

Crystallization temperature dependence of interference color and morphology in poly(trimethylene terephthalate) spherulite

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Abstract

The relationship between retardation and morphology in highly birefringent poly(trimethylene terephthalate) spherulites was studied from the viewpoint of crystallization temperature dependence. Both the retardation and the morphology relate with the degree of orientation of the molecular chains. Therefore, the degree of orientation of the crystal lamellae was estimated by image processing of transmission electron microscope (TEM) images of the spherulite. It was found that the degree of orientation changed remarkably between the non-banded and the banded morphology and the temperature dependence of the degree of orientation correlated with that of the retardation. Based on the image-processed TEM images, it was recognized that the crystal lamellae formed bundles in the banded spherulite, while few bundled lamellae were observed in the non-banded ones. It is suggested that the formation of bundled lamellae played the significant role for both the magnitude of retardation and determination of the morphology; i.e. whether to form banded spherulites or non-banded ones.

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1. Introduction

Poly(trimethylene terephthalate) (PTT) is an aromatic semicrystalline polyester which has a repeating unit of three methylene groups in the backbone. Until recently, there were only several reports about PTT based on academic interest, since one of the starting materials for the synthesis of PTT, 1,3-propanediol, was very expensive and it was difficult to produce it in large quantity. However, the development of mass-production methods of 1,3-propanediol in the mid-1990s created increasing commercial interest in PTT in the past several years. In particular, a number of researches on PTT fiber have been performed due to its excellent elastic deformation recovery [1] compared to the two similar aromatic polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). In addition, the crystallization behavior of PTT has also been investigated recently. For PTT spherulites, analyses of crystallization behavior [2–5] and crystal structure by using wide angle X-ray diffraction (WAXD) and electron diffraction (ED) [6–8], and morphology observation under polarized light

microscopy (PLM), atomic force microscopy (AFM), and electron microscopy [4,6,7,9,10] have been reported. Among them, PTT banded spherulites have been extensively studied, which are formed under a specific crystallization condition. Moreover, PTT spherulites show a vivid interference color without a sensitive tint plate under PLM and various interference colors such as blue, magenta and green are observed in films from 10 to 20 μm thick depending on the crystallization temperature [11].

Interference color is attributed to the retardation that is expressed by (birefringence, Δn) \times (thickness of the sample, d) and the relationship between interference color and retardation is described in an interference color chart such as the Michel–Levy chart. According to the chart, black and white is observed below approximately 300 nm of retardation, and yellow color appears at 300 nm and various interference colors are observed with increasing retardation value. Therefore, the fact that vivid interference colors are seen in PTT spherulites means high birefringence of PTT spherulites, while black and white color is observed in spherulite of many other polymers. Although, to our knowledge, there are few reports on birefringence of PTT spherulites [11], there are some reports on the birefringence in PTT fiber. It was reported that the birefringence of the fiber was smaller than that in PET and PBT fiber, even if the PTT fiber was highly oriented [12,13]. Moreover, the intrinsic birefringence of PTT fiber was also much smaller than those of PET

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and PBT [14]. The small birefringence in PTT fiber does not agree with high birefringence of PTT spherulite. When the orientation direction of PTT molecular chains in the spherulite is compared to that in the fiber, it was reported that the growth direction of crystal lamellae in PTT spherulites was the *a*-axis direction of unit cell while PTT fibers have the *c*-axis orientation [6,7]. In our calculation of intrinsic birefringence for each axial orientation of PTT unit cell, it was clarified that the intrinsic birefringence for *a*-axis orientation was much larger than that for *c*-axis orientation. Therefore, *a*-axis orientation of crystal lamellae in the PTT spherulite is one of the principal factors for the vivid interference colors under PLM in PTT spherulite [15].

In the present work, the relation between interference color and morphology in PTT spherulite was investigated from the viewpoint of the crystallization temperature dependence. Additionally, the factors for the change of retardation with crystallization temperature were also discussed.

2. Experimental section

PTT was supplied by Asahi Kasei Chemicals Corporation. The intrinsic viscosity of the PTT measured in a phenol/tetrachloroethane (60/40) mixed solution at 25 °C was $[\eta]=$

