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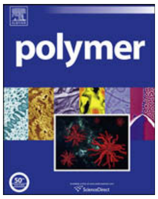

Feature Article

How atomic force microscopy has contributed to our understanding of polymer crystallization

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ABSTRACT

Over the past two decades atomic force microscopy (AFM) has become one of the most frequently used tools for studying polymer crystallization. The combination of high resolution, minimal sample preparation and the ability to image non-destructively has allowed visualisation of crystallization, melting and re-ordering processes at a lamellar and sub-lamellar scale, revealing complexities that could only previously be guessed at. Here the insights that AFM has provided into some of the main over-arching questions relating to polymer crystallization are reviewed. The emphasis is on the use of AFM to image growth in real time, and on contributions that have been made to our understanding of polymer crystallization in general, rather than to specific systems.

1. Introduction

The excellent and varied mechanical properties of many polymers result from their complex semicrystalline morphology. However, despite more than 50 years of intensive study [1–4], the way in which polymers crystallize, and the fundamental processes that result in their highly complex nanoscale architectures, remain areas of active research [5,6]. Over the past 15 years the various scanning probe microscopy techniques [7–9] have been applied to this area, and have produced solutions to old controversies and posed new questions that have fed into developing an improved understanding of the field. In this article the new insights into polymer crystallization that have been obtained from scanning probe microscopy (SPM), and in particular atomic force microscopy (AFM) will be reviewed. This is a very broad area, so here we will concentrate on work that has led to new general principles, rather than the specifics of individual systems, and on data that could not straightforwardly be obtained with other technologies.

Putting aside the specifics of individual systems, there are a number of questions in polymer crystallization that have focussed attention over recent years: How sharp is the transition from disorder (the melt) to 'order' (the crystal)? What controls the morphology, i.e. why do we get particular structures? How does flow affect crystallization? What influences do different types of confinement have on the crystallization process? What controls the stability of crystals – is it just thickness? Although less frequently studied, crystal nucleation is often as important as growth, and it is still an open question whether the classical models are correct or if there is something else, perhaps polymer specific, occurring? As new techniques have been developed they have naturally been applied to try to answer these questions. Over the past 20 years the two most significant changes in instrumentation available to the polymer scientist have been the growth in availability of synchrotron radiation [10–12], and the development of the large family of scanning probe microscopes.

SPM, and AFM in particular, has been widely applied to questions in polymer crystallization. The technique has several strengths that make it ideally suited for such studies. It is a high resolution technology, routinely resolving sub 10 nm features [13,14], and hence allowing the fundamental length scale of the polymer lamellar crystal, its thickness, to be observed. AFM requires no staining or metal coating of the sample, so sample preparation is relatively straightforward. Also, it is non-destructive under many circumstances. This allows images to be obtained while a process such as crystal growth or melting is occurring, giving time-resolved data at lamellar or sub-lamellar resolution [15–18]. It is this final feature that provides many of the most exciting possibilities of AFM for studying polymer crystallization, as it is now possible to watch crystal growth, crystal melting, and re-organisations within crystals at the lamellar scale, seeing how structure evolves and local conditions influence kinetics. AFM has a wide range of different measuring modes, and, with the ever increasing number of functional semicrystalline polymers available (e.g. [19]), the breadth of experiments that can be

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carried out with a single machine is also one of the techniques attractions.

Although a powerful tool for investigating polymer crystallization, AFM also has some drawbacks. It is a surface technique, and if it is being used to infer information about the bulk, it is easy to misinterpret images and to draw false conclusions. Images are usually obtained relatively slowly, so it is hard to obtain good sample statistics for ex-situ studies, and under many crystallization conditions in-situ observation is not possible because the rapid kinetics are incompatible with the slow imaging rates. Finally, the contrast mechanisms in AFM, and particularly in the commonly used 'phase' imaging, are often non-intuitive, with changes and inversions in contrast occurring as the imaging conditions are varied [20–22]. This can obviously lead to confusion in the interpretation of data.

In the following the contributions made by atomic force microscopy to our understanding of the questions on transitions, morphology, flow, confinement, stability and nucleation outlined above will be addressed in turn, following a brief overview of how the technique works and the main instrumental factors involved in its application to polymer crystallization. The ability of AFM to follow the growth (or melting) process in real time will form the focus, as it is the area of the authors' own work. The article will finish with a brief look at the prospects of the technique and its application in this area in the future.

2. Introduction to AFM and developments for the study of polymer crystallization

In AFM a sharp tip attached to a cantilever beam is brought into contact with the sample surface. There are many different modes of operation but the two most commonly used for imaging semicrystalline polymers are 'contact mode' and 'tapping mode'. In 'contact mode' the force interaction between the tip and the surface is measured through the deflection (bending) of the cantilever, which is usually monitored using an optical lever set up. A feedback loop adjusts the height of the base of the cantilever to maintain the cantilever deflection (and therefore the force applied to the tip as the cantilever acts as a linear spring) at some user controlled value (the set point). The cantilever is scanned point by point over the sample surface, the feedback loop continuously adjusting the vertical position of the cantilever so as to maintain constant deflection, and this vertical control signal is then used to form a topographic image of the surface. As the name suggests, this mode maintains constant tip-sample contact and therefore the lateral forces exerted on the sample by the tip are rather high, frequently leading to damage to soft or loosely bound samples. Although initially used extensively for AFM studies of polymer crystals and crystallization, it is unable to image most molten polymers without causing damage and the disruption of any growth process.

In 'tapping mode' AFM the AFM cantilever is oscillated at or close to its resonant frequency [20]. The tip comes into intermittent contact with the surface and the amplitude of the oscillation is damped by that contact. This amplitude is used as the feedback parameter and kept at a constant value. The lateral forces are considerably reduced compared to contact mode and soft samples such as polymer melts can be stably imaged if care is taken. The cantilever is driven at a set frequency, and access to the surface material properties can be obtained by monitoring the difference between the phase of the drive signal and the phase of the cantilever response – the 'phase' image. The information obtained in this image is difficult to quantify and depends on imaging parameters, but is related to the viscoelastic and adhesive properties of the sample [20–22]. The very large difference in mechanical and adhesive properties between a liquid and a crystalline polymer mean that this mode of operation is ideally suited to the study of polymer crystal growth.

To follow crystallization and melting of most polymers it is necessary to have control over sample temperature. The development of stable controlled temperature accessories to AFMs has allowed a wide range of polymers to be imaged during crystallization at temperatures from 0 °C to 250 °C [15,23–25]. Environmental control, with the use of both vacuum and inert gas atmospheres [25,26], has allowed polymers that are susceptible to oxidation and hydrolysis to be studied at high temperature.

Following crystallization in many polymers with AFM is limited to temperatures close to T_g or T_m, where crystal growth is slow. Recently a novel high speed scanning AFM was developed, VideoAFM, that allows images to be collected at video rate [27,28]. There has been some initial progress in applying this to crystal growth [29], but this is hampered by the relatively large tip-sample forces as VideoAFM requires constant tip-sample contact. Future advances of this or other technologies [30,31], allowing an intermittent contact imaging mode at rates of at least 1 frame/s are required if fast scanning is to make a considerable impact on our understanding of polymer crystal growth in a wide range of systems.

Unless otherwise mentioned, in the work detailed below tapping mode AFM has been used, and the data collected is either the topographic image, or the phase image (viscoelastic/adhesive contrast), or sometimes the amplitude image which is the error signal in the feedback loop controlling tip height (and accentuates changes in height).

