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Crystal Growth Rate in a Blend of Long and Short Polymer Chains

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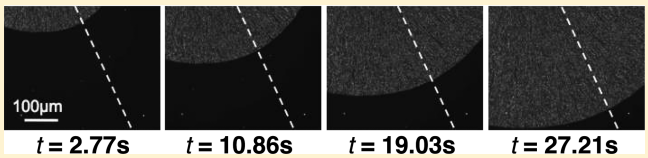
ABSTRACT: Since short polymer chains have a higher mobility than long molecules, conventional expectations are that the growth rate, G, of polymer crystals should decrease as the concentration of large chains increases in a binary blend. Here we present results on G as the blend concentration, ϕ, is varied from short chains of poly(ethylene oxide) (PEO), which are well above the entanglement molecular weight, to long PEO chains. Contrary to the simple mobility argument, $G(\phi)$ is nonmonotonic—clear evidence that another mechanism can dominate. We propose a tentative model based on the simple idea that chain ends retard the crystal growth. Thus, increasing the chain end concentration with the addition of short chain molecules can reduce the crystal growth rate.



■ INTRODUCTION

Even though polymers are long chain molecules, typically dominated by entropy, they can form a crystalline structure. Much of the process of crystal growth is generally very well understood.[1−3] Starting from an initial crystal nucleus, segments of a chain pull out of the amorphous melt and sequentially attach to the growth front. When chains are short enough and the supercooling relatively small, crystallization proceeds slowly and extended chain crystals can form. However, with long chain systems or large supercooling, a perfectly aligned and fully extended chain arrangement is rarely realized. Such a crystal would require the chain to fully disentangle from the melt at a huge entropic cost—a cost that is too large to overcome on the time scale of growth. Instead, long chain molecules attach subchain segments to the growth front via a chain folding process to form well-defined nanoscale crystalline lamella. Defects like entanglements and chain ends are sequestered to thin amorphous layers separating the lamellae. The resulting structure is semicrystalline and driven by kinetics rather than equilibrium thermodynamics. The larger superstructures that form are round spherulites which exhibit linear growth rates, G, for a given crystallization temperature, T_c.[1−3]

There is a very extensive body of experimental and theoretical work to describe the crystallization process for monodisperse systems where the entire sample is of similar molecular weight. However, what has been generally overlooked is a means to describe the effect of polydispersity. Given the industrial importance of semicrystalline polymers, where highly polydisperse materials are the norm, this is perhaps surprising. Part of the difficulty in treating polydispersity is a lack of a solid understanding of the effect of molecular weight on crystallization kinetics. The experimental observations are complex and depend on chain length, temperature, and polymer type, to name a few, in ways that cannot be described within a single theoretical framework. For example, in a seminal study Kovacs and co-workers showed a stepwise change in growth rate as a function of temperature for short chain poly(ethylene oxide) (PEO), whereas longer chains demonstrated a continuous change.[4] This effect has been attributed to transitions from fully extended chain crystals to integer-folded crystals in the short chain systems, which contrasts with noninteger chain folding in the long chain systems. Other studies have demonstrated a complex molecular weight dependence for the growth rate of PEO spherulites, which also lacked a simple temperature dependence.[5]

One way to understand polydispersity and molecular weight effects on crystal growth is to look at blends of different monodisperse chain lengths. A large body of work exists for blends of short chain systems, like the *n*-alkanes.[6−11] These systems are ideal because perfectly monodisperse fractions have become available in recent years, making the preparation of perfectly bidisperse blends possible. Such perfectly monodisperse samples do not exist for long chains. Because simulating long chain crystallization remains very challenging, studies have focused on short chains.[12] By understanding these simpler model systems, extrapolations may be made to more complex, long-chain blends. Such studies have lent insight into chain alignment, chain-end effects, integer and noninteger chain folding, spherulite formation, etc. Work by Hosier and co-workers looked at binary blends of relatively long, monodisperse *n*-alkanes.[6−8] Differences in size between the two blend chain lengths played an important role in the resultant morphology, and growth rates were seen to decrease when small amounts of the guest molecule, whether shorter or longer, were added to the melt of the host molecule. Such nonmonotonic changes in growth rate as a function of blend composition have also been observed in simulations of short chain blend systems.[10,13]

