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In situ AFM study of the growth of banded hedritic structures in thin films of isotactic polystyrene

Yongxin Duan[a], Ying Zhang[a], Shouke Yan[a,*], Jerold M. Schultz[b,*]

[a]State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
[b]Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

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Abstract

The growth of banded hedrites of isotactic polystyrene (iPS) is followed in situ, using atomic force microscopy (AFM). The melt layer surrounding the growing hedritic front is much thinner than both the hedrite front and the far-field melt. Growth occurs simultaneously in three dimensions: radially, circumferentially and height. The height of the hedrite growth front being so much higher than the adjacent molten pool, the observed propagation of the front requires that it be covered by a thin film of molten material, likely drawn up the face of the front by capillarity. As the hedritic front grows in height, it demands material at a higher rate than can be delivered from the far-field melt and the stacked lamellae stop growing, layer by layer, from the top downward, until only the basal lamella continues to grow (at a constant velocity). The kinetics of the position of the lowest point ahead of the growth front slows with time during this process. Supplying only the basal layer, the adjacent molten pool is replenished and now begins to feed new layers of growing lamellae as the process repeats itself. The creation of the new lamellar layers appears to be coupled to morphological instability of the basal layer, in the form of growth front serrations, likely causal of the giant screw dislocations.

Keywords: Crystallization; Thin film; Isotactic polystyrene

1. Introduction

We recently reported on banded hedrites in thin films of isotactic polystyrene (iPS) [1]. The hedrites exhibit no change in orientation across the bands; the chain axis is uniformly normal to the plane of the film. The bands manifest a periodic variation in film thickness. There is a similarity between these structures and the non-banded spherulites reported a half century ago by Schuur [2], Schramm [3], and Keith [4]. It was demonstrated in the previous work that the banding derives from a competition of the growth velocity and the rate at which new molten polymer can be transported to the growth front. A conceptual model for this behavior was suggested. In the model, as the hedrite grows laterally, the growth velocity outstrips the rate at which melt from the far field can replenish the depleted melt at the growth front, the depletion arising from the specific volume difference between crystal and melt. Further, it was observed that the decrease in film thickness from peak to valley is steep, while the increase in thickness from the valley to the next peak is more gradual. It was suggested that this more gradual increase in thickness relates to the rather slow rate of formation of the giant screw dislocations necessary to creating new layers of crystal lamellae. The intention was to close our investigation of this phenomenon, but some further study has shed additional light on the banded hedrites, qualitatively validating features of the model and also revealing surprising new information on crystallization in thin films.

2. Experimental

iPS powder with $M_w = 400{,}000$ and isotacticity of 90% was purchased from Scientific Polymer Products, Inc. M_w/M_n is approximately 2.8. iPS has a fairly slow

* Corresponding authors. Tel.: +1 302 831 8145; fax: +1 302 831 1048.
E-mail addresses: skyan@iccas.ac.cn (S. Yan), schultz@che.udel.edu (J.M. Schultz).

