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Fine Structure and Nucleation Mechanism of Extended Chain Crystal of Polyethylene

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The fracture surfaces of extended chain crystal were observed with 100 kV electron microscope for samples obtained from linear polyethylene ($M_w=64,000$) by isothermal crystallization under elevated pressure. Some fracture surfaces were prepared after uniaxial compression was given to the samples. The obtained results were as follows: the samples were irregular aggregation of block-bands and the bands consisted of the bundles of extended-chain crystal strings (rod-like crystals of 300–500 Å diameters). Some of the strings penetrated into adjacent block-bands. These crystal strings were considered to be the nuclei of extended chain crystal which were precipitated from extended chain molecules directly.

INTRODUCTION

After polyethylene spherulites were discovered by Bunn and Alcock¹⁾ in 1945, the earlier investigation of the molecular arrangement in the spherulites suggested that the molecules seemed to be arranged in the radial direction, based on the model of fringed micell, due to fibrillar structure radiated from the center of the spherulite. On the other hand, the molecules were found to be arranged in the tangential direction from the observation of the spherulites with a polarizing microscope. Such ideas were inconsistent with each other.

Four investigators, Till,²⁾ Keller,³⁾ Kobayashi,⁴⁾ and Fischer⁵⁾ independently reported the growth of the lamellae or the single crystals of polyethylene in 1957. These crystals consisted of thin platelets about 100 Å thick, which was revealed by the shadow length in the electron micrograph, and the molecular arrangement should be normal to the platelets, that was deduced from the selected area diffraction patterns of the platelets, and the fact was the same as Storks' earlier suggestion in 1938.⁶⁾ These results required that molecules should be folded back and forth on themselves in the platelets. Many polymer single crystals grown from dilute solutions that have been reported have same general appearance. The recognition of the folded chain crystals not only solved above mentioned inconsistency but also presented a new model of the molecular arrangement in the solid states of polymers instead of fringed micell. The inconsistency was solved by explaining as follows; the radial fibrillar structure was the aggregation of twisting lamellae in a radial manner and the molecules in the lamellae were arranged in the tangential direction of the spherulite. During the early 1960's owing to overemphasis of folded chains in polymer crystals, the fringed micell was almost forgotten. However, not so much later, extended chain crystals were discovered under some limiting conditions and fringed extended chain crystals and

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the fringed micell have been renewed as a type of molecular arrangement in polymer crystals although the folded chain crystal is a more general form.

Up to present, extended chain crystals or fringed micellar structures have been obtained under four different conditions for several polymers; *i.e.* the extended chain crystals of polyethylene,⁷⁾ polytetrafluoroethylene,⁸⁾ and polychlorotrifluoroethylene,⁹⁾ crystallized from melt under elevated pressure, the shish-kebab back bone of stirrer-crystallized polyethylene¹⁰⁾ or polypropylene, the nascent crystals¹¹⁾ of polyethylene or polypropylene precipitated at polymerizing points by Ziegler-Natta's Catalysers, and spinning induced crystal of stiff molecules such as Kevlar fibers.

The extended chain crystal of polyethylene can be obtained from melt under elevated pressure more than 3 Kbar. The most common feature of all fracture surfaces of the extended chain crystals is that they consists of the aggregation of block-bands having striations. The striations run parallel to the molecular chain direction as deduced by comparison of the electron micrographs with the selected area diffraction patterns of the extracted replica specimen. However, the fine texture has not yet been revealed enough. In addition two different growth mechanisms of the extended chain crystal have been reported, one is the thickening of the folded chain crystals under high pressure,¹²⁾ the other one is the direct condensation of the extended molecules.¹³⁾ The main purpose of this investigation was to make clear the fine structure or texture and the nucleation mechanism of the extended chain crystal of polyethylene.

EXPERIMENTAL

A commercial polyethylene (Sholex F 6150) was used as the original material. The molecular weight determined by viscosity measurement was 64,000 ($M_w/M_n=4.12$). To prepare specimens with a cylindrical shape of 12 mm diameter and about 5 cm length, the original polyethylene was melted and subsequently crystallized under 6.4 Kbar at 240°C for 2 hours. The obtained specimens mainly consisted of extended chain crystals, con-

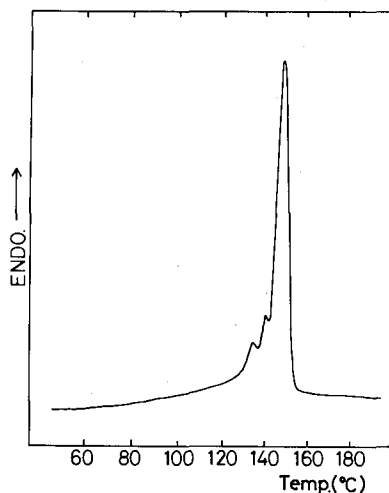


Fig. 1. An example of the DSC thermogram of the samples (extended chain crystals of polyethylene).

taining folded chain crystallites slightly. This fact was confirmed by DSC measurement for the obtained cylinders as shown in Fig. 1.

