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The Superstructure of Melt-Crystallized Polyethylene. I. Screwlike Orientation of Unit Cell in Polyethylene Spherulites with Periodic Extinction Rings

YASUNA FUJIWARA

Department of Physics, Faculty of Science, Kyoto University, Kyoto, Japan

INTRODUCTION

Investigations on spherulite structure have been carried out by many workers in connection with a fundamental problem on the association of crystalline polymer: the problem of the linking of amorphous and crystalline parts. Single crystals of polyethylene have been obtained from solution. Studies of these single crystals led to an interesting discovery: the folded configuration of the polymer chain. It is not known whether this configuration is characteristic only of single crystals or whether it is, more generally, a fundamental feature of polymer association. Also in question is the chain configuration of melt-crystallized material.

To attempt to resolve these problems, the present study of the ringed structure of spherulites was undertaken. This structure has, of course, been studied by many workers, but no definite model has been presented nor have x-ray diffraction data which explain this structure been reported. Nevertheless, diffraction is a direct and effective method; in this work, an x-ray microbeam method was used.

EXPERIMENTAL

To carry out the x-ray microdiffraction, a microcamera was set up. A lead shield with a pinhole slit of 2.5 $\mu \times 5\ \mu$ was set to the camera. In contact with this shield a sample holder with a hole about 0.7 mm. in diameter could be placed which could be slid smoothly up to the slit by use of a screw micrometer and a steel spring. Figure 1 is the front and top view of the camera. Here, P is the pinhole slit in the lead shield (0.5 mm. thick), with the pinhole opening conically toward the specimen, H is the sample holder, S is the specimen, F is the x-ray film (placed about 9 mm. from the slit), and M is the screw micrometer head which drives the sample holder up and down. The camera was built as thin and compact as possible, so that it could be fixed to the side of x-ray tube to keep away from any vibrations between the tube and camera introduced from outside. Unfiltered Cu radiation was used. The distance from the focus of the target to the pinhole slit was about 7 cm., and the apparent x-ray focusing area on the target was about 0.3 mm. (horizontal) $\times$ 0.2 mm. (vertical); therefore the beam divergence on the specimen was about 2 μ (horizontal) and 1.3 μ (vertical). Accordingly, taking into account the dimensions of the pinhole slit, a selected portion of the specimen about 7 μ (horizontal) $\times$ 4 μ (vertical) in area could be subjected to x-ray diffraction.

The material examined was low pressure polyethylene. A piece of it was placed into a split transparent mica plate, and this "sandwich" was heated above the melting point and then pressed. The thin film of polyethylene thus prepared between mica plates was again heated on the hot stage of an optical microscope and then crystallized just below the melting point. In this way large spherulites about 0.5–1 mm. in diameter showing extinction rings with intervals of about 50 μ could be obtained. Figure 2 shows one of these spherulites as it appears under the polarization microscope. As seen, it is somewhat fibrous in appearance, yet the phase relation of the extinctions of these neighboring fibers are maintained fairly well. The film, several microns in thickness, was sufficiently thick to show the birefringence effect under the polarization microscope but too thin for x-ray diffraction, and exposure times of about 8 hr. were needed to produce the two strongest x-ray reflections (110) and (200). Before setting the specimen in the holder, excess mica was split away as much as possible to reduce the x-ray absorption;

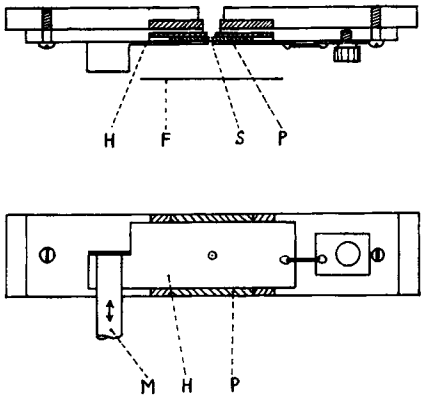

Fig. 1. Microdiffraction camera.