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A limited number of studies have explored high molecular weight blends.[14−20] These studies have mostly focused on cocrytallisation, where both chain lengths are homogeneously distributed in the crystal, contrasted with segregation, where one component is expelled from the growing crystal. Work by Cheng and co-workers thoroughly examined a large number of blends of short PEO chains (with number-averaged molecular weight ranging from $M_n \sim 3.5$ to 20 kg/mol) with much longer chains.[14−16] Segregation was seen to persist with a short chain component of 20 kg/mol. Balijepalli and co-workers examined blends of very short 5 kg/mol and long 270 kg/mol PEO molecules.[20] For temperatures where cocrystallization took place, they found a crystal lamella thickness dependence based on blend composition. Whether short or long, the majority component was responsible for templating the crystal thickness with the minority component conforming to this restriction. The authors suggested that this behavior was caused by a balance between the energy of folding long chains and the inclusion of more chain end defects for the short chains.

While nonmonotonic growth rates as a function of blend composition have been seen before in systems where integer chain folding or chain segregation are important, such effects do not play a role in high molecular weight polymers. For high molecular weight chains the expectations are more simple: increasing chain length decreases the mobility. Thus, adding a low molecular weight component should result in monotonically increasing the crystallization kinetics.

Here we present results on the spherulite growth rate, G, of high molecular weight blends of PEO. In contrast with expectations, we demonstrate a robust, *nonmonotonic change in the growth rate as a function of blend composition*. Such an effect has not been previously reported in the literature for chains of this length. From the experimental results we can only conclude that that there is a secondary mechanism, not previously accounted for, that is responsible for the nonmonotonic results. We propose a tentative model that is consistent with the experimental results.

■ EXPERIMENT

Three different narrow molecular weight species of PEO were used for this study. The molecules, which will be referred to as 57K, 102K, and 330K, had weight-averaged molecular weight M_w = 57, 102, and 330 kg/mol and polydispersity index M_w/M_n = 1.10, 1.08, and 1.18, where M_n is the number-averaged molecular weight (Polymer Source, Inc., Canada). Blends of the three molecular weights were dissolved in acetonitrile and spin-cast onto Si substrates to obtain uniform films with $h \sim 500$ nm. We note that all growth rates presented can be considered bulk measurements since h was chosen well above that for which thin film effects become important.[21] The films were vacuum annealed (10^{-6} Torr) about 5 °C above the melting temperature for PEO ($T_m \sim 65$ °C) for ~24 h to remove residual solvent and relax the polymer chains. After annealing, samples were transferred to an optical microscope heating stage (Linkam, UK) and flushed with argon gas to ensure a dry environment. Samples were annealed for at least 10 min above T_m to erase thermal history and then cooled rapidly to the desired crystallization temperature, T_c, for spherulite growth measurements. Dark field optical microscopy was used to measure the spherulite growth rate, G, as shown in Figure 1.

■ RESULTS AND DISCUSSION

With dark field microscopy, the growing crystal appears bright with a very sharp boundary in contrast with the surrounding amorphous melt. G is readily obtained from the position of the growth front as a function of time. A plot of G as a function of the blend concentration ϕ is shown in Figure 2a for all three binary blends. We note that each composition data point represents an average of 4−8 measurements (multiple measurements of G were obtained on several individual film samples for each ϕ). Here the concentration ϕ is the number fraction of long chains in a blend. For example, for the 57K/102K blend data set, $\phi = 0$ is a film of entirely 57K PEO chains, $\phi = 0.5$ has an equal number of 57K and 102K molecules, and $\phi = 1.0$ is a film of entirely 102K PEO chains. It is important to note that the molecular weights used in this study fall in the regime of decreasing G with increasing chain length.[5] Thus, for binary blends, the mobility argument described above would predict a monotonic decrease in G for increasing ϕ. Such expectations are clearly not observed in the data. A distinct nonmonotonic change in growth rate is evident for two of the three blend compositions. While G seems to decrease monotonically with ϕ for the 102K/330K blends, the 57K/102K and 57K/330K blends exhibit an upturn in the growth rate for larger values of ϕ. The result is counterintuitive: *adding more mobile short chains to a system of long chains slows the growth kinetics of the crystals.*

