A Direct Observation of the Formation of Nuclei and the Development of Lamellae in Polymer Spherulites

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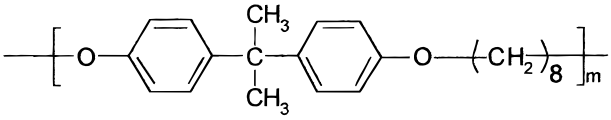
Since polymer spherulites were observed using optical microscopy and single polymer crystals were prepared from solution,[1,2] the internal structure of polymer spherulites has been investigated widely with electron microscopy.[3−9] For most crystalline polymers, it is generally accepted that spherulites are developed from a single crystal through unidirectional growth, and the spherical shape is attained through continuous splaying apart and occasional branching of lamellae,[5] though there are ongoing debates concerning the details of the branching in the literature. More recently, atomic force microscopy (AFM) has been utilized to study the organization of spherulites and the crystallization process of polymers.[10,11]

A copolymer, poly(bisphenol A-*co*-octane),[12] was synthesized with the following structure:



This polymer is attractive for analyses of the formation of nuclei and growth of lamellae because its glass transition temperature is close to room temperature, and it crystallizes at room temperature at a rate that allows imaging of the crystallization process by AFM without a hot stage. The glass transition temperature, melting point, and number-average molecular weight for this polymer were respectively measured to be 6.9 °C, 83.5 °C, and 5.7×10^3 g/mol. The crystallized sample exhibited several X-ray diffraction peaks at $2\theta = 5.6°$, 15.2°, 18.6°, and 19.8°. A thin film of about 300 nm was prepared by spin-coating the polymer solution on a silicon chip, and the crystallization process was observed directly under tapping-mode AFM phase imaging.

Embryos of the lamellae, as fine dots, with a dimension smaller than 10 nm, appeared and disappeared on the surface of the initially amorphous polymer film during scanning (Figure 1a,b). 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. We believe that this is the first experimental evidence in a polymer to show that, as predicted by thermodynamics, embryos smaller than a critical dimension are unstable and may not ultimately grow. The initial nucleating lamella grows along the length of the lamella at both ends (Figure 1c). During the growth stage, it breeds more lamellae (Figure 1d). When their lengths are longer than 0.5−1.0 μm, the lamellae begin to form branches (Figure 1e), and some lamellae splay apart from each other (Figure 1f). As a result of continual splaying and branching of the lamellae, the initial lamellae gradually develop into a lamella sheaf and a spherulite skeleton (Figure 1g,h). We believe that all lamellae except at the "eye" of the spherulites are viewed edge-on because the "width" (this dimension is likely to be the thickness of the lamellae) of the lamellae, as viewed in this direction, is approximately 10 nm.

