Real-Time AFM Study of Lamellar Growth of Semi-Crystalline Polymers

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Summary: Atomic force microscopy (AFM) has been used to study the lamellar development during the crystallization and melting processes of poly(bisphenol A-co-alkyl ether) (BA-Cn) films. High-resolution and real-time AFM phase imaging enables us to observe the detailed growth process of the lamellae. At the early stage of the lamellar growth, embryos appeared firstly and some disappeared on the film surface after a period of time. The stable embryo developed into a single lamella. Then the lamella developed into a lamellar sheaf through branching and splaying. Our results revealed that the branches of the lamellae were formed by induced nucleation and it was also dependent on the crystallization temperature. Real-time AFM study of the melting, recrystallization and remelting processes of lamellae indicated that the thermal stability of different segments of a single lamella is different and that the thermal stability of the different lamellae is also different even if they develop at the same annealing temperature. The orientation and the development of the lamellae at the characteristic eyes and boundaries of the spherulites are observed in details.

Introduction

Spherulites are common crystalline structures observed not only in polymers but also in a large variety of inorganic substances. In the case of polymers, the detailed structure and formation mechanisms of spherulites have been studied using polarized optical microscopy (POM) and transmission electron microscopy (TEM)[1,2]. It is generally accepted that the three-dimensional geometry of spherulites develops from a stack of lamellae. During the growth process, the stacked lamellae splay apart continually and branch occasionally. Not until were AFM used to observe the growth process of spherulites, this process is hypothetical because the description is not based on direct observations of the formation of spherulites[3,4].

The invention of atomic force microscopy (AFM) made it possible to observe the lamellar growth of a semi-crystalline polymer in real time. The development of tapping-mode AFM (TM-AFM) has made it easier to map soft, adhesive and fragile samples. Many studies have been performed to interpret the height and phase images recorded by TM-AFM. Results

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clearly indicate that phase images can provide enhanced contrast on heterogeneous surfaces. TM-AFM has been shown to be a powerful tool to study the surfaces of polymer blends, copolymers, and semicrystalline polymers. Most recently, hot-stage atomic force microscopy has been applied to image crystallization and melting of polymers in real time.

By utilizing the advantages of AFM, spherulites and lamellae of various semi-crystalline polymers have been investigated[5-9]. It was found by Vancso et al. that polypropylene lamellar thickness and hedritic morphology were identical to the values in the literature as revealed by other techniques. The growth rate of a spherulite and the internal lamellar arrangement of a poly(hydroxy-butyrate-*co*-valerate) copolymer have been determined by Barham and colleagues using TM-AFM[7]. Their results indicate that the overall gross growing front of a spherulite propagated at a constant rate, but the growth rate of internal lamellae were variable. Poly(bisphenol A-co-alkyl ether)s (BA-Cn) are the ideal candidates to investigate the fundamental issues associated with the development of lamellae and spherulites by real-time AFM due to their slow crystallization rate at room temperature and relatively low melting temperatures (about 90 ^{o}C). Here, we summarized our results of real-time AFM imaging of the lamellar growth, branches and melting of the BA-Cn spherulites. We believe that the studies on the detailed lamellar structure and development in this paper will provide a better understanding of crystallization mechanisms of polymers.

Experiment

The BA-Cn polymers were prepared as described previously[3, 4]. The thin films for AFM observations were prepared by spin coating a 20 ~ 40 mgml^{-1} polymer-chloroform solution at 3000 rpm onto silicon wafer surface or freshly cleaved surface of mica. The samples were dried in a vacuum at room temperature for 30 minutes. The thickness of the amorphous BA-Cn films was estimated to be 300 to 400 nm by a profilometer.

Real-time AFM measurements were carried out using the tapping-mode AFM (Digital Instrument Nanoscope IIIA) equipped with a hot stage. Both height and phase images were recorded simultaneously using the retrace signal. Si tips with a resonance frequency of approximately 300 kHz and a spring constant of about 40 Nm^{-1} were used, and the scan rate and the scanning density were 0.5-1 Hz and 512 lines/frame, respectively. A set point amplitude ratio was around 0.8.

