

OBSERVATION OF GROWTH PULSATIONS IN POLYMER DENDRITIC CRYSTALLIZATION IN PEO/PMMA BLEND FILMS

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Introduction

One of the outstanding questions in the study of dendritic crystallization is the relation between side-branch and tip growth and the global crystallization geometry. The highly symmetric appearance of snowflakes and metallurgical dendrites has led many to suggest that oscillatory hydrodynamic modes govern dendritic growth. Early models of dendritic growth gave support to this intuition, but careful measurements of the crystallization of succinonitrile and other small molecule liquids from the melt has provided no evidence for growth oscillations.¹ We investigate the existence of growth pulsations in dendritic growth using polymer blend films where the crystallization morphology can be studied at high undercooling and over long timescales due to the relatively slow rate of crystallization.²

Experimental

Montmorillonite ("Cloisite" clay) was supplied by Southern Clay Products.³ This clay has exchangeable Na^+ ions and a cation exchange capacity of ca 120 meq per 100 g. PEO and PMMA were purchased from Aldrich. The polydispersity indices k ($k = M_w/M_n$) and 'weight-averaged' molecular masses were determined by gel permeation chromatography to equal $k(\text{PMMA}) = 1.8$ ($M_w = 7.3 \times 10^3 \text{ g.mol}^{-1}$) and $k(\text{PEO}) \approx 4$ ($M_w = 1.5 \times 10^5 \text{ g.mol}^{-1}$).⁴ 41g of clay and 50 ml of distilled water at 353 K were placed in 100-ml beaker along with 1 g of distearyldimethyl ammonium chloride. The mixture was stirred vigorously for 1h and then was filtered and washed 3 times with 100 ml of hot water to remove NaCl. After being washed with ethanol (50 ml) to remove excess ammonium salt, the product was freeze-dried, and dried in a vacuum oven at room temperature for 24 h. The blend components were dissolved in chloroform at a concentration between 0.3 % and 3 % relative weight of polymer to solvent and thin blend films of this solution were spin-coated onto Si substrates (Semi-conductor Processing Co., orientation (100), Type P) at a spin speed of 2000 rpm. This procedure results in uniform films having a thickness between 100 nm and 500 nm. Prior to spin coating, the polished Si substrates were treated for 2 h with a solution of 70% H_2SO_4 / 30% H_2O_2 at 353 K, rinsed with deionized water. Reflective optical images were obtained with a Nikon optical microscope with a Kodak MegaPlus CCD camera attachment. Each digitized image has a 1028 x 1028 pixels resolution and was obtained with a (x 100) objective (1028 pixels = 154 μm). Error bars in the figures correspond to a maximum measurement uncertainty of 0.15 μm . This uncertainty is associated with the pixel resolution. After spin-casting, the film samples were melted to 377 K and then cooled down to the desired PEO crystallization temperature, T_c . The melting temperature T_m of pure PEO was determined to equal $T_m = 338 \text{ K}$ by differential-scanning calorimetry on thick (20 μm) evaporated PEO/chloroform films and the glass transition temperature T_g of the PEO and PMMA films were found to equal $T_g = 213 \text{ K}$ and 377 K , respectively.

Results and Discussion

Symmetric dendritic crystallization (SDC) is a familiar phenomenon from our everyday experience with snowflakes and frost and **Figure 1** illustrates this phenomenon in the case of a polymer blend film. We utilize thin blend films of the crystalline polymer (PEO) and the amorphous polymer (PMMA). Clay particles are added to nucleate the crystallization and these particles are apparent as dark spots at the center of the dendrite. The blend films are relatively thin [thickness < 500 nm] and previous studies of phase separation in blend films have shown that the films can reasonably be described as two-dimensional for a thickness on the order of 10 nm. The thin film geometry facilitates our measurements and comparisons to simulations of two-dimensional crystal growth detailed below. PEO/PMMA blend films are unusual because we can *tune* the crystal morphology by varying the relative polymer composition, an effect we have attributed elsewhere to a change of the surface tension anisotropy ϵ with relative polymer composition.⁵

Figure 1 shows optical images of a growing polymer dendrite over a sequence of times from 60 to 460 min. The film thickness is 160 nm and the dimensionless undercooling equals, $\delta T = (T_m - T_c) / T_m = 0.10$ where T_m is the

melting temperature and T_c is the crystallization temperature. Note the cusplike shape of the envelope curve describing the tip positions of the dendrite arms. The side-branches of the SDC in **Figure 1a** grow perpendicularly to the slender and nearly parabolic main dendrite branch. Crystallization images were acquired at a rate of one picture per 5 min and in **Figure 2** we show the increase in the distance of the tip position from the center of the dendrite, the *dendrite radius*, $R(t)$. We observe that $R(t)$ (data corresponds to the dendrite arm indicated by arrow in **Figure 1**) grows in an oscillatory manner about an average linear growth. The data in **Figure 2** yields an average growth rate, $R_0 = 0.171 \mu\text{m} / \text{min}$ and the growth oscillation period $P \approx 180 \text{ min}$ (see below). Uncertainties in the data shown in **Figures 2 and 3** are discussed elsewhere.²

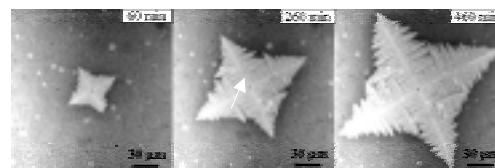


Figure 1. Dendritic crystallization of PEO in a PEO/PMMA blend film.