Fig. 2. Polyethylene spherulite with extinction ring system.

the specimen was then fixed by paste to the holder. Here the extinction ring system was set so that the direction of translational motion with the screw micrometer was at right angles to the tangent to the rings, that is, along the spherulite radius. Then the holder was set against the camera so that the long axis of the slit is parallel to the rings, i.e., the shorter axis is parallel to the spherulite radius. After setting the sample holder in position the whole camera was placed under the optical microscope. With oblique illumination from above together with the ordinary illumination from the bottom, a bright spot from the pinhole could be seen in the dark circle of the sample holder hole. The spot of light looked dim owing to diffraction of light but was sufficient to indicate the position. By moving the fine adjustment the pinhole spot was set to pass through the center of the dark circle. By use of the screw micrometer the pinhole spot could be moved back and forth along the diameter of the dark circle. By comparing enlarged photographs of specimens in the sample holder, any intermediate position along the diameter could be obtained approximately by turning the micrometer handle to the scale corresponding to that point. Thus any desired position of specimen along that diameter could approximately be set before the pinhole slit without direct aiming. After these adjustments the camera was fixed to the x-ray tube, ring system being kept horizontal. This procedure was not always sufficient for aligning the pinhole slit with a given desired position of rings, the narrower the ring intervals, the larger the error. Even in this case the periodicity of the ring system along the spherulite radius and any periodicity in the diffraction patterns could be expected to correspond to each other.

THE DIFFRACTION PATTERNS

Figure 3 shows one such diffraction pattern. The direction of the spherulite radius is indicated by the arrow. Laue spots in the photograph are those from mica. The *b*-axis orientation is apparent from the arcs. But in place of the simple fiber

Fig. 3. Unsymmetric diffraction pattern.

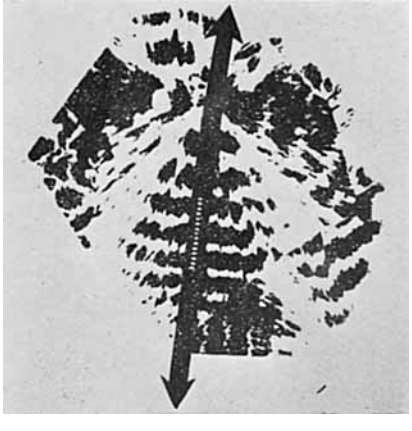

Fig. 4. Direction of microdiffraction series (negative).

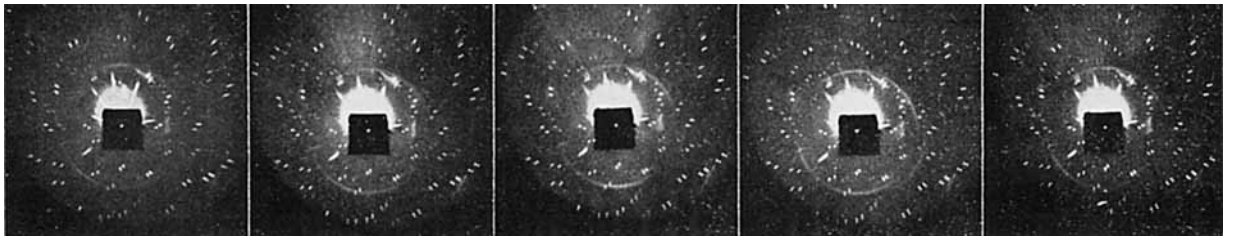

Figure 5. Figure 6. Figure 7. Figure 8. Figure 9.

pattern as reported by many workers[1-3] here a highly oriented feature is seen. That is, the (110) arc is split in two, a finding which was not observed by other workers; also, the pattern is not symmetric in the radial direction. This indicates that in this area of the spherulite the unit cells never randomly oriented around the *b*-axis but have nearly similar orientations. In the next stage a diffraction series was taken as shown in Figure 4. The direction of translation of the pinhole slit on the specimen is shown by the arrow, which is nearly at right angles to the extinction rings. Every diffraction photograph was taken at intervals of 13 μ by turning the screw micrometer. Figures 5–9 show these diffraction photographs. In Figure 5, the (110) arcs of the right side are somewhat stronger than the left, but they are joined.

