

IN-SITU AFM OF POLYMER CRYSTALLIZATION

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Abstract Atomic force microscopy images taken during the crystallization of polyethylene both from processed and quiescent melts are presented. Crystallization from processed melts provides further evidence of a region in front of a growing lamella that is influenced by the crystallization process, but extending only 40 nm into the melt. High-resolution images of the growing crystal tip, taken during crystallization, show no direct evidence of the existence of intermediate phases. The growing tip is shown to be slightly rounded. In-filling crystallization, occurring after the initial flush of growth, is imaged in polyethylene for the first time, and shown to continue to a temperature 8°C below the initial crystallization temperature.

Keywords AFM, Polymer crystallization, Polyethylene

INTRODUCTION

Polymer crystallization has been an area of intense study and debate since the surprising discovery in the 1950s of the lamellar texture and chain folding^[1], in direct contradiction to the theoretical predictions at the time^[2]. However, despite an enormous experimental effort, a consensus has still not been reached as to what are the fundamental mechanisms and processes involved in crystallization. One reason for this continued confusion is the local complexity of the structures that grow, the so-called morphological hierarchy^[3], and the lack of real-space information at lamellar resolution, due to the susceptibility of organic molecules to damage in an electron microscope. Atomic force microscopy, with its capability of obtaining images at nanometer resolution without damaging the surface being studied, has the capability of supplying answers to some of the long standing questions in the area.

Atomic force microscopy was first used for *in-situ* studies of polymer crystallization in the mid 1990s^[4–8]. Since then there has been a rapidly increasing body of work, largely facilitated by the advent of hot-stages which enabled commercially important polymers to be imaged during growth. Several significant new findings have been made, such as the observation that growth, when viewed on a lamellar scale, is often not a constant at a particular temperature, but rather varies both from lamella to lamella, and in time for each lamella^[5, 9]. In this paper we will present some new data on the crystallization of polyethylene using AFM which provides additional confirmation of some of our previous studies as well as some new insights into the secondary processes that occur following the primary crystallization stage.

EXPERIMENTAL METHOD

A sharp fraction of polyethylene from the National Bureau of Standards was used, $M_w = 119.6$ k, $M_w/M_n = 1.19$. The polymer was dissolved in xylene at 120°C. The resulting suspension was then cast onto a glass cover-slip at 145°C, held at that temperature for two minutes to drive off the solvent, and then cooled to room temperature.

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The thin film was re-melted at 160°C, held for two minutes, and then cooled to the desired crystallization temperature ready for imaging with the AFM.

A Digital Instruments — Veeco Dimension D3100 AFM was used. This is a tip-scanned device that provides sufficiently large sample space to allow the use of a conventional Linkam hot-stage. The same AFM set-up was used as described previously^[9, 10], and the same problems relating to the exact calibration of the sample temperature apply. Imaging conditions were maintained so as to just enable the sample to be imaged, without damaging or interfering with the surface in any discernable way. In most cases scan rates were optimized for following the process of interest, rather than for necessarily obtaining the best image quality and resolution. In certain instances this lead to severe degradation of image quality, with the AFM tip failing to track the surface for part of the image. However, this was regarded as a necessary evil to enable the growth process to be followed with the desired time resolution.

In order to obtain oriented samples, the initial heating to 160°C was performed with an additional glass slide on top of the thin film, allowing the molten polymer to come into contact with the top slide. The sample was then cooled to 145°C and the top slide slid off, shearing and elongating the polymer film. The resulting flow caused the formation of chain extended fibrils (“shish” crystals), which then provided a nucleating backbone for further growth.

RESULTS AND DISCUSSION

Figure 1 is a series of images showing the growth and inter-digitation of lamellae growing from two extended chain backbones formed using the simple technique outlined above. The images are amplitude images, highlighting edges. Several interesting features are visible.

The two lamellae labeled A can be seen to be growing on a collision path in Fig. 1(a)–(b). In Fig. 1(c) they are nearly in contact with each other. Figure 1(d) shows that they both changed direction subtly just prior to impact. This same behavior was reported previously^[9] and is a common feature of crystallization in this geometry. The possible reasons for this behavior were discussed extensively in^[9]. However, what is new here is that the experimental set up had sufficient stability to enable an estimate to be made of how close together the two lamellae were before changing direction. This gives a distance of not more than 40 nm, so, if the change in direction is due to some sort of flow or disruption field in front of the growing crystal, as suggested in^[9], it does not extend significantly beyond 40 nm. This size, being of the same order as the radius of gyration of a molecule in the system studied, is not surprising. Even a simple growth process must at least influence the melt over the size scale of a molecule as if one side of the molecule is crystallizing, the other side of the molecule will be pulled towards the growth front with a resultant effect on all the molecules with which it is interlinked.