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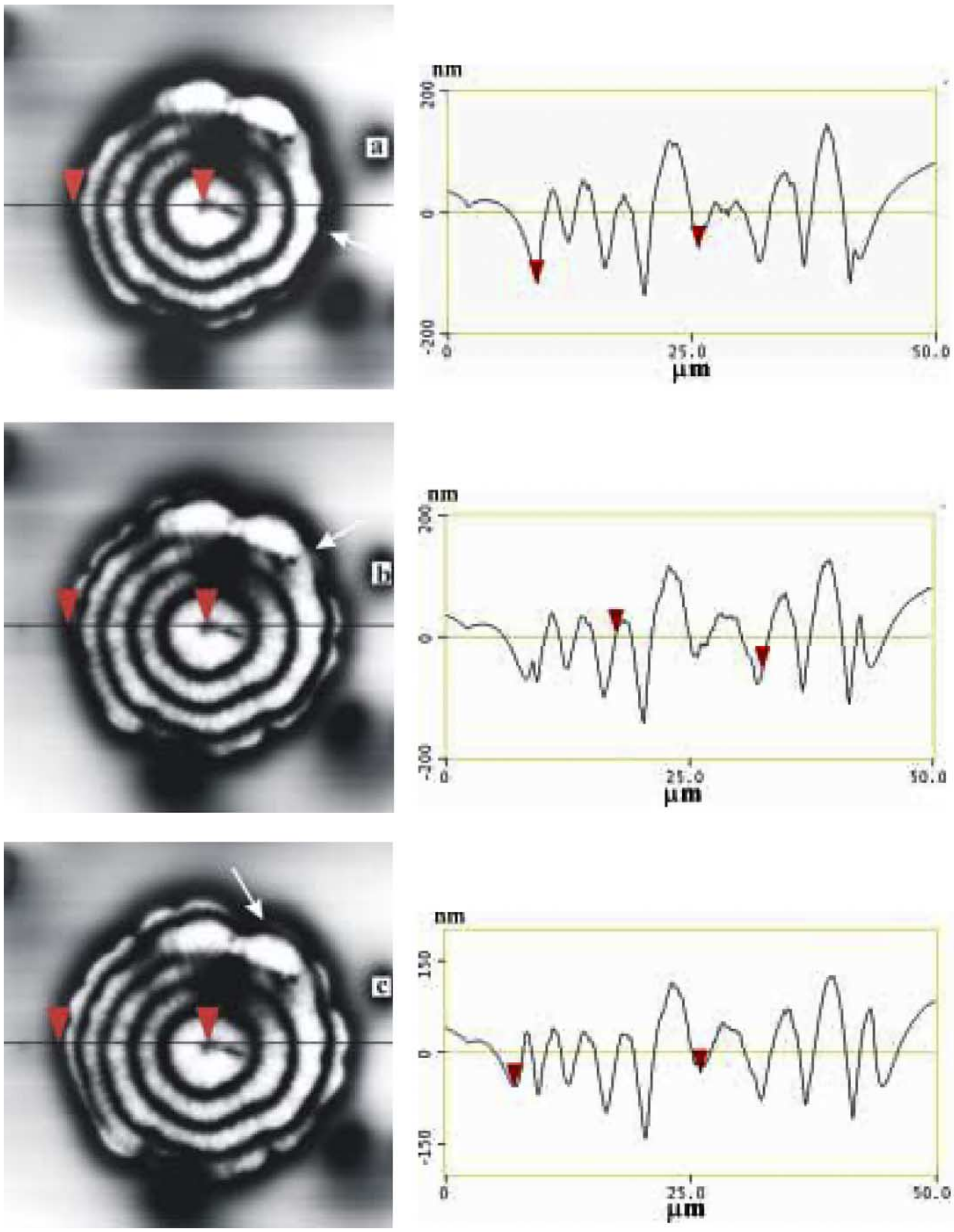

Fig. 1. A set of AFM height images of a banded iPS hedrite taken at different stages during crystallization at 160 °C, along with radial traces of height.

crystallization rate, which makes it easy to observe crystal growth in situ and to fix the structure by quenching.

Thin iPS films about 150–200 nm used for this banding morphology study were prepared by spin-coating 1.0 wt% iPS-xylene solution onto clean glass slides, (for TEM observation, onto carbon-coated mica). After complete evaporation of the solvent, the films were heat-treated at 250 °C for few minutes and then transferred directly to another hot stage preset at 160 °C for isothermal melt crystallization. The crystallization process at 160 °C was observed directly under tapping-mode AFM. A typical value for the set-point amplitude ratio (rsp) (defined as the ratio of the cantilever's oscillating amplitude to its freely oscillating amplitude) was 0.7–0.9. The amplitude of the free-oscillating cantilever was approximately 40 nm. TESP tips with a resonance frequency of approximately 300 KHz and a spring constant of about 30 N/m were used. For TEM observation, the thin iPS films experienced the same thermal treatments. The films, together with the carbon coated layers, were floated onto the surface of distilled water and mounted on 200-mesh copper grids. Electron microscopic observations were

