THE ROLE OF VISCOSITY IN
BANDED-SPHERULITIC GROWTH

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Abstract

We studied solidification in mixtures of ethylene carbonate polyacrylonitrile at high undercooling. Within a certain range of undercoolings, we observed a periodic structure, which has been identified as banded-spherulitic growth. Although known and documented for over a century, this growth mode has no clear explanation to date. In this work, we build on previous studies in an attempt to find a relation between the period of the bands and the hydrodynamics of flows caused by the growing crystal. Using a hydrodynamic scaling law derived by Tiller et al., we collapsed the band-spacing data obtained from samples with different viscosity/polymer-concentration onto a single curve. However, when the polymer's chain-length was modified while keeping the viscosity constant, this scaling failed. Further investigations of the undercooling dependence of the band spacing gives the clearest evidence to date that the transition to banded growth is a second-order morphological transition.
To Marnie and Nadav.
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Chapter 1

Introduction

The study of free-growth solidification dates back at least to Johannes Kepler [1], and, although there has been considerable success in explaining some of the physical laws governing the solidification of low-viscosity fluids [2, 3], this is not the case for high-viscosity fluids.

Solidification studies often focus on the effect of undercooling, which is defined as $\Delta T = T_0 - T$. Here, $T_0$ is the temperature at which the liquid and solid are in thermodynamic equilibrium, while $T$ is the temperature imposed at the system's boundary. The actual freezing temperature need not equal $T_0$ because the liquid can exist in a metastable undercooled state, where its temperature is lower than $T_0$. This is possible because, in order to freeze, the liquid must overcome an energy barrier, which is lowered as $\Delta T$ is increased.

At very small undercoolings, near equilibrium, ordered single-crystal solids are formed. As the undercooling is increased, diffusion of latent heat causes the planar solid-liquid interface to become wavy. At much higher undercoolings, the rate at which liquid molecules can bond to the solid surface (attachment kinetics) may start to control the growth. The solids formed in these two distinct regimes have distinct structures. In the high-undercooling, kinetics-limited regime, the single crystal may break into a polycrystalline aggregate. Increased undercooling is related to an increase in viscosity, since the mobility of molecules in the melt decreases with temperature. It follows that, in viscous materials, attachment kinetics will often become important at higher undercoolings.
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Figure 1.1: Spherulites in the liquid crystal 10 OCB. (a) Non-banded spherulite; (b) banded spherulite.

Often, the crystallites in the polycrystalline materials formed at high undercoolings are themselves ordered. An example of this is spherulitic growth and, in particular, banded spherulitic growth (Fig. 1.1). In spherulitic growth, the aggregate consists of needle crystals that are arranged in a radial pattern. In contrast to low-undercooling crystals, the branching angle of crystallites is not confined to crystallographic angles. In banded spherulites, a second type of ordering is imposed on the structure. In this case, the needles twist as they grow outwards, giving rise to a modulation in the index of refraction (for birefringent crystallites). It is particularly interesting to note that the twist in single needles is not independent, as adjacent needle crystals twist with some degree of coherence. These two morphologies appear in a wide variety of materials, ranging from elemental selenium [4], to liquid crystals [5], to polymers [6]. The spacing of the bands varies over many orders of magnitude in different systems. The largest spacings reported to date are on the order of 1 cm [7], while the smallest are on the order of 1 μm [8].

Spherulitic growth poses two main problems: First, what causes the non-crystallographic branching that gives rise to the radial pattern? Second, what mechanism is responsible for the twisting and the correlation of the crystallites? To date, there are no accepted quantitative models explaining either of these problems. However, there have been attempts at generating scaling laws for the phenomena. One such model, derived by Tiller et al. [9], relates the radial splay to a hydrodynamic scaling factor (see Ch. 2). Tiller's model stands out because it is completely general. Other models tend to be system specific: they assume behavior that is particular to the material under
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observation. For example, polymer folding has been used to explain the twist in the crystallites; however, banding occurs in many non-polymeric systems. Tiller et al.'s system does not display the banded morphology, and therefore no hydrodynamic scaling law for the banding was determined. The goal of this study was to extend Tiller et al.'s work, to see whether a hydrodynamic scaling law could be associated with the banding.

In order to realize this goal, we did two sets of experiments. In the first set, we prepared a number of mixtures of ethylene carbonate (EC) with polyacrylonitrile (PA), a soluble polymer. Each sample had a different concentration of PA, and hence a different viscosity. As in previous experiments [10], the band spacing diverges at a finite critical undercooling, \( \Delta T_c \). When we plotted the band spacing vs. the hydrodynamic pressure, following Tiller's analysis, we found that the previously spread-out data collapsed onto a relatively narrow band. In order to test this data collapse, we then carried out a second set of experiments. We prepared samples with viscosities similar to, or lower than those used in the previous set of experiments, but this time we used PA with a different chain length. The data from this experiment did not agree with the first one (see Ch. 4).

This is a very complex system, with many interacting variables. In order to fully understand why the two experiments disagree with each other, we need to make a detailed study of the front velocity, band spacing, and correlation length as a function of chain length, viscosity, and concentration. Furthermore, the macroscopic view that we have adopted here will probably need to be rethought, as many different microscopic morphologies may look the same on this scale. In order to distinguish these morphologies, one must make complementary studies under a polarizing optical microscope equipped with a high-magnification objective. The drawback to this (optical) microscopic study is that the undercooling is shifted by the latent heat released during solidification. Although this problem has been reduced in the apparatus discussed in Ch. 3, a parallel study would still be necessary in order to accurately determine the undercooling, while simultaneously monitoring the micro-structure.

The plan of the thesis is as follows: In Chapter 2, I outline some theories and models that are relevant to our understanding of spherulitic growth. In Chapter 3, I describe in detail of the apparatus and chemistry used to carry out the experiments.
In Chapter 4, I present results from these experiments.
Chapter 2

Theoretical Background

This chapter gives an overview of the phenomena observed in a system undergoing a liquid-solid phase transition at high undercooling. We begin with a brief introduction to low-undercooling phenomena. For a more thorough description of the low-undercooling regime, see the book *Solids Far From Equilibrium* [11]. For more discussion of the high-undercooling regime, see [9], [12] or [13].

Although the experiments in this thesis focus primarily on systems undergoing phase transitions at high undercoolings, the theory for this regime is poorly developed. In order to give an intuition for high-undercooling phenomena, I will outline the relevant theory for the low-undercooling regime and relate it, at a phenomenological level, to the high-undercooling case. In the first section, I will explain the origin of the undercooled, metastable liquid state, whose existence makes it possible to explore systems with a high undercooling and also explains the origin of the freezing front. In the second section, I will outline some of the typical regimes observed in freezing systems and present an argument explaining why a flat front becomes unstable to perturbations when subject to a finite undercooling. In the last section, I will describe the spherulitic and banded-spherulitic regimes, which are the main focus of this work.

2.1 Classical Model For Nucleation

From equilibrium thermodynamics, we know that cooling a liquid to below its solid-liquid coexistence temperature $T_0$ decreases the bulk free energy of the solid
relative to that of the liquid. At these temperatures, fluctuations in the local density, configurations, and heat content of the liquid lead to the continuous formation of solid clusters. However, most of these clusters are too small to survive the collisions from molecules in the surrounding melt, and redissolve into the surrounding liquid. For the solidification to begin a stable solid cluster larger that a critical size must form [9].

The formation of solid germs from the liquid (or gas) bulk is known as "homogeneous nucleation." Although many systems undergo "heterogeneous nucleation," in which solid germs condense onto pre-existing solid impurities, I will neglect this case for the sake of simplicity.

The nucleation rate is defined as the rate of formation of critical clusters and is subject to the free-energy changes associated with crystal formation and the kinetics associated with moving material to create/grow the cluster. In order to understand why the liquid does not freeze as soon as $T < T_0$, we need to model this nucleation rate in terms of the undercooling.

The classical nucleation rate can be derived by assuming that nucleation is an activated process; that is, the steady-state number-density of critical germs in a sample, $n^*$, is given by a Boltzmann distribution,

$$n^* \propto e^{-\frac{\Delta G^*}{k_B T}},$$

(2.1)

where $k_B$ is the Boltzmann constant, $\Delta G^*$ is the nucleation barrier, and $T$ is the absolute temperature. For a nucleation to occur the critical nucleus must continue to grow, rather than shrink back to zero. The rate that critical nuclei cross the nucleation barrier is given by the product $I \propto n^* \cdot D$, where $D$ is the molecular diffusion constant, given by

$$D \propto \frac{k_B T}{\eta},$$

(2.2)

where $k_B$ is the Boltzmann coefficient, and $\eta$ is viscosity. It follows that

$$I \propto \frac{k_B T}{\eta} e^{-\frac{\Delta G^*}{k_B T}}.$$  

(2.3)

Fig. 2.1, shows the typical undercooling dependence of $I$. At low undercoolings, the rate of homogeneous nucleation is limited by $n^*$, while at low temperatures (high $\Delta T$), it is limited by $\eta$. 

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Figure 2.1: Nucleation rate $I$ vs. temperature and undercooling.

Figure 2.2: The free energy of a solid germ, $\Delta G$ vs. its radius, $R$. Only germs with $R > R^*$ will experience a decrease in free energy with increasing $R$. 
CHAPTER 2. THEORETICAL BACKGROUND

An estimate of $I$ in terms of temperature can be found by analyzing the free energy of a single solid cluster. The change in bulk free energy per unit volume upon solidification is given by

$$\Delta \mu = \mu^s(T) - \mu^l(T),$$

where $\mu^s(T)$ and $\mu^l(T)$ are the chemical potentials of the solid and liquid, respectively, and $T$ is the temperature of the system. Note that $\Delta \mu < 0$ for $T < T_0$. However, the bond configurations at the boundary of the solid cluster introduce a surface-energy term into the free-energy equation. The total change in the free energy (excess) is given by [14]

$$\Delta G = \iiint_{\text{Volume}} \Delta \mu \, dv + \iiint_{\text{Surface}} \gamma \, da,$$

where $\gamma$ is the surface energy per unit area. Eq. 2.5 can be greatly simplified by assuming that the solid phase nucleates as spherical “clusters.” $\Delta G$ is then given by

$$\Delta G = \frac{4}{3} \pi R^3 \Delta \mu + 4\pi R^2 \gamma,$$

where $R$ is the radius of the cluster. In order for this solid germ to be stable and initiate the phase transition, its growth should decrease the system’s free energy. Fig 2.1 shows the $R$ dependence of $\Delta G$. For small $R$, the surface term dominates, and $\Delta G$ increases with $R$. In contrast, for large $R$, the bulk energy dominates, and $\Delta G$ is a decreasing function of $R$. The crossover between these two regimes occurs when

$$\frac{\partial G}{\partial R} = 4\pi R^2 \Delta \mu + 8\pi R^2 \gamma = 0.$$  

Solving this equation for $R^*$, the critical radius, leads to

$$R^* = -\frac{2\gamma}{\Delta \mu}.$$  

The energy barrier to homogeneous nucleation, $\Delta G^*$, is found by substituting $R^*$ into Eq 2.6,

$$\Delta G^* = \frac{16}{3} \pi \frac{\gamma^3}{\Delta \mu^2}.$$  

A more useful form for $R^*$ and $\Delta G^*$ is obtained by looking at the limit where $T \approx T_0$. In this case, one can expand $\Delta \mu$ around $T_0$, giving

$$\Delta \mu \approx [\mu^s(T_0) - (T - T_0)s_s] - [\mu^l(T_0) - (T - T_0)s_l],$$
where \( s_s \) and \( s_l \) are the entropy densities of the solid and liquid phases, respectively. If equilibrium conditions apply, then

\[
\begin{align*}
L &= T_0 (s_l - s_s), \\
\mu^l (T_0) &= \mu^s (T_0),
\end{align*}
\]

(2.11)

where \( L \) is the latent heat released per mole of liquid frozen. Now \( \Delta \mu \) can be approximated as

\[
\Delta \mu \approx -\frac{L \Delta T}{T_0},
\]

(2.12)

where \( \Delta T = T_0 - T \) is defined as the undercooling. By substituting this result into Eqs. 2.8 and 2.9, we can express the critical radius and the excess free energy in terms of the undercooling and capillarity:

\[
\begin{align*}
R^* &= \frac{2 \pi T_0}{L \Delta T} = 2 d_0 \frac{T_0}{\Delta T}, \\
\Delta G^* &= \frac{16}{3} \pi \frac{\gamma^3 T_0}{L^3 \Delta T^2} = \frac{16}{3} \pi \frac{d_0^3 L T_0^3}{\Delta T^2},
\end{align*}
\]

(2.13)

where \( d_0 = \frac{\gamma}{L} \) is known as the capillary length and is typically on the order of a few Angstroms.

Rewriting \( I \) in terms of \( T \) gives

\[
I \propto \frac{k_B T}{\eta} e^{-\frac{16 \pi d_0^3 L T_0^3}{3 k_B T \Delta T^2}},
\]

(2.14)

If one takes into account the temperature dependence of \( \eta \) (see below Sec. 2.2.2), plotting eq. 2.14 would give a curve that resembles Fig 2.1. The small \( I \) at low undercoolings makes it possible to cool a liquid to temperatures below \( T_0 \). In practice, nucleation will occur at a temperature below \( I_{\max} \).

The formation of critical germ(s) initiates the phase transition from metastable liquid state to solid. The growth of the critical germ(s) into the surrounding liquid gives rise to solidification fronts, which in turn determine the structure of the solid formed. One factor that affects the growth dynamics is the undercooling of the liquid at the time of the phase transition. Systems frozen at low undercoolings will show an ordered crystal structure, as seen in Si crystals grown for the electronics industry. Conversely, those frozen at high undercoolings, far from equilibrium, will exhibit less-ordered structures. These show an accumulation of stresses and/or defects in the solid,
that prevent them from reaching their global free-energy minimum. Occasionally, one can cause these stresses to relax by annealing, or heating the sample to temperatures just below $T_0$. In these cases, the high temperatures facilitate the transition from the initial metastable solid to one with a lower free energy.

In the next section, I will try to give an intuitive explanation of how the freezing front depends on undercooling, and I will try to relate low-undercooling to high-undercooling phenomena.

### 2.2 Diffusion- and Kinetics-Limited Regimes

Roughly speaking, solidification phenomena in liquids can be divided into two main classes: In the first, the growth rate of the solid is limited by the diffusion of latent heat and/or excess impurities away from the solidification front.$^1$ In the second, the solid's rate of growth is limited by the microscopic rate at which particles in the liquid phase can undergo epitaxy on the solid surface. If these were the only two mechanisms at work, the transition from the diffusion to the kinetic regimes would occur when the undercooling exceeded a critical value of $L/c_p$, where $c_p$ is the specific heat capacity of the solid and $L$ is the latent heat of crystallization. Above this undercooling, not enough latent heat is produced by the growing solid to raise the front temperature above $T_0$.

In practice, many other effects limit, or modify, the growth of the front. For example, in systems where the densities of the solid and liquid are not equal, solidification requires the liquid to flow towards (away) from the interface. In this case, growth may be limited by the rate at which molecules are delivered (removed) to (away from) the front. Other sources of fluid flow, such as convection (where the necessary heating may be due to the crystallization or to some other external sources) or mechanical mixing of the melt (as is done in some industrial applications), will also modify the temperature field and require corrections to the diffusion model that I will be presenting [9]. Apart from flows in the liquid, the temperature field can also be altered by using a thin sample sandwiched between thermally conducting plates. In this case,

---

$^1$In systems that freeze from the vapor phase, growth may be limited by the rate at which material diffuses towards the solid interface, as happens in snow crystals.
CHAPTER 2. THEORETICAL BACKGROUND

the latent heat is removed from the front via the thermally conducting walls. This lowers the front temperature, reducing the effects of latent heat production.

Thermal effects and flows are not the only sources of complication; another is the nature of the growing surface. Typically, faceted surfaces will grow at different rates than rough surfaces. In the faceted case, adding an atomic layer requires the creation of a 2-D critical island (similar to the 3-D critical germ), while the rough surface has many readily available "dangling bonds" to which molecules can attach. Although all these effects are very important if we wish to have a good understanding of solids, I will ignore them until the last section, where I will discuss how a density change at the interface may generate flows in the melt.

2.2.1 Diffusion-Limited Growth

If $\Delta T \leq L/c_p$ and no heat transport processes take place, the temperature of an imaginary volume of liquid undergoing a phase transition to solid would be raised to beyond $T_0$; this is clearly impossible. In order for solidification to proceed, this latent heat must be removed from the front. In the simplest case, the heat transport will be by diffusion, and the thermal field satisfies

$$\frac{\partial T}{\partial t} = D_h \nabla^2 T, \quad (2.15)$$

where $D_h$ is the heat-diffusion constant and may have different values in the solid and liquid phases.

