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The observation of rapid surface growth during the crystallization of polyhydroxybutyrate

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ABSTRACT

A two stage growth during isothermal cold crystallization of PHB has been observed in the temperature range 5–40 °C when a free surface is present. This growth has been investigated with optical and atomic force microscopy both in-situ and ex-situ. Initially, crystal growth is observed to be composed of lamellae oriented approximately flat-on relative to the free surface. At later stages of growth there can be a change to a distinctly different form of crystal growth that is composed of edge-on lamellae which grow at a substantially higher crystallization rate. This change in growth rate at constant temperature gives rise to curved interfaces between the slower growing flat-on growth and the faster growing edge-on growth. Several possible explanations for this change in growth rate are put forward.

1. Introduction

Crystal morphology can greatly influence the mechanical and optical properties of any crystalline material [1,2]. In the case of semi-crystalline polymer materials it is the morphology of the typical polycrystalline aggregate, the spherulite, composed of individual plate-like lamellae, which affects the physical and mechanical properties of the final polymer material. It should be expected that crystallization behaviour will differ between that in the bulk, and that at surfaces and interfaces. Hence it is important that the crystallization process and conditions that give rise to changes in the crystalline morphology of polymers, especially in relation to surfaces, is well understood so that materials with the desired physical properties can be produced repeatedly and effectively.

Poly(3-hydroxybutyrate) (PHB), a member of the polyhydroxyalkanoates (PHA) family, is a biologically synthesized polyester that has been investigated as a possible biodegradable alternative to more common thermoplastics [3,4]. However due to the high crystallinity and low glass transition temperature of this polymer it generally produces stiff and brittle materials [5]. One environment where PHB and PHAs in general are being utilised is for medical applications and tissue engineering in particular [3]. This material offers a good candidate for the study of some aspects of polymer crystallization due to properties such as a low homogeneous nucleation rate while displaying little heterogeneous nucleation [6]. For this reason, spherulites in samples of PHB can usually be followed over quite large distances during their growth. This, coupled with the fact that crystallization rates are accessible by a number of in-situ observation techniques including atomic force microscopy (AFM) where the capture of a single image can take several minutes, make PHB (and its copolymers [7]) an ideal system to follow the growth of polymer crystals. In addition, the easily accessible glass transition and melt temperatures mean that crystal growth through a whole range of undercoolings can be followed without large temperature gradients between sample and equipment.

Here the crystallization behaviour of PHB is studied with particular focus on crystallization at the free surface of thick (>1 μm) supported films and how this differs from crystallization in the bulk. This thickness is selected so that the films thickness is greater than either the lamellar thickness or the radius of gyration for a molecule of the polymer. It is expected that surface behaviour will differ from that in the bulk [8] and previous experimental [9–11] and simulation [12] work has provided evidence for differences between molecular dynamics, and hence crystallization behaviour, between material near to a surface and that in the bulk. New insights into the effect of a free surface on crystal growth will be important for both an understanding of polymer crystallization in general, and for applications such as thin films that are composed of essentially all surface and interface. The latter are becoming more commonplace, for example as barriers, as membranes, and for applications such as data storage

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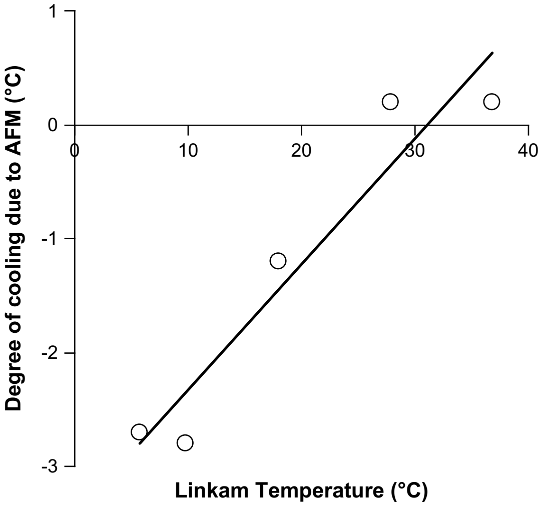

Fig. 1. Calibration plot showing the cooling effect of an AFM tip in close proximity to a heated sample between 5 °C and 40 °C. The linear line of best fit was used to correct recorded temperatures.

and medical implants. In this work an unusual dual morphology is observed during the isothermal cold crystallization of PHB.

2. Experimental method

Poly(3-hydroxybutyrate) was obtained from Fluka ($M_w = 300{,}000$, $M_w/M_n = 2.75$). The PHB was first dissolved in hot chloroform then this solution was precipitated in methanol leaving a fine PHB suspension. The powder was extracted, dried under vacuum and then dissolved in hot chloroform for sample preparation. PHB films were cast from this solution onto glass slides which were then dried under vacuum at room temperature for several hours producing films with thicknesses between 1 and 5 μm.

Optical micrographs were captured on a Nikon Eclipse ME600 attached to a computer controlled Pixelink PL-A742 CCD camera. For accurate temperature control samples were kept on an FTIR600 Linkam hot stage during image capture so that in-situ observations of isothermal crystallization could be made.

AFM images were captured on a Dimension 3100 AFM (Veeco, Santa Barbara) attached to a Nanoscope IIIa controller and a phase extender unit. Tapping Mode™ was employed using Olympus microcantilevers with nominal spring constants of 42 N m^{-1}. Again, in order to facilitate in-situ observations at various crystallization temperatures an FTIR600 Linkam hot stage was used in conjunction with the AFM as in Ref. [13]. Due to the temperature difference that exists between the AFM scan head and the sample with this experimental setup a calibration was made in order to account for the cooling effect of the scan head with sample temperatures above room temperature, and the heating effect of the scan head at temperatures below room temperature (see Fig. 1). This effect is described in detail in Ref. [14] on a slightly different experimental setup. The calibration was produced by looking at *n*-alkane melting points while undergoing AFM observation. All quoted sample temperatures in this work while under AFM observation have had this calibration applied to them.

3. Results

Fig. 2a shows a bright field optical micrograph of a PHB film undergoing crystallization at 23 °C under ambient conditions. The three spherulites in the image area display two circular and clear boundaries in contrast to the single boundary seen around typical spherulites. In the outer regions of the spherulites showing two boundaries the crystal morphology appears rough and less predictable in its ordering than that in the smoother central region.

