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Direct observations of the growth of spherulites of poly(hydroxybutyrate-co-valerate) using atomic force microscopy

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Atomic force microscopy (AFM) has been used to observe, in real time, the growth of two-dimensional poly(hydroxybutyrate-co-valerate) (PHB/V) 'spherulites' in thin films. The AFM permits us to image the growth over a wide range of magnifications, from the macroscopic spherulitic growth down to observations of growth of individual lamellae. The lamellar growth images are obtained using a special, high resolution, phase-imaging technique. Low magnification images show, in common with optical microscope techniques, sharp circular growth fronts which move at a constant growth rate. At higher magnifications the rough nature of the growth front on a lamellar scale is clearly revealed with dominant lamellae leading the growth. The most remarkable observation is that these dominant lamellae do not grow at a fixed, constant rate, as predicted by most growth theories, but rather they initially spurt forwards at a rate substantially faster than the macroscopic growth rate, and then slow down or stop. A new theory, in which the spherulite growth rate is controlled not by the growth rate of the individual lamellae, but rather by the rate at which new lamellae nucleate on existing, dormant lamellae, is suggested. It is believed that these observations, although only made on one system, may be more widely applicable.

(Keywords: spherulite; AFM; crystal growth)

INTRODUCTION

Spherulites are an ubiquitous form of crystalline aggregate, occurring in a wide range of substances from minerals to polymers. The overall texture of spherulites has been much studied over the last century[1–16], initially through the use of optical microscopy[1,3–9] and, during the last 40 years, using the various electron microscopes as they have been developed[10,11]. More recently, several workers have examined spherulitic structures using the scanning probe microscopes[12,13]. All the early studies of spherulites were performed on inorganic minerals[9], later studies took into account some organic systems[1], but most of the recent studies have used polymeric materials as paradigms for the spherulitic state.

The initial optical microscopy studies revealed the approximately spherical symmetry of these aggregates. Further, it was deduced that they consisted of radiating fibrous crystals which branched to fill space[5]. It was also possible to identify, in some systems, a regular helicoidal twist of these radiating fibrous crystals[3,6–8]. In experiments where the growth of spherulites was observed directly in the optical microscope, it was noted that spherulites grew with a constant radial growth rate. Further, it was found that the temperature dependence of this constant radial growth rate was precisely that expected for a secondary nucleation process.

Once electron microscopes became available, the detailed internal morphology of spherulites could be investigated. A central sheaf-like structure was identified and, in many systems—especially the polymeric systems—it could be seen that the underlying crystals were not fibrous, but rather lamellar or ribbon-like[10]. More detailed studies of polymeric systems showed that there were two distinct types of lamellar crystals present in the spherulites[14–16]. Dominant, or leading, lamellae could be characterized by a thicker appearance and were identified as growing first to provide a skeleton for the spherulite. Secondary, or in-filling, lamellae were seen as being rather thinner and having a less well defined orientation within the spherulite. These secondary lamellae were taken to have grown behind the main growth front, after the dominant lamellae, and served to fill in the spaces between the primary, leading lamellae.

In recent years, experimental work on spherulites has concentrated in two areas. First, many authors have been concerned to measure the growth rates of spherulites as a function of growth temperature, etc.[17,18]. Secondly, a good deal of effort has been put into mapping out the detailed internal architecture of spherulites. Especially to attempt to explain the underlying cause of the regular twist that occurs in so many different systems[19–21,12].

Parallel to all this experimental work there has been a good deal of theoretical work attempting to elucidate all aspects of the spherulitic state. At the most fundamental level, many authors have addressed the problem of what causes the branching within the aggregates and leads to the final spherical symmetry. Most of these studies are based on solutions to the diffusion problem with moving boundary conditions (e.g.[22]). Such models lead to 'densely branched' structures and can be compared with experiments with

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highly idealized model systems such as Hele–Shaw cells, where the diffusion aspects of the problem can be separated from the crystallization aspects[23].

On a more pragmatic level, many workers have concerned themselves with diffusion and crystallographic models to explain the local branching and splaying apart of lamellae and the twist of growing lamella (e.g.[21]). In these models the authors normally rely on observations in a particular system (usually polymeric) and attempt to generalize to all spherulitic structures. In particular, authors often take a specifically polymeric effect (such as cilia pressure) to explain a more general effect (such as the splaying apart of growing crystals). Nevertheless, a good deal of progress has been made and the present understanding of the internal architecture of spherulites seems to be relatively complete.

Another area where a great deal of modelling and theoretical effort has been applied is in the understanding of the growth mechanism of the lamellar crystals that make up the spherulites and in the prediction of the overall growth rates of spherulites[24–26]. The observation that the growth of spherulites followed the general pattern of secondary nucleation has led to the development (and generally widespread acceptance) of a model where the growth of the underlying, dominant, lamellar crystals is itself through a secondary nucleation process at the crystal growth front[27–29].

While there are some differences of opinion concerning the details of the growth of spherulites, it is commonly accepted at present that a spherulite begins with a stack of lamellar crystals that splay apart and start to branch out, until all evidence of the initial orientation is lost. These dominant lamellae then continue to grow at a constant growth rate, branching occasionally to provide for space filling, and in some systems also twisting, to form the spherulite skeleton. A short distance behind the growth front defined by these dominant lamellae, secondary lamellae nucleate on the dominant lamellae, and grow until they are stopped by meeting with another lamellae, in such a way as to fill up the spaces between the dominant lamellae.

Although it is possible to reconstruct the detailed internal architecture of a spherulite by careful sectioning and microscopy[16], the actual mechanisms by which the structures are formed remain open to question unless they can be observed directly at a lamellar resolution during the growth of a spherulite. This is the objective of the present work. One of the strengths of atomic force microscopy (AFM) is that it allows real-time imaging of dynamic processes[30]. The commonly used tapping mode[31] minimizes lateral forces, so that in all but the softest of systems the process under examination is unaffected by the imaging technique.

