On the Properties of Large Banded Spherulites in a Maleic Anhydride–Polyacrylonitrile Mixture

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Abstract

We investigate the solidification of a mixture of maleic anhydride and 2% (by wt.) polyacrylonitrile as the undercooling is varied. Such mixtures show banded spherulites with band spacings over an order of magnitude larger than any seen before. We show that these large banded spherulites share many of the same properties as banded spherulites found in other systems. Our experiments suggest an explanation for the minimum undercooling threshold commonly observed for banded spherulites.

Key words: Solidification, spherulites, banded spherulites, maleic anhydride, polyacrylonitrile
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1 Introduction

Although the solidification of low-viscosity fluids is by now fairly well understood, that of high-viscosity fluids continues to pose fundamental problems. The generic high-viscosity morphology is the spherulite, a spherical aggregate of radially oriented microcrystals. There are many subvarieties of spherulites; one in particular, banded spherulites, has aroused considerable interest for over a century.

Banded spherulites have been observed in many kinds of materials, including polymers[1–3], organics[4], liquid crystals[5–7], and elemental selenium[8].

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These materials show typical band spacings of 500 μm or less. Recently, Lagasse and coworkers have observed band spacings on the order of 10 mm, over an order of magnitude larger than seen before. The material studied was a blend of a low-molecular-weight organic solvent, maleic anhydride, and a small amount of the polymer polyacrylonitrile[9,10].

Lagasse et al. studied this blend using wide-angle and small-angle X-ray scattering. They also studied the polyacrylonitrile foams remaining after removing the maleic anhydride by sublimation. Their studies confirm that this blend shows the crystallite rotation observed in other materials. Furthermore, the polyacrylonitrile foams also show the same rotation in the orientations of pores left behind after removal of the maleic anhydride[9–11].

Although Lagasse and his colleagues show that the banding is associated with a rotation of the crystallite axis, they looked at only two samples and were thus unable to examine the detailed dependence of the banded spherulites on undercooling. In this paper, we expand upon Lagasse et al.'s work with a more thorough survey of the effects of undercooling. We present further evidence that the banded spherulites in this system are the same phenomena as seen in other materials and highlight a number of their features. We also take advantage of the large spatial scales to examine aspects of the transition from non-banded to banded spherulites that are not accessible in other systems.

2 Experiment

The procedure followed here is similar to that used by Lagasse[9]. The melts used are mixtures of maleic anhydride and 2% (by wt.) polyacrylonitrile (Fig. 9, shown in an Appendix). Both chemicals were purchased from Aldrich and used as received. The solid-liquid coexistence temperature for this melt is $T_{sl} \approx 51.8\,^{\circ}\mathrm{C}$.

First, the polyacrylonitrile is dissolved in the maleic anhydride under vacuum at $\approx 165\,^{\circ}\mathrm{C}$. Next, the melt is poured into a heated ($> 65\,^{\circ}\mathrm{C}$) silicone mold that is placed on an aluminum stage held at the desired undercooling $\Delta T \equiv T_{sl} - T_{\infty}$, where T_{∞} is the temperature of the melt, imposed at the container's boundaries. The temperature of the stage is regulated by flowing water from a recirculating bath through it. Finally, a heated glass plate is placed over the silicone mold, but not in contact with the melt.

Four different silicone molds have been used, according to the predicted size of the resulting structures. The first is round, with a 76 mm diameter. The second and third are square, with sizes of $80\,\mathrm{mm} \times 80\,\mathrm{mm}$ and $150\,\mathrm{mm} \times 150\,\mathrm{mm}$ respectively, while the fourth is an $80\,\mathrm{mm} \times 300\,\mathrm{mm}$ rectangle. All four molds

have side walls at least twice as thick as the bottoms, ensuring unidirectional heat flow.

The temperature of the melt is measured via a thermistor immersed directly in it. Once the melt has cooled to the desired ΔT, the glass cover plate is removed and crystallization induced by either a cold point or a seed crystal.

As described in an Appendix, an examination of the cooling curve allows measurement of the specific heat $c_p = 1.8 \pm 0.2$ J/°C gm and the latent heat $L = 100 \pm 15$ J/gm of the melt. Once L and c_p are known, we can define a dimensionless undercooling

$$\Delta \equiv \frac{\Delta T}{L/c_p}. \tag{1}$$

Given that $L/c_p = 55 \pm 10$ °C and that $\Delta T < 30$ °C for all of the work reported here, $\Delta < 0.5$ in our experiments. This means only a fraction of the melt, Δ, freezes during the initial crystallization. The remaining melt reheats to the coexistence temperature and stays there for the next few minutes while the heat is removed. This two-stage cooling, or secondary crystallization, is observed in many systems that exhibit banded spherulites[1,9], although not all[7].

