

Influence of the Thin-Film Thickness and Crystallization Temperature on the Spherulitic Structure of Polymer Thin Films

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ABSTRACT: The spherulitic structure and morphology of poly(3-hydroxybutyrate) (PHB) thin films crystallized from the melt were observed with a polarizing optical microscope. Depending on the thickness of the PHB thin film and crystallization temperature, banded and non-banded spherulites could form. Reducing the thin-film thickness and crystallization temperature was favorable for the formation of the banded structure. The morphology transition from banded spherulites to nonbanded spherulites was related to the ratio of the crystallization rate to

the diffusion rate. The formation mechanism of the banded structure was examined with the discontinuity growth theory. A depletion zone was considered to appear periodically at the crystal growth front because of the slow diffusion rate, and this may have resulted in the banded spherulites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1616–1621, 2010

Key words: crystallization; diffusion; growth; morphology; thin films

INTRODUCTION

Banding in polymer spherulites is a common feature that is often observed in some semicrystalline homopolymers^{1–7} and polymer blends^{8–12} crystallized in bulk or in thin films. More and more polymer physicists are becoming interested in the formation mechanism of the banded structure because this special crystal morphology is very important for the study of polymer condensed physics. Up to now, it has been widely believed that the formation of the banded structure can be attributed to the twisting of lamellar crystals along the radial growth direction of the spherulites; this idea has been advanced by Keller, Keith, and Padden.^{13–21} Furthermore, Bassett and coworkers^{22,23} reported transverse S-bending in lamellae within banded polyethylene spherulites. They concluded that the generation of the screw dislocation induced by S-bent lamellae was the reason for the formation of banded spherulites. On the basis of a simulation, Kyu et al.²⁴ proposed that the twisting of lamellar crystals may not be the only reason for the formation of the ring-banded structure, and

the concentric ring-banded structure may be a result of the rhythmic crystal growth resulting from nonlinear diffusion during growth.

It has been widely observed that a polymer can form either banded or nonbanded spherulites and that this depends on the crystallization temperature.^{25–27} Moreover, Janjmak et al.²⁸ studied the spherulitic morphologies of metallocene-catalyzed polyethylenes of different molecular weights and found that banded spherulites more easily formed when the molecular weight was more than 100,000. Beekmans et al.⁴ found that *S*-poly(propylene oxide) more easily formed banded spherulites than *R,S*-poly(propylene oxide) at 60°C. On the basis of this result, they concluded that the chiral chains more easily formed the banded structure. Recently, it was determined that banded spherulites could be formed in polystyrene-*b*-poly(L-lactide) thin films crystallized from the melt. In contrast, no banded spherulites could be obtained in crystallized poly(L-lactide) homopolymer under similar crystallization conditions.²⁹ In this work, the influences of the thin-film thickness and crystallization temperature on the spherulitic structure and morphology of poly(3-hydroxybutyrate) (PHB) were studied. The formation mechanism of the banded spherulite was examined.

PHB is commercially available, and a number of applications in medicine and agriculture have been proposed on the basis of its biocompatibility and biodegradability. In particular, PHB can easily form