3. The transition from disorder to order

Polymer molecules in the melt adopt a Gaussian random coil conformation characterised by a high level of disorder. Below the equilibrium melting temperature of the polymer this state is unstable with respect to the ordered crystalline state in which the positional ordering of the chain is maximised. Crystallization kinetics prevent the most highly ordered state from being reached, and result in the well known lamellar structure of most semicrystalline polymers [32]. As the molecules re-organise themselves at, or close to, a growth front, they may pass through intermediate degrees of order that are metastable, i.e. have a free energy lower than the melt but higher than that in the final state. Whether such states exist, and, if they do, how long they last, is central to our understanding of crystallization. Several different models have been proposed that predict the existence of metastable states [33–36], the most widely studied of which is that due to Strobl [36–38]. This model suggests an intermediate partially ordered state that occurs at the growth front and is characterised by molecular alignment but that maintains translational and rotational freedom more similar to that of the melt. Crystallization is suggested to occur initially in this partially ordered state, similar to the well known high pressure hexagonal phase in polyethylene [39]. Growth occurs in discrete bundles that then merge and ultimately transform into the final crystal form, some distance behind the growth front. There are strong similarities between this model and an earlier one due to Keller et al. [33]. The Keller model was more specifically applied to polyethylene, and considered the possible size dependence of the relative stability of the hexagonal and orthorhombic forms of polyethylene.

AFM played a role in the original development of the Strobl model as it was observed that in many cases the surface of lamellae crystallized from the melt had a knobbly texture, suggesting a lateral sub-structure to each 'crystal' [40,41]. Fig. 1 shows examples of such data. In-situ AFM has the potential to directly image the growing crystal tip, and hence to observe any intermediate structures. Despite a large number of observations of polymer crystal growth at the lamellar scale in many different systems [42–52], unambiguous observation of the formation of bundles in front of a growing lamellae have not been made. The surface nature of AFM

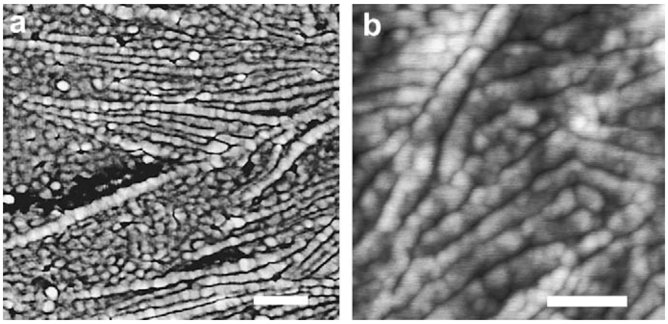

Fig. 1. AFM phase images of the surface of semicrystalline polymers, showing the frequently observed "knobbly" sub-structure that it has been suggested is due to initial crystallization in discrete blocks. Scale bars represent 200 nm and 100 nm in (a) and (b) respectively. (a) Taken from Ref. [40] and used with permission.(b) Taken from Ref. [41] and used with permission of ISC Publications.

images does cause some potential for misinterpretation [24]. We have made a considerable effort to image the growing crystal tip at high resolution with the aim of 'seeing' if an intermediate state exists. Fig. 2a–b shows a pair of AFM images of individual polyethylene lamellae growing as part of a shish–kebab structure. This structure constrains the crystal growth so that each lamella is lying perpendicular to the film surface, at least close to the oriented backbone. There is a strong contrast in the 'phase' image because of the difference between the (soft, sticky) melt and the (hard) crystal, but no apparent variation in the phase contrast along the length of the lamellae, or in the melt in front of the growing crystals. As phase imaging is not quantifiable under most circumstances, this observation does not preclude the existence of a slow transition towards order, but it implies [54] that any intermediate state is probably more similar in properties to the crystal than to the melt. The images also show some evidence of tapering of the lamellar growth front, albeit very subtle, in agreement with some predictions [33] and simulations [55] of crystal growth.

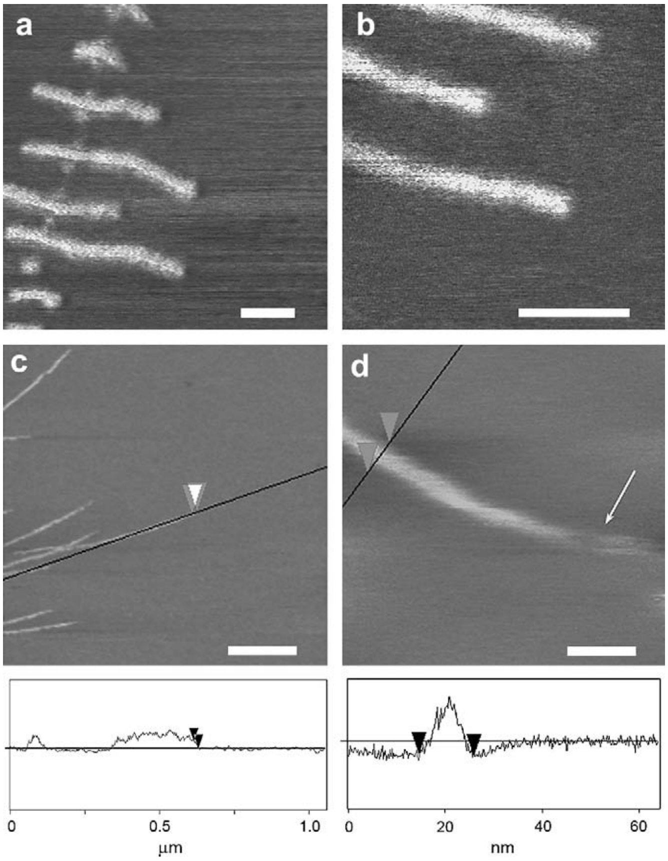

Fig. 2. (a) and (b) AFM phase images showing polyethylene lamellae growing from an oriented backbone, showing the sharp contrast transition from the amorphous to the crystalline phase. The scale bars represent 100 nm. Taken from Ref. [53] and used with permission of World Scientific. (c) and (d) AFM phase images of a growing lamella tip with the corresponding cross sections taken along the lamella (c) and across the lamella (d). The arrow indicates the gradual transition in phase contrast from the melt to the crystal. The scale bar in (c) is 200 nm, and in (d) is 20 nm. Re-used with permission of ACS Publishing, taken from Ref. [44].

In other systems, there is some evidence that the growth tip has different properties from the rest of the crystal. Li et al. [44] have shown that during imaging of growing lamellae there is a difference in the phase contrast at the tip relative to that of the mature lamella, and have associated this with a higher number of crystal defects in the tip region. Fig. 2c–d shows the relevant growth data. It is hard to quantify the difference in material properties with current technology, and the problem is obviously complicated by the fact that the growth tip is growing, so the region of interest is moving across the imaging window. However, the data provides evidence that in this system the growing tip is softer than the rest of the lamella for a distance of some 30 nm, arguably in agreement with the Strobl model. The difference between this result (in poly(bisphenol A octane ether)) and the findings for polyethylene may come from the difference in the rate of re-organisation within the crystalline phase of the different materials. Polyethylene is known to re-order very rapidly at high temperatures, undergoing thickening growth [56,57], and thus may reach its stable state a shorter distance down the lamella. However, our studies of another polymer close to its glass transition temperature, polyhydroxybutyrate-co-valerate, which should not re-order rapidly both because of the proximity of T_g and the presence of hydroxyvalerate monomers that are not easily incorporated into the hydroxybutyrate lattice, similarly show no evidence of a transition region [58]. AFM is not able to provide a definitive answer here, but it does not provide strong evidence supporting the idea of a gradual transition to order in many systems.

The exact nature of the knobbles on top of lamellae as imaged with AFM is unclear, but in-situ AFM has allowed their melting behaviour to be explored. If the fine structure reflects variations in order within a lamella, it would be expected that the less ordered parts would melt at a different temperature from the more ordered parts (whether higher or lower temperature depends on if there is also a difference in the phase, see [37] for a thorough review on the Strobl model and crystal melting). Fig. 3 shows an example series of images taken during the slow melting of a lamellar aggregate of polyethylene, which is one of several investigations of this process [24]. The heterogeneous surface texture of the lamella lying flat in the plane of the surface is clear. On heating the crystal melts back from the edge, although the melting process is not the reverse of crystallization. The knobbly sub-structure does not appear to influence the melting behaviour. Either the surface texture, at least in the case of polyethylene, is not an indicator of variations in stability across a crystal, or else any variations that do exist re-organise and 'heal' on heating prior to melting.