We have also measured the viscosity of the maleic anhydride-polyacrylonitrile melt, as described in the Appendix. In the experiments discussed below, viscosities ranged from $\approx 9 \rightarrow 15$ cS.

The thickness of the samples ranged from 2.5mm to 12.5mm, with the majority at ≈ 6 mm. No property (band spacing, front velocity, ...) was found to vary over this range of thicknesses.

Observations during and after solidification are made by reflection with the unaided eye or an ordinary charge-coupled-device (CCD) camera, recorded on videotape, and later analyzed by computer. The optical properties of these thick samples are dominated by multiple scattering. Because the many scattering events effectively average over polarization states, no variation in the banding is observed with polarization of the light, in either reflection or transmission. This is in contrast to observations in optically thin slices of banded spherulites in other systems where the birefringence dominates the optical properties[2].

This mixture has two complicating factors: First, the polymer is not completely miscible in the solvent at the crystallization temperatures. For this reason, the fluid turns opaque at ≈ 110 °C because of a phase separation[9]. Lagasse et al. have shown variations in the morphologies and band spacings

depending on how completely the polyacrylonitrile is dissolved prior to cooling[11]. In all of the measurements reported here, we first completely dissolve the polymer. Repeating the measurements using different melting and cooling protocols gave the same band spacings and front velocities. Furthermore, stirring the melt after the phase separation and before nucleation is induced has no measurable effect on the banded spherulites. Thus, we conclude that the phase separation is not responsible for the unusually large banding scales.

The second complication is that the maleic anhydride reacts with water to form maleic acid, which may be detected via the color of the mixture. But mixtures with different concentrations of maleic acid solidified at the same undercooling show the same front velocities and same band spacings. This supports Bassett's observations that impurities in the melt are *not* responsible for spherulitic growth[3]. The stability of spherulitic growth to changes in the amount of maleic acid impurities is in sharp contrast with observations in diffusion-limited crystallization, where even small impurity levels dominate the solidification behavior[12].

3 Results

The most distinguishing feature of the banded spherulites formed in the blend studied here is the band spacing, λ, which is over an order of magnitude larger than that seen in other substances. Are these then the same banded spherulites seen in other materials?

Lagasse et al. showed that X-ray diffraction patterns imply a radial twist in the crystallite orientation, one of the commonly observed features of banded spherulitic growth[9,10]. Here, we show further evidence for classifying the observed growth phenomenon as banded spherulites. These observations also highlight the universality of the banding phenomenon.

3.1 Band Spacing.

The first common feature of banded spherulites is the observation of larger band spacings at lower undercoolings[1]. Our data, presented in Fig. 1, follows this common trend. The band spacings range from 40 mm at the lower undercoolings to 6mm at the highest achievable undercoolings. (Numerous attempts were made to reach higher undercoolings, but the melt always spontaneously nucleated at $\Delta T < 30\,^{\circ}\mathrm{C}$.) No bands are observed for $\Delta T < 8.3\,^{\circ}\mathrm{C}$.

The solid curve in Fig. 1 is a fit to the data with a power law of the form

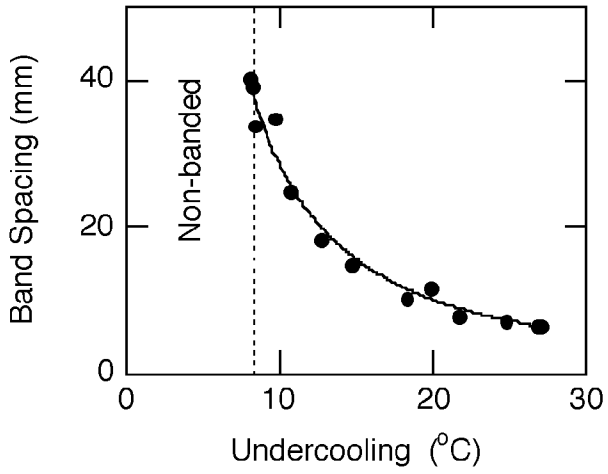

Fig. 1. (a) Band spacing vs. Undercooling. The solid curve is a fit with $\lambda \propto \Delta T^{-1.5}$.

