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# Giant Single Crystals of Poly (ethylene oxide)

Kazuo MONOBE and Yuhiko YAMASHITA

*Department of Industrial Chemistry*

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The preparative method of giant single crystals of PEO and the experimental results of them by x-ray diffraction and electron microscopy are described. The crystallization of PEO was carried out in a two dimensional crystallization apparatus. From the tridirectional x-ray diffraction patterns on the resulting plate-like crystals, it was confirmed that these crystals have a single crystal-like orientation at high supercoolings, the [401] axis is parallel to a growing direction and the [001] axis is perpendicular to the wide surface, and a double orientation at low supercoolings, two axes of [421] and [42$\bar{1}$] are parallel to a growing direction and the [001] axis is perpendicular to the wide surface.

## § 1. Introduction

Various high polymers have been obtained in the form of single crystals in which the molecular chains are folded in segments of 100 Å since the polyethylene single crystal was discovered in 1957[1-3]. Notwithstanding the intrinsic interest of these crystals, much of current work is, nevertheless, concerned with the morphology and the structure on these crystals with electron microscopy[4]. The investigation of the mechanical properties on these crystals may ultimately lead us to a comprehension of the situation in bulk polymers. However, their dimensions are too small to examine them. Furthermore, the structural investigation of single crystals by means of x-ray, infrared, nmr and other techniques is also confronted with the handicap of their smallness. In order to remove this handicap we attempted to prepare giant single crystals employing the nature of spherulite growth in polymer and succeeded by moving thin molten sample of PEO placed between two pieces of glass in a steep temperature slope toward lower temperature at constant speed.

The present paper shows the preparative method of giant single crystals of PEO and the results of our studies on them by x-ray diffraction and electron microscopy.

## § 2. Principle for Preparation of Giant Single Crystals

Fujiwara's oriented crystallization method[5] was improved in order to obtain giant single crystals of PEO. The crystallization was carried out in a two dimensional crystallization apparatus with a steep temperature slope. Fig. 1 shows a thin molten sample placed between two pieces of glass moving with velosity $v_m$ away from melt region to crystallization region, a

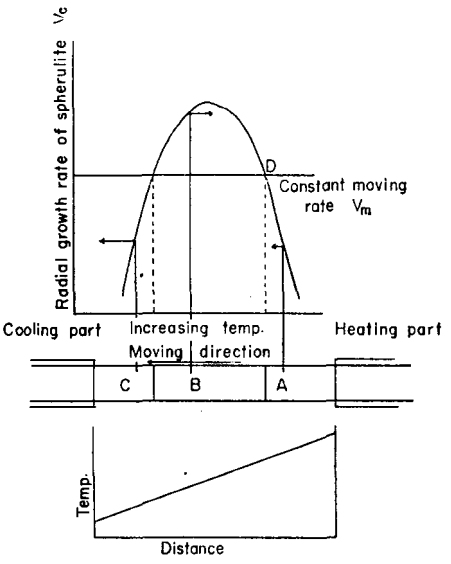


**Fig. 1** Schematical representation of principle for preparation of giant single crystals.

typical curve for radial growth rate $v_c$ of spherulites in crystalline polymer and a temperature slope between heating part and cooling part. If a nucleus forms at A region, the crystallization will then proceed in all directions. The crystalline boundary on the left side will move to the left at a speed $(v_m+v_c)$ and when $v_c$ has fallen to a negligible value, the crystallization will stop. However, on the right side the crystalline boundary will move to the left at a speed $(v_m-$

