Direct Observation of Polyethylene Shish-Kebab Crystallization Using in-Situ Atomic Force Microscopy

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Introduction. The crystallization of polymers into oriented structures, caused by extensional flow fields in the melt, has been the subject of extensive study for many years.[1−4] Recent advances in atomic force microscopy (AFM) have allowed samples to be heated and imaged in situ, in real time, with nanometer resolution. This has already been applied to polymer crystallization,[5−8] following earlier work in our laboratory on the room temperature crystallization of poly(hydroxybutyrate-*co*-valerate) (PHB/V)[9] using AFM. To date, all the AFM studies have dealt with quiescent melts, in which spherulitic growth dominates. However, it is well-known that under normal polymer processing conditions the melt is submitted to severe shear and extensional flow fields, frequently resulting in oriented microstructures.

In this communication we present our preliminary AFM results imaging the crystallization of preprocessed melts, revealing directly, for the first time, the lamellar scale growth as it occurs from the oriented molecular backbone. From observations such as these, significant new insights into the mechanisms underlying the formation of morphologies that occur during industrial polymer processing can be gained. Here our intention is to place this new observation on the map, leaving a fuller presentation and discussion of the work to a future publication.

Experimental Details. A sharp polyethylene fraction was used, supplied by the National Bureau of Standards, M_w 119 600, M_w/M_n 1.19. A 1% suspension of the polymer in *p*-xylene was prepared by dissolving for 20 min at 120 °C and quenching to room temperature. A drop of the suspension was then placed on a glass coverslip on a hot bench at 150 °C and held in the melt for 2 min. The resulting thin film was then quenched to room temperature. This film was remelted on a Linkam hot stage at 160 °C for 2 min and cooled to 145 °C. A razor blade was dragged across the glass coverslip in order to cause oriented crystallization in the melt. When this process was observed using an optical microscope, it was clear that the melt started to crystallize as soon as the blade was brought into contact with the melt, due to the drop in temperature that this caused. A highly oriented birefringent area was formed where the razor blade had sheared and extended the melt. As soon as the razor blade was removed, the unoriented regions remelted, but the high birefringence remained in the oriented part of the film.

The Linkam was cooled to 135 °C and then moved into position under the scan tube of a Digital Instruments D3100 AFM. To protect the piezoelectric crystal from the heat, a sheet of aluminum foil and a sheet of Kapton were placed between the scan tube and the heater, the cantilever projecting through a small hole in these protective sheets. The AFM was operated in Tapping mode, and phase, height, and amplitude images were collected simultaneously. Imaging conditions were maintained so as to just allow the surface to be tracked while maintaining the fast scan rates necessary to follow the process. All images were taken at 256 × 256 pixels.

Owing to the proximity of the (unheated) cantilever and the heat shield to the sample surface, a temperature difference of ∼7 °C was estimated between the nominal value given by the Linkam and that of the sample surface. However, the sample was being cooled, and we have not been able to accurately calibrate the Linkam−AFM system on cooling due to slight differences between each experimental setup. The temperatures quoted in the rest of this paper are those given on the Linkam

