The Birth of an Embryo and Development of the Founding Lamella of Spherulites As Observed by Atomic Force Microscopy

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Introduction. Spherulites are common crystalline structures observed in polymer systems. Many studies have been performed to investigate the detailed structure and formation mechanisms. Phillips and Edwards studied the spherulitic morphology and growth kinetics of *cis*-polyisoprene under different pressures with transmission electron microscopy (TEM).[1,2] Heterogeneous and homogeneous nucleations were both observed.[2] Bassett et al. investigated the spherulite lamellar morphology of melt-crystallized polymers using optical microscopy (OM) and TEM. They proposed that dominant lamellar first grew into the melt to form a skeleton of a spherulite by splaying and branching, interdominant lamellae regions were filled with subsidiary lamellae, and branching occurred mainly through giant screw dislocations.

Atomic force microscopy (AFM) provides a powerful technique to investigate spherulitic morphology and growth kinetics of various semicrystalline polymers because of its high resolution, easy sample preparation method, and ability to image dynamic processes.[5−12] A detailed spherulitic growth process was clearly described by Li et al.[6,7] However, the initial stages of formation of a lamella were still not visualized in situ. In this study, the formation of a primary nucleus and its growth to a lamellar sheaf were observed in real time using AFM at room temperature.

Experimental Section. A sample of poly(bisphenol A octane ether) (BA-C8) was synthesized by condensation polymerization of bisphenol A and 1,8-dibromoctane.[13] The glass transition temperature, melting point, number-average molecular weight, and polydispersity indexes of the polymer were measured to be 10.5 °C, 83.3 °C, 13 750 g/mol, and 2.36, respectively. Thin BA-C8 polymer films were prepared by spin-coating a 30 mg mL^{-1} polymer−chloroform solution onto silicon wafers ($\sim$10 mm $\times$ 10 mm) at 4000 rpm. The samples were dried in a vacuum at room temperature for 30 min. The thickness of the amorphous BA-C8 films was estimated to be approximately 300 nm by a profilometer.

Tapping-mode AFM images were obtained at ambient conditions using a NanoScope III MultiMode AFM (Digital Instruments). Si tips with a resonance frequency of approximately 300 kHz and a spring constant of about 40 N m^{-1} were used, and the scan rate was 0.805 Hz. The scanning density was 512 lines/frame. A set point amplitude ratio of 0.8 was used.

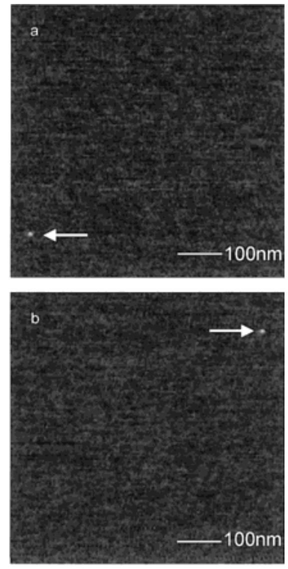

Figure 1. The data scale is 30 deg. (a) An embryo. (b) The embryo in (a) disappeared, and a new embryo appeared at a different location.

Results and Discussion. Figure 1 shows two continuous AFM phase images of the same area. The time interval between the two images was 10.6 min, and the image size was 600 nm. It can be seen clearly that an embryo appeared as a 10 nm diameter dot in the left-hand lower corner of Figure 1a. After 10.6 min, this embryo could not be found (Figure 1b); however, a new embryo appeared in the upper right-hand corner of the image. These results demonstrate that embryos below a certain critical size can disintegrate, as predicted by thermodynamics. However, the accurate measurement of this critical size could not be obtained with AFM.

Studies have been performed to investigate the nucleation induced by AFM tips during the crystallization experiments.[8−10,14] Pearce and Vansco investigated the possibility of tip-induced nucleation during crystallization of poly(ethylene oxide) (PEO) near the melting point.[8,9] They concluded that the tip did not induce nucleation. A similar conclusion was made by Godovsky and Magonov during their study of PE crystallization using AFM.[10] However, Beekmans found that tip-induced nucleation was possible in the study of crystallization of poly(ϵ-caprolactone) (PCL).[14] The difference in the behavior between PEO and PCL was attributed to the difference in the shear force. High shear forces will cause chain alignment at the surface of the melt. It is important to point out that in the studies of PCL[14] and PEO[8,9] the contact mode, which in general produces high shear forces during scanning, was used at temperatures near the melting points of the polymers. In the current study, the tapping mode was used, and the experiments were performed at a high degree of supercooling ($\Delta T \sim 60$ °C). During the experiments, the amorphous areas around the growing crystallites were scanned for a long time without detection of nucleation.

