

The Optical Behavior of Polyethylene Spherulites

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Polyethylene was crystallized from the molten film under temperature gradient. As a result, the optically positive spherulites were observed, though only the negative spherulites had been observed previously in polyethylene. When the radial structure units twisted regularly in a spherulite are formed parallel to the surface of the film, the spherulite is usually optically negative in polyethylene. In this study, the temperature gradient normal to the surface of the film gives so significant tilt of the radial structure units formed to the surface of the film that the radial refractive index becomes larger than the tangential one under the transmitted polarized light and the spherulites have optically positive behavior. The optical behaviors of the polyethylene spherulites and the crystallizing condition were studied and discussed.

§ 1. Introduction

The topography of polymer spherulites can best be observed by crystallizing the polymer as a film with an unrestrained surface, facilitating their observation in the optical microscope. These two dimensional spherulites are usually assumed to have the same structure as diametral sections of three dimensional spherulites. Though this is not always correct in detail, much structural information and relation of structure to crystallization condition can be generally deduced from the two dimensional spherulites.

Polymer spherulites, as spherulites of low molecular material, have radiating fibrous (or lamellar) structure, and the radial structural units often twist regularly to form a helical type structure. In the spherulite, polymer molecules are, on the average, tangentially oriented. Between crossed polaroids most polymer spherulites display a Maltese cross whose arms are parallel to the direction of the polarizer and analyzer, and optically two distinct types, positive and negative, are assumed basing on the magnitude of the birefringence. We shall be concerned mainly with the optically negative or positive behavior of polyethylene spherulites.

The tangential refractive index has larger value than the radial one in the negative

spherulites. It is this negative type spherulites that there has been often observed in polyethylene. We found the positive type spherulites of polyethylene by crystallizing the molten film under temperature gradient. The optical behaviors and the crystallizing condition were studied and discussed.

§ 2. Experiment

Polyethylene used in this study is Marlex 50. A pellet of Marlex 50 is cut thinly, molten and then pressed to form the thin circular film with about 0.2 mm thickness and 3~5 mm diameter. The film prepared above is held between the slide glasses and is moved at the speed of 1 mm/min. by a synchronous motor, in the temperature gradient glass tube as shown in Figure 1. The diameter of the glass

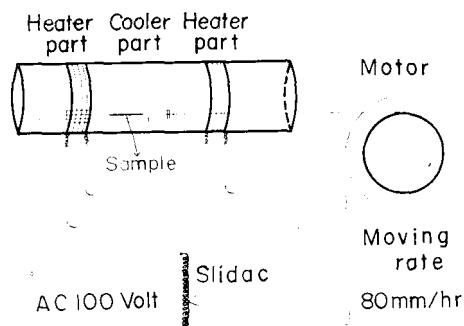


Fig. 1 Apparatus for crystallization.

tube is 16 mm and the length of heating part and cooling part are 10 mm and 50 mm, respectively.

Molten sample at the heating part (about 180°C) crystallizes gradually as it moves into the cooling part. Thus, the crystallized specimen were observed under optical microscope between the crossed polaroids with gypsum plate. The sign of the birefringence was determined by the use of a gypsum plate. Basing on the arrangement of the refractive index ellipsoids representing an average array of individual crystallite in the spherulite, the color appeared by insertion of the gypsum plate is illustrated as shown in Figure 2. The blue and

yellow observed in quadrant 2 and 4 indicate the negative and positive spherulites, respectively.

In order to examine the effect of oxygen in air,^{1,2)} some sample films exposed previously in air at higher temperature (240°C) over the melting temperature were used.

§ 3. Results

The microscopic observations of polyethylene spherulites crystallized under the condition described above are shown in the following figures. Moving rate of the molten film is 80 mm/hr along the horizontal temperature gradient. Beside the horizontal temperature gradient, it is considered that there is the temperature gradient normal to the surface of film, since the space of cooling part is relatively large.

In general, both the negative and the positive spherulites were observed under the microscope as shown in Figure 3. In the main part near the center of the circular film crystallized, there were observed the negative spherulites. In the part near the film edge, the positive spherulites were observed. In Figure 3, upper half part corresponds to the former and the lower half part corresponds to the latter.