Growth kinetics have frequently been measured to provide input data for crystallization theories. If mesophases do exist they would be expected to influence the growth kinetics, at least if measured at the molecular scale. For instance, variations in the density or structure of the melt, as suggested in [34], would cause corresponding variations in lamellar growth rate. There has been extensive work on the rates of crystallization of individual lamellae and lamellar aggregates using AFM (e.g. [15,18,51,54]). In all the aggregate systems studied, i.e. when there are multiple lamellae growing near to each other, it has been found that the

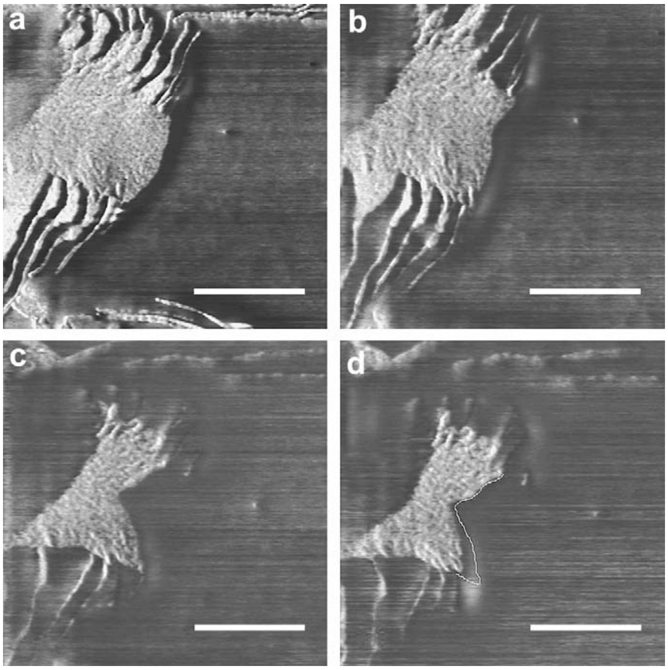

Fig. 3. A series of AFM phase images of a polyethylene crystal during slow melting, in which the 'knobbly' sub-structure is visible. The dotted line in (d) shows the outline of the crystal in (c), as there is no temperature change between the two images. The scale bars represent 1 μm. Reproduced from Ref. [24] with permission from Springer-Verlag.

growth rate varies from crystal to crystal and for each crystal with time. Fig. 4 shows an example of lamellae growing in a film of polyhydroxybutyrate at high supercooling close to T_g and an example of polyethylene lamellae growing close to T_m. The growth rate undergoes apparently random fluctuations, as can be seen from the graphs in Fig. 4e and j. Similarly, the growth front of lamellae that grow flat in the surface of a film can be seen to fluctuate in their shape, with a growth front that is irregular on a 10 nm scale [24]. An example of polyethylene lamellae is shown in Fig. 5. It may be that these two observations are manifestations of the same phenomena, as fluctuations in shape when viewed edge-on would lead to changes in the measured growth rate. Such fluctuations might be expected in an interface at elevated temperature, but clearly need to be accounted for in crystallization theories. Most crystallization theories [32,59,60] assume that the growth rate is essentially constant at a particular temperature as this is the observation of optical microscopy. At temperatures close to the melting point the Hoffmann theory predicts growth for the polyethylene used for some of these studies is in regime II, where growth is still layer by layer although there are multiple secondary nucleation events on each layer. This implies a relatively flat growth front, or one with a continuous curvature, and does not allow for such fluctuations. Other theories similarly do not account or predict fluctuations that occur over tens of nanometres, rather than over the distance of a few unit cells, while detailed computer simulations have not as yet simulated sufficiently large volumes to really contribute to this question. Here there is a need for theories of crystal growth to develop to encompass the observations coming from AFM.

Growing crystals always create or induce changes in their environment, setting up fields in, for example, concentration, density, temperature or even stress [61]. Such fields are expected to influence the growth kinetics, as well as the structure (see the next section). Although not directly related to the transition from randomness to order, these self-induced fields will influence and perhaps control the growth process. In polymers there is also a natural length scale over which a growing crystal must interact with the surrounding melt, as not all of a chain need enter the crystal at one point during growth. In-situ observations of crystal growth in both polyethylene [46] and polyethylene oxide [29] point to some interaction between growing lamellae that reduces growth rate or hinders/alters growth once they come within a distance of approximately 40 nm. The same length scale has been observed when lamellae are growing directly towards each other (when nucleated from parallel shish in shish–kebab aggregates), when observing the growth of in-filling lamellae between neighbouring lamellae in polyethylene [46], when following the growth of surface crystals of polyethylene oxide at high speed using Video-AFM [29], and even when observing crystallization in a phase separated block copolymer (see below) [62]. It may be that this indicates either the length scale of an induced field, or that growth is only affected once neighbouring growing structures are trying to share a single chain, and is, therefore, a uniquely polymeric effect. Further work, in particular a study of the effect of molecular weight on this observed length scale, is required to determine its origin.

4. What determines the morphology of semicrystalline polymers?

Watching how a structure grows can give an insight that is not available simply from looking at the final form. However, semicrystalline polymers have been exhaustively studied by both transmission (TEM) and scanning (SEM) electron microscopy, and quench techniques have been used to access intermediate growth structures [4,63–66]. More recently, advanced electron tomographic approaches have also been used to elucidate the 3-D structure [67]. A wealth of knowledge has been obtained using these ex-situ techniques, but they are always open to question because of the possibilities of artefacts caused by sample preparation, so some of the value of AFM is also in confirming the conclusions reached in these earlier studies.

Many of the in-situ studies of crystal growth have concentrated on understanding how different structures are formed. The formation of spherulites has been extensively studied, both in thick and thin films [48,68–70]. The progression of structure from single lamella, to multiply branched lamellae, ultimately to spherulite, has been followed in situ, confirming in a single experiment [48] the extensive ex-situ work of Phillips [64], Bassett [4], and others. AFM provides height information, and a number of studies have shown the depletion of material that occurs in front of a growing spherulite under certain growth conditions [15,18]. In many cases initial crystal growth is followed by a protracted period of in-filling growth and possibly crystal re-organisation. This has been studied in a number of systems [43,48,49,53]. In a study of the crystallization of a poly(ε-caprolactone) with poly(vinyl chloride) blend [43], quantitative analysis of the data showed a gradual thickening of the entire lamellar population with time, as well as a perfecting through the merging of micro-fragmented objects to form longer crystals. An example series of data for polyethylene [53], following growth and the subsequent development of structure, is shown in Fig. 6. The sequence of events, with an initial framework of fast growing 'primary' lamellae oriented away from the nucleus, followed by slower in-filling 'secondary' lamellar growth, can be seen. In this case, where initial crystallization has occurred at a small supercooling, it is necessary to cool the sample quite substantially before growth is relatively complete. Interestingly, it is apparent that some lamellae that appeared edge-on to the surface were actually at quite a large angle to the perpendicular, even though only the edge was visible initially. As material is depleted by further growth the lamellar surfaces are revealed. Determining the orientation of lamellae relative to the surface with AFM is extremely difficult.