1.06 ml/g. The PTT sample was first dried at 80 °C for 6 h under vacuum before sample preparation. The isothermally crystallized PTT thin film for PLM observation was prepared by the following process. A thin film specimen of thickness of about 10 μm was prepared by pressing a PTT fragment between two cover glasses at 280 °C. After the specimen was melted at 280 °C for 3 min, it was rapidly transferred onto a hot stage with the desired crystallization temperature from 140 to 210 °C and crystallized until the truncation of spherulite growth by impingement occurred. After crystallization, the sample was quenched at room temperature. The morphology of the spherulite was observed under PLM (Olympus BH2-BHSP). For the small-angle X-ray scattering (SAXS) measurement, the bulk PTT sample was prepared by the same condition as that for PLM observation and then the long period of PTT lamellae was determined. Density of the isothermally crystallized PTT was determined by using a density gradient column filled with *n*-heptane/carbon tetrachloride mixture at 25 °C. WAXD data for the samples were obtained by using a Rigaku D/max diffractometer with graphite-monochromatized Cu K_α radiation at 40 kV and 40 mA with a scanning rate of 1°/min. For transmission electron microscopy (TEM) analysis, ultra-thin sections of the PTT spherulite were microtomed at −40 °C and stained with ruthenium tetroxide (RuO₄) in the

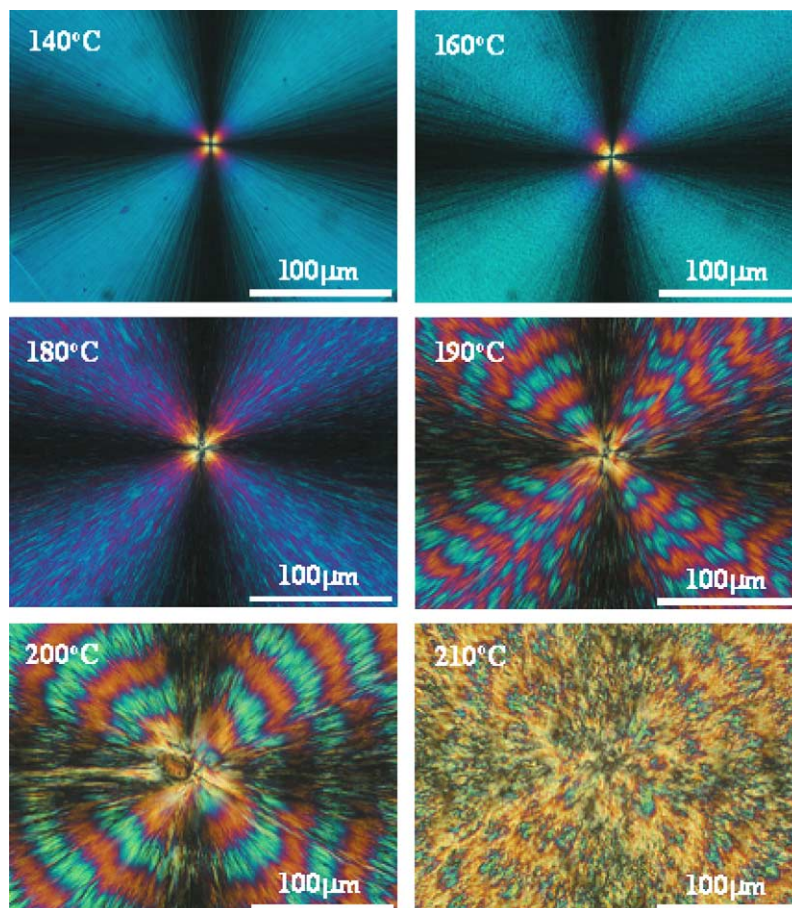


Fig. 1. PLM micrographs of PTT spherulite isothermally crystallized at each temperature (without a tint plate).

gas phase. The lamellar morphology was observed under TEM with an acceleration voltage of 100 kV (JEM-100CX, JEOL Ltd).

3. Results and discussion

3.1. Crystallization temperature dependence of morphology of PTT spherulite

Fig. 1 shows a series of PLM micrographs for PTT spherulite crystallized at various isothermal melt-crystallization temperatures from 140 to 210 °C. Vivid interference colors, such as yellow, blue, magenta, and green were observed in all of the PTT spherulites under PLM without a sensitive tint plate. Non-banded spherulites were observed for the temperature range from 140 to 180 °C, while banded spherulites were formed above 190 °C. Moreover, periodically arranged concentric rings within the banded spherulite were gradually disturbed above 200 °C. When the micrographs were observed in detail, a mottling pattern appeared above 160 °C of crystallization temperature, and the pattern became rougher with increasing isothermal crystallization temperature; finally, the periodic banded pattern was formed around 190 °C. That is, the morphology of PTT spherulites continuously changed from non-banded to banded spherulites. The reason why such a detailed morphological change could be observed under PLM was that the value of retardation was above 600 nm because of the high birefringence of PTT spherulites, while such a detailed morphological observation may be difficult for the other polymer spherulites with low retardation.