In Figure 6, equal (110) reflections of both sides are approached and completely joined.

In Figure 7, the converse of Figure 5, the left (110) is stronger than the right. The left (200) reflection appears.

Figure 8 is nearly symmetrical. The (110) arcs are split, and both (200) arcs are clearly seen.

In Figure 9, the right side is stronger than left. The right (200) arc is scarcely visible. The orientation is nearly the same as in Figure 5.

These orientations can be shown most briefly by using the reciprocal space. Fig. 10a shows the reciprocal lattice points with some distributions. The x-ray beam is reflected to the direction where the reflection circle cuts the reciprocal lattice points from the center of reflection sphere. As lattice points have some distribution, the reflected beam forms an arc on the photograph. For the sake of easier visualization, a projection to the a^*-c^* plane is shown in Figure 10b. For different directions of the incident x-ray, the orientation of reflection differs, e.g., for seven angles of the incident beam, I, II, III, IV, V, VI, and VII, the intersection of the lattice points is tabulated in Figure 11. From the above demonstration, it is clear that the diffraction photographs of Figures 5–9 correspond to the directions of the incident x-ray noted at the bottom of Figure 11.

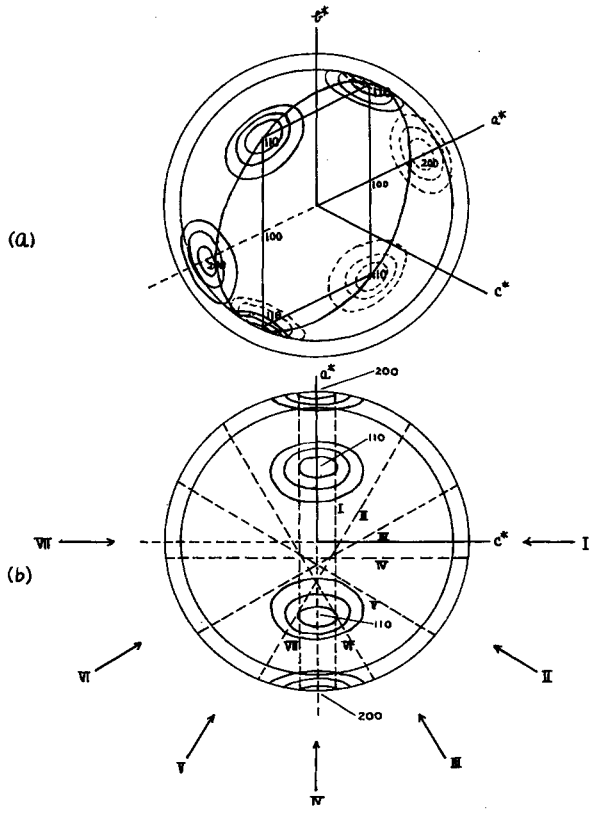

Fig. 10. Intersection of reflection sphere with reciprocal lattice points.

In other words, the unit cells are distributed in a counterclockwise helix like a screw along the spherulite radius, with the *b* axis parallel to the spherulite radius.

The orientations of Figures 5 and 9 are nearly equal. The radial translation between these photographs is 13 $\mu \times 4 = 52$ μ, and this distance corresponds to 180° rotation of the unit cell or half the pitch of the screw. The model of unit cell distribution along the spherulite radius and corresponding rotation of the index ellipsoid is illustrated in Figure 12.

		I	II	III	IV	V	VI	VII
UPPER SIDE	(200)	+	−	−	−	−	−	+
	(110)	+	+	(+)	−	(+)	+	+
LOWER SIDE	(110)	+	+	+	(+)	+	+	+
	(200)	+	+	−	−	−	+	+
DIFFRACTION PATTERN		◯	◯	◯	◯	◯	◯	◯

Fig. 11. The appearance of reflections according to Fig. 10*b*.