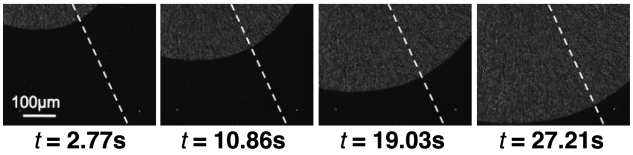

Figure 1. Dark field optical microscopy images of a growing spherulite in a PEO (57K) film at T_c = 50 °C. G is obtained from position of the growth front as a function of time.

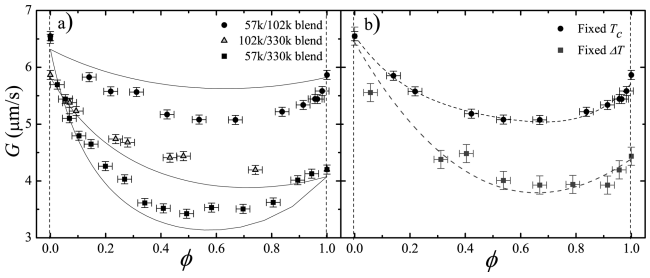

Figure 2. (a) $G(\phi)$, for three different blends crystallized isothermally at T_c = 50 °C. Nonmonotonic changes in G can be seen for two of the blends. Lines are the best fit of the model presented in the text. (b) $G(\phi)$ for 57K/102K blend as in (a) and with fixed supercooling. Lines drawn to guide the eye.

In addition to investigating binary blends, $G(\phi)$ has also been obtained for ternary systems (see Figure 3). In this ternary plot, the vertices represent films of the pure components. Each edge represents one of the binary data sets in Figure 2a, while the interior of the plot is composed of data points from the ternary blends. This plot represents hundreds of individual growth rate measurements of various blend compositions, underlining the robust nature of this anomalous nonmonotonic trend in $G(\phi)$.

From the experiments we can state with certainty that there is a second mechanism which opposes the simple mobility argument and results in an increase in the growth kinetics as the short chain component vanishes. While we cannot be certain about the cause of this mechanism, in what is to follow we speculate as to the origin and propose a simple model.

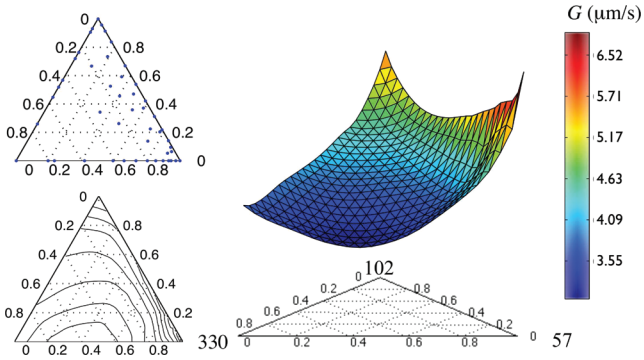

Figure 3. Ternary plot of G for all blends. Vertices represent growth rate of the pure components, edges are that of binary blends, and ternary blends fill the middle of the plot. Color scale indicates range of G values represented.

The chain lengths were chosen to be well above those where integer chain folding effects exist,[4] where chain segregation of the two components can play a role,[14] and above the entanglement molecular weight ~1.6 kg/mol.[22] For long chains, as in our system, it has been shown that the energy barrier for chain segments attaching to the crystal front is not dependent on the amount of chain left to be incorporated into the crystal.[23] Thus, from the point of view of of the growth front, the three chain lengths should be indistinguishable from one another.