$\lambda \propto \Delta T^{-1.5}$. The choice of exponent is prompted by a model due to Owen[13], a variation on earlier work by Keith and Padden[1,14], which attributes the banding phenomena to surface stresses on the crystallites. The surface stresses cause a twisting of the crystallite that is balanced by bulk bending energy, a process conceptually similar to warping. Further discussion of this model appears below.

Another observation is that the $\lambda \propto \Delta T^{-1.5}$ dependence implies that the band spacing diverges at $\Delta T \simeq 0$, even though banded spherulites are not observed for $\Delta T < 8.3\,^{\circ}\mathrm{C}$. How can these two observations be reconciled?

3.2 Core Region.

The solution to the discrepancy between fits that yield no critical undercooling and experiments that show no bands at $\Delta T < 8.3\,^{\circ}\mathrm{C}$ begins with a closer examination of the solidified melt near the nucleation site. We identify a "core region" as the area between the nucleation site and the first dark band, which can be seen in Fig. 2a. Such core regions are commonly observed in banded spherulites[15].

We plot the size of the core region (R) (defined as the distance from the nucleation site to the first dark band) as a function of undercooling in Fig. 2b. Since the first band is not typically spherical, two sizes, the maximum and minimum, are shown. Fits to the data in Fig. 2b with a power law show that the size of the core region diverges at $\Delta T_{\mathrm{core}} = 8.3\,^{\circ}\mathrm{C}$. Given this divergence and the lack of a critical undercooling in the band spacing, we interpret this as implying that bands "exist" for $\Delta T < 8.3\,^{\circ}\mathrm{C}$; however, the first band appears infinitely far from the nucleation site. Inspection of Figs. 1 and 2b shows that

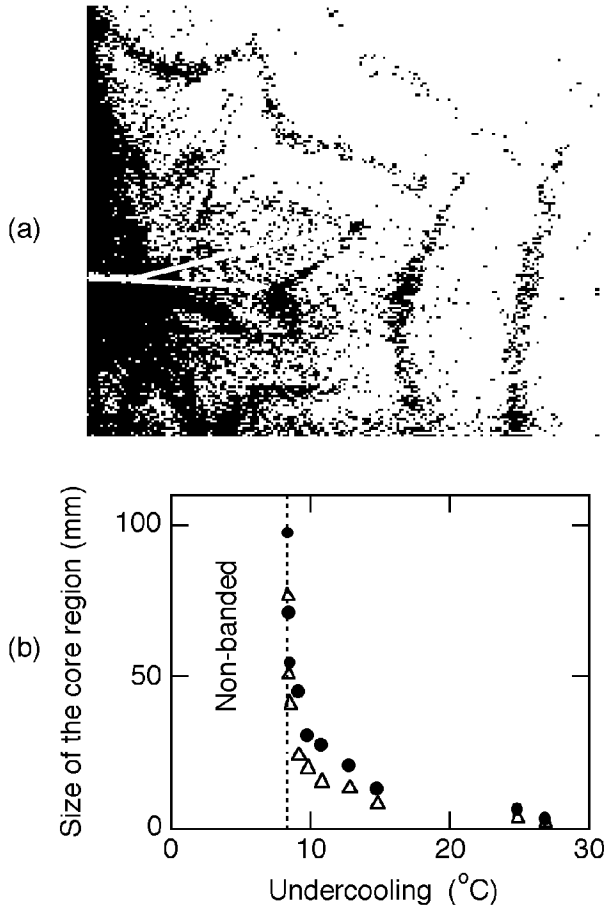

Fig. 2. (a) Photograph showing the core region and first few bands of a banded spherulite grown at $\Delta T = 24.9\,^{\circ}\mathrm{C}$. The probe used to induce nucleation is visible on the left side of the image and two lines indicate the relevant distances to the first band. (b) Size of the core region vs. Undercooling. (•) denotes the maximum and (△) the minimum.

the band spacing is already smaller than the core region for $\Delta T < 9\,^{\circ}\mathrm{C}$.