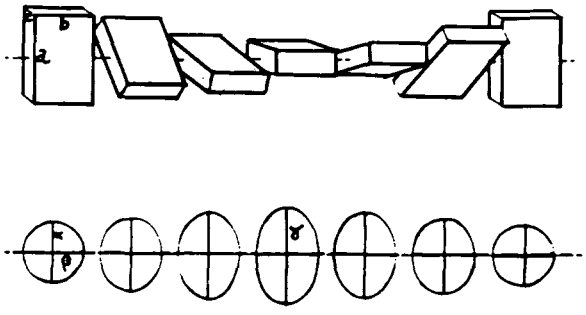

Fig. 12. Screwlike arrangement of unit cell along the spherulite radius and corresponding rotation of index ellipsoid.

Another microdiffraction series was taken with the same specimen and a larger pinhole slit (5 μ × 12 μ), the shorter dimension being parallel to the spherulite radius); the exposure time was thus reduced to 4 hr. and the translation along the radius was 9 μ, which is about two thirds of that in the preceding series. Owing to the wideness of selected area, the obtained patterns were more broad but the screwlike orientation was again observed over two periods of unit cell rotation.

DISCUSSION

According to the above x-ray evidence, the unit cells are not randomly distributed around the radial direction with only the *b* axis of the unit cell parallel to the radius, nor do there exist any fine, closely coiled helices as considered previously by Keller.[4] The neighboring unit cells have nearly similar orientations. In the area selected for study orientations of all unit cells in this range do not differ much, and, further, the unit cells gradually change their direction along spherulite radius in a screw-like way as described above. One period or pitch of such screw corresponds of course to a full rotation of the *a*- or *c*-axis, but a rotation through 180° is sufficient to return orthorhombic lattice to the identical position, and this is the apparent period of orientation which is about 50 μ in this experiment.

From the aspect of optical birefringence, the above evidence leads to a model in which the index ellipsoids, which are approximately uniaxial (γ-axis) in the case of polyethylene, gradually change their direction along spherulite radius in a way such that γ-axes, which are always perpendicular to spherulite radius, gradually rotate around the radius (Fig. 12). In positions where the γ-axes are also perpendicular to the spherulite plane, no birefringence effect is seen where light passes perpendicularly to the spherulite plane, hence these positions look dark when examined under polarization microscope. In other positions where the γ-axes are not perpendicular to the spherulite plane, some birefringence occurs, and this has the largest value where the γ-axes lie perfectly flat in the spherulite plane; hence these positions appear brightest. Accordingly, two dark positions are seen in one rotation of the index ellipsoid. Direct measurement of the interval of extinction rings by microscopy proved this interval to be about 50 μ, which is in good agreement with the value of 52 μ for the half-rotation period of unit cell obtained from the above x-ray data. The ringlike appearance of extinction fringes indicates that the unit cell orientations are maintained along a tangent to the spherulite radius. This is very marked in spherulites grown at low temperature, and the rings are so narrow and concentric that they are apt to be mistaken for interference fringes. The higher the crystallization temperature, the wider the ring intervals become; in this case irregular, fibrous features also appear, until the rings are no longer seen except as an irregular, circular aggregation of fibrils at temperatures very close to the melting point. In such a case the regular orientation along the tangent to the spherulite radius no longer exists; nevertheless, in each fibril the above-mentioned screwlike orientation of unit cells would be preserved.

The positions where the γ-axis of the index ellipsoid are perpendicular to the spherulite plane of course show an extinction effect regardless of the direction of the analyzer or polarizer of the polarization microscope. In addition, at the positions on the spherulite at which the optic axes of the index ellipsoid are parallel to the analyzer or polarizer an extinction effect appears. At these points on the spherulite radius, in the course of the screw-like rotation of the index ellipsoid, one of the optic axes lies parallel to the polarizer and perpendicular to the analyzer, and the other axis is parallel to the polarizer. This zero birefringence effect causes the appearance of a Maltese cross.

