressure, several attempts have been made to clarify the nature and the origin of the band. Czornyj and Wunderlich studied the band optically[2]. Sakaoku *et al.* showed, using transmission electron microscopy, that at least the striations in the band are single crystals[3]. But there has been no definite study on whether this band as a whole is a single crystal.

On the other hand, Bassett[4,5] postulated that extended chain crystals were formed on crystallization under high pressure through the hexagonal phase[6]. Hikosaka and Tamaki[7] suggested that the single crystals were formed in the hexagonal phase and transformed to the orthorhombic phase without any change in shape. It is an interesting problem as to how the band structure originates from single crystals in the hexagonal phase through the phase transition. Using a diamond-anvil cell, Yasuniwa and Takemura[8] observed that the lens-like polyethylene crystals were divided into band structures on this phase transition. Bassett[9] also observed the change in birefringence on this transition.

In this study, firstly we report on the success of achieving an isolated extended chain single crystal of polyethylene through high pressure crystallization. Secondly, using this result, we discuss the morphological features of the phase transition of polyethylene from the hexagonal to the orthorhombic phase.

## EXPERIMENTAL

The material used in this study was unfractionated high density polyethylene, Sholex 6009 ($\bar{M}_n = 1.4 \times 10^4$, $\bar{M}_w/\bar{M}_n = 8.4$). High pressure crystallization was carried out with a high pressure d.t.a. cell[10]. Pressure was measured with a calibrated manganin gauge. Temperature was measured with a copper–constantan thermocouple. The pressure-transmitting fluid was a silicone oil (Toshiba TSF451).

The sample preparation was as follows. A polyethylene plate (15 mm × 10 mm × 1 mm) was melted at 0.6 GPa, and the phase change process was examined by d.t.a. with a heating rate of 5°C/min under this pressure; the transition temperature from the orthorhombic to the hexagonal phase was 253°C and the melting temperature was 268°C. The temperature of the cell was then lowered to 260°C at a rate of 5°C/h and kept at this temperature for one day; the sample was kept in an undercooling state of 8°C at 0.6 GPa. The temperature was then lowered further to room temperature at a rate of 5°C/h. With such a slow cooling rate, the transition point could not be detected by d.t.a., but it does ensure that crystallization has occurred in the hexagonal region and the crystals were subsequently transformed to the orthorhombic phase by further cooling.

*Figure 1* shows a scanning electron micrograph of the fractured surface of the specimen. Bands of a few μm thickness with many striations perpendicular to the band surface are seen.

The sample was etched with fuming nitric acid at 60°C for a week to cut tie molecules, and rinsed with water and ethanol. Since the specimen became very fragile after this treatment, the specimen was broken and dispersed into fragments ultrasonically in benzene. A photograph of fragments thus obtained is shown in *Figure 2*, where one can see that the bands were well separated. One of these fragments was picked up and was set on a supporting film of amorphous polystyrene (~10 μm thick). This fragment was examined with an optical microscope with crossed and parallel Polaroids. When the fragment became uniformly dark in the crossed Polaroids, X-ray oscillation photographs of the fragment were taken; the oscillation angle was ±45°. The X-rays were unfiltered CuKα radiation. A collimator with a hole about 100 μm in diameter was used. Following the X-ray study, the

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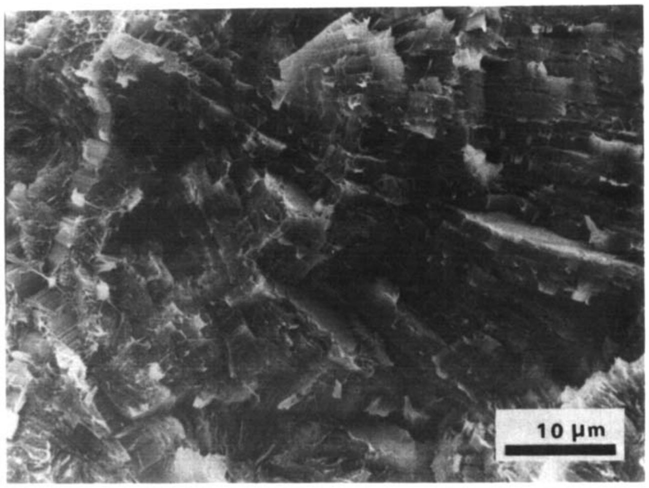