One model that attempts to explain the crossover between a core region and an outer spherulitic region has been proposed by Tiller[16]. In Tiller's model, the core region is dendritic, and there is a radius at which the growth changes to spherulitic. This model attributes the splay of the crystallites (necessary so that the crystallites eventually adopt a radial orientation) to viscous forces caused by the hydrodynamic flows generated by the density difference between the solid and liquid (here, $\approx 9\%$; see Appendix). The magnitude of these forces depends on the length of the crystallites and hence the distance from the nucleation site. This model says that the size of the core should vary with the front velocity v as $R \propto \nu^{-0.5}\, v^{-2}$ with ν as the viscosity of the liquid. Tiller successfully applies this scaling to the core region of a water/glycerol mixture. The data from Fig. 2b are shown as a function of Tiller's scale factor

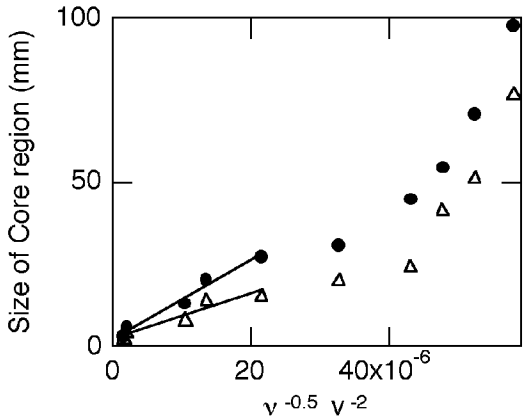

Fig. 3. Size of the core region vs. Tiller's scale factor. (•) denotes the maximum and (△) the minimum. The solid lines serve as guides to the eye and indicate the region where Tiller's model appears to be most applicable.

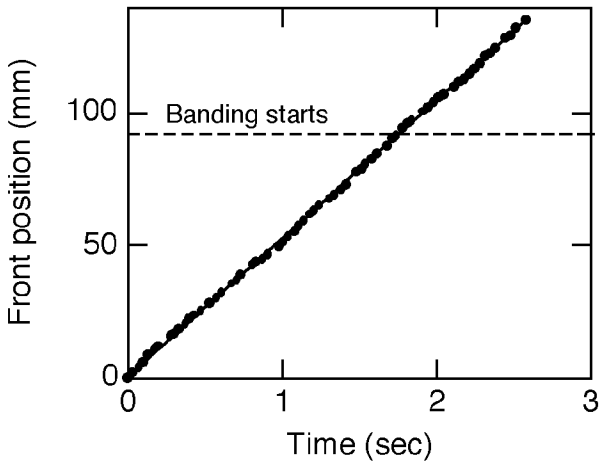

Fig. 4. Position of solidification front vs. Time at $\Delta T = 8.3\,^{\circ}\mathrm{C}$. Specific origins of position and time are arbitrary, although near the nucleation site. The dashed line in indicates the position of the first dark band. No change in slope is noticeable in the graph.

in Fig. 3. The solid lines in Fig. 3 show that the model qualitatively accounts for the behavior in the high velocity, or high undercooling, region. However, the model does not predict a divergence of the core region and thus fails near the undercooling threshold ($\Delta T = 8.3\,^{\circ}\mathrm{C}$).

3.3 The Solidification Front.

In order to further investigate the transition from the core region to the spherulitic region, we analyzed the motion of the solidification front as it

proceeds through the melt. A change in the front velocity at the appearance of the first band would indicate a change in the solidification mode[6]. With this in mind, we plot the position of the solidification front as a function of time for two undercoolings in Fig. 4. The time step between successive points is $1/30^{th}$ second in Fig. 4. The origin (in space and time) is approximately the nucleation site (within 1 mm and 0.05 sec).

Three features emerge from Fig. 4: First, the acceleration of the front is too rapid to be seen at our resolution and thus does not appear to influence any of the phenomena reported here. Second, there are no changes associated with the appearance of bands; i.e., there is no discontinuity in the slope, implying no change in the front velocity when banding begins. Unfortunately, this does not explain the transition from the core region to the spherulitic region but rather indicates that something more subtle is happening. Third, the front velocity is constant during the banding, a commonly observed feature of banded spherulites[1]. We note, however, that Wang et al. recently observed small oscillations in the front velocity associated with the formation of the bands[17]. Because our temporal resolution is relatively coarse, we cannot rule out small velocity oscillations during banding.

3.4 Front Velocity.

We next investigated whether a change in the front velocity could be associated with the divergence of the core region. Fitting lines to position of the front vs. time plots, such as that shown in Fig. 4, gives the front velocities as a function of undercooling, Fig. 5a. The data in Fig. 5a are fit to a power law

$$v = B\,\Delta T^{\beta}, \tag{2}$$

which gives $B \approx 2.6$ and $\beta \approx 1.54$ with both parameters free. Setting $\beta = 1.5$ produces the solid curve shown in Fig. 5a[18].