Once an embryo grew larger than the critical size as predicted by thermodynamics, the embryo could grow

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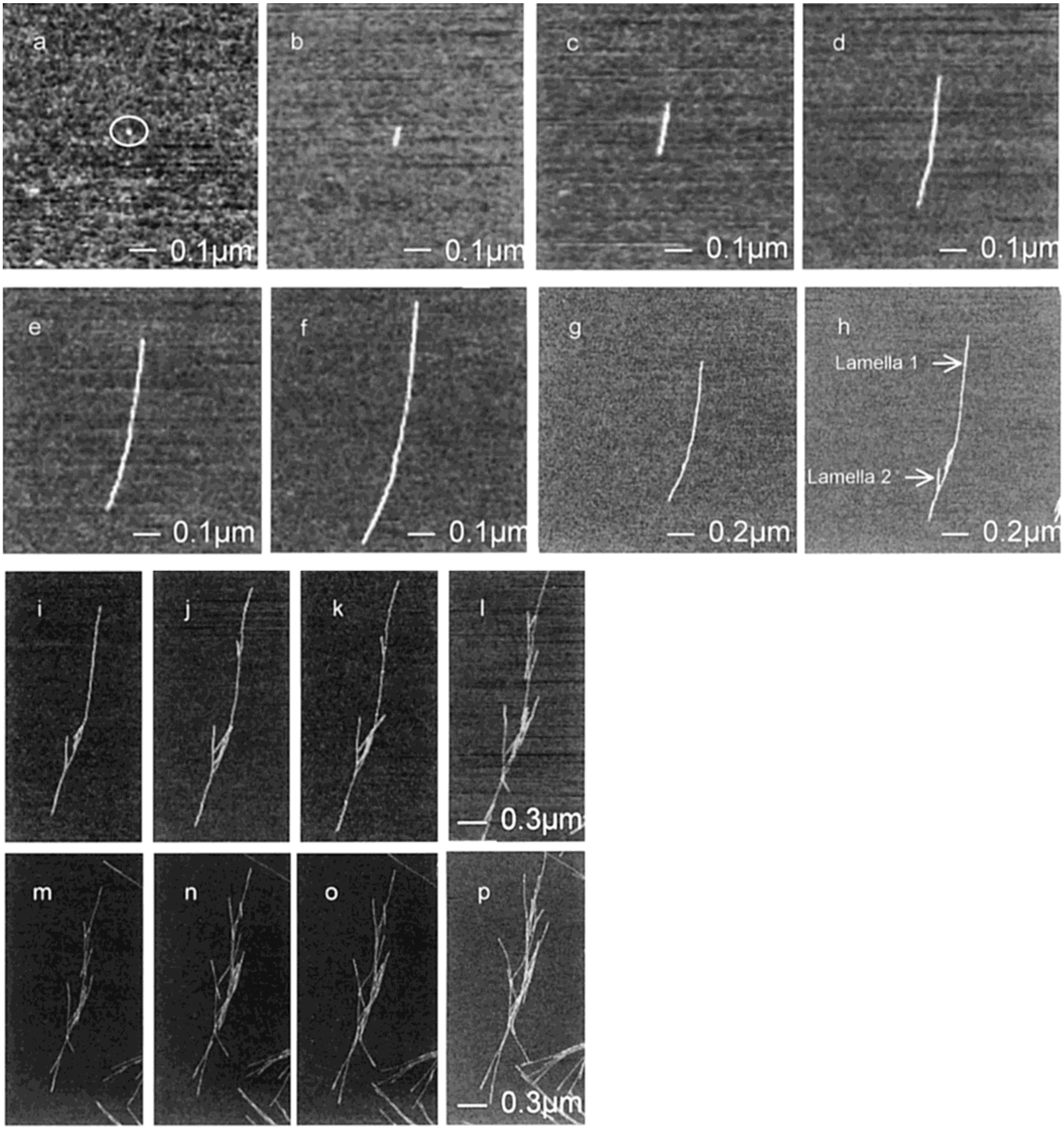

