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Homogeneous Crystallization of Poly(Ethylene Oxide) Confined to Droplets: The Dependence of the Crystal Nucleation Rate on Length Scale and Temperature

Michael V. Massa and Kari Dalnoki-Veress*

Department of Physics & Astronomy and the Brockhouse Institute for Materials Research, McMaster University,
Hamilton, Ontario, Canada L8S 4M1

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We present a study of homogeneous nucleation in polymer crystallization. Crystal nucleation is observed within discrete droplets of poly(ethylene oxide) that are formed by the dewetting of a thin film. The samples provide an ensemble of impurity-free droplets, with length scales that can easily be measured. Droplet crystallization is found in two distinct temperature regimes corresponding to homogeneous and heterogeneous nucleation. Here we focus on homogeneous nucleation and show that the nucleation rate scales with the volume of the crystallizable domain, indicating that we are observing homogeneous nucleation in the bulk of the droplets. In addition, the dependence of the nucleation rate on temperature is consistent with classical nucleation theory.

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It is perhaps surprising that macromolecules like polymers, which are long amorphous chains in the melt, have the ability to crystallize. Because of the large conformational entropic barrier to obtaining a crystal array of fully extended chains, crystallizable polymers typically compromise by forming a *semicrystalline* state. The chains fold back and forth to form crystalline lamellae separated by amorphous layers which contain most of the defects of the system. The lamellae often self-assemble into spherulites—large (μm's to mm's) spherical superstructures—in which the lamellar sheets grow out from the center [1,2].

Currently there is much interest and fruitful debate about the existence of a precursor to crystallization and the exact mechanism by which the crystals nucleate (for a current review, see [2] and a series of articles [3–6]). The interest in the initial stages of crystal formation transcends the field of polymer science with current studies being carried out on a range of systems, proteins [7], water [8], and colloids [9] being a few examples. The nucleation rate can affect the total crystalline content in the semicrystalline material and the size of the spherulites. This in turn affects properties such as material strength, optical clarity, and the processability of the polymer. Typically, *heterogeneous nucleation* is observed whereby nucleation occurs at defects inherent in the sample. However, under certain unique conditions it is also possible to observe *homogeneous nucleation* or self-nucleation—a fundamental process that is spontaneous and intrinsic to the material itself. It is homogeneous crystal nucleation that we focus on in this Letter. Specifically we aim to address the dependence of the nucleation rate on the crystallization temperature and on the length scale of the sample.

The difficulty in studying the nucleation rate is that it is not easily accessible in bulk measurements. The *crystallization rate* is dependent on *both* the nucleation rate and the growth rate of existing crystals. Few experiments probe these two aspects independently. The first crystal nucleation experiments were carried out by Vonnegut on tin [10]. This same approach was later used by others to study metallic and also organic systems [11–14]. The principle of Vonnegut's approach is both simple and elegant: Small droplets of the crystallizable material are dispersed into an immiscible matrix, providing an ensemble of simultaneous experiments. There are several aspects that make experiments like these ideal: (i) The only way for a droplet to crystallize is if a nucleation event has taken place in that compartment. (ii) If the number of droplets is larger than the number of defects, then some of the droplets *must* nucleate via a homogeneous nucleation event. (iii) For a small compartment the time scale for nucleation is much longer than the time it takes for the crystal to grow to the full size of the compartment. It is this *separation of the time scales* that makes the study of nucleation accessible.

More recently, the use of block copolymers has provided fascinating information on crystallization by confining the crystallizable block into microdomains [15–24]. In these samples large supercooling was required in order for the domains to crystallize, which was considered to occur homogeneously. Of great relevance to the work discussed here is the study by Reiter and co-workers who used atomic force microscopy (AFM) to *directly image* the crystalline domains of poly(ethylene oxide) (PEO) in an amorphous matrix [18].

In our work we combine the earlier approach of Vonnegut with the advantages of direct visualization of the crystallization by using dewetted samples (tiny droplets of PEO on a substrate). We have recently shown that this sample geometry provides an ideal system in which to study the fundamental properties of nucleation [25]. Because the droplets are all on the substrate plane, it is straightforward to study nucleation in these droplets using optical microscopy. Our previous work focused on demonstrating that it was possible to distinguish between homogeneous and heterogeneous nucleation. Here we show that (i) the homogeneous nucleation rate depends on the length scale of crystallizable compartments, (ii) this dependence indicates that homogeneous nucleation occurs in the bulk of the droplet rather than on the surface, and (iii) the dependence of the nucleation rate on temperature is consistent with classical nucleation theory [1].