To date, work using the new family of scanning probe microscopes has largely been limited to confirming the observations made previously using both optical and electron microscopes. The principal advantages are that the spherulites can be observed over the whole magnification range in a single instrument, thus allowing direct comparison of structure at all observable levels, and that it is not necessary to treat the sample in any way before observation. In melt crystallized samples, a number of studies have used these capabilities to study spherulite morphology. Polycarbonate films have been imaged[32] after annealing at high temperatures and spherulitic structures resolved. Spherulites of isotactic polypropylene have been imaged after crystallization at various temperatures[13] and good agreement with the literature values for lamellar thickness obtained. Atomic force microscopy has been used to image spherulites of optically active polyethers[12]; in this study the AFM allowed the dependence of the inclination of the lamellae on molecular chirality to be determined, adding support to their theory on the source of the banding structure in spherulites. In a series of papers[33–35], the real time degradation of poly(seboic anhydride) poly(DL-lactic acid) blends has been observed using AFM. The closest in approach to our work is that in[36], in which thin films (~10 nm) of polycarbonate were progressively crystallized by the action of a plasticizer and imaged using both contact and tapping mode AFM. A spherulitic morphology was observed. In this study, high resolution images were obtained after the sample had been dried and the amorphous material had become glassy. However, real-time imaging of spherulite growth was not obtained.

In the work reported here we have been able to obtain real-time images of spherulitic growth. These images raise many questions concerning the mechanism of spherulite growth that will be addrressed later. To be able to image the crystallization on a lamellar scale directly in real time, we have applied a modification of the normal tapping mode AFM imaging, namely phase imaging[37]. To provide a suitable slow growing system for AFM investigation we chose to use a poly(hydroxybutyrate-co-valerate) (PHB/V) copolymer growing at a temperature well below its melting point. As we shall show, the observations we have made do not agree with the commonly accepted model as described above. Rather than individual lamellae growing with constant growth rates, we can see separate lamellae spurting forward at the growth front and stopping growing—an observation which may have serious implications for the derivation of crystal surface energies from optically observed spherulite growth rates. Nevertheless, we do observe that the overall growth rate of the growth front as a whole remains constant.

Spherulites of the bacterial thermoplastic poly(hydroxybutyrate) (PHB), and its copolymers with hydroxyvalerate (PHB/V), have been extensively studied using standard techniques[17,38]. They provide ideal systems for the study of spherulites as the polymer's bacterial origin makes it very pure. The lack of heterogeneous nuclei leads to very large spherulites (sometimes several millimetres in diameter) with a clearly defined optical banding structure over a crystallization temperature range of ~100°C, down to the glass transition temperature of approximately 0°. The radial spherulite growth rate is relatively slow, becoming slower with increasing copolymer content, allowing the growth rates and nucleation behaviour to be studied over a very wide range of temperatures[17,38–41]. The behaviour observed is closely similar to that seen in most other spherulite forming polymer systems, the only unusual feature being the uncommon ease with which morphologies and growth kinetics can be studied.

In this paper, we first describe the techniques used to image the growing spherulites and the individual lamellae at the growth fronts. We are able to observe for the first time the existence of dominant lamellae in front of the main crystal–amorphous interface as they grow. Their exact length and the magnification at which they become visible can be seen. Secondly, we present details of our findings, illustrating that while the overall gross growth front does have a constant growth rate, the individual lamellae do not. Thirdly, we will present a simple model that lays the basis for understanding how such a situation can arise. Finally, we

discuss some implications of our observations for the existing models of spherulite growth and morphology.

In a companion paper[42], the details of the new techniques, and the way in which this work can give an insight into the nature of the tapping mode phase-imaging process used, will be reported in more detail. In the present paper the emphasis will be upon the implications of this work to spherulite growth in PHB/V, and in polymer spherulite systems in general.

EXPERIMENTAL DETAILS

A Nanoscope III multimode AFM (Digital Instruments, Santa Barbara, U.S.A.) was used in tapping mode. Integrated silicon tips and cantilevers with a nominal spring constant of 30 N m^{-1} were used without further modification. A phase extender unit incorporating a lock-in amplifier (Digital Instruments) was used to record the phase lag between the cantilever oscillation in free space and that when the cantilever was tapping the surface. Two types of data were recorded: constant force data in which the feedback control circuit is used to maintain a constant cantilever tapping amplitude, and phase data. The former data type is the same as that commonly used in topographical imaging. Both types of data were recorded on the same trace or retrace line to eliminate the effects of piezo drift, and because the surface was expected to be changing during the imaging process.

Two different methods of phase imaging were adopted. Slow speed, feedback-controlled imaging was carried out to image the macroscopic growth of spherulite. This is the method used in *Figures 1 and 2*. In these images, the slow scan direction was always from top to bottom. In order to investigate the spherulite growth at higher resolution, it was necessary to scan substantially faster if multiple scans of the same area were to be obtained before growth had completed. In this case the feedback gains were adjusted to minimize oscillation and optimize the phase image, as the phase image was found to give more detail at these high resolutions. Scan speeds of at least 10 Hz were typically used for this high-speed imaging, giving a time between successive scans of the same area of 25 s or less. In this high-speed imaging, the sample was scanned continuously, so the slow scan direction alternated between successive images. The cantilever was driven at its resonant frequency, at which the slope of the relationship of phase angle with frequency is greatest.

A random hydroxyvalerate poly(hydroxybutyrate-co-valerate) copolymer containing 24% hydroxyvalerate units, with a Mw of 297 000 from batch P05, supplied by Zeneca Bioproducts Business was used. The polymer was placed on a glass slide and melted on a hot bench for 2 min at 200°C. The thickness of the sample was controlled by scraping with a razor blade. The surface of the resultant film was optically flat over areas of several hundred microns. After removal from the hot bench, the thin film was quenched to room temperature by placing on a metal block, and then inserted into the AFM for scanning. The quenching process was sufficiently fast that no optically visible crystallization had occurred.