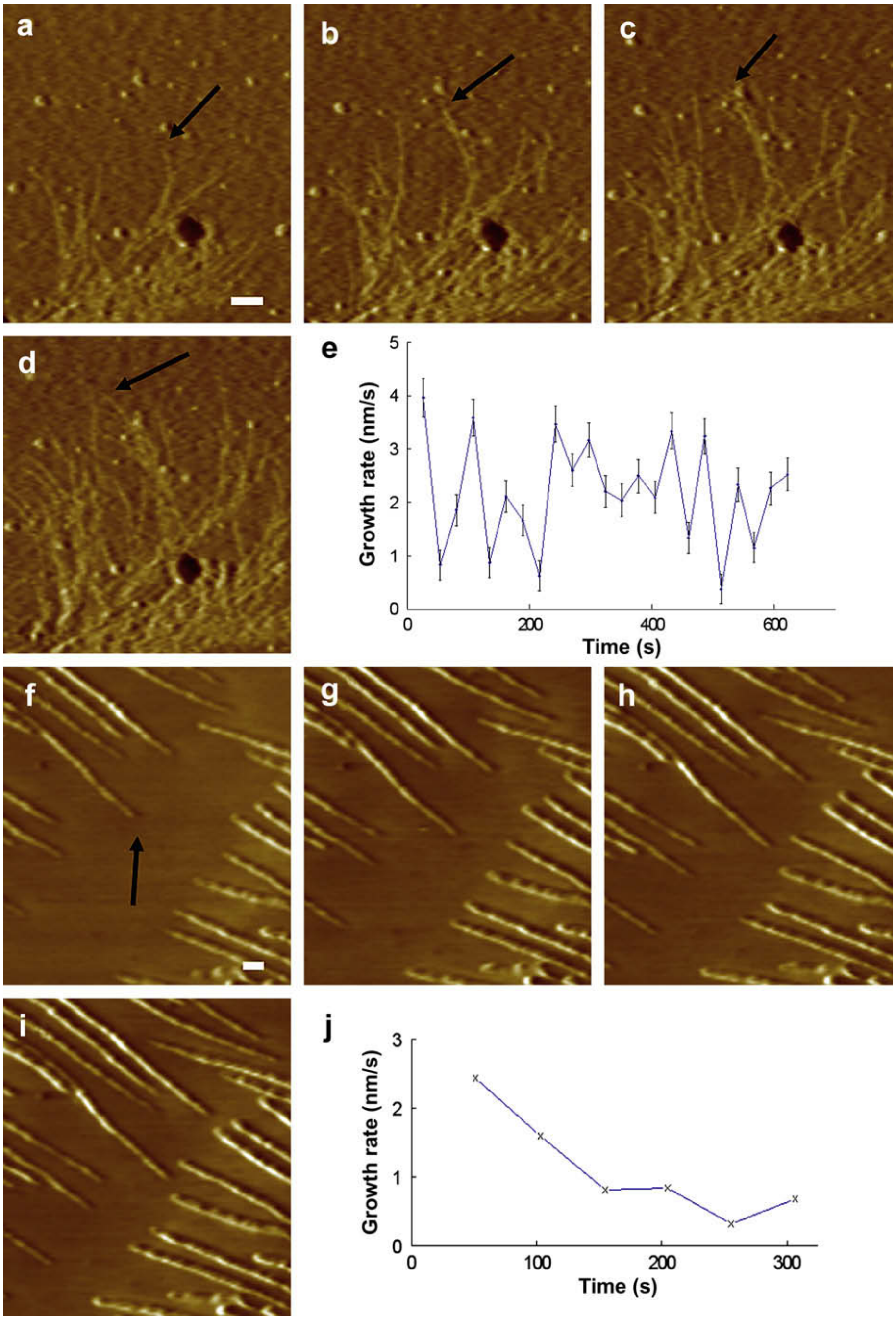

Fig. 4. (a)–(d) A series of AFM phase images showing the crystallization of polyhydroxybutyrate at 6 °C ($T_g = 3$ °C). The arrow indicates a growing lamella, the growth rate of which as a function of time is plotted in (e). (f)–(i) A series of AFM phase images of polyethylene during crystallization, with the corresponding growth rates of the arrowed lamella shown in (j). The scale bars represent 100 nm. (f)–(i) Adapted from Ref. [54], and used with permission of Springer-Verlag.

In many polymers lamellae within spherulites twist to create banded spherulites (so-called because of their optical appearance between crossed polarisers [71–73]), and in-situ observation has shown that this twist can be a continuous process over at least a substantial fraction of the rotation [69]. This is in agreement with X-ray studies [74], but somewhat in contradiction to the inferences drawn from some EM studies [75], and supplies supporting evidence for some models of how this intriguing long distance self-organisation occurs [76,77].

Spherulites require branching that is non-crystallographic over a lamellar length scale, as the final spherulite usually has one crystallographic axis radial if averaged over a distance of a few micrometres. Branching mechanisms have been observed in situ, and although a surface imaging technique is limiting, there have been many observations of screw dislocation branches in several polymers (e.g. [47,51,58]), as well as suggestions of other branching mechanisms [44], and even the observation that the AFM tip can be used to induce branching [68]. The formation of a screw dislocation branch from a defect or fluctuation at the edge of a growing lamella is believed to be one of the main sources of branching in polymers. Fig. 7 shows an example of such a process observed in polyethylene [58]. A novel tomographic method [78] has also been used to etch away the surface following in-situ observation of crystal growth and reveal the structure beneath that was responsible for the

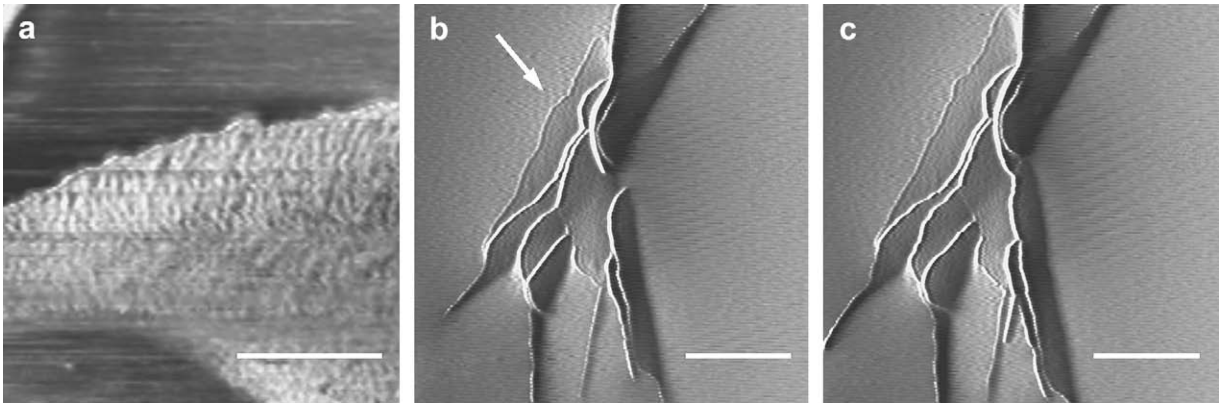

Fig. 5. (a) An AFM phase image, and (b), (c) AFM amplitude images showing polyethylene lamellae growing in the surface. The undulating growth front can be seen. Scale bars represent 1 μm. Reproduced from Ref. [24] with permission from Springer-Verlag.

surface observation [79]. Fig. 8 shows some data from this study, in which a branch is identified as coming from a screw dislocation following the tomographic reconstruction. Although time consuming, it is only through studies such as this that the full story of what is happening during crystal growth can be revealed.

Ex-situ observation of crystal growth using AFM has also been extensively used (e.g. [80]), and has provided information leading to an important new concept in how spherulites grow. Toda et al. [81,82] have carried out very careful studies on the branching behaviour of polyethylene, and the role played by interfacial instabilities in that branching. They have determined by variation of molecular weight that the growth front instability, that ultimately leads to a lamellar branch (the so-called screw dislocation branch), is due to a self-induced pressure gradient caused by the difference in density between the crystalline and amorphous phases. By combining methodologies usually associated with TEM, with the relative ease of use of AFM, a new insight into this long standing question has been obtained.

All of the above has concentrated on the shape and the conformation of polymer lamellae. However, AFM offers the hope of molecular [14] or even better [83] resolution, and it was a goal of many early AFM studies to try to image the morphology at a single chain level [84]. This has not been convincingly achieved for three dimensional crystals, but there have been some exceptionally high resolution images obtained of 2-D crystals. Fig. 9 shows an example, in which the ‘crystals’ are formed by very slow compression of a Langmuir Blodgett film prior to depositing onto a mica structure [85]. The resultant images show individual chains that have formed crystals of limited “thickness” along the chain axis, i.e. crystals that look remarkably similar to how one might imagine a 2-D slice through a 3-D polymer lamellar aggregate would appear. Individual folds within chains are even visible. The 2-D geometry during crystallization, now a true 2-D confinement as only minimal motion out of the plane of the Langmuir trough surface is possible, will considerably change the thermodynamics of crystallization. In particular, there are very few conformations available for a chain in which it re-enters a crystal that it has left which do not involve a reasonably tight fold, so the observation of tight folding cannot be taken as proof that this is the favoured conformation in the bulk. However, the images do give a remarkable snapshot of how chains *can* look within a polymer crystal.

