

Two Distinct Types of Spherulite in Poly (ethylene oxide)

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Fujiwara's oriented crystallization method was applied to poly (ethylene oxide) to obtain a uniform texture composed of parallel fibrils which correspond to the structure of a radial direction of spherulites. Two different x-ray diffraction patterns in crystallite orientation of the spherulite radius were obtained. From these patterns and crystallization conditions it could be determined that the spherulite radius has a [401] rotation axis below about 50°C and two [421] and [4 $\bar{2}$ 1] rotation axes above about 50°C.

A reasonable interpretation was given for these two ways of spherulitic crystallization, based on the growth features of lamellar crystals of poly (ethylene oxide). That is, it is concluded that a second order transition in poly (ethylene oxide) lamellar crystals near the temperature of 50°C is responsible for the change of the rotation axis in spherulite radius.

We wish to report that two distinct types of spherulite are formed at different supercoolings from the melt in poly (ethylene oxide) (PEO) and to give this fact a reasonable interpretation.

Price and Kilb reported two distinct types of PEO spherulite in Carbowax 4000 and Carbowax 6000 for the first time¹⁾. They have indicated that at low supercoolings spherulites develop scalloped edges, with each scallop sector having branched structure reminiscent of a fern frond, and at high supercoolings they develop smooth circular boundaries. A x-ray diffraction study was also made the capillary samples of spherulites and the crystallite orientation with respect to the spherulite radius was examined. They have concluded that [401] rotation axis is $\pm 45^\circ$ to the radius at low supercoolings and is perpendicular to the radius at high supercoolings. This conclusion that the polymer chains are generally not in the tangential orientation, in-

terests us in contrast with evolving concept of molecular orientation in polymer spherulites²⁾. To examine their results, Fujiwara's oriented crystallization method^{3,4)} was applied to PEO.

By this method, oriented rods of PEO, Carbowax 6000, about 1 mm. in diameter, were produced for various values of moving speed ranging from 0.008 mm./min. to 1 mm./min. The crystallization temperatures in these conditions are estimated to be approximately from 54°C to 45°C based on the data of the radial growth rate of Carbowax 6000 which were measured by Price et al⁵⁾. Two different x-ray diffraction patterns in crystallite orientation were obtained from these specimens as shown in Fig. 1 (a) and (b). All reflections of them can be identified and indexed as from the monoclinic crystal structure proposed for PEO by Tadokoro et al⁶⁾. From these patterns and crystallization conditions it can be determined that the spherulite radius has a [401] rotation axis below about 50°C and two [421] and [4 $\bar{2}$ 1] rotation axes above about 50°C. In both cases the fact that these rotation axes are perpendicular to the *c* axis makes chain molecules the same tangential orientation as that in other polymer spherulites. The transition temperature of the rotation axis is consistent with that of morphologically different spherulites suggested by Price and Kilb¹⁾. However, our results on the crystallite orientation for the

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** In this method isothermal crystallization can be realized by moving a specimen rod, which is enclosed in a glass capillary, with a constant speed along a steep temperature slope since most polymer spherulites have negative values of temperature dependence of radial growth rate. Thus, the whole specimen rod comes to possess a uniform texture composed of parallel fibrils which correspond to the structure of a radial direction of spherulites.

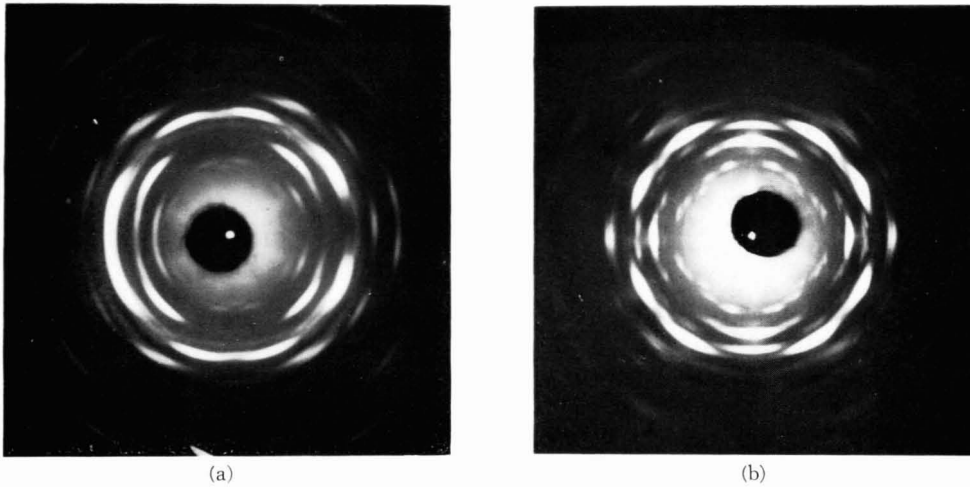


Fig. 1. X-ray diffraction patterns of spherulites prepared by oriented crystallization method.
 (a) Pattern obtained from the specimen crystallized below 50°C. Oriented rod axis vertical. The spherulite radius has a $[401]$ rotation axis.
 (b) Pattern obtained from the specimen crystallized above 50°C. Oriented rod axis vertical. The spherulite radius has two $[421]$ and $[\bar{4}21]$ rotation axes.

radius are apparently inconsistent with those of them. These discrepancies seem to be due to the following situations. In their capillary samples formed at high supercoolings, a transcristalline layer seems to be produced for the reason that the whole capillary was cooled at a time. That is, spherulite nuclei at glass surface are so closely spaced that the spherulites grow in perpendicular direction to the capillary. In the spherulites formed at low supercoolings above mentioned discrepancy can not be understood, for it is likely that in their capillary samples as well as ours the spherulite radius is parallel to the capillary since the nucleation rate is very low at these temperatures. It, however, should be noticed that in our determination the $[401]$ axis is not rotation axis but is oriented to $\pm 45^\circ$ for the radius.