RESULTS

We show in *Figures 1–6* several series of AFM images taken during the growth of PHB/HV spherulites. *Figure 1* is a low magnification view where the growth of the whole

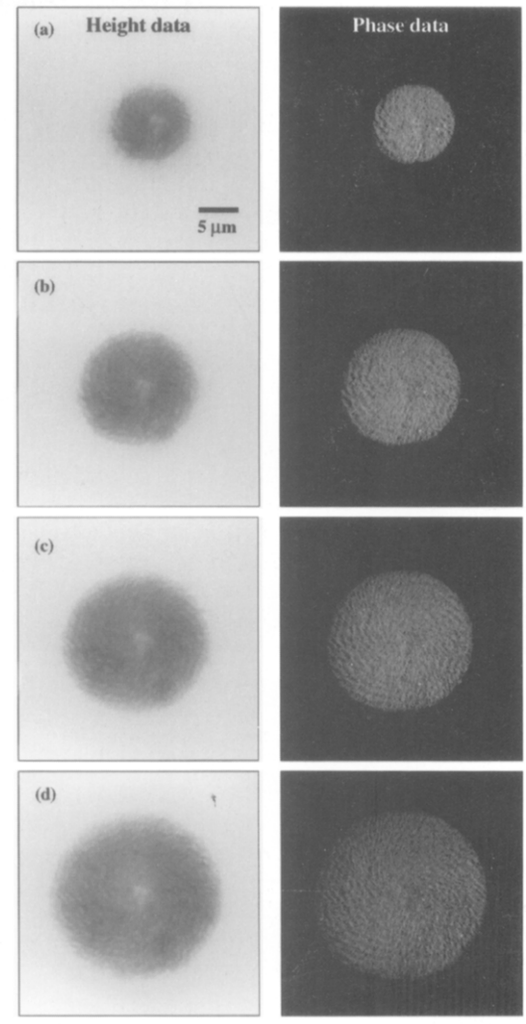

Figure 1 A series of AFM images showing a single growing spherulite. The left-hand images are height images in which the black-to-white colour scale represents 0–300 nm. The right-hand image shows phase data: (a) collected at 0 s; (b) collected at 338 s; (c) collected at 742 s; (d) collected at 1084 s

spherulite can clearly be seen. The successive images closely resemble optical micrographs as they display a sharply defined growth front. It is a simple matter to measure a growth rate from the advance of the growth front in successive images, although care must be taken to ensure the correct time interval between the moments the probe passed over the relevant reference points is used. We find that the growth rate for this particular spherulite is (5.1 ± 0.8) nm s^{-1}. This value corresponds to the growth rate at a temperature of 29°C, measured by optical microscopy. It has been observed that the temperature within the AFM sample space increases by about 3°C relative to the ambient temperature during use. This has been ascribed primarily to energy dissipation in the piezo-electric transducer with the laser optical system also contributing. The ambient temperature in the room was 25°C, so the spherulite growth rate can be used as a reasonably accurate measure of the sample temperature, and therefore of the heating effect of the AFM. The band spacing can be clearly discerned from both height and phase images and is in agreement with that expected from optical observation of spherulites crystallized at this temperature.

Figure 2 shows a higher magnification set of images of a different spherulite in both height and phase mode. The