The cylinders were cut into disks having about 6 mm thickness. A uniaxial compressive deformation of about 50% was given to some of the disks at several different temperatures between 70° and 130°C. The all disks were fractured at liquid nitrogen temperature. Some of fractured disks were exposed to the hot vapour of a mixed solvents (benzene/toluene=2.1/60) which selectively dissolves the folded chain crystallites in the disks as reported in the previous paper.¹⁵⁾

To reveal or observe the fine texture of the extended chain crystal with 100 kV electron microscope, one step extraction replica method was employed for the fracture surfaces following the next procedure. Pt-carbon was shadowed on the fracture surfaces at an angle of about 45° in a vacuum of 5×10^{-6} Torr, and then carbon was evaporated uniformly on to the surfaces while those specimens supported by a gimbals with a tilt were rotating. The casted replica membranes on the fracture surfaces were removed by a current procedure using polyacrylic acid. The replica membranes were fixed on specimen grids for electron microscopy. To observe the selected area diffraction pattern or the dark field image of the extended chain crystal, the extracted crystallites were examined with very weak beam intensity. On the other hand, to take bright field image of the structure, the extracted crystallites on the replica membranes were washed away in the hot vapour of xylene before observation with the electron microscope.

RESULTS AND DISCUSSION

Irregular aggregation of block-bands was observed on the fracture surfaces of the sample disks as shown in Fig. 2. All surfaces of the bands were covered with parallel striations having periods of between 300 and 3000 Å. The surfaces of the striations corresponded to the hko planes and the direction of them were parallel to the molecular chains in polyethylene crystal. These facts were also verified in this investigation by comparison of the electron micrograph with the selected area diffraction pattern of the extended chain crystal strings as shown in Fig. 3. It was difficult to recognize from the evidence mentioned above whether the striations were produced by the artefacts on the

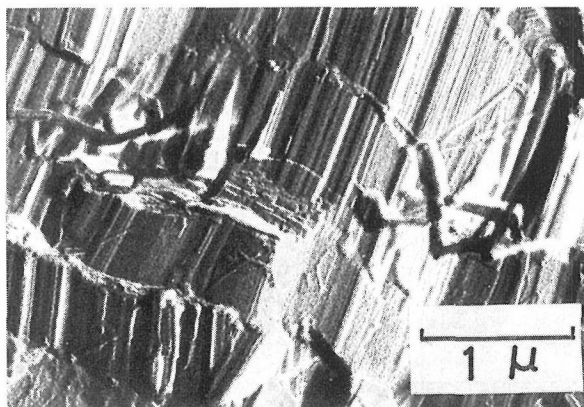


Fig. 2. The fracture surface of the sample (extended chain crystal of polyethylene).

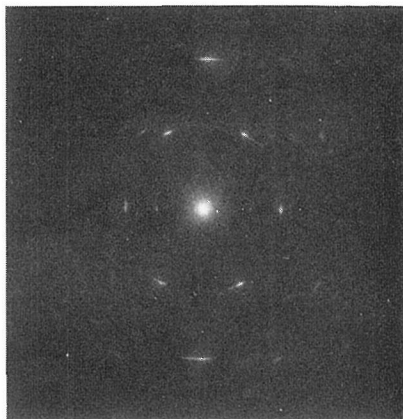


Fig. 3. The selected area diffraction pattern from the extracted crystal string.

fracture process or partly reflected the fine structure of the extended chain crystal.

The striations on the hko surfaces disappeared and a wave-like structure developed on the surfaces in the case of exposing the samples to the vapour as shown in Fig. 4. The streaks of the wave-like structure were nearly perpendicular to the chain direction in the block-bands and the period was about 200 Å which corresponded to the lamellar thickness of folded chain crystal. The vapour treated samples, which have wave-like structure observed in the electron micrographs, always showed the peak due to the melting of the folded chain crystallites in the thermograms of DSC measurement.

Generally, in the case of highly drawn crystalline polymers, the similar wave-like texture has been recognized to be due to the rearrangement of the molecules on the surfaces through an over growth or self epitaxial growth by annealing.

When the exposure time to the vapour was more than 4 hours, the wave-like structure on the hko surfaces of the block-bands disappeared completely and the parallel striations reappeared, and in DSC measurement of the samples the peak due to the melting of the folded chain crystallites was no more observed although the melting peak of the extended chain ones almost unchanged.

It can be recognized from above facts that the wave-like structure of the block-bands consisted of folded chain lamellae. The reason of formation of the folded chain lamellae would be explained as follows. By exposing samples to the vapor, only the component of folded chain crystallites dissolved selectively without effect to the extended chain crystallites as the first step; this might suggest that there was no tie molecules between the folded chain crystallites and the extended ones. And next, the dissolved molecules recrystallized as the folded chain lamellae on the hko surfaces of the extended chain crystal through the self epitaxial growth as far as the folded chain component existed.

A grain-like structure, the size of which was between 300 and 500 Å, was observed on the 001 surfaces of the extended chain blocks as shown in Fig. 4. The structure will be referred later in relation to the fine structure of the extended chain crystal.