An alternative presentation of the data on a log-log scale appears in Fig. 5b. A fit to Fig. 5b with a line shows a slope of 1.3 with no change at the appearance of bands, indicated by the vertical dotted line at $\Delta T = 8.3\,^{\circ}\mathrm{C}$. This suggests that the divergence of the core at $\Delta T_{\mathrm{core}} = 8.3\,^{\circ}\mathrm{C}$ is not related to any changes in the front velocity. Also, the lack of any significant changes in the front velocity at the appearance of bands is in contrast to Hutter and Bechhoefer's observation of a decrease in the slope of the v vs. ΔT curve associated with the appearance of bands in a liquid crystal melt[5,6].

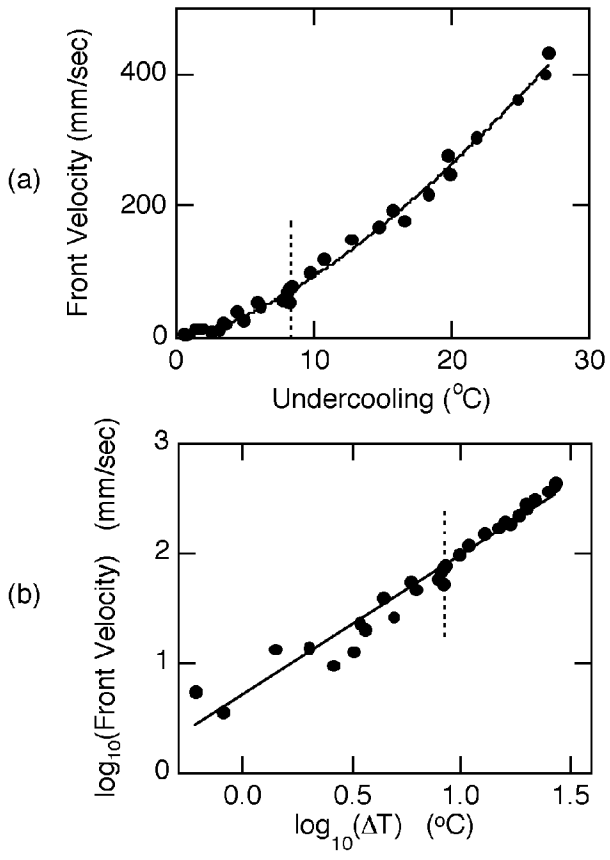

Fig. 5. (a) Front velocity vs. Undercooling. The solid curve is a fit with $v \propto \Delta T^{1.5}$. (b) log(Front velocity) vs. log(Undercooling). The vertical dotted lines indicate the appearance of bands at $\Delta T = 8.3\,^{\circ}\mathrm{C}$. No change in the slope is associated with the appearance of bands.

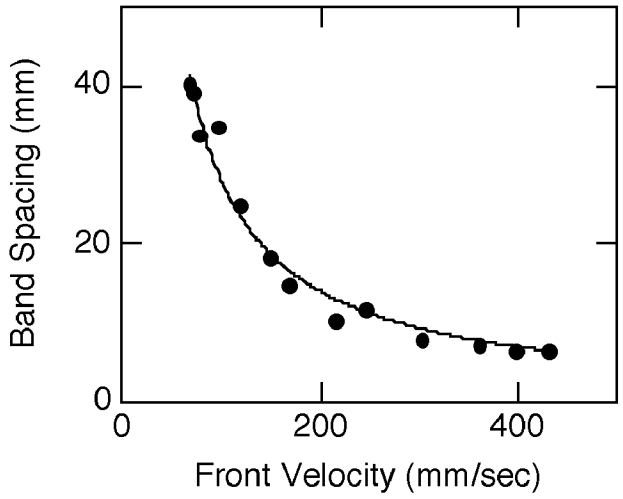

Fig. 6. (a) Band spacing vs. Front velocity. The solid curve is a fit with $\lambda \propto 1/v$.

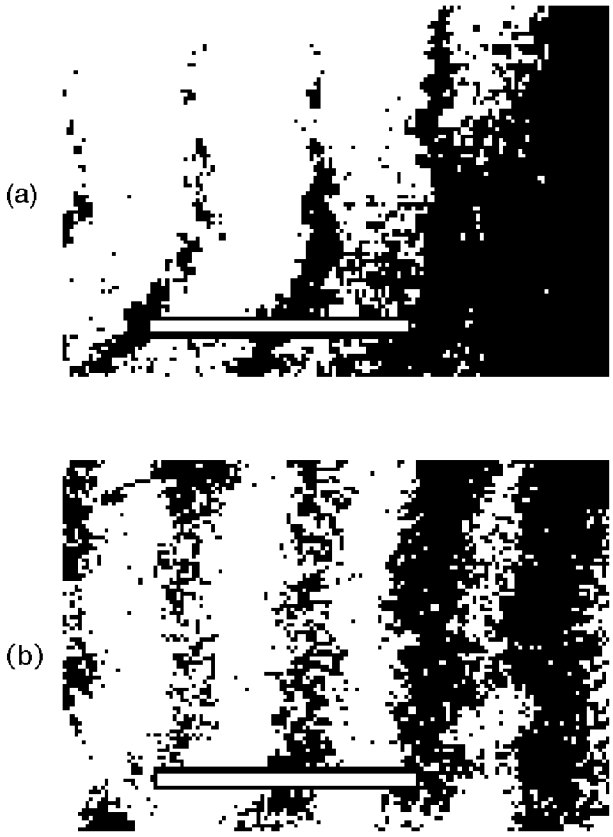

Fig. 7. Photograph showing banded spherulite solidified at $\Delta T = 14.9\,^{\circ}\mathrm{C}$. (a) just after freezing and (b) $\approx 1\,\mathrm{hr}$ later after cooling to room temperature. The scale bars in both photographs represent 30 mm.

3.5 Band Spacing vs. Front Velocity.

Considering the undercooling dependence of the front velocity ($v \propto \Delta T^{1.5}$) and that of the band spacing ($\lambda \propto \Delta T^{-1.5}$), we see that $\lambda \propto 1/v$ (Fig. 6). For polymeric materials, one typically observes $\lambda \propto v^{\gamma}$ with $0 > \gamma > -1$[19–21]. On the other hand, $\gamma \approx -7$ in a liquid-crystal system[5]. Therefore, the dependence of band spacing on front velocity varies significantly with the material under consideration.

3.6 Sizes of the Light and Dark Bands.

Since the nature of the variation of band spacings with undercooling is not understood, numerous models have been proposed to explain the various observations. Hutter and Bechhoefer conjectured that this transition may be "soliton-like"[6]. This model is typified by the unwinding of a cholesteric liquid crystal in an external field. The transition is characterized by a fixed-size

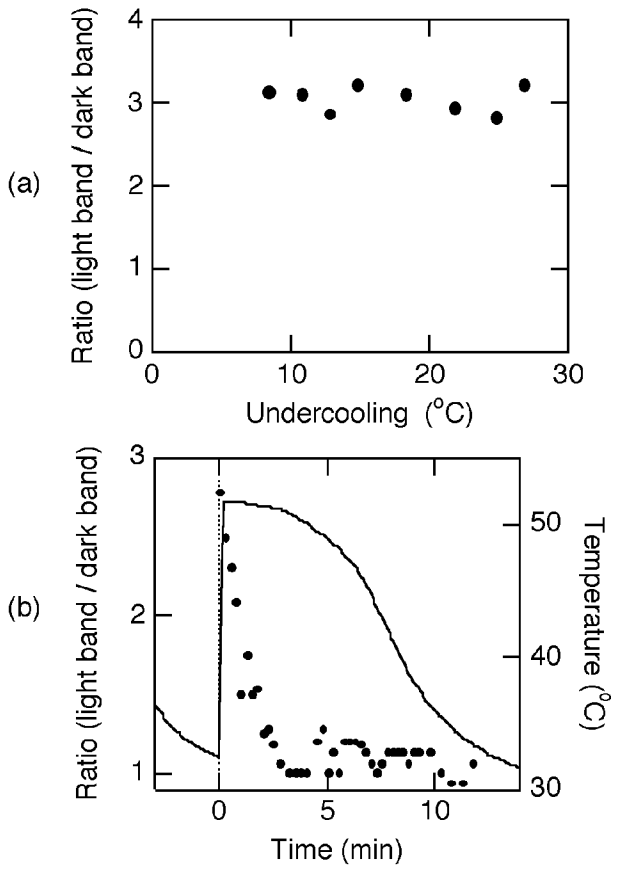

Fig. 8. (a) Ratio of the sizes of the light band to the dark band vs. Undercooling. Measurements were taken immediately after passage of the solidification front. (b) The temporal evolution of the ratio of the band sizes (○) after passage of the solidification front for $\Delta T = 19.3\,^{\circ}\mathrm{C}$. The moment of nucleation is defined as time = 0. The solid curve is the temperature of the melt.

twist region (the "soliton") separated by untwisted regions, whose size diverges as the external field is increased, becoming infinite at a finite field. If we identify one of the bands with the twist region, its size should stay constant as the undercooling (the analog of the external field) is varied. Therefore, according to this model, the size of the other band should diverge with undercooling as the total band spacing diverges. It is useful to consider the sizes of both bands jointly by examining their ratio, which should diverge to infinity as the total band spacing diverges.

Inspection of Fig. 7a indeed shows that the light and dark bands have different sizes, lending credibility to this idea. However, when the ratio is plotted at various undercoolings in Fig. 8a, one sees that it does not diverge, but rather stays constant (≈ 3) over the complete range in undercooling. This observation is incompatible with a soliton model of the transition from non-banded to banded spherulites.

The band sizes in Fig. 8a are measured immediately after the solidification front passes, as shown in Fig. 7a. However, when the sample is left to completely freeze and cool to room temperature, the bands end up with a size ratio of ≈ 1 (Fig. 7b). The temporal evolution of the ratio for a particular ΔT appears in Fig. 8b, which includes the cooling curve for comparison. The ratio of the bands starts to relax from ≈ 3 to ≈ 1 immediately after passage of the solidification front and does not follow the temperature of the system, suggesting that the evolution of the ratio is not associated with the secondary crystallization process. The overall band spacing (the combination of a light and dark band) does not change; instead, the dark band grows at the expense of the light band. It is possible that this change is caused by a relaxation of built-in stresses in the spherulites, as has been suggested by Keith and Padden[14]. These spherulites have been observed to spontaneously crack after cooling to room temperature and the spherulites in other materials have been known to break up explosively[15], which indicates that large built-in stresses are present in banded spherulites. We are currently investigating the band relaxation in more detail.

4 Discussion

We have observed many of the generic features common to banded spherulites, including

(1) Radial orientation of crystallites,
(2) Constant band spacing as a function of distance from nucleation site,
(3) Larger bands observed at lower undercoolings,
(4) Constant growth velocity as a function of distance from nucleation site,
(5) A core region distinct from the outer spherulitic region,
(6) Stress in samples.

All of these observations, together with those by Lagasse et al.[9,10], imply that the banded spherulites observed in mixtures of maleic anhydride and polyacrylonitrile are the same phenomena as observed in other materials.

The commonly accepted explanation of banding is a twisting of the optical axis of the crystallites along the radial direction[1,22,23]. Indeed, Lagasse and coworkers have shown the presence of twisted crystallites in this mixture with X-ray scattering[9,10]. However, the source of this twisting is not understood.

One of the models of the twisting, as mentioned above, is due to Owen[13], which is a variation on earlier work by Keith and Padden[1,14]. This model attributes the twisting to surface stresses on the crystallites. Owen begins by using standard elasticity theory to equate surface energies to bulk bending

energies and argues that $\lambda = A(E/\sigma)^{0.5}\, d^{1.5}$ with A being a geometrical factor on the order of one, E Young's modulus, σ the surface energy density, and d the thickness of the crystallite. Owen then invokes the Thompson equation, $d \propto 1/\Delta T$, to arrive at the final relationship $\lambda \propto \Delta T^{-1.5}$, the observed dependence for our system. Owen also shows similar behavior in two polymer systems. Furthermore, if we assume the pore size ($5 - 10\ \mu$m) measured by Lagasse et al.[9–11] to be similar to the crystallite thickness in the model along with $A \approx 1$ and $\lambda \approx 10$ mm, we can calculate $E/\sigma \approx 10^{11}\ \mathrm{m}^{-1}$. This value is of the same order as the value that Owen presents for a polymer system ($E/\sigma \approx 1.6 \times 10^{11}\ \mathrm{m}^{-1}$), lending further credibility to this model.

However, while Owen's model accounts for many of the observations, some open questions still remain: First, how generally applicable is the model? Keith and Padden report exponents that range from ≈ 1.25 to ≈ 15 in various polymers, suggesting that Owen's model is either incorrect or at least not always applicable[1]. Second, what is the exact origin of the surface stresses? Owen (and Keith and Padden) suggests that the surface stresses are produced by chain folding at the surface of the crystallite in a polymer system. However, since the exact origin of the surface stresses does not enter into the model, a different source for the surface stresses may play a role in the system investigated here, with only 2% polymer. And third, why do the crystallites twist coherently?

5 Conclusions

We studied the effect of undercooling on banded spherulites observed in a mixture of maleic anhydride and 2% polyacrylonitrile. We take advantage of the exceptionally large band spacings to investigate new aspects of banded spherulites. Band spacings range from ≈ 6 mm at the highest achievable undercoolings up to ≈ 40 mm, with $\lambda \propto \Delta T^{-1.5}$. Although no critical value of the undercooling was found from the data fits, no bands were observed for $\Delta T < 8.3\,^{\circ}\mathrm{C}$.

This discrepancy was explained by monitoring the size of the core region (defined as the area between the nucleation site and the first dark band) as the undercooling was varied. This size of the core region diverged at a critical value of the undercooling $\Delta T_{\mathrm{core}} = 8.3\,^{\circ}\mathrm{C}$. We interpret this as implying that for $\Delta T < 8.3\,^{\circ}\mathrm{C}$, bands would start infinitely far from the nucleation site. This suggests that the undercooling threshold necessary to observe bands depends on the transition from the inner core region to the outer spherulitic region rather than being a feature of the banding phenomenon.

One model that attempts to explain the transition from a core region to a

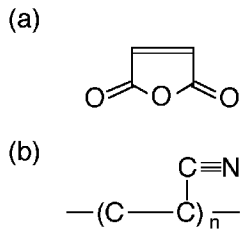

Fig. 9. (a) Maleic anhydride, (b) Polyacrylonitrile.

spherulitic region has been proposed by Tiller[16]. This model yields a relation between the size of the core, the front velocity and the viscosity of the melt, which qualitative accounts for the observed behavior in the high-velocity region. However, the model fails to account for the divergent behavior near $\Delta T_{\rm core} = 8.3\,^{\circ}$C.

Finally, a conjecture by Hutter and Bechhoefer that the transition from non-banded to banded spherulites is solitonic in character was shown to be inconsistent by examining the ratio of the light to dark bands as the undercooling was varied[6]. It would be interesting to see whether the new observations reported here—the divergence of the core region and the constancy of the light-dark band spacings—holds for other banded spherulites, as well.

Acknowledgements

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Appendix Some relevant material properties

In order to compare the results reported here with those from other materials, it is necessary to measure some of the material properties of maleic anhydride–polyacrylonitrile system, whose chemical structures are shown in Fig. 9. The molecular weight of the polyacrylonitrile is reported to be $M_w = 150,000$ by the distributor.

We have measured the densities of the solid and liquid to be $\rho_s = 1.47\,\mathrm{gm/cm^3}$ and $\rho_l = 1.35\,\mathrm{gm/cm^3}$. This implies a density change $\Delta\rho/\rho_l \approx 9\%$ upon solidifying.

Next, by examining a series of cooling curves such as shown in Fig. 10, we can measure the specific heat c_p and latent heat L of the melt. First, the rate

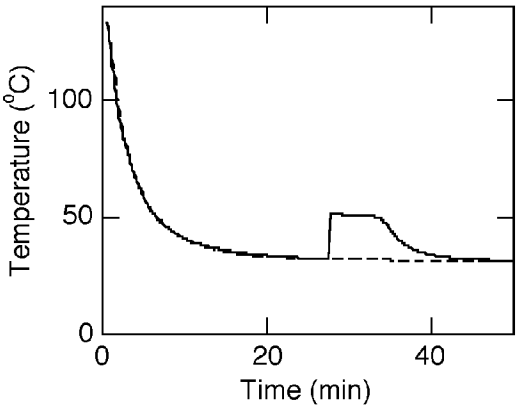

Fig. 10. A typical cooling curve. The dotted curve is an extrapolation of the initial cooling, and the shaded region represents the additional latent heat released during freezing.

of heat loss through the mold to the temperature stage is calibrated using cooling curves of hot water, which has a known c_p. Next, the initial cooling in Fig. 10 is fit with a double exponential, shown as the dashed curve, which indicates two separate time scales are present in the cooling. The first time scale is on the order of ≈ 1 min and is associated with heating of the silicone mold by the hot melt, as shown by varying the initial temperature of the mold. The second time scale is on the order of ≈ 10 min and is the heat loss through the mold to the temperature stage. From this rate of heat loss and the mass of the mixture, we calculate $c_p = 1.8 \pm 0.2$ J/°C gm. We calculate L from the "extra" area between the actual cooling curve and the extrapolated initial cooling, indicated by the shaded region in Fig. 10. This method yields $L = 100 \pm 15$ J/gm.

We have also measured the viscosity of the melt using a capillary tube viscometer[27]. The viscosity is found to obey the Andrayde-Eyring equation $\nu = \nu_o \, e^{T_o/T}$, with $\nu_o = 0.07 \pm 0.01$ cS and $T_o = 1580 \pm 60$ K[28].

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