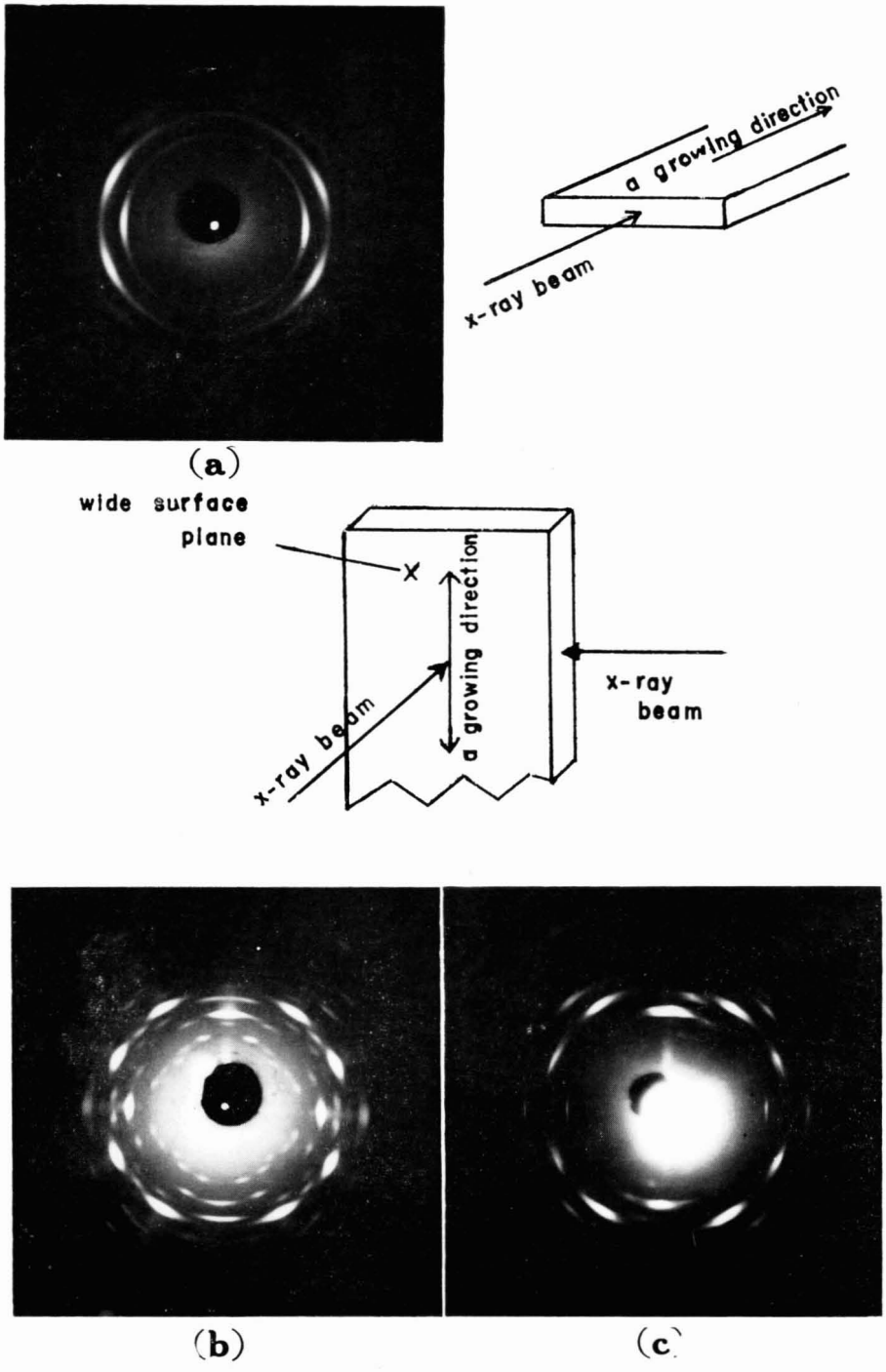


**Fig. 2** Tridirectional x-ray diffraction patterns of the plate-like crystal formed at a moving speed 0.01 mm./min.

(**a**) X-ray beam parallel to a growing direction. A wide surface plane horizontal.

(*b*) X-ray beam perpendicular to a growing direction and a wide surface plane. A growing direction vertical.

(**c**) X-ray beam perpendicular to a growing direction and paralllel to a wide surface plane. A growing direction vertical.

$v_c$) and when the boundary reaches **D**, $v_m = v_c$ and a steady state will be achieved. If the initial nucleus forms at **B** region where $v_c$ is larger than $v_m$, then on the right side the crystalline boundary will move to the right with a speed $(v_c - v_m)$ until the boundary reaches **D**, when a steady state will again be achieved. On the other hand, if an initial nucleus forms at **C** region, no position of stability can be reached. Therefore, if the initial nucleus forms at **A** or **B** region, a single giant spherulite originates from one nucleus and the type of texture which would result from this form of growth shows perfect orientation of spherulite radius parallel to the axis of the moving direction. If such spherulites are parallel in one line, the whole sample will possess the same structure. It is known[6] that the fibril twisting along a radius occurs in PEO spherulites as in other polymers. However, if the lamellar width of fibrils is larger than the sample thickness, lamellar surfaces will be parallel to the glass surfaces. That is, the molecular chains will be perpendicular to the wide surface plane of the sample. In such a principle we have obtained a giant single crystal of PEO.

## § 3. Experimental

The samples of PEO used in this study were Carbowax 6000 (The Carbide and Carbon Chemical Company). By the above mentioned method, plate-like crystals, 1 mm. in thickness, 20 mm. in width and 30 mm. in length, were produced for various values of a moving speed ranging from 0.008 mm./min. to 1 mm./min. The resulting samples were studied by x-ray diffaction and the fracture surfaces of the samples were also examined by electron microscope using the standard replication.

