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Depletion-Induced Nonbirefringent Banding in Thin Isotactic Polystyrene Thin Films

Yongxin Duan, Yong Jiang, Shidong Jiang, Lin Li, and Shouke Yan

State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

Jerold M. Schultz*

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

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Introduction

Banding in the spherulites of polymers crystallized from the melt is a common occurrence. For crystallization in the bulk or in thick films, the banding results from a periodic change in crystal orientation along the radius of the spherulite,[1,2] related microscopically to the regular twisting of ribbonlike crystalline lamellae along their growth direction (the spherulite radius). These typical bands appear in sharp contrast under all specimen orientations of plane-polarized light but exhibit very poor contrast under unpolarized light. In contrast, in the 1950s, Schuur,[3] Schramm,[4] and Keith[5] reported observations of banded spherulites in which the bands appeared in sharp contrast in unpolarized light as well as under polarized light. Further, under plane-polarized light, the bands disappear when the plane of polarization is perpendicular to the bands. These unusual bands appear to occur only in thin films[3,6] and have been attributed by Schramm to radially periodic differences in the degree of order.[3,6] In the present work, we report on and explain the character of such banding in thin films of isotactic polystyrene (i-PS).

Experimental Section

Isotactic polystyrene (iPS) material with an isotacticity of 90%, MW = 400 000, and $M_w/M_n \cong 2.8$ (Scientific Polymer Products). For atomic force microscopy (AFM) observation, iPS films ranging from 100 to 300 nm in thickness were prepared by spin-coating 1.0 wt % iPS-xylene solution onto clean glass slides. The crystallization process from the melt at 160 °C was observed directly under tapping-mode AFM, using a Nanoscope III MultiMode AFM equipped with a heater (Digital Instruments).

Results

Figure 1 shows two optical micrographs of iPS thin films melt-crystallized at 160 °C for 6 h. Figure 1a was taken under crossed-polarizers. Nonbirefringent ring-banded structures can be seen. After removing the analyzer (Figure 1b), the ringed-banded structures are even more clearly seen. The strongly birefringent central parts of the objects are intriguing but are outside the scope of this note. The period of the rings in the banded structures is quite uniform and is estimated to be ~3.5 μm. The initially hexagonal shapes of the objects and the absence of birefringence suggest that the objects are stacks of crystals viewed along the chain axis; i.e., they are hedrites. Similar microstructures are observed in the still thinner films prepared under the same thermal history for transmission electron microscope (TEM) observation (not shown). The electron diffraction patterns are almost identical at all positions over the banded object and confirm that the chain axis is everywhere normal to the film plane. Thus, the banding is not associated with orientation changes (e.g., lamellar twisting).

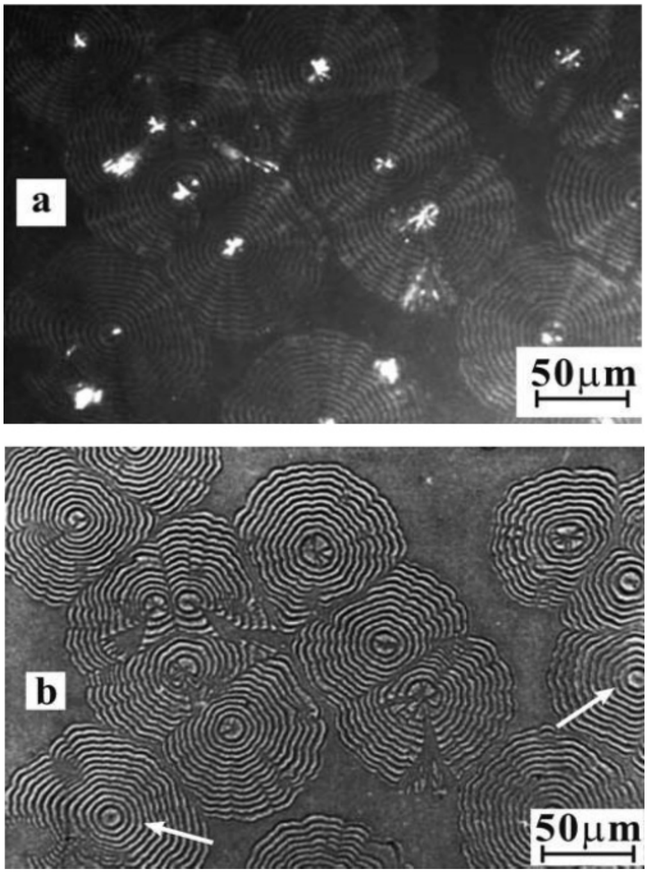

Figure 1. Optical micrographs of iPS hedritic entity melt-crystallized at 160 °C for 6 h: (a) taken under crossed-polarizers; (b) taken after removing the analyzer.