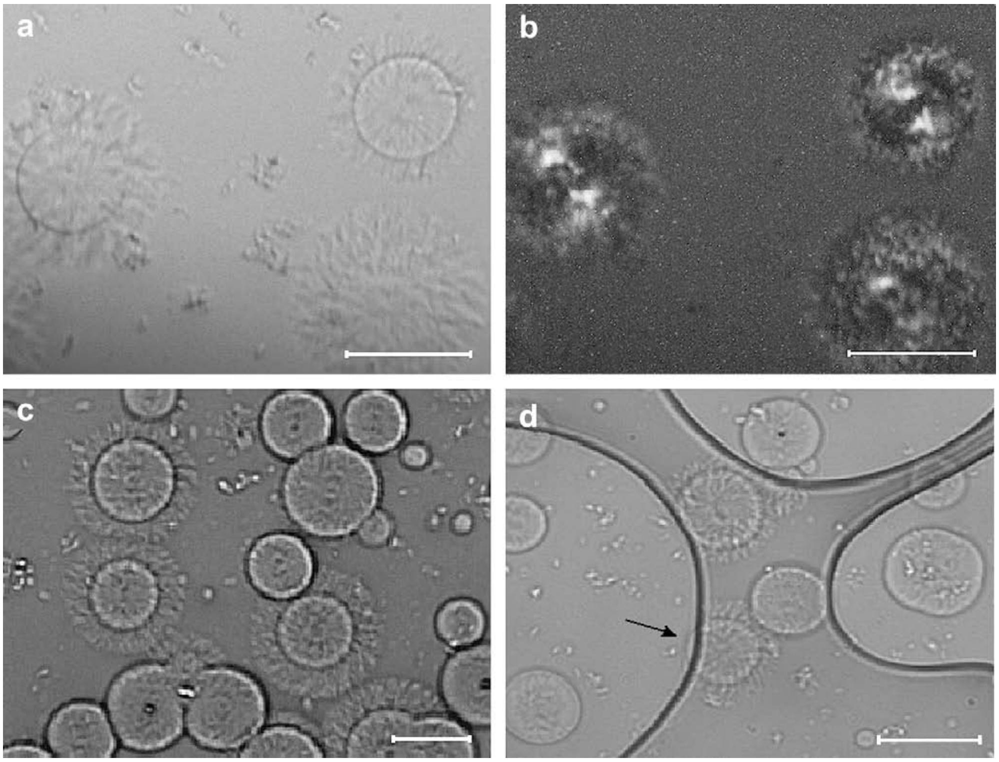

Fig. 2. Optical micrographs captured during isothermal crystallization. (a) 23 °C in air. (b) same area as (a) with crossed polarisers. (c) 24 °C under a nitrogen atmosphere and in the presence of a desiccant. (d) Partially sandwiched PHB film between two glass slides undergoing crystallization at 30 °C. All scale bars represent 20 μm.

Similar observations to this have been made before with PHB [15] where the occurrence of the rough crystal morphology was associated with the presence of water, as the rough morphology only appears when crystallization is conducted either under water or in air where atmospheric moisture is present. When the crystallization was repeated between glass slides the rough morphology was no longer seen and in [15] it was assumed that this was due to the lack of water in the case between two glass slides.

However, PHB crystallization in the absence of water has been investigated and an example of this is shown in Fig. 2c. This shows a PHB film crystallizing under a nitrogen atmosphere and in the presence of a desiccant (phosphorus pentoxide) to ensure that no water was present and demonstrates that the rough morphology can still form in dry conditions.

In addition to PHB crystallization under air and nitrogen, PHB crystallization when the film was sandwiched between two glass slides was also investigated. Fig. 2d shows a region of a PHB film undergoing crystallization at 30 °C while partially sandwiched between two glass slides. Within this image there are two distinct domains due to the PHB film not totally wetting the top covering glass slide, resulting in regions with a free surface where the film has not wet the cover slide, and regions with no free surface where the PHB film has wet the covering glass slide. In Fig. 2d the three regions that display no free surface appear slightly lighter than the region which does possess a free surface. Fig. 2d then clearly shows that spherulites displaying the outer optically rough morphology only appear in the areas with a free surface present and in the regions with no free surface the rough morphology is not seen. Spherulites displaying the rough morphology which then grow into an area with no free surface only display the inner spherulite boundary, indicating that the rough morphology stops growing when there ceases to be a free surface (arrowed in Fig. 2d). This image clearly demonstrates that in order for the observed rough morphology to form it is necessary for a free surface to be present. This is consistent with previous observations on this phenomenon despite the different conclusions reached for the necessary conditions for the formation of the rough morphology.

Similar optical micrographs taken with cross-polars (Fig. 2b) reveal a reduction in birefringence on approaching the outer edge of the spherulite where the rough morphology appears. These observations are consistent with the notion that the rough morphology only grows in the free surface region of the PHB film. It seems likely that the rim of faster growth (i.e. the optically rough surface growth) will initiate further crystal growth away from the surface and down into the bulk. This is supported by the reduction in birefringence as the outer edge of the spherulite is approached.

In addition to optical microscopy, in-situ AFM studies were conducted on crystallizing PHB films to investigate the crystal growth and morphology in the free surface region. Fig. 3a shows an