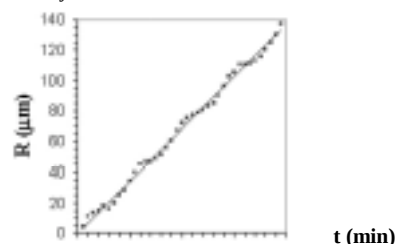
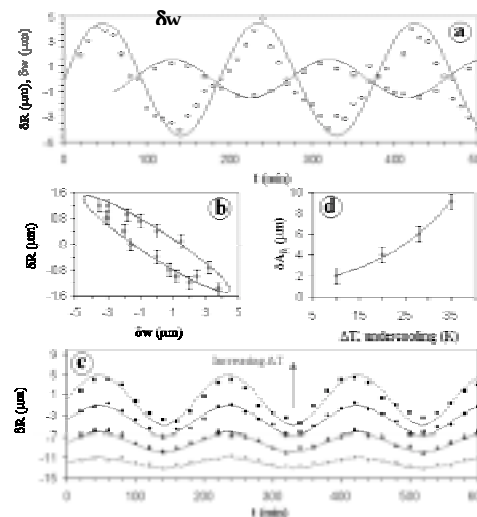


Figure 2. Distance of tip of dendrite trunk tip from dendrite center, $R(t)$.

The tip pulsations in **Figure 2** are quantified by subtracting the *average dendrite tip radius*, $R(t) = R_0 t$ (straight line in **Figure 2**) from $R(t)$. **Figure 3a** shows that the *tip position fluctuation*, $\delta R(t) = R(t) - R_0 t$ is nearly sinusoidal; the solid curves correspond to a fit of $\delta R(t)$ to $\delta A_R \sin(2\pi t/P)$ where δA_R is the *oscillation amplitude* and P is the *pulsation period*. We next compare $\delta R(t)$ to fluctuations in the dendrite arm width, $\delta w(t)$. To measure $\delta w(t)$ we choose an arbitrary sidebranch (denoted by arrow in **Figure 1**) and define $\delta w(t)$ as the orthogonal distance from tip of the sidebranch to the center line of the main dendrite arm. $\delta w(t)$ shows "out of phase" oscillations with $\delta R(t)$ and a "phase plot" of $\delta R(t)$ and $\delta w(t)$ in **Figure 3b** reveals that the dendritic growth in δA_R increases with δT (**Figure 3c**; curves offset from zero average for clarity) and **Figure 3d** shows this amplitude growth is nearly exponential in δT . The amplitude **Figure 1** is governed by a limit-cycle with a phase angle α difference of $\alpha \approx 164 \pm 4^\circ$. Although there have been suggestions of growth pulsations in dendritic growth, this is apparently the first convincing



observation of limit-cycle growth dynamics in SDC.

Figure 3. Amplitude of trunk tip and sidebranch width oscillations.

Since theory offers limited guidance about the factors governing the period P of dendrite growth pulsations, we explore the influence of system parameters under our control: undercooling, polymer composition and film thickness, L . In **Figure 3c**, we show $\delta R(t)$ for a range of undercooling $\Delta T = (T_m - T_c)$ values in the range (15-35 K). Apparently, P has no appreciable dependence on ΔT . A change in the relative polymer composition has a large influence on the pulsation rate, but this effect can cause a *qualitative* change in the crystallization morphology⁵ [e.g., spherulites, seaweed, fractal, etc.] so we restrict ourselves to a composition range where SDC is observed. A decrease of the PMMA concentration causes a decrease in P and an increase in δA_R for a fixed $\Delta T \approx 35$ K (e.g., $P \approx 105$ min and $\delta A_R \approx 15$ μm for a 35/65 blend (PEO / PMMA relative mass fraction) while $P \approx 180$ min and $\delta A_R \approx 9$ μm for a 30/70 blend). We next explore the change in growth dynamics and morphology associated with reducing the film thickness.