Heat-diffusion problems involving Eq. 2.15 require boundary conditions, at infinity and at the heat source. In the free-growth problem, we have an additional unknown, the position of the front. Therefore, in order to solve Eq. 2.15, we must provide a second boundary condition at the front: the effect of curvature and motion on the temperature of the front.

The first boundary condition at the front requires that the heat production at the front be balanced by the thermal flux and is essentially a statement of energy conservation:

$$\hat{n} \cdot \left[ D_h^L c_p(\nabla T)|_{Liq} - D_h^S c_p(\nabla T)|_{Sol} \right] = -L(\vec{v} \cdot \hat{n}), \quad (2.16)$$

where the diffusion constants in the solid and liquid phases, given by $D_h^S$ and $D_h^L$, are not necessarily equal. The L.H.S of this equation gives the heat flux through an
imaginary surface surrounding the front, while the R.H.S gives the heat production at the front. The presence of the latent-heat source at the front causes a discontinuity in the temperature gradient. In Eq. 2.16, $v$ is the local front velocity and $\hat{n}$ is the unit vector normal to the front.

The second boundary condition at the front states that the temperature at the interface, $T_{int}$, depends on the curvature and on the growth rate:

$$T_{int} = T_0(1 - d_0\kappa) - \tilde{\beta}(\vec{v} \cdot \hat{n}),$$

(2.17)

where $\kappa$ is the mean curvature of the front and $d_0$, the capillary length. The depression of the freezing temperature due to the curvature is known as the Gibbs-Thompson effect. The third term in Eq. 2.17 arises because a front in equilibrium with its surroundings will not move. In order for growth to occur, the front must be out of equilibrium. At low $\Delta T$, this “kinetic” term is small, but it becomes more relevant at higher $\Delta T$.

The third boundary condition applied to all other boundaries states that the temperature of the sample will asymptotically approach the imposed temperature as we move away from the solid-liquid interface,

$$T(z \rightarrow +\infty) = T_\infty.$$  

(2.18)

Generally, the experimental system is not infinite, and a more realistic requirement would be

$$T(z \gg l) = T_{set},$$

(2.19)

where $l = D_{\text{heat}}/v_n$ is the diffusion length and $T_{set}$ is the temperature set at the boundary of the sample. The solution to this free-boundary problem yields the position of the solid-liquid front.
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Figure 2.3: Phase diagram of a typical low-concentration binary mixture. For low concentrations, the freezing point of the mixture is lower than that of the pure solvent. Mixtures with initial conditions that fall between the solidus and the liquidus, an "excluded region" labeled L+S, phase separate into a solute-rich liquid of concentration $c_L$ and a solute-poor solid of concentration $c_S$.

A Note on Solute Diffusion

Although thermal diffusion limits growth in pure materials at low undercoolings, in impure materials and mixtures such as binary alloys solute diffusion must be taken into account. Impurities (or solutes) incorporated into the solid lattice will usually have a higher free energy than those dissolved in the liquid. Therefore, a fraction of these impurities are excluded from the growing solid, increasing the impurity concentration ahead of the front. For low concentrations, the typical phase diagram is shown in Fig. 2.3. The temperature where solidification just begins is known as the liquidus temperature, $T_l$, and is given by

$$T_l = T_0 - \frac{k_B T_0^2}{L} \left(1 - \frac{c_s}{c_L}\right) c, \quad (2.20)$$

\[\text{[ll]}\]

---

\[\text{2The Gibbs-Thompson equation states that the chemical potential of a solid sphere in equilibrium with a surrounding liquid will be a function of the curvature: } \Delta\mu = 2v\gamma\kappa \text{ where } v = V/N \text{ is the specific volume, } \gamma \text{ is the surface energy, and } \kappa = 1/R_1 + 1/R_2 \text{ is the local mean curvature. A higher } \kappa \text{ raises the internal pressure of the solid, creating a higher } \Delta\mu \text{ and therefore a lower coexistence temperature [11].}\]
where \( k_B \) is the Boltzmann constant, and \( c, c_s, \) and \( c_L \) are the initial impurity concentrations and concentrations after partition in the solid and liquid phases, respectively. Eq. 2.20 holds for sufficiently small concentrations, \( c \). It follows that the impurity concentration and freezing temperature are coupled. Therefore, an increase in the impurity concentration decreases the local undercooling and slows the front. By contrast, the removal of impurities from the front via diffusion in the liquid phase accelerates solidification.

The concentration-undercooling coupling yields a set of equations that is very similar to that derived for the case of latent-heat diffusion. Since in general \( D_{\text{heat}} \gg D_{\text{impurity}} \), heat will diffuse away from the front much more rapidly than the solutes. Therefore, impurity diffusion will usually limit the growth.

As the solution to the free-boundary partial differential equation is technically involved and can be found in many standard texts [11], I will not repeat it here. However, it leads to a good description of phenomena such as dendritic growth, side-branching, and the effects of crystal-lattice anisotropy. In the next section, I will focus on a qualitative description of the freezing front that forms in the presence of a thermal (or solute) diffusion field.

**The Front Shape**

Both latent heat and impurity fields increase in the vicinity of a growing front, causing it to slow down. However, these fields have another, more interesting consequence: they are responsible for the pattern formation observed at low undercoolings. Mullins and Sekerka [3] showed that in rough growth (Section 2.2.2), the planar front is unstable at finite undercoolings. The essence of their argument is that perturbations to the planar front protrude into regions of higher undercooling, thereby causing a local compression of the isotherms ahead of the perturbation and, thus, an increase in the temperature gradient (Fig. 2.4). Because the heat current is proportional to the temperature gradient, the isotherm compression accelerates the heat diffusion away from the perturbation and causes an increase in the local velocity. The increased velocity of the protrusions relative to the surrounding planar front creates the instability.

The size of the protrusions is limited by the the surface energy, which increases
CHAPTER 2. THEORETICAL BACKGROUND

Figure 2.4: The Mullins-Sekerka instability. Perturbations to the planar front sample regions of higher undercooling and compress the isotherms in their vicinity.

with increased surface area (Eq. 2.5). The resulting protrusions are a product of the competition between the stabilizing effect of surface tension and the destabilizing effect of the temperature/impurity gradient. Mullins and Sekerka showed that a linear-stability analysis of the diffusion equations yields a characteristic length scale for the perturbations given by

$$\lambda \sim 2\pi \sqrt{d_0 l_D},$$

(2.21)

where the capillary length, \(d_0\), can be thought of as a typical “width” of the solid-liquid interface, and \(l_D \equiv 2D_k/\nu\) is defined as the diffusion length.

2.2.2 Kinetics-Limited Growth

In the idealized model I am presenting, the crossover from the diffusion- to the kinetics-limited regime occurs when \(\Delta T > L/c_p\). Solving the free boundary equation for \(\Delta T > L/c_p\) in the absence of kinetics (\(\bar{\beta} = 0\)) will give an accelerating front since the latent heat cannot raise the interface temperature above \(T_0\). In practice, these fronts are not observed; instead, the rate at which molecules can attach onto the surface begins to limit the growth rate of the front. This attachment rate may also be responsible for the pattern formation seen in this regime. In order to understand how the transition from diffusion- to kinetics-limited growth occurs, we need to formulate
an equation for the growth rate as a function of the material parameters. In general, the growth rate will depend on specific physical factors such as the roughness of the growing surface at the interface, the presence of screw dislocations, the direction of growth relative to the lattice, and other surface phenomena. Here, we will assume a rough interface. In this case, the growth rate can be modeled as [14]

\[ v_K \propto D \frac{1 - e^{\frac{-\Delta G}{k_B T}}}{d}, \]  

(2.22)

where \( k_B \) is the Boltzmann factor, \( T \) is the absolute temperature, and \( \Delta G \) is the decrease in free energy due to solidification. Each molecule arriving at the surface must diffuse a distance on the order of its physical size \( d \) in order to be incorporated into the solid lattice; therefore, the growth rate is proportional to \( D \), the self-diffusion constant, and inversely proportional to \( d \), the lattice/molecule size.

Although other growth mechanisms may have a different \( \Delta T \) dependence, the pre-factor will always include \( D/d \). Diffusion and viscosity are connected by the Stokes-Einstein relation [15],

\[ D = \frac{k_B T}{6\pi a \eta}, \]  

(2.23)

where \( a \) is the hydrodynamic radius of the diffusing molecule and \( \eta \), the viscosity of the fluid. Therefore, the transition to the kinetics regime is related to an increase in the viscosity of the freezing fluid. Because the temperature dependence of the viscosity follows an Arrhenius law [15], we write \( \eta \propto e^{(\beta F)} \). From Eq. 2.23, \( D \propto e^{-\beta F} \), which can be substituted into Eq. 2.22 to obtain

\[ v_K \propto e^{-\beta F} \left[ 1 - e^{-\beta \Delta G} \right]. \]  

(2.24)

At low temperatures, this equation is dominated by the \( e^{-\beta F} \) term, which causes the growth to slow. This slowing is caused by the restricted mobility in the melt due to the increased viscosity at low temperatures. At high temperatures, the \( [1 - e^{-\beta \Delta G}] \) term in Eq. 2.24 dominates. It can be approximated as \( v_K \propto \Delta T/T \) for small undercoolings. The growth rate is limited by the small driving force. A qualitative plot of this curve can be seen in Fig. 2.5(a).

In practice, the transition from diffusion- to kinetics-limited growth rarely takes place at \( \Delta T = L/c_p \). This can happen for several reasons. A straightforward one is
that the solidification geometry is such that the latent heat can be extracted more efficiently than is implied by the $\Delta T = L/c_p$ criterion. For example, consider a thin layer of liquid in contact with a plate that has a high thermal conductivity. As the liquid freezes, most of the heat is removed from the interface by the conducting plate. (See Ch. 3 for more discussion.)

Figure 2.5: (a) Qualitative plot of the growth rate in two regimes vs. undercooling $\Delta T$ imposed at the sample boundaries. At low undercoolings, diffusion limits the growth ($v_D$); at higher undercoolings ($\Delta T < \Delta T^*$), growth is dominated by the transport kinetics at the growing interface ($v_K$). (b) The undercooling at the interface $\Delta T_i$ vs. the imposed undercooling, $\Delta T$. In diffusion-limited growth, $\Delta T_i \approx 0$. $\Delta T_i$ increases only when the growth is no longer diffusion limited. In a thick sample, $\Delta T^* = L/c_p$; while in an ideal thin sample, $\Delta T^* = 0$.

A graphic representation of the determination of the transition undercooling can be seen in Fig. 2.5(a). Here, a sketch of the growth rate of a kinetics-limited front is shown, along with that of a diffusion-limited one. The slowest growth law at a given $\Delta T$ will determine the growth rate of the front; therefore, the transition from diffusion-limited to kinetics-limited growth takes place at the intersection of the two curves. Removing latent heat via a conducting boundary, as described above, will steepen the diffusion-limited-growth curve, lowering the $\Delta T^*$ of the transition.

In the diffusion-limited regime, the undercooling of the interface is essentially zero. In Fig 2.5(b), the imposed undercooling is plotted against the undercooling of the
interface. Here, we see that in a thick sample, the front's undercooling remains zero so long as the growth is diffusion limited. If the latent heat produced by solidification is too small to lower the undercooling to zero, the undercooling starts to increase and the growth becomes kinetics limited. In an ideal thin sample, where all the latent heat is removed from the front via conducting boundaries, the imposed undercooling is equal to the interface's undercooling, and the transition to kinetics-limited growth is essentially at $\Delta T = 0$. The conditions in our system are close to this limit.

### 2.2.3 Pattern Formation at High Undercooling

In the diffusion-controlled limit, pattern-formation studies have focused on the growth of a single crystal [11]. Solids are assumed to be composed of a small number of such domains. However, when driving the system further from equilibrium by increasing the undercooling, one can no longer make this assumption. The mechanical stresses and defects that result from the high growth velocities, viscous flows, impurity trapping, etc., cause the solid to break up into an aggregate of many small crystallite domains. One particularly interesting case is spherulitic growth, where the crystalline aggregate exhibits ordering on a scale much larger than the size of the individual crystallites.

### 2.3 Spherulites

Spherulites, as their name suggests, are spherical aggregates of crystallites. They are observed in the freezing of viscous melts at high undercoolings and occur in a variety of materials, including polymers [16] and polymer blends [17], liquid crystals [18], elemental selenium [4], minerals [4, 16, 19], organic materials [20], and low-molecular-weight organics with polymer impurities [7, 21]. Although spherulites are commonly encountered in both industry and science and have been studied for about a century, there is still no quantitative theory that can make predictions about their growth [22]. Existing theories tend to focus on the phenomena seen within a particular subset of materials, as opposed to explaining them in a more general way.
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2.3.1 Phenomenology

A spherulite has three important length scales [13]: At large length scales, there is the spherical aggregate, whose size depends on that of the sample and on the number of spherulitic domains formed. At a much smaller length scale, there are the individual crystallites or lamellae. Finally, at intermediate scales, there are filamnetary arrays, formed by bunching together the crystallites/lamellae. The formation of spherulites may result from feedback among these scales. For example, growth at the crystallite scale may generate flows in the liquid, which will determine the growth at the macroscopic scale, while the macroscopic shape modifies these flows and may be responsible for modifying the microscopic interactions [9]. The coupling of effects from the microscopic scale to larger scales is familiar from low-undercooling systems such as snowflakes, where the atomic symmetry has a macroscopic effect on interfacial patterns. (For example the hexagonal symmetry of ice crystals is responsible for the six-sided snowflake [11].) However, in spherulites, there is a possibility that the reverse is occurring: macroscopic growth may be responsible for pattern formation on the lamellar scale through the imposition of hydrodynamic flows.

A feature common to spherulites is that the crystallites that form the aggregate are oriented radially around a small, non-spherulitic core region. In contrast to dendrites and faceted morphologies, the angles between the crystallite domains are not confined to crystallographic values. Instead, they can branch at any angle, so long as they maintain an overall average radial orientation. This “radial splay” of the crystallites results in an approximate radial symmetry for the coarse-grained aggregate. Evidence for the radial orientation is found when viewing a slice of a spherulite between crossed polarizers [23]. Under these conditions, one sees a cross-shaped extinction pattern\(^3\) (Fig. 1.1(a)). Extinction occurs when the crystal’s optical axis is parallel to the polarization axis of the analyzer, or the polarizer. Since the optical axis is parallel to the crystallite, we conclude that the crystallite orientation must rotate as one moves around the core region.

A particular subclass of spherulites known as “banded spherulites” exhibits an additional ordering. In this case, when viewed between crossed polarizers, one observes

\(^3\)this pattern is sometime referred to as a “Maltese Cross.”
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Figure 2.6: The optical axis of a lamellar crystal twists along a helical path as the crystal grows radially. This twist can be seen by rotating the crystal along its own axis on a universal stage between crossed polarizers. In this case, the bands move continuously as the crystal is rotated [23].

concentric dark and light bands (similar to a target pattern), as shown in Fig. 1.1(b). The band spacing, defined as the distance between two light bands, is constant with radius but varies with the material and with the undercooling. The bands are believed to result from a twist in the individual crystallites [24], [21]. This twist requires that the optical axis follow a helical path, as seen in Fig. 2.6, with the dark bands appearing whenever the optical axis is parallel to the line of sight [23].

In materials that exhibit banding, the transition from the unbanded to the banded regime occurs when the undercooling, \( \Delta T \), is increased past a critical value, \( \Delta T_c \). The band spacing near \( \Delta T_c \) is large, and the bands highly disordered. As \( \Delta T \) is increased further, the banding becomes more ordered and the spacing decreases. The disordering and eventual disappearance of the bands as \( \Delta T_c \) is approached from above is typical of a continuous pattern transition. We shall return to this topic in the discussion of our results (Ch. 4).

The band spacing is not only a function of temperature but also varies from system to system. In fact, the band spacings for different materials may vary over several orders of magnitude. For example, spherulites formed by freezing pure polymers have typical band spacings\(^5\) of 1 to 10 \( \mu \)m, while in systems where a polymer is added

\(^4\)Since the band-spacing depends on undercooling, and not on the initial nucleation conditions, changing the undercooling during the growth will change the band spacing.

\(^5\)The typical band spacing, \( \lambda_{\infty} \), is defined as the band spacing far from the divergence, at high
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to a low-molecular-weight organic compound, the band spacings are on the order of millimeters to centimeters [7] [21].