Lastly, we will give an interpretation for two distinct spherulitic crystallization, based on the growth features of lamellar crystals of PEO. It has already been shown by many investigators^{7,8,9,10} that PEO is crystallized from dilute solution in the form of square tabular crystals thickening by way of screw dislocation mechanism. In our previous paper⁸ it has been determined that the four growing faces are $\{120\}$ of monoclinic cell and two diagonals are the $[401]$ and $[010]$ axes, respectively. Here, it should be noticed that two axes of the $[401]$ and $[010]$ are different in notation but very similar in nature since single crystals are square

in shape and their electron diffraction patterns have an approximately tetragonal symmetry. From more concentrated solution a dendritic development of lamellar crystals whose morphological habits are intermediate between single crystals and spherulites was obtained. These crystals have a pronounced tendency for rapid growth to the diagonals as shown in **Fig. 2**. The extension of this marked habit for spherulitic crystallization from the melt seem to give a simple interpretation for two distinct types of spherulite as shown schematically in **Fig. 3** if it is assumed that at low supercoolings two axes of the $[401]$ and $[010]$ possess the similar tendency** for rapid growth and at high supercoolings only a $[401]$ axis possesses the tendency for rapid growth. This assumption seems to be reasonable from following facts. It can be pointed out that the temperature at which two axes of the $[401]$ and $[010]$ possess similar habit corresponds to that of beginning of sliding diffusion¹¹ of chain molecules in crystals. The viscoelastic absorption α_c characteristic of crystalline regions in polymers such as polyethylene is also attributed to the sliding diffusion¹³. The peak of the α_c absorption for solution grown crystals of PEO is located near the temperature of 50°C¹⁴. Furthermore, we have previously⁸

** The change of crystal structure above 50°C from monoclinic to tetragonal was ruled out by photographing x-ray diffraction patterns of fiber samples of PEO at a constant temperature of 55°C¹²,



Fig. 2. Electron micrograph of dendritic crystals crystallized from solution. These crystals have a pronounced tendency for rapid growth to the diagonals. This growth mechanism is due to the way of screw dislocation. $\times 10,000$

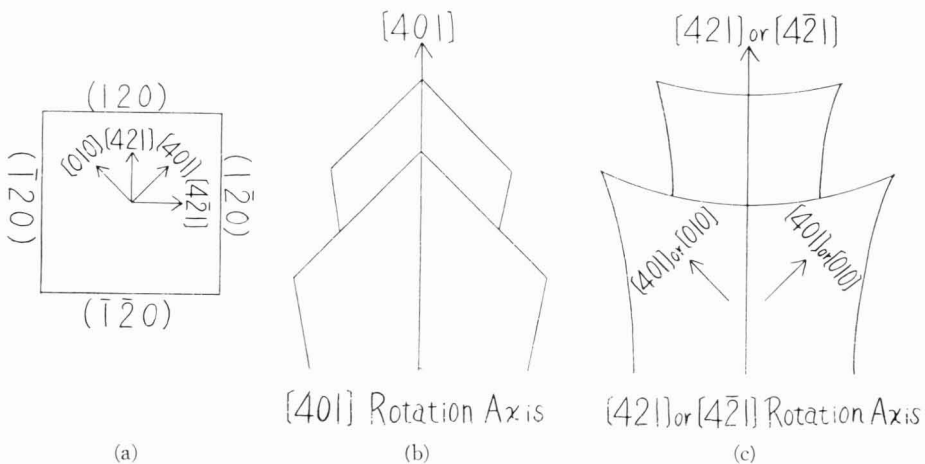


Fig. 3. A simple interpretation for two distinct types of spherulite in PEO is shown schematically.

- (a) Diagram which schematically represents growing planes and main crystallographic axes.
- (b) Since at high supercooling only a $[401]$ axis possesses the tendency for rapid growth, spherulite radius has a $[401]$ rotation axis.
- (c) Since at low supercoolings two axes of the $[401]$ and $[010]$ possess the tendency for the rapid growth, spherulite radius has $[421]$ and $[4\bar{2}1]$ rotation axes. One should notice that in these crystals $[401]$ and $[010]$ axes are not rotation axis as shown in x-ray diffraction pattern of **Fig. 1 (b)**.

pointed out that the radial growth rate of spherulites also changes abruptly at about 51°C. Therefore, it is not questionable that near the temperature of about 50°C lamellar crystals of PEO have a second order transition point and this transition in crystalline regions is responsible for the change of rotation axis in spherulite radius.

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