3.2. Crystallization temperature dependence of retardation

In order to compare the retardation value of the spherulites crystallized at each temperature, the thickness of samples should be exactly controlled and measured. In particular, when there is an error in measuring the thickness of a highly birefringent sample, even a low error in thickness will bring about a large error in the retardation value. However, PTT can form large spherulites with diameter from several hundreds micrometers to a few millimeters easily, and the crystallization rate is not so fast in the high temperature range. By using these features, the sample was isothermally crystallized by step sequencing of the temperature at 200, 190, 180, and 140 °C in one spherulite. Consequently, the thickness of the whole regions isothermally crystallized at different temperature in one spherulite could be regarded as the same value. Fig. 2 shows the retardation values measured by a Berek compensator at some points located in the radial direction from the center of the spherulite. The abscissa axis of the plot indicates the distance from the center of the spherulite; the ordinate axis indicates the retardation value $\Delta n d$. A part of the micrograph of step crystallized PTT spherulite is also shown at the upper part of the plot. At 200 and 190 °C, the retardation value took both higher and lower values periodically because a banded spherulite was formed and the retardation differed in each band region. The retardation varied from 1650 to 1035 nm at

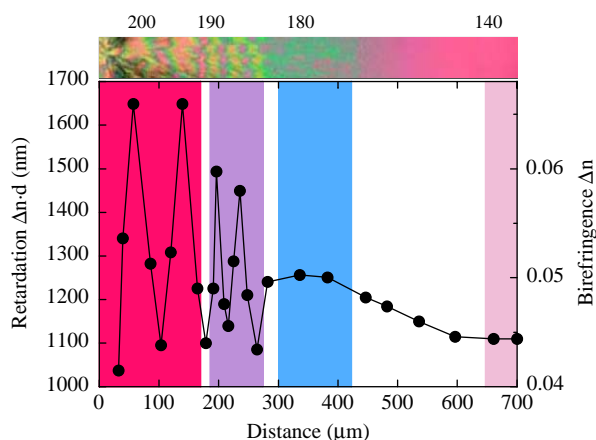


Fig. 2. Retardation at each position in one PTT spherulite isothermally crystallized by step sequence of temperature at 200, 190, 180, 140 °C.

200 °C, while the change of retardation at 190 °C became smaller than that at 200 °C, having a value from 1490 to 1085 nm at 190 °C. Moreover, below 190 °C, banded spherulites were not formed, the retardation took a smaller value than the average value at 190 °C, and the retardation became lower as the crystallization temperature decreased.

There are some factors that affect the crystallization temperature dependence of the retardation. If the retardation of a spherulite, R , was mainly derived from the crystals in the spherulite, the retardation can be expressed under the condition that the crystal lamellae orientation direction is approximately uniform in the direction of sample thickness as follows

$$R = f\phi_c\Delta n_{\text{Imax}}(r)d, \quad (1)$$

where f is the degree of orientation of the molecular chain in the PTT crystal with respect to the radial direction of a spherulite at each position, ϕ_c is the degree of crystallinity, $\Delta n_{\text{Imax}}(r)$ is the local maximum birefringence depending on the position, r is distance from the center of spherulite and d is the thickness of the sample.

The value of $\Delta n_{\text{Imax}}(r)$ depends on the position due to the coherent twisting of crystal lamellae for banded spherulites,

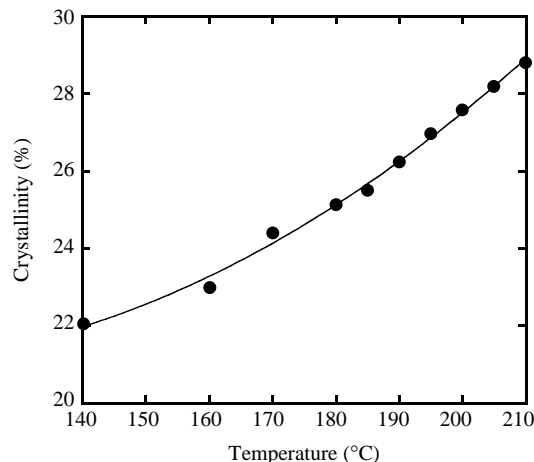


Fig. 3. Crystallization temperature dependence of degree of crystallinity in PTT spherulite.