When viewed with phase contrast, rings are seen. This is naturally a result of phase difference

between light passing along the optical axis of the index ellipsoid and that passing perpendicular to it.

With an ordinary microscope, the rings are still seen, although they are very faint compared to those seen with phase contrast. This effect has been noticed and explained by Keith and Padden[5] as follows. The visibility, i.e., the contrast, of rings, is weak when the numerical aperture of the microscope condenser is large and great when the numerical aperture is small. The visibility of rings with unpolarized light is attributed to the loss of intensity due to diffraction of light out of the accepting cone of the objective by some structures in the rings, a structure which is resolvable only by objectives having a large numerical aperture. From these data, Keith and Padden concluded that these structures at each point of a ring behave as linear phase gratings. Keith and Padden present a model for the structure of ringed spherulites in which the strongly birefringent rings are composed of radial bundles of fine, crystalline fibrils, separated by narrower isotropic rings (dark between crossed nicols) of amorphous or randomly oriented crystalline polymer devoid of microscopic birefringent superstructure, and that the fibrils and the medium in which they are embedded are both transparent but have different refractive indices. Therefore the dark ring acts as a diffracting slit since it consists of a narrow strip bounded by material of different refractive index.

This concept of phase grating appears to be correct on the one hand, but does not hit the truth on the other hand. The diffracting phase grating may well correspond to fluctuations of refractive indices between 1.55 and 1.50. The former is the region where the γ-axis of the index ellipsoid is vertical (perpendicular with respect to the spherulite plane) and the latter the region where the γ-axis lies flat (parallel to the spherulite plane). This is a direct conclusion of the above x-ray evidence. Alternate arrangement of crystalline and isotropic or randomly oriented crystalline polymer, however, does not seem to be substantiated.

Claver et al.[6] examined a thin film of polyethylene under the electron microscope and found a ringlike, fine structure consisting of zones with considerable contrast. This film was prepared by solvent casting (xylene) technique and then slowly cooled through the melting range. They conclude that this ringlike fine structure cannot be due to birefringence, but is attributable primarily to fluctuations in density or mass of the material within the spherulite brought about by the crystallization mechanism and its dependence on time and temperature.

However, the appearance of rings as a result of the birefringence effect seems to be not necessarily inconsistent with the effect of fluctuations in density or mass; sometimes both effects may be superposed, especially in cases where the specimen has a free surface, as in solvent-cast film. It is possible on the basis of these data that dark rings of the type corresponding to the extinction contours usually seen on a bent single crystal, which may be explained by the above x-ray evidence, might also appear. On the other hand, if we assume that the spherulite is composed of curled, flat, single crystals, there are regions where these flat crystals may stand on end; here, the film thickness may be somewhat greater than in regions where the crystals lie flat (parallel to the plane of the films). Both of these effects are possible, but they act in opposition to each other with respect to the brightness of rings. Which effect is dominant may differ from case to case, depending on the method of preparation of specimens. It seems unnecessary to introduce the rhythmical growth mechanism.

When the spherulite is grown at higher temperature, the fibrous nature becomes marked, and, when grown at a temperature close to the melting point, the spherulite no longer shows any concentric structure but is changed into a radially symmetrical aggregate of feather-shaped units. In this stage the expression "spherulite" is not appropriate; rather the unit resembles a "hedge-hog" of crystal when viewed on the hot stage. Here, of course, the shell models proposed previously[7–9] by several authors are not applicable. Instead, the fibrous character of the spherulite must be emphasized, as Keller does.[4] He visualized the spherulites as consisting essentially of fibrous crystals, but the nature of the fibrous crystal is not yet clear. As to the morphology of these fibers, he has proposed two explanations. One is that such fibrous units can be formed through rolling up of flat sheets along the b axis, a mechanism deduced from the thickening of flat single crystals along the b axis.[10] The other is that the spherulite appears to be composed of regularly curled flat crystals, the curling of which gives rise to the periodic extinction effects.[11]

The former seems to be inconsistent with our x-ray data, as the unsymmetric diffraction pattern cannot be explained from this standpoint. The

latter second possibility, however, is in accord with our data.