Thin polystyrene (PS) films with thickness $h \sim 200$ nm were spincast out of toluene onto clean Si substrates ($M_w = 2\,100\,000$, $M_w/M_n = 1.16$). The Si-PS samples were annealed at 115 °C at a pressure of 10^{-6} Torr for 12 h to remove residual stress and solvent in the film. Subsequent films of PEO ($M_w = 27\,000$, $M_w/M_n = 1.09$, and $h \sim 70$ nm) were spincast out of acetonitrile onto the Si-PS substrates to provide a final Si-PS-PEO sample (polymer obtained from Polymer Source Inc., Canada). The samples were annealed in vacuum at 90 °C, which is below the glass transition temperature of the PS ($T_g = 98\,^\circ$C) yet above the observed melting temperature of the PEO ($T_m = 64\,^\circ$C). The PS film provides a reproducible and unfavorable interface from which the PEO dewets. After annealing for a long time (> 24 h) the samples consisted of small droplets (spherical caps) of PEO on the PS substrates that were not connected as verified by optical microscopy and AFM. Dewetting enables control over the distribution of droplet sizes by changing the PEO film thickness. After vacuum annealing, the sample was transferred to a microscope heating stage flushed with argon.

In Fig. 1 we show a typical image taken with optical microscopy. Under nearly crossed polarizers it is possible to see both the amorphous droplets (dark) as well as the crystalline droplets (white). From a sequence of images we can obtain the time at which a specific droplet crystallizes, as well as the length scale of the droplet. More precisely, the contact angle of PEO droplets on PS is found to be $\theta = (20 \pm 1)^\circ$ with AFM, while the base area of the droplets is obtained with optical microscopy. From these measurements, and the assumption of the spherical cap, we can obtain the volume, V, of the droplets (even for droplets that are slightly ellipsoidal the assumption made contributes a negligible error). Because optical microscopy measurements provide the base area directly (i.e., the area of the PS/PEO interface), it is the base area, A, or the radius of the circular contact area, R, that is quoted to describe the "length scale" of the droplets. The use of a high resolution CCD camera ensures that we capture ~1000 droplets *simultaneously*, while still having enough resolution to measure A for each droplet. As we make clear in the following, the ability in the experiment to track a statistically relevant number of droplets of various sizes is crucial to the results and provides a powerful tool to study nucleation kinetics.

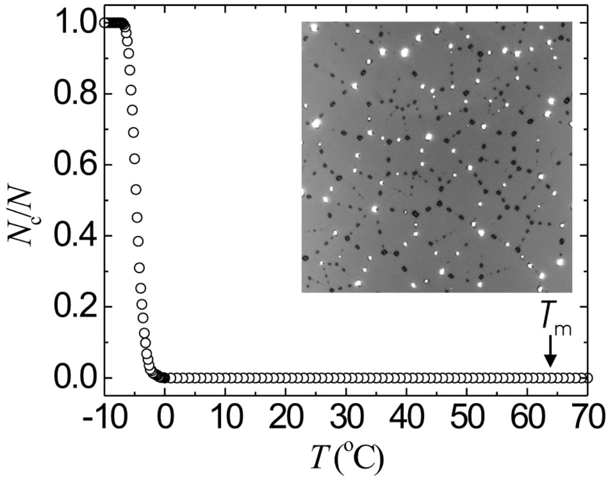

FIG. 1. Optical microscopy image of a small section of the sample (1000 μm wide) obtained at $T_c = -2.6\,^\circ$C. Amorphous droplets appear dark and semicrystalline droplets appear white under nearly crossed polarizers. The plot shows the fraction of crystallized droplets as a function of temperature upon cooling (0.4 °C/min) for homogeneous nucleation.

The results of a sequence of images obtained upon cooling are shown in Fig. 1, where we plot the fraction of crystallized droplets to the total number of droplets in view (N_c/N) as a function of temperature. The data shown are for a sample with droplets which have a base area ranging from $A = 200$ to 500 μm^2 (volume range: $V = 140$ to 560 μm^3). We see that as the sample is cooled below T_m, nothing happens until at a temperature of $\sim -2\,^\circ$C (i.e., $> 65\,^\circ$C below the melting temperature), *all* the droplets spontaneously nucleate. We ascribe this nucleation process to *homogeneous nucleation* where the sample is supercooled sufficiently so that the driving force to crystallization can overcome the *intrinsic* barrier to nucleation. We note that with care in the sample preparation all ~1000 droplets crystallized at $T \lesssim 0\,^\circ$C and no droplets crystallized at higher temperatures, indicative of heterogeneous nucleation [25]. In addition, there is no sample-to-sample variation in the temperature at which homogeneous nucleation occurs for droplets with this length scale (i.e., the peak in the nucleation rate dN_c/dt occurs at $T = -5\,^\circ$C). The dewetting process is crucial to achieving droplets that are free of defects because the dewetting process is *self-cleaning*: for the thick films used, holes form in the film preferentially at the same defects that would promote crystallization (*nucleated* rather than *spinodal* dewetting) and as a result the PEO dewets away from the defect.