**Figure 1** Scanning electron micrograph of fractured surface of polyethylene crystallized at 0.6 GPa and 260°C for one day

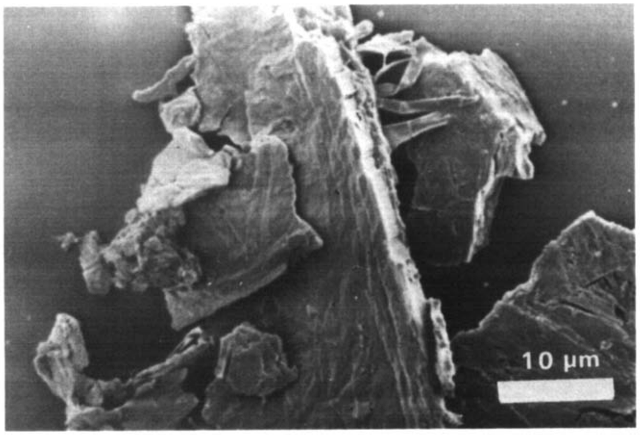

**Figure 2** Scanning electron micrograph of fragments of polyethylene. The sample was roughly broken and ultrasonically dispersed after the fuming nitric acid treatment

specimen was studied with a scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

We have succeeded in obtaining an isolated 'large' extended chain single crystal of polyethylene crystallized under high pressure. *Figure 3* is an optical micrograph of a fragment of the polyethylene. This fragment is very thin pentagonal shaped plate, which was then examined by X-ray diffraction. *Figure 4* shows the X-ray oscillation photographs of this fragment; the oscillation axis is vertical. In *Figure 4a*, the oscillation axis is identical to vertical axis in *Figure 3*, and in *Figure 4b* the oscillation axis is perpendicular to the pentagonal plate. *Figure 4a* shows four 110 and two 200 reflections. Therefore, the vertical axis in *Figure 3* is the *b*-axis. In *Figure 4b*, 110 reflections can be seen on the equator; the axis perpendicular to the pentagonal plate is the *c*-axis (chain axis[3]). With these X-ray diffraction patterns, we can conclude that this fragment is a single crystal. The lattice constants are $a = 7.38$ Å, $b = 4.94$ Å. The scanning electron micrograph of this crystal is shown in *Figure 5*. This single crystal is made of a single band 2 $\mu$m thick. Therefore, a single band is identified as a single crystal at least several tens of $\mu$m wide. There are many striations on the lateral surface of this single crystal. If these striations were grain boundaries, X-ray diffraction should not have given the spots observed in *Figure 4* but continuous arcs. These striations are presumably cleavage planes of the $\{110\}$ planes. However, more detailed morphological studies on these striations are required to confirm this. It is remarkable that the end surface of the band is not flat; i.e. many ridges can be seen. These ridges are traces of lateral edges of other bands not parallel to this band.

*Figure 6* shows an optical micrograph and the X-ray diffraction pattern of another type of fragment. *Figure 7* is the reciprocal lattice corresponding to *Figure 6b*. From this pattern, it turns out that this fragment is made up of two single crystals; these single crystals are not twins but are merely rotated around each other by 60° around the *c*-axis. The contrast of the optical photograph in *Figure 6a* shows that a small single crystal overlaps on a large one.