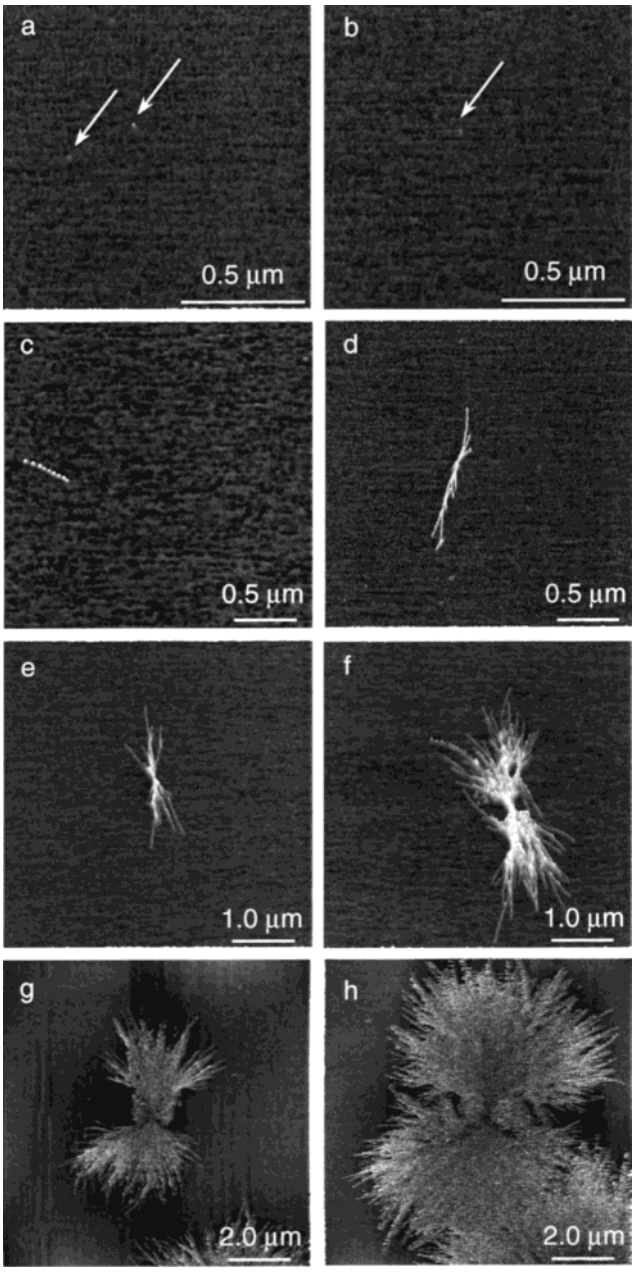


Figure 1. Nucleation, growth, and formation of a spherulite: (a) formation of lamella embryos; (b) disintegration of one of the lamella embryos; (c) growth of a lamella embryo; (d) breeding of more lamellae from the initial nucleating lamella; (e) branching of the growing lamellae; (f) splaying apart of the lamellae; (g) a lamella sheaf; and (h) a spherulite skeleton.

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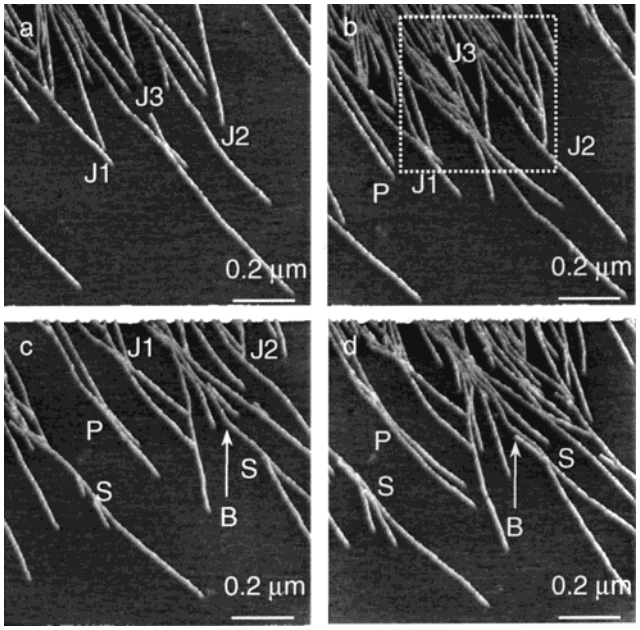

Figure 2. A series of phase images of the growing front of a spherulite in a consecutive time sequence. The time interval between the consecutive images was about 8.7 min. J1 and J2 = joining of a growing lamella with an existing lamella. J3 = joining of opposite growing lamellae. P = joining of parallel lamellae. S = branching of lamellae induced by secondary nucleation. B = bending of lamellae.