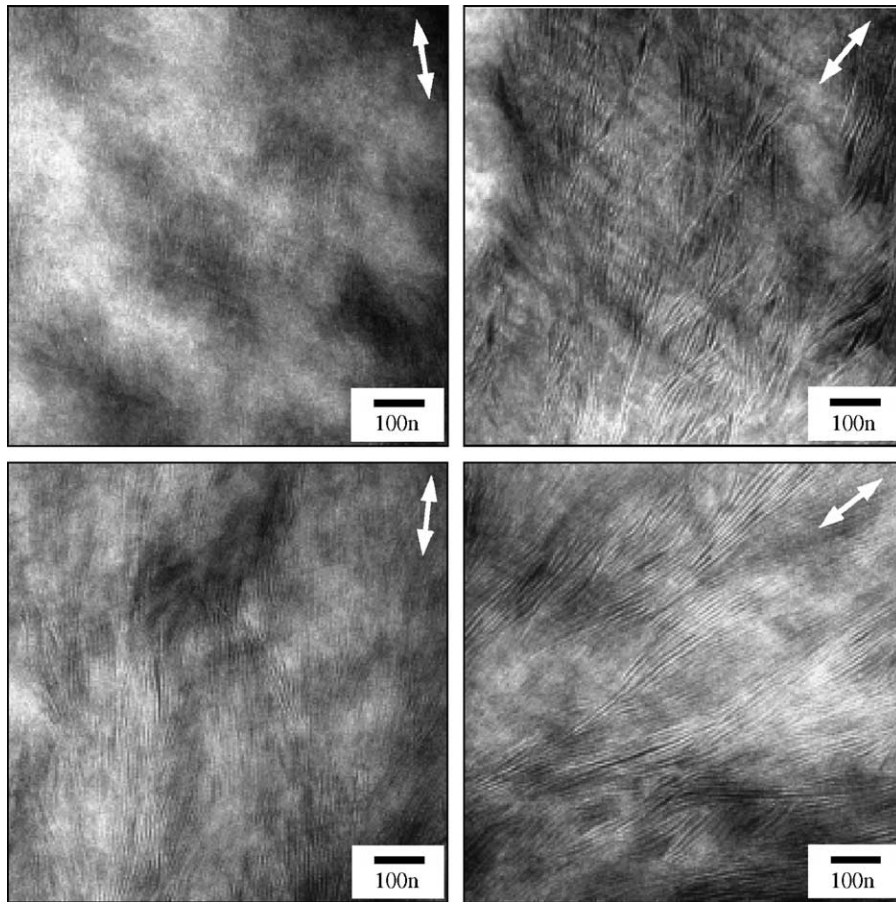


Fig. 4. TEM images in PTT spherulites crystallized at (a) 140 °C, (b) 180 °C, (c) 190 °C, and (d) 200 °C. Radial direction of the spherulite is indicated by a white arrow.

while it is independent of the position in a spherulite for non-banded spherulites. However, the space mean value of $\Delta n_{lmax}(r)$ in a spherulite must take a constant value irrespective of existence or non-existence of a banded pattern in the whole temperature region examined in this study; since the crystal lamellae twist in banded spherulites then the mean value of $\Delta n_{lmax}(r)$ in banded spherulites should be same value as that in non-banded ones.

From the equation, it can be thought that degree of crystallinity and degree of orientation are the principal factors for the determination of the retardation. Thus, the relation between the retardation and these factors will be discussed in the following sections.

3.3. Temperature dependence of degree of crystallinity

Degree of crystallinity of PTT films crystallized at the various temperatures was estimated by the density gradient method. The weight fraction crystallinity ϕ_c from density can be expressed by density of a sample ρ , crystal ρ_c , and amorphous ρ_a as follows

$$\phi_c = \frac{\rho_c}{\rho} \frac{\rho - \rho_a}{\rho_c - \rho_a}, \quad (2)$$

with $\rho_c = 1.432 \text{ g/cm}^3$, $\rho_a = 1.295 \text{ g/cm}^3$ [16,17]. Fig. 3 shows the degree of crystallinity of PTT films isothermally crystallized at various temperatures. The degree of crystallization monotonically increased with the crystallization temperature. The result agrees with the tendency of the retardation below 180 °C, shown in Fig. 2, the retardation becoming higher with increasing crystallization temperature. Above 190 °C, banded spherulites are observed; usually it is considered that the banded pattern originates in crystal lamellar twisting. Consequently, the direction of the unit cell should vary in the region where the retardation changed significantly, and then the birefringence varies in this region. Thus, the mean value of the retardation in the banded spherulite was estimated and they were about 1290 nm at 190 °C and 1340 nm at 200 °C. The average values of retardation between 190 and 200 °C also increased with increasing of crystallization temperature.