Frequently we obtained bulky fragments which gave almost hexagonally symmetrical X-ray diffraction patterns. A typical example is shown in *Figure 8a*, which is an X-ray diffraction pattern with the oscillation axis perpendicular to the *c*-axis. This sample fragment is a

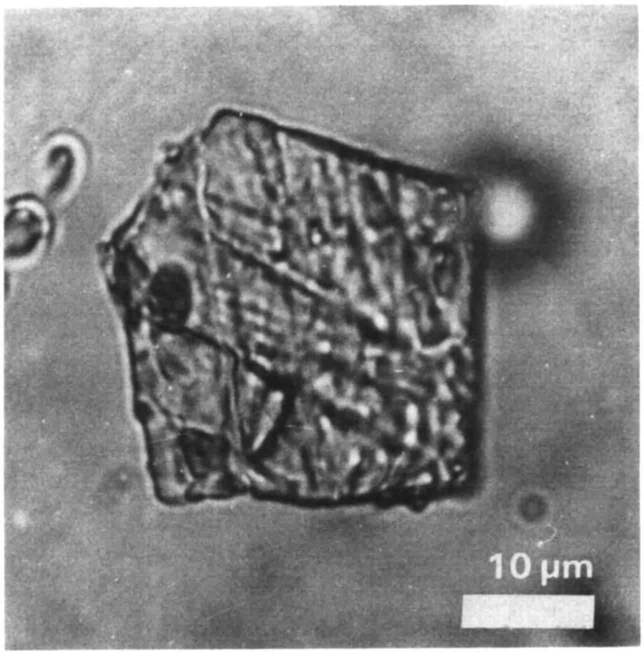

**Figure 3** Optical micrograph of a single crystal of polyethylene crystallized under high pressure

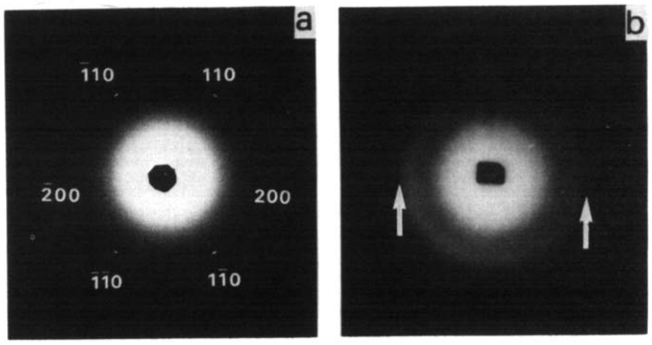

**Figure 4** (a) X-ray diffraction pattern of a single crystal of polyethylene crystallized under high pressure. The sample was oscillated around the vertical axis in *Figure 3*. Inner reflection of each 110 reflection is due to CuK$\beta$ radiation. (b) X-ray diffraction pattern of the same sample as in (a). The sample was oscillated around the axis perpendicular to the end surface of the plate in *Figure 3*