## § 4. Results and Discussion

X-ray diffraction patterns on the resulting plate-like crystals confirmed that these crystals have a single crystal-like orientation at high supercoolings and a double orientation containing twin structure at low supercoolings. The facts that these two type crystals are formed at different supercoolings are consistent with our previous results[7] in PEO spherulites, that is, a growing direction (a moving direction) possesses a [**401**] axis below 50°C and two axes of [**421**] and [**42$\bar{1}$**] above 50°C. Fig. 2 illustrates x-ray diffraction patterns of the plate-like crystal formed at a moving speed 0.01 mm./min. with the beams (Ni-filtered CuK$\alpha$ radiation) parallel to three mutually perpendicular directions. The x-ray diffraction pattern shown in Fig. 2 (a) was taken on a sample so held that the wide surface plane was horizontal with the x-ray beam parallel to a growing direction. If the plate-like crystal possesses a rotation axis along a moving direction, the pattern will not exhibit the arcs or spots as shown in Fig. 2 (a), but only the ring pattern. The indices of the main reflections of the patterns in Fig. 2 are asigned reasonably by the monoclinic crystal structure proposed for PEO by Tadokoro et al[8]. From these tridirectional x-ray diffraction patterns it can readily be concluded with the aid of the reciprocal lattice that the plate-like crystal has a double orientation, two axes of [**421**] and [**42$\bar{1}$**] are parallel to a growing direction and the [**001**] axis are perpendicular to the wide surface. A closer verification for this conclusion is obtained by studying the reflections individually, the (120) reflections providing the clearest evidence. In Fig. 2 (a) two (120) reflections are in equater, in Fig. 2 (c) two (120) reflections are in meridian and in Fig. 2 (b) the intensities of all four (120) reflections are equal, which mean that the reciprocal lattice is corresponded for the crystal as shown in Fig. 3. Other reflections can be also

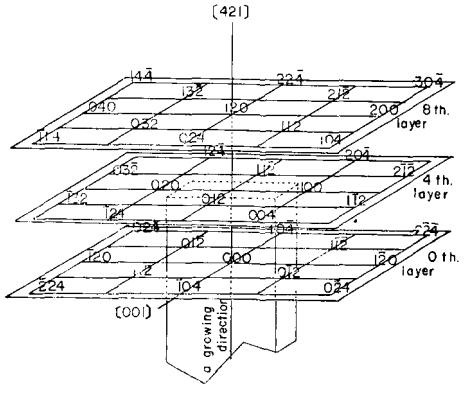


**Fig. 3** Schematical representation of the plate-like crystal and its corresponding reciprocal lattice. The reciprocal lattice represents conveniently the 0, 4 and 8th. layers containing main reflections.

interpreated by this asignment for the crystal. However, it should be noted that a spread of each reciprocal lattice point has been occurred with a small disturbance of orientation.

**Fig. 4** Electron micrograph of fracture surface of the plate-like crystal. ×25000

X-ray diffraction studies on the crystals prepared with a high moving speed also concluded that the plate-like crystal has a single crystal-like orientation, the [**401**] axis are parallel to a growing direction and the [**001**] axis are perpendicular to the wide surface.

Electron micrograph of fracture surfaces of these crystals is shown in Fig. 4. This shows the texture of the crystal composed of parallel lamellae which grow to one direction. Therefore, this observation is an additional supporting evidence for x-ray diffraction studies.

Employing the nature of polymer spherulite growth, we succeeded in preparing a giant single crystal or a double oriented crystal of PEO and give the confirmations on their orientation by the use of x-ray diffraction and electron microscopy. These crystals are accommodated with the studies of various physical properties on the contrary of tiny single crystals obtained from the solution. Therefore, it is very valuable that the above mentioned principle for preparation of giant single crystals is applied to other polymers. Basing on this concept, experiments for the application to other polymers are going on in our laboratory.

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## References

1) P. H. Till: *J. Polymer Sci.*, 24, (1957) 301.
2) A. Keller: *Phil. Mag.* [8], 2, (1957) 171.
3) E. W. Fischer: *Z. Naturforsch.*, 12a, (1957) 753.
4) P. H. Geil: *Polymer Single Crystals*, Interscience (Wiley), New York, (1963).
5) Y. Fujiwara: *J. Appl. Polymer Sci.*, 4, (1960) 10.
6) F. J. Baltá Calleja, I. L. Hay and A. Keller: *Kolloid-Z. und Z. Polymere*, 209, (1966) 128.
7) Y. Yamashita and K. Monobe: *This Memoirs*, 1, (1966) 59.
8) H. Tadokoro, Y. Yoshihara, S. Tahara and S. Murahashi: *Makromol. Chem.*, 73, (1964) 285.