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Oriented Crystallization of Polyethylene at High Pressure from Flowed Melt

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Synopsis

In the course of the study of polymer crystallization at high pressure, oriented crystallization of extended chain crystals of polyethylene were examined. Molten polyethylene were extruded into a die at a few hundred atm, and follwed by crystallization by high pressure application above 3000 atm. Resulting sample shows chain orientation to extruded direction. Thick lamella nearly a few thousand angstrom, which are typical feature of high pressure crystallization, were observed to be stacked parallel each other. In spite of favorable condition for crystals to grow to chain direction, remarkable growth to normal direction to them were also observed.

1. Introduction

One of the characteristic feature of polymer crystallization is that the long chain molecules crystallize in the form of thin lamella only in a few hundred angstrom thick, in which the chains are folded back and forth normal to the lamellar surface. However, Wunderlich et al revealed that polyethylene (PE) crystallize in the form of thick lamella nearly a few thousand angstrom above 3000 atm 1). The length correspond to the chain length. It was very interesting subject, therefore, whether the polymer crystals can grow to exceed their chain length. Hatakeyama et al reported the crystal grown up to 40 microns by isothermal crystallization at about 5000 atm 2). In a previous

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paper 3), authors suggested that such a crystal developed when the polymer was melted thoroughly at high pressure and crystallized slowly lower rate than 0.05°C/min. However, it seems difficult to grow the crystal above the thickness in isotropic system. One of the crystallization process of polymers are regarded as the chain oirentation process within the isotropic system. Therefore, it is valuable to study the crystallization on chain oriented state in melt. At atomospheric pressure, folded chain habit is well known to be remained in the system and these lamella are stacked parallel each other normal to chain oriented direction.

In present paper, the crystallization from oriented melt at high pressure was examined.

2. Experimental

Samples used in this study is unfractionated linear PE (Mv=54000). The high pressure apparatus is shown in Fig. 1 schematically.

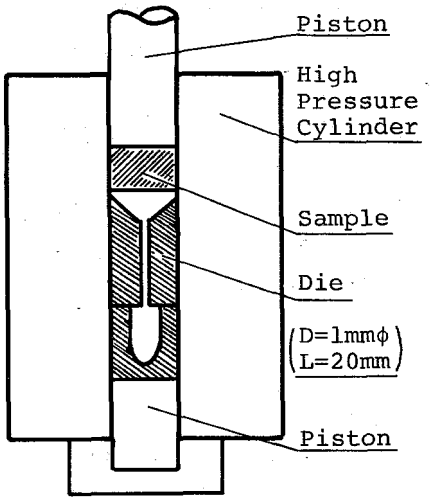


Fig. 1. Schematic representation of crystallization apparatus.

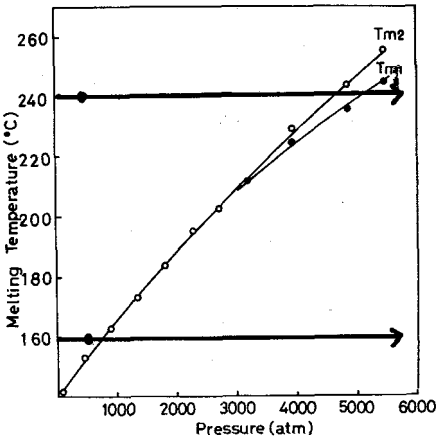


Fig. 2. Crystallization procedures.

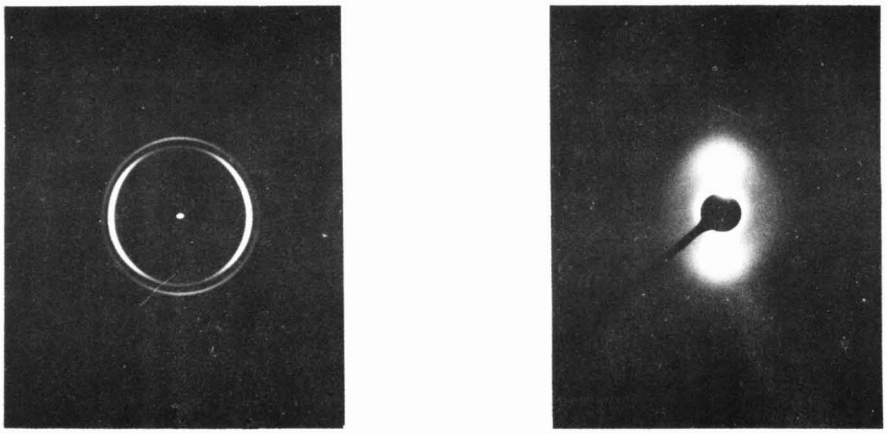
- Extruded position.
- Crystallization process.