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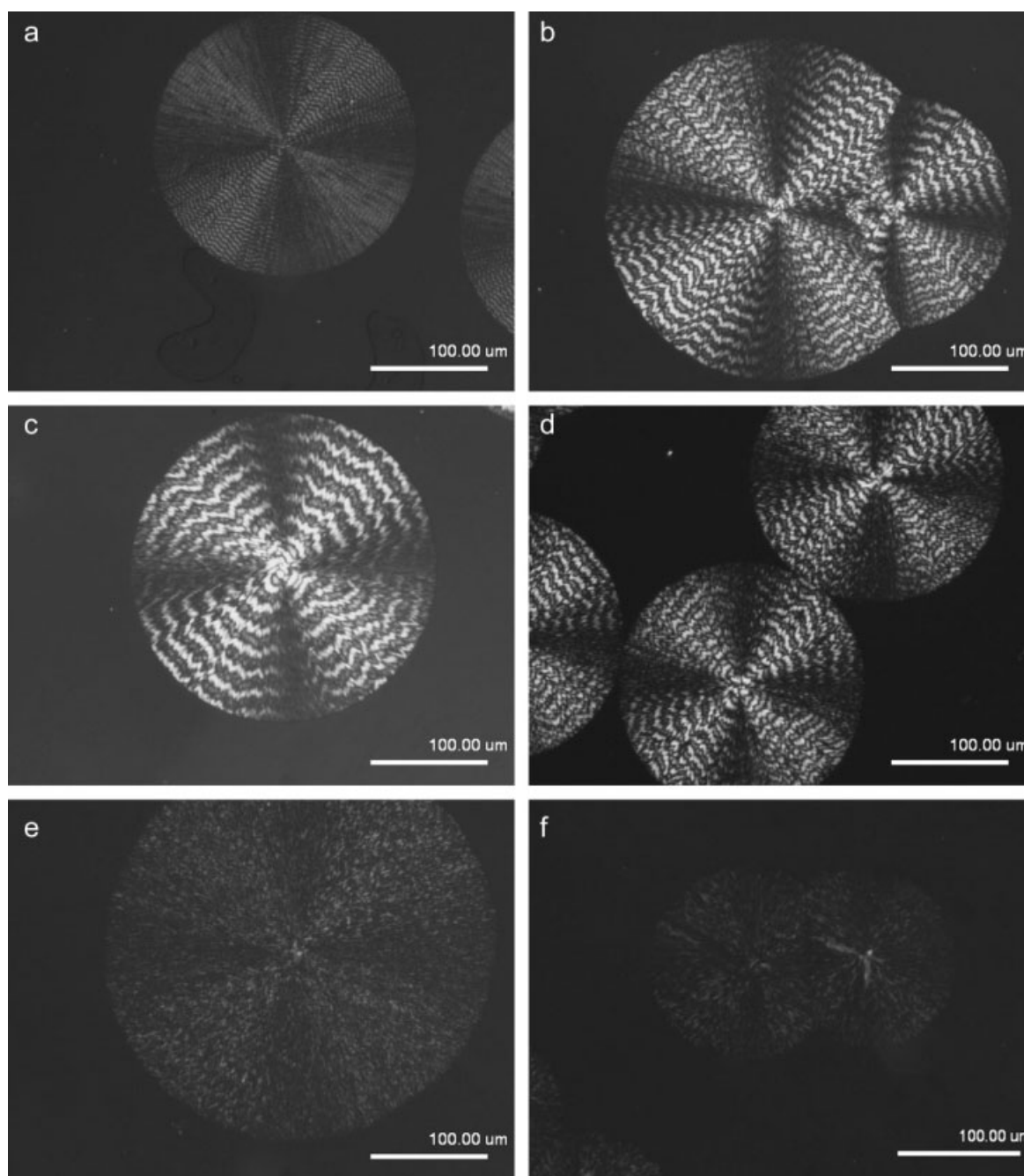


Figure 1 Observations of the spherulitic structure and morphology of PHB spherulites crystallized at different crystallization temperatures with a thin-film thickness of 8.3 μm : (a) 80, (b) 90, (c) 100, (d) 110, (e) 120, and (f) 130°C. A dramatic transition in the spherulitic structure from a banded form to a nonbanded form was observed between 110 and 120°C.

regular banded spherulites, and this makes it ideal for studying the formation mechanism of banded spherulites.^{12,30–33}

EXPERIMENTAL

PHB (glass-transition temperature = 3.2°C, melting temperature = 176.4°C) was purchased from Aldrich (Steinheim, Germany). The thin films of PHB were prepared on clean glass slides by a solution spin-coating method. The concentration of a dimethylfor-

mamide solution of PHB and the spin speed were selected to be approximately 8 wt % and 800 rpm, respectively. To obtain thick films, spin coating was repeated several times. The thickness of each PHB thin film was measured with a TPY-2 spectroscopic ellipsometer (Tianjin, China) [ΔI (Precision of thickness) = ± 0.5 nm, wavelength = 632.8 nm, θ (variable angle) = 20–90°].

The morphology and growth of the spherulites were observed with a Nikon Eclipse E400 polarizing optical microscope (Tokyo, Japan) with an Instec