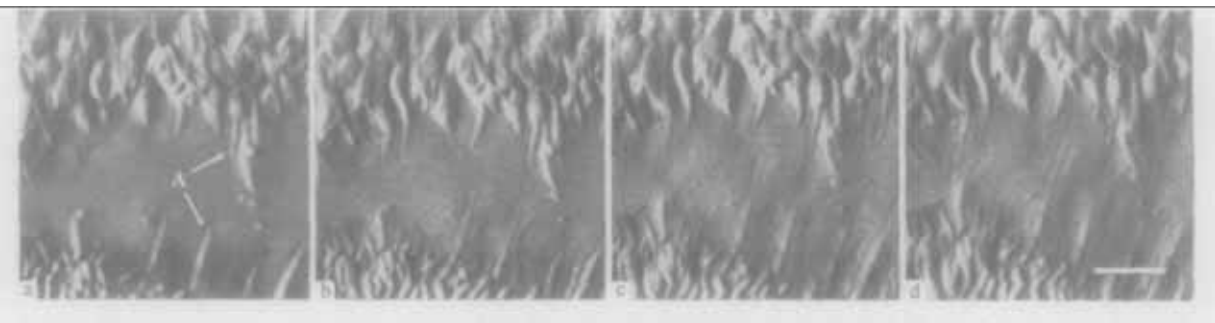


Fig. 1 A series of images showing the crystallization of polyethylene from two parallel oriented backbones (a) at 130°C; (b) at 129.5°C; (c) and (d) at 129°C

All images are amplitude images, black to white representing a change in amplitude of 0.3 V. The scale bar represents 500 nm.

By examination of these and other images taken as part of this series, it is clear that the growth rate of all the lamellae is not the same, but rather varies from lamella to lamella. This behavior has been reported elsewhere^[9], and has implications for secondary nucleation theory. The data presented here is further confirmation of these previous studies.

Figure 2 shows a series of images taken during the isothermal crystallization of a shish kebab structure. The initial shish with overgrowing lamellae is shown in Fig. 2(a). Subsequent growth, after offsetting the scan area, is shown in Fig. 2(b)–(c). These two images were obtained at a relatively slow scan rate and at 512×512 pixels so as to maximize the quality of the data. The growth of the lamellae themselves is very slow. The thickness of the lamellae can be observed, and, at ≈ 20 nm, corresponds well with what is expected at these temperatures. This is perhaps slightly surprising considering the well known tip convolution effect in AFM, but it can be argued that this effect will be minimized in this case as the surface is virtually flat, and the image consists of a property map of that surface. If there is no change in height when going from the amorphous to the crystalline phase then there will be no effect of tip convolution. As the amorphous phase is softer than the crystalline phase, we expect there to be more penetration of the tip into the melt than into the crystal, causing some effective height difference for the lamellae and the melt. It must also therefore be assumed that the tip in this case is relatively sharp. Indeed, in many cases much broader crystal widths have been measured, and it is only approximately one in three tips that give a width that agrees with other techniques, while other tips always give wider lamellae, as expected when considering tip convolution.

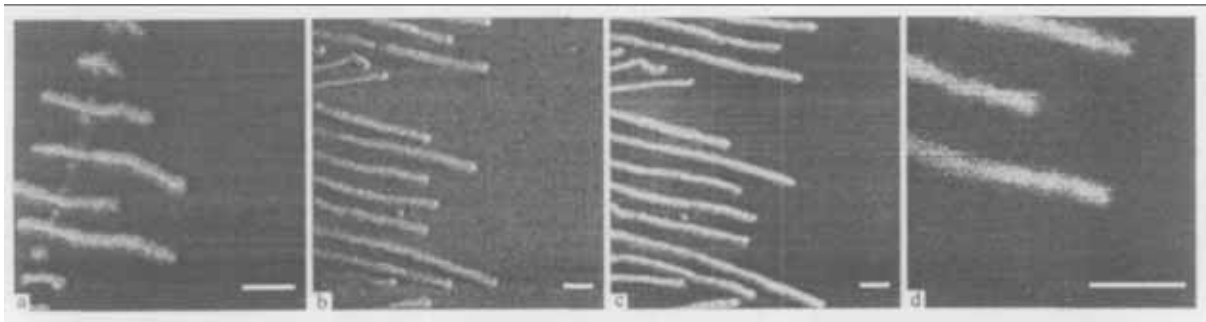


Fig. 2 A series of phase images taken at high-resolution showing polyethylene crystallization from an extended chain backbone. Scale bars represent 100 nm