The assertion of homogeneous nucleation can be strongly justified by the difference in the character of the two nucleation mechanisms. This difference can be illustrated by a unique analysis of the data which rules out the possibility of the low temperature nucleation being heterogeneous [25]. We have previously shown that a correlation plot, where the nucleation temperature of a droplet during a cooling run is plotted against that of a subsequent run, can be used to conclusively determine if the nucleation process is homogeneous or heterogeneous. For homogeneous nucleation, the data are not correlated in subsequent cooling cycles, which is to be expected: Since the homogeneous nucleation barrier is intrinsic to the PEO, there is an equal probability of a nucleation event for each droplet, *provided that the volume of the droplets is equal.* The data discussed here are all of homogeneous character as determined by correlation plots described in [25].

Having established that the nucleation data shown in Fig. 1 is homogeneous, we shift to the main focus of this Letter: the dependence of nucleation on the droplet length scale R. The assumption that the volume of each droplet is equivalent is not quite right, since Fig. 1 reports on the homogeneous crystallization of droplets with a *range* of base areas. Correlation plots reveal that when the droplets are binned in groups according to the base area, large droplets nucleate faster than the small droplets. This is to be expected—a larger droplet has greater volume and hence a higher probability of a nucleation event than a small one.

The length-scale dependence is an important issue since it is not clear if the homogeneous nucleation is susceptible to finite-size effects. Isothermal crystallization experiments were carried out on samples which exhibit homogeneous nucleation. For droplets with *identical volume* which nucleate homogeneously (i.e., an activated process) we write the change in the uncrystallized fraction with time as

$$\frac{d}{dt}\left(\frac{N_a}{N}\right) = -P\left(\frac{N_a}{N}\right) = -\frac{1}{\tau}\left(\frac{N_a}{N}\right); \tag{1}$$

where N_a is the number of amorphous droplets, P is the probability per unit time of having a nucleation event, and τ is the time constant associated with nucleation events (P and τ have a length-scale dependence which is to be determined below). From this we obtain $N_a/N = \exp(-t/\tau)$.

In Fig. 2 we plot the logarithm of the uncrystallized fraction as a function of time for the droplets binned according to their base area. It should be noted that in this sample there are ~1500 droplets visible with various length scales. The data are fit well by straight lines with a slope of $-1/\tau$, and it is clear that small droplets nucleate much more slowly than do the large droplets.

The crucial question regarding length scale is how the time constant scales with the size of the droplets: if $\tau \sim R^{-n}$, what is n? We might expect the following two possibilities: if $n = 2$, then nucleation is surface dependent; however, if $n = 3$, then we observe *homogeneous bulk nucleation.* The scaling of τ with the length scale R of the droplets is shown in Fig. 3.

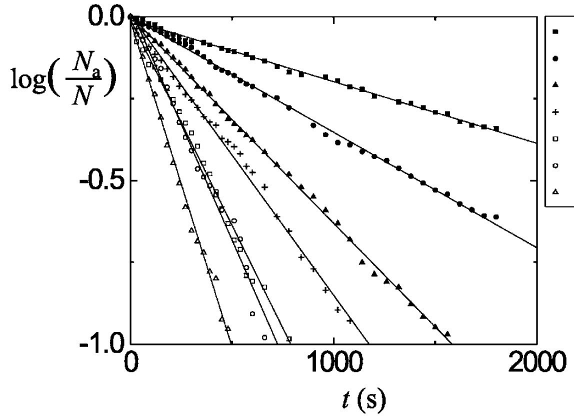

FIG. 2. Plot of the logarithm of the *uncrystallized fraction* as a function of time for the isothermal *homogeneous* crystallization of droplets at $T = -5\,^\circ$C. The data have been binned according to the base area of the droplets. The center of the bin range for the data sets is indicated in the legend [bin range: (44, 50, 75, 100, 125, 150, 175, 225) μm^2].

It is immediately clear from the logarithmic plot that the *time constant depends on the volume of the droplet* and not on the surface area. A fit to the data reveals that $\tau \sim R^{-(3.2\pm0.3)}$ and that we observe homogeneous bulk nucleation. The result, though new, is to be expected: a droplet with twice the volume is twice as likely to nucleate in a given amount of time.

In Fig. 4 we plot the time constant normalized by the volume, V, of the droplets as a function of temperature.