At the boundary regions between the neighboring positive spherulites (they are indicated

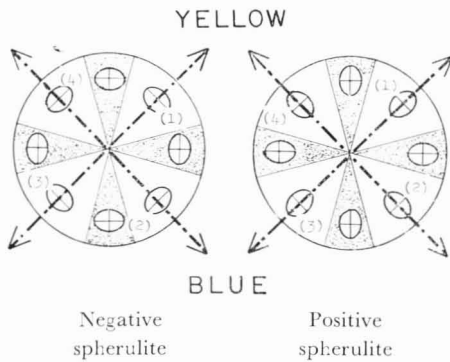


Fig. 2 Schematic patterns of two different types of spherulite between the crossed polaroids with gypsum plate.



Fig. 3 Micrograph of polyethylene spherulites between crossed polaroids. ($\times 400$)

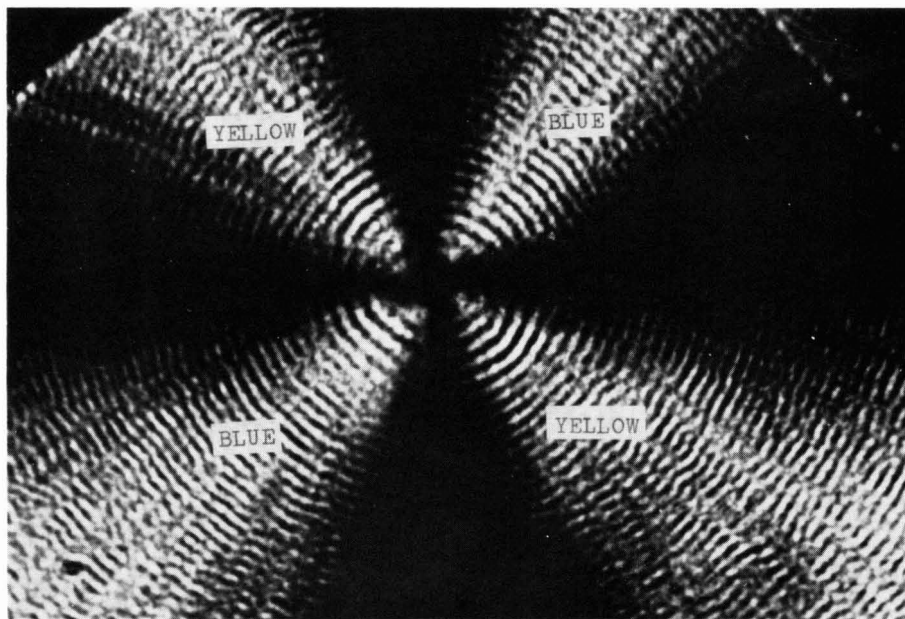


Fig. 4 Positive spherulite of polyethylene observed between crossed polaroids with gypsum plate. ($\times 800$)

by two arrows in the figure.) the optically extraordinary behavior due to the optical interference is observed. This is the characteristic behavior of the positive spherulites. There are also the undistinguishable spherulites in the intermediate part of the figure.

Figure 4 is a typical type of the positive spherulite. Figure 4 shows the monochromatic optical micrograph of a spherulite which we call as positive spherulite. The letters, yellow and blue, in Figure 4 represent the corresponding colors in the real photograph, respectively. Even if the stage is rotated with the sample, the position of the colored part is not changed. However, observation in detail indicates the following points.

- (1) Small part of the center of the spherulite is optically negative.
- (2) Yellow bands weekly appear parallel to the extinction rings in the blue section and also blue bands weekly appear in the yellow section in Figure 4. This suggests the existence of the optically negative bands which depend on the larger twist angle of the radial structure unit as discussed later.

These positive spherulites are usually observed near the edge of the film. In this part of the film, however, the sections grown inward are optically negative in the same spherulites. This is shown by the signs of plus and minus in Figure 5.