(a) Black to white represents 25° , scan rate 4.9 Hz, 256×256 pixels; (b) and (c) black to white represents 30° , scanned at 6.1 Hz, 512×512 pixels; (d) black to white represents 15° , scanned at 4 Hz, 256×256 pixels

Crystallization temperature 32.4°C

Examination of the growing tips of the lamellae shows that they are slightly rounded. This is particularly clear in the higher magnification image, Fig. 2(d). Although this is close to the resolution limit, and should be treated with some caution, it is possibly an indication of a period of rapid thickening growth just after the chains initially crystallize, in order to reach the final lamellar thickness. The end of a crystal is not a taper, but rather very slightly curved. This same morphology was observed in the data collected in both scan directions, *i.e.* both when the tip was scanned from left to right, and when scanned from right to left into the growing crystal. Such behavior has been suggested to occur, and it has been argued that a mobile, hexagonal phase exists in polyethylene at the initial stages of growth^[11, 12]. If such a phase does exist, it might be expected that the hexagonal and orthorhombic phases would have different mechanical properties, and as such would perhaps provide different phase shifts to the cantilever and hence appear with a variation in contrast in the image. Such a difference is not observed, so the existence of a hexagonal phase, associated with rapid thickening growth, must only occur at the very tip of the growing crystal, if at all.

It has recently been suggested that polymer crystallization occurs through the initial formation of a mesophase that transforms, via the creation of blocks, into the final crystalline phase^[13]. In these images of

growing lamellae we see no evidence of the crystallization of such a phase, and no evidence of the formation of blocks.

It has also been suggested that the supercooled polymer melt is unstable to fluctuations in density, and will undergo spinodal decomposition into phases rich and poor in crystallizable units^[14]. Again, direct imaging of the molten polymer does not give support for this view, although whether or not such small density differences would be observable is unclear.

Figure 3 shows a series of images taken during the crystallization of a sample crystallized without having first deformed the melt, *i.e.* a quiescent melt. The first four images were taken during isothermal crystallization at 133°C, the last two were taken during cooling at 0.5 K/min. In these images the initial flush of growth occurs almost immediately, and is followed by a slower infilling growth consuming the remaining amorphous material. Although the immediate interpretation of the difference in growth speed would be that the secondary crystallization does in fact happen more slowly than the primary growth, this must be treated with some care as the shape and position of the lamellar aggregate being imaged, relative to the surface, is unknown. It is possible that it is growing up from below and this is leading to the observation of very fast rates. However, there are several interesting features of the growth that can be commented upon which would not be available without direct, real-time imaging.