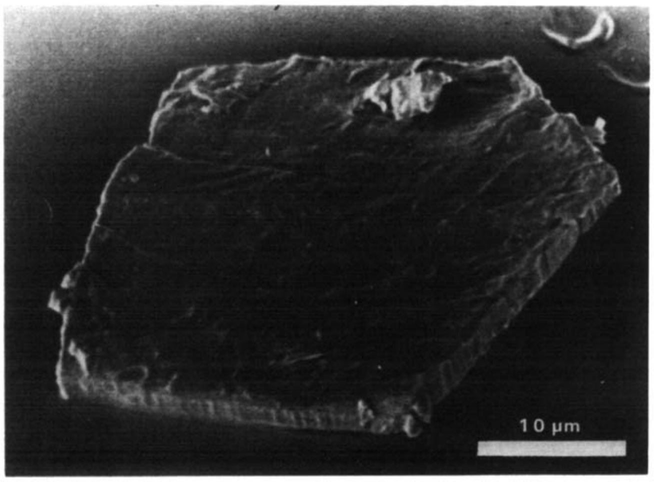

**Figure 5** A scanning electron micrograph of a single crystal of polyethylene crystallized under high pressure

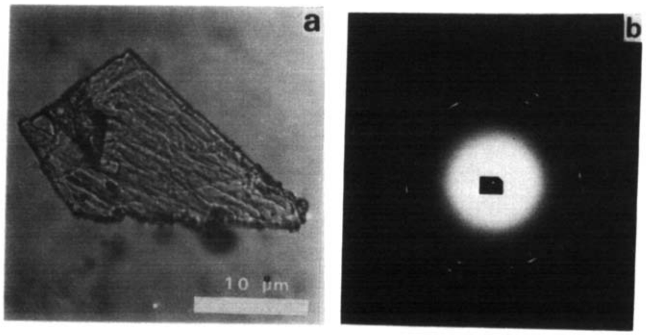

**Figure 6** (a) An optical micrograph of a fragment composed of two single crystals. (b) X-ray diffraction pattern

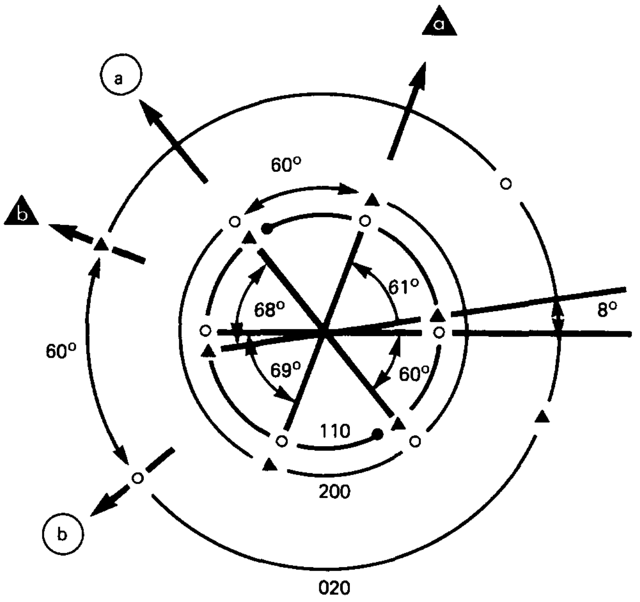

**Figure 7** Reciprocal lattice construction for *Figure 6b*. There are two crystals; (○) represents the reciprocal lattice points of one single crystal and (▲) represents those of the other single crystal. The arrows drawn by thick line represent the *a*- and *b*-axes of the two crystals

polycrystal. These crystals can be almost superimposed by rotation around the *c*-axis through an angle of 60°. *Figure 8b* is a scanning electron micrograph of this fragment. We can see that this fragment is made up of several sheets of bands overlapped. Since a band is a single crystal at least a few tens of µm wide, these bands are superimposed crystallographically by six-fold rotation around an axis perpendicular to the band surface.

It should be noted that a single band much wider than the bands discussed above may be made up of several single crystals approximately a few tens of µm wide. *Figure 9* is an X-ray oscillation photograph along with a scanning electron micrograph of a very wide single band (more than 0.1 mm wide). This single band gives a hexagonally symmetrical diffraction pattern; this wide band comprises several single crystals.

It is known that polyethylene crystal in the hexagonal phase contains many defects along chain axis[6] such as kinks and jogs. On the phase transition from the hexagonal to the orthorhombic phase, these defects are excluded from the crystal by molecular motions and aggregated on a plane perpendicular to the chain axis to form the boundaries between the bands. Consequently this process minimizes the free energy of the system. A thick single crystal in the hexagonal phase splits into several bands on the phase transition (*Figure 10*). This model agrees with the optical observations of Yasuniwa and Takemura[8]. Therefore, it may be inferred that the fragment shown in *Figure 8b* was a single crystal, as a whole in the hexagonal phase at high pressures and high temperatures. The hexagonal symmetry in the X-ray diffraction pattern (*Figure 8a*) of the specimen results from the symmetry of the hexagonal phase. The hexagonal phase has three equivalent crystallographic *a*-axes. It is reasonable that the ⟨100⟩ direction of the hexagonal phase turns out to be either the ⟨010⟩ or the ⟨110⟩ direction of the orthorhombic phase[11]. These cases are schematically represented in *Figure 11*. Since the hexagonal phase has a larger specific volume than the