As expected from the scaling $\tau \sim R^{-3}$, droplets of different volumes have the same value of τV. The normalized time constant decreases with increased supercooling, which reflects the simple fact that the larger the

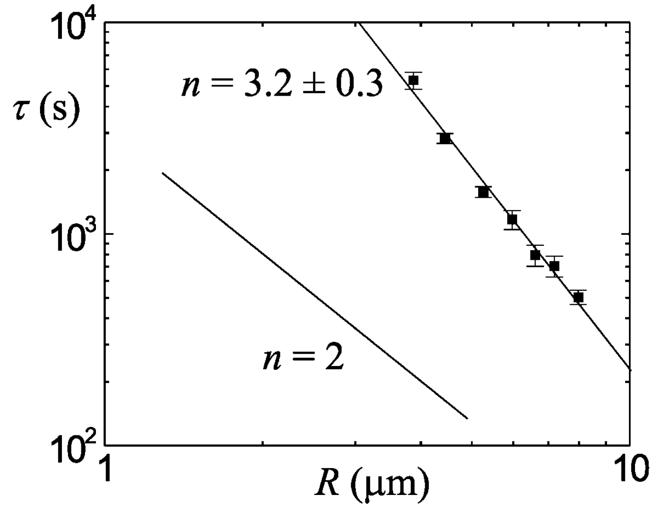

FIG. 3. Logarithmic plot of the time constant for the crystal nucleation of droplets as a function of the length scale of the droplets. The dependence of the time constant follows a power law: $\tau \sim R^{-n}$, where $n = 3.2 \pm 0.3$.

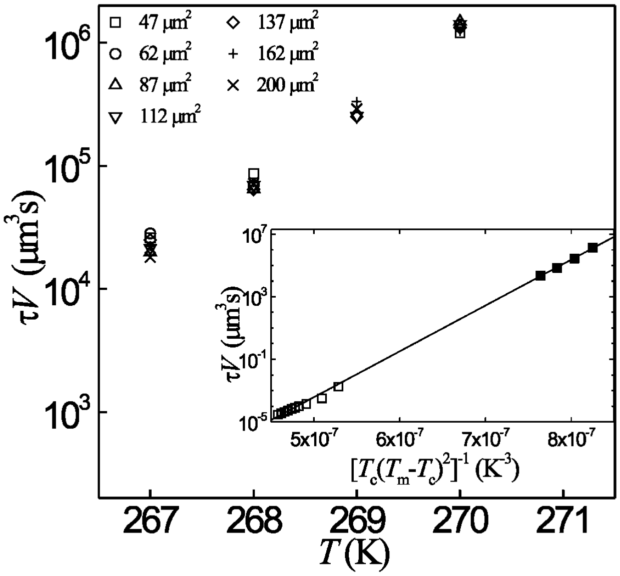

FIG. 4. Semilogarithmic plot of the volume-normalized time constant, τV, as a function of temperature. The data show a linear dependence when τV is plotted as a function of $1/[T_c(T_m - T_c)^2]$ as is expected from classical nucleation theory (see the inset). A fit to the averaged dewetted droplet data (solid symbols) is in remarkable agreement with the data from [19] (open symbols).

driving force to nucleation, the faster the process. It is often stated that if nucleation is observed at a low temperature, then any higher temperature nucleation must be heterogeneous. This is not the case. A most extreme example is obtained in comparison with the work by Reiter and co-workers [18,19]. The authors studied nucleation in spheres of PEO that were 12 nm in diameter at significantly lower temperatures (~ −25 °C) than where homogeneous nucleation occurs in dewetted droplets (~ −5 °C). The crystallizable volume plays a crucial role in determining the nucleation rate when the volume is small. In the inset to Fig. 4 is shown a semilogarithmic plot of τV for both the dewetted droplets as well as the diblock data [19] as a function of $1/[T_c(T_m - T_c)^2]$. Classical nucleation theory predicts a straight line on such a plot over a small temperature range [1]. It is remarkable that a best fit line to the droplet data, when extrapolated by ~8 orders of magnitude in τV, is in close agreement with the data for diblocks—*consistent with the interpretation* that nucleation is not affected down to length scales of ~10 nm. It is also important to note that this agreement is obtained for two very different systems, which suggests that it is the bulk of the domains which dominate nucleation for both cases.

The data presented in this Letter are the result of a unique sample geometry of dewetted crystallizable droplets. Each droplet acts as its own nucleation experiment. The ability to measure the volume of each droplet and the time at which it nucleates for a statistically relevant ensemble enables detailed studies of the nucleation process. We have shown that homogeneous nucleation can be observed and that fundamental properties can be easily studied in this system. A broad distribution of droplet volumes facilitates the measurement of the dependence of the nucleation rate on the length scale of the droplets. We find that the probability of nucleation depends on the *volume* of the droplets, which indicates that *homogeneous bulk nucleation* is observed rather than surface nucleation. Furthermore, we have investigated the nucleation rate as a function of the crystallization temperature and find that the temperature dependence is consistent with classical nucleation theory. The sample geometry and analysis presented provides a tool with which it is possible to study