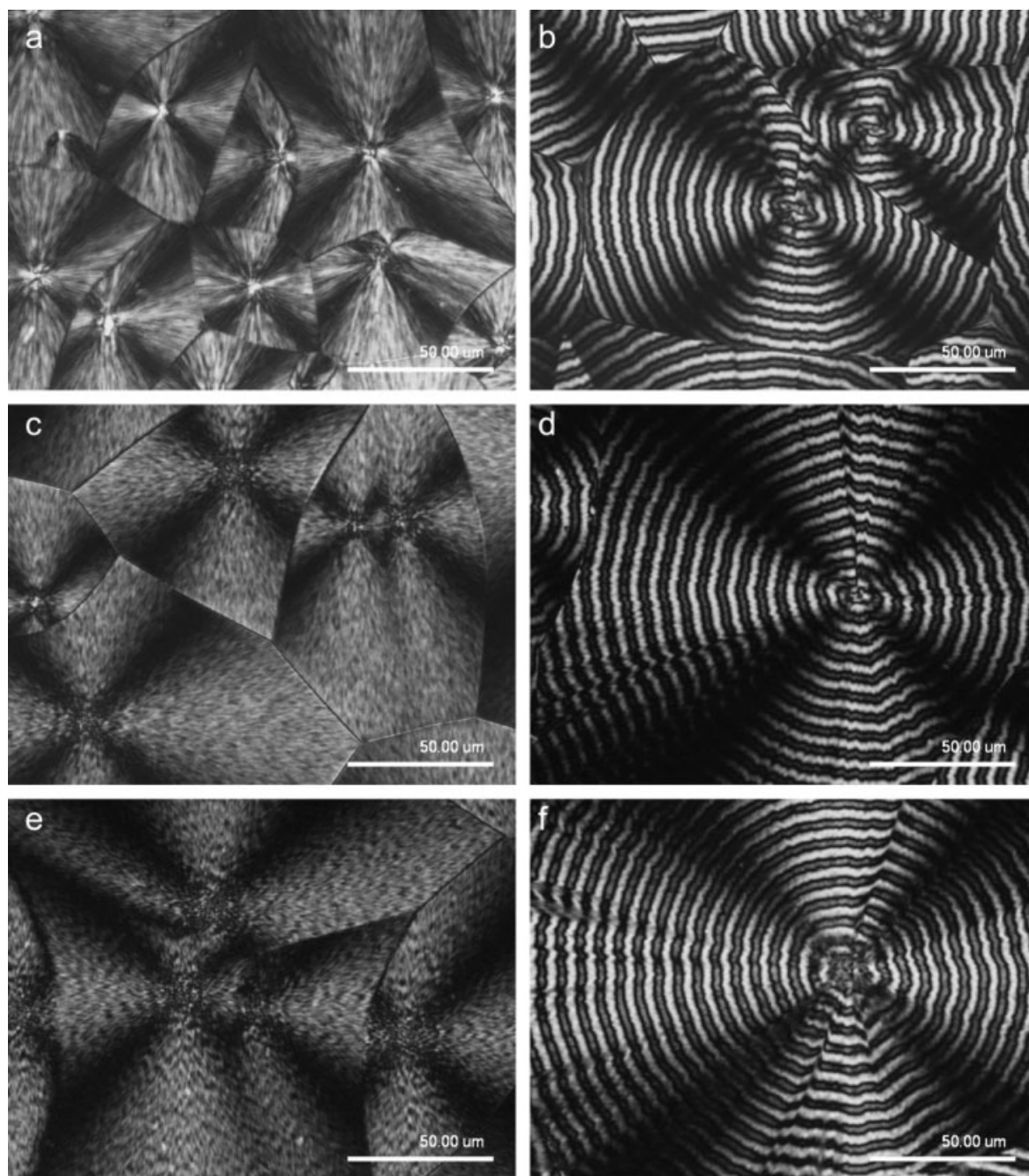


Figure 2 Observations of the spherulitic structure and morphology transitions of PHB spherulites crystallized at different crystallization temperatures and with different thin-film thicknesses: (a) 50°C and 32 μm , (b) 50°C and 30 μm , (c) 60°C and 23 μm , (d) 60°C and 15 μm , (e) 70°C and 13 μm , and (f) 70°C and 11 μm .

STC200 microscopy hot stage (USA). Thin films of PHB of various thicknesses were first put onto a hot stage and heated to 190°C in air for 10 min to get an equilibrium melt. The melt samples were then transferred as quickly as possible to the Instec STC200 microscopy hot stage with a preset temperature. Different temperatures (50–130°C) were selected for the isothermal crystallization of PHB. The spherulitic morphology of the PHB thin films was recorded as a function of the crystallization time. To prevent the

degradation of PHB, each experiment was carried out with a new sample.

RESULTS AND DISCUSSION

The crystallization behavior of PHB thin films with a thickness of 8.3 μm at various temperatures was studied with a polarizing optical microscope. Two types of spherulites, banded and nonbanded, were