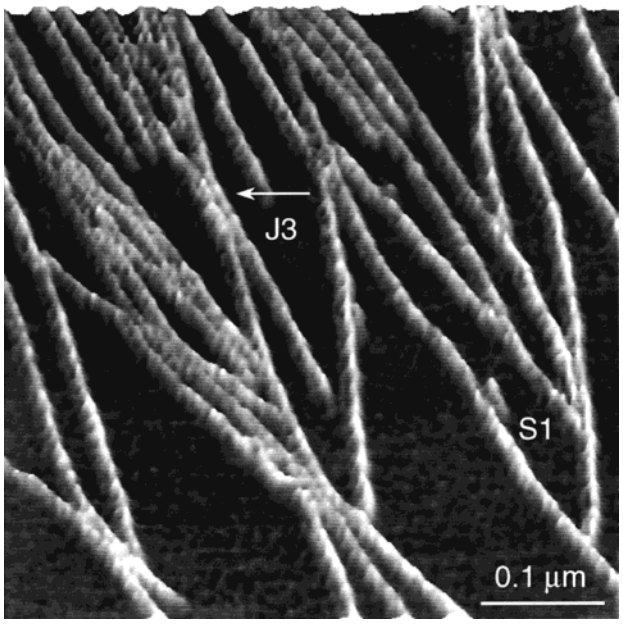

Figure 3. A magnified image of the area around J3 in Figure 2b, showing the joining of two opposite growing lamellae. J3 = joining of opposite growing lamellae. S1 = separation of a daughter lamella embryo and the parent lamella.

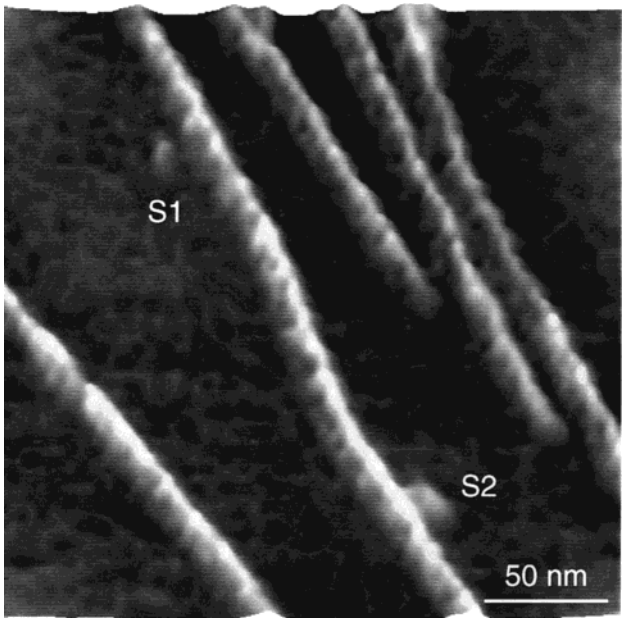

Figure 4. An image showing the separation (S1) and the joining (S2) of a daughter lamella embryo and the parent lamella.

It has been suggested that a polymer spherulite develops from a single lamella through unidirectional growth and continuous branching and splaying apart.[5,8] Our examination of the growth of a lamella embryo into a mature spherulite provides direct evidence to support this view. Furthermore, our experiments revealed that the periphery of the developing spherulites is not as smooth as that observed under optical microscopy. The growth front of the spherulites looks like a hedgehog, as shown in Figure 1h, and the growth rate of an individual lamella varies with time and location.

The growth front of a spherulite was examined at a higher magnification. Figure 2 shows a series of AFM phase images of a growth front in a consecutive time sequence. The time interval between the consecutive images is about 8.7 min. Branching of the lamellae is obvious at the growth front, as shown in Figure 2a,b. It normally occurs approximately 0.5 μm behind the growth front of the parent lamellae (S in Figure 2c). Evidently, the branching is initiated by secondary nucleation of the parent lamellae. High magnification reveals that the induced nuclei are separated from the parent lamellae (S1 in Figures 3 and 4); sometimes they are joined to the parent lamellae (S2 in Figure 4). We have found that there is, indeed, no observable difference in the thickness between the parent and daughter lamellae. In fact, most of the dominant lamellae may be considered as daughter lamellae because their nuclei consist of only a few lamellae immediately after the stable nuclei are formed (Figure 1d). The daughter lamellae inevitably become the parent lamellae and then induce secondary nucleation, which explains why lamellae grow in bundles in a spherulite.