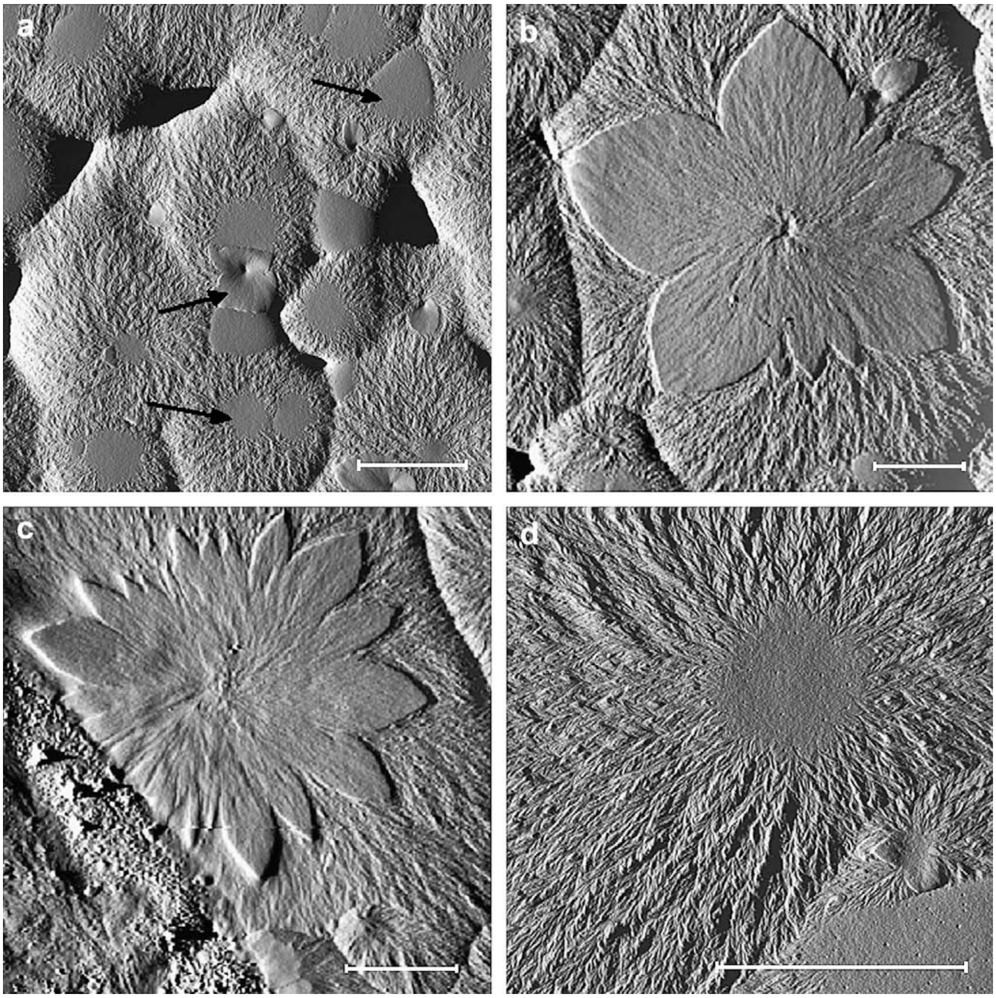

Fig. 3. AFM amplitude images showing four examples of crystallized PHB samples. Image (a) was captured after crystallization at 20 °C. Images (b), (c) and (d) were captured after crystallization at 27 °C demonstrating the differing spherulite morphologies that can develop when crystallized under the same conditions. All scale bars represent 15 μm.

AFM image taken on a PHB sample crystallized under air at 20 °C with several spherulites in the image area. The central regions of each spherulite seen in this image show a topographically smooth morphology (three examples are arrowed in Fig. 3a) which at some later stage of growth must switch to the topographically rougher morphology that is seen in the outer regions of these spherulites. These features are similar to what is observed under the optical microscope.

In order to investigate the crystal morphology at a lamellar scale, higher resolution AFM images were captured both in-situ during growth and ex-situ. Examples of these images are shown in Fig. 4a–i. In-situ observations were made on both the slow growing smooth morphology and fast growing rough morphology crystallizing at high resolution and at low crystallization temperature so that the growth could be followed via AFM (Fig. 4a, b, d and e). Also, high resolution ex-situ observations were made on one of these areas after crystallization in order to identify differences between the crystal lamellae (Fig. 4c and f).

From the images in Fig. 4 a clear difference in the lamellar orientation can be seen between the observed rough and smooth crystal morphologies. The slower growing smooth morphology displays what appear to be approximately flat-on oriented lamellae (Fig. 4a and d) with respect to the free surface whereas the faster growing rough morphology displays approximately edge-on lamellae (Fig. 4b and e). From the AFM images it is not possible to precisely define the angle that the plane of a lamella makes with the surface. The 'flat-on' lamellae are seen as stacked or terraced plates with a spacing between successive edges of approximately 20 nm, with less than 1 nm variation in height between successive edges. From this we can estimate that the angle these lamellae make with the surface is 15° or less (taking the lamellar spacing as 5 nm for PHB [6] and the geometry outlined in the schematic in