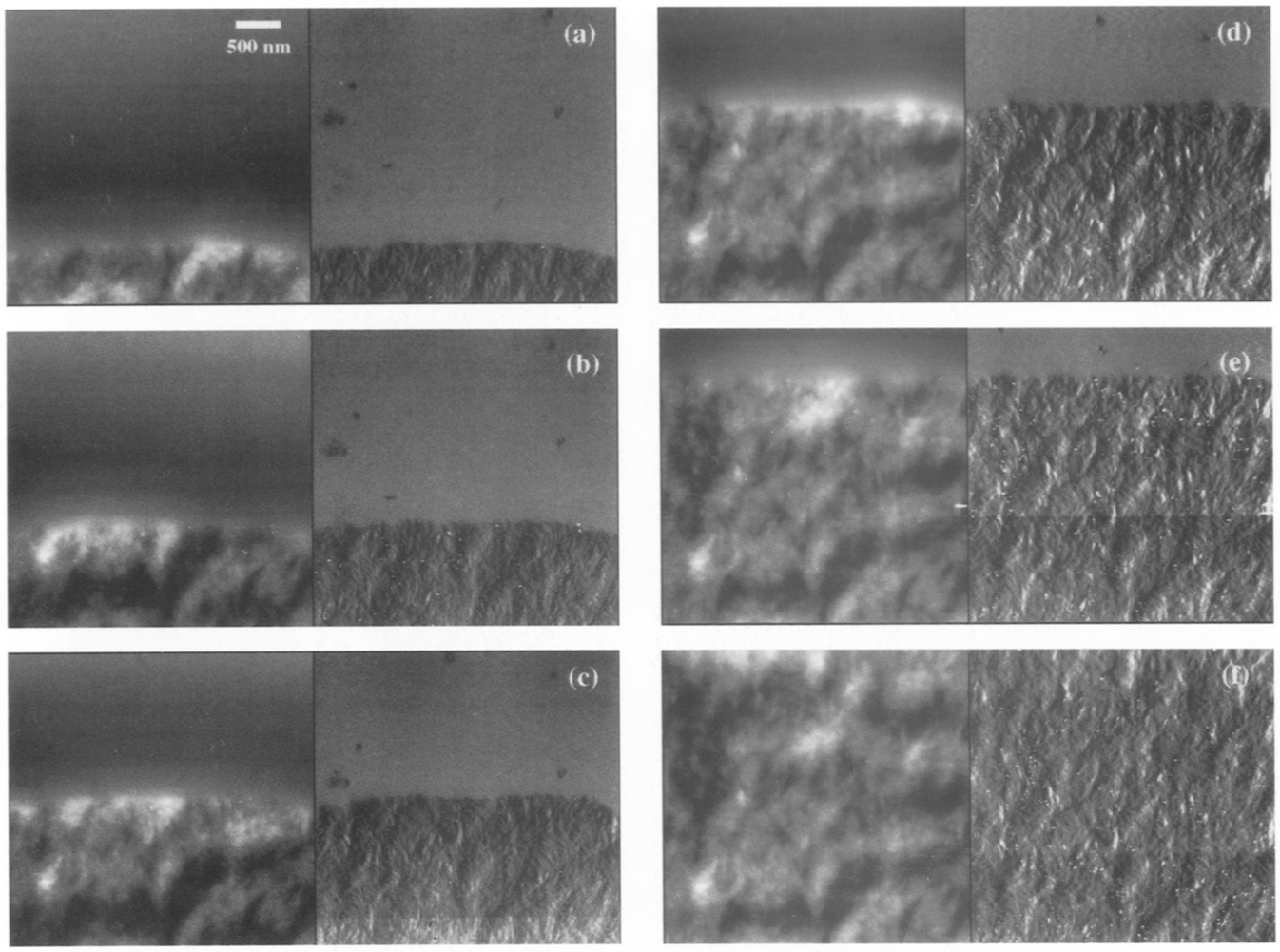

Figure 2 A series of AFM images showing part of a growing spherulite. The left-hand images are height images in which the black-to-white colour scale represents 0–40 nm. The right-hand image shows phase data. Successive images are collected at 170 s intervals. The slow scan direction is down the image in all cases

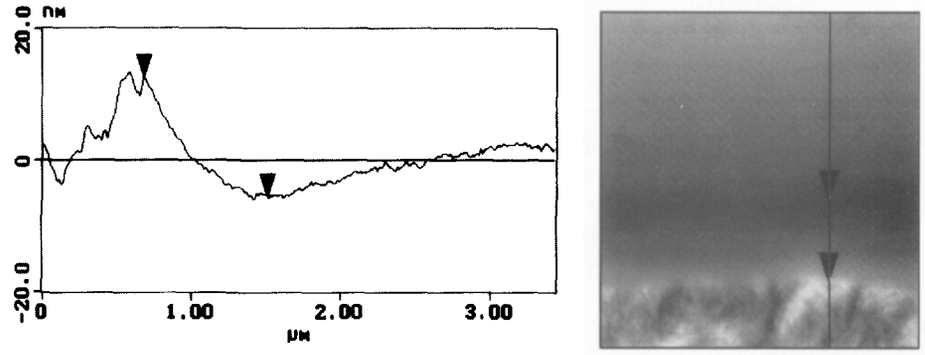

Figure 3 A height profile taken across the height image in *Figure 2a* showing how the amorphous material dips down in front of the growth front

height mode images still maintain a banded structure. From the height profile shown in *Figure 3* it is clear that in front of the growth front the melt dips down to a level below that of the subsequent crystal, indicating a surprising rate of material transport in such a rubbery liquid. This phenomenon has been seen in a number of separate spherulites, although in many others, such as those shown in *Figure 1*, the crystalline region was consistently lower than the amorphous region, as would be expected considering the volume reduction that occurs during crystallization. The band structure is much less clear in the phase image which now has a fine texture that closely resembles the lamellar texture seen in TEM replicas. At this magnification the growth front is still relatively smooth. From this set of images, taken on a cooler day, the growth rate can be measured as (4.0 ± 0.5) nm s^{-1}.

At higher magnification the height image no longer gives useful information, as the feedback gains had been adjusted to minimize oscillation and optimize the phase image, so only the phase image will be shown for these images.