Figure 4 shows that P first *increases* sharply with *decreasing* film thickness L , but then *drops precipitously to zero* below a critical film thickness², $L_c \approx 80$ nm. The left inset to **Figure 4** shows an example of dendritic growth in a thin film ($L < L_c$; $L \approx 50$ nm thickness) where the crystallization conditions (temperature, composition) are the same as in

Figure 1. Notably, this dendrite *does not* exhibit growth pulsations and has a more disordered appearance and overall square-like shape. The right inset shows a crystallization pattern for $L > L_c$ (same film as **Figure 1**, but $t = 800$ min). Thus, we have evidence for a *morphological transition* for $L < L_c$, accompanied by a change in the dynamics of the dendrite tip. The lack of pulsations in the "two-dimensional" blend film dendrites is also reflected in the extent of correlation in the position of the sidebranches on each side of the growing, near-parabolic dendrite trunk arms. The registry of sidebranches and the cusp-like envelope curve describing the positions of the sidebranch tips in the symmetric dendrite shown in **Figure 1** are contrasted with the "two-dimensional" dendrite ($L < L_c$) shown in the inset of **Figure 4**. There is little correlation in the sidebranch positions on either side of this dendrite. This enhanced regularity of structure in the pulsing dendrite is reminiscent of the regular sidebranching found in the growth of dendritic growth subjected to periodic external perturbations.⁶ We therefore suggest that the oscillatory tip tip mode imparts regularity to the growing dendrite.²

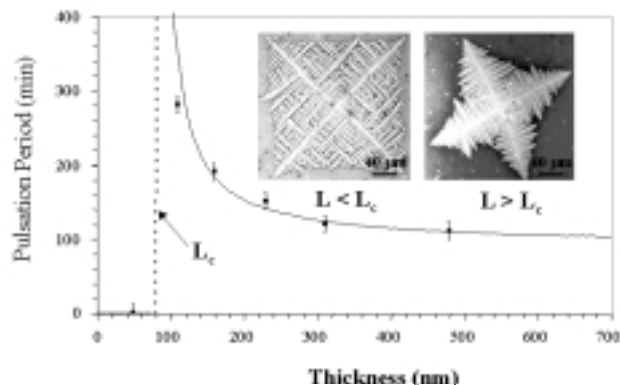


Figure 4. Effect of film thickness on pulsation period, P .

There have been other measurements indicating the presence of hydrodynamic modes in non-equilibrium crystallization. Limit-cycle dynamics have been observed in the directional solidification in succinonitrile.⁷ In this case, the crystallization front forms an array of finger-like "cells" and the oscillations involved the tip position relative to the average position of the moving crystallization front and the width of the cells. Oscillatory tip-splitting has been observed in seaweed dendritic crystallization in succinonitrile / PEO mixtures.⁸ There has also been reports of radial growth oscillations in spherulitic polymer crystallization.⁹ All these observations point to the importance of tip hydrodynamic modes in influencing the morphology of dendritic growth.

We obtain some insight into these growth patterns by comparing to phase field simulations of two-dimensional SDC in a two-dimensional fluid mixture.¹⁰ The simulation in **Figure 5** corresponds to a Ni-Cu alloy ($\Phi_{Ni} = 0.59$) where a large surface tension anisotropy ϵ is assumed (ϵ has apparently

never been measured for polymers so that direct comparison of simulation to measurement is not currently possible) and $\delta T = 0.013$. Growth pulsations are *not observed* in the phase field simulation¹⁰, but we find a close resemblance to the "two-dimensional" polymer dendritic growth shown in the inset of **Figure 4**.



Figure 5. Phase field simulation of dendrite growth. ($\delta T = 0.013$; $\epsilon = 0.012$)

Conclusions

Many physical effects can lead to oscillations in the velocity of propagating non-equilibrium growth fronts² and further experiments and simulations are necessary to resolve their origin in our blend film measurements. Nonetheless, the present measurements prove that growth pulsations can occur spontaneously in free dendritic growth, accompanied by coherent and periodic emission of sidebranches and this suggests that hydrodynamic modes in the growth front can have a large impact on the regularity of crystallization morphology. We can expect to exert control of the crystallization morphology through forcing these oscillations with periodic external perturbations, as demonstrated with pressure and thermal oscillations in small molecule non-equilibrium crystallization⁶.

The properties of semi-crystalline materials created under conditions of non-equilibrium crystallization depend on the complex domain wall structures resulting from the interaction of growing crystalline domains in the late-stage of crystallization. Preliminary data indicates that the growth pulsations have a strong influence on the inter-dendrite interactions. Future work should examine whether the dendrites exhibit phase-locking in their pulsations and whether there are effective interactions between the dendrites associated with the commensurability of their oscillation frequencies. Investigation of growth oscillations and other periodic growth phenomena for the other crystallization morphologies and the influence of this type of oscillatory phenomena on the late-stage crystallization morphology would also be of interest.

We are hopeful that the interplay between simulation and measurements on non-equilibrium crystallization and other related pattern formation processes will lead to an improved understanding of the properties of semi-crystalline polymer and metallurgical materials.

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- (3) Certain commercial materials and equipment are identified in this article in order to specify experimental procedure, but these items are not necessary the best available for this purpose.
- (4) We thank Ronald Heddon and Charlie Guttman of the Polymers Division at NIST for characterizing the polydispersity of our PEO and PMMA samples by gel permeation chromatography.
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