3.4. Estimation of degree of orientation of crystal lamellae in a spherulite by image processing of TEM image

It was considered that PTT crystal lamellae grow approximately in the radial direction from the center of a spherulite. However, the orientation of molecular chains in a spherulite cannot be measured by usual methods, such as

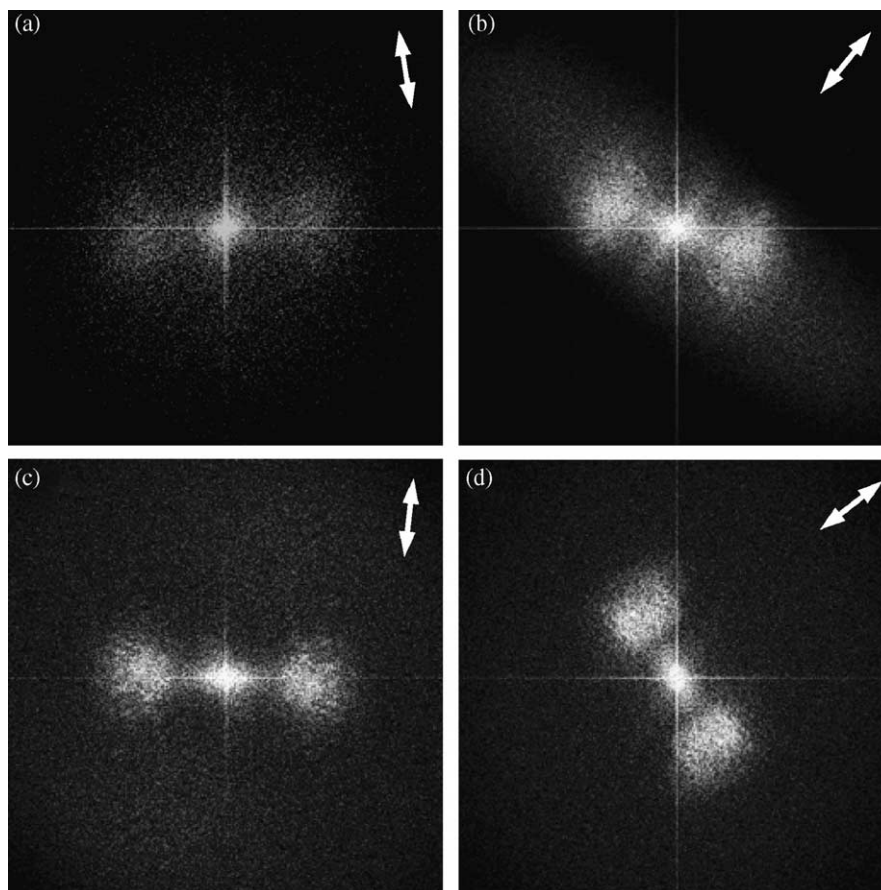


Fig. 5. Two-dimensional Fourier transformed images of TEM images of (a) 140 °C, (b) 180 °C, (c) 190 °C, and (d) 200 °C. Radial direction of the spherulite is indicated by a white arrow in each image.

normal WAXD and Fourier transform infrared spectroscopy, due to the small size of a spherulite compared to the beam diameter of X-ray or infrared, respectively. Accordingly, a suitable method should be adopted to study the degree of orientation of molecular chains in a local area of spherulite, such as microbeam X-ray diffraction with synchrotron radiation. In this study, the degree of orientation was estimated from a TEM image of each sample; however, this only permitted determination of the degree of orientation of the crystal lamellae instead of molecular chain orientation but the degree of orientation of lamellae correlates with that of molecular chains. In a banded spherulite, it is considered that the crystal lamellae twist around the radial direction of a spherulite. However, only edge-on crystal lamellae were observed, while flat-on lamellae were not. Thus, if it is assumed that both the edge-on and the flat-on lamellae appear at the same frequency in the radial direction, the degree of orientation of lamellae is same as that of edge-on lamellae.

For the TEM observation, the spherulites were prepared under similar conditions as those used for PLM observation and ultrathin sections were microtomed from the surface of the film after staining by RuO_4 . Fig. 4 shows TEM images of the PTT spherulite crystallized at each crystallization temperature. Bright areas in the images correspond to PTT crystal lamellae parallel to the surface; dark lines correspond to the inter-lamellar regions. It seems that the lamellar orientation varies

with crystallization temperature. A two-dimensional Fourier transform (two-dimensional FT) was carried out for each image, as shown in Fig. 5, in order to extract the features of these images and examine them in detail. The spots in Fig. 5 originate from the periodic structure of the PTT crystal

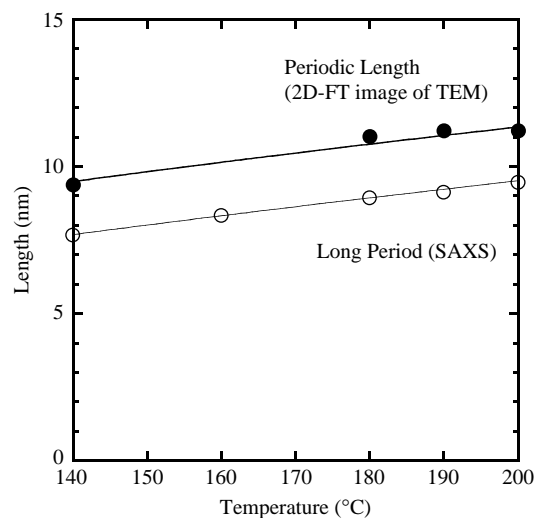


Fig. 6. Crystallization temperature dependence of both (●) periodic length estimated from two-dimensional Fourier transformed image, and (○) long period measured by SAXS.

