



Short communication

On nucleation in miscible polymer blends



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ABSTRACT

The effects of diffusion of crystallizable polymer to a developing spherulite embryo are treated. Using the classical nucleation theory result for the size of a critical-size embryo and an existing model for the growth of a small pure component sphere in a bicomponent matrix, the time τ_b for a critical-size embryo to develop under diffusion control is given. The nucleation rate is lowered inversely proportionally to τ_b . The dependence of τ_b on crystallization temperature exhibits a minimum. At temperatures above that minimum, τ_b for a blend becomes increasingly larger with temperature than the time to form a nucleus in a pure system with similar diffusivity. Below the minimum, τ_b decreases with increasing crystallization temperature. Decreasing the activation energy for diffusion causes the minimum to move to higher temperatures.

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It is known that in some [1–5], but not all [6,7], miscible polymer blends the spherulite nucleation rate is depressed below that of the neat polymer, resulting in larger spherulite diameters and, thereby, poorer failure behavior. Further, the magnitude of the blending effect on decreasing the spherulite nucleation rate, relative to the neat polymer, increases with increasing crystallization temperature [2]. In this note the possibility that the lower nucleation rate is determined principally by the transport of chains to the region adjacent to growing embryos is explored.

In the classical (Vollmer-Becker- Döring) theory of nucleation, ephemeral small embryos are taken to form and dissolve by the accretion and dissociation of individual molecules at the surface(s) [8]. When a spherical embryo attains a critical radius r_c , the sphere grows spontaneously; reaching the critical size is the nucleation event. The saddle point Gibbs free energy for nucleation is

$$\Delta G^* = \frac{4}{3} \pi \sigma r_c^2 \quad (1)$$

where σ is an isotropic surface energy and the critical radius r_c is given by

$$r_c = -\frac{2\sigma T_m}{\Delta h_f \Delta T} \quad (2)$$

where T_m is the equilibrium melting temperature, ΔH_f is the

enthalpy of fusion, and $\Delta T = T_m - T$ is the undercooling.

The nucleation rate (nuclei per unit volume per unit time) of spherical nuclei from surroundings of the same concentration is

$$I = 4\pi r_c^2 q_0 e^{-\frac{\Delta G^*}{kT}} \quad (3)$$

where q_0 is the number of times per second and per unit area that molecular segments join or leave an embryo. The nucleation rate can be thought of as the product of the probability ($e^{-\frac{\Delta G^*}{kT}}$) of finding a critical size embryo and the rate at which one more molecule joins its surface ($4\pi r_c^2 q_0$). For nucleation of a pure component from a blend with concentration c_i of crystallizable component in the melt adjacent to the embryo, a dilution factor c_i is placed in the preexponential term [9]. In the following, we will not be interested in the volumetric rate of nucleation (given by (3)), but rather in the time τ_n for a given embryo to grow from radius zero to radius r_c .

When nucleation of spherulites of one component from a bicomponent blend is the case, the depletion of crystallizable molecules in the melt adjacent to the embryo must be taken into account. Some time ago, Gornick and Mandelkern treated crystallization from a miscible blend, including in their model all effects of blending on the thermodynamics of the phase change and on the kinetics of spherulite growth [10]. However, they did not attempt to analyze the effect of diffusion currents on nucleation. More recently, two models to include diffusive delivery of crystallizable molecules to the surface of embryos have been proposed. Yang et al. have given a very detailed distribution kinetics model of the

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nucleation of polymer spherulites in blends [9] Their model includes all the thermodynamic parameters suggested by Gornick and Mandelkern, but uses what appears to be an ad hoc coupling of diffusion to the embryo growth rate: $k_g = 4\pi D r_c$ where D is the diffusivity of the crystallizable species in the blend and r_c is the momentary size of the embryo. A very satisfactory model of diffusion-coupled nucleation has been given by Kelton [11,12]. This model follows the stepwise detailed balancing of classical nucleation theory, but includes the diffusion-controlled concentration of crystallizable moieties at the surface of the embryo. Kelton's simulation scheme should produce correct results. However, its implementation is via numerical computation and is cumbersome. In the following, we propose a simple means of assessing qualitatively the effect of "long-range" diffusion on the nucleation rate.

The case which we wish to compare with the classical nucleation model is that of the growth of a sphere of composition c_s from a mixture of composition c_0 from zero size to the size of a critical embryo. Embryonic polymer crystals are certainly not spherical, with isotropic surface energy. Nevertheless we use here the convenience of sphericity to develop a model, recognizing that a fully quantitative model requires more detail. Extant analytical models

describe the kinetics of growth in this case as controlled only by the rate at which crystallizable molecules are delivered by diffusion to the surface of the sphere. Like the accretion of molecules to embryonic crystals, the growth of a sphere is likewise a stepwise process, with molecules joining and leaving the surface at a rate q_0 . The growth of a sphere of pure B in a random melt of A and B molecules at initial concentration c_0 is a classical problem in diffusion theory. A solution is known for the case in which the rate of growth is given by the rate at which B molecules arrive at the surface [13,14] Here the radial growth is parabolic in time:

$$r = A\sqrt{Dt} \tag{4}$$

where A is a constant, containing c_0 and c_i , the concentration of solute in the melt at the interface (assumed to be the thermodynamically equilibrium concentration). Importantly, (4) holds also for spheroidal particles of any eccentricity [14]. The time τ_D for a sphere to grow to the size of a critical embryo is then

$$\tau_D = \frac{r_c^2}{A^2 D} \tag{5}$$

Since both nucleation and growth processes represent the stepwise accretion of molecules to a growing body, the time τ to grow an embryo to size r must be a combination of τ_n and τ_D (something near $\tau_n + \tau_D$).