Figure 2a,b shows an AFM height image and a through-diameter height trace of a hedritic entity in a thin film crystallized at 160 °C for 6 h. In Figure 2c, an enlargement of Figure 2a, we see everywhere flat-on lamellae (crystals viewed along the *c*-axis). This invariable orientation, along with the TEM results, demonstrates the absence of crystal orientation differences through the bands. The radial growth velocity at 160 °C, taken from AFM image sequences, is approximately 100 nm/min.

Demonstrating that the nonbirefringent banding is a rather general phenomenon in iPS thin films, we have obtained very similar iPS structures on (a) different substrates (glass, mica, carbon film, and silicon wafer) and (b) different iPS materials (M_w = 400 000 and 90% isotacticity; M_w = 750 000 and 97% isotacticity) and different preparation methods (solvent-casting, spin-coating). The banded structure can be formed over a wide temperature range, 140−190 °C, regardless of

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* To whom all correspondence should be addressed: Fax 302-831-1048; e-mail schultz@che.udel.edu.

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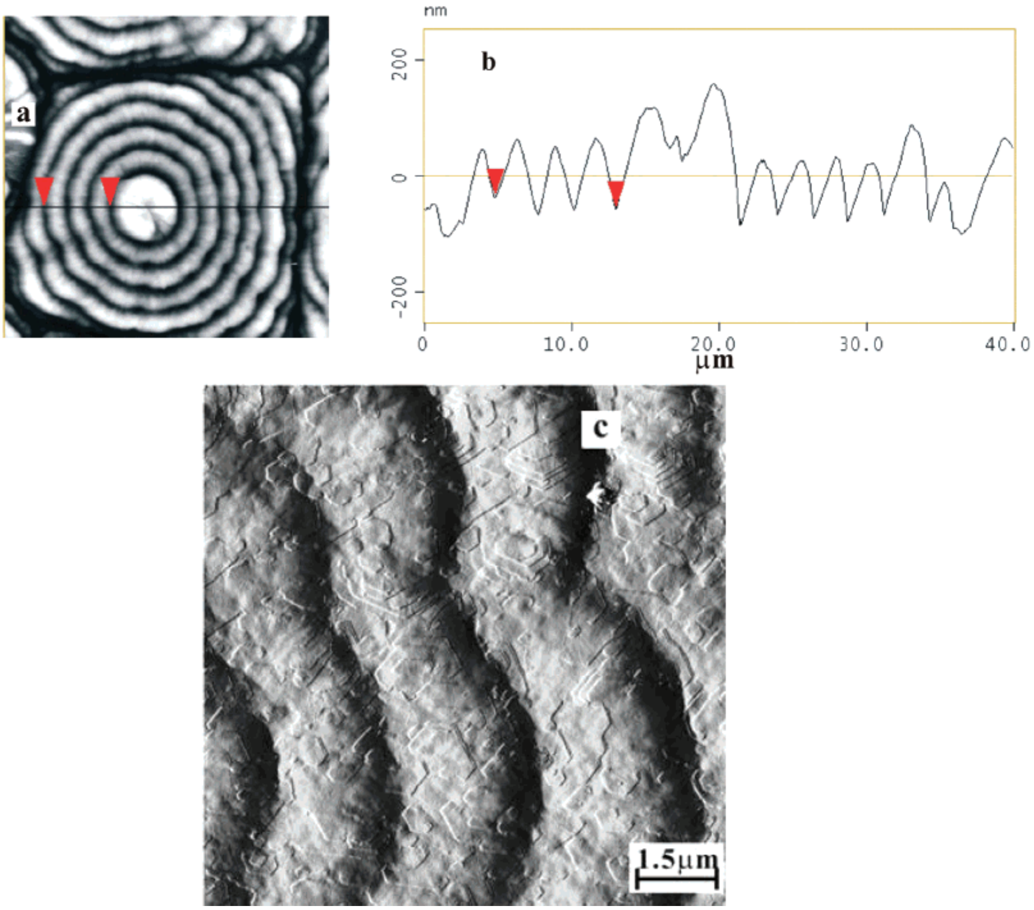

Figure 2. (a) AFM height image of a hedritic entity in a thin film crystallized at 160 °C for 6 h, (b) a through-diameter height trace, and (c) an enlargement of a portion of (a).

whether crystallization occurred from the melt or the glass. No banding is seen above 190 °C.