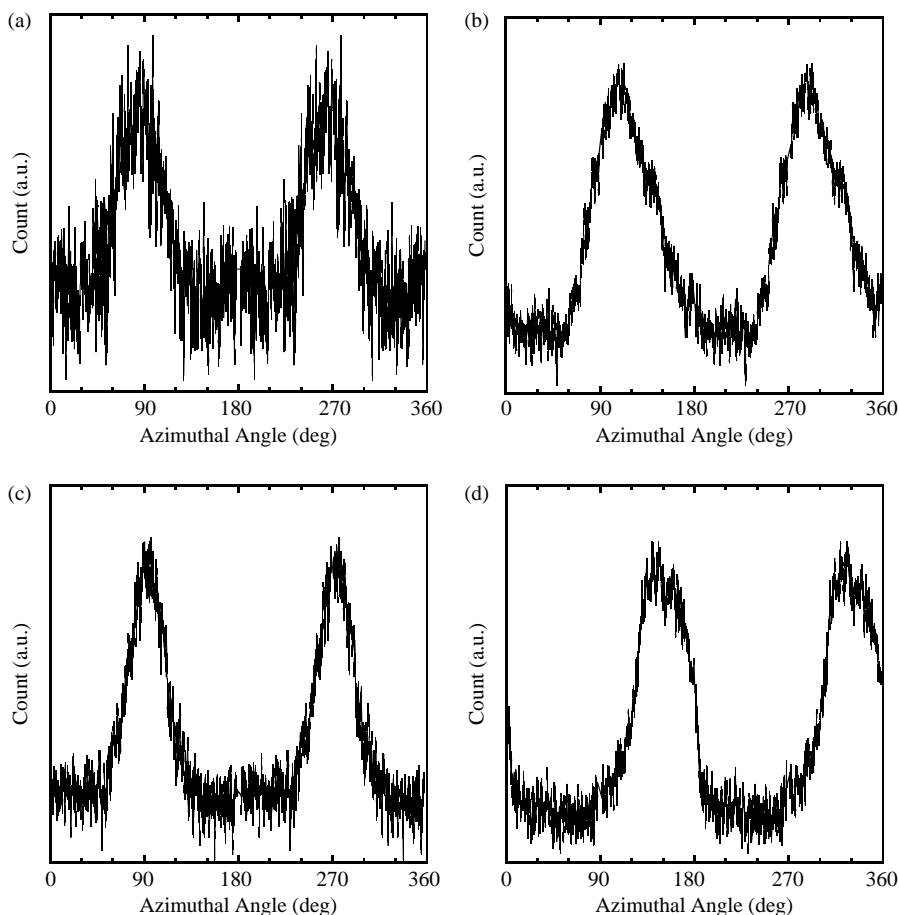


Fig. 7. Intensity profiles for azimuthal angle in two-dimensional Fourier transformed images. (a) 140 °C, (b) 180 °C, (c) 190 °C, and (d) 200 °C.

lamellae. To confirm this, the periodic length estimated from the wavenumber of the brightest point in the spot in the two-dimensional FT image was compared with the long period of PTT crystal lamellae measured by SAXS as shown in Fig. 6. Both lengths were approximately 10 nm, and became larger as crystallization temperature increased, confirming that the periodic distance estimated from the two-dimensional FT image corresponds to the long period of PTT crystal lamellae. Consequently, to examine the orientation of lamellae, the azimuthal distribution of intensity in two-dimensional FT image at the wavenumber of the brightest point in the spot was plotted in Fig. 7. The azimuthal angle was taken clockwise starting from the direction of 12 o'clock in Fig. 5. From the plots, the degree of orientation of the crystal lamellae was estimated under the assumption that the direction of the peak angle was almost the perpendicular direction to the radial direction of the spherulite; thus, it was considered that the angular distribution of the intensity corresponded to the orientation distribution of the crystal lamellae. The information obtained from the TEM image is the orientation distribution in a two-dimensional plane of the edge-on lamellae and then the two-dimensional degree of orientation $f = \langle \cos 2\theta \rangle$ was estimated as the indicator giving the orientation distribution of the lamellae. That is, the degree of orientation of lamellae in a PTT spherulite was estimated from the deviation of orientation direction of edge-on lamellae from the radial

direction. The radial direction was assumed as being perpendicular to the peak angle (that is, $\theta = 0$) in the plots in Fig. 7, and the estimation of the degree of orientation was carried out by calculating the f within the range of angle θ from -90 to 90° . Fig. 8 shows the crystallization temperature dependence of degree of orientation of PTT crystal lamellae in a spherulite. As a result, it seems that the degree of orientation changed largely around the temperature from 180 to 190 °C