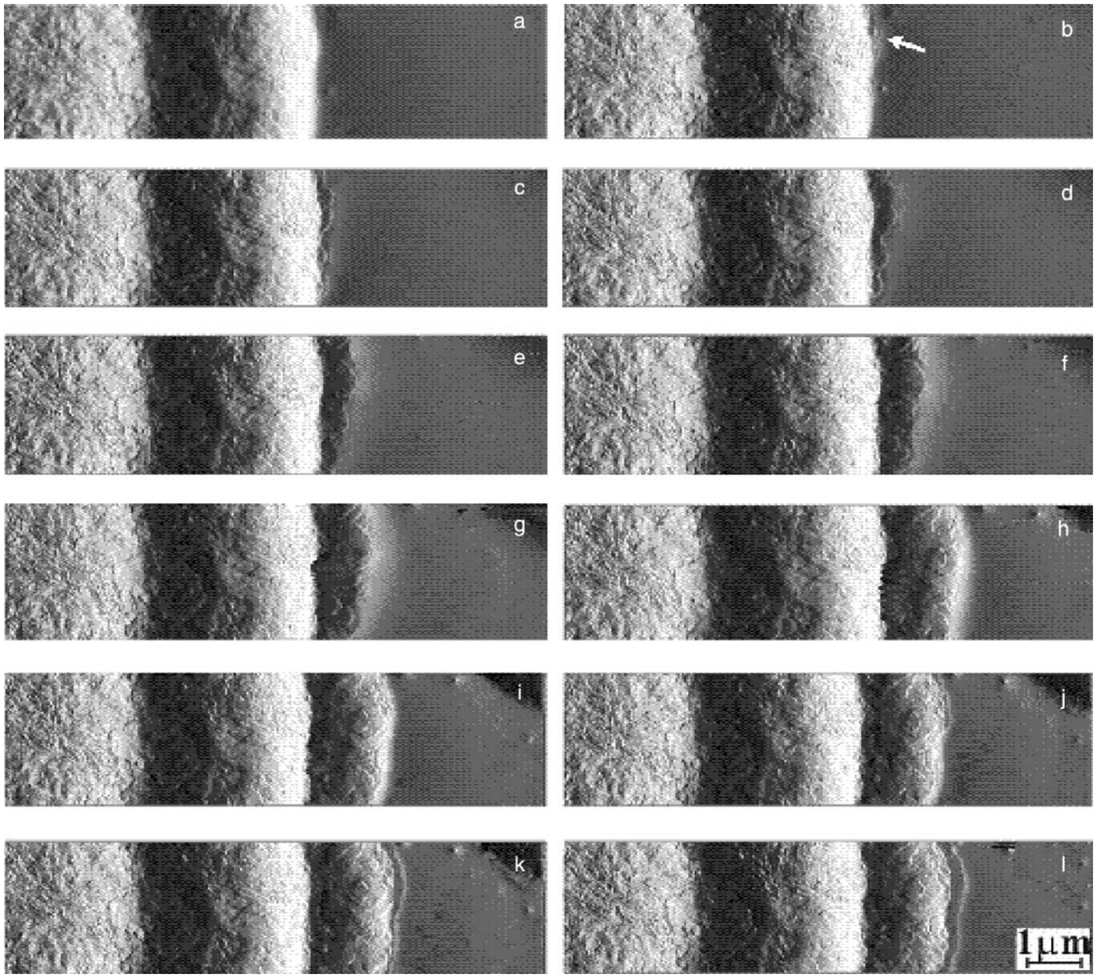

Fig. 2. A set of AFM phase images indicating the growth process at 160 °C of an iPS hedrite band. The images are taken at intervals of 1.9 min.

made using a JEOL JEM-100CXII transmission electron microscope operated at 100 kV.