The optically positive spherulites are assumed to form under the temperature gradient normal to the surface of the film as discussed later. Negative spherulites are also sometimes observed near the film edge. The effect of the horizontal temperature gradient of the growth of these spherulites was observed. The radial structure units (fibrils) draw the curved lines to the direction of horizontal temperature gradient as shown by arrow in Figure 6.

We chose 80 mm/hr. as a moving rate of the sample from the heating part to the cooling part. The speed is significantly high compared with the radial growth rate⁷⁾ of polyethylene spherulites. In order to make a large temperature gradient normal to the surface of the sample film in our crystallizing apparatus, it is desirable, we think, to choose a relatively large moving rate.

§ 4. Discussion

We shall discuss principally on the problem of the optically negative or positive. The positive spherulites have such optical property that radial refractive index is larger than tangential one in the spherulites. On the contrary, in the negative spherulites, the tangential refractive index is larger than radial one. Only the negative spherulites have been observed previously in polyethylene. The optically positive spherulites observed were shown

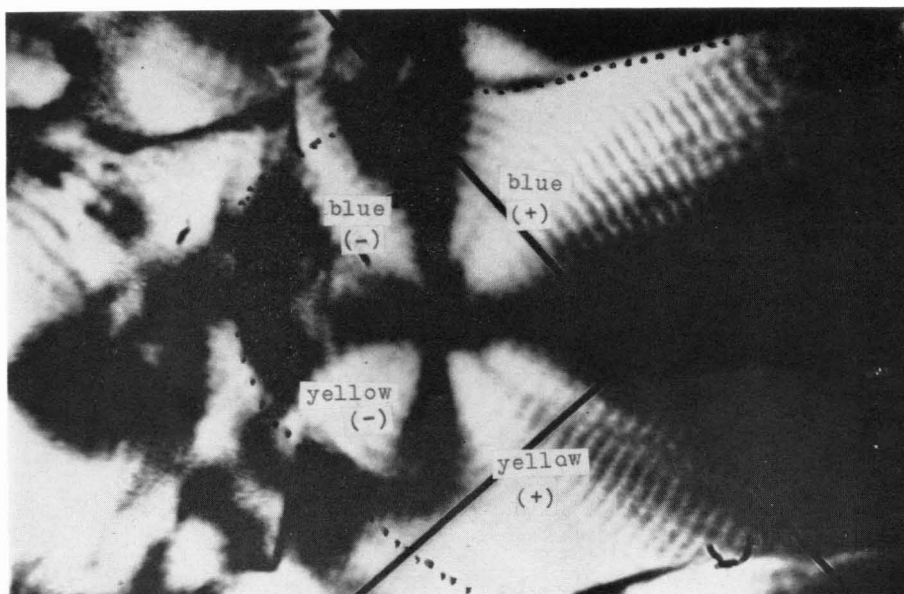


Fig. 5 Peculiar spherulite grown near the edge of the sample film.

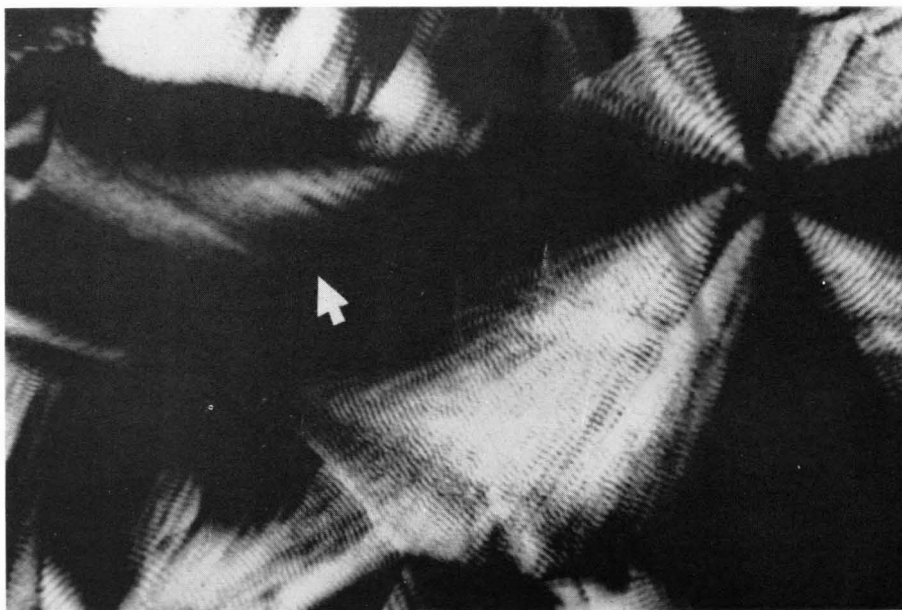


Fig. 6 Negative spherulite of polyethylene.

here.