2.3.2 Theories for Phenomenology

Splay

There are two main theories that attempt to explain the non-crystallographic splay of the crystallites forming the spherulite. The first is due to Basset and Keller [25] (both polymer scientists) and proposes that the splay is due to an intrinsically polymeric phenomenon. When polymers freeze, they form plate-like crystallites known as lamellae. The lamellae are formed by folding the polymer chains onto the growing interface. Typically, growth will proceed in one direction, resulting in very long, thin crystals. The thickness is controlled by the undercooling and is related to the length of the chains and the number of folds each chain undergoes. However, the folding process is not perfect, causing dangling “ends” and “loops” to be left hanging off the top and bottom surface of the lamella, as seen in Fig. 2.7. Basset et al. have proposed that the “entropic pressure” of these dangling ends (loops) causes the lamellae to bend into an approximate radial direction. Although this theory may explain the appearance of non-crystallographic angles in spherulites formed from polymer melts, it does not explain how the splay occurs when only a small concentration of polymer, or no polymer at all, is present [4].

A competing theory proposed by Tiller et al. [9] proposes that the splay is a consequence of hydrodynamic flows imposed by the growing crystal on the surrounding fluid that are then fed back onto the growing crystallite. Unlike the theory of Basset et al., this theory does not assume a particular class of materials but, rather, relies on more general hydrodynamic flows in the fluid and on the general observation that spherulites tend to freeze from viscous liquids. The essence of Tiller’s argument is that the solid and liquid, having different densities, will generate flows in the liquid upon freezing. If, for example, the solid is denser than the liquid, the flow will be towards the front. The direction of the flow is not critical to the model, as splay is predicted to occur independently of the flow direction.
Figure 2.7: A polymer crystallizes by folding chains onto the growing surface. Because the folding is not perfect, many dangling loops and ends remain unfolded, protruding from the top and bottom surfaces.

Tiller’s original model is for spherulites formed in a water-glycerol mixture. In this system, the crystallites forming the spherulite can be approximated as deformed dendrites. Although Tiller’s derivation relies on this observation, it is not essential to make this approximation. Here, I give a modified version of Tiller’s model for a general dense array of cylindrical crystallites.

The array (see Fig. 2.8 for definitions of variables) grows in the radial direction, $z$, while each crystallite thickens in the $R$ direction. Liquid must enter the aggregate through small channels between the crystallites in order to feed their growing surfaces. It is important to note that the channels are not cylindrical tubes but rather consist of the space left between densely packed crystallites of radius $R$ (Fig. 2.8). If the crystallites can thicken as they grow, then as $R$ increases, the channels will become narrower, eventually closing up. In crystals formed from polymers, the thickness of the lamella is fixed by the undercooling and remains constant over the entire length of the crystal [26]. The following is a derivation for crystals that thicken as they grow.

To describe the steady-state flow, we start from the steady-state Navier-Stokes equation for slow laminar flows [27],

$$\frac{dP}{dx} = \eta \nabla^2 v_L(z), \quad (2.25)$$
(a) Array of crystallites formed in spherulite

(b) Side view of segment of (a)

(c) View of (b) along the growth axis

Figure 2.8: Fluid flows in a dense crystal array, a generalization of Tiller's model. (a) 2-D slice of the spherulite with radial crystallites. (b) Enlargement of a segment of (a). (c) View of 'b' along the radial growth direction.
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where $\frac{dP}{dx}$ is the pressure gradient, $\eta$ the viscosity, and $v_L$ the liquid velocity. We can estimate the pressure drop $\Delta P$ produced by a flow in a channel of cross section $w^2$ and length $l$ as

$$\frac{\Delta P}{l} = \eta \frac{V_L}{w^2},$$ 

(2.26)

where $V_L$ is the liquid velocity at the mouth of the channel (at $z = l$). In Eq. 2.26, we note that the Laplacian operator is dominated by the smallest length scale in the channel geometry, $w$. Rearranging, we obtain

$$\Delta P \propto V_L \eta \frac{l}{w^2}.$$ 

(2.27)

As fluid flows through a channel, it is converted into solid on the channel walls. If the crystallites are thickening uniformly along their length, $v_L(z)$ must decrease linearly as one goes deeper into the channel. Therefore, if $v_L(z = 0) = 0$ and $v_L(z = l) = V_L$, we can write $v_L(z) = \frac{V_L}{l} \cdot z$.

Mass conservation across a length segment $\delta z$ of the channel requires that

$$R \frac{dR}{dt} \Delta \rho \delta z \propto \delta v_L \rho_L w^2 = \frac{V_L}{l} \cdot \delta z \cdot \rho_L w^2,$$ 

(2.28)

where $\frac{dR}{dt}$ is the change in crystallite radius with time, $\Delta \rho = \rho_S - \rho_L$ is the change in density upon freezing, and $\delta z$ is the length of a short channel segment. The L.H.S. of Eq. 2.28 is proportional to the change of mass within $\delta z$, while the R.H.S. is proportional to the difference between the mass flux in and out of the segment $\delta z$. We use proportionalities rather than equalities since it is not clear exactly what the geometry of the crystallites is. (For example, we have assumed here that the crystallite has a circular cross section; however, rectangular cross sections are also possible, giving rise to a geometrical factor.)

As mentioned above, this derivation is for crystals that thicken with time. In this case, the growth rate in the $R$ direction is proportional to the growth rate in the $z$ direction, as they are both functions of the undercooling.\(^6\) Therefore, $\frac{dR}{dt} \propto V_S$, where $V_S$ is the front velocity, which is proportional to the undercooling, $V_S \propto \Delta T$. The crystallite radius can also be related to undercooling using the Gibbs-Thompson,

\(^6\)Note that this does not require the crystallite to maintain a constant aspect ratio, as growth rate in one direction may still be much larger than the others.
equation which states that \( R \propto \Delta T^{-1} \). It follows that \( R \frac{dR}{dt} = \text{constant} \) and Eq. 2.28 reduces to

\[
V_L \propto \frac{\Delta \rho}{\rho_L} \frac{l}{w^2}. \tag{2.29}
\]

From Eqs. 2.27 and 2.29, we find

\[
\Delta P \propto \Delta \rho \frac{l^2}{w^4} \nu, \tag{2.30}
\]

where \( \nu = \eta/\rho_l \) is the kinematic viscosity of the liquid. The width of the channels \( w \) should scale with \( R \), but \( R \propto 1/V_s \). Therefore, \( w \propto 1/V_s \). Replacing \( w \) in Eq. 2.31, we get

\[
\frac{\Delta P}{\Delta \rho} \propto l^2 V_s^4 \nu. \tag{2.31}
\]

Tiller's argument assumes that the crystallites forming the spherulite are essentially dendrites that have bent to accommodate the fluid flow. This explains the origin of the crystallites (the Mullins-Sekerka instability). In this case, the core region will also be dendritic, the only difference between it and the remaining spherulite being in the branching angles and envelope shape (polygonal versus round/spherical). Furthermore, the radius of the core should scale with the hydrodynamic pressure. At higher flow rates, the pressure field would cause an increase in the bending force and a smaller core. We define the critical pressure as \( \Delta P^* \) and the critical crystal length (which is the same as the critical core size) as \( L^* \). Substituting, we find that the critical core should scale as

\[
L^* \propto \nu^{-1/2} V_s^{-2}. \tag{2.32}
\]

In order to test this scaling law, Tiller and Geering froze mixtures of water with varying glycerol concentrations at different undercoolings. Indeed, \( L^* \) was observed to scale with \( \nu^{-1/2} V_s^{-2} \) for each concentration [9, 13].

The original motivation of this thesis was to see whether this scaling law, which empirically holds for the core size of spherulites, also holds for the band spacing, \( \lambda \). In other words, we need to test whether \( \lambda \propto \eta^{-1/2} V_s^{-2} \). The motivation for this was that it seemed plausible that the same forces responsible for the splay could also be responsible for the twist. As we shall see in Ch. 4, we ultimately conclude that such a scaling does not hold. This has led us to consider other more explicit mechanisms for the twist, as outlined in the next section.
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Banding

There are currently four classes of models for the twist instability responsible for the banding [28]:

1) Surface stresses within the crystallite. As far back as 1888, Lehmann suggested [29] that surface stresses may be the cause of twisting in ribbon crystals. Possible sources of the stress include the dilation of lattice parameters near the solid-liquid interface [30], dilation of the lattice parameter due to imperfect folding of polymer chains on the lamella surface [8, 31, 32], and dilation due to the preferential incorporation of impurities at the surface of the crystallite [6]. Here, we give a simple estimate of the expected twist due to surface stresses, following Owen [33]. In this case, the source of the surface stress may be a particular folding mechanism of the polymer chains within the lamella.

According to elastic theory [34] \( W \), the work per area to bend a plate of thickness \( d \) is given by

\[
W \propto \frac{\alpha d^3}{R^2}, \tag{2.33}
\]

where \( \alpha \) is the elastic modulus and \( R \) the radius of curvature of the bending. The exact \( R \) required to create a helix with period \( \lambda \) would depend on many geometrical factors; however, in general, it should scale with \( \lambda \),

\[
R \propto \lambda, \tag{2.34}
\]

It is reasonable to assume that the intrinsic surface energy does not change much with undercooling, and therefore \( W \) (the energy per unit area of plate) is also constant. From Eqs. 2.33 and 2.34, the band spacing and the thickness of the crystallite is

\[
\lambda \propto d^{3/2}. \tag{2.35}
\]

A modified version of the Gibbs-Thompson equation for polymers states that the thickness of a lamella is inversely proportional to the undercooling [31]. Replacing \( d \) with \( (\Delta T)^{-1} \) in Eq. 2.35 gives

\[
\lambda \propto \Delta T^{-3/2}. \tag{2.36}
\]

The result is a power law with a divergence at \( \Delta T = 0 \). We discuss this result below.
2) Surface stresses induced by the melt surrounding the crystallite. The surface stress may also result from an interaction between the interlamellar melt and the lamella's surface. For example, Keith and Padden [35–37] have proposed that dilation of one crystal face relative to its opposing face would cause the crystal to bend. This differential dilation of the faces could result when the growing face is not normal to the growth direction, as depicted in Fig. 2.9. Basset et al. have proposed that entropic pressure from unfolded cilia between the closely packed lamella may cause screw dislocations to form on the surface, which would also be a source of surface stresses [38–40].

Whatever the source of the surface stress, the arguments follow along lines similar to a derivation presented by Owen, with the power law of the divergence depending on the particular mechanism. For example, Keith and Padden conclude that $\lambda \propto \Delta T^{-\alpha}$, with $2 < \alpha < 4$, depending on the angle of the growth face.

3) Giant Isochiral screw dislocations. Kinloch and Shultz [22] have showed that queues of isochiral screw dislocations in the lamella would cause a twist (Fig. 2.10). The source of the dislocations is assumed to be thermal, with the chirality determined by the stress in the lamella. Bassett et al. have proposed a similar argument where the source of the stress is uncrystallized interlamellar material, as described above.

If the screw dislocations are thermal, the probability density of a dislocation's occurring is given by

$$p(\text{dislocation}) \propto e^{-\frac{\gamma M^2}{kB T}} \quad (2.37)$$
where $c_1$ is a constant, $b$ is the Burger's vector and $l$ is the length of the dislocation. The spacing between screw dislocations is inversely proportional to the probability density, and the angular rotation is given by

$$\phi = c_2/S,$$  \hspace{1cm} (2.38)

where $c_2$ is a constant, and $S$ the average spacing of dislocations. If the length and Burger’s vector of the dislocation scale with the lamella’s thickness $w$, we can write

$$\phi = c_2 e^{-\frac{c_1 w^3}{k_B T}}.$$  \hspace{1cm} (2.39)

Since $w \propto \Delta T^{-1}$, we have

$$\phi = c_2 e^{\frac{-S}{\Delta T k_B T}}.$$  \hspace{1cm} (2.40)

As in Owen’s theory, this theory also predicts a divergence of band spacing at $\Delta T = 0$, albeit with a different functional form.

4) Escape from impurity concentrations. A recent model also due to Schultz [28] proposes that lamellar crystallites may rotate around their axis in order to avoid regions of concentrated impurities. By twisting or bending, the crystallites avoid regions of high impurity concentration that build up ahead of the solid-liquid interface. Although Schultz’s paper focuses on impurity concentration, he claims that a similar mechanism should hold for the pressure field, thus generating a model depending on flows and the Navier-Stokes equation rather than on impurity concentration and the
diffusion equation. Although Schultz raises this possibility, he does not pursue this calculation; however, this calculation suggests an interesting way to explore theoretical links between hydrodynamic effects and crystal morphology.

The four types of models above have some general shortcomings:
(1) Excepting the isochiral-screw model, all models are system specific and do not account for the broad range of material in which banding is observed.
(2) Excepting the last, all assume equilibrium growth conditions, while these systems are obviously far from equilibrium, and dynamic conditions probably play an important role in the instability.
(3) None of the models predicts the measured length scales.
(4) The experimental observations show that the twist in adjacent lamellae is correlated. However, all models ignore this correlation and instead focus on the twist in individual lamellae.

2.4 Summary

I have outlined the origin of the freezing front and of the interfacial instabilities that form at low undercooling. At high undercoolings, one observes a quite different morphology: bundles of fine crystallites forming spherulites. I have presented two types of models for the splay of these crystallites: a general hydrodynamic model, which should apply to all materials [9], and a material-specific model which, in this case, should apply only to a specific polymer [33]. I have also presented four types of banding models, which share some common shortcomings. The goal of this thesis is to see whether experimental evidence for hydrodynamic-controlled scaling laws can be found for the banding instability. I will also try to show that an important aspect of the banding is the coherent twist of crystallites, which is not discussed in the above models.
Chapter 3

Experimental Methods

Since this will perhaps be the most useful chapter for future students continuing this work, I will give a detailed description of the experimental methods and techniques. The first section explores the reasons for choosing the system we work with. In the second section, I explain in detail the sample-preparation procedures. The third section describes the apparatus and data-collection methods. The fourth section outlines the image-analysis methods used. The last section describes briefly the cone-plate viscometer we used to measure sample viscosities.

3.1 Choice of Experimental System

Although banded spherulites are observed in many different systems, most of the experimental work has been done on systems with a viscosity that is not adjustable independently of the temperature.\(^1\) The possibility that the band spacing, like the core size [9], may have hydrodynamic origins requires a systematic study of the bands as a function of some hydrodynamic parameter. For this purpose, we sought to use a material in which the viscosity at a given temperature was adjustable. An obvious approach is to use a binary mixture where the concentration of the minority component changes the liquid viscosity at a fixed temperature. Of course, one needs to test whether any phenomena that are observed are affected in other ways by having

\(^1\) Although Tiller [9] and Geering [13] explored spherulitic growth in a system with variable viscosity, their system (water+glycerol) does not exhibit banding.
two components. Degen et al. [7] explored the strategy of using a low-molecular-weight material to which a small amount of polymer is added. In particular, they looked at maleic anhydride, to which a small amount of polyacrylonitrile had been added. Banded spherulites of extraordinarily large size had been observed previously in this system[21], but no systematic studies had been done. Unfortunately, the solubility of polyacrylonitrile in MA is low, implying that only a very limited range of concentrations and, hence, viscosities could be explored.

Later, Degen identified an alternative system consisting of melted ethylene carbonate (EC) with a small amount of polyacrylonitrile (PA) dissolved in it. By varying the polymer concentration from 2.6 Wt.% to 7 Wt.%, at a typical freezing temperature of 25 °C, one can vary the viscosity of the mixture from 120 to 2200 cP (Sec. 3.10). Apart from the tunable viscosity, this system has two other advantages: a convenient banding scale and a convenient freezing temperature. Previously, I mentioned that the scale of the banding can vary considerably between materials. A typical banded spherulite grown from a liquid crystal or polymer melt has a band spacing on the order of 2 μm-10 μm [5] [41], while the MA+PA the band spacing was about 1 cm. EC+PA has an intermediate band spacing on the order of 1mm [10]. Although larger band spacings make for easier visualization and probing of the crystal orientation [21], they also require larger samples which makes temperature control difficult, since thermal inhomogeneities tend to scale with the sample’s area. The millimeter bands formed in centimeter-size EC samples form a good compromise between the temperature-control and optical constraints. The second advantage is that the coexistence temperature, $T_0 = 38.6$ °C, is only slightly above room temperature, which makes temperature control relatively easy.

One must still ask how important the polymeric nature of the PA is in the crystal growth observed in this set of experiments. In pure polymers and polymer blends, spherulitic growth is the standard mode of solidification [12]. It may be the case that the banding observed here is intrinsically related to the chemical properties of the polymer in the sample rather than to the increased viscosity associated with its presence. I will try to clarify this point below.