5. How does flow change crystal growth?

One of the advantages of polymer systems is that the final properties of a product can be radically changed by the processing route that is selected. Oriented crystallization, resulting from flow during or prior to growth, is one of the main tools for this control over properties [86–88]. The formation of highly oriented polymer crystals, and the resulting ‘shish–kebab’ structure [89,90], has been used since the 1960s to provide materials with greatly increased modulus compared to the same polymer crystallized quiescently. With the recent push towards molecular design leading to control over properties at the molecular scale [91], there has been renewed scientific interest in these intriguing structures.

AFM is not at first glance the tool of choice to study crystal growth in processed melts, as it is not currently possible to image anything but the most mechanically stable system, so imaging during processing is not available. However, in many processing situations the polymer is only subjected to extensional and/or shear fields when at a temperature above that at which it would conventionally crystallize. In this case much of the growth occurs on cooling. The molecular orientation imposed during this initial stage can be partially locked in by the formation of oriented ‘shish’ crystals. Subsequent lamellar growth under real processing conditions may occur while some orientation in the melt is retained, but arguably some insight into this process can be obtained by watching the growth of lamellae from the oriented backbone under conditions when the remaining molecules have doubtless largely relaxed. The extreme is to introduce a nucleating fibre, and then watch the subsequent growth from it into the never deformed melt [92], a sort of artificial shish–kebab similar in effect to the nanotube nucleated structures [93].

Hobbs et al. have carried out a number of studies on thin films that have been sheared at high temperature prior to imaging during cooling in the AFM [45,46], as well as using the controlled orientation of the lamellae to study questions relating to growth in quiescent melts. The inter-digitation process that occurs when neighbouring shish–kebabs grow towards each other has been observed in situ. Some unexpected re-orientations are observed as lamellae approach within 40 nm of each other, and these are partially responsible for the highly interwoven morphology that gives these structures their strength. The initiation of growth from the ‘extended’ chain backbone has been followed, with the density of nucleation sites appearing to be rather random, some gaps that are clearly wide enough to support growth nonetheless not crystallizing. The melting of shish–kebabs has been followed in real time [94], showing extensive thickening of the lamellae where they meet the backbone, in agreement with previous models [86], and showing that these lamellar overgrowths can indeed be melted off the backbone. Fig. 10 shows a series of images taken close to and during the final stages of melting.

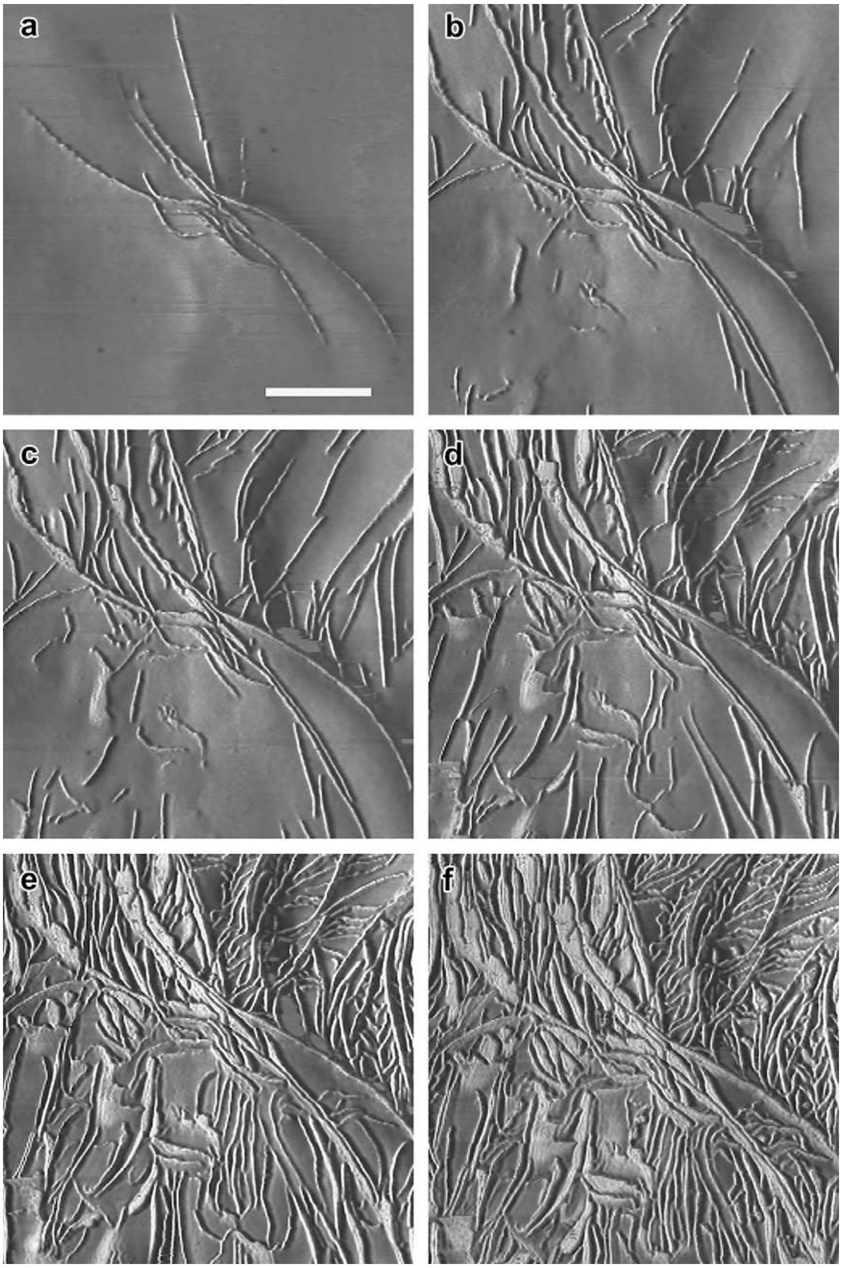

Fig. 6. A series of AFM phase images taken during the crystallization on cooling of a polyethylene film, showing initial growth (a)–(d) and growth on subsequent cooling (e)–(f). Scale bar represents 1 μm. Reproduced from Ref. [53] with permission of World Scientific.

6. The effect of confinement on polymer crystallization

In most of the above work the aim was to gain an improved understanding of how polymers crystallize under ‘normal’ circumstances, as a continuation of the extensive studies carried out in this area over the last 50 years and in comparison to other, often necessarily bulk, techniques. Much AFM work has concentrated on confined crystallization in very thin films and monolayers, in which the behaviour is likely to be considerably different from that seen in the bulk [95], and in which the interest is often in the specific constraint placed on growth by the geometry. An extreme example of this is the crystallization of Langmuir Blodgett films described above. Here the ‘problem’ that AFM is a surface technique becomes an advantage. Confinement into essentially two dimensions in a thin film is of interest both because of the important industrial applications of thin films as barriers etc., and because of the scientific interest in the interplay between the crystal thickness, the film thickness, and the molecular size.