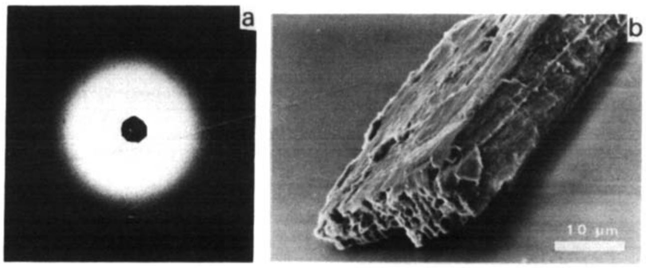

**Figure 8** (a) X-ray diffraction pattern of a bulky polyethylene fragment. (b) A scanning electron micrograph. This fragment is made of several sheets of bands overlapped

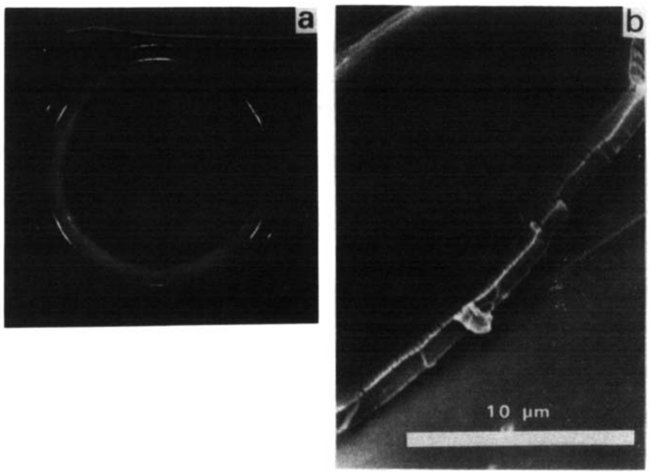

**Figure 9** (a) An X-ray diffraction pattern of a band more than 0.1 mm wide. (b) A scanning electron micrograph of the fractured portion

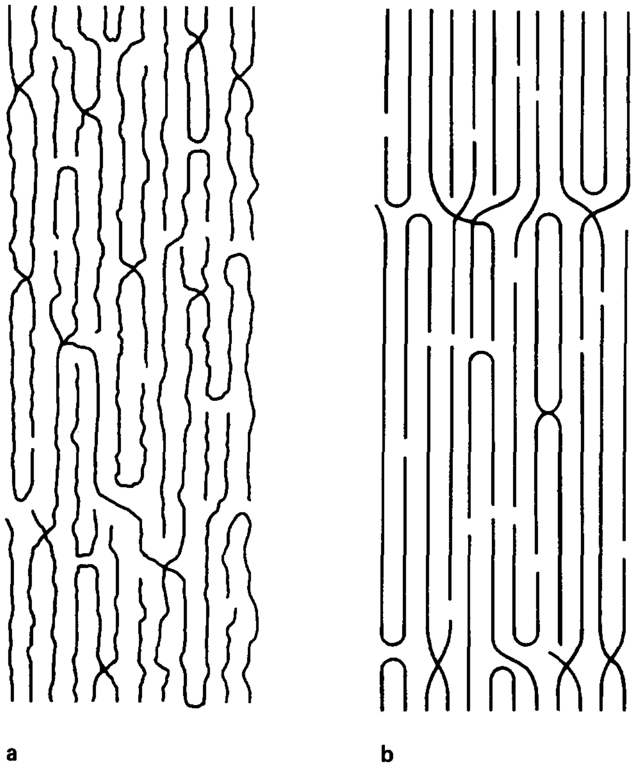

**Figure 10** Model for the phase transition of polyethylene from the hexagonal to the orthorhombic phase. (a) In the hexagonal phase, there are many defects along *c*-axis (kinks, jogs). (b) On the phase transition, these defects are excluded to form boundaries between bands

orthorhombic phase, the dilatational strain as well as shear strain in the phase boundary causes the orientational fluctuation in the orthorhombic crystals during the phase transition.