The induced lamella embryos not only grow in the same forward direction as their parent lamellae, but most of them grew in the backward direction after the forward growth reached about a certain length (0.1−0.5 μm, S in Figure 2d). The backward growing may be stopped by another parent lamella. When a forward-growing lamella meets a backward-growing counterpart (J3 in Figure 2a), they may join together (J3 in Figure 2b). Figure 3 is a magnified image of the area around J3 in Figure 2b, showing the joining of two opposite growing lamellae. Lamellae joining does occur not only in the opposite growing lamellae but also in already existing lamellae (J1 and J2 in Figure 2a,b). One of the most interesting phenomena that we observed is the growth of two parallel lamellae. These two lamellae propagated almost parallel to one another at first (P in Figure 2b). Then, the two lamellae grew closer to each other and finally joined together (P in Figure 2c). We posit that polymer chains that were trapped between the parallel lamellae caused the joining of these two

lamellae. The tension exerted on these polymer chains as the chains crystallized in the lamellae pulled the two lamellae together. After the contact, the growth of the lamellae did not stop completely but proceeded at an extremely slow rate. The growth rate resumed at a normal pace after the two lamellae propagated separately (P in Figure 2c,d). A bend of lamellae was also observed during the lamella growth (B in Figure 2c,d).

Although the process of organizing the random polymer coils into a spherulite in bulk may be more complicated than that in a thin film, the above AFM observations can provide very valuable information on the development of the random polymer coils into spherulites. We believe that the nucleation we observed was homogeneous nucleation. Under supercooling, an ordered embryo of a lamella is generated in a random coil by adjusting the conformation of the chain segments through molecular thermal motion. Some of the embryos may disintegrate with the thermal motion, but some may survive and develop into spherulites. When the embryos are large enough, they become stable and grow continually. The growth of lamellae may be such that the nearby chain segments adjust their conformations and fit themselves into the lattice of the existing lamellae.

There is certainly some mass migration during crystallization because the chain segments are compacted more densely in the lamellae. However, long distance migration of the polymer chains is not favorable because of high viscosity and physical entanglements. Consequently, the two faces ($a-b$ planes) of the lamellae will consist of a high concentration of loose loops or protruding cilia of polymer chains. When one end of these polymer chains is trapped in the lamellae, the mobility of these polymer chains is reduced. Hence, they have more chances to arrange in order and form lamella embryos close to the parent lamellae; i.e., there is an induced secondary nucleation. In this way the initial nucleating lamellae branch and develop into a lamella sheaf and finally into a spherulite.

Because it will take some time for the chain segments to change orientation or adjust conformation, the induced nuclei are always produced after the parent lamellae have propagated for a certain distance (about 0.5 μm). This also explains why when two growing lamellae meet, their growth rates could be significantly slowed. After the secondary nuclei have been formed, they may grow in the forward and/or backward direction, depending on the lattice orientation and the availability of the crystallizable materials. In the backward direction, the supply of the crystallizable materials is limited because most of the polymer chains are trapped by the adjacent parent lamellae. Hence, the organization of the polymer chains into the lamellae will take more time, which leads to slower growth rates in the backward direction.

Even for the protruding lamellae, the original orientation of chain segments near the tips of the growing lamellae may be different at various locations. They may take different periods of time to adjust their conformations to fit themselves into the lattice of the lamella. Therefore, the lamellae cannot propagate at a constant rate. When two lamellae propagate parallel and very close to each other, their growth rates and directions can be affected by the orientation of chain segments near the tip of the growing lamellae. We believe that the parallel lamellae are pulled together by the polymer chains trapped in the tips of the lamellae.

A newly formed lamella usually does not assume a perfect order. The defects will diffuse out of the lamella continually even before the lamella has formed completely. If a daughter lamella has the same lattice orientation as its parent lamella and the materials in the gap between them do not contain other structural defects, the daughter lamella can join with the parent lamella. In the same way, the growing lamellae can join with already existing ones, provided that the majority of the mismatched structures are removed from their growth paths. However, we should point out that the joint between the lamellae is not defect-free. It is highly possible that defects in the joint are more severe than in the lamellae themselves.

We have shown that AFM can provide detailed information on the formation of the nuclei and the growth of the lamellae. We believe that we have produced the first experimental data that show the appearance and disappearance of embryos, as predicted by thermodynamics. In addition, our results have shown that branching is initiated by secondary nucleation of the parent lamellae, and lamellae can join with each other and branch in many different ways that have never been observed by any other techniques.

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