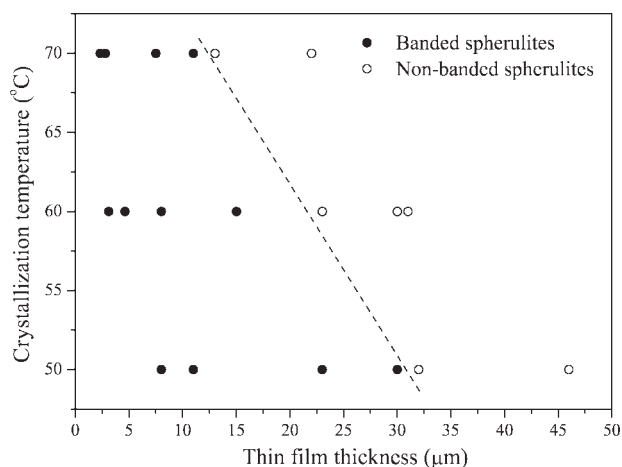


Figure 3 Spherulitic morphology with banded and non-banded spherulites with different thin-film thicknesses and at different crystallization temperatures.

observed, as shown in Figure 1. The transition temperature from banded spherulites to nonbanded spherulites was between 110 and 120°C. For the thin films with the same thickness, the PHB banded spherulites formed at a lower crystallization temperature. Figure 2 shows the spherulites formed in PHB thin films with different thicknesses at the same crystallization temperature. When the crystallization temperature was fixed, banded spherulites usually formed in the thinner films. These experimental results indicate that a lower crystallization temperature and a thinner film are favorable for the formation of banded spherulites. The transition of the spherulitic structure should depend on the crystallization temperature and the film thickness. On the basis of all of the experimental observations, the spherulitic transition from the banded structure to the nonbanded structure with the crystallization temperature and thin-film thickness is shown in Figure 3.

It is well known that the crystallization of a polymer is composed of the arrangement of the crystalline entities (chain folding) and the diffusion of the chains from the melt to the crystal front. The diffusive displacement rate (v_d) and the growth rate of the crystalline entities (v_c) can be defined as follows:

$$v_d = \frac{d}{dt} [6D(T_c)t]^{1/2} \quad (1)^{34}$$

$$v_c = G_0 \exp \left[-\frac{U^*}{R(T_c - T_\infty)} \right] \exp \left[\frac{K_g}{T_c \Delta T f} \right] \quad (2)^{35}$$

where D is the whole chain diffusion constant, T_c is the crystallization temperature, t is whole diffusion time, G_0 is a pre-exponential factor, generally

assumed to be constant, U^* is the activation energy, R is gas constant, T_∞ is the temperature at which all motions associated with viscous flow cease, f is a factor that corrects for variations in the heat of fusion with temperatures below the equilibrium melting point (T_m^0), f is determined as $2T_c/(T_m^0 + T_c)$, ΔT is the supercooling, and K_g is a parameter related to the growth regime. The actual crystallization morphology and structure of the polymer spherulites depend on the ratio of the diffusive displacement of chains to the growth rate of the crystalline entities. This ratio, in turn, can be controlled by suitable choices of the crystallization temperature and film thickness for the crystallization of polymer thin films.^{33,36,37}

It is thought that the banded spherulites that form in thin films may come from rhythmic crystal growth, that is, discontinuity growth. A depletion zone of the polymer melt may be formed at the growth fronts of the spherulites because of the slow diffusion rate and the volume shrinkage during the crystallization solidification process. Ridge and valley structures are formed periodically on the spherulitic surface.^{38–40} The crystallization growth rates at ridges and valleys are different because of the formation of the depletion zone at the growth front.^{21,41} In this work, the banded structure for the banded spherulites, observed with a polarizing microscope, was still observed after the removal of the analyzer, as shown in Figure 4. This result supports the idea that the banded structure of PHB banded spherulites should come from the fluctuation of the thickness, and this supports the aforementioned growth model. According to the growth model, banded spherulites should more easily form when the diffusive velocity of the chains is less than the growth rate of the crystalline entities. This is also the reason that polymer

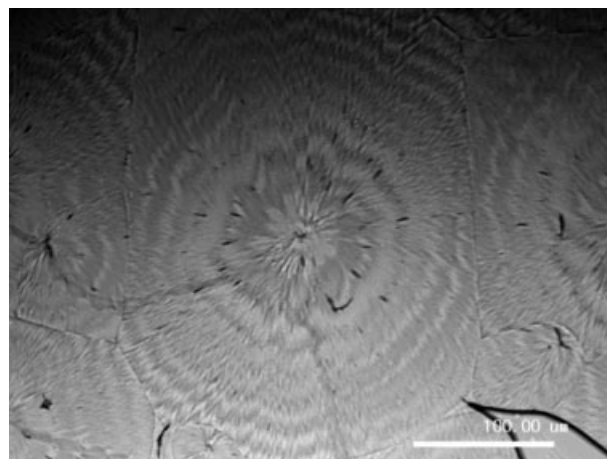


Figure 4 Optical micrograph of a PHB banded spherulite crystallized at 100°C with a thin-film thickness of 8.3 μm after the removal of the analyzer.

blends more easily form banded spherulites, even though the crystallization temperature is higher. For polymer blends, the diffusion rate of the crystalline component dramatically decreases with the addition of the second component.