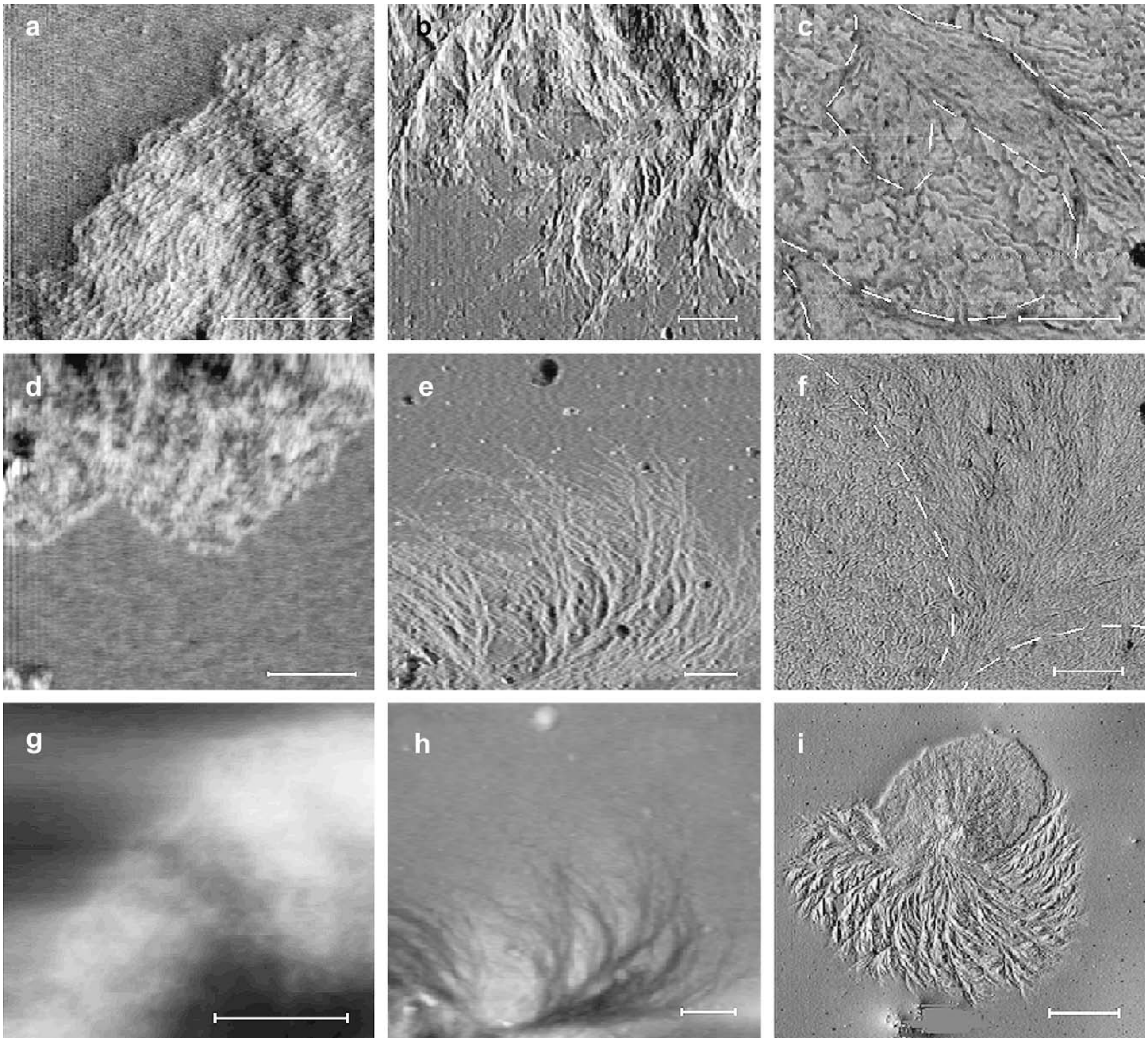

Fig. 4. High resolution AFM phase images showing both in-situ (all except c and f) and ex-situ (c, f) observations of PHB crystal lamellae. (a) flat-on crystallization at 8 °C with corresponding height image (g), (b) edge-on crystallization at 8 °C, (c) unclear flat-on to edge-on transition region with dashed line indicating boundary regions captured after crystallization at 40 °C, (d) flat-on crystallization at 10 °C, (e) edge-on crystallization at 6 °C with corresponding height image (h), (f) flat-on to edge-on transition region with dashed line indicating boundary regions, captured after crystallization at 30 °C, (i) simultaneous flat-on and edge-on crystallization at 15 °C. Scale bars for images (a) to (h) represent 250 nm, scale bar in image (i) represents 2.5 μm.

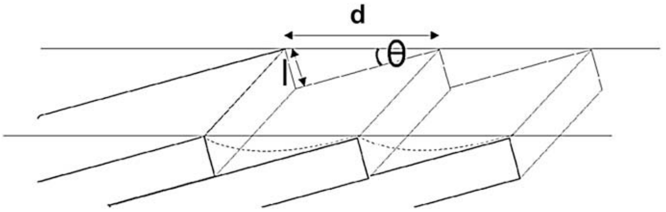

Fig. 5. A sketch showing a lamella oriented approximately flat-on to the sample surface. Theta is the angle to the sample surface discussed in the text. The crystal thickness, *l*, is approximately 5 nm in PHB, and the measured separation between crystals intersecting the surface, *d*, is 20 nm or more, giving an angle *θ* of less than 15°. The dotted parabolic lines represent the assumed position of the amorphous surface.

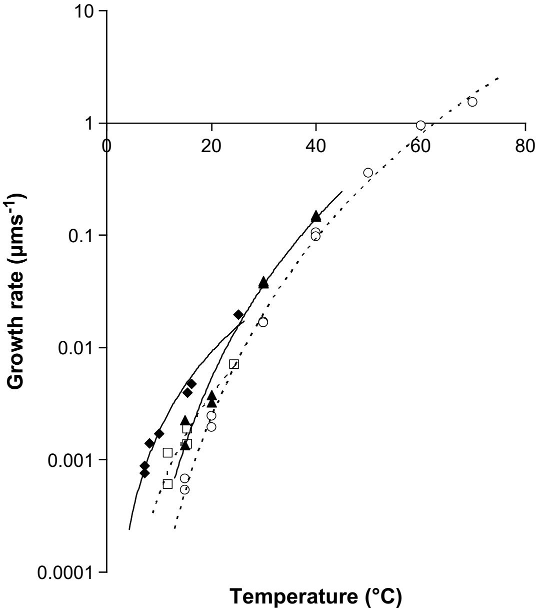

Fig. 6. A plot showing the growth rates as a function of temperature for flat-on and edge-on PHB lamellae measured by both AFM and optical microscopy. (□) AFM of flat-on growth, (◆) AFM of edge-on growth, (▲) optical microscopy on edge-on growth and (○) optical microscopy of flat-on growth.

Fig. 5). For the 'edge-on' case it is more difficult to define the angle as a tilt of the lamella with respect to the surface normal would only be visible as a broadening of the measured lamellar thickness until large angles are reached, and the measurement of thickness is strongly limited by the radius of curvature of the AFM tip. From our data we estimate that the lamellae are at an angle of more than 45° to the surface. In the following we will refer to the two types of growth as 'edge-on' and 'flat-on' for the sake of contrast between the two clearly different modes of growth.

In the case where flat-on lamellae are observed the crystal melt interface is abrupt in comparison to the case where edge-on lamellae are observed (seen as fine filaments). The crystallization of the edge-on lamellae gives rise to a rougher crystal melt interface due to the presence of the primary lamellae growing ahead of the main crystal growth front. This is demonstrated in Fig. 4i on a larger length scale where both the flat-on and edge-on oriented morphologies are shown growing alongside one another.

In addition to observations of spherulite and lamellar morphology, in-situ observations of PHB crystallization recorded with both optical and atomic force microscopy at various magnifications were used to directly measure crystal growth rates of both morphologies (i.e. the flat-on and edge-on oriented crystal morphologies as seen with AFM, or the smooth bulk and rough surface crystal morphologies as seen with optical microscopy). This data is shown in Fig. 6. It can be seen that at all temperatures where AFM data was recorded the edge-on morphology grows faster than the flat-on morphology at a given temperature, and this is also true for the surface and bulk morphologies as observed with optical microscopy. This difference in growth rates is implied by the curved nature of the interface between the flat-on and edge-on regions. Due to the surface nature of this unusual crystallization behaviour observations were difficult to obtain with optical microscopy of the edge-on crystal morphology growing at the same time as the flat-on morphology, as typically when one type of growth was in focus the other was not.