It is instructive to consider the temperature dependence of τ_D . Using (2) and the temperature dependence of D in (5),

Table 1
Values of Q and T used.

Polymer	Q kJ/mol	T_m °K
PE	4.7 [15]	417 [16]
iPS	90 [13]	516 [14]
PLLA	75 [17]	453 [15]

$$\left(\frac{1}{\Delta T}\right)^2 e^{\frac{Q}{RT}} \text{ vs. } T$$

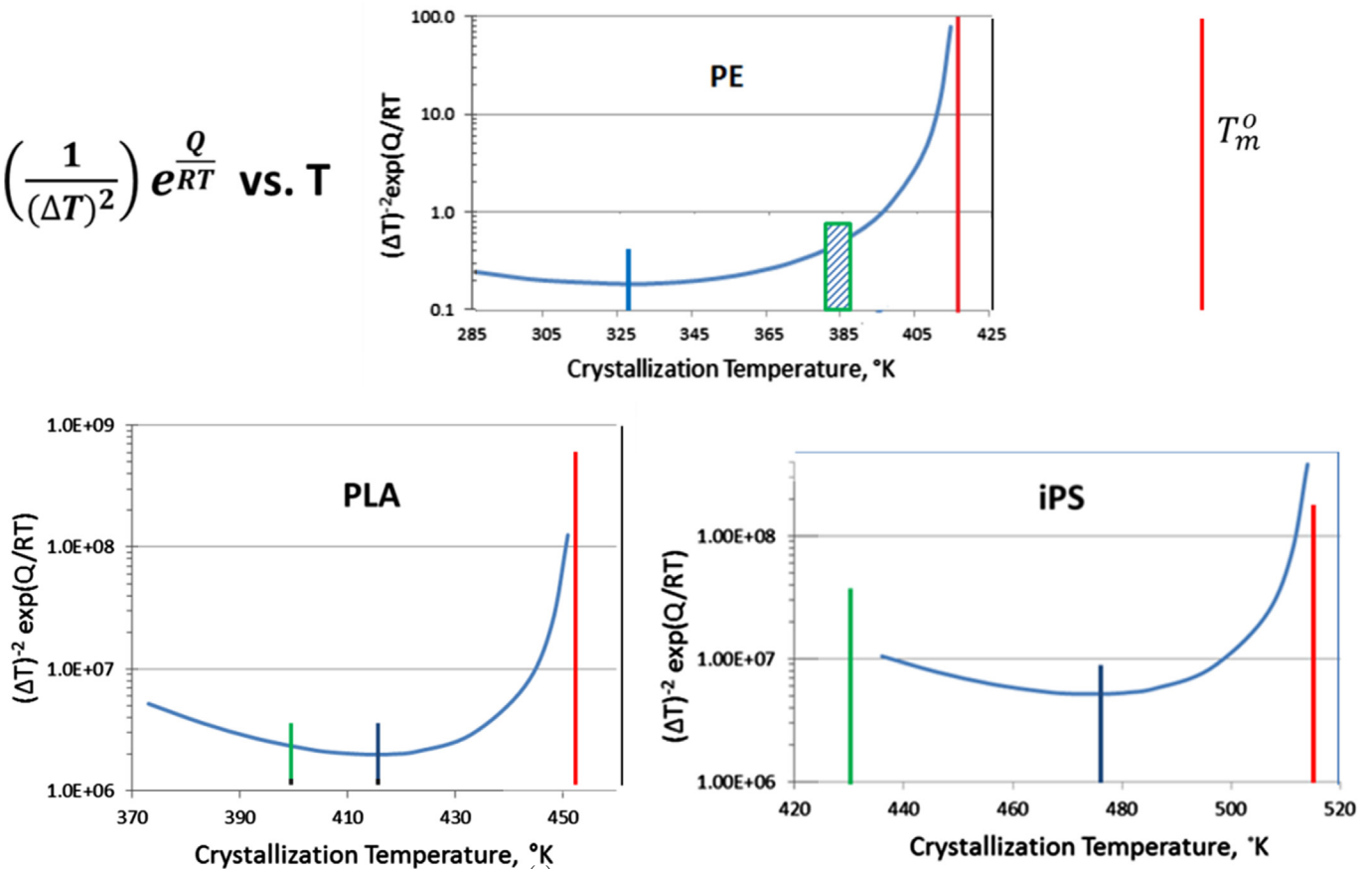


Fig. 1. $\frac{\exp(\frac{Q}{RT})}{(\Delta T)^2}$ vs. T for blends containing PE, PLA, and iPS.

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