AFM has been used to follow the effect of film thickness on growth morphology. In very thin films, comparable to the lamellar thickness or thinner, crystal growth is controlled by the need to transport material to the growth front (e.g. [96–101]). At small supercoolings single crystals are observed, but at lower temperatures the surface instability breaks up the growth front and a dendrite is formed. At even larger supercooling the dendrite growth tip becomes unstable and a densely branched or seaweed morphology is found. This range of morphologies has been observed in a number of systems with AFM [96–98], in some cases with additional features coming from, for example, the chirality of the molecule. In-situ observation of dendritic growth has revealed

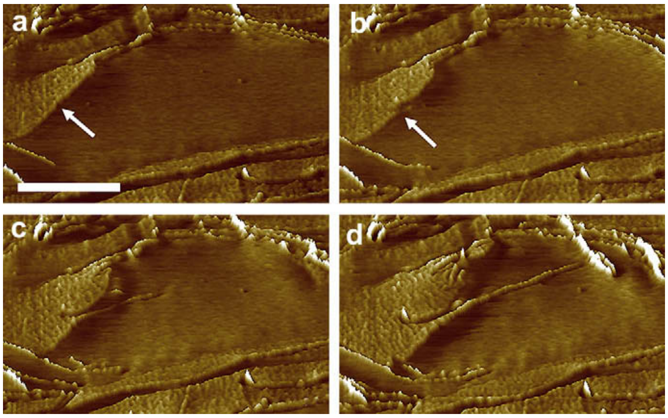

Fig. 7. A series of AFM phase images showing the formation of a screw dislocation branch in a polyethylene lamella. The arrow indicates the branch point. The scale bar represents 1 µm. Adapted from Ref. [58] and used with permission of Wiley-VCH.

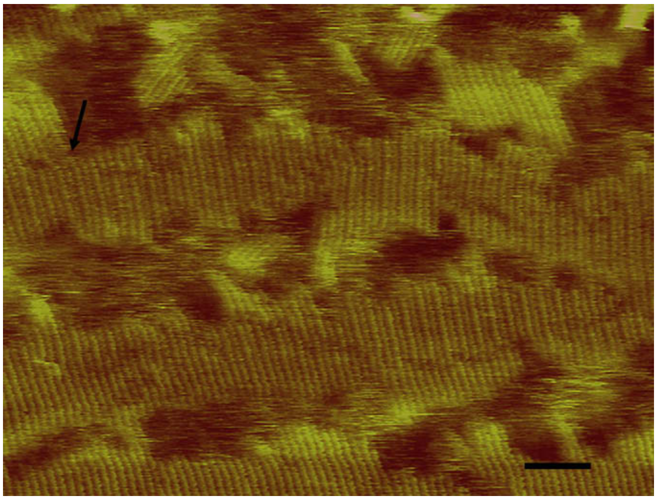

Fig. 9. An AFM topographic image of an it-PMMA Langmuir Blodgett film. The scale bar represents 10 nm. Reproduced from Ref. [85], with permission of ACS Publishing.

a cyclic growth process [101]. Similar transitions in behaviour have been observed in diffusion controlled growth in small molecule systems [102,103], but it is rare to see the full range of morphologies in a single system, while it appears to be relatively common in the case of polymers. In polymers it is also often necessary to use AFM or an alternative high resolution technique for these studies as the length scale of the dendrites (e.g. the ‘arm’ width) is rather small compared to that found in many small molecules, where such structures have been studied with optical microscopy.

Polymer crystallization has also been studied under more complex confinement, particularly in block copolymers with one crystallizable block, where the formation of micro-phase separated structures gives access to growth under conditions of cylindrical and spherical confinement [62,80,104]. In this case by necessity the confinement is on a length scale similar to the molecular size, as the block copolymer itself sets the maximum extent of separation. In complex architectures such as block copolymers it is even harder to carry out meaningful TEM studies of growth, and AFM is the primary real-space tool for these investigations.

In block copolymers the degree of confinement of the growing crystalline material depends on the level of segregation of the two melt phases, the temperature of the sample relative to the glass transition temperature of the non-crystallizable material and also the rate of growth of the crystal [105]. In the case where the system is softly confined (i.e. growth can disrupt the phase separated structure and cross between domains), the melt domain structure alters the crystal growth morphology considerably. In a softly confined sphere forming block copolymer the growth morphology becomes dominated by the need for material to diffuse across the non-crystallizable domain, and a densely branched structure with branching angles controlled by the crystallography of the phase separated melt is observed [62]. In a similarly confined cylinder former it is observed that the domain orientation affects growth rates, and that the growth front only causes very minimal re-organisations within the previously existing domain structure [62]. Transport of material is found to occur through diffusion rather than through flow, as there is no distortion of the domain structure ahead of a crystal growth front. In more strongly confined systems, the melt phase largely acts as a template for crystal growth, although there is still some re-organisation of the domain structure near a growing crystal tip. Surprisingly multiple nucleation is observed along a single domain as growth causes the depletion of available material and slows itself down, allowing time for fresh nucleation events to occur further along the same cylinder [80].

The nucleation process within a strongly confined sphere forming block copolymer has also been studied [104], finding that individual domains behave completely independently despite being separated from their neighbours by only a few nanometres. On heating these domains re-organise and perfect, disrupting the originally rather well ordered domain structure. This ability of AFM to follow both growth and re-organisation on heating is one of its

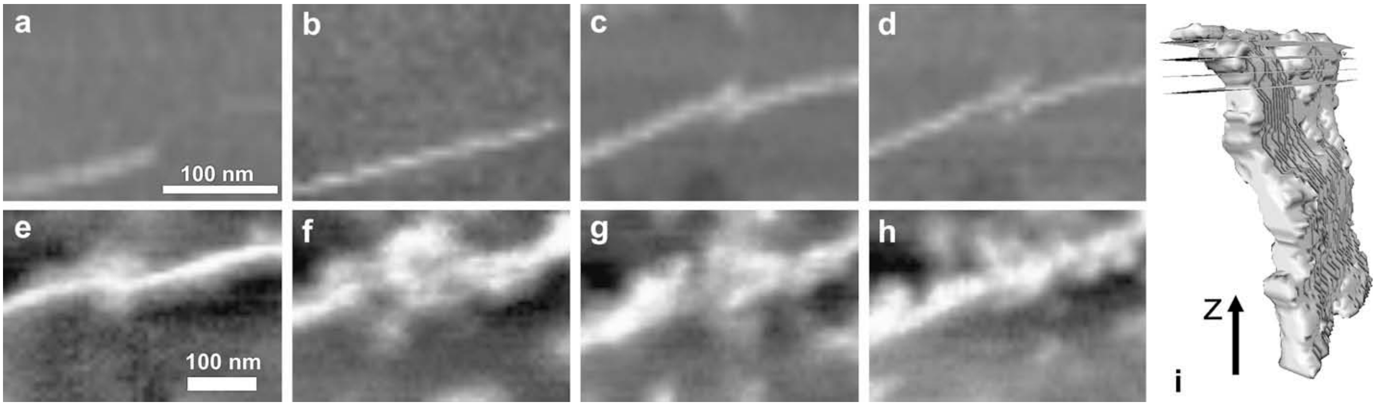

Fig. 8. A series of AFM phase images, showing initial crystallization of an iPP lamella (a)–(d) and then the tomographic slices observed through gradual etching (e)–(h). (i) The resulting tomographic reconstruction. Adapted from Ref. [79] and used with permission of ACS Publishing.

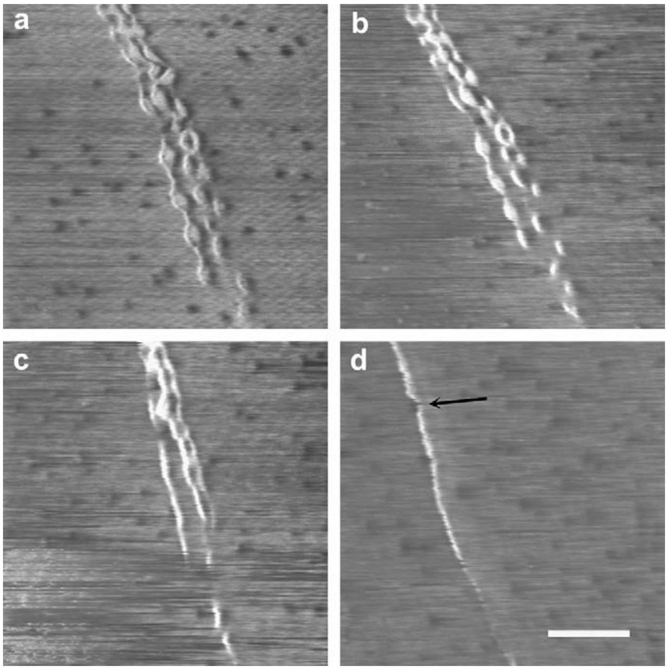

Fig. 10. A series of AFM phase images during the heating and melting of polyethylene shish–kebabs. The arrow indicates a kink caused by instrumental drift. The scale bar represents 250 nm. Reproduced from Ref. [94] with permission of Elsevier.

strength, as the re-organisation process can often give greater insight into the nature of the original crystal growth.