When the radial structure units twisted regularly³⁾ in a spherulite are formed parallel or nearly parallel to the surface of the film, the spherulite displays optically negative property in polyethylene because of tangential orientation of molecular chain. Therefore, in order to display the optically positive property, it is necessary that the polymer chains tilt to the axis of microscope along the radial direc-

tion of the spherulite. It is considered the following two cases. One is the inclination of the radial structure unit composed of lamellae to the film surface, which molecular chains orient normal to the lamellar surface. The other is the inclination of the molecular chain to the normal direction of the lamellar surface along the radial direction, and the lamellar surface orients parallel to the film surface.

Keith and Padden showed³⁾ that polyethy-

lene spherulites nucleation usually occurred on the surface of the film in contact with the substrate and subsequent radial growth occurred at a constant angle ($3\sim 10^\circ$) with this surface.

They showed also that larger values ($10\sim 15^\circ$) of this angle were found in spherulites grown at the edge of the film, where the vertical component of the temperature gradient was probably greatest because of a thin air gap.

Here, we shall consider our positive spherulites of polyethylene, and we shall also assume the greater temperature gradient normal to the film surface in our experiment. Thus, the inclination angle of the fibril to the film surface may be at least more than 35° . When the two dimensional negative spherulites are tilted at the angle of more than 35° by using universal stage,⁴ the optically positive pattern along the direction tilted can be observed. Nucleations occur predominantly on the surface and subsequent growth is directed downward gradually to have considerable inclination with large angle under the influence of local temperature gradient. This is associated with the facts that there is the optically negative behavior at the center of the positive spherulites as shown in Figure 4 and that there exist both positive and negative sections in the same spherulite as shown in Figure 5. Figures 7 and 8 indicate the vertical sections of the spherulites corresponding to Figures 4 and 5, respectively.

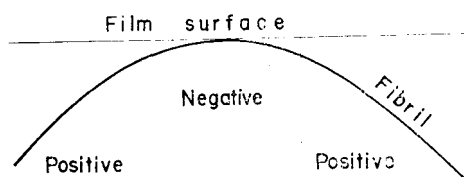


Fig. 7 Diagram of the positive spherulite in vertical section.

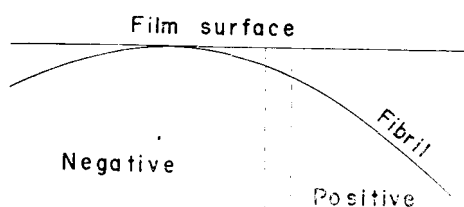


Fig. 8 Diagram of the spherulite shown in Figure 5 in vertical section.

On the other hand, molecular chains orient nearly perpendicular to the radial direction generally in polyethylene, according to the x-ray diffraction study. However, from the theoretical point of view, Price took account for the inclination of the molecular chains to the radial direction for estimation of the optical properties.⁵⁾

Now, we shall explain theoretically the optical behaviors of polyethylene spherulites concerning with the positive spherulites observed here. We shall take as our model an idealized two dimensional spherulite in which along a given spherulite radius the crystalline fibrils composed of lamellae are arranged, and the fibrils twist uniformly about the radial direction. The lamellae constructing a fibril are essentially the same as in a single crystal. The variation of the crystallographic orientation along the radius in a spherulite can be represented as the rotation of the refractive index ellipsoid along the radial direction. Our calculation was carried out by conventional algebraic solid geometry, while Keith¹⁾ and Price⁵⁾ used matrix method.