3. Results

Fig. 1 shows a set of AFM height images taken at different stages during crystallization of an iPS banded hedrite, along with radial traces of height. We found that the nascent band developed in three directions simultaneously: It progressed radially, it advanced anticlockwise about the central part of the hedrite, and its height developed. Periodic peaks and valleys are seen. In these in situ images the banded hedrite is fairly isolated and the melt immediately in front of the growing hedrite is much lower than the hedrite and the far-field polymer melt. The azimuthal position of the front of a band is indicated in subsequent images by an arrow. The counter clockwise development is evident. The height profile along the line indicated in the height image shows that the surface of the valleys is about 150 nm lower than surface of the far-field melt and the hedrite. Considering the thickness of the film, the surface of the valleys cannot be more than one or two lamellae thick.

A surprising feature of the radial traces is that as the crystalization moves forward it is always significantly higher than valleys in front of it. This can be seen in either the left-hand or right-hand front of the traces; as the height of a new peak grows, there is always a deep valley in front of it. Thus the propagating crystal front is not in contact with a molten pool of its own height, strongly suggesting that there is a molten layer adhering to the crystallization front, and that this layer is continuously replenished with molten material which has climbed the front from the valley ahead. This adhering and climbing action would be driven by capillarity; that is, the energy of the system is decreased when the propagating crystal faces are in contact with melt, rather than air. As the front continues to propagate, the rate at which melt can diffuse to the base of the front is insufficient to maintain the molten layer and the number of crystalline layers decreases until the need for new material matches the rate of supply.

The more detailed growth process of the bands was investigated through a sequence of amplitude images during

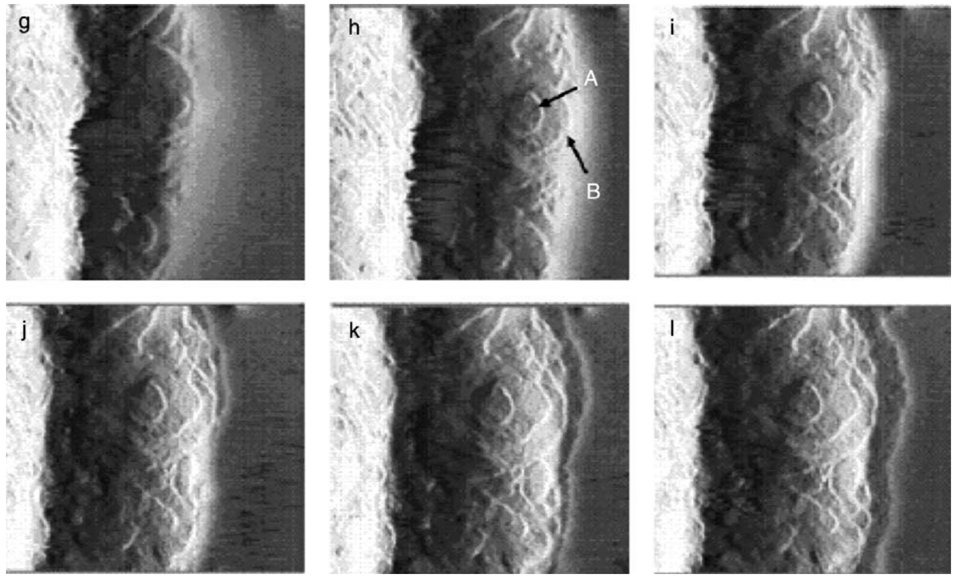

Fig. 3. Higher magnification of images g–l of Fig. 2.