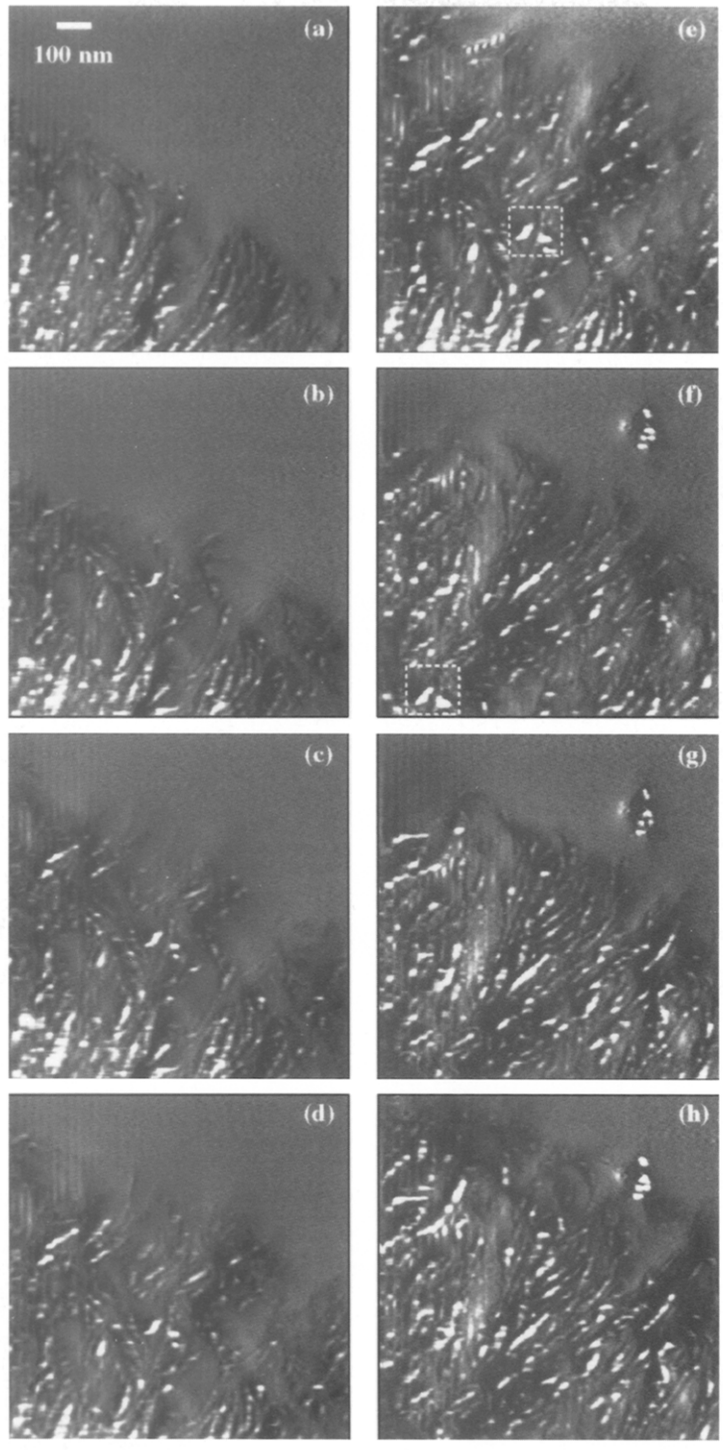

Figure 4 A series of high magnification phase images of part of a growing spherulite. The slow scan direction is up the page in image (a) and alternates in successive images. Images have been captured continuously. Images collected at 25.2 s intervals. The scan area has been moved between image (d) and (e), and a common feature is indicated by the white box

Figure 4 shows a sequence of higher magnification phase images of growth of the same spherulite as that shown in *Figure 2* above. Between *Figure 4e* and 4*f* the scan region has been shifted to keep the growth front in the field of view. A feature present in both images is marked. On reducing the magnification after taking these images, no change in the growth in the area imaged at high magnification was apparent. The scanning tip does not appear to interfere with the growth process in any way.

From the thickness of the linear features in *Figure 4* it is reasonable to associate them with the edges of individual lamellae. The rough nature of the spherulite growth front on a microscopic scale is clearly visible. Individual lamellae can be seen protruding in front of the main growth front. It can be seen that the protruding dominant lamellae do not grow forwards at a constant rate, maintaining dominance until for some reason they are no longer primarily forward facing, but rather continuously swap their furthest forward situation with neighbouring lamellae. The coarse texture of the growth front is continuously changing, with small sections of the growth front speeding up to overtake their neighbours before slowing down and themselves being

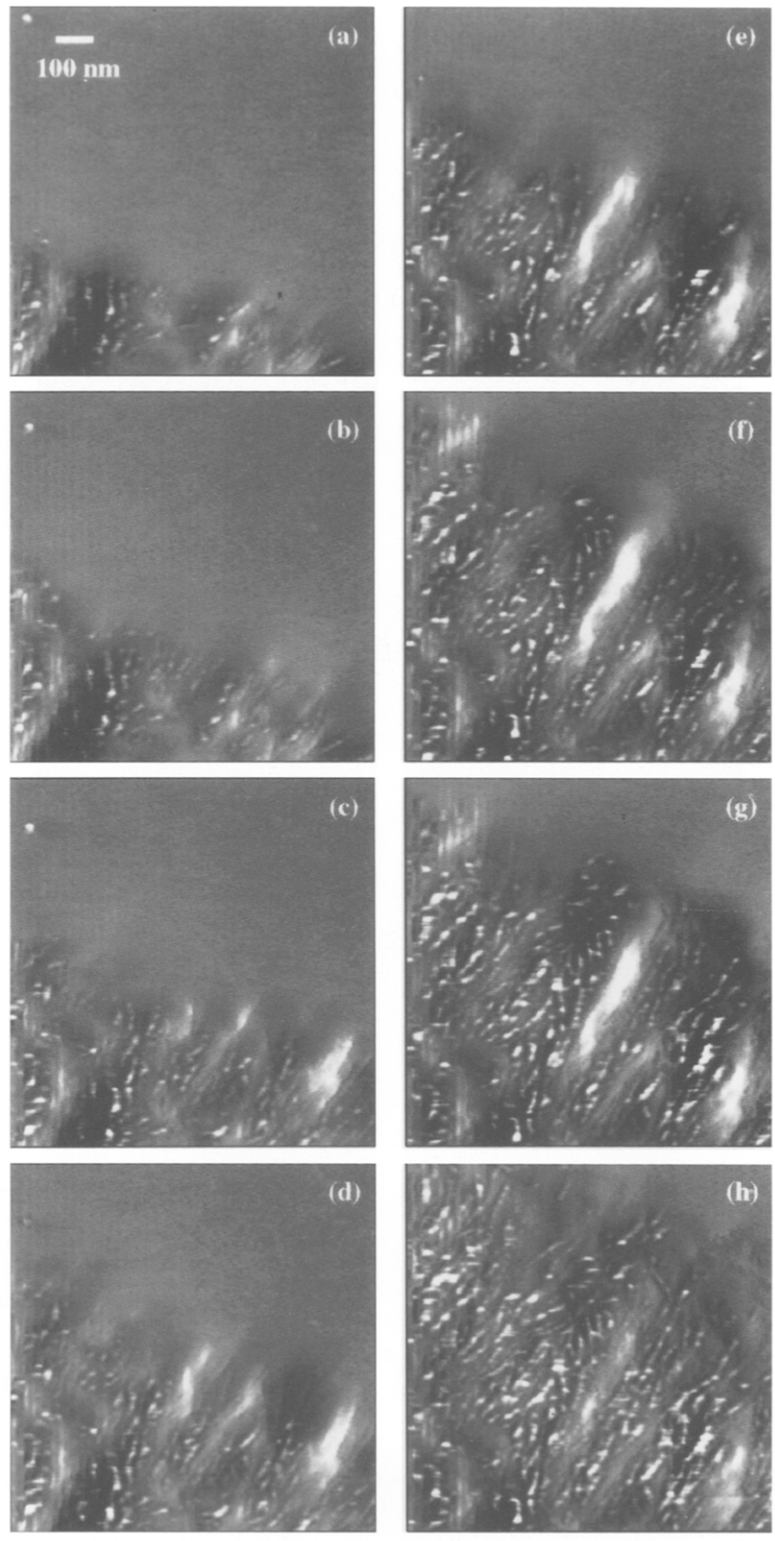

Figure 5 A series of high magnification phase images of part of a growing spherulite. The slow scan direction is down the page in image (a) and alternates in successive images. Images have been captured continuously. Images collected at 25.2 s intervals

overtaken. In *Figure 4b* there is a particularly clear example of a set of lamellae that have grown extensively between successive scans. However, in the subsequent image the rest of the growth front has 'caught up' with this faster growing region.