4. Discussion

The data presented above demonstrates that PHB displays unusual two stage growth during isothermal crystallization where, in the presence of a free surface, the crystallization morphology and growth rate change. This is characterised by a faster than bulk growth rate for lamellae oriented largely edge-on to the surface, while lamellae oriented largely parallel to the surface maintain the same growth rate as the bulk. At least qualitatively similar behaviour has been observed previously in other systems [16,17], although it is not a universal feature of surface crystallization in polymers.

The increase in crystal growth rate associated with the change in crystal morphology gives rise to the observation of double spherulite boundaries with optical microscopy and "flower" like shapes with AFM. The appearance of the interface between the smooth and rough regions can appear different from spherulite to spherulite even within the same sample where all spherulites grew under identical conditions. For example, the three spherulites shown in Fig. 3b–d here are all examples of PHB spherulites grown at 27 °C, yet the interfaces between the edge-on and flat-on crystal morphologies appear different. The main difference between these three spherulites is the number of "petals" involved around the edge of each of the flat-on regions. Considering the spherulite as a "flower" (e.g. Fig. 3b) which is composed of a number of "petals", the number of these petals depends on the number of instances that the growth front has switched from the flat-on morphology to the edge-on morphology. Then each "petal" forms because the edge-on morphology grows faster than the flat-on one (Fig. 6). Thus at each point where the morphology changes from the slow growing flat-on type to the faster growing edge-on type opposite edges of neighbouring "petals" will be produced as the edge-on morphology overtakes the flat-on one. This gives rise to the curved interfaces that are observed. The closer together that these switching points are (i.e. the more frequent) the smaller each petal will be and the more abrupt the interface between the two growth regimes will appear.

An adequate explanation of this unusual behaviour should explain why this transition is only seen in the presence of a free surface and also why the points where the transitions occur are not regular in their position or frequency from spherulite to spherulite (unlike in [17]).

This behaviour is only seen at the free surface as this is the only region where the edge-on lamellae grow faster than the flat-on ones. Indeed away from the free surface in the bulk of the sample different lamellar orientations are equivalent as there is no interface to orientate with respect to. As the free surface is approached the lamellae are orientated with respect to it having either their fold planes more parallel to the surface (flat-on) or more perpendicular to it (edge-on). From the data collected in this work it is not clear why the edge-on lamellae grow faster than flat-on ones. A model that attempts to account for the observed crystallization morphologies along with a number of possible explanations for the observed difference in growth rates will now be presented.

A simple model is proposed that plots out the boundary between flat-on and edge-on growth based on three variables; the growth rate of the fast and the slow lamellae (G_{fast} and G_{slow} respectively) and the time after the initial nucleation of the spherulite where the transition between slow and fast growing lamellae occurs (t). The model assumes that the curvature of the boundary region is simply due to the difference in growth rates between the slow and fast growing lamellae. Because the edge-on lamellae are observed to grow faster than the flat-on ones (Fig. 6) one would expect that the faster growing region would gradually overtake the slower growing region. The larger the difference between the growth rates of the different regions the greater the degree of curvature of the boundary region between them. Presented below (derivation given in Appendix 1) are the two equations used to plot out the boundary region in plane polar coordinates where Δt represents the time that has passed since the transition from slow to fast growing lamellae occurred, R and ϕ are the radius and angle respectively of the boundary position in plane polar coordinates.

$$R = G_{\text{slow}}(t + \Delta t) \tag{1}$$

$$\cos\phi = 1 + \left(\left(1 - \frac{G_{\text{fast}}^2}{G_{\text{slow}}^2}\right)\cdot\frac{\Delta t^2}{2t(t+\Delta t)}\right) \tag{2}$$

The radial distance of the boundary from the centre of the spherulite is the distance that the slowest growing, flat-on lamellae would have grown in the time that the spherulite had been growing. The equation for the angular position of the boundary is derived using trigonometry, by considering where a faster growing spherulite that has nucleated on the edge of an already partially developed slower growing spherulite would meet.

Shown in Fig. 7 are two such plots made with this model based on the observed spherulite also shown. The plots were made by measuring the initial distances and angular positions of the transition points where flat-on oriented lamellae change to edge-on ones with respect to the centre of the spherulite. This distance was converted to the time (t) by dividing the measured distance by the observed growth rate of the slower growing, flat-on lamellae at the temperature that the spherulite grew at.

In Fig. 7a an AFM image of a PHB spherulite crystallized at 27 °C is shown alongside two plots of the boundary between the two different regions using the model described above. The plot shown in Fig. 7b is made using the transition points measured from the AFM image and growth rates corresponding to those shown in Fig. 6, which are 0.0108 μm s^{-1} and 0.0242 μm s^{-1} for G_{slow} and G_{fast} respectively. As can be seen from Fig. 7, the plot does not represent the observed boundary shape when measured crystallization rates are used. The use of measured crystallization rates over predicts the degree of curvature of the boundary region between flat-on and edge-on lamellae suggesting that the difference between the crystallization rates of the slower and faster growing regions is less than that shown in Fig. 6. Fig. 7c shows a similar plot but using different values for G_{slow} and G_{fast} in order to try and correctly plot the shape of the boundary region observed in Fig. 7a. The plot shown in Fig. 7c employs a ratio of 1.5 for $G_{\text{fast}}/G_{\text{slow}}$ whereas the values used in Fig. 7b correspond to a ratio of 2.23 indicating that the boundary does curve less than expected from growth rate data. It should be mentioned that the growth rates shown in Fig. 6 are made up of measurements recorded away from any boundary regions. It is possible that the growth rates of the edge-on lamellae at and near to the boundary with the flat-on lamellae are slower than those measured away from such boundaries or, alternatively, that the flat-on lamellae grow faster than expected near the boundary.