the formation of a band, taken at intervals of 1.9 min. In the first image, Fig. 2(a), at the left is half of a ridge, to the right of it a valley, then a ridge which contacts the polymer melt. In the next image, Fig. 2(b), the bottommost lamella, which we term the basal lamella, propagates ahead of the ridge, as indicated by a white arrow. As the basal lamella propagates forward, the position of the leading edge of the lamellae composing the ridge dos not change; the growth of these lamellae has stopped, creating a relatively precipitous drop to the valley floor. It is to be noted that as the basal layer propagates forward, it quickly becomes serrated. When the growth front of the basal lamella has propagated some 400 nm from the edge of the ridge, new layers begin to appear on the top of it. As more and more layers appear, these nascent layers and the base lamella grow forward together. The accretion of new layers creates a new ridge. The several layers of the new ridge form a common growth front; that is, the growth fronts of the several layers are all at the same position forward of the left side of the image, as seen, for instance, in Fig. 2(g). The next stage, that of the creation of the valley, is seen in the higher magnification of images 2g–2l in Fig. 3. The topmost and the second topmost are labeled A and B. It is seen that as A stops growing, B continues. Subsequent layers in depth continue to grow when the layer above stops. This provides a sloping descent into the valley. In Fig. 3(i) and (j) the base layer continues to propagate, while all layers above have stopped. So, a new valley emerges. This process begins to repeat itself in Fig. 3(k) and (l). Ultimately periodic ridges and valleys are created, forming the banded hedrites.

From a series of images such as those shown in Figs. 1 and 2, kinetic data can be obtained. The data measured at 160 °C are plotted in Fig. 4. Fig. 4(a) is a plot of the front of the bottommost lamella vs. time-the velocity at which the base of the hedrite propagates forward. We note that this bottommost crystal propagates at a constant velocity, as expected from interface kinetics models, such as that of Lauritzen and Hoffman [5]. Fig. 4(b) is a plot of the movement of the lowest valley point vs. time. The absolute height of this minimum is very low and does not vary greatly with time. Molten material has diffused to this valley from the far field, prior to climbing the crystallization front. Since the height of this minimum is approximately constant, the motion of this valley measures the rate of consumption of melt. The valley minimum moves with complex kinetics, reflecting the delivery of molten polymer from the far-field. In Fig. 4(b), the region denoted as I represents the valley in front of a mature growth front, as the front is about to stop. In this case, the propagation of lamellae above the bottommost has nearly stopped, because the supply of fresh melt cannot keep up with the demand of the large number of lamellae in the stack. The positions represented by region II are those occupied by the newly building next ridge and clearly can never exhibit a minimum. Region III represents the valley minimum as the new ridge grows in height and propagates forward. In region III, melt is initially rapidly consumed, but as the stack of lamellae matures and the thickness of the melt locally thins, this rate must slow down and the stack of crystallites must decrease in height in order to match demand and supply.

4. Discussion

In this section we first summarize and comment on the sequence of steps which take place in the formation of the banded hedrites. The earliest stages of formation of the hedrite have not been observed and will not be discussed. We first observed the propagation outward of a multilayered hedrite. Its leading edge terminates rather abruptly, the