Finally, the relationship between the band thickness and molecular weight should be discussed. It is noted that the fuming nitric acid treatment has little effect on lamella thickness[12,13]. The band thickness of 2 $\mu$m is larger than the thickness corresponding to the weight averaged molecular weight of $1.2 \times 10^5$. This discrepancy has been reported by several authors[14-16]. A model explaining this discrepancy is illustrated in *Figure 10*, where a single crystal may include many chain ends.

How the phase boundary between the hexagonal and orthorhombic phases occurs and why a band-like single crystal has a fairly uniform thickness are interesting problems. To clarify these using the above model, a study of the molecular motion and kinetics of the transitions such as nucleation and growth are required.

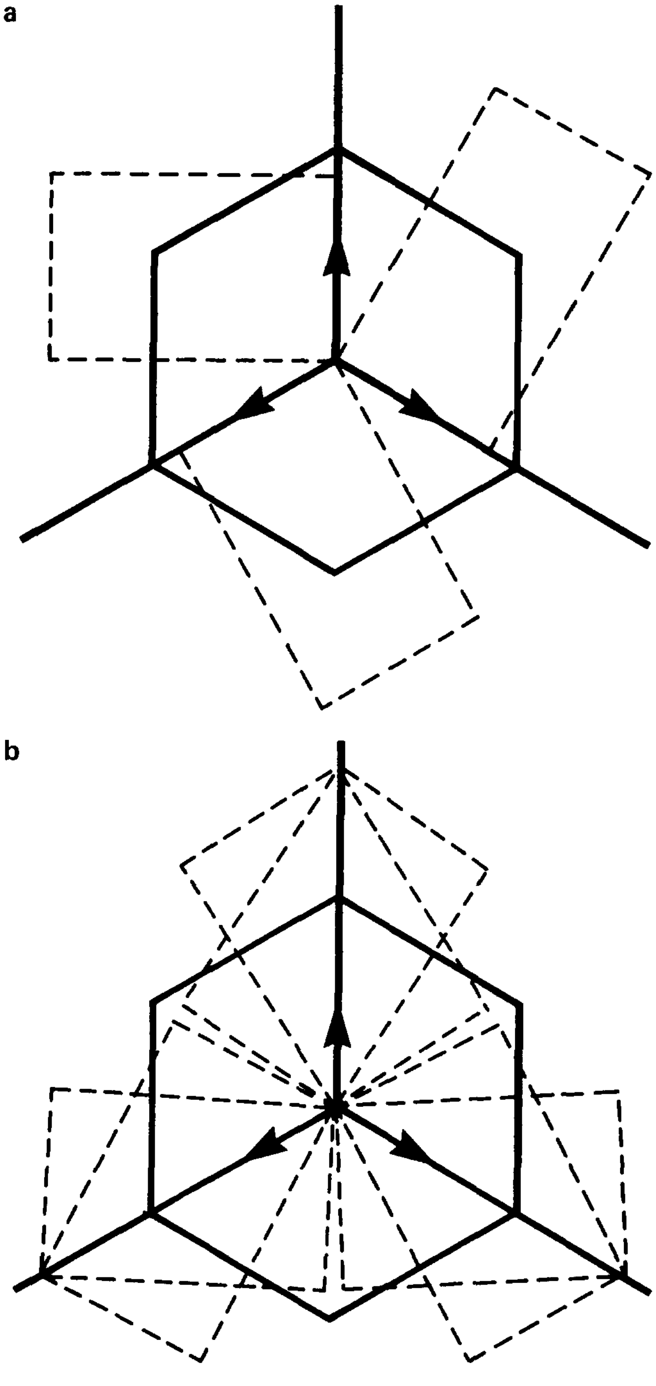

**Figure 11** Schematic representations for the possible orientations from the hexagonal to the orthorhombic phase. (a) $\langle 100\rangle_{\text{hex.}} \rightarrow \langle 010\rangle_{\text{orth.}}$; (b) $\langle 100\rangle_{\text{hex.}} \rightarrow \langle 110\rangle_{\text{orth.}}$

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