Having ruled out integer chain folding and chain segregation effects, consideration must be given to the degree of supercooling in the experiments. For simplicity, all values of $G(\phi)$ were obtained at T_c = 50 °C. However, the relevant parameter for determining the growth rate is not T_c, but rather the degree of supercooling below the melting temperature, $\Delta T = T_m - T_c$. Since T_m is chain length dependent, the degree of supercooling was not identical for all measurements and hence the driving force to crystallize not equal. Experiments were carried out to ensure that the variation in the degree of supercooling is not the reason behind the nonmonotonic trends. For the three fractions considered in this work, differences in T_m were measured to be less than 1 °C, in agreement with proposed empirical relationships (see for example Figure VIII.15 in ref 24). While this is a small difference, by measuring the values of T_m for a number of 57K/102K blends, $G(\phi)$ could be obtained for fixed supercooling as shown in Figure 2b. From the data it can be seen that while the differences in T_m certainly add a correction to G, the nonmonotonic trend is still present in the fixed supercooling experiment. Thus, we can definitively conclude that the slight difference in the degree of supercooling is also not responsible for the paradoxical results. Furthermore, we have examined the morphological features of the blends both with optical microscopy and atomic force microscopy. No unusual features were noted for compositions at the minimum of the growth rate. More precisely, the morphology appears to transition from the low composition case to the high composition case in a continuous fashion.

The increase in G near ϕ = 1 suggests a mechanism that opposes the mobility argument (i.e., one would expect G to decrease with increasing ϕ because when ϕ increases, so does the fraction of longer, more sluggish, molecules). The mobility contribution modifying the growth rate can be described by a power law[3]

$$G_{\text{mobility}} \sim \left(\frac{A}{\langle M_n \rangle}\right)^{\alpha} \tag{1}$$

where A is a prefactor, $\langle M_n \rangle$ is the number-average molecular weight of the blend, and the exponent, α, is found to take a value between 0 and 1, depending on T_c. A mechanism resulting in the upturn in G with ϕ is elusive and has not been previously reported. How can one account for a reduction in the growth kinetics with the addition of *more mobile* shorter molecules? While there may well be other possible origins, we suggest that the mechanism can be explained by the increasing number of chain ends in the system with the addition of shorter molecules. In general, chain ends can be thought of as defects in the system that, because of the thermally driven entropic fluctuations, are more mobile than the midchain segments. Work by Richter and co-workers has directly verified that chain ends are much more mobile than midchain segments.[25] It is reasonable to assume that this increased motion will decrease the likelihood of a chain end attaching to the growth front compared to a stem from the midchain region. As a result, chain ends are more resistant to being folded into a compact crystalline form and are more likely to end up in the amorphous interlamellar region.[1]

We propose that the chain ends, which act as entropic defects at the crystal growth front, slow the dynamics of crystal growth. Adding short chains to a long chain system increases the concentration of chain ends or, in other words, increases the defects at the growth front. Then the increase in chain ends is responsible for the slowing of the growth rate as the concentration of small chains increases. This is consistent with the qualitative observation that the 57K/330K blend, which has the largest difference in chain lengths, also shows the greatest upturn in G near ϕ = 1. To model this mechanism, we assume that a chain end, of average length γ, has a larger time constant, τ_a, for incorporation into the growing crystal front than that for the remaining midchain, τ_b. The average time it takes for a chain of total length M to incorporate into the growth front is $t(M) \sim (M - 2\gamma)\tau_b + 2\gamma\tau_a$, which results in a growth rate contribution for a single chain given by

$$G_{\text{ends}}(M) \sim \frac{M}{(M - 2\gamma)\tau_b + 2\gamma\tau_a} \tag{2}$$