At first, it is assumed that polymer chains orient normal to the lamellar surface. The birefringence in the spherulite depends on the tilting of the axes of the refractive index ellipsoids to the axis of a polarizing microscope. The tilting of the axes of the ellipsoids is prescribed by the two quantities, namely, the twist angle δ of lamella about the radial direction, and tilting angle θ of the spherulite radius to the horizontal plane, the surface of the sample film. It corresponds the twice transformations of the coordinates system that the major axis of the ellipsoid is tilted by θ to the Z coordinate (the axis of microscope), and subsequently tilted by δ about the radial direction as it is.

As a result, the vertical section of the ellipsoid to the axis of microscope is represented by the equation;

$$\frac{x^2 \cos^2 \theta + \{y \cos \delta - x \sin \theta \sin \delta\}^2}{a^2} + \frac{\{x \sin \theta \cos \delta + y \sin \delta\}^2}{c^2} = 1 \quad (1)$$

where a and c represent the minor axis and the major axis of the refractive index ellipsoid, respectively. The X coordinate was chosen along a radial direction of spherulite projected

to the horizontal plane, and the Y coordinate is normal to it.

Substituted that $y=0$ and $\delta=0$ in equation (1), it yields,

$$x = \frac{ac}{(a^2 \sin^2 \theta + c^2 \cos^2 \theta)^{1/2}} \quad (2)$$

When $a = 1.512$ and $c = 1.556$ obtained by Bunn⁶⁾ are substituted in Equation (2), we obtained 1.53 as the value of x for $\theta = 35^\circ$ $\delta = 0$. This value of x nearly equals to the mean value between a and c . This value of x or θ is assumed to be a turning point of either the optically positive or the negative, because maximum refractive index along spherulite radius should be considered when $\delta=0$. However, we must estimate the following quantity as a measure of both the magnitude and the sign of the spherulite birefringence of the system at any point along the radius of the spherulite;

$$R^2 = \frac{\eta_t^2}{\eta_r^2} = \frac{c^2 \cos^2 \theta + (c^2 \sin^2 \delta + a^2 \cos^2 \delta) \sin^2 \theta}{a^2 \sin^2 \delta + c^2 \cos^2 \delta} \quad (3)$$

where η_r and η_t represent the radial and tan-

$$R^2 = \frac{c^2 (\cos \theta \cos \varphi - \sin \theta \cos \delta \sin \varphi)^2 + c^2 \sin^2 \theta \sin^2 \delta + a^2 (\sin \theta \cos \varphi \cos \delta + \sin \varphi \cos \theta)^2}{c^2 \cos^2 \delta + c^2 \sin^2 \delta \sin^2 \varphi + a^2 \sin^2 \delta \cos^2 \varphi} \quad (4)$$

where φ represents the tilting angle to the normal direction of the spherulite radius along the radial direction. The result of numerical calculation for R as functions of θ , δ , and φ indicates qualitatively similar to that from Equation (3). Positive birefringence is, however, enhanced for larger values of φ . The appearances of both positive and negative birefringences are inevitable depending on the value of δ . This is the same result as that from the numerical calculation of Equation (3). From this, a uniformly positive birefringence is unable to expect. One of the reasons for optically complex behavior of the positive spherulites we call so seems to be suggested from Equations (3) and (4).

gential refractive indexes are calculated by substituting $y=0$ and $x=0$ in Equation (1), respectively.

Hence, if R is greater than unity, the system is negatively birefringent. If R is less than unity, the system is positively birefringent. If R is unity, the system has zero spherulite birefringence. When $\delta=0$ in Equation (3), it results Equation (2) and the values of R are less than unity for all values of θ as mentioned above. However, R as a function of δ have the value more than unity for larger values of δ . The values of R depend significantly upon the twist angle, δ , and Equation (3) represents the appearances of positive and negative birefringences alternatively for smaller and larger values. This seems to be reflected in the observation of optically negative bands in the optically positive section of spherulite.

Next, we shall consider in the case of oblique orientation of polymer chains to spherulite radius along the radial direction. Similar calculation by the transformation of coordinates system differed a little from the method used above produces the equation for R^2 ;

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