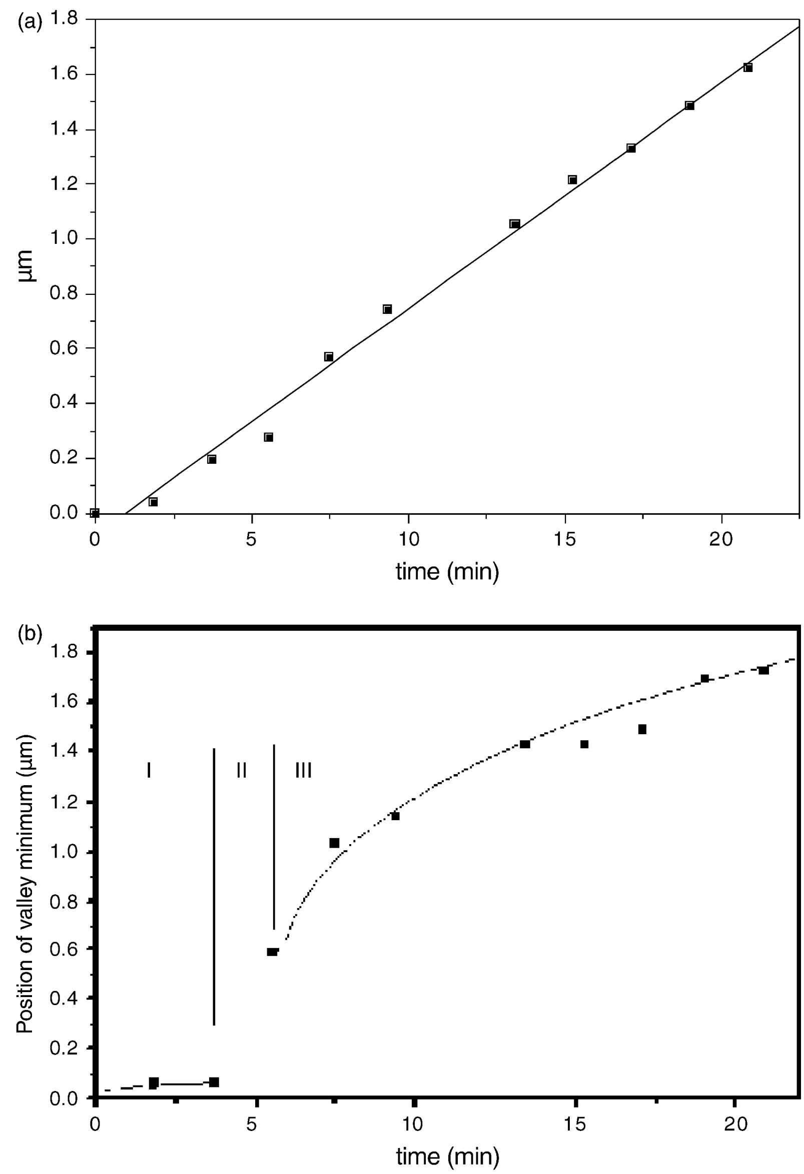

Fig. 4. Plot of the position of (a) the lowest point of the melt ahead of the growing hedrite and (b) the basal lamella versus time.

growth surfaces of all lamellae being at approximately the same lateral position. Because of the lower specific volume of the crystal phase, vis-à-vis the melt, a material deficit is created in the melt at the growth front and the height of the melt must decrease locally. As the leading edge of the hedrite propagates forward, it is fed by a molten pool much lower in height than that of the crystal front. Thus, in order for the front to propagate, the existence of a thin layer of molten material covering the almost vertical leading edge is suggested. Presumably it is the reduction in surface energy of the lamellae, which would drive the melt up the face of the front. The lamellae propagate at the velocity dictated by conditions at the crystal/melt interface, as modeled, for instance by Lauritzen and Hoffman [5]. The large number of lamellae propagating at this velocity demands a high rate of supply of molten material. The diffusion of new chains to the molten pool at the base of the growth face ultimately cannot meet the demand of the ever-increasing stack of lamellae and the growth sequentially stops, from the topmost lamella down, until only the basal lamella continues to propagate forward. This and the subsequent steps are sketched in Fig. 5. As the basal lamella propagates, it becomes heavily grooved, possibly a morphological instability caused by the buildup of uncrystallizable molecules in the melt at the growth front [6]. As suggested originally by Reneker and Geil [7] and recently observed by Keith and Chen [8], it is likely that the crystal portions on opposite sides of a groove overgrow each other, creating the giant screw dislocations which in turn continuously produce the lamellar layers of an emerging stack, and forming the next ridge of the banded structure. The process then repeats itself, producing the rhythmic banding, as Schram [3]