Results and Discussion

Embryos and Primary Nuclei

The development of a stable embryo into a single lamella can be clearly observed, as shown in a series of AFM phase images (c.f., Figure 1), where polymer of BA-C8 crystallized at 22 °C. Lamellar embryos, as the fine dots with a dimension smaller than 10 nm, appeared and disappeared on the surface of an initially amorphous polymer film during scanning (Figures 1a and 1b). Figure 1a shows the presence of two embryos. In Figure 1b, which was obtained approximately 8.7 min after the image shown in Figure 1a, one of the embryos disappeared. As predicted by thermodynamics, embryos smaller than a critical dimension are unstable and may not ultimately grow. The stable embryo, a primary nucleus, can grow along the length of the lamella at both ends (Figure 1c, d). We name this lamella, which originates from a primary nucleus, as the founding lamella because all other lamellae presented in the spherulite are its descendants.

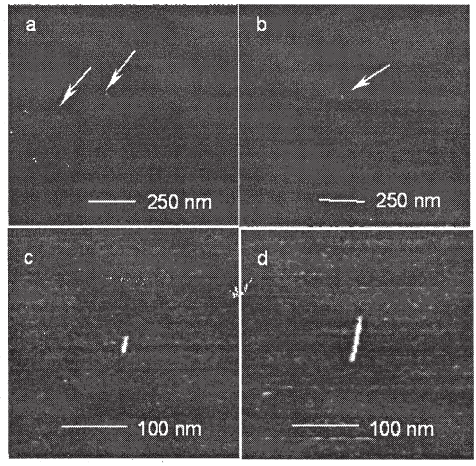

Figure 1 The formation of embryos and the growth of a stable embryo to single lamellae

In our experiments, the dimension of primary nuclei was measured to be smaller than 10 nm, however, the critical size of a stable embryo could not be accurately measured with AFM.

Induced Nuclei and Lamellar Branches

After the founding lamella grew to a certain length, it would develop into a lamellar sheaf through extensive branching and splaying. Usually, the branching of the parent lamellae appeared at some distance behind its growing tip. The effect of crystallization temperature on

the formation of lamellar branches was studied using AFM with a hot stage. The branching of parent lamellae at different temperatures (16, 22 and 28 °C, respectively) is presented in Figure 2. It can be clearly observed that crystallization temperature strongly influenced the formation of lamellar branches. At the lower temperature, such as 16 and 22 °C as shown in Figures 2a-d, there was no branching as the lamellae grew to about 0.5 μm in length. However, branching appeared before the parent lamellae grew to 0.5 μm at 28 °C. This result suggests that the branching of parent lamellae can occur easier at the higher crystallization temperature. However, the rate of branching was found to decrease at temperatures near the melting point of the polymer,

In our earlier papers[3, 4], we proposed that branching of a parent lamella is initiated by induced nucleation, which is caused by trapping one end of a polymer chain in the parent lamella. The reduced mobility and the accumulation of the stress of the trapped chain segments induce the formation of a nucleus near the parent lamella. The induced lamellar embryos could also appear and disappear. This result suggests that the screw dislocation at the parent lamella does not cause the formation of an induced nucleus. Induced nuclei did not grow only in one direction; they also could grow in the opposite direction (Figure 2f). In this way, the parent lamellae gradually branch and splay apart to develop into a lamellar sheaf[3].

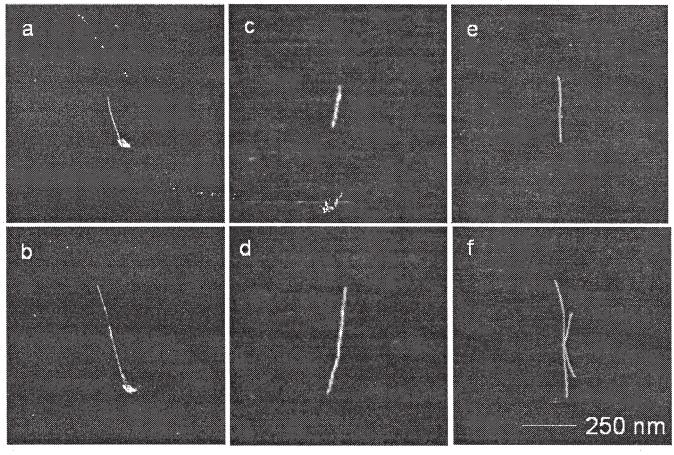

Figure 2 AFM phase images of the lamellae grown at a-b: 16 °C c-d: 22 °C and e-f: 28 °C