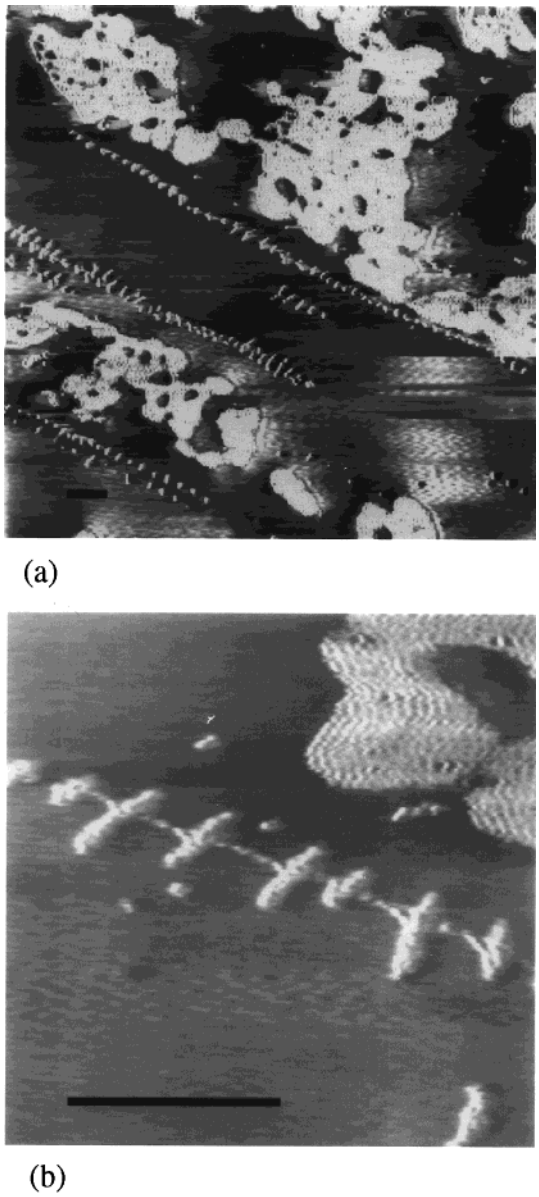

Figure 1. Two AFM phase images showing dormant shish-kebab crystals at a nominal temperature of 135 °C. Black to white represents a change in phase angle of 30°. (b) is a ×1.27 software zoom. Scale bars represent 300 nm.

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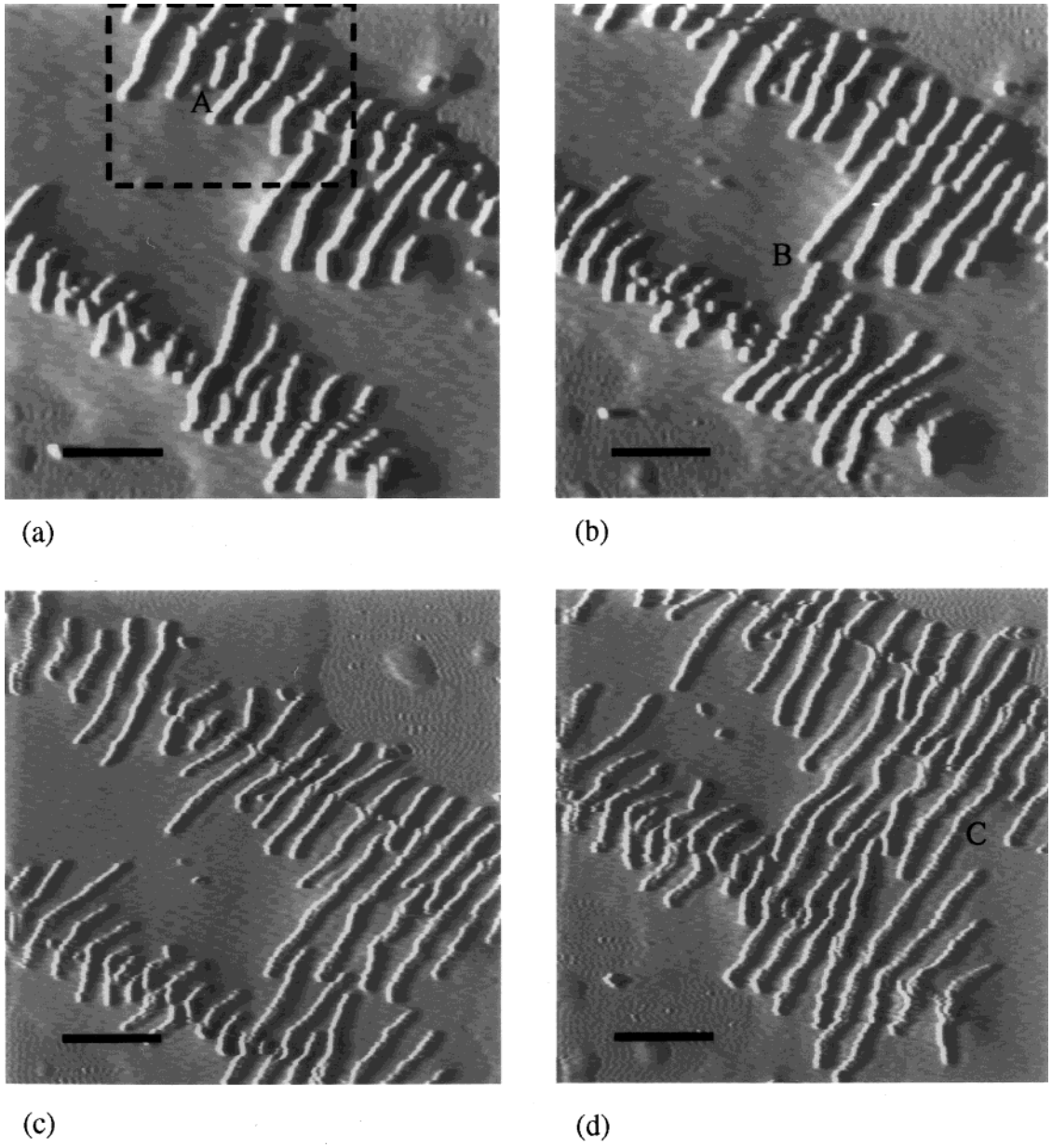

Figure 2. A series of AFM amplitude images showing the growth of lamellae from the oriented backbone. (a) and (b) are ×2 software zooms. (a) Taken at 132.5 °C; (b) taken at 132.3 °C; (c) taken at 132 °C; (d) taken at 131 °C. The scale bars represent 300 nm.

and are therefore ~7° higher than the true temperature.