The set of images in *Figure 4* covers a distance of slightly more than one band spacing. There does appear to be a periodic bending away of the lamellae from the mean, forward facing, direction. This is clear in *Figure 4a* and *Figure 4h*, in which some of the newly grown lamellae are almost perpendicular to the growth direction.

Figures 5 and 6 show more sequences of images taken at the spherulite growth front. These figures provide further evidence that the individual lamellae do not grow at a constant rate, but rather spurt forwards and reduce their growth rate as they become longer. There are a number of instances where an individual lamella can be seen which has not noticeably grown in successive images, although

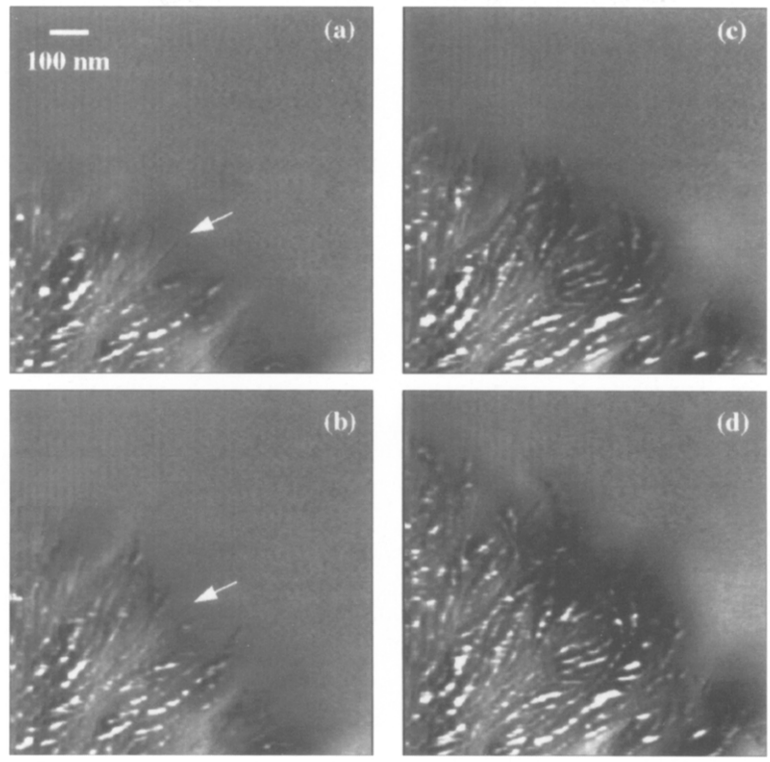

Figure 6 A series of high magnification phase images of part of a growing spherulite. The slow scan direction is up the page in image (a) and alternates in successive images. Images have been captured continuously. Images collected at 31.4 s intervals

nothing else appears to have grown across in front of it. An example of this behaviour is arrowed in *Figure 6a–b*.

In the high magnification images, some evidence of a change in orientation between successive dominant lamellae can be seen. It is possible that the overall twist in orientation is not a continuous change with each lamella twisting in itself, but it could arise from small differences in the orientation in successive lamellae as they grow outward.

We can make some very rough estimates of the speeds at which individual lamellae grow from images such as those in *Figures 4–6*. In many sequences of images, lamellae that have grown from behind the growth front in one image do not appear to have grown any further in subsequent images. In these cases we can only note that they grew some measurable distance (and then stopped) within the time between the probe reaching that part of the image for the second time. Such cases provide a minimum average growth rate for the lamellae, since the lamellae have stopped growing their actual average growth rates should be significantly higher. Typically we find this minimum average growth rate to be in the region 5–12 nm s^{-1}, depending on the individual lamella measured. This value should be compared to a bulk spherulite growth rate measured on the same day of (4.0 ± 0.5) nm s^{-1}. It is clear that the individual lamellae are growing considerably faster than the macroscopic spherulite growth rate.

DISCUSSION

In this report we have shown for the first time images of a growing spherulite with an optically smooth growth front showing individual dominant lamellae protruding in front of the bulk of the crystal. We have been able to map out the distance which these lamellae protrude and to show, on the same growing spherulite, images which closely resemble those taken optically as well as confirming the inferences previously made by those taken using TEM.

Using the ability of the AFM to give the surface profile of the growing spherulite, we have obtained evidence that in some instances the crystalline region is actually higher than the surrounding amorphous material from which it has crystallized. The reason for this is unclear, and seems counter to our present understanding of the crystallization process.

From the observations reported here we find the lamellar crystals that form at the front of a growing spherulite, do not grow continuously with a constant growth rate, but rather nucleate sporadically and grow rapidly outwards and then either stop growing or continue growing with a substantially reduced growth rate. New lamellae form behind the growth front and grow past these now inactive lamellae to continue the growth process. Despite these complications, we nevertheless find that the overall rate of growth of the spherulite is itself constant.

Comments on the validity of this experimental approach

Perhaps the most important issue to be raised is whether the observations we have made can be caused by any form of artefact. Since our observations are clearly challenging the accepted growth mechanism where lamellae grow in a continuous manner, we should examine the possibility that this is the case and the apparent stopping of growth of leading lamellae is some form of artefact. There are two immediate considerations. First, in our experiments we are not growing full three-dimensional spherulites, but rather thin two-dimensional discs, which appear to have the same overall symmetry. Secondly, our observations are not of the bulk, but are limited to the surface of the growing system.