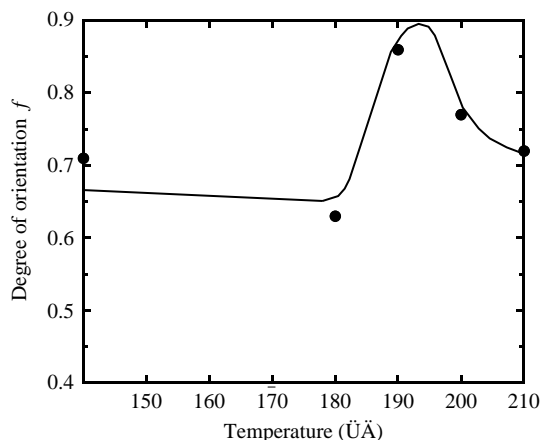


Fig. 8. Crystallization temperature dependence of degree of orientation of PTT crystal lamellae in the spherulite.

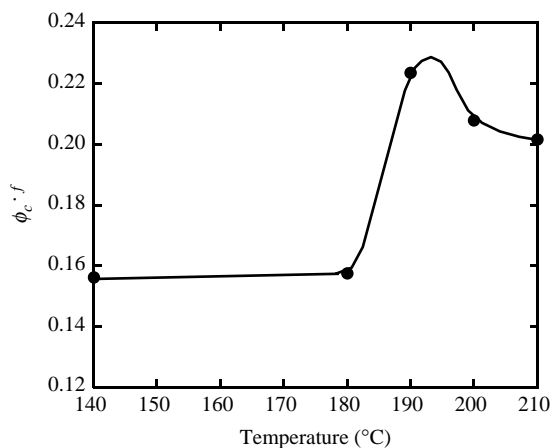


Fig. 9. Temperature dependence of (degree of crystallinity, ϕ_c) (degree of orientation of crystal lamellae, f) in PTT spherulite.

and the change corresponds to the banded spherulite formation. Moreover, the crystallization temperature dependence of (degree of crystallinity, ϕ_c) \times (degree of orientation of crystal lamellae, f) is plotted in Fig. 9 and the plot was compared with both the plots of degree of crystallinity (shown in Fig. 3) and the degree of orientation (shown in Fig. 8). As the result, the temperature dependence of $\phi_c f$ in Fig. 9 remarkably changed between 180 and 190 °C along with that of the degree of orientation in Fig. 8 while that of the degree of crystallinity in Fig. 3 gradually increased and did not show such a marked change around the temperature region. This suggests that the degree of orientation played a more important role for the

retardation change between non-banded and banded spherulites than the degree of crystallinity.

On the other hand, it was expected that the $\phi_c f$ at 200 °C would be larger than that at 190 °C because the maximum value of retardation at 200 °C was larger than that at 190 °C, as shown in Fig. 2. However, the value of $\phi_c f$ at 200 °C was smaller than that at 190 °C, as shown in Fig. 9; the relation between this smaller f value and the larger retardation at 200 °C is re-examined in the following section.

3.5. Interference color and morphology of PTT crystal lamellae

The arrangement of PTT crystal lamellae was re-examined based on the TEM images shown in Fig. 4. To extract only the information regarding the arrangement of the crystal lamellae, the area without the spots was eliminated in the two-dimensional Fourier transformed images in Fig. 5 and then the images were inverse two-dimensional Fourier transformed to obtain the real images of the crystal lamellae and binarized as shown in Fig. 10. The images are magnified in order to recognize the features. From the images, it can be seen that the crystal lamellae are well oriented, independent of the crystallization temperature, but the orientation features are different. At 140 °C, it seems that the lamellae are orientated separately and intersected each other or bend all over the image. However, at 180 °C, it seemed that several lamellae locally formed bundles of the width and the length of several tens nm to 100 nm, such as the areas surrounded with the white circles in Fig. 10(b). Furthermore, at 190 °C, the length of crystal lamella bundles became 100 nm and the orientation direction of the