Initially, the sample was imaged at 135 °C and then cooled at 0.5 °C/min to a final temperature of 128 °C, imaging continuously and held every 0.5 °C for various lengths of time in order to observe the crystallization process.

Results and Discussion. Figure 1a shows a phase image of part of the polyethylene film. The large bright areas (corresponding to high phase angle) are the glass substrate, while the dark areas are the molten polymer. From the height image the molten polymer is ~50 nm thick. The rows of small bright ellipses are the crystalline polyethylene. Figure 1b shows a higher magnification area taken from just above the center of Figure 1a. A classic "shish-kebab" morphology is clearly visible, with the narrow crystalline backbone running between individual platelike overgrowths. The direct observation of the oriented backbone is particularly striking, as is the close resemblance of this melt-grown morphology to the solution-grown crystals frequently referred to in the literature. This is, to our knowledge, the first observation of a shish-kebab structure during growth using SPM and the first nondestructive imaging of such a structure using any technique.

The backbone shown in Figure 1b is only ~9 nm wide (measured width at half-maximum), which is close to the maximum resolution at this scan size (the pixel size is 3.7 nm). This width is in good agreement with observations made with electron microscopy [e.g., ref 10]. We would expect the width measured to be somewhat wider than the true width because of the broadening effect of the AFM tip. Such close agreement with the expected width might be because the surface is nearly flat, and we are recording differences in mechanical and adhesive properties, leading to a reduced impact of tip size on measured width.

It can be assumed that the oriented regions crystallized during the shearing/extending process. Most of the lamellae would then have melted as the sample temperature returned to the temperature of the heater (145

°C), leaving a few crystals behind, which were particularly stable. It can be seen that these lamellae are not equally spaced along the backbone. It may be that these crystals contain parts of chains that are also in the backbone,[10] fixing their position along the backbone.

Figure 2 shows a series of images taken during the slow crystallization of the lamellae growing from the central backbone. The images were taken during occasional cooling from 132.5 to 131 °C. The cooling was carried out so as to allow the complete growth of the lamellae during the time available for the experiment. The bright lines are the individual lamellae growing from the central backbone and imaged edge on. The occasional slight ripples and kinks in these lines are due to drift in the scanning cantilever caused by air movements in the room, which have an accentuated effect at these high temperatures, and are not real features of the growth. It can be seen from comparison of Figure 2a with Figure 1b that an additional nucleation event of a lamella on the backbone has occurred—marked A in Figure 2a. The dashed box marks the part of Figure 2a that is shown in Figure 1b. This nucleation event occurred on cooling from 133 to 132.5 °C. Following this event, there is no further primary nucleation on the backbone until the sample is cooled from 131 to 130.5 °C, which is surprising as there are sites sufficiently wide to accept new crystal growth at the same thickness as the other crystals already growing.

A number of features of lamellar growth are clear from the series of images shown in Figure 2. In some cases, as in the lamellae marked B, as the lamellae approach each other, they adjust their direction slightly so as to interdigitate. This interdigitation has been frequently observed "post-mortem" by TEM and is believed to play a role in the toughness of oriented structures.[11] The mechanism that allows the direction of growth to adjust is unclear, but this is an area where a high-resolution, in-situ observation may make a significant contribution. In a few cases the lamellae join together when they meet to form what appears to be a single, long crystal—an example of this form of behavior is labeled C in Figure 2d.

By examining consecutive images of the same lamellae, it is possible to assess their relative growth rates. It is apparent that a single growth rate does not apply to the whole population of crystals; some grow faster than others, while some lamellae lie dormant. In this very thin film depletion of material may play a role in slowing down the growth rates, although the height images do not consistently support this hypothesis. This is an observation which could be of considerable significance for our understanding of polymer crystallization, especially considering our previous observations on the crystallization of poly(hydroxybutyrate-*co*-valerate) using AFM,[9] and will be dealt with in more detail in a future publication.

Conclusions. We have presented the first in-situ, high-temperature images of shish-kebab crystallization of polyethylene using AFM. These are also the highest resolution in-situ AFM images of polyethylene crystallization published so far and are a clear indication of the possibilities of the technique.

The close similarity between the melt-crystallized and solution-crystallized morphology has been confirmed using a nondestructive technique. A number of other important observations have been made relating to the growth rate, the cooperative motion of interdigitating lamellae, and the nucleation behavior.

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