Some interesting observations of Fischer[12] are also in good agreement with the second possibility. Fischer obtained electron micrographs of replica from broken surfaces of melt-crystallized polyethylene which contained spherulite with periodic extinction rings. These electron micrographs revealed that the samples consisted of lamellae reminiscent of single crystals. The lamellae changed their orientation periodically along the radius of the spherulite, the period being identical with that of the extinction rings seen under the polarizing microscope.

That these lamellae of melt-crystallized film are flat single crystals is uncertain at the present. If we assume however, that this is so, and the lamellae are twisted single crystals, the chain folding proposed by Keller about single crystals grown from xylene solution would probably occur in melt-crystallized film, as well.[10,11,13,14] Although the low-angle scattering is not so sharp as in single crystals from solution, it is certain that the folding configuration would be less regular in melt-crystallized film; however, the data do not rule out the possibility that such a folded configuration exists. In the author's recent study, the low-angle scattering from the spherulite structure shows sharp orientation of large spacings perpendicular to the spherulite radius, which is in accordance with such a folded configuration.

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Synopsis

The ringed structure in polyethylene spherulites was investigated by an x-ray microdiffraction method. A spherulite with extinction rings whose interval is about 50 μ was observed when viewed under the polarization microscope. An asymmetric x-ray diffraction fibrous pattern about the *b* axis was obtained for this specimen. This indicates that in the area of spherulite (several microns in diameter) the unit cells are never randomly oriented around a common *b* axis but have nearly similar orientations. A series of microdiffraction patterns was obtained at intervals of 13 μ (about $1/4$ the extinction fringe interval), and it was shown that the unit cells have screwlike orientations with their common *b* axis along the spherulite radius. The distance corresponding to one-half the pitch of the screw is just in accordance with the extinction ring interval.

Résumé

La structure annulaire des sphérulites de polyéthylene a été étudiée au moyen des méthodes de microdiffraction de rayons-x. Un sphérulite possédant des anneaux d'extinction séparés par un intervalle d'environ 50 μ a été observé au microscope polarisant. A l'aide de ce spécimen on a obtenu un diagramme de diffraction de rayons-x asymétrique fibreux autour de l'axe *b*. Ceci signifie que dans la surface du sphérulite (d'un diamètre de quelques microns) les cellules unitaires ne sont pas orientées au hasard autour de l'axe commun *b* mais possèdent une orientation sensiblement identique. Des séries de microdiffraction ont été prises à des intervalles de 13 μ (environ un quart de l'intervalle de franges d'extinction) et il a pu être démontré que les cellules unitaires possédent des orientations en spirale avec leur axe commun *b* suivant le rayon du sphérulite. La distance correspondant au demi pas de vis est en accord avec l'intervalle des anneaux d'extinction.

Zusammenfassung

Die ringförmige Struktur von Polyäthylensphärolithen wurde mittels Röntgen-Mikrobeugungsmethoden untersucht. Ein Sphärolith mit Extinktionsringen, deren Abstand etwa 50 μ beträgt, wurde unter dem Polarisationsmikroskop beobachtet. Mit dieser Probe wurde ein um die *b*-Achse unsymmetrisches Röntgenbeugungs-Faserdiagramm erhalten. Das bedeutet, dass im Bereiche eines Sphärolithen (einige Mikron im Durchmesser) die Elementarzellen nicht statistisch um die gemeinsame *b*-Achse orientiert sind, sondern eine weitgehend ähnliche Orientierung besitzen. Eine Reihe von Mikrobeugungsdiagrammen wurde mit Abständen von 13 μ (etwa $1/4$ des Abstandes der Extinktionsfransen) aufgenommen und es wurde gezeigt, dass die Elementarzellen eine schraubenartige Orientierung, mit ihrer gemeinsamen *b*-Achse längs des Sphärolithradius, besitzen. Der Abstand, der einer halben Ganghöhe der Schraube entspricht, stimmt gerade mit dem Abstand der Extinktionsringe überein.

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