Some rod-like crystal strings were observed between the block-bands and penetrated into adjacent bands as shown in Fig. 5. These crystal strings were considered to be the bundle of the extended chain molecules, since these were not dissolved by exposing to the vapor.

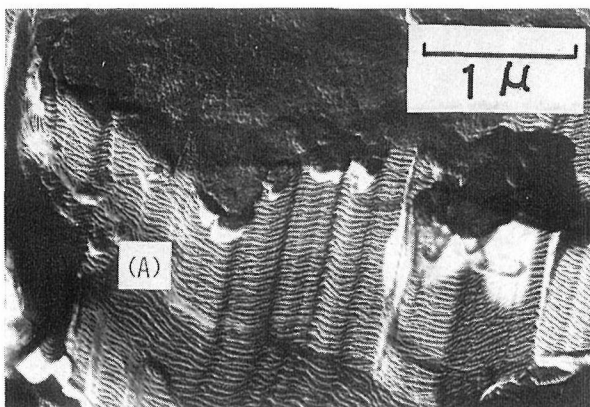


Fig. 4. The fracture surface of an exposed sample to vapor. (A): the hko surface, and (B): the 001 surface.

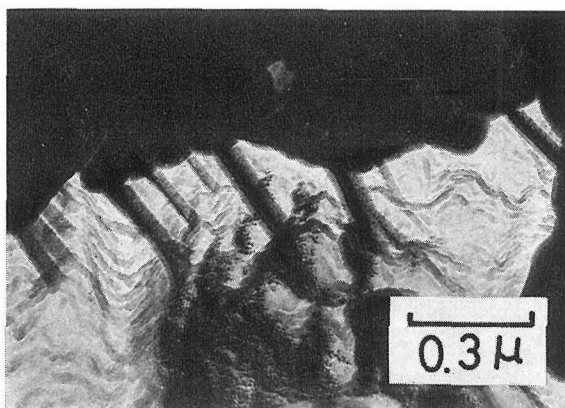


Fig. 5. The rod-like crystal strings of extended chain molecules between block-bands.

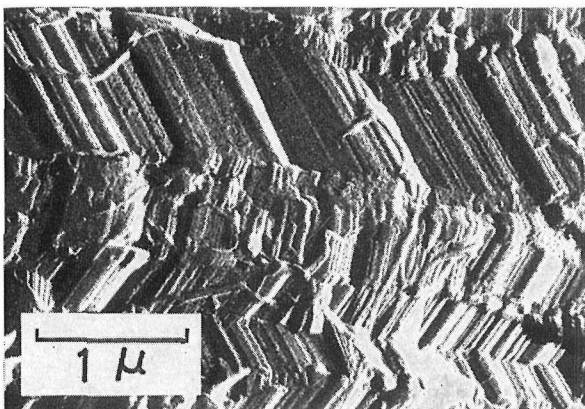


Fig. 6. The fracture surface of a uniaxial compressed sample.

The crystal strings of the extended chain bundles were observed also in the fracture surfaces of uniaxial compressed samples as shown in Fig. 6. The structure indicated that sliding between the strings or tilting of them would occur after some of the block-bands split up into crystal strings on the initial deformation process. However, the deformation

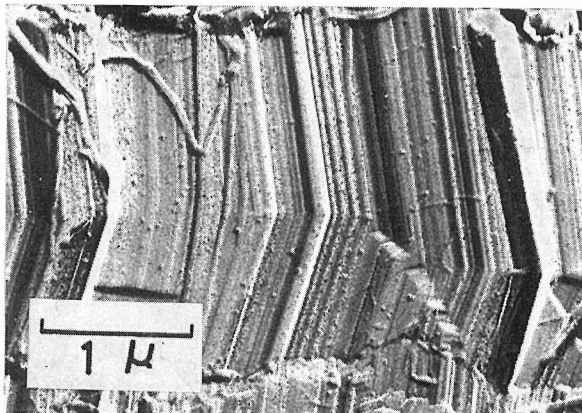


Fig. 7. An example of kink-bands in extended chain crystal.

of thick block-bands and gliding between individual extended chain molecules were hardly observed for all samples compressed at various temperature. It might be because the stress in the samples due to compression was not uniformly distributed, *i.e.* the stress was released preferentially in the weak boundaries in the texture because of no tie molecules.

The kink-bands, as shown in Fig. 7, were found in the same probability for the compressed and uncompressed samples. This also suggested that kink-bands were hardly produced in the block-bands by uniaxial compression because of unequal stress distribution in the sample.

The following conclusion can be deduced from above obtained evidence. The block-bands consisted on the bundles of extended chain crystal strings having 300–500 Å diameters. Each string consisted of extended chain molecules. The penetrating strings through adjacent bands were considered to be nuclei that were directly formed from the extended chain molecules in the isothermal crystallization process under elevated pressure.

Finally, however, the dependence of the diameter of the crystal strings on pressure and temperature in the crystallization and the arrangement of the chain ends in the long strings were not obtained in this investigation and it was necessary to develop more investigation about extended chain crystal.

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