We do not regard the fact that we are using two-, rather than three-dimensional spherulites to be of any real concern

to the growth mechanism of the lamellae. Most observations on the growth rates of spherulites, as well as many of the morphological studies, have been made on similar systems. It is the restriction of growth in thin samples that enables good optical microscopic observations to be performed. Thus, even if the growth in bulk three-dimensional spherulites were different and the stopping of growth were to be caused by the two dimensional nature of these crystal aggregates, the observation would still have significant implications, since nearly all the available growth rate data for polymer spherulites come from similar two-, rather than three-dimensional systems.

The second issue, that we are only observing growth at a free surface, could be more important. If a particular lamellae were to change its growth direction so that it moved away from the surface, then we might be misled into believing that it had stopped growing. There is clearly the potential for artefacts of this kind to occur and to lead to a false conclusion. We can, however, be confident that this is not the case with many of the lamellae which we observe to have stopped growing. In many cases the average gowth rate of a particular lamellae which has stopped growing (as assessed from successive AFM images) is significantly faster than the overall rate of advance of the growth front. If the lamellae were all to grow continuously, with a constant growth rate similar to that of such lamellae, then the overall spherulite growth rate should be very much higher (and more or less equal to the individual lamellae growth rate).

It is possible that the unexpectedly fast growth rate is caused by the fact that we are only observing growth at the surface. It may be that the growth front that is observed at the surface is slightly behind that in the bulk. In this case the lamellae could be growing up from this lower level and only be observed when they protrude from the surface. If this were the case, very fast forward growth rates would be possible, even when the bulk growth rate was constant and slow. Assuming the front of the growing lamella is flat, the growth rate of the lamella growing at some angle θ to the surface is related to the observed growth rate by

$$G_{\text{observed}} = \frac{G_{\text{lamella}}}{\cos\theta} \quad (1)$$

From this it is apparent that angles greater than 60° will give at least a doubling in the observed growth rate. Considering the continued observation of similar rough growth fronts in spherulites with radii of several tens of microns (compared to a film thickness of $\sim 1\ \mu$m) there is no reason to expect the lamellae to be growing at so steep an angle. It might be expected that if the rapid growth rates were due to growth from below, isolated sections of lamellae might occasionally be imaged in front of the main growth front. In no case was this observed, all the forward facing lamellae imaged consisted of a continuous line emanating from the spherulite growth front. In fact, as the AFM laser will cause a small increase in the surface temperature, and the polymer grows faster at higher temperatures in the temperature range examined, the growth rate at the surface would be expected to be faster than in the bulk.

Considering the above arguments, we confirm that, at least in this particular system, the normally accepted growth mechanism for spherulites where lamellae grow continuously outwards (with occasional branching) at a constant linear growth rate is not consistent with the experimental observations.

Comments on the application of these results to spherulite crystallization in general

We shall next address the question of the generality of this newly observed growth mechanism. The particular system we have used, PHB/HV crystallizing at a temperature only some 20–30°C above its glass transition temperature, is obviously not very typical. The system was chosen for the ease with which the AFM images could be obtained. However, when we have observed the growth of spherulites from this and other similar systems in the past[17], we have found no obvious differences in the overall morphology and no discontinuities in the growth rates over the entire crystallization temperature range from *ca.* 15°C to *ca.* 120°C. There is, therefore, no reason to suppose that the growth mechanism we have seen does not persist over the same temperature range. Further, PHB/HV spherulites, although generally larger than those in other polymers, have appearances in both optical and electron micrographs closely similar to all other polymer spherulites. Accordingly, although we have only made observations on a single system, at a rather low growth temperature, we argue that in the absence of evidence to the contrary we should, for the present, assume that this growth mechanism is the general case.

Although the currently widely accepted view is one where lamellae grow continuously out with a constant growth rate, this is not usually explicitly suggested by the various authors when describing their models. In practice the morphological models that describe the internal architecture of spherulites and attempt to explain the branching, splaying and twisting in terms of, for example, cilia pressure and arrays of dislocations[21], should not be greatly affected by the present observations. With suitable minor modifications they could easily fit in with a scheme where each lamella grows to only a limited extent. For example, the models of Bassett which attempt to describe the regular twist of lamellae in terms of arrays of screw dislocations are quite compatible with the present observations. All that is necessary is to note that crystals only grow to a certain size before stopping. The branching of crystals through screw dislocations in a regular manner would then lead to a closely similar morphology to that which led Bassett to his model in the first place.

A new model for spherulite growth rates

When we consider the models for the interpretation of the growth rate data for spherulites, there is a very different situation. The arguments made by the current secondary nucleation models[27] all rely on the underlying lamellae growing at constant linear growth rates on the scale observed here. If the lamellae do not behave in this fashion, then the models are not tenable. We have, therefore, tried to provide the basis of a model that is at least consistent with our observations.

First, we should briefly speculate on the possible reasons for the observations of the sudden growth of lamellae which just as quickly stop growing. One obvious mechanism which could cause such behaviour is a build up of internal stresses causing lattice strains which lead to a maximum possible size before crystal symmetry is lost. The existence of lattice strains arising during polymer crystals growth has been noted experimentally and theoretically in several past works[43,44], albeit in different contexts. In polymeric systems, the need for chains to fold back into the crystall caused by the density defect that would occur at the surface

Table 1 Values for the various constants in equation (5) used to generate *Figure 7*

T_∞	σ_e	$\sigma_A = \sigma_B$	ΔH	T_m^0	U^*
−52°C	6×10^{-2} J m^{-2}	7.7×10^{-3} J m^{-2}	1.85×10^8 J g^{-1}	188°C	10250 kJ mol^{-1}

ΔH and U^* are taken from[42], T_m^0 is taken from[17]. The surface energies are similar to those found in[17] but adjusted slightly to give a good fit.

in the absence of any folding, provides an obvious source of cumulative lattice strain that can affect crystallization rates. Other possible mechanisms for limiting the size of growing crystals come from arguments concerning the accumulation of impurities at the growth front, from limited thermal diffusion at the growth front leading to a reduced driving force for crystallization (an argument that clearly could not apply in the present case of PHB/HV spherulites which would grow faster at higher temperatures around room temperature) and from considerations of packing at the surfaces.