For the blend system the appropriate average of $G_{\text{ends}}(M)$ is given by the harmonic mean

$$G_{\text{ends}}(\varphi) = \left[\frac{\varphi}{G_{\text{ends}}(M_l)} + \frac{1-\varphi}{G_{\text{ends}}(M_s)}\right]^{-1} \tag{3}$$

where M_l and M_s are the molecular weights of the long and short chains. The total contribution to the growth rate from both the mobility and our proposed chain-end mechanisms is given by the product, $G = G_{\text{mobility}}G_{\text{ends}}$. Fits to the experimental data with this functional form are shown in Figure 2a. While the fits are not in quantitative agreement, this simple model captures the observed behavior with reasonable values for the parameters: A = 1205 kg/mol, α = 0.9 (consistent with the expected range as discussed above), τ_a/τ_b = 290 (midregion of the chain is incorporated into spherulite much faster than the ends), and γ = 0.4 kg/mol. Most interesting among these parameters is the result that the chain end length, γ, which acts as a defect, corresponds to about 10 monomer units. While the model captures the qualitative features, deviations are likely due

to the need to include a more complex form of the mobility term $G_{mobility}$.[26] Furthermore, the model assumes perfectly sharp molecular weight distributions of the PEO used in the blends, but in fact the polymers are not perfectly monodisperse.

Polymer crystal growth rates are strongly dependent on temperature. Lowering T_c is equivalent to increasing the driving force for crystallization. As a last test of the model, we investigated the effect of changing the degree of supercooling on the $G(\phi)$ as shown in Figure 4. As T_c is lowered, the nonmonotonic trend weakens, with a return to the expected monotonic decrease in G with increasing ϕ for the lowest T_c. This trend is also consistent with the model we have presented. Crystals grown at larger supercoolings are typically less perfect due to the fact that they are formed under much larger growth rates.[1] It should be expected that a more imperfect crystal will be less sensitive to defects at the growth front than one formed at higher temperatures where greater crystal perfection has time to be achieved.

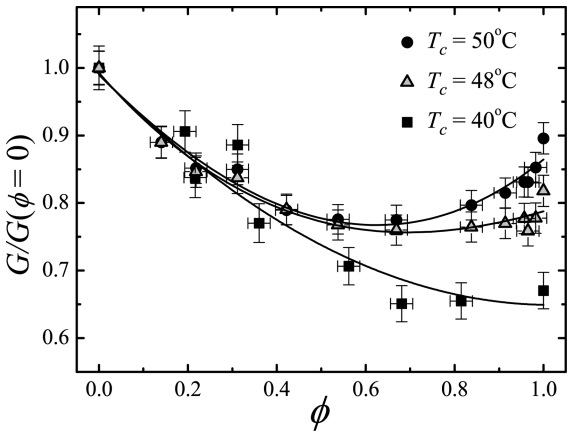

Figure 4. $G(\phi)$ for a 57K/102K blend at different values of T_c. Each data set has been normalized by $G(\phi = 0)$ to aid comparison. Lines have been drawn to guide the eye.

CONCLUSIONS

Here we have demonstrated, for the first time, that there is a nonmonotonic change in spherulite growth rate as a function of blend composition for binary and ternary blends of PEO. The conventional expectation is that as one adds short chains to a long chain system kinetics should become faster and hence the crystal growth rate should increase. This was not found to be the case, and from the experiments we can state with certainty that there is a mechanism which opposes the simple mobility argument and results in an increase in the growth kinetics as the short chain component vanishes. We suggest a tentative model based on the simple idea that the chain ends are more mobile. As a result, the ends act as defects that are more difficult to incorporate into the crystal. Thus, increasing the chain end concentration increases the defects which reduces the crystal growth rate. While the simple model fails to provide quantitative agreement, the model does capture the nonmonotonic observations in $G(\phi)$. Furthermore, from the model one would expect the chain-end retardation to become less important for greater supercooling—this expectation is also observed. The experiments provide robust proof that the conventional mobility argument is not sufficient to describe the observations. It is hoped that the simple model presented provides a starting point for more complete theoretical models.

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