7. What controls the stability of polymer crystals?

A basis of many theories of crystal growth is that at small supercoolings polymers form crystals that are only just thick enough to be stable, i.e. if they are heated slightly above their crystallization temperature they will melt [32]. The Hoffman–Weeks equation [106] shows that the melting temperature depends on the crystal thickness, in agreement with the Gibbs-Thomson relationship. However, polymer crystals will often contain defects, and may be the result of a series of transformations (see above), so it would be expected that behind this gross behaviour there is additional complexity. Crystal re-organisations have been extensively studied by AFM both in situ and ex situ. In this article, the aim is to concentrate on data that is relevant to what happened during growth, rather than to examine the thickening process itself in detail.

The effect of heating on single crystals, grown in dilute solution and then dried onto substrates, has been extensively studied with AFM, following many similar ex-situ studies with electron microscopy [107–109]. This geometry is arguably prone to artefacts caused by the stresses induced by drying, secondary effects that may have come from material that crystallized on cooling the solution, and also the possibility that the solution growth structure is not similar to that found in the melt. However, the advantage is that the crystallography is usually obvious from the crystal shape, and there is no pool of molten material to complicate or hide the re-organisations. A related morphology is that found in the thin films discussed above [110,111], where crystals are again isolated on a surface, without the problems associated with drying, but also without the control and knowledge of crystallography given by the shape of single crystals grown in solution. Thickening is found to be a nucleated process in most studies, clear thickening fronts progressing through the crystal, with particular activity occurring at the edges of the crystals where mobility is highest.

Of particular relevance to theories of crystal growth is the observation that crystal thickness is not the only thing that controls crystal stability or melting. Melting starts at the edges of crystals in most (but not all) cases. This is in agreement with in-situ studies of the melting of polyethylene crystallized in relatively thick films [94]. However, in the single crystal geometry it is possible to measure crystal thickness accurately, and it is found that melting does not occur at a single, thickness controlled temperature, but rather over a range of several degrees for a particular thickness [109]. The interpretation of this is complicated by the fact that there are re-organisations occurring within the crystals that have minimal impact on the structure observed with AFM but do change the crystal stability. It may be that the variation in melting temperature for a particular thickness is caused by these re-organisations, rather than being a property of the original single crystal, i.e. rather than there being a spatial variation in the degree of stability within the same crystal. Fig. 11 shows an example of such a data set, in which melting (seen clearly in the AFM 'phase' image, not shown here) stops, and recrystallization occurs at increased thickness, but leaving material behind that has not yet thickened. Such data does seem to support the proposal that there must be some other factor, beyond simple thickness, that is influencing the melting process, as has been suggested by Strobl [37].

Watching the melting of a sample that has been observed during growth is particularly useful for determining how crystal growth conditions affect the subsequent stability of a crystal. Such experiments are still technically very demanding, as they require stable high temperature imaging for several hours while frequently changing temperature, but the results can be compelling. It had been suggested from electron microscopy studies that in-filling growth that happens after the primary lamellar structure has been laid down, is less stable than the primary structure [112]. Fig. 12 shows a series of images collected during crystallization and subsequent melting of a shish–kebab morphology [46]. The small in-filling crystal arrowed has grown under confinement caused by

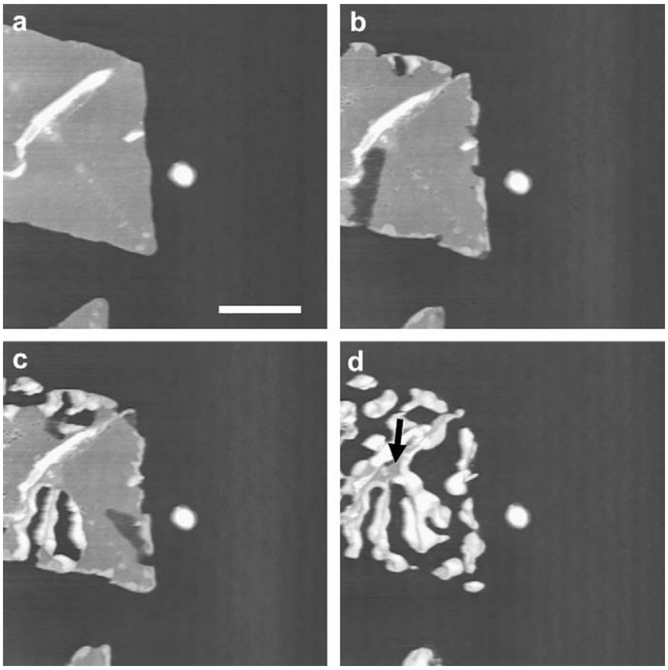

Fig. 11. A series of AFM topographic images showing the melting and re-organisation on heating of a polyethylene single crystal grown from dilute solution. The arrow in (d) shows an area that has not thickened or melted despite having the same thickness as the initial crystal. The scale bar represents 1 μm. Adapted from Ref. [94] and used with permission of Elsevier.

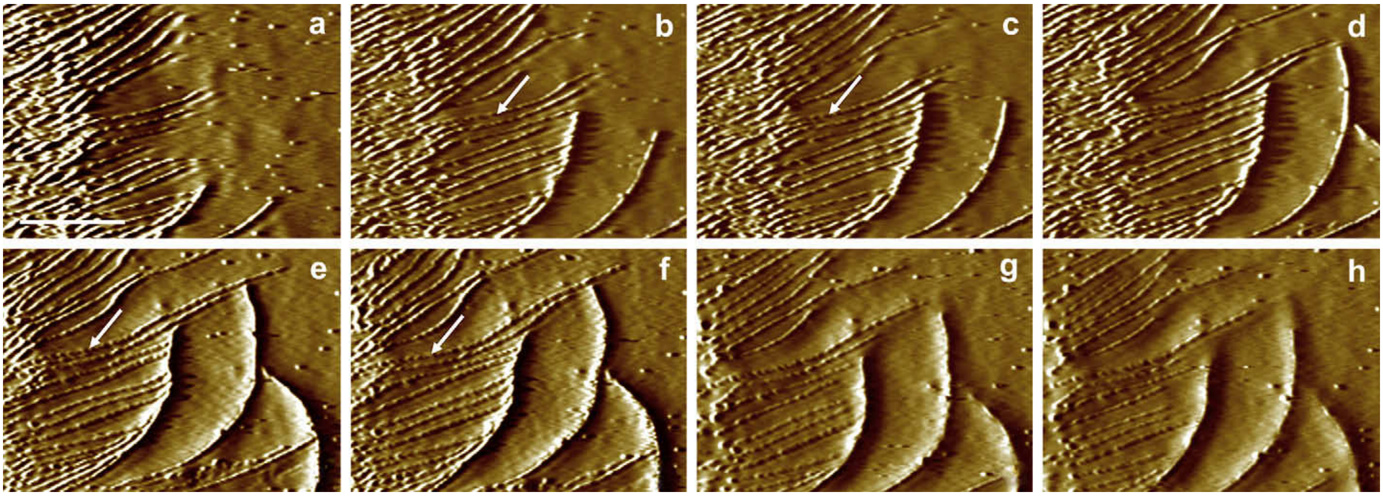

Fig. 12. A series of AFM images showing the crystallization (a)–(d) and subsequent melting during heating (e)–(h) of polyethylene lamellae grown from an oriented backbone. The arrows in (b) and (c) indicate a lamella that has grown in a small gap, while the arrows in (e) and (f) show its subsequent melting at a temperature below that of its neighbours. The scale bar represents 1 μm. (a)–(d) Adapted from Ref. [46] and used with permission of ACS Publishing.

its neighbours and its growth is ultimately stopped once the gap becomes too small (an example of the distance over which crystals impact upon their neighbours mentioned above). On heating it is found that this same crystal melts at a temperature a few degrees lower than its neighbours, despite crystallizing at the same temperature. Similar behaviour has been found in a number of cases [94], and indicates that this crystal has a reduced stability, or possibly a reduced ability to re-organise on heating, caused by the constraints imposed on it during growth. The semicrystalline polymer aggregate is a highly complex object, and the order in which lamellae grow, how close they are to their neighbours during growth and subsequently, constraints placed on the local environment into which they grew, and a myriad of other factors can influence the stability of the final lamellae. Considering the lamellae as a homogeneous population is bound to result in confusion. In-situ AFM provides an important tool to probe such factors that ultimately control the material properties.