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2This viscosity-concentration data is for a PA sample with a molecular weight of 102700 Daltons.
3.2 Chemistry

3.2.1 Materials

The samples used consisted of an ethylene carbonate-polyacrylonitrile mixture (EC+PA). EC is a small organic molecule that is typically used as a solvent for hydrophobic polymers (See Fig. 3.1(a) for its chemical structure). The chemical properties are given in Table 3.1. PA, a polymer that dissolves readily in EC, was used to increase the sample viscosity (See Fig. 3.1(b) for its chemical structure). Three batches of PA with varying dispersity and molecular weight were used. The dispersity is a measure of the chain-length distribution variance and is defined as

\[
PDI = \frac{\langle M_W \rangle}{\langle M_N \rangle},
\]

where \( PDI \) is the polydispersity index, \( \langle M_W \rangle \) is the average weight of the molecules and \( \langle M_N \rangle \) is the weight of a chain of average length. These are respectively given as \( \langle M_W \rangle = \frac{\sum N_i M_i^2}{\sum N_i M_i} \) and \( \langle M_N \rangle = \frac{\sum N_i M_i}{\sum N_i} \), where \( N_i \) is the number of chains of molecular weight \( M_i \) in the sample. Note that if the sample is monodisperse, \( M_i = \text{constant} \) and \( M_W = M_N \), yielding a \( PDI = 1 \). The relevant chemical properties of the PA samples are presented in Table 3.2.

We first obtained 98% pure EC from Aldrich-Sigma. However, since the impurity concentration in the vicinity of the front can limit the growth of a crystal, we needed either to purify the EC or to find a source of purer EC. After some attempts at purifying EC using recrystallization, as described in the Appendix, I concluded that the method would not yield an EC purity much higher than that supplied by Aldrich.

![Chemical structure](image)

Figure 3.1: Chemical structure of (a) ethylene carbonate; (b) the monomer of polyacrylonitrile.
CHAPTER 3. EXPERIMENTAL METHODS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>88.06 gr.mol⁻¹</td>
<td>[42]</td>
</tr>
<tr>
<td>Melting point $T_0$</td>
<td>36.4 °C</td>
<td>[42]</td>
</tr>
<tr>
<td>Boiling point (760 mm Hg)</td>
<td>248 °C</td>
<td>[42]</td>
</tr>
<tr>
<td>Liquid Density $\rho_L (T = 39 , ^\circ C)$</td>
<td>1.3218 kg.lit⁻¹</td>
<td>[10]</td>
</tr>
<tr>
<td>Solid Density $\rho_L (T = 39 , ^\circ C)$</td>
<td>1.45 ± 0.03 kg.lit⁻¹</td>
<td>Estimated⁴</td>
</tr>
<tr>
<td>$C_p,\text{liquid}(T = 323.15K)$</td>
<td>133.9 J.mol⁻¹ K⁻¹</td>
<td>[42]</td>
</tr>
<tr>
<td>$C_p,\text{solid}(T = 298.15K)$</td>
<td>117.44 J.mol⁻¹ K⁻¹</td>
<td>[10]</td>
</tr>
<tr>
<td>Thermal conductivity $\lambda_c$ (liquid, $T \approx T_0$)</td>
<td>0.1526 W.m.K⁻¹</td>
<td>[43]</td>
</tr>
<tr>
<td>Latent Heat</td>
<td>2.41kJ.mol⁻¹</td>
<td>Derived</td>
</tr>
<tr>
<td>Characteristic undercooling $\frac{\lambda_c}{C_p,\text{liquid}}$</td>
<td>18.0 °C</td>
<td>Derived</td>
</tr>
<tr>
<td>Thermal diffusivity $\frac{\lambda_c}{\rho_L C_p,\text{liquid}}$ (solid,liquid)</td>
<td>(0.0765, 0.0760) m².s⁻¹</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Table 3.1: Thermodynamic properties of pure ethylene carbonate.

Later, we found a supplier³ of 99.98% pure EC [42]. Since the final EC+PA samples consist of less than 7 Wt.% PA, the purity of the PA is less relevant than that of the EC.

3.2.2 Mixture Preparation

EC+PA mixtures were prepared by mixing PA into the pure EC. The range of concentrations that can be mixed is fixed by two constraints and depends on the chain length of the polymer used. For the 102,700 Dalton PA samples, mixtures with $c_{PA} < 2.6$ wt.% did not exhibit banding. Above 7.0 wt.%, the PA could not be dissolved in the EC without employing more sophisticated mixing methods. The longer-chain PA was much less soluble (< 3 wt.%) and showed banding at concentrations as low as 0.5 wt.%. I did not find the lower limit for banding for the high-molecular-weight PA.

In order to avoid contaminating the EC supply, I prepared aliquots of EC by

³Huntsman Scientific, 500 Huntsman Way Salt Lake City, Utah 84108, www.huntsman.com (.)
CHAPTER 3. EXPERIMENTAL METHODS

Table 3.2: Thermodynamic properties of polyacrylonitrile samples.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle M_W \rangle ) (Dalton)</td>
<td>(~100000)</td>
<td>102700</td>
<td>193100</td>
</tr>
<tr>
<td>( \langle M_N \rangle ) (Dalton)</td>
<td>N.A</td>
<td>46600</td>
<td>60600</td>
</tr>
<tr>
<td>( PDI = \frac{\langle M_W \rangle}{\langle M_N \rangle} )</td>
<td>N.A</td>
<td>(~2.2)</td>
<td>(~3.2)</td>
</tr>
<tr>
<td>Length</td>
<td>N.A</td>
<td>(~1\mu m)</td>
<td>(~2\mu m)</td>
</tr>
<tr>
<td>Melting point</td>
<td>((317.0 \pm 0.5) ^\circ C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.185 \pm 0.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

decanting pure EC into 10 ml vials and sealing them. In order to prepare an EC+PA mixture, I melted an aliquot of EC, weighed it, and held it at a temperature of 40 °C. Next, I ground the PA into a powder and added it to the liquid EC. In order to calculate the Wt. concentration, I weighed the EC+PA mixture rather than the PA directly, thus avoiding the error resulting from PA loss during the transfer from the weighing boat to the EC. The mixture was kept at 40 °C and stirred using a teflon-coated magnetic stirring bar on a magnetic stirring table for 1-10 hours (the higher the PA concentration, the longer it took to dissolve). After the liquid became clear, the mixture was allowed to freeze.

Because the vapor pressure of EC is much higher than that of PA, evaporation from the mixture can lead to an increase in PA concentration. In order to avoid this source of error, we always sealed the mixtures. Since evaporation is especially likely during the long mixing process, when the mixture’s temperature is elevated, the mixtures were weighed before and after mixing to make sure no losses had occurred. Samples that showed a significant change in mass (\(\Delta m > 0.1\%\)) were discarded. After mixing, the viscosity of the mixture was measured using a cone-plate viscometer (see section 3.10.1). For each mixture, the viscosity was plotted as a function of temperature.

The liquidus temperature of the EC+PA mixtures drops and the coexistence range
increases as the concentration of PA is increased. In order to find the experimental phase diagram of the EC+PA mixtures, I heated frozen samples very slowly \( \left( \frac{dT}{dt} \sim 1 \; ^{\circ}\text{C/hr} \right) \). The liquid fraction of each sample was plotted vs. temperature in order to determine the solidus and liquidus temperature, \( T_s \) and \( T_l \), as described in Sec. 2.2.1. From Fig. 3.2, we see that the slope of the liquidus line is \( \frac{dT_l}{dc} \sim 0.1 \; ^{\circ}\text{C per wt.\%PA} \). The solidus temperature was much harder to determine, since it seemed to depend on the heating rate. The problem is probably that it takes a very long time for the solutes to reach equilibrium when a large amount of solid is present.

Figure 3.2: The liquidus temperature, \( T_l \) vs. PA concentration, \( c_{PA} \). A linear fit gives \( T_l = b - m \cdot c \), with \( b = (36.24 \pm 0.09) \; ^{\circ}\text{C} \) and \( m = (0.12 \pm 0.02) \; ^{\circ}\text{C per wt.\%PA} \).

3.3 Sample Holder

3.3.1 2-D Spherulites

In three dimensions, spherulites grow as balls whose radius increases linearly with time. In a thin, quasi-two-dimensional geometry, spherulites grow as thin disks, which makes them much easier to observe. Furthermore, as we discussed above in Sec. 2.2.2, the thin sample geometry helps to remove latent heat from the interface, allowing us to reach the kinetics-limited regime more easily. It has been previously observed
that parameters such as the band spacing and the front velocity are unaffected by thickness changes, suggesting that phenomena observed in the quasi-two-dimensional case apply to the full three-dimensional geometry.

3.3.2 Geometry

The liquid sample is a flat disk of liquid (or solid) roughly 4 cm in diameter and nominally 25 \( \mu m \) thick that is constrained between a 3-mm-thick glass plate and a nickel-coated copper plate. Wire spacers are used to set the nominal 25 \( \mu m \) gap between the glass and copper plate. The gap is sealed around its edges with vacuum grease in order to prevent contamination and evaporation of the sample (sec. 3.4.2). The glass plate is fixed to the copper plate with an aluminum bracket. A schematic of the sample holder is shown in Fig. 3.3.

Nucleating Sealed Samples

Typically, in non-sealed samples, nucleation was initiated by touching the liquid at the edge of the sample with a small previously frozen seed crystal or with a “cold-finger.” However, in order to nucleate the sealed samples, where one cannot access the sample directly, a method due to Schaeffer et al. was adopted and modified to suit our sample’s geometry [48]. In this method, the sample holder is connected to a capillary tube and they are both filled with liquid EC+PA, as shown in Fig. 3.3. The end of the tube that is farthest from the sample is frozen and sealed off with a rubber stopper. The bottom end of the tube, closest to the sample, is held at a temperature which is above \( T_0 \) with a small heating coil. The heated region prevents the solid from growing down the tube and into the sample plane. After the heating coil is de-energized, the liquid in the tube cools and the solid can spread into the sample plane, where solidification phenomena can be observed. The capillary tube used was a 24-gauge blunt hypodermic needle inserted through a 0.5 mm diameter

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5 They are unaffected after one controls for temperature shifts due to latent-heat release.
6 The coating is approximately 1μm thick and gives the plate more resistance to abrasion and corrosion with minimal loss in thermal conductivity.
7 The heating coil was made from 5 turns of Nicrome wire with \( V \sim 4 \text{ volts} \) and \( I \sim 0.2 \text{ A} \).
Figure 3.3: Schematic of sample holder.

hole that was drilled\(^8\) through the glass cover plate, as seen in Fig. 3.4.

\(^8\)Drilling glass is hard! The holes were drilled by a professional who was contacted through the S.F.U glass-shop.
3.4 Sample Preparation

3.4.1 Cleaning

In order to avoid contaminating the sample with material from previous runs, we must thoroughly clean the sample holder before each run. We remove the glass cover plate and copper plate from the aluminum heat-sink, rinse them with ethanol, and wipe them clean with "Kim-wipes". The ethanol rinsing is repeated as needed until the plates are relatively clean. Next, the plates are sonicated\(^9\) in a 2% Micro-90 solution\(^{10}\) for half an hour. The capillary tube is cleaned by first injecting hot EC through it (in order to remove polymer residues) and, then, ethanol (in order to remove the EC). The ethanol is removed from the tube by sonicating it with the plates. After sonication, the assembly is rinsed in deionized water in order to remove the detergent residue, and it is oven dried at 100 °C for 30 min.

3.4.2 Filling and Sealing

The sample can be filled either by capillary action or by squeezing a measured quantity of fluid between the plates. Although the capillary method gives a sample with no air bubbles, it creates a chemical gradient in the sample, as EC evaporates during the filling. After gaining some experience with the second method, I found that I could make uniform samples with no chemical gradient. Although some gas bubbles may form during this filling process, one can omit these regions during the final analysis. This filling method also allows an estimate of the average sample thickness, by dividing the volume of mixture deposited by the area it covers. Measuring the sample volume directly is hard since the EC+PA sticks to the inside of the micro-pipet. Instead, mass is determined by weighing the pipet before and after the EC+PA mix is deposited on the sample holder. The weight is divided by the density of liquid EC, \(\rho_L\) (see Table 3.1) to get the volume (this volume has a 1% accuracy because of measurement errors and neglecting the presence of PA). The liquid-covered area is

\(^9\)Branson 1200 ultrasonic bath.
\(^{10}\)Micro-90, concentrated cleaning solution. Int. Product Corp. P.O. Box 70, Burlington NJ, 08016-0070, USA.
measured by capturing an image of the sample and analysing it with NIH-Image.\textsuperscript{11} (the liquid-air boundary is determined to approximately 5% accuracy; the errors arise from averaging over the width of the rough interface) it follows that the average thickness can be determined to roughly ±5%. Results from this method are shown in Tab. 3.3.

<table>
<thead>
<tr>
<th>Concentration (Wt.%)</th>
<th>Thickness (μm) ± 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.70</td>
<td>25</td>
</tr>
<tr>
<td>6.08</td>
<td>22</td>
</tr>
<tr>
<td>4.04</td>
<td>28</td>
</tr>
<tr>
<td>3.57</td>
<td>25</td>
</tr>
<tr>
<td>2.95</td>
<td>26</td>
</tr>
<tr>
<td>2.80</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 3.3: Average sample thickness found from volume-to-area ratios for the samples presented here.

Because open samples will develop a chemical gradient due to preferential evaporation of EC,\textsuperscript{12} it is important to seal the sample holder. I tried many different sealing materials but ultimately found that they almost all had an adverse effect on the samples. Finally, I settled for vacuum grease.\textsuperscript{13} It formed a good seal, was easy to work with, and did not seem to react with the EC. After sealing the samples, I realized that having the EC+PA in contact with gas along the edges of the sample also caused drifts in the measured properties, perhaps due to small gas bubbles getting sucked into the fluid upon freezing. In order to remove the air around the sample edge, I deposited a “grease-bead” around the edge of the glass, leaving a small gap for the air to escape during filling. After the grease was in place, approximately 0.1 ml of EC+PA was deposited in the center of the copper plate. Immediately, the sample was covered with the glass cover which was pushed down squeezing the air, EC+PA

\textsuperscript{11}NIH-Image; rsb.info.nih.gov/nih-image

\textsuperscript{12}This gradient caused some confusion in preliminary work [10]. The PA-rich areas tend to exhibit larger bands and slower front velocities. As a result, in the former unsealed configuration, the PA rich area near the edge of the sample was mistaken for the dendritic core discussed by Tiller [9].

\textsuperscript{13}Dow-Corning high vacuum grease.
mixture, and grease until the glass and copper were both touching the spacer wires. The EC+PA should touch mostly grease around the edges, with very little contact with air. The assembly was then fastened together with an aluminum bracket that was held down with four screws. If the grease bead did not close the gap in the grease ring, it was sealed off with a bit more grease. In order to seal the gap between the capillary tube and the hole in the glass, I used a soft rubber gasket.

![Image](image_url)

Figure 3.4: The nucleation device used in sealed samples.

### 3.5 Temperature Control

The temperature of the sample is controlled with a commercial temperature regulator\(^\text{14}\) containing a Peltier element.\(^\text{15}\) The Peltier element is used to heat or cool the copper plate and, consequently, the sample, depending on the polarity of the current passing through it. It is set inside an aluminum casing, which doubles as a heat sink and is cooled with a small fan (Fig. 3.5). In contrast to directional-solidification studies, where a thermal gradient is imposed on the growing crystal, this apparatus is designed to avoid thermal gradients across the sample. Gradients are eliminated by manufacturing the sample holder from copper, a good thermal conductor, and also by insulating the sample and sample-holder. The sample temperature was measured

\(^{14}\)Wavelength Electronics HTC3000; www.wavelengthelectronics.com (.)

\(^{15}\)Tellurex Co, CZ1-1.0-127-1.27 Z-max module.
3. EXPERIMENTAL METHODS

Figure 3.5: Apparatus for setting the temperature in the sample holder.

with a thermistor\textsuperscript{16} that is glued inside the top of the aluminum casing, between the sample-holder and the Peltier element. The thermal contact between the sample holder and aluminum heat-sink was improved by filling the thin gap between them with paraffin wax. The sample holder is insulated from the surrounding air with a closed-cell foam box that has a glass viewing window inserted into its top side.

3.5.1 Thermistor Calibration

Because every thermistor is different (readings vary by about 5\% among nominally identical units), they require calibration. The resistance of the thermistor was measured while in thermal equilibrium with a mercury thermometer\textsuperscript{17} over temperatures ranging from 5 °C to 50 °C.\textsuperscript{18} The data, represented in Fig. 3.6, were fit to a standard

\textsuperscript{16}Thermistor: Thermometrics Cat. # BR42KB503M.

\textsuperscript{17}The thermometer had 0.1 °C gradations.

\textsuperscript{18}The temperature was set using a Neslab water bath of nominal stability ±0.01 °C. Model: RTE110; Thermo NESLAB, 25 Nimble Hill Rd, Newington, NH 03801; www.thermo.com (.)
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phenomenological form for thermistors [49]:

\[ T(R) = \left[ a + b \cdot (\ln(R)) + c \cdot (\ln(R))^3 \right]^{-1}, \]

where \( R \) and \( T \) are resistance and temperature and \( a, b, c \) are fitting coefficients. Typical values which correspond to the calibration in Fig. 3.6 are given in Tab. 3.4.