It is important to note that although the first grown lamellae do not proceed forward in an uninterrupted manner, we sometimes do observe long, apparently uninterrupted lamellae behind the growth front. The above explanations, however, do not preclude the possibility that a lamella whose growth has slowed significantly could undergo a process of rearrangement so as to allow itself to become active again. Indeed, this may be expected to occur, and as long as the crystallizable material in front of it has not been exhausted it may grow through a number of separate 'spurts'.

Whatever the cause of the stopping of growth of lamellae as they grow beyond some size, we can for the present purposes take this as an experimental fact and proceed from there to build up a simple model. We make the simplifying assumption that a lamella will grow to a length L (m), before stopping, and that it will do so at a mean growth rate much faster than the overall rate at which the growth front of the spherulite progresses. We will further assume that new lamellae are formed by some secondary nucleation process on existing lamellae behind the growth front at a rate I events (m^{-2} s^{-1}), and that the lamellae all have mean width, W (m). With these assumptions it is relative simple to calculate the overall spherulite growth rate G as

$$G = \frac{IL^2W}{2} \tag{2}$$

since G is given just by the distance grown beyond the growth front by lamellae before they stop ($= L/2$) divided by the time between nucleation events ($= (ILW)^{-1}$).

Now if we use a secondary nucleation model for I, we can take matters further and derive a temperature dependence of the growth rate. The simplest case is to assume that the nucleus is on one of the basal surfaces of a lamellar crystal. If the nucleus has a height of C, and the lateral surface energies are denoted by σ_A and σ_B the nucleation rate I is given by

$$I = I_0 \exp\left(-4C\sigma_A \frac{\sigma_B}{\Delta f kT}\right) \exp\left(-\frac{U^*}{R(T-T_\infty)}\right) \tag{3}$$

where Δf is the free energy gained on crystallization, U^* is an activation energy for molecular motion, k is Boltzman's consistent, R is the gas constant, T_∞ is the temperature at which motion is frozen out, and T is the actual temperature. If, in the case of polymers, we take C to correspond to the lamellar thickness, l, then we can substitute the normal form

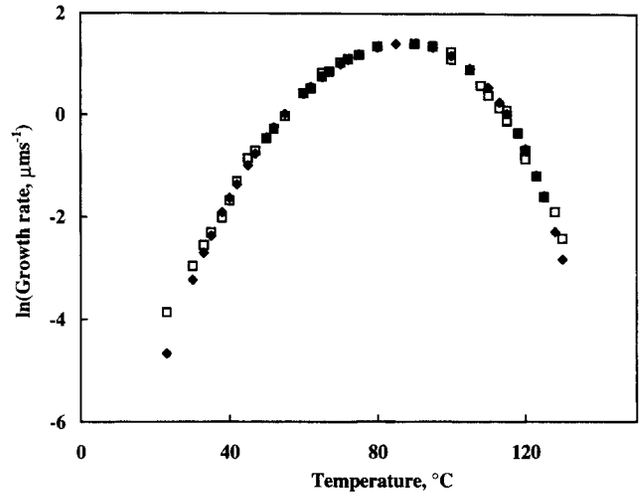

Figure 7 A graph showing experimental data for the variation of log(growth rate) with temperature for PHB plotted with data generation from equation (5), using the values for the various constants from *Table 1*: □—experimental data; ◆—data generated from equation (5)

of l given by

$$l = \frac{2\sigma_e}{\Delta f} + l_0 \tag{4}$$

into the equation for G to give

$$G = I_0 L^2 W \exp\left(-\frac{U^*}{R(T-T_\infty)}\right) \exp\left(-\frac{8\sigma_e\sigma_A\sigma_B}{\Delta f^2 kT}\right) \times \exp\left(-\frac{4l_0\sigma_A\sigma_B}{\Delta f kT}\right) \tag{5}$$

The form of this equation, using estimated values of the various parameters appropriate to PHB shown in *Table 1* and taking L to be a constant independent of temperature, is illustrated in *Figure 7* along with some experimental data. Clearly, it is possible to obtain a reasonable fit to the experimental data. However, this fit could be much improved if the length of the crystals L was allowed to be temperature dependent.

In order to proceed beyond this simple model, it would be necessary to gain more experimental information about some of the assumptions made above. The relationship between the forward growth rate of the lamellae and their rate of nucleation will have a controlling influence over the spherulite growth rate. By simulating the growth process it may be possible to see the extent to which these can vary while still maintaining the experimentally observed relationship between temerature and growth rate.

CONCLUSIONS

In this paper we have shown, for the first time, conclusive evidence of the existence of a microscopically rough spherulite growth front in a system where the growth front appears smooth on an optical scale. Spherulite growth has

been followed in real time on a lamellar scale using phase-imaging AFM, enabling us to compare the growth rates of the individual lamellae with that of the bulk spherulite. It has been observed that these two growth rates are different.

The technique of AFM phase imaging has been found to give particularly good data at the high magnifications and scan rates required by this study, and opens up the possibility of performing similar studies on other spherulite-forming systems.

The currently accepted models for the growth of spherulites, where the underlying crystals grow out from the centre continuously at a constant rate, are not consistent with experimental observations in this work. A new model for growth is necessary, at least for the PHB/HV system described here, and we have attempted to lay the basis for such a new model. We expect that this may be a more general problem.

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