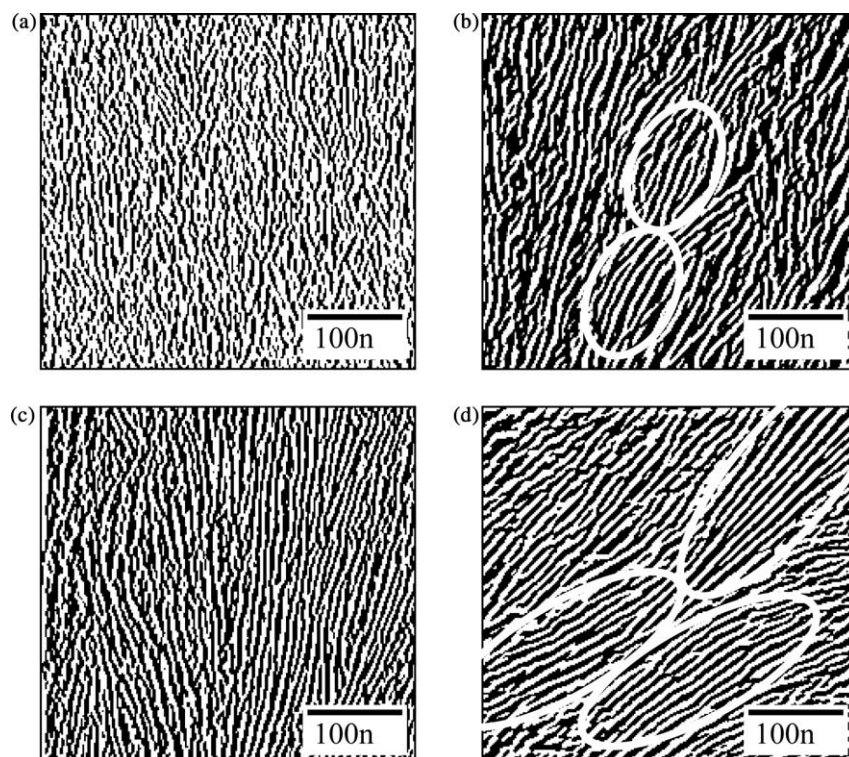


Fig. 10. Inverse two-dimensional Fourier transformed and binarized images of the spots in Fig. 5. (a) 140 °C, (b) 180 °C, (c) 190 °C, and (d) 200 °C.

lamellae more regular. On the other hand, it seemed that the degree of orientation of lamella bundles in the entire image was lower at 200 °C than that at 190 °C. However, from the local view, the width of the lamellar bundles became wider, arranged more linearly and the degree of orientation became higher at 200 °C than those at 190 °C (areas surrounded with the white circles in Fig. 10(d)).

The resolution δ of the optical microscope can be expressed as follows

$$\delta = \frac{0.16\lambda}{n \sin \theta}, \quad (3)$$

where λ is wavelength of light, n is refractive index of medium, θ is angle between diffracted light and optical axis, that is, maximum angle of incident light into objective lens and $n \sin \theta$ is numerical aperture of objective lens. When the sample is observed in the air, n is 1 and the numerical aperture is 1 or less. The interference color observed under PLM is caused by the retardation resulting from structure with size of the order of the wavelength of light, because the resolution of optical microscope is approximately the order of wavelength of light as understood from Eq. (3). When Fig. 10 is reviewed from such a viewpoint about the resolution, it was considered that, at 200 °C, the higher degree of orientation of crystal lamellae than 190 °C in the local areas with the size of wavelength of light brought about the higher retardation. That is, in the local area with the size of wavelength order of light, the degree of orientation increased along with the increasing crystallization temperature, and then the retardation increased between 190 and 200 °C.

4. Conclusion

It is known that there are many polymers forming both non-banded spherulites and banded spherulites with high birefringence. Among them, PTT has the combined features of forming large size spherulites easily and having relatively wide band spacing in banded spherulite. Therefore, PTT is a suitable sample for structure analysis by PLM observation.

In this study, the retardation of PTT spherulites was measured under PLM by a Berek compensator, and the crystallization temperature dependence of the retardation was

discussed from the viewpoint of the relation with the morphology. Because the spherulite was symmetrical about a point, the degree of orientation can be estimated in a local area of the spherulite. In this paper, the degree of orientation of crystal lamellae was estimated based on TEM images, and the relation between the degree of orientation and the retardation was discussed. As a result, it was clarified that the degree of orientation of crystal lamellae in PTT spherulite correlates with the retardation. However, it is noted that the degree of orientation inside an area of the size of the wavelength of light is important, and that in an area with size much larger than the size of the resolution of the microscope, the orientation might not necessarily correlate with the retardation.

The degree of orientation of crystal lamellae accompanied by the formation of lamellar bundles, and thus it is suggested that the lamellar bundles formation is closely related with both the magnitude of retardation and the formation of banded spherulites.

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