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A possible explanation for nonlinear spherulitic growth rates

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Nonlinear growth of polymer spherulites has been repeatedly reported in blends containing a low-molecular weight amorphous polymer. A new explanation for this behaviour is proposed. Results of numerical simulations of the growth of lamellar stacks are presented. The model incorporates diffusion of amorphous polymer and assumes that the lamellar growth rate is depressed by the presence of amorphous chains at the growth front. It is shown that steady-state growth is reached only after long times when the diffusion coefficient of amorphous chains is large or when the lamellar growth rate is small. It is proposed that nonlinear growth in blends containing a low-molecular weight amorphous polymer (large diffusion coefficient) is, in some cases, due to the long times needed for a steady state to be reached and not a diffusion-limiting process. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

The general behaviour of polymer spherulitic growth is that it is linear; the growth rate is constant in time. Under certain conditions, nonlinear growth (i.e., growth rate decreasing with time) has been reported. This behaviour is most often seen in melt miscible blends containing a low-molecular weight amorphous polymer which is excluded from crystalline regions. For example, Keith and Padden[1] observed linear growth (i.e. a constant growth rate) of isotactic polypropylene ($M_n = 178\,000$) when blended with an atactic polypropylene of $M_n \geq 2600$, but observed nonlinear growth when blended with a low-molecular weight atactic polypropylene ($M_n = 540$). Similarly, Okada *et al.*[2] observed linear growth of isotactic polystyrene ($M_n = 400\,000$) when blended with a high-molecular weight atactic polystyrene ($M_n = 1\,300\,000$), but observed non-linear growth when blended with a low-molecular weight atactic polystyrene ($M_w = 420$). Other examples are given in Ref. 2.

Both Keith and Padden[1] and Okada *et al.*[2] proposed explanations for the nonlinear growth they observed. Keith and Padden argued that when diffusion of impurities (i.e. non-crystallisable species) is slow (high-impurity molecular weight) and crystal growth is fast, impurities are trapped in interfibrillar regions and a steady state develops since diffusion of impurities occurs in a direction normal to the growth direction. Hence, growth is linear. Conversely, when diffusion of impurities is fast (low-impurity molecular weight) and crystal growth is slow, they argue that diffusion of impurities will mainly occur in the radial direction and this will result in an ever increasing impurity concentration at the growth front and nonlinear growth. However, these two cases should not be strongly distinguished. Assuming that impurities can reside in interlamellar and/or inter-fibrillar regions, both of the cases above are diffusion-coupled problems. A steady state is attainable, but the condition of that state should be a function of impurity diffusion rate, growth rate, overall impurity concentration, and lamellar and fibrillar spacings. This is similar to the way

a steady state can develop during eutectic or dendritic growth.

A diffusing impurity follows a random walk which usually results in a net flux down a concentration gradient. Impurities will reside in interlamellar or interfibrillar regions (neglecting rejection due to thermodynamic considerations) regardless of the magnitude of the rate of diffusion. However, the impurity concentration in these regions and at the growth front are influenced by the rate of diffusion and the other parameters given above.

Okada *et al.*[2] argue that when the impurity (atactic polystyrene) molecular weight is low, crystal growth is controlled by the process of secondary nucleation which is influenced by the exclusion of isotactic chains by atactic chains at the growth front. As growth proceeds and atactic chains are rejected from the growing crystal, exclusion of isotactic chains increases and nonlinear growth results. They further argue that when the impurity molecular weight is high, growth is controlled by surface spreading kinetics which are not affected by the presence of atactic chains. Hence, growth will be linear in this case.