8. Polymer nucleation

Crystallization is a two stage process, with an initial nucleation step in which fluctuations result in the formation of a stable nucleus, usually, in the case of polymers, with the help of a foreign surface (nucleating agent or impurity), followed by crystal growth. The latter process in the most widely studied, both because of convenience, as observing a rare event such as nucleation that occurs in only a tiny proportion of the total sample volume is difficult, and because in the case of polymers some characteristics of the initial nucleus, such as its thickness, are soon lost. However, in polymers that can crystallize into multiple polymorphs the initial nucleation event does tend to control the final crystal structure at the atomic scale, and nucleation is also of wider scientific interest.

There have been comparatively few studies of polymer nucleation with AFM, and the surface nature of the technique is particularly problematic here as in the case of heterogeneous nucleation the

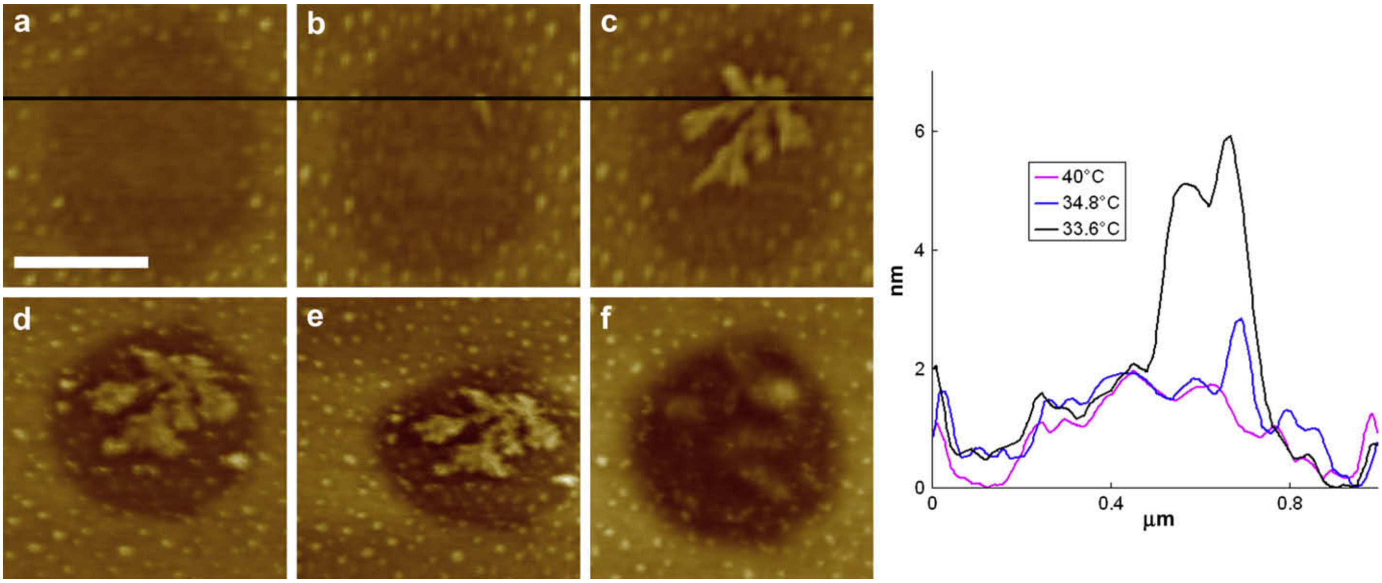

Fig. 13. (a)–(c) A series of AFM phase images showing the nucleation and growth of an iPP crystal taken during cooling. (d)–(f) The melting of the crystal on heating at a temperature indicating it may have been in the smectic phase. The graph shows line profiles across (a) at 40 °C, (b) at 34.8 °C and (c) at 33.6 °C, taken along the black line marked in the figure. The thickness of the lamella doubles between (b) and (c). Scale bar represents 500 nm. Adapted from Ref. [120] and used with permission of ACS Publishing.

nucleating surface will be hidden by the polymer itself. The effect of a nucleating surface on chain organisation has been examined by carefully cleaving between a polyethylene sample and the graphite substrate on which it grew [113]. This has shown that a surprising degree of chain sliding must occur at the nucleating interface, the strength here of the AFM technique being that just the polymer layer that was in contact with the substrate is visible, so the influence of the nucleant can be separated from subsequent growth. This work is in agreement with several studies on the re-organisation of ultra-long alkanes and polyethylene on graphite, where crystals are found to effectively 'wet' the graphite surface [114,115]. The molecules re-organise so as to lie down on the graphite surface, completely changing the original crystal structure. Another study looking at melt crystallization in a thin film observed crystals appearing and disappearing before finally leaving a stable nucleus [116], although it is difficult to say for sure if these apparently transiently crystallized regions are due to the fluctuations prior to growth of a crystal.

Following the example of traditional studies on nucleation, it is possible to increase the number of events occurring in a sample by breaking it up into discrete volumes, or droplets [117]. AFM has been used in a recent study on the nucleation behaviour of polyethylene oxide using this approach, the nucleation rates being monitored optically while sample shape and morphology can be observed ex situ, confirming a conventional lamellar morphology despite the sometimes very small volume of material [118,119]. In another case in-situ AFM has been used to observe the nucleation event, in this case in isotactic polypropylene [120]. Here an extra level of interest comes from the very low temperature at which the process is occurring, which should result in the formation of the highly disordered mesomorphic or smectic phase. Fig. 13 shows a series of images in which the nucleation event is caught soon after its initiation, and is followed by subsequent growth. The growth process occurs both laterally and vertically, the crystal nearly doubling in thickness. Subsequent heating reveals a melting temperature between 80 and 90 °C, implying that the crystal is indeed in the smectic phase. In this study it was found, perhaps not unexpectedly, that only when the droplets were extremely thin could the growth process be separated from nucleation. Only in such thin 'droplets' was growth slow enough at such a high supercooling to not occur essentially instantaneously on the time scale of an AFM image. To take such a study further and gain real insights into, for example, the geometry of the initial nucleus, both higher resolution and considerably faster imaging rates are required.

9. Summary and outlook

This paper has provided an overview of the use of atomic force microscopy to understand the crystallization of polymers. It has concentrated on the insights gained from in-situ observations, and the wide and successful application of the technique as an adjunct to other methods is beyond the scope of this article.

When AFM was initially applied to polymer crystallization, it was hoped that the molecular resolution obtainable in some other systems would provide a breakthrough in understanding. Perhaps not surprisingly, this has not happened, the reality of rapid and random thermal motion within an interpenetrating network of neighbouring molecules making such a simplistic, but highly desirable outcome, unobtainable. Instead, progress has been more incremental. Much of the strength of AFM has been in confirming what was already 'known' about the structural evolution of polymers. Real-time observation of processes such as growth and crystal thickening have revealed a world of complexity and diversity that are easy to ignore with bulk measurements. The roles played by fluctuations, by transport, and by interactions between neighbouring growth structures, become clear. New ideas about how growth occurs have not been proven or categorically disproven, but new information that must be included in any such theory if it is to be complete, has been provided.

AFM is only 24 years old as a technique, and the instruments which have been used for almost all of the research mentioned above utilise technology that is now far from cutting edge. The technology is constantly advancing, with high speed scanning [27], methods of materials mapping [121] and high resolution imaging [122], being areas that are potentially of particular importance to future applications of AFM to polymer crystals.

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