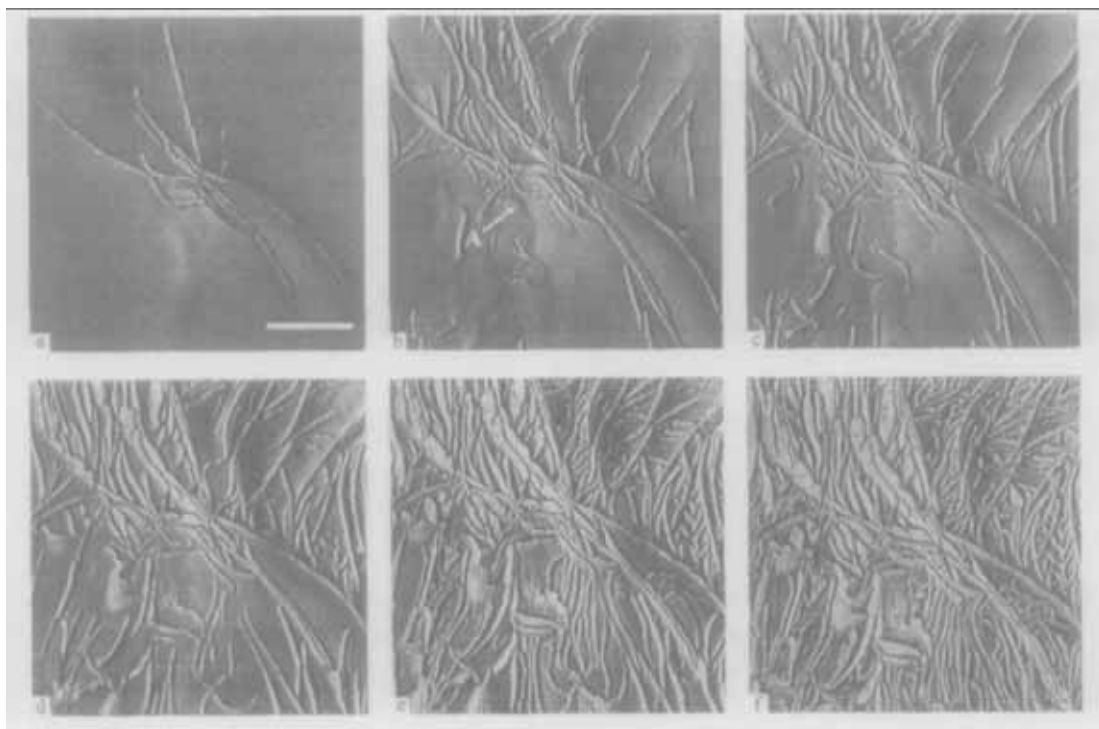


Fig. 3 A series of phase images of polyethylene crystallization from a quiescent melt (a)–(d) taken at 133°C; (e) taken at 128.3°C; (f) taken at 125.4°C
Black to white represents a change in phase of 50°. Scale bar represents 1 μm

Firstly, it is clear that the generally accepted model for structure formation, that the primary lamellae grow, followed by branching and infilling of the secondary lamellae, is correct^[15]. This is the first in-situ, real-space observation of this process in polyethylene. It is also apparent that although some of this secondary crystallization occurs at the initial crystallization temperature, it is necessary to cool the sample before much of the infilling growth can occur, at least in this instance when the initial crystallization temperature is relatively high.

It should be noted that the majority of the lamellae are initially seen to be growing edge on. It is only once

most of the amorphous material has been consumed that the fold surfaces of many of the lamellae become visible. This is to be expected, considering the very large lateral dimensions of the lamellae relative to their thickness, so if the surface remains relatively undistorted only edges will be observed for almost all orientations to the surface. It is only once the sample is cooled, and the remaining melt is sufficiently driven to crystallize, that more of the fold surfaces are revealed.

Figure 3(b) shows a crystal growing flat on in the surface of the melt, the growth front being visible (labeled A). In Fig. 3(c) the same area does not have the characteristic phase signal of the crystalline phase, although the growth front is still visible. It appears that a layer of amorphous material still lies on top of the flat on lamella. This is confirmed by observation of Fig. 3(e) in which further growth of a presumably very narrow lamella can be seen, edge on, over the top of the original flat on lamella. This secondary growth only occurs on cooling, as the driving force becomes sufficiently high to force these highly constrained chains to crystallize. Thus the presence of the surface here is most probably causing a change in the crystal morphology.

If Fig. 3(d) and 3(f) are compared, it is apparent that there is a large degree of further crystallization during cooling. There are still large amorphous regions visible until the sample is cooled 8 °C below the initial isothermal crystallization temperature. There are several possible reasons for this temperature dependence of the crystallization of the remaining amorphous material. It could be that the initial growth excludes the low molecular weight material, and further crystallization only occurs once this has reached a temperature sufficiently below its (lower) melting point. This is known to occur and is doubtless part of the effect. Another possibility is that some of the remaining material consists of chains that are already partially crystalline, that is they are either very long loops or cilia. In this case, crystallization might be slowed by reduction in mobility of these chains. The existence of such a constrained phase has been the subject of extensive study, and most probably contributes to the effect here. Although it is not possible to determine the exact reasons behind this behavior, the application of in-situ AFM observation opens up new possibilities for understanding the formation of structure in semi-crystalline polymers. Coupled with melting studies, this approach promises to clear up many long-standing questions in polymer science, particularly with regard to the allocation of melting peaks obtained with DSC. Such a study will be the subject of a future publication.

CONCLUSIONS

Atomic force microscopy images of polyethylene have been presented, taken during isothermal crystallization and on cooling, as well as crystallization from both processed and quiescent melts. In agreement with previous studies, it has been shown that lamellae cause some disturbance of the melt in front of them, but that this disturbance is not significant beyond 40 nm from the growth front. An attempt has been made through careful, slow scanning of crystallization to observe whether or not there is an intermediate step between the amorphous and crystalline phases. No such step has been observed, although it is unclear whether or not a difference would be discerned. Unfortunately lower crystallization temperatures, where such an intermediate phase may be longer lived, or more clear, cannot be conveniently studied in polyethylene due to the very high crystallization rates.

In-situ, real-time imaging of the secondary crystallization process has directly revealed the complex way in which the final crystalline structure develops. As expected, this is largely in agreement with the inferences that have been made from previous studies using electron microscopy.

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