Keith and Padden[1] observed that nonlinear growth is not only favoured by a reduction in impurity molecular weight, but also by a reduction in the growth rate (achieved by changing the crystallization temperature). The explanation of Okada *et al.*[2] cannot account for this observation. A new explanation will be proposed here which is consistent with the observations of Keith and Padden and Okada *et al.*

Numerical modelling. Consider the problem of zone refining in which a material is forced to crystallise at a prescribed constant rate from an impure, single phase melt. Smith *et al.*[3] have given a time-dependent solution for the one-dimensional impurity concentration profile in the melt ahead of an infinite planar growth front by solving the diffusion equation with appropriate boundary conditions. The impurity concentration in the melt at the growth front as a function of time, $C^*(t)$, is

given by

$$C^*(t) = \frac{C_0}{2k}\left\{ 1 + \mathrm{erf}\left(\sqrt{\frac{V^2 t}{4D}} \right) \right.$$

$$\left. + (2k - 1)\, e^{-kqV^2 t/D}\, \mathrm{erfc}\left(\frac{2k-1}{2}\sqrt{\frac{V^2 t}{D}} \right) \right\}. \quad (1)$$

where C_0 is the initial, homogeneous impurity concentration, V is the imposed growth velocity, D is the impurity diffusion coefficient, k is the segregation coefficient (or the fraction of impurities in the melt at the growth front which are incorporated into the solid), and $q = 1 - k$. It can be seen that C^* will approach a steady-state value of C_0/k as the quantity $V^2 t/D$ becomes large. For a given value of k, the time that it takes for the system to reach a steady state (or a virtual steady state) will be proportional to D/V^2. Indeed, a metallurgical rule of thumb[4] states that a steady state is reached after a time of $4D/V^2 k$. A similar dependence on the time it takes a growing stack of polymer lamellae to reach a virtual steady state would be consistent with Keith and Padden's observation[1] that nonlinear growth is observed when either D is large or V is small. When the converse is true, steady state is reached quickly, and the transient behaviour may be missed experimentally.

I have a developed a space–time finite element model[5] to simulate the growth of a stack of lamellae from an impure, single-phase melt. Assuming that the impurities are completely excluded from the lamellae ($k = 0$), the model determines the impurity concentration in the melt surrounding the growing lamellae by solving the time-dependent diffusion equation. It is assumed that the system is isothermal and that the growth rate, V, of each lamella is given by

$$V = V_n f(C^*) \quad (2)$$

where V_n is the growth rate of lamellae from a pure melt, $f(C^*)$ is a monotonically decreasing function of C^*, and C^* is the impurity volume fraction in front of the crystal. The form used here for $f(C^*)$ is $1 - C^*$. This would apply for a binary blend of weakly interacting polymers such as isotactic and atactic polystyrene, because the melting point and transport properties should not be functions of impurity concentration. Therefore, the growth rate is reduced only due to the dilution of crystallisable species.

Results of two such simulations will be presented. The space–time formulation which has been used is non-dimensional. Each simulation is defined by the parameter $D/V_n L_c$ where L_c is the lamellar thickness. Time is scaled using the quantity D/V_n^2. For these simulations, a linear degree of crystallinity (ratio of crystal thickness to long period) of 0.3 and an initial impurity volume fraction of 0.5 were used. Also, for the purposes of plotting the data in *Figure 1*, $L_c = 5$ nm was chosen. These are typical values for isotactic polystyrene. The results in *Figure 1* are for two systems in which the values of D/V_n (usually designated as δ, the diffusion length) are equal to 1 and 1000 nm. The absolute time scale can be fixed by choosing either a value for D or V_n. If a value of 2 nm s^{-1} is chosen for V_n, the time unit on the abscissa is 1 s, and the two diffusion coefficients are 2 and 2000 nm^2 s^{-1} (2×10^{-14} and 2×10^{-11} cm^2 s^{-1}). A growth rate of 2 nm s^{-1} (0.12 μm min^{-1}) is typical for isotactic polystyrene.
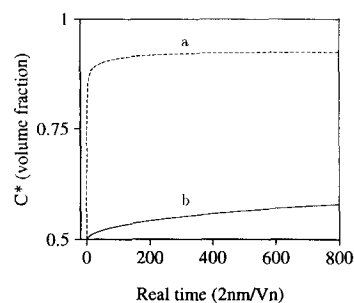

Figure 1 C^* as a function of time: (a) $\delta = 1$ nm, (b) $\delta = 1000$ nm. See te? for explanation of abscissa time units

The impurity concentration at the growth front of crystal contained within an infinite stack is plotted in *Figure 1 versus* time. When $\delta = 1$ nm, C^* rises quickly and levels off. When $\delta = 1000$ nm, C^* rises more slowl initially but continues to increase at an appreciable rate for longer time. After 800 s, $C^* = 0.58$. Although not shown $C^* = 0.65$ and 0.68 after 5000 and 10000 s, respectively Therefore, for small values of δ, both C^* and the growth rat will vary only over a very short time. After this time, the rat of increase of C^* (and hence the rate of decrease of growtl velocity) becomes very small, and the experimenta observation of nonlinear growth will become unlikely. Fo larger values of δ, a longer time is needed for C^* and the growth rate to reach a steady state. During this time, the growth rate continuously decreases, and observation o nonlinear growth is more likely. Thus, it is reasonable tc suggest that the time necessary for a steady state to develor will scale with δ.