The above provides a quantitative description of what is happening, but provides no explanation for why it happens. There have previously been a number of studies on the effect of film thickness on crystallization rate, in which a slowing of the growth rate with decreasing film thickness has been observed [18–20]. In very thin films an additional reduction in growth rate and a significant change in morphology occurs, as once the crystal is thicker than the melt it is necessary for there to be substantial diffusion accompanying growth. This transition to largely diffusion controlled growth leads to dendritic and related morphologies. In contrast, our experiments are carried out in relatively thick films, and similar surface growth is observed optically in films that are many microns thick, so outside the range where film thickness has been observed to affect growth rate. In thin films such behaviour may also occur, but it would be in addition to the effects imposed by the confinement of the film geometry, and may be of lesser importance. In films thinner than 100 nm or so we have not observed initial crystallization in the flat-on orientation, but only edge-on, so comparative growth rates have not been made. PHB

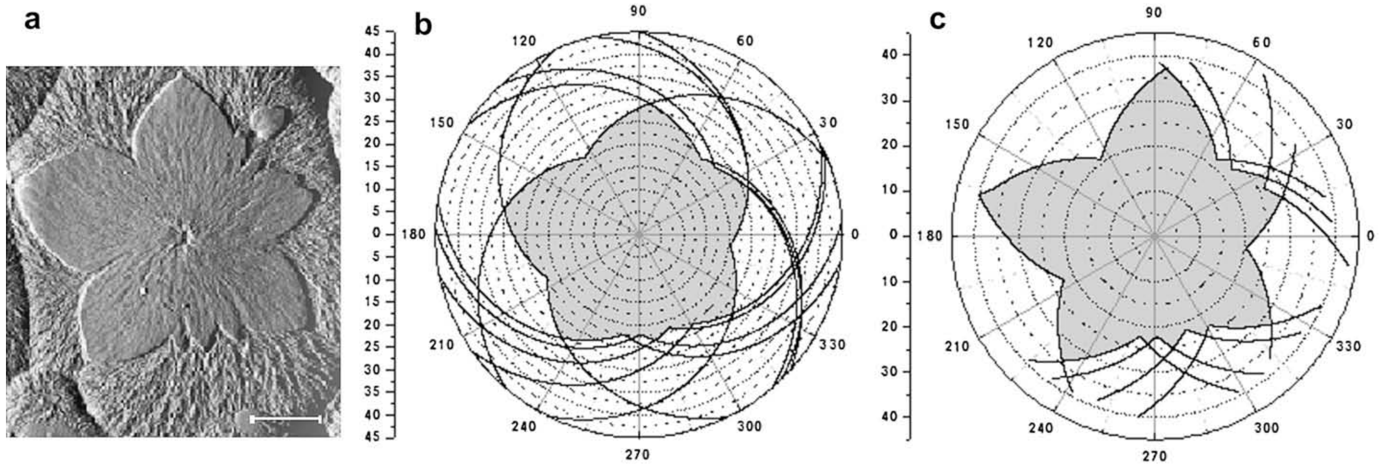

Fig. 7. Depiction of model to account for curvature of flat-on edge-on boundary. (a) AFM image of a typical PHB spherulite displaying the dual crystal growth crystallized at 27 °C where the scale bar represents 15 μm. (b, c) fits to observed curvature based on the above model where vertical scales represent μm. Growth rates used in the model are; the observed crystallization rates at 27 °C of 0.0108 μm s^{-1} and 0.0242 μm s^{-1} for G_{slow} and G_{fast} respectively shown in (b) and rates giving best fit to data of 0.006 μm s^{-1} and 0.009 μm s^{-1} for G_{slow} and G_{fast} respectively shown in (c).

nucleates so rarely that it is very difficult to do experiments on thinner films. In the following we will put forward several possible explanations that could account for our observations.

(i) A build up of stress during growth that retards growth in the bulk but is relieved by the presence of the surface. Crystallization is accompanied by a volume reduction due to the higher density of the crystalline phase than the amorphous phase. It has been argued [21–23] that this volume reduction means that material transport (flow) is required in the amorphous phase to maintain constant density, and that this flow is driven by a pressure gradient. It is known that there can be cavitation of the melt, or cracking of the growing crystal which it has been suggested is due to the transfer of stress from the melt to the crystal [5,24]. The existence of a pressure gradient will result in an effective lower supercooling for a crystal at the growth front than for a hypothetical crystal that is not surrounded by a lower pressure region. The lower supercooling leads to a lower driving force for crystallization and hence a lower growth rate, if any possible concomitant reduction in T_g can be ignored. At the melt-air interface, stress can be relieved simply by deforming the free surface, resulting in the depletion zone that is frequently observed in front of growing spherulites when imaged with AFM e.g. [5]. If the above argument relating to a self-induced pressure gradient or stress is correct, we might expect somewhat faster growth at the surface than in the bulk.

Although the above provides a possible explanation for why growth should be faster near to the surface, it does not explain why only edge-on crystals grow faster. It may be that the deformation of the free surface in front of the growing spherulite will interact with the lamellae in different ways depending on their orientation. In the case where a lamella is oriented flat-on relative to the free surface the deformation will significantly alter the path along which molecules will have to diffuse in order to reach the growth front. Further growth flat-on relative to the surface will occur more easily just below the surface, where it is not hindered by the formation of the depletion zone. A lamella in this lower position will then undergo the same process as the initial one of forming a depletion zone ahead of it until eventually slows and so on. Hence the growing flat-on lamellae will always have a limited source of material that is easily capable of attaching to the growth front because of the deformation of the melt surface caused by the volume reduction of growth and its resultant stress. Such a mechanism would result in a series of stacked or terraced flat-on lamellae at the free surface which is consistent with observations presented above (Fig. 4a, c, d and f). This should also lead to the growth front of the flat-on crystal morphology being higher than the melt into which it is growing, as the formation of the depletion zone means that the height of the melt ahead of the growing crystal will be lower than that of the growing crystal itself. This is consistent with the height data displayed (Fig. 4g).

However, after the formation of this depletion zone at the free surface and the slowing of growth of the initial flat-on lamellae, further growth could continue in an edge-on orientation relative to the free surface rather than a flat-on one. In the event of such a transition, lamellar growth would become less dependant on location relative to the surface than in the flat-on case as most of the growing lamella is not in contact with the free surface. The edge-on lamella is free to grow more rapidly just below the surface (i.e. below the depleted melt deformation) but in a region that is not at reduced pressure (and hence grows more rapidly than in the bulk). Such behaviour should lead to a volume reduction in this region just below the surface and hence one may expect that the edge-on growth is lower than the surrounding melt which is consistent with observations presented above (Fig. 4h). Once this transition to edge-on growth occurs it will most likely lead to the growth front becoming more irregular. Lamellae that are further away from their neighbours will also be less affected by any residual problems with a pressure reduction leading to slow growth, as the pressure reduction is caused by a large number of adjacent lamellae simultaneously growing and creating a volume reduction. This relief of stress through the transition to edge-on growth can only occur at the free surface. In the bulk the stress could be relieved by the formation of a less dense growth front, but this density of the growth front is presumably controlled by some other inherent characteristics (such as the number of dislocations leading to branches that occur in the growing lamellae) which can only be varied by changing the material chemistry. We suggest that the reason that such behaviour is not universally observed is that in many other materials the growth front is less dense, the high density of the PHB growth front possibly being caused by its exceptional stereoregularity due to its biological origin, and hence the impact of stress build up on growth is often less significant.