Experimental procedures are summerlized in Fig.2. The samples which is placed on the extrusion die in the cylinder was melted at suitable temperatures at atmospheric pressure. The molten sample was extruded into the die at a few hundred atm for a few minutes and followed by crystallization with application of high pressure up to 6000 atm. The samples are analyzed by x-ray and electron microscope.

3. Results and Discussion.

The samples obtained are oparque strands. The strands crystallized at 160°C is comparatively flexible and ductile. On the other hand, the strands crystallized at 240°C is rather brittle and easily break to normal direction to the length.

X-ray diffraction patterns of the strand crystallized at 160°C are shown in Fig. 3. Wide angle x-ray diffraction pattern (WAXD) shows that a-axis oriented to extruded direction. And small angle x-ray diffraction pattern (SAXD) shows the meridional scatter corresponding to 270 A. These feature coincide with familliar flow-induced crystallized materials at atomospheric pressure. Phase transition pressure at this temperature is nearly 900 atm. Therefore, at this pressure, obvious pressure effect was not observed. Odell showed shish-kebab structrue developed by the similar procedures 4).



(a) (b)

Fig. 3 X-ray diffraction patterns of the extrudate at 160°C. Extrusion direction on this and subsequent patterns are vertical. (a): WAXD, (b) SAXD corresponding to about 270 A.

On the other hand, WAXD of the strands crystallized at 240°C shown in Fig. 4 shows that the chains oriented to nearly parallel to extruded direction. Therefore, the chain alignment seemed to be easier at this conditions, although the polymer extruded at higher temperature. At this temperature two transition pressures present as shown in Fig. 2 at 4500 atm and 5100 atm. The former is the transition from melt to hexagonal and the latter is one from hexagonal to solid.

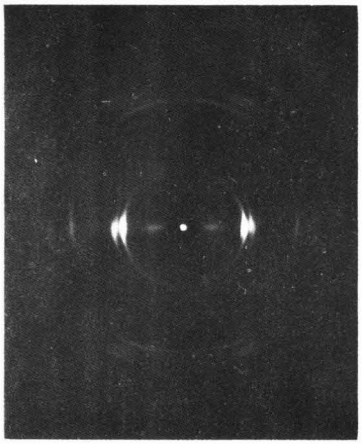


Fig. 4 WAXD of the extrudate at 240°C.

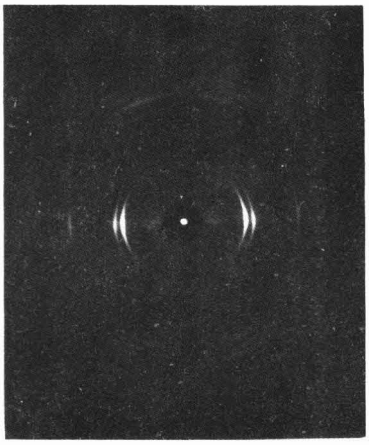
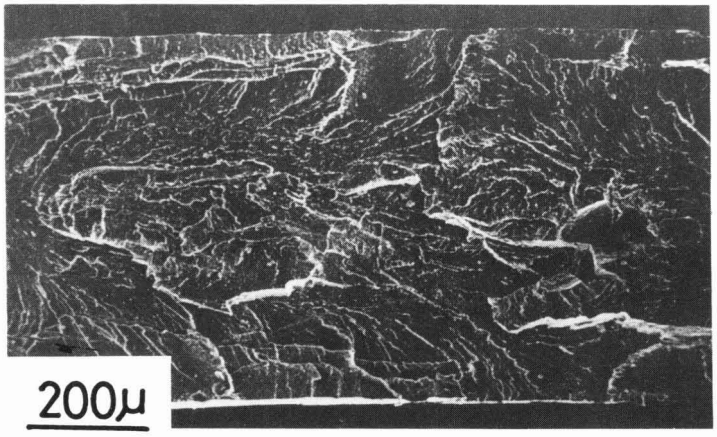


Fig. 5 WAXD of thin section of the sample in Fig. 4

In this diagram another features are observed. Two sets of spots are observed in (110) and (200) reflections each other. They are slightly displaced each other to equatorial direction and rotated around the diffraction center. On the higher reflections this feature is also observed. The sliced samples of the strand, which were cut parallel to strand length in width 0.2 mm avoided central core, disappear a pair of reflections as shown in Fig. 5. However, the slight rotations are remainded and their intensity relations does not obey the relations on usual fiber diagram. For example, (200) reflections are weak extreamly and (020) reflections are stronger than usual. These feature is specific one on the sample crystallized at high pressure in this method. These observation suggest that each reflections arrived from separated and comparatively larger crystallite than usual fiber, which has conical symmetry around the strand core.