Lamellae at the Eyes of Spherulites

Spherulites with two characteristic eyes at the center can be clearly seen on the BA-C8 films, as shown in Figure 3. The top column displays the AFM topographic images and the bottom

column shows the AFM phase images. The data scales of the AFM height images are 20 nm. The time interval between each consecutive image of Figures 3a-c is about 15 minutes. From the AFM height images, it is clear that the height of the eye area is different from the other areas of the film surface. This result suggests that the lamellar structure of the eyes may also be different from that in other parts of the spherulite. However, the lamellae at the eyes, as labeled by "e" in the AFM phase images, were formed at a relatively late stage of the spherulitic growth. Comparing the AFM height and phase images of Figure 3a, the height changes of the eyes can be seen clearly, but the lamellae of the eyes have not been formed yet. During the growth of the spherulite, the "flat-on" lamellae were formed at the area of the eyes. The growth of "flat-on" lamellae at the eyes was limited and stopped by surrounding "edge-on" lamellae. The boundaries between the "flat-on" and the "edge-on" lamellae at the eyes can also be identified. This observation suggests that the chain segments at the boundaries of the eyes are difficult to fit perfectly into the different orientations of the "flat-on" and "edge-on" lamellae.

The detailed lamellar structures of the eyes show that the central area of the eyes is lower than the boundary areas (Figure 3d). The layer structure of the "flat-on" lamellae surrounded by the "edge-on" lamellae can be seen in the AFM phase images. However, the formation mechanism of the eyes at the center of a spherulite is not fully understood. For example, the height changes within the eye areas occurred at the initial stages of the spherulitic growth, but the layer structures of the "flat-on" lamellae within the eye areas were formed at a later stage.

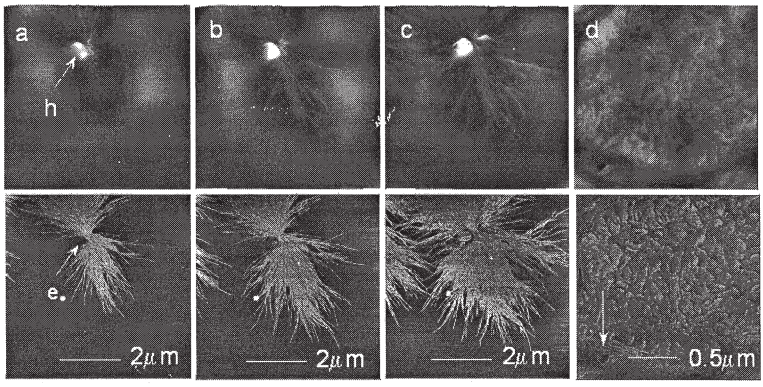

Figure 3 A series of AFM images showing the formation of the eyes at the center of a spherulite

Lamellae at the Boundaries of Spherulites

It is well known that lamellae of spherulites can penetrate into and impinge each other during the later stages of crystallization. However, when lamellae impinge each other at the boundaries of spherulites more defects are created, resulting in less constriction of the film. Therefore, the boundaries are higher than the other parts of spherulites. Figure 4 shows a series of AFM phase images of the lamellar propagation at the boundaries of spherulites. When the lamellae from different spherulites grew closer to each other, the lamellae that growing in opposite directions could penetrate each other, as indicated by the arrows in Figures 4a and 4b. The penetrated lamellar sheaf, which consisted of a stack of parallel lamellae from different spherulites, formed a "lamellar bridge" connecting the spherulites. Many "lamellar bridges" could be formed at the boundaries of the spherulites, as shown in Figures 4c and 4d. However, when the lamellae from different spherulites grew in different directions, they met and stopped one other at the boundaries of the spherulites producing many defects, as indicated by arrows in Figures 4e and 4f.

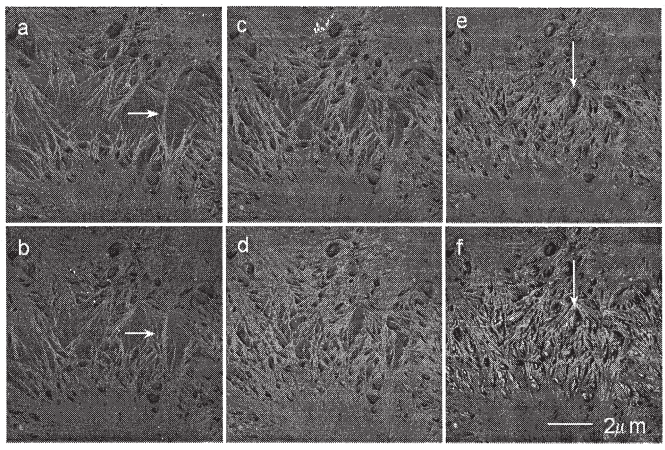

Figure 4 A series of AFM phase images showing lamellae propagation at the boundaries of spherulites