This possible account for the observed unusual behaviour in films of PHB may also offer an explanation for why the model presented above (Fig. 7) does not accurately predict the degree of curvature of the boundary region between the flat-on and edge-on oriented lamellae. The edge-on crystals grow most rapidly when the melt is not supporting a stress. In close proximity to the transition region there will still be residual stress, and hence reduced growth rate. Once growth has continued for some time in the morphologically less dense edge-on morphology, the stress will be completely relieved and growth will reach its maximum possible value. Thus it may be expected that in the boundary region where edge-on lamellae are crystallizing near to the flat-on ones, the growth rates of the edge-on lamellae are reduced from the value that is measured away from the boundary (such as those rates measured in Fig. 6). This would then cause the model presented above (Fig. 7) to over account for the curvature of the boundary region.

(ii) Contaminants or impurities that segregate to the surface. If sample contamination occurred, maybe due to the cleaning via precipitation not removing all impurities or some other source of contaminants, then this could account for the difference in growth rates of lamellae oriented in different directions [25–28]. It is plausible that any impurities will tend to migrate to one of the film interfaces, one of which is the free surface [31]. The orientation of the crystalline lamellae relative to the free surface will then become relevant to the lamellar growth rate. Lamellae oriented edge-on to the impurity enriched free surface could grow and incorporate the impurities into the amorphous layers between the lamellae, whereas flat-on lamellar growth would have the amorphous layer further away from the free surface (approximately a lamellar width ~10 nm) thus making incorporating the impurities more difficult. So the growth rate of the flat-on lamellae would be slower as the impurities have further to diffuse in order to be incorporated into the semi-crystalline structure than in the edge-on case. Such a contaminant related explanation for the observed behaviour seems unlikely, however, as the polymer used has first been cleaned via precipitation and on some occasions the precipitation process was repeated several (up to 5) times and no difference in the occurrence of two stage crystallization behaviour between samples cleaned once and a number of times was observed. Also, one would expect such behaviour to lead to faster crystal growth rates in the bulk when compared to those at the free surface which is not observed.

(iii) Order induced by the presence of the surface prior to crystallization. Ordering could occur due to preferential segregation of certain groups or chain ends to the free surface, or possibly due to polymer chains near to the free surface experiencing spatial confinement and so not assuming a random coil conformation [30–32]. For example, the polymer molecules may preferentially align parallel to the free surface (as suggested in [29]) and effectively experience biaxial orientation. Such an orientation is known to increase crystallization rate, and edge-on lamellar crystallization would require less reorganization of the crystallizing molecules. This would give a faster edge-on lamellar growth rate than the flat-on rate. In other words, there is only rotational diffusion of molecules around the *z*-axis (the axis running through the thickness of the film) rather than the three dimensions as in the bulk. If this situation does give rise to the observed two stage crystallization behaviour in PHB it would be difficult to explain why this phenomenon is not a common feature in many different crystallizable polymer systems.

(iv) Increased mobility at the surface. A related explanation invokes the suggested increase in molecular mobility in a small (~10 nm thick) region at the surface [32,33] and thus we could expect faster crystallization rates at the free surface. A study related to ours on the orientation of lamellae at the surface of films of different thicknesses [34], suggested a primary role for the nucleation step in the orientation in that system, but also a change in mobility at the surface. In our system it is difficult to see why the flat-on lamellae would crystallize more slowly than the edge-on ones when growth is observed at the surface.

(v) The free surface affecting the nucleation barrier. If there is a difference between the interfacial energies of the edge-on and flat-on crystal lamellae when at the free surface then the barrier to crystallization in the two cases will be different and thus so will the growth rates. For example, a lamella growing in the bulk will differ from a flat-on lamella at the free surface because at the free surface one of the interfaces has changed. In this case a fold plane–melt interface will have changed to a fold plane-free surface interface which will likely have different interfacial energies associated with them. An edge-on lamella at the free surface will differ from a flat-on oriented one in that it will have an edge-free surface interface with all other interfaces being melt interfaces whereas a flat-on lamella will have a fold plane-free surface interface with all others being melt interfaces. Thus different orientations of crystalline lamellae with respect to a surface can give rise to different interfacial surface energies and thus a different barrier for crystallization leading to different growth rates.

From our data it is not possible to choose categorically between these, or any other, explanations for the observed behaviour.

Individual PHB spherulites can appear different even when crystallized from the same sample and under the same conditions (Fig. 3a). They can display different distances from the spherulite centre to where the transition from flat-on to edge-on lamellae occurs and also different numbers of transition events around different spherulites. This is not the case with PESU crystallization reported elsewhere [17] where similar curved boundaries are observed between flat-on and edge-on oriented lamellae with respect to the free surface. These clear differences between otherwise similar behaviour may be because in the case of the PESU observations the transition region is located at the corner of a well defined and symmetrical lozenge whereas in the case of PHB we are dealing with lamellae twist in a polycrystalline aggregate.

In the above we have not considered the exact nature of the transition from ‘flat-on’ to ‘edge-on’ growth, but rather the question of why one orientation should grow faster than the other. Why such a large change in orientation should occur at a branch point is unclear, but is related to the question of branching and splaying in polymer lamellae that has been considered for many years in the context of spherulite growth in general as well as in lamellar twist in banded spherulites [34,35]. It may be that new experimental methods, such as the nanotomography used in [36], could help to answer this question.

5. Conclusions

In this paper unusual two stage crystal growth has been reported in PHB during isothermal crystallization between 5 and 40 °C. It has been shown that lamellae initially prefer to grow flat-on relative to the free surface of the PHB film but, at later stages of spherulite development, a transition from flat-on oriented lamellae to edge-on oriented lamellae occurs. A significant difference in the growth rates of these two lamellar orientations has been measured and this difference results in curved interfaces between regions composed of the two different orientations.

Several possible explanations attempting to account for the observed crystallization behaviour have been presented. The build up of stress due to the volume reduction on crystallization, coupled to the stress relieving capability of the surface and the resultant selection between edge-on and flat-on growth, seems most likely of the explanations offered in this paper. This mechanism is able to account for more than just a difference in growth rates for different orientations of PHB lamellae. It is clear that, at least in the case of PHB, the presence of a free surface has a profound effect on both the crystallization dynamics and the resultant crystal morphology.