The crucial factor for forming the banded structure is the thickness of the film. Ultrathin films (<100 nm) do not show this structure (see, e.g., refs 7−10). Thickness in the range 100−300 nm is suitable for the formation of the banded structure, and the band spacing increases with increasing film thickness.

The banding is associated with the change of specific volume upon crystallization from the melt. The evidence for this is twofold. First, it is seen from the magnitude of the mean change in thickness. Examination of numerous height traces shows that the level of the peaks of the bands is approximately the same as that of the surrounding melt. The *mean* level of the height of the crystallized object is some 35−65 nm below the level of the melt. The exact film thickness is not known but lies between 200 and 500 nm. The mean change in height lies then between 7 and 33%. The density difference between crystalline and amorphous iPS is approximately 7%.[11] This order of magnitude agreement suggests that the mean height decrement coordinates to the shrinkage upon crystallization.

The second evidence derives from a comparison of the behavior of flat-on and edge-on crystallites; while rare, edge-on crystals are found in some regions of the thin films. In Figure 3a, the regions exhibiting banding are all flat-on crystals. The remainder of the image is composed of edge-on crystals. Where flat-on structures come together, as at A, there is a gap containing no polymer. The gap results from the density difference between crystal and melt; all the melt has been used up in forming crystals before the neighboring objects have grown together. On the other hand, where regions of edge-on crystals grow together, as at B, there is no gap. (In fact, the boundaries between edge-on regions appear thicker than the interiors, a phenomenon which we cannot yet explain.) In this orientation, the specific volume difference is accommodated by voids between stacks of lamellae. This behavior is well illustrated in Figure 3b, in which a wedge of edge-on-oriented crystals forms part of an object composed otherwise of flat-on crystals. Elongated (black) voids between lamellar stacks are seen within the wedge. Here the density difference has been accommodated by the formation of voids. On the basis of these two pieces of evidence (height difference and voiding), it becomes clear that the bands are formed as a means to accommodate the specific volume decrement upon crystallization; i.e., these are *depletion* bands. As a general empirical observation, edge-on crystallites are found to become more and more dominant as the film thickness increases. Thus, the increasing dominance of edge-on crystals forces an upper bound to the thickness at which depletions bands can occur.

The height trace in Figure 2b shows further intriguing details: the height decreases sharply into the valley of a band but increases more slowly toward the peak; the band is asymmetric. In AFM images (not shown) one generally observes that the crystal stacks end rather abruptly during the descent from the ridge to the valley but that new layers develop more gradually when climbing to the next ridge.

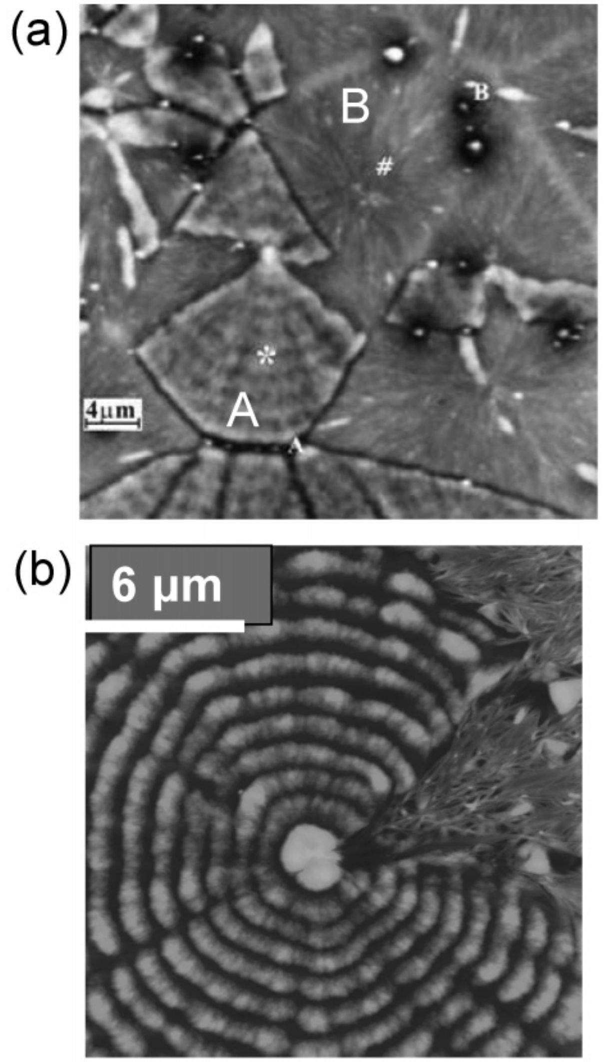

Figure 3. AFM height images showing mixed flat-on and edge-on structures.