Due to the penetration and impinging of the growing "edge-on" lamellae at the boundaries, some areas in these regions were divided into many small "island-like" areas with various shapes, which contained amorphous materials. The size of these small islands of amorphous phase decreased with the propagation of the lamellae at the boundaries, as indicated by the arrows shown in Figure 4. It is also possible that the polymer crystals inside the small areas

were formed by the induced nucleation of the "edge-on" lamellae around the small areas. Hence, the boundary areas among the spherulites of the BA-C8 polymer thin films consisted of amorphous polymer and various orientations of lamellae, such as "edge-on", "flat-on" and "tilt" orientations.

Melting and Recrystallization of Lamellae

The melting process, which usually is accompanied by lamellar thickening, perfection and recrystallization, has been extensively studied by differential scanning calorimetry (DSC), wide angle x-ray scattering (WAXS) and small angle x-ray scattering (SAXS). Recently, AFM with a hot stage has been applied to image the crystallization and melting processes of polymers in real time.

Figure 5 presented a series of images of the melting and recrystallization and remelting processes of lamellae. All temperature measurements were accurate to ± 1°C. Figure 5a is the image of the lamellae crystallized at 35 °C. The lamellae with edge-on orientation can be clearly observed. All lamellae are uniform in appearance. As seen in Figure 5b, before the temperature was increased to 80 °C there was no obvious sign of melting. When the annealing temperature was increased to 80°C, (c.f., Figure 5c), some parts of the lamellae melted. With an increase of the annealing time, some of the broken lamellar segments joined together with the formation of new lamellar segments (c.f., Figures 5d). Different lamellae showed different

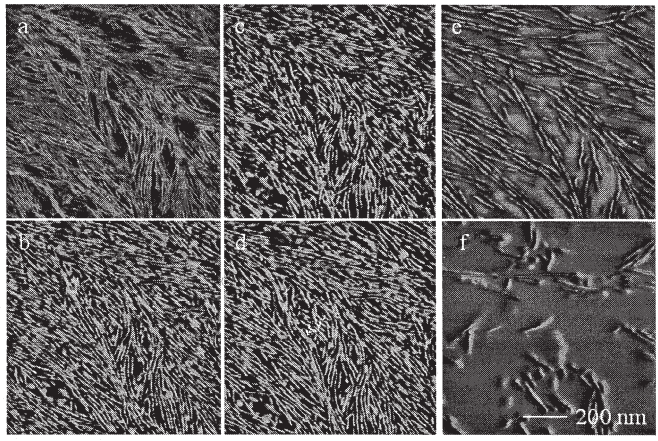

Figure 5 AFM phase images of the lamellar structure of the BA-C10 polymer thin film annealing at a: 35 °C; b: 78 °C; c: 80°C; d: 80 °C, about 9 min after c; e: about 9 min at 90°C; and f: about 9 min at 92 °C

melting and recrystallization behaviors. These results suggest that the stability and the degree of perfection of the lamellar crystals are very different in different lamellae and even in the different locations of one lamella. When the annealing temperature was continually increased, more and more lamellae melted and the broken segments did not join together again (Figure 5e,f). The lamellar thicken also can be seen clearly (Figure 5e).

Conclusion

In summary, our *in-situ* AFM investigations revealed some important features of the crystallization process of polymers, such as, embryos appeared and disappeared when they were smaller than a certain critical size. A stable embryo grew into a founding lamella. The branching of parent lamellae was a result of induced nucleation and then the induced nuclei developed into daughter lamellae or subsidiary lamellae. Crystallization temperature has strong influence on the rate of lamellar branching. When lamellae were heated to near their melting temperature, melting, re-crystallization and remelting occurred simultaneously. The areas of the two characteristic eyes at the center of a spherulite and boundaries among the spherulites were higher than the other areas of the semi-crystalline film surfaces. The "flat-on" lamellae inside the eyes could be observed clearly using AFM phase imaging. There were many "lamellar bridges" formed by "edge-on" lamellar sheaves at the spherulitic boundaries. This "lamellar bridges" should have a major contribution to the mechanical properties of the semi-crystalline polymers.

Acknowledgements

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