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Appendix 1

To calculate the position of the interface between the flat-on and edge-on crystals, the intersection between a spherulite growing at rate G_{slow} for some time t_2, and a spherulite (or spherulites) growing at rate G_{fast} that had nucleated at the growth front at time t is calculated. The diagram (Fig. A1) shows the situation.

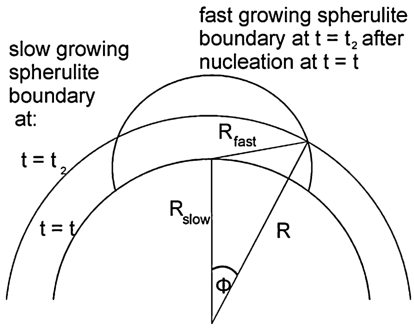

Fig. A1. A sketch showing the nomenclature used to calculate the observed interfaces.

From the diagram we can define the following:

$$t_2 - t = \Delta t$$
$$R_{\mathrm{slow}} = G_{\mathrm{slow}} t$$
$$R = G_{\mathrm{slow}} t_2$$
$$R_{\mathrm{fast}} = G_{\mathrm{fast}} \Delta t$$

The Law of cosines gives.

$$\cos\phi = \frac{R_{\mathrm{slow}}^2 + R^2 - R_{\mathrm{fast}}^2}{2R_{\mathrm{slow}}R}$$

Which can be rearranged to give R and $\cos\phi$.

$$R = G_{\mathrm{slow}}(t + \Delta t) \tag{A1}$$

$$\cos\phi = 1 + \left(\left(1 - \frac{G_{\mathrm{fast}}^2}{G_{\mathrm{slow}}^2}\right) \cdot \frac{\Delta t^2}{2t(t + \Delta t)}\right) \tag{A2}$$

References

[1] Davis GT, Eby RK, Martin GM. Journal of Applied Physics 1968;39(11):4973–81.

[2] Leisen J, Beckham HW, Sharaf MA. Macromolecules 2004;37(21):8028–34.

[3] Williams SF, Martin DP, Horowitz DM, Peoples OP. International Journal of Biological Macromolecules 1999;25(1–3):111–21.

[4] Sudesh K, Abe H, Doi Y. Progress in Polymer Science 2000;25(10):1503–55.

[5] Hobbs JK, McMaster TJ, Miles MJ, Barham PJ. Polymer 1996;37(15):3241–6.

[6] Barham PJ, Keller A, Otun EL, Holmes PA. Journal of Materials Science 1984;19(9):2781–94.

[7] Hobbs JK, McMaster TJ, Miles MJ, Barham PJ. Polymer 1998;39(12):2437–46.

[8] Backus EHG, Bonn M. Journal of Chemical Physics 2004;121(2):1038–49.

[9] Forrest JA, DalnokiVeress K, Stevens JR, Dutcher JR. Physical Review Letters 1996;77(10):2002–5.

[10] Pu Y, Rafailovich MH, Sokolov J, Gersappe D, Peterson T, Wu WL, et al. Physical Review Letters 2001;8720(20):4.

[11] Wu WL, Sambasivan S, Wang CY, Wallace WE, Genzer J, Fischer DA. European Physical Journal E 2003;12(1):127–32.

[12] Mansfield KF, Theodorou DN. Macromolecules 1991;24(23):6283–94.

[13] Hobbs JK, Humphris ADL, Miles MJ. Macromolecules 2001;34(16):5508–19.

[14] Schonherr H, Bailey LE, Frank CW. Langmuir 2002;18(2):490–8.

[15] Hobbs JK, Barham PJ. Polymer 1997;38(15):3879–83.

[16] Reiter G, Botiz I, Graveleau L, Grozev N, Albrecht K, Mourran A, et al. Progress in understanding polymer crystallization. In: Reiter G, Strobl G, editors. Lecture notes in physics. Berlin: Springer-Verlag; 2007 [chapter 11].

[17] Kawashima K, Kawano R, Miyagi T, Umemoto S, Okui N. Journal of Macromolecular Science-Physics 2003;B42(3–4):889–99.

[18] Massa MV, Dalnoki-Veress K, Forrest JA. European Physical Journal E 2003; 11:191.

[19] Taguchi K, Toda A, Miyamoto Y. Journal of Macromolecular Science B Physics 2006;45(6):1141–7.

[20] Sawamura S, Miyaji H, Izumi K, Sutton SJ, Miyamoto Y. Journal of Physical Society of Japan 1998;67(10):3338.

[21] Schultz JM. Polymer crystallization: the development of crystalline order in thermoplastic polymers. Oxford University Press; 2001 [chapter 10].

[22] Toda A, Okamura M, Taguchi K, Hikosaka M, Kajioka H. Macromolecules 2008;41:2484–93.

[23] Toda A, Taguchi K, Kajioka H. Macromolecules 2008;41(20):7505–12.

[24] Galeski A. Progress in Polymer Science 2003;28(12):1643–99.

[25] Keith HD, Padden FJ. Journal of Applied Physics 1964;35(4):1270.

[26] Keith HD, Padden FJ. Journal of Applied Physics 1964;35(4):1286.

[27] Keith HD, FJP. Journal of Applied Physics 1963;34(8):2409–21.

[28] Reijme MA, van der Gon AWD, Draxler M, Gildenpfennig A, Janssen FJJ, Brongersma HH. Surface and Interface Analysis 2004;36(1):1–7.

[29] Durell M, Macdonald JE, Trolley D, Wehrum A, Jukes PC, Jones RAL, et al. Europhysics Letters 2002;58(6):844–50.

[30] Factor BJ, Russell TP, Toney MF. Physical Review Letters 1991;66(9):1181–4.

[31] Ma Y, Hu WB, Reiter G. Macromolecules 2006;39(15):5159–64.

[32] Forrest JA, Dalnoki-Veress K. Advances in Colloid and Interface Science 2001;94(1–3):167–96.

[33] Kawana S, Jones RAL. Physical Review E 2001;6302(2):6.

[34] Wang Y, Chan CM, Ng KM, Li L. Macromolecules 2008;41:2548.

[35] Bassett DC. Journal of Macromolecular Science Physics 2003;B42(2):227.

[36] Franke M, Rehse N. Macromolecules 2008;41:163.