![Figure 3.6](image)

**Figure 3.6**: Thermistor resistance vs. temperature with phenomenological best fit.

<table>
<thead>
<tr>
<th>( a )</th>
<th>(2740.3 ± 1.2) ( \times 10^{-6} ) ( °K^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b )</td>
<td>(2464.0 ± 7.5) ( \times 10^{-7} ) ( °K^{-1} )</td>
</tr>
<tr>
<td>( c )</td>
<td>(24.7 ± 3.8) ( \times 10^{-8} ) ( °K^{-1} )</td>
</tr>
</tbody>
</table>

**Table 3.4**: Fit coefficients for thermistor.

From the residuals in Fig. 3.6 the typical systematic errors were less than 0.1°C. Using this thermistor, in conjunction with a 16-bit data-acquisition card\(^{19}\), one can detect temperature shifts as small as 1.5 \( \times 10^{-4} \) °C.\(^{20}\) In practice, two factors lead to a much poorer accuracy. First, the sample is separated by about 7 mm of copper from the thermistor. Since gradients in the copper can be important, especially when the sample is being heated or cooled by the Peltier, the stated accuracy can only be

\(^{19}\) National Instruments PCI MIO E series.

\(^{20}\) This precision was achieved by acquiring data in 10,000 point blocks at 100 kHz and averaging over the block.
achieved if the whole system is in thermal equilibrium. I found that it typically took about 15 minutes for the system to equilibrate at an undercooling of approximately 10 °C. (This is equivalent to a temperature of 28 °C). Once the sample reaches the set point temperature, gradients in the copper become small, as little or no heat-pumping is required to maintain this state. If, however, the sample is frozen, latent heat is released, and this quasi-equilibrium state is lost.

![Sample cooling curve](image)

Figure 3.7: Sample cooling curve, showing the change in the slope of the temperature curve as the sample approaches the set point temperature. Since a proportional controller is used, there will always be a difference between the actual temperature and the set point temperature.

### 3.5.2 Latent-Heat Correction

In this study, we aim to correlate the viscosity with the band spacing and front velocity. Since the viscosity of the EC+PA mixtures is a function of temperature (Sec. 3.10), we must have an accurate estimate of the undercooling or temperature at the interface in order to calculate the viscosity. In practice, the interface temperature is a bit higher than the set-point temperature because the sample is only quasi-two

---

21 The temperature was considered to have “equilibrated” when the change in the measured temperature was less than 0.01 °C/min. Because we used a proportional control algorithm for temperature regulation, the steady-state temperature differed slightly from the setpoint. We use the actual steady-state value in our recorded temperature.
dimensional and because the copper has a finite thermal conductivity. Ideally, we would measure the temperature of the front directly. This requires the temperature probe to be in direct contact with the front until thermal equilibrium is reached. This is quite hard to do, since the front is moving; we would need either a very fast thermistor or a thermistor that could be moved with the front. Instead, we chose to find a correction for the front temperature analytically, by numerical simulation.

![Numerical simulation data showing the temperature increase at the front, $\delta T$, due to latent heat. $\delta T$ is plotted vs. $vh$, where $v$ is velocity (values from 0.5 to 2.5 mm/sec), and $h$ is the sample thickness. (Five thicknesses were simulated, ranging from 22 to 36 $\mu$m.) A linear fit to the data yielded Eq. 3.2.](image)

In order to correct accurately for the latent heat production, a PDE describing the heat flow in the system needs to be solved. This problem can be solved numerically or analytically [5, 10]. In both cases, the correction depends on the thermal conductivity of the glass, $EC$, and copper, on sample thickness, and on front velocity. It follows that each run will have a unique temperature correction. Results from an analytic calculation of the temperature increase at the interface for this apparatus can be found in [10]. In Fig. 3.8, I present the results from a more recent numerical calculation [43]. The temperature increase is plotted vs. $vh$, the front velocity multiplied by the sample thickness. From the plot, we note that temperature is roughly linear. Although the residuals show a systematic trend, the magnitude of this trend is very small within our range of interest ($\frac{\text{residual}}{\delta T} \leq 1\%$). We can also see that an extrapolation to zero of
vh will cause the temperature increase to approach zero. The results of the fits can be summarized as

$$\delta T = (0.0445 \pm 0.0044) hv,$$

where the sample thickness h is in \( \mu m \), and the front velocity v is in \( mm/sec^{-1} \). The 10% systematic uncertainty in the simulation data comes from the difficulty in estimating how to average the numerical result. The simulation gives a front temperature that varies with height. The result quoted is the range between the maximum temperature rise at the front and the average temperature rise (over the sample thickness).

### 3.6 Visualization

![Diagram of illumination setup](Image)

Figure 3.9: Illuminating a sample off axis.

Movies of the freezing samples were captured through a telezoom video lens\(^{22}\) with a CCD\(^{23}\) camera connected to a frame-grabber,\(^{24}\) installed in a G4 Powermac running

\(^{22}\)Visualtek 18-108mm 1:2.5
\(^{23}\)Pulnix TM-7CN CCD with maximum frame rate: 1/60 sec. Pulnix America Inc. 770 Lucern Dr., Sunnyvale, CA 94086.
\(^{24}\)Scion LG-3 82 Worman's Mill Court, Suite H, Frederick, Maryland 21701, USA;
NIH-Image. Typically, bands are visualized between crossed polarizers; however, in this experiment, we used off-axis illumination (Fig. 3.9), since it is less sensitive to imperfections on the copper substrate than the polarized-light method. The explanation for the optical contrast has been studied previously in different systems. There are several different contributions that have been noted:

1. The scattering intensity is a function of the index of refraction that is changing with the bands [23, 50].
2. The dark and bright regions have different defect concentration causing different scattering rates [50, 51].
3. In cases where the lamellae have a wide and narrow edge, the scattering intensity is a function of the visible width of the lamellae, changing as the lamellae rotate [41].

3.7 Automation

Previous data taken on the EC+PA system [10] showed a drift in the sample characteristics as the samples aged. In order to understand the nature of these drifts and to eliminate them, we compared the results of many repeated freezing cycles. To facilitate gathering data from a large number of runs, we automated the experiment. A schematic of the control loop, as well as a diagram showing the physical connections of elements in the system, is shown in Fig. 3.10. In brief, a master computer\textsuperscript{25} equipped with a data-acquisition card\textsuperscript{26} running Igor-Pro 4.0\textsuperscript{27} was used to control all the elements in the experiment and to coordinate the timing of events. However, since the experiment must run independently for many hours, we needed to observe the state (solid/liquid) of the sample at all times during the experiment and to react accordingly. For example, if a sample were to spontaneously freeze, it would be necessary to restart the cycle by first melting the sample and next recooling it. We achieved this by creating a sort of "visual-feedback" loop, where the state of the

\textsuperscript{25}www.scioncorp.com ()
\textsuperscript{26}Powermac-7600
\textsuperscript{27}National Instruments PCI MIO E series; Nat. Inst. Corp. 11500 N Mopac Expwy, Austin, TX 78759-3504; www.ni.com ()
\textsuperscript{27}Wavemetrics, Inc. P.O. Box 2088, Lake Oswego, OR 97035, USA; www.wavemetrics.com ()
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Figure 3.10: (a) Physical connections and feedback diagram; (b) Flow chart of control loop. The master computer gets visual feedback on the state of the sample from the CCD via the frame grabber and the image-processing computer. If the sample nucleates prematurely, the system resets the run.

The system is interpreted by an image-processing computer\(^{28}\) which measures the average intensity of the scattered light incident on the CCD. When illuminated off-axis (Fig. 3.9), a liquid sample appears dark, while a solid one scatters light into the lens and thus appear lighter. The information about the state of the system is transmitted to the master computer, which responds accordingly, as in a feedback loop. The “visual-feedback” loop is also used to trigger the movie capture as the sample is freezing. When the sample temperature has equilibrated, the heating coil is de-energized, the capillary cools, and the pre-frozen solid starts to grow down the capillary tube towards the

\(^{28}\)G4 Powermac: www.apple.com (.)
sample-plane. The time it takes for the solid to reach the sample-plane varies from one to five minutes, depending on the imposed undercooling. In order to avoid collecting useless images, we programmed the image-processing computer to trigger the movie capture from the CCD image. By presetting freezing and melting temperatures on the master-computer, we could capture many data sets with accurately repeated timings and temperatures.

3.8 Image Analysis

The data consist of movies that show consecutive images of the spherulite as it grows. From this data, we extract the front velocity, band spacing, and a measure of the correlation of the bands.

3.8.1 Front velocity

In order to extract the velocity of the solid-liquid front from a stack, I wrote a front-tracking algorithm in the NIH-Image macro language. In this algorithm, a difference stack is generated by subtracting image \((i + 1)\) from image \(i\), for all \(N\) images. The result is a stack that shows only the moving front\(^\text{29}\) and CCD shot noise, while all the static features of the image are subtracted out. An example is shown in Fig. 3.11(b). In order to locate the position of the front in the image, we take the cross section. In the cross section the front shows up as a maximum (Fig. 3.11(c)). In order to achieve sub-pixel resolution of the front location, we find the parabola that passes through the highest three points around the maximum. The position of the front is taken as that of the maximum of this parabola. When the front position is plotted vs. time (Fig. 3.12), the slope is a measure of the local velocity.
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Figure 3.11: (a) Image of growing front; (b) difference image; (c) cross section of difference image.

Figure 3.12: Front position vs. time, fit to a linear relation. The residuals show the deviation of the local velocity from a constant. This deviation increases with the number of freeze-thaw cycles.
3.8.2 Band Spacing and Correlation

Far from $\Delta T_c$, the critical undercooling for banding, the bands are small and ordered; as $\Delta T_c$ is approached, the band spacing increases and becomes less regular. In order to quantify this behavior, I took a 2-D FFT of the last image in the stack, as shown in Fig. 3.13. The FFT has two peaks: one around zero frequency, resulting from non-uniform illumination and other low frequency noise, and a second, resulting from the periodic intensity modulation of the bands. The second peak is generally broad in the

\[ \text{Occasionally, other motions in the sample are visible, such as the liquid meniscus or air bubbles trapped in the liquid moving towards the solid as a result of the fluid flow that is driven by the density change. These contribute a low intensity compared to the front and do not interfere with the image processing.} \]
direction parallel to the bands, and narrow in the other direction. The perpendicular width is a measure of the correlation length of the bands: a narrow peak in this direction is a result of ordered banding, while a wide peak, means that the banding is disordered. The width in the direction parallel to the banding is a measure of the lateral correlation between regions that have grown side by side. In order to find the position and width of the banding-peak, I fit two 2-D Gaussians to the zero-order peak and to the banding peak. To obtain the band spacing and a measure of the correlation length in image-space from the banding peak, I used

$$\begin{cases} \lambda = \frac{1}{k}, \\ \xi \propto \frac{1}{\sigma}, \end{cases}$$

where $\lambda$ is the band spacing and $\xi$ is the correlation length, $k$ is the location of the peak in $k$-space and $\sigma$ is the full peak width at half maximum.

Correlation lengths were also determined by calculating the autocorrelation function of a cross section of the image and fitting a decaying exponential to the envelope. (See Fig. 3.14.) In this case, the correlation length was defined as the “e-folding” length associated with the exponential. The correlation lengths found using these two methods agreed up to a proportionality constant.

Figure 3.14: Autocorrelation function of a cross section of an image of a banded spherulite for a 6.7 Wt.% PA sample, grown at $\Delta T \approx 10 \, ^{\circ}C$. The envelope of the autocorrelation is fit to a decaying exponential (dashed line).
3.9 Limitations Due to Drifts

Previous work has showed that in a uniform sample, if one ignores the core, the front velocity should either be constant, or modulated with the banding. In either case, a linear relation can be fit to position vs. time data with the slope giving the average velocity, as shown in Fig. 3.12. A constant velocity front would only have random noise in the residuals. In practice, the velocity of our samples varies as the front moves through the sample. Typically, the front is slower as one approaches the sample edges. This variation in front velocity can also be seen, less clearly, when one looks at the local band spacing of the crystal. We find that regions with increased velocity form wider bands. The origin of the variation can be traced to thermal and/or chemical gradients in the sample.

![Graphs showing velocity vs position for sealed and unsealed samples.](image)

Figure 3.15: The effect of sealing on the front-velocity drifts in EC+PA samples. (a) shows the velocity as a function of position in a sealed sample. The velocity is plotted for 13 runs. The runs are repeated once every 25 minutes. (b) shows the same for an unsealed sample. Although the drift in the sealed sample is smaller than the unsealed one, it is not eliminated.

By analyzing movies of repeated freeze-thaw cycles, we saw that the velocity change across the sample increased with time but did not seem to depend on the particular undercooling used (Fig. 3.15(b)). If the gradient were thermal, it would not change with time and would depend on the undercooling. It follows that the change in velocity is probably caused by a time-dependent chemical gradient. This hypothesis is further reinforced by the observation that the velocity in low-viscosity
samples tends to drift faster than that in high-viscosity ones. The chemical gradient could have a number of sources, the most obvious one being evaporation of EC from the sample into the surrounding air and contamination of the sample by diffusion of impurities in from the sample edge (as discussed above). In order to avoid these sources, we sealed the samples with vacuum grease. A comparison of drifts in sealed and unsealed samples is showed in Fig. 3.15. In this figure one can see that sealing the samples reduces but does not eliminate the drifts altogether. The remaining chemical gradient may be caused by solute segregation due to fractionalization or by impurities diffusing into the sample from the sample-air edge (from air pockets trapped between the grease seal and the sample). Ideally, in order to eliminate this chemical gradient, one would mix the sample after every run. This is not possible with thin samples. In order to minimize the effects of this drift, the number of freeze-thaw cycles per sample must be limited.

If fractionalization were the source of the gradient in the sample, it would mean that each run depended on the sample history, making the analysis of samples with multiple “freezings” very complex. In order to verify that this was not the case, we checked whether the gradient was a function of the sample age or of the number of freeze-thaw cycles the sample had been exposed to. If fractionalization were the source of the gradient, we would expect it to increase with the number of freeze-thaw cycles; if, however, it were caused by impurity diffusion, it would depend on the sample age directly. We compared the drifts in two samples aged for approximately 200 minutes each. The first sample was frozen eight times, once every 25 minutes (Fig. 3.16(a)); the second was frozen sixteen times, once every 12 minutes (Fig. 3.16(a)). We subtract the first velocity profile from the last, for both samples, and compare these differences ($\delta v$'s) in Fig. 3.16(c). The magnitude of $\delta v$ for the samples is roughly the same, meaning that the number of freeze-thaw cycles is irrelevant and that the sample age determines the gradient size. This implies that the velocity drift is caused by diffusion of impurities from the sample's edge. The difference between the two $\delta v$'s in Fig. 3.16(c) may be caused by the slightly different impurity profile of the samples. The impurity concentration at any point in the sample depends on its distance from the sample edge; therefore, a change in the shape of the sample boundary (which is not exactly repeatable for the samples) may cause a change in the impurity profile.
Figure 3.16: The effect of repeated freeze-thaw cycles on chemical gradients in the sample. (a) front velocity vs. position for a sealed sample frozen eight times, every 25 minutes. (b) same for a sample frozen sixteen times, every 12 minutes. (c) is a comparison of $\delta v = v_{last} - v_{first}$ for the velocities shown in (a) and (b).

Since drifts were not totally eliminated by sealing, it was necessary to limit the amount of time a sample was used. In order to determine whether a sample was still usable, we periodically returned to a baseline undercooling during the acquisition. After the acquisition was completed, runs taken with the baseline undercoolings were analyzed to see how much drift had occurred. All runs that were taken while the velocity drifts were less than 2% of the total velocity were allowed. Data taken after the velocity drift was beyond this limit were discarded.
3.10 Viscosity Measurements

The viscosities of the individual mixtures were measured with a cone-plate viscometer\textsuperscript{30} using the procedure laid out in the manual [52]. The viscosity of polymer solutions is a strong function of the temperature [53] and was, therefore, measured over temperatures from 20 °C to 40 °C. The temperature range is larger than the range over which solidification is observed so that better fits could be made to the viscosity data. The temperature of the viscometer was set by circulating water of known temperature around the cone-plate assembly using a water bath,\textsuperscript{31} and it was measured with a thermocouple temperature probe that is embedded inside the cone-plate assembly. The thermocouple has a nominal uncertainty of ± 1 °C.