Discussion

Several predictions can be made based on these results When the impurity molecular weight is large, the impurity diffusion coefficient will be small. Thus, δ is small, a steady state will be reached quickly, and constant growth rates should be observed. Conversely, when the impurity molecular weight is small, a steady state is reached slowly, and nonlinear growth should be observed. Also, a reduction in growth rate (larger δ) would increase the time necessary for a steady state to develop and favour observation of nonlinear growth. These predictions agree qualitatively with the experimental observations mentioned above and with the temporal behaviour of the zone solidification process.

Nonlinear growth is also known to be a result of diffusion-limited crystallisation[6]. However, the behaviour of nonlinear growth when due to a diffusion-limited process is quite different than when due to initial transients as discussed here. A steady state will develop only if all of the impurities can be accommodated in interlamellar or interfibrillar regions. If this condition is not met, long-range diffusion of impurities must occur parallel to the growth direction, resulting in diffusion-limited nonlinear growth.

Cahn[7] has derived an equation describing the isothermal growth of a spherical particle from a supersaturated matrix. In this analysis, long-range diffusion parallel to the growth must occur, and both interfacial and diffusional kinetics are taken into account. It was found that growth is linear in time when the particle is small or diffusional kinetics are rapid, and that growth is parabolic in time when the particle is large or diffusion kinetics are slow. These results contradict

the observations of Keith and Padden[1] and Okada *et al.*[2]. They reported linear growth when diffusion kinetics are slow (high-molecular weight impurities) and nonlinear growth when diffusion kinetics are fast (low-molecular weight impurities). This is strong evidence that long-range diffusion in the growth direction does not occur during crystallisation in the aforementioned blends. Therefore, a steady state will eventually develop; and nonlinear growth must be due to transients which exist prior to the attainment of that steady state.

The degree of solute redistribution upon crystallisation is affected by the parameter δ and by the lamellar morphology (crystal thickness and long period). When δ is small, there is little time for diffusion, and impurities are trapped in interlamellar regions. For the simulation presented above with $\delta = 1$ nm, the average impurity volume fraction in the interlamellar regions was 0.7. Since interlamellar regions account for 70% of the volume of the lamellar stack, the impurity fraction within the lamellar stack is then 0.49 (compared to the initial impurity fraction of 0.5). Therefore, most of the impurities are indeed being trapped in interlamellar regions.

When δ is large, diffusion kinetics are fast compared to crystallisation kinetics, and a greater number of impurities are able to diffuse away from the lamellar stack. (For the simulation presented above with $\delta = 1000$ nm, the average impurity volume fraction in the interlamellar regions was 0.54.) Diffusion of impurities from the growth fronts will occur in all directions including the growth direction. However, this is not a diffusion-limited case because diffusion in the growth direction is not necessary, and a steady state will eventually be reached.

Conclusions

It has been proposed that nonlinear growth of polymer spherulites from impure melts is, in some cases, due to initial transients in local crystallisation conditions and not a diffusion-limiting process. If the fraction of noncrystalline regions within a lamellar stack or spherulite is high enough to accommodate all of the impurities, steady state crystallisation conditions will eventually develop. Results of numerical simulations of crystal growth show that the time needed for a steady state to develop are related to the parameter δ. When δ is small, a steady state will be reached quickly, and measured growth rates will be constant in time. However, when δ is large, longer times are needed for a steady state to be reached, and measured growth rates will change in time. These predictions are consistent with several observations reported in the literature. Although the numerical results presented here are for an infinite lamellar array, the behaviour of a radially symmetric spherulite should be qualitatively similar.

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