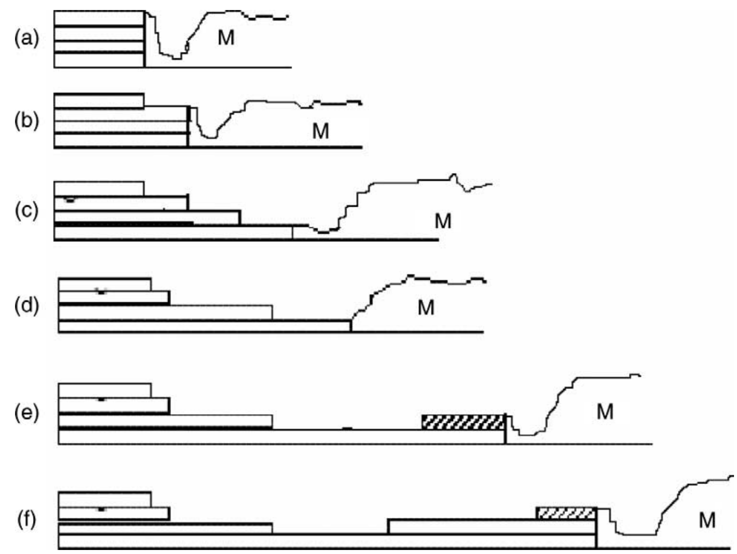

Fig. 5. Model of depletion band formation. (a) Lamellar stack is at its highest position; the adjacent melt (M) is much lower than lamellar stack and far-field melt and the nearly vertical growth front is covered by a thin layer of molten material. (b) Melt depletion begins; topmost crystals cannot grow. (c) At valley of band; only the basal lamella grows. (d) and (e) Melt is locally replenished and new lamellar layers are initiated (via giant screw dislocations). (f) Continued building of a lamellar stack.

named a similar process. This directly observed sequence of events supports the model proposed in the previous paper, but adds the observation of the growing stack being fed through a thin molten layer covering its nearly vertical front.

Two puzzling phenomena which have been observed (but not commented upon) in the crystallization of polymers from thin molten films on a solid substrate are (1) that the central feature of a hedritic or spherulitic structure can be much thicker than the molten film and generally consists of edge-on lamellae [1] and (2) that the height of growing edge-on lamellae can be very much greater than the surrounding molten material [9]. The present observation of melt climbing the steep hedritic crystallization front suggests that a like process operates in this case. The sequence of events would be as follows: (1) A lamellar stack nucleates and grows edge-on above the substrate. (2) Surface energy directs melt up the fold surfaces of the lamellae, where it feeds the growth of the lamellar stack. The rate of this process should be limited by the rate of diffusion to and along the vertical molten pool. (3) Branching and splaying of new lamellae in the stack ultimately produces lamellae lying flat on the surface, where they grow unhindered by the supply of melt. (4) The growth of the flat-on lamellae occludes the original edge-on feature from the melt and halts its growth.

5. Conclusions

The principal conclusions of this work are as follows:

1. The growth front of banded hedrites in thin molten iPS films develops in three dimensions simultaneously, forward, tangentially, and in the thickness direction.
2. The leading edges of the crystals comprising the growth front are at approximately the same radial position, forming a nearly vertical growth face.
3. The basal crystal layer propagates at a constant velocity.
4. The molten pool immediately in front of the growth face is much lower than both the front and the far-field melt, indicating that the supply of material from the far-field melt cannot keep pace with the demand of new material by the propagating stack of crystals. Further evidence for this behavior is found in the decreasing kinetics of the motion of the base of the molten trough.
5. Since the propagating growth front is much higher than the adjacent melt, it must be covered with a thin layer of molten polymer. The ability of molten polymer to climb the steep growth front is presumably capillarity-driven.
6. As the melt becomes more and more depleted, lamellar growth stops, sequentially from the top lamella downward, forming a sloping front from top to bottom.
7. As the layers stop growing, the demand for polymer at the front decreases and the molten pool available for crystal growth is replenished, allowing new lamellar layers to develop, via a giant screw dislocation mechanism.

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