Figure 5 shows the overall growth rates of spherulites formed in PHB thin films with various thicknesses at various crystallization temperatures. According to eqs. (1) and (2), the diffusive displacement rate increases evenly with the temperature, and the spherulite growth rate, in contrast, exhibits a maximum between the glass-transition temperature and the equilibrium melting point. Two relationships of the spherulite growth rate and diffusion velocity can be considered according to the literature⁴² and the experimental results in this work. For the thicker films (16.5 and 8.3 μm in Fig. 5), the diffusive velocity of chains may be less than the growth rate of the crystalline entities at a lower crystallization temperature, so banded spherulites are formed. In contrast, at a higher crystallization temperature, the diffusive velocity of the chains may be faster than the growth rate of the crystalline entities. Non-banded spherulites are formed in these cases. When the thickness of the PHB thin film decreases, the transition temperature from nonbanded spherulites to banded spherulites should shift to the higher temperature because the diffusive velocity of the chains decreases with decreasing film thickness. For the thinner films, the diffusive rate may be less than the growth rate at all crystallization temperatures because of the smaller thickness. Banded spherulites were observed over the range of crystallization temperatures used. We observed that banded structures also formed at the ends of the nonbanded spherulites, as shown in Figure 6. The formation of banded structures should come from the reduction of the film thickness during the late crystallization stage.

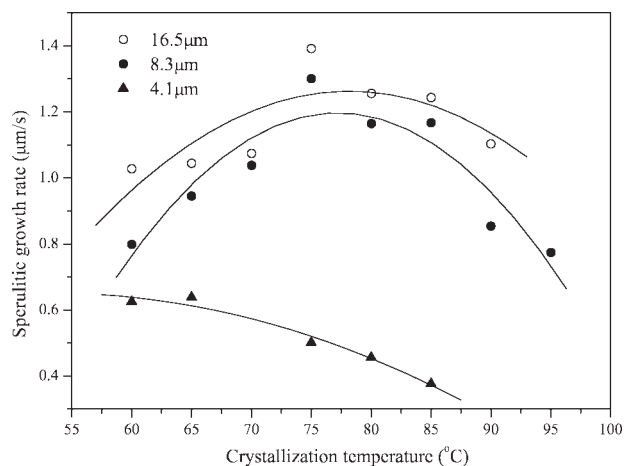


Figure 5 Plots of the spherulitic growth rate versus the crystallization temperature with different thin-film thicknesses.

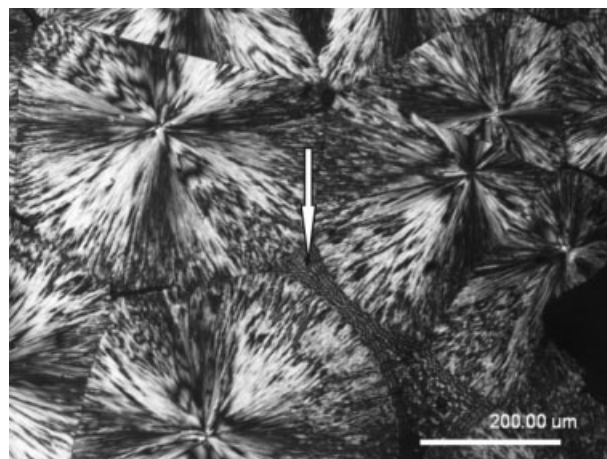


Figure 6 Spherulitic morphology of PHB crystallized isothermally at 120°C with a thin-film thickness of 8.3 μm . The arrow points to the banded area.

CONCLUSIONS

Banded and nonbanded spherulites of a polymer can be formed under certain crystallization conditions. The rhythmic crystal growth (discontinuity growth) of spherulites is the main factor for the formation of banded spherulites formed from thin films from the melt. The discontinuity growth of spherulites may result from the slower diffusion rate and the depletion zone of the melt phase formed at the crystal growth front. This rhythmic growth process is controlled by the ratio of the growth rate to the diffusion rate. The structure and morphology of spherulites are strongly affected by the film thickness and crystallization temperature for polymer thin films isothermally crystallized from the melt. Banded spherulites can be formed when this ratio is more than 1 for pure homopolymers. Decreasing the film thickness and crystallization temperature of polymer thin films can lead to the formation of the banded structure because of the slower diffusion rate.

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