Figure 2. The data scale is 30 deg. (a) An embryo. (b) A short lamella (founding lamella) developed from the embryo shown in (a). (c−f) The growth of the founding lamella. (g−p) Branching and splaying apart of the subsidiary lamellae.

continuously at its two ends and develop into a single lamella, as shown in a series of images (cf. Figure 2). We can see an embryo as a round dot in the center of the image in Figure 2a and the development of the embryo into a short lamella of approximately 60 nm in length in Figure 2b. The appearance of this short lamella in Figure 2b at the same location as the round dot in Figure 2a provides solid evidence that the dot is an embryo. After about 60 min, as shown in Figure 2c−f, this lamella had grown in length to approximately 1 μm. We name this lamella, which originates from an embryo, as the founding lamella because all other lamellae that are present in the spherulite are its descendants.

The founding lamella grew into a lamellar sheaf through branching and splaying. In our earlier work,[7] we observed on a similar polymer film that a growing lamella might branch at about 0.5 μm behind its growing tip. It is very interesting to find that the founding lamella did not branch until it grew to a fairly long length of about 1 μm (Figure 2f,g). The results suggest that during this period the growth rate of the founding lamella is much faster than the rate of branching. Branching was found to occur on both folding surfaces of the founding lamella (cf. Figure 2k).

Bassett was the first to propose that branching occurs at screw locations.[3,4] In our earlier paper,[7] we proposed that branching is caused by secondary nucleation which

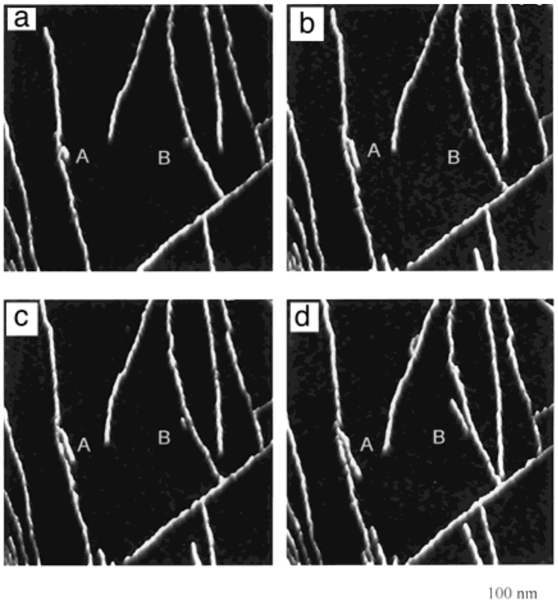

Figure 3. A sequence of AFM images showing the formation and growth of induced nuclei. The time interval between each consecutive image is approximately 5.8 min.

is induced by trapping one end of a polymer chain in a lamella. The reduced mobility of the trapped segments induces the formation of a nucleus near the parent lamella. Our choice of the term secondary nucleation to describe this phenomenon overlaps with the term generally used to describe the nucleation of stems onto a growing surface of a propagating lamella. Thus, we would like to rename this phenomenon induced nucleation. The nucleus formed in this process is the induced nucleus. Because some of the induced nuclei were formed at a certain distance away from the parental lamellae, we believe screw dislocations may not be the cause of branching unless the screw dislocations were formed at the subsurface level and grew to the surface. Figure 3 shows the formation and the growth of two induced nuclei (marked by A and B). These images clearly show the formation of induced nuclei at some distances away from the parent lamellae. The newly formed nuclei grew and became subsidiary lamellae. Of course, on the basis of the current results, we cannot determine unequivocally the cause of the branching observed in this system. Therefore, we propose that there are at least three possible causes for branching: (1) screw dislocations as suggested by Bassett, (2) induced nucleation as a result of a trapped polymer chain in the parent lamella, and (3) the stresses induced by the crystallization of a parent lamella in its nearby regions.

Branching also occurred after the subsidiary lamellae grew to a certain length (Figure 2m,n). In this way, an embryo gradually developed into a lamellar sheaf (Figure 2p). A spherulite was generated after extensive branching and splaying apart of the subsidiary lamellae.[7] The lamellar splaying is clearly seen in Figure 2k–p.

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