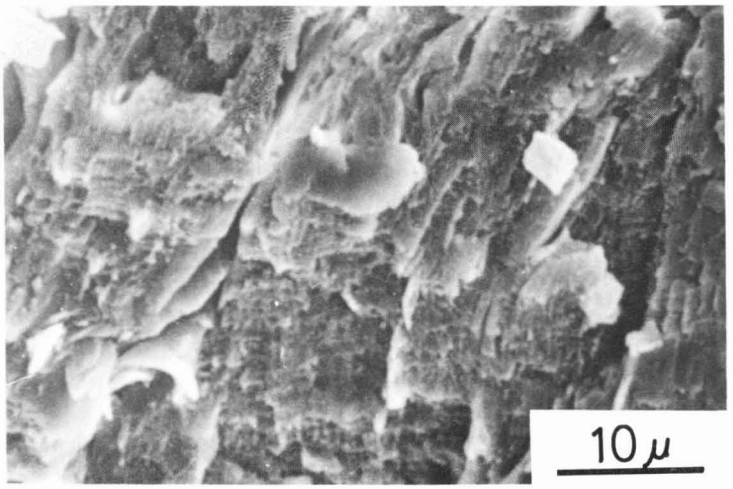


Fig. 7 SEM of the fracture surface of the extrudate at 240°C. Higher magnification of the surface shown in Fig. 6

Scanning electron micrograph (SEM) of the fracture surface of the strand is shown in Fig. 6. The surface is parallel to strand direction. The fracture surface is rather flat and is not fibricated as in usual fiber sample. Stacked layer structure are observed in Fig. 7. Transmission electron micrograph of the same sample is shown in Fig. 8. Thick lamella nearly a few thousand angstrom, which is characteristic feature of high pressure crystallization on PE, were observed to be stacked parallel each other. Lamellar surface is not normal to chain direction, although they are usually normal each other

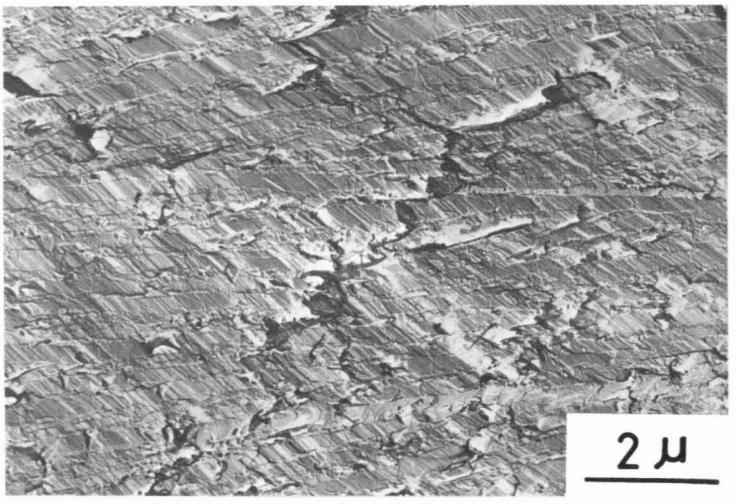


Fig. 8 TEM of the fracture surface of the extrudate at 240°C.

at isotropic crystallization. Degree of obliquity is varied from position to position of the sample.

X-ray and morphological observations mentioned above suggest that the crystallization was occured after the chain orientation by flowing. However, it is noteworthy that remarkable growth was permitted to nor-

mal direction to chain length. This seems to be general phenomena of PE whether the crystallization take place in oriented conditions or isotropic, and at atomospheric pressure or at high pressure.

5. conclusion

1) It is clearized that chain oriented thick lamella are obtained by means of high pressure crystallization of flowed melt of PE.

2) The lamella are, however, developed pronouncedly to normal direction to chain length rather than the chain length in present conditions.

3) Therefore, the crystallization conditions should be analyzed at nearer equilibrium conditions on flowing melt.

References

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