Discussion

The formation of nonbirefringent depletion bands is dictated by the inability of new molten polymer to diffuse to the growth interface as rapidly as the interface moves forward. It is the relative magnitudes, then, of the growth velocity V and the diffusivity D which are important. Indeed, the ratio D/V is the diffusion length, a measure of the distance traversed by a molecule in reaching the crystallization front. The observed presence of depletion bands suggests that D/V is small; the crystallization front drains molecules only locally, and the height of the melt adjacent to the growth surface must shrink during growth. In the present case, D (see ref 12) and V (this work) are approximately 1.0×10^{-13} cm^2/s and 1.7×10^{-7} cm/s, respectively, and the diffusion length D/V is of the order of 10^{-6} cm, confirming the very local nature of the process. As the crystalline region becomes thinner and thinner, the few remaining crystals demands less and less melt replenishment, and the new melt diffusing constantly in from the far field now refills the depression in front of the growth surface. With this replenishment, the crystalline material again thickens, creating the backside (valley to ridge) of the band. The process should repeat itself periodically. This process is sketched and described in Figure 4.

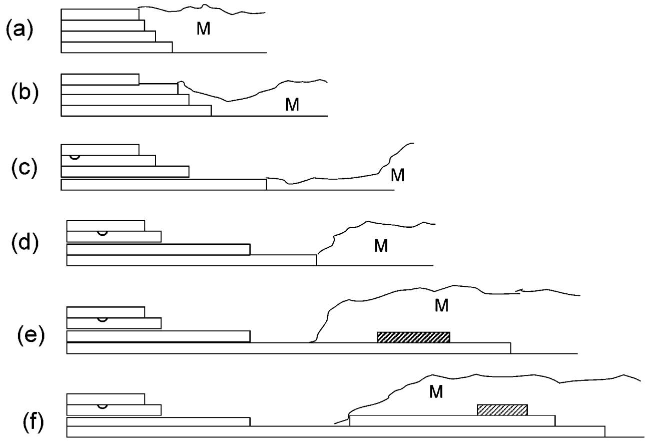

Figure 4. Model of depletion band formation: (a) At ridge of band (M marks the melt). (b) Melt depletion begins; topmost crystals cannot grow. (c) At valley of band; replenished melt at the interface is not sufficient; growth of most layers has stopped. (d) At valley of band; melt is locally replenished. (e) Initial climbing from valley; screw dislocation initiates new layer (hatched) in replenished melt. (f) Climbing further from valley.

The depletion bands demonstrated here bear similarity to rhythmic crystallization processes and the development of Liesegang rings, phenomena known, particularly in mineralogy, since the late 19th century (see refs 13 and 14 for reviews). These phenomena result from an interplay of diffusion (dependent on a concentration gradient) and precipitation or crystallization (dependent on local concentration level), analogous to the thickness and thickness gradient in the present case.

We propose that the asymmetry of the front and back slopes of the bands relates to the necessary formation of new crystal layers about giant screw dislocations, as sketched in Figure 4. The random generation of giant screw dislocations is a kinetic phenomenon[9] and should occur, on average, only after the basal crystal has grown forward to some extent. It is likely that this dislocation generation kinetics dictates the rather gradual increase in film thickness as growth propagates outward from valley to ridge.

Conclusions

Depletion of material at the growth front, due to the specific volume decrement between crystal and melt, in melt-crystallized iPS films results in nonbirefringent banded hedritic structures. The periodic banding is a result of the inability of the diffusive process replenishing melt at the growth front to keep up with the crystal growth velocity. This rhythmic process is associated with a small diffusion length D/V. When the structures are composed of edge-on lamellae, no bands are found; here the specific volume deficit is accommodated by voiding between lamellar bundles. It is suggested that the observed slow ascent from the valley of each band to the next ridge is due to the low rate of creation of the required giant screw dislocations.

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