3.10.1 The Cone-plate Viscometer

A diagram of the viscometer is presented in Fig. 3.17. In this viscometer, the cone rotates at a constant angular velocity $\omega$ around the axis of symmetry, and the viscosity of the sample is inferred from the resistance to rotation, as measured by the torsion spring. The advantage of the cone-plate geometry is that the shear rate $\frac{dv}{dz}$ is constant throughout the entire sample. From Fig. 3.17, the separation between the cone and plate is given by $z = \tan \theta \cdot r$, while the tangential velocity at a point on the rotating cone is given by $v_t = \omega \cdot r$, with $\theta$, $\omega$, and $r$ as defined in Fig. 3.17. The velocities of the fluid at the boundaries are $v_{cone} = v_t$ and $v_{plate} = 0$. Therefore, the shear-rate $\frac{dv}{dz} = \omega / \tan \theta \approx \omega / \theta$ for small $\theta$, independent of $r$ and $z$ before approximation. In the Brookfield viscometer, the cones we used had angles of $\theta = 0.8$ degrees and $\theta = 1.565$ degrees.
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3.10.2 Fits to Viscosity Data

The viscosity of a polymer solution is a function of temperature and typically follows an Arrhenius relation [54],

\[ \eta = \eta_e(c) \cdot e^{\frac{E}{k_B T}} + \eta_0, \]  

(3.4)

where \( \eta_e(c) \) is a prefactor for the exponential which depends on \( c \), the concentration of polymer in the sample, \( E \) is an activation energy, \( k_B \) is the Boltzmann constant and \( \eta_0 \) is the viscosity of pure EC (a constant over the relevant temperature range). In order to determine the temperature dependence, we plotted viscosity vs. temperature for all the samples (Fig. 3.18) and then fit this data globally to Eq. 3.4. The global fit allows \( \eta_e \) to vary from sample to sample while constraining \( E \) and \( \eta_0 \) to have a single value for all the curves in Fig. 3.18.

In dilute polymer solutions, the concentration dependence of the viscosity is given by

\[ \eta = \eta_e(1 + 2.5\psi), \]  

(3.5)

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30 Brookfield digital viscometer DV-I+; 11 Commerce Boulevard, Middleboro, MA 02346 U.S.A; www.brookfieldengineering.com (.)

31 Neslab water bath of nominal stability ±0.01 °C. Model: RTE110; Thermo NESLAB, 25 Nimble Hill Rd, Newington, NH 03801; www.thermo.com (.)
where $\eta_s$ is the solvent viscosity and $\psi$ is the polymer volume fraction [54]. However, for this equation to apply, the solution must be in the low-concentration limit. The crossover from this limit is defined by the concentration where individual chains begin to overlap. A scaling theory by de Gennes [54] estimates the crossover concentration, from the dilute to the semi-dilute regime, at $c^* \sim a^{-3} N^{-\frac{1}{4}}$, where $a$ is the persistence length of independent polymer segments (this is not necessarily the monomer length) and $N$ is the number of such segments in a chain. Using this criterion, we find that the critical volume fraction, $\psi$, for a polymer with $10^6$ base units is on the order of $10^{-3}$ [54]. The volume fraction of PA in our solutions can be estimated by taking $\psi = \frac{V(\text{PA})}{V(E)} \approx c_{\text{PA}} \frac{\rho_{\text{PA}}}{\rho_{\text{EC}}}$. It follows that the smallest $\psi$ obtained for a 2.95% sample is $\psi \sim 0.03$, placing our solutions well into the semi-dilute regime ($\psi^* \sim 10^{-3}$ $\ll$
Figure 3.19: log $\eta - \eta_0$ vs. concentration, $c$, for $T = 30$ °C. Within our dynamic range, an empirical linear relation can be derived.

3.10.3 Shear Thinning

The constant shear rate makes the cone-plate viscometer an ideal candidate for measuring how Newtonian a fluid is.\footnote{In a Newtonian fluid, viscosity is independent of the shear rate.} Polymer solutions generally show “shear-thinning.” When no shearing is present, polymer chains form spherical globules. Large shears may cause elongated globules to form, that resist the flow less than...
spherical ones do [54]. Thus, viscosity tends to decrease as a function of the shear rate. In order to determine whether the crystal growth is indeed influenced by the viscosity of the liquid, we need to have a good estimate of the viscosity in the vicinity of the front. For a Newtonian fluid, the viscosity measured in the viscometer will be the same as that “seen” by the growing crystal, provided the temperature is the same. However, the viscosity of a non-Newtonian fluid is a function of the imposed shear. In this case, there is no guarantee that the viscometer and the crystallite “see” a liquid with the same viscosity, as the shear-rate in the sample will depend on the length scales and flow rates relevant to the crystallization. We then need to estimate the shear rates in the fluid that are associated with the flows, which arise from the density difference between solid and liquid.

An order-of-magnitude estimate of the shear rate relevant to the crystal growth is given by $\frac{dv}{dt} \approx \frac{v}{l}$, where $v$ is the local fluid velocity at the growing solid-liquid interface and $l$ is the lamella thickness. Investigations with an optical microscope$^{33}$ showed that $l$ for a typical EC+(102kD PA) spherulite is on the order of 1 $\mu$m. The typical fluid velocity can be found using mass conservation,

$$v_f = \frac{\rho_s - \rho_f}{\rho_f} v_s,$$

where $\rho_{f/s}$ is the density of the fluid/solid and $v_{f/s}$ is the velocity of the fluid/solid. The denser solid requires fluid to be supplied to the front. Using the material parameters for EC in Tab. 3.1, I found $v_f \approx 0.1$ mm/sec and $\frac{dv}{dt} \approx 100$ sec$^{-1}$.

The maximum shear rate of the viscometer is determined by how much the torsion spring can be torqued. It follows that low-viscosity samples can be subjected to much higher shear rates than high-viscosity ones. The maximum shear rate for a sample with $\eta \approx 1000$ cP (a typical viscosity for the 102-kD PA) is on the order of 10 sec$^{-1}$. This shear rate is one order of magnitude less than the shear rate present in the crystal growth experiment. However, measurements of $\eta$ for shears between 0 and 10 cP in the 102-kD PA mixtures showed no shear thinning at all.

In contrast to the 102-kD samples, mixtures with the 200-kD PA did show a power-law variation in viscosity as a function of shear rate (Fig. 3.20). The stronger

$^{33}$Olympus BHM Universal equipped with a 100 X, NA=1.4, lens; Olympus Optical Co. Ltd.; www.olympus.com (.)
Figure 3.20: Shear-thinning in a 200-kD 0.5 wt.% mixture at 36 °C. This data was taken by using two different cones, the first gave data up to \( \frac{dv}{dz} \approx 10 \text{ sec}^{-1} \) the second from 10 sec\(^{-1}\) to 200 sec\(^{-1}\). This can be seen as a 10-cP jump in the fit residuals at \( dv/dz \sim 10/\text{sec} \). The best fit is \( \eta = A \cdot \left( \frac{dv}{dz} \right)^\alpha \), where \( A = 114 \pm 4 \), and \( \alpha = -0.125 \pm 0.005 \). The point at \( \frac{dv}{dz} \sim 0.3 \text{ sec}^{-1} \) was ignored in the fit.
dependence on shear in the longer polymer is not surprising, since the longer chains give rise to larger, “floppier” globules, which are more easily influenced by the flows. From Fig. 3.20, we note that the dependence on shear persists to very low values of the shear rate, overlapping those used to analyse the 102-kD samples.

In conclusion, although the shear rate in the viscometer is an order of magnitude smaller than that estimated during crystal growth of the 102-kD samples, the qualitative agreement between the viscosities of the various mixtures (Fig. 3.18) could imply that any deviations from the measured viscosity during crystal growth (and beyond the dynamic range of our viscometer) occur in a uniform way. In this case, a scaling argument should not be affected by this “global shift.” Furthermore, the viscosities relevant to the crystal growth in the 200-kD sample, which did show shear thinning, can simply be estimated by extrapolating the power-law curve. Estimates of the shear for these samples are not made here since no microscopic observation of the 200-kD samples was made.

3.11 Appendix: Purification Procedure for EC

The ethylene carbonate (EC) obtained from Aldrich was only 98% pure. To purify the sample, it was first dissolved in warm (≈ 34 °C) anhydrous ether, a poor solvent for EC. When the solution was saturated, it was filtered through a warm funnel in order to remove large chunks of debris. After filtering, I introduced a seed of solid EC as the solution was slowly cooled (first in air and next in an ice-water bath). As the temperature drops, the EC becomes less soluble in the ether, and as a result, the existing solid seed grows in size. The slower the cooling, the better the segregation of impurities out of the EC. After the solid has precipitated the dirty ether is filtered off. In order to remove the remaining ether, the EC crystals are put under a weak vacuum and allowed to sublime on a cold surface, as shown in Fig. 3.21. The purity of a chemical can be gauged by looking at the range of coexistence temperatures. As seen in Fig. 2.2.1, the purer a chemical, the smaller the coexistence range. Unfortunately this method was not effective enough to change the EC purity by a measurable factor.

34A poor EC solvent is used, so that impurities will have a better chance of staying in the solvent after cooling.
Later we discovered a supplier of ultrapure EC and abandoned our purification efforts.
Chapter 4

Results

4.1 Introduction

Here, I revisit band-spacing and front-velocity measurements for EC doped with a short-chain polymer (102-kD PA). Although a preliminary set of data had previously been taken [10], there were no accurate undercooling measurements available. In addition, there were problems with concentration drifts (see Sections 3.4.2 and 3.9).

4.1.1 Velocity and Band Spacing as a Function of Undercooling

A well-documented feature of banded spherulites is the strong dependence of band spacing on undercooling. I measured the band spacings of six samples as a function of undercooling and PA concentration, $c_{PA}$, using the method described in Ch. 3. For sample images see Fig. 4.1, for $\lambda$ vs. undercooling see Fig. 4.2. In contrast to most theoretical predictions, the band spacing diverges at a non-zero critical undercooling, $\Delta T_c$. Samples with higher $c_{PA}$ exhibit wider bands near this divergence (Fig. 4.4 (a)). The largest “clear” bands observed were about 2 mm wide and were seen in the 6.7 wt.% PA sample. Although in some cases bands larger than 2 mm were seen, these observations were not repeatable and therefore were ignored.

The smallest bands observed using the video lens were on the order of 0.08 mm. Beyond this limit, the resolution of the lens was very poor. In order see whether bands
Figure 4.1: Images of bands formed in a 102-kD $c_{PA} = 6.08$ wt.% sample. The band spacing gets larger and more disordered as the critical undercooling is approached.
beyond the resolution of our lens were forming, a very thin sample of 5.9 wt.% (102 kD PA)+EC was made between two glass cover slides. The sample was frozen at high undercoolings and observed under an optical microscope\(^1\) in the polarized transmission mode. Bands in this sample did not get much smaller than those observed using the video lens and seemed to vanish beyond an undercooling of \(\sim 20 \, ^\circ\text{C}\). The mechanism by which banding disappeared was not investigated.

Figure 4.2: Band spacing \(\lambda\) vs. corrected undercooling. The undercooling is found by subtracting the corrected sample temperature from the liquidus temperature (Fig. 3.2). The sample temperature is corrected for latent heat (Sec. 3.5.2).

We also measured the front velocity of the growing spherulites. Observed velocities ranged from 0.5 to 1.5 mm/s (Fig. 4.3). As expected, the velocity increases with undercooling and decreases with \(c_{PA}\).

\(^1\)Olympus BHM Universal Metallurgical Microscope. Equipped with 100X NA=1.4 lens. www.olympus.com(\(\))
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Figure 4.3: Velocity vs. undercooling for six concentrations at undercoolings that produced banded spherulites.

4.1.2 The Effect of PA concentration

Bands are only visible in EC samples that have $c_{PA} > 2.75$ wt.%. To understand the source of this threshold, we analyzed two observable quantities, the normalized correlation length and the optical contrast, as functions of $c_{PA}$.

The normalized correlation length, $\xi/\lambda$, is defined as the number of correlated bands in a given domain, where $\xi$ is the correlation length and $\lambda$ is the band spacing. Preliminary studies showed that spherulites formed from samples with a higher $c_{PA}$ tended to be more ordered than those formed from lower concentration samples. In order to quantify this effect, eight EC+PA samples were frozen at a relatively high undercooling of 12 °C. At this undercooling we are far from $\Delta T_c$, thus avoiding complications due to the divergence and the concentration dependence of $\lambda$. (In Fig. 4.2, we see that at $\Delta T \sim 12$ °C, $\lambda$ is almost independent of concentration.)

The correlation length was determined by fitting a decaying exponential to the envelope of the image cross section’s autocorrelation function (See Ch. 3 and Fig.
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Figure 4.4: Normalized correlation lengths in PA samples at high undercooling vs. concentration compared with $\lambda_{\text{max}}$. (a) $\lambda_{\text{max}}$ vs. $c_{PA}$. (b) $\xi/\lambda$ vs. $c_{PA}$. Note that $\lambda_{\text{max}}$ decreases with $c_{PA}$.

We see that the correlation length decreases linearly with decreasing concentration, reaching zero at $c_{PA} \approx 2$ wt.%. This vanishing correlation length agrees with observations made by [10], that bands were not visible in mixtures with $c_{PA} < 3$ wt.%. By comparing Fig. 4.4(a) and (b), we see that the vanishing correlation length corresponds to the decreasing size of the largest observable bands near the divergence for each concentration.

If banding depended only on the polymer in the samples, we would expect the amount of "banded" material present and the optical contrast of the bands to decrease with $c_{PA}$. Fig. 4.5 shows that the optical contrast, defined as $\frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}}$, does decrease slightly as lower concentrations are examined; however, this decrease is much smaller than the one seen in the normalized correlation lengths. We conclude that the main factor in the vanishing of the bands is the decorrelation in the rotation of adjacent
CHAPTER 4. RESULTS

crystallites.

\[ \text{Figure 4.5: The optical contrast decreases slightly as } c_{PA} \text{ decreases.} \]

The decrease in \( c_{PA} \) is related to a decrease in viscosity. From Fig. 4.3, we note that the decrease in \( c_{PA} \) also leads to an increase in growth rate. It may be that, in lower-viscosity samples, the faster kinetics limit the correlation between adjacent lamellae, thereby limiting the size of correlated domains. Beyond a threshold, the correlation length goes to zero and the bands vanish altogether. The threshold is determined by either concentration and undercooling (if surface stresses are the cause of bands) or by viscosity and velocity (if hydrodynamics is the source of bands). In the next section, I will describe a method for determining which of these two pairs of variables is fundamental to this system.

4.2 Hydrodynamic Collapse

The idea that banding may be induced by hydrodynamic flows in the sample, as opposed to surface stresses in the crystallites, was outlined in Ch. 2. In order to clarify the need for a hydrodynamic model, we first plot the band spacing vs. velocity rather than undercooling (Fig. 4.6 (a)). In each sample, bands start to form at a threshold velocity (rather than undercooling). As the sample viscosity decreases, this threshold increases; in other words, higher flow rates are needed to cause banding in
Figure 4.6: Data collapse according to hydrodynamic model. (a) Plot of $\lambda$ vs. velocity showing a family of self-similar curves with power-law functional form. (b) Using the hydrodynamic scaling law described in Ch. 2, we see that the curves collapse towards a trend line with the form, $\lambda = \lambda_0 + Ae^{a v^{-2} \eta^{-1/2}}$ where $\lambda_0 = 0.075$ mm, $A = 0.002057$ mm, $a = 64 (\text{mm/s})^2 \sqrt{cP}$.

less-viscous samples. Following Tiller (See Ch. 2), we plot the band spacing (rather than the critical core size) vs. $v^{-2} \eta^{-1/2}$ (Fig. 4.6 (b)). The self-similar curves of band spacing vs. velocity seem to collapse onto a broad "strip" (rather than onto a perfect line). The data follow the trend: $\lambda = \lambda_0 + Ae^{a(v^{-2} \eta^{-1/2})}$. The uniqueness of
this "collapse" was tested by plotting $\lambda$ vs. $v^a \eta^b$, where $a$ and $b$ are varied from $-40$ to 20, and from $-10$ to 5, respectively. Each set of curves was fit to a single 5th-order polynomial, and the $\chi^2$ of this fit was extracted. Reasonable collapses will tend to yield lower values of $\chi^2$. This method allows us to quickly scan the $a, b$ space for candidate exponents of reasonable collapses. Fig. 4.7 shows the values of $\chi^2$ obtained with this method. The actual fitting function does not need to be a polynomial. Any functional form that roughly fits the data can be chosen for this task, as the $\chi^2$ minima always falls within a narrow valley which roughly preserves the ratio $a:b = 4:1$, independent of the fitting function used. Note that while the 4:1 ratio was well determined the overall scale factor was not, as indicated by the "long valley" shape of the $\chi^2$ surface.

Figure 4.7: Plot of the $\chi^2$ statistic for polynomial fits made to $\lambda$ vs. $v^a \eta^b$ plotted vs. the exponents $a$ and $b$. A minima in $\chi^2$ corresponds to a good fit, or in this case, collapsed data. The minimum is at the bottom of a long narrow valley with an $a:b$ ratio close to 4:1. Attempts to use different fitting functions gave different shape minima, but the 4:1 ratio was always conserved.

Despite the uniqueness of this exponent ratio, the results from this analysis are inconclusive. First, in Tiller's original model the core size was linear with the scaling factor. In our case, the relation between band spacing and the hydrodynamic factor
seems to follow an exponential. Without a clear model, we cannot fit the data to optimize the collapse and cannot obtain a conclusive minimum in our $\chi^2$ surface. Second, since viscosity is a function of concentration a similar collapse could have been obtained for concentration. To obtain clearer results with respect to the roles of concentration and viscosity we must vary a second parameter. An obvious candidate is the polymer chain-length.

4.2.1 Failure of the Hydrodynamic Collapse

In this section, I will present data taken with the 200-kD PA sample. The initial aim was to replicate some of the measurements presented in the previous section as a means of determining whether viscosity was in fact a fundamental parameter in the formation of spherulites. The reasoning was that, if the system was controlled by the viscosity rather than by $c_{PA}$, the 200-kD data would collapse onto the same curve as the 102-kD data did. However, the long-chain mixtures showed qualitatively different behavior from the short-chain ones, making a quantitative comparison impossible.

4.2.2 Band Spacing and Velocity

Plots of band spacing vs. both undercooling and velocity, and velocity vs. undercooling are shown in Fig. 4.9. Both the velocity and the typical band spacing are an order of magnitude higher than those found in the 100-kD samples, while the viscosity is on the order of 100 cP. (See Sec. 3.10.3.)\(^2\) No divergence is visible in the band-spacing data because it is “cut off” by a new discontinuous first-order morphology transition that tends to nucleate at low undercoolings. The first-order transition originates from the nucleation of a faster, non-banded mode on the growth front. This faster mode competes with the banded mode, eventually dominating the growth. A picture of a typical crystal grown, including the faster-growing, non-banded, mode is shown in Fig. 4.8. The experiment was repeated for $c_{PA} = 1$ wt.% but bands were not observed because of a similar first-order “cut off.”

\(^2\) Shear thinning reduces the viscosity by a factor of four near the growing front. While this may account for a small discrepancy in $\lambda$, no reasonable amount of shear thinning can reconcile the data sets for the two polymers.
In Fig. 4.9 (a) and (b), we see that the range of undercoolings for the 200 kD samples is lower than the range used in the 100 kD samples. This is partly because of the high growth velocities, resulting in a large release of latent heat. The range is also reduced because we expect to see a divergence at low undercooling.

The band spacing of the 200-kD samples is an order of magnitude higher than that in the 100-kD samples at comparable viscosities (Fig. 4.9 (a)). It was impossible to scale this data with the 100-kD data using our hydrodynamic arguments. However, if the band spacing were scaled with velocity, the collapse would work. There is no theoretical motivation for this \( \lambda \) scaling.

The 200-kD samples also tended to age much faster than the 100-kD ones. After heating the mixture a few times, it became yellow, rather than transparent, and also looked more “gummy.” This could be caused by polymer crosslinking or by some other chemical reaction. The aging may explain some of the unexpected trends in the data, such as the slight increase in band spacing with undercooling.

As a preliminary conclusion, we may say that the hydrodynamic-scaling hypothesis failed; however, we cannot rule out the possibility that hydrodynamics play a role in the banding. It may simply be that our adaptation of Tiller’s model is flawed.
4.3 Tests for Existing Band Spacing Models

Since our data did not scale with the simple hydrodynamic model, we decided to revisit some of the existing models, to see how well they explained the data. Below we consider three possibilities: Owen’s model, Schultz’s screw-dislocation model, and a power-law divergence reminiscent of a continuous-bifurcation transition proposed by Hutter et al. [5]. All models excluding the last are developed in Ch. 2. A discussion of the continuous transition model is given in Sec. 4.3.3 below.
4.3.1 Owen’s Surface-Stress Model

Owen’s model predicts a divergence at $\Delta T = 0$ with exponent $-3/2$. Although the data do diverge with an exponent that is close to this (see below), the divergence is at a finite undercooling. The data for the 6.7 wt.% sample is plotted along with a best fit in Fig. 4.10. Clearly, this model is incompatible with our data.

![Figure 4.10: Band spacing vs. undercooling (c_p =6.70 wt.%). Solid line is the best fit to Owen’s model, $\lambda = A\Delta T^{-3/2}$.](image)

4.3.2 Screw-dislocation Model

As we saw in Sec. 2.3.2, Shultz’s screw-dislocation model predicts $\lambda = Ae^{(\Delta T)^{5/2}}$ [22]. A preliminary fit was made to the 6.70 wt.% sample (Fig. 4.11 (a)). Although this initial fit is much better than Owen’s was, there is a systematic trend in the residuals. In an attempt to remove this trend, I allowed an offset in the temperature scale. Such an offset could conceivably be caused by a systematic error in our temperature scale but could be no larger than 1 °C. The modified fit and residuals are compared with the original fit and residuals in Fig. 4.11 (a) and (b). The modified model does not improve the fit. These trends can be seen more clearly when we plot the linearized data (Fig: 4.12) Next, I made a global fit to the entire data set with the unmodified model. The globally fitted data are plotted in Fig. 4.13, and results are tabulated.
in Tab. 4.1. We note that both the parameters in the fit do not vary much with concentration.

<table>
<thead>
<tr>
<th>$c$ (Wt.%)</th>
<th>$A$ (mm)</th>
<th>$c_0/10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.70</td>
<td>$0.0721 \pm 0.0013$</td>
<td>1.02 $\pm$ 0.01</td>
</tr>
<tr>
<td>6.08</td>
<td>$0.0701 \pm 0.0020$</td>
<td>1.22 $\pm$ 0.02</td>
</tr>
<tr>
<td>4.04</td>
<td>$0.0661 \pm 0.0021$</td>
<td>1.18 $\pm$ 0.04</td>
</tr>
<tr>
<td>3.57</td>
<td>$0.0779 \pm 0.0025$</td>
<td>1.17 $\pm$ 0.04</td>
</tr>
<tr>
<td>2.95</td>
<td>$0.0764 \pm 0.0033$</td>
<td>1.23 $\pm$ 0.05</td>
</tr>
<tr>
<td>2.80</td>
<td>$0.095 \pm 0.012$</td>
<td>1.17 $\pm$ 0.16</td>
</tr>
</tbody>
</table>

Reduced $\chi^2 = 3.5$

Table 4.1: Parameters for exponential fit to $\lambda$ vs. $\Delta T$.

4.3.3 Power-Law Model

A third possible explanation for the band spacing was suggested by Hutter et al. [5]. In this case, the bands are said to originate from a continuous-bifurcation morphology transition, with $\Delta T$ being the control parameter. The continuous bifurcation has a few generic signatures: At a critical, finite undercooling, the band spacing should diverge as a power law. We define the critical undercooling of the transition as $\Delta T_c$. The transition should be smooth; that is, as $\Delta T_c$ is approached, bands should both diverge and vanish as fluctuations become more important. The bifurcation results from a discontinuity in one of the systems parameters; therefore, all observables should show some kind of singularity when the critical undercooling is traversed.

The data on band spacing vs. undercooling were globally fit to the power law $\lambda = \lambda_\infty + A(\Delta T - \Delta T_c)^{-\alpha}$, where $\lambda_\infty$ is the band spacing at infinity, $A$ is an amplitude, $\Delta T_c$ is the critical undercooling, and $\alpha$ is the power of the divergence (Fig. 4.14(a)). Since the curves are self-similar, it is reasonable to take $\alpha$ as a global variable, independent of $c_{PA}$. However, we expect none of the other parameter to show any universality so we set $A$, $\lambda_\infty$ and $\Delta T_c$ as local variables in the fit. Results for the local variables, $\lambda_0$ and $\Delta T_c$, are plotted in Fig. 4.14(b,c). Results for all variables can be found in Tab.
Figure 4.11: Band spacing vs. undercooling for $c_{PA} = 6.7$ wt.% fit to screw dislocation model [22]. In (a), I fit the data to the unmodified fitting function ($\lambda = Ae^{(-\Delta T)\beta}$). In (b), I introduce an offset in the undercooling scale as a fit parameter ($\lambda = Ae^{(-\Delta T-\Delta T_c)\beta}$). Although the residuals in both (a) and (b) are smaller than the estimated random error, they do show a systematic trend, with no clear improvement in (b) relative to (a).

4.2.

From the results of the fit, we note that the divergence temperature, $\Delta T_c$, decreases steadily as the concentration increases but is roughly equal to 5 °C; the power, $\alpha = 1.08 \pm 0.08$, does not agree with 3/2 (the exponent predicted by Owen); however, is compatible with $\alpha = +1$. $\lambda_\infty$ seems to decrease slightly with concentration, however, measurements on lower concentration also have a much higher error associated with them.

Fig. 4.15 compares the residuals from the screw-dislocation model with those from the power law fit. From the residuals, we see that the power-law fits better, especially near the divergence. However, a major source of concern with the power law is the
CHAPTER 4. RESULTS

Figure 4.12: Linearized screw dislocation model $c_{PA} = 6.7$ wt.%.

Figure 4.13: Band spacing vs. undercooling fit to Schultz's screw-dislocation model [22]. Here, we fit Schultz's unmodified model to the data.
Figure 4.14: (a) A power-law fit to band spacing vs. undercooling shows that (b) \( \lambda_{\infty} \) remains roughly constant (c) the critical undercooling decreases with \( c_{PA} \).

lack of dynamic range. Typically, for fitting a power law, one would like to have data spread over a few decades, on both the x and y axes, in order to fit a power law reliably. In this case, we have just over a decade's range on both axes. Fortunately, we are fitting to multiple data sets within this range, thus reducing the overall error in the fit parameter.

Noting that the fit was very good, we attempt to collapse the data by plotting \( \log \lambda - \lambda_{\infty} \) vs. \( \log \Delta T - \Delta T_c \), where \( \lambda_{\infty} \) and \( \Delta T_c \) are found in the power-law fit (Fig. 4.16). We see that all the data fall on a very tight line with the power-law form \( A\Delta T^{-1.08} \). Although this procedure does collapse the data, the source of the shifts in undercooling and band spacing has yet to be determined. Further investigation showed
Reduced $\chi^2 = 1.43$

Table 4.2: Parameters for power law fit to $\lambda$ vs. $\Delta T$.

<table>
<thead>
<tr>
<th>$c$ (Wt.%)</th>
<th>$\lambda_{\infty}$ (mm)</th>
<th>$\Delta T_c$ °C</th>
<th>$\alpha$</th>
<th>$A$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.70</td>
<td>0.040 ± 0.008</td>
<td>4.61 ± 0.04</td>
<td>1.08 ± 0.08</td>
<td>0.39 ± 0.02</td>
</tr>
<tr>
<td>6.08</td>
<td>0.041 ± 0.004</td>
<td>4.89 ± 0.04</td>
<td>&quot;</td>
<td>0.40 ± 0.03</td>
</tr>
<tr>
<td>4.04</td>
<td>0.047 ± 0.006</td>
<td>5.02 ± 0.05</td>
<td>&quot;</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>3.57</td>
<td>0.075 ± 0.008</td>
<td>5.54 ± 0.06</td>
<td>&quot;</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>2.95</td>
<td>0.072 ± 0.013</td>
<td>5.61 ± 0.16</td>
<td>&quot;</td>
<td>0.23 ± 0.051</td>
</tr>
<tr>
<td>2.80</td>
<td>0.0 ± 0.4</td>
<td>3.8 ± 4.2</td>
<td>&quot;</td>
<td>1.4 ± 3.4</td>
</tr>
</tbody>
</table>

Figure 4.15: Comparison of residuals from the screw-dislocation model (Fig. 4.13) with those of the power-law model (Fig. 4.14). The power-law fit matches the data better than the screw-dislocation model near the divergence.

that similar collapses can be generated for a wide range of exponents, $0.8 < \alpha < 1.2$; however, further investigation showed that this range was in fact too large. (See Appendix-A. to this chapter.)

The second criterion for the continuous transition is decorrelation of the domains, caused by fluctuations, as one approaches the critical point. The degree of correlation can be estimated by measuring the width of the band-spacing peak in $k$-space (See Sec. 3.8.2), where a correlated structure will show a narrow peak and vice versa. We define the normalized correlation length $\xi/\lambda$ as the number of correlated bands in a given domain, where $\xi$ is the correlation length and $\lambda$ is the band spacing. Fig. 4.17 shows
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Figure 4.16: Shifted band spacing $\tilde{\lambda}$ vs. shifted undercooling $\Delta T$. The band spacing is shifted by taking $\tilde{\lambda} = \lambda - \lambda_\infty$, where $\lambda_\infty$ is the band spacing at infinity. The undercooling is shifted by $\Delta T = \Delta T - \Delta T_c(C)$, where $\Delta T_c(C)$ is the critical undercooling for the power law fit. Superimposed on the data is a line of slope -1.08.

The normalized correlation length as a function of $\Delta T$ for four PA concentrations. We see that the bands in spherulites become uncorrelated as their respective $\Delta T_c$ is approached, independent of concentration. It is also evident that spherulites formed from samples with a higher $c_{PA}$ tend to be more ordered than those formed from lower-concentration samples, as we saw in Fig. 4.4.

According to this model, near the divergence the maximum observed band size is limited by fluctuations in temperature and sample chemistry. To see bands on the order of 3 mm $\pm$ 10%, temperature gradients in the sample would need to be less than 0.01 °C/mm, and PA-concentration gradients would need to be less than 0.2

\[^{3}\left|\frac{d\Delta}{d(\Delta T)}\right| \approx 10 \text{ mm/°C and } \Delta \lambda \approx 0.3 \text{ mm, therefore the maximum } \Delta (\Delta T) \approx 0.03 \text{ °C over a distance of 3mm.}\]
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Figure 4.17: The normalized correlation length, $\xi/\lambda$, vs. undercooling for four concentrations. Except in the case of 2.95 Wt.% (the lowest concentration), $\xi/\lambda$ undergoes a sharp decrease as the critical undercooling is approached from above.

The magnitude of gradients can be estimated by observing changes in the front velocity and/or in the band-spacing through the sample (Sec. 3.9). 4

The final criterion for the continuous bifurcation is that other parameters should also show a discontinuity or change as $\Delta T_c$ is crossed. In Fig. 4.18, the velocity profile of the 6.7 Wt.% sample is plotted over a wide range of undercoolings and compared to the band spacing curve. A continuous change in the slope of $v$ vs. $\Delta T$ starts close to $\Delta T_c \approx 4.8^\circ$ (the critical undercooling for banding). The slope continues to decrease over the “transition zone” as the band spacing becomes smaller. $\frac{dv}{d(\Delta T)}$ becomes constant at roughly the undercooling where the curve of band spacing vs. undercooling flattens out.

A possible physical mechanism for the change in $\frac{dv}{d(\Delta T)}$ may come from a change in the driving force as the bands start to form. The banded morphology is a metastable structure that has a higher free energy than the unbanded one because of the elastic-

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4In theory, one can distinguish between chemical and temperature effects by repeating the freezing process many times. In this case, the $\nabla T$ would act like a constant background while diffusion, zone-refining, solute segregation, evaporation, etc. would modify $\nabla c$ with time. In practice, this is very hard to do because of the many factors involved in $\nabla c$. An example of the evolution of the velocity gradient over time can be seen in Fig. 3.15.
Figure 4.18: Velocity and band spacing vs. undercooling for 6.7 wt.% 102-kD PA sample. This data is plotted over a range of undercoolings that shows the transition from the non-banded to the banded morphology. A continuous change in $dv/d[\Delta T]$ starts at $\Delta T_c$, simultaneous with the divergence of the band spacing.

twist energy stored in the crystallites. Since the driving-force for crystalization is a function of the change in free energy, an increase in the free energy of the solid will cause the front to slow down. If elastic twist were the only source of extra free energy, we would expect the velocity curve to resume its original slope once the “transition zone” had been passed and $\lambda$ became approximately constant. However, the slope of $v$ does not increase at undercoolings beyond the “transition zone.” One possible explanation for this may be that the dissipation in the high undercooling system does not allow the system to reach a lower-energy state. In other words, defects other than crystallite twist are continuously forming, reducing the velocity.

Although the exponent for the divergence and the critical undercooling are not compatible with the ones predicted by Owen’s model (See Ch. 4.5), this model does predicts a power-law. One could attempt to correct the model, for example, by finding a source for $\Delta T_c \neq 0$. One possibility is that $\Delta T_c$ is a “special” undercooling for this system. For example, $\Delta T_c$ could be a temperature where the polymer starts to adsorb onto the crystallite’s surfaces. PA surface adsorption could supply the surface stresses and dangling ends required for the twisting and the correlation between adjacent
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crystallites, as has been suggested by [24]. If this were the case, we would expect the free energy of the crystals to start increasing at $\Delta T_c$, as PA adsorbed onto the crystallite surfaces. The change in $v$ would occur until the EC crystal surface was saturated with PA. Here, we note that as more PA gets adsorbed onto the surfaces, the bands get tighter (since the twisting increases). However, the twisting may depend on many other factors, such as the crystallite size, geometry, and rate of growth. From the correlations in Fig. 4.4, we also note that, as $c_{PA}$ increases, so does the degree of correlation among adjacent twisting crystals. Furthermore, when the “transition zone” is passed, we do not expect the slope of $v$ to increase back to its pre-banding value, because the change in free energy comes from a change in the chemistry of the crystal rather than from elastic twisting.

4.4 Summary

The hydrodynamic scaling failed because of the lack of agreement between samples of 100 kD and 200 kD, despite agreement of data within the 100-kD samples. During further investigation, we tested four models for the band spacing. This analysis showed that two models were compatible with our data, the screw dislocation model and the continuous-transition model. Where the data’s fit to the continuous-transition model was much better than it was for the screw dislocation model. Furthermore, J. Schultz, who originally proposed the screw dislocation model, has recently abandoned it in favour of the “escape from impurities” model\textsuperscript{5}. Although the continuous transition model does not supply a physical mechanism for the banding, it does give specific requirements that any future models must meet.

4.5 Appendix A: Discussion of Errors.

In order to obtain meaningful error estimates for parameters in the fits, it was necessary to estimate both systematic and random errors for each. The main source of

\textsuperscript{5}A more recent publication (found after defense) shows that the screw dislocations form after the twist has occurred, and can not be responsible for it [55].
systematic error in $\lambda$ and $v$ was the chemical drift, described in Ch. 3. By limiting the amount of time a sample is used, the systematic error in $\lambda$ is limited to less than $\pm 0.1$ mm and the error in $v_{avg}$ to less than $\pm 0.02$ mm/s. Random errors in $\lambda$ come from the inherent decrease in order as the critical point is approached (See Ch. 4). This error is estimated by propagating the error in peak-position, found when fitting to the FFT of the bands in $k$-space. In this case, $\Delta \lambda = \Delta k/k^2$ (See Sec. 3.8.2). Typical random errors range from 0.01 mm to 0.3 mm and increase as $k$ decreases, close to the divergence. Since the random error in $\lambda$ is dominant, we use this error as the standard deviation of the fits of $\lambda$ vs. $\Delta T$.\(^{6}\)

Random errors in $T$ are small if one takes the prescribed precautions outlined in Ch. 3 ($\sim 0.01$ °C). However, systematic errors in $\Delta T$ may be large. These may come from errors in temperature measurement or from corrections applied to the measured temperature, $T_{measured}$. Two corrections are applied to $T_{measured}$. First, we must correct for latent heat using data from numerical simulations (Fig. 3.8). The temperature at the solid-liquid interface is given by $T = T_{measured} + \delta T$, where $\delta T$ is the estimated rise in temperature at the interface due to latent heat. Second, we need to convert temperature to undercooling using $\Delta T = T_l - T$, where $T_l$ is the liquidus temperature, determined experimentally for $c_{PA}$. The uncertainty in $T_l \sim 0.1$ °C (Fig. 3.2).\(^{7}\) The latent heat corrections have a 10% confidence interval, which leads to a maximum error of 0.3 °C. Since both errors are independent, $\delta[\Delta T] \sim 0.35$ °C. The existence of $\delta[\Delta T]$ introduces an extra source of error into the viscosity measurements at the interface. More important, being much less than 4 °C, it does not account for the non-zero divergence found in the power law fits.

Further analysis of the power-law fits led us to believe that the confidence intervals on the exponent $\alpha$ and on $\Delta T_c$ may be too small. The confidence intervals generated by Igor were $\delta \alpha \sim \pm 0.08$ and $\delta[\Delta T_c] < 0.16$ °C. However, attempts to fit the data with other exponents yielded results that were almost indistinguishable “by-eye”. The source of this discrepancy is correlations among the variables in the power-law fit.

---

\(^{6}\)In other words $\chi^2$ is calculated as $\chi^2 = \sum_{i=0}^{N} \frac{(\lambda_i - f(\Delta T_i))^2}{\sigma_i^2}$, where $\sigma_i$ is the standard deviation in the estimate for $\lambda$.

\(^{7}\)It is not obvious that $T_l$ is the correct choice of “zero”; $T_s$ could have also served this purpose. Without a reliable estimate for $T_s$, we cannot estimate how much of an error this choice introduces.
These correlations are summarized by the correlation matrix

\[
C_{proj} = \begin{pmatrix}
1 & 0.41 & -0.94 & -0.84 \\
0.41 & 1 & -0.67 & -0.82 \\
-0.94 & -0.67 & 1 & 0.96 \\
-0.84 & -0.82 & 0.96 & 1
\end{pmatrix},
\]

where the vector of variables used in the fit is given by \( \langle \lambda_\infty, A, \alpha, \Delta T_c \rangle \). The correlation matrix gives the degree of correlation between these variable. Uncorrelated variables will have a zero at their intersection in \( C_{proj} \), while completely correlated and anticorrelated variables will have a 1, or \(-1\), respectively. From \( C_{proj} \), we see that \( \alpha \) is strongly correlated with \( \Delta T_c \) and strongly anticorrelated with \( \lambda_\infty \). Curve fits where there is a strong correlation (or anticorrelation) between variables may cause "identifiability" problems. That is, the fit does not distinguish between the correlated parameters very well [56]. As a result, a fit that does not incorporate an independent estimate of \( \Delta T_c \) will have a large range of possible exponents.

In order to check Igor's estimate of the errors, we look at the projection of \( \chi^2 \) onto the \((\alpha, \Delta T_c)\) plane for a power-law fit to a single curve.\(^8\) An estimate of the errors is given by looking at the range of the \( \Delta \chi^2 = 1 \) ellipse, for each variable, where \( \Delta \chi^2 \) is defined as \( \chi^2 - \chi_{min}^2 \) [57] (Fig. 4.19). We see that our "chi-by-eye" estimate was in fact wrong and that the uncertainty estimates given by Igor are accurate. In conclusion, despite the seeming "good fits" generated by a range of exponents and despite the large correlations among the variables, the errors in the exponents and in the critical undercooling are relatively small. Furthermore, the predictions by Owen's model that \( \alpha = (-3/2) \) and \( \Delta T_C = 0 \, \text{°C} \) are not with the range of our results, \( \alpha = 1.08 \pm 0.08 \) and \( \Delta T_C = 5.0 \pm 0.5 \, \text{°C} \).

### 4.6 Appendix B: Spiral Domain Boundaries

As mentioned above, spherulites formed in the long-chain PA samples show a competition between two growth modes, a slow-growing banded mode and a fast-growing

\(^8\)The global fit has six independent values of \( \Delta T_c \), making the \( \chi^2 \) space more complex (7-D) and visualization harder. For the sake of this argument, one curve is enough. We also note that the \( \alpha \) for this curve is not exactly the same as that found in the global fit.
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Figure 4.19: Projection of $\chi^2$ onto the $(\Delta T, \alpha)$ plane, for $c_{PA} = 6.7\text{wt.\%}$. The error in $\alpha$ is given by the extremities of the $\Delta \chi^2 = 1$ ellipse.

"smooth" mode, which are observed at the same undercooling. When both morphologies are present, one observes a characteristic curved boundary between them (Fig. 4.21 (c)). It has previously been shown that the boundary between two spherulitic domains growing at equal velocities can be described by a hyperbolic curve. In this experiment, we observed boundaries between domains of equal velocity and also boundaries between domains of different velocities. In particular, we see a slow-growing banded domain, which serves as a nucleation source for a fast-growing, "smooth" domain that tends to dominate the growth at long times. In this section, I will show that the boundary between the smooth mode and the slower-growing banded mode can be described by a logarithmic spiral.

The radial velocity, $v_r$, of a point $A$ on the boundary is given by

$$v_r = (r_2 - r_1)/\Delta t,$$

where $\Delta t$ is a time interval and $r$ is the distance between the origin and the point. From Fig. 4.20, the radial velocity at this point is just the velocity of the slow-growing mode. The velocity along the boundary can be approximated as the velocity of the
Figure 4.20: Schematic of the boundary formed between slow- and fast-growing modes. The origin, \( N \), is chosen at the point where the slow banded-mode nucleates. The \( x \) axis is chosen as horizontal. \( r_1 \) and \( r_2 \) are two cords to the boundary points \( A \) and \( B \) and are equal in length to \( v_s \cdot t \). The fast growing mode nucleates on the dashed line.

fast-growing mode. It follows that the tangential velocity of the point is given by the Pythagorean theorem (applied to \( \Delta ABC \) which is right angled in the limit of large \( r \)).

\[
(\Delta tu_f)^2 = (\Delta tu_s)^2 + (\Delta \phi v_s t)^2 \Rightarrow \\
\frac{\Delta \phi}{\Delta t} = \frac{1}{t} \sqrt{\frac{v_s^2 - v_f^2}{v_f^2}},
\]

(4.2)

where \( v_{f/s} \) are the velocities of the fast/slow growing modes and \( \Delta \phi \) is the change in \( \phi \) during the motion. Here, we have chosen \( \phi \) to be the angle subtended between the \(-x\) axis and the line \( NA \) (Fig. 4.20). Taking the limit \( \Delta t \to dt \) and integrating gives \( \phi = \phi(t) \). By integrating Eq. 4.1 and substituting \( t \) with \( t(\phi) \), we find

\[
r = v_s \times e^{(\phi-\phi_0)\sqrt{\frac{v_s^2-v_f^2}{v_f^2}}},
\]

(4.3)

where \( \phi_0 \) is the angle subtended between the \(-x\) axis and the chord, from the origin, on which the fast mode nucleated. Here, we have chosen the origin as the point where the slow mode nucleated (labeled "\( N \)" in Fig. 4.20). In order to correct for cases where the nucleation of the two modes is not at the same point, one must add an offset to Eq. 4.3,

\[
r = |(v_s \times e^{(\phi-\phi_0)\sqrt{\frac{v_s^2-v_f^2}{v_f^2}}})\phi + r_0 \phi_0|,
\]

(4.4)
where \( \vec{\phi} \) and \( \vec{\phi}_0 \) are unit vectors and \( r_0 \) is the distance between \( N \) and the point at which the fast-mode nucleated (which can be anywhere along the chord subtended by \( \phi_0 \)).

In order to test this model we captured a movie showing the growth of the competing modes. The velocities of the two modes were determined from the movie using the method described in Ch. 2. These velocities were substituted into Eq. 4.4, which was fit to \( r \) vs. \( \phi \) data (extracted from the final image of the movie) (Fig. 4.21(a)). This

![Graph of radius vs. phi with data points and fitted line.](image)

Figure 4.21: Fit to spiral interface. (a) Our model, fit to a set of points \( r(\phi) \) extracted from image (b). (b) The fit superimposed on the image.
fit is superimposed on the actual image in 4.21(b). Since the velocities are determined from the movies rather than from the boundary fit, the only free parameters in this fit are $\phi_0$ and $r_0$. Results from the boundary fit are tabulated in Tab. ??.
Chapter 5

Conclusions

We have shown that the banded spherulitic growth observed in the EC+PA system has properties that are similar to those observed in other related systems. In particular, we have shown that the band spacing diverges as a critical growth velocity or undercooling is approached and that this divergence is accompanied by a loss of coherence in the bands.

We attempted to collapse curves of band spacing vs. velocity using the viscosity, as suggested by previous studies. The attempts were somewhat successful, showing a ratio of 4:1 in the ratio of exponents of the velocity:viscosity, as expected in Tiller’s model. However, since viscosity is a function of concentration, a similar data collapse using the polymer concentration rather than viscosity could be made. Spherulites grown from the 200-kD samples showed qualitatively different behavior. The 200-kD samples showed a much higher growth rate and band spacing, along with very ordered bands and no divergence. This is confusing since typically lower viscosity/concentration samples showed a lower degree of correlation. Furthermore, attempts to collapse data from 200-kD samples onto the curve formed by the 100-kD data failed. These qualitative differences made it impossible to compare the 100-kD and 200-kD spherulites.

When comparing spherulites frozen from samples with different \( c_{PA} \), we noted that the bands tend to lose their coherence as \( c_{PA} \) is decreased. It is still unclear whether it is the viscosity or the polymer concentration that is responsible for the coherence of the bands. In the 100-kD samples, the threshold for the observation of bands is
$c_{PA} = 2.8\ \text{wt.\%}$, while preliminary observations have showed that the 200-kD samples are banded well below this threshold. Since the 200-kD samples show correlated bands at lower concentration and viscosity, it is hard to know how one should interpret this result.

In order to understand how these two data sets are related, in terms of both correlations and band spacing, we would need to do a future study incorporating at least two more chain lengths. This study should attempt to correlate variables such as the typical band spacing and typical velocity with the viscosity, concentration, or the chain length. The goal of this study would be to understand the role of polymer length and dispersity in the formation of spherulites. Our preliminary results show that we should be very careful in our assumption that spherulites formed in the EC are independent of the type/chain-length/dispersity of the polymer used for “thickening.”

Since the hydrodynamic model we were testing failed, we attempted to analyse the data using some existing models. We showed that the data on band spacing vs. undercooling can be fit to two models: The first model assumes that bands are forming as a result of crystal twist generated by isochiral thermal screw-dislocations. Although this model fits the data fairly well, a much better fit is obtained using a power law, with the reservations that both the critical undercooling and the band spacing at infinite undercooling are non-zero. Power-law divergences are generic in “continuous transitions.” We show that two other generic requirements for a continuous transition are also met, namely that the bands tend to lose their coherence as the critical undercooling is approached and that along with the appearance of bands, a discontinuity (or change) in front velocity occurs. Continuous transitions are very common. A familiar example from equilibrium thermodynamics occurs when the temperature of a ferromagnet is lowered to below its Curie temperature.

Preliminary microscopic observation of a banded spherulites formed in a sample with $c_{PA} = 5.9\ \text{wt.\%}$ showed that the crystallites are on the order of a few microns in diameter and seem to originate in clusters at nucleation sites that form on the bands. The crystals seem to “fan out” from these sites. This is important because in the macroscopic study, periodicity due to twisting or defects cannot be distinguished, while observations under an optical microscope resolve the two effects very clearly. The preliminary microscope investigation also showed that the assumption
that bands could not be resolved beyond a certain undercooling in the macroscopic system because of optical limitations is incomplete. Beyond some maximum undercooling, bands vanish altogether. It would be interesting to try to correlate microscopic phenomena with the macroscopic phenomena observed in this experiment.

In order to understand why experiments that use two different chain lengths disagree with each other, we need to make a detailed study of the front velocity, band spacing, and correlation as a function of chain length, viscosity, and concentration. Furthermore, the macroscopic view that we have adopted here will probably need to be rethought, as many different microscopic morphologies may look the same on this scale. In order to distinguish these morphologies, one must make further studies under a polarizing optical microscope equipped with a high-magnification lens. The drawback with the microscopic study is that the undercooling is shifted by the latent heat released during solidification. Although this problem has been reduced in the apparatus described in Ch. 3, a parallel study with this apparatus is still necessary in order to accurately determine the undercooling for a given front velocity.

Future experiments should also try to determine the effect of impurities that diffuse into the sample. Our study showed that impurity-rich areas had wider band spacings, slower velocities, and shorter correlation lengths. Under air and with sealed samples, the impurity problem was not solved. One possible solution is to work under an inert gas (e.g., argon). Since the dispersity of the molecular weights of the polymer can be regarded as a type of impurity field, this study should also try to explain how the dispersity affects the banding.

This study has shown that the EC+PA system is more subtle than originally presumed [47]. The length and perhaps the dispersity of the molecular chains have large effects on the banding and front velocity, even when the viscosity is held constant. Although we have explored a number of possible mechanisms, our efforts to test these were hampered by the rudimentary nature of the work that has been done, which goes little beyond back-of-the-envelope calculations. More realistic calculations are needed to solve the 3-D partial differential equations that couple front growth, hydrodynamic flows, elasticity, and surface forces. While theorists have shied away from such complicated systems, advances in computer software and hardware suggest that relevant simulations are now possible. I hope that the results presented here will
help stimulate such work. The real issue in such a computer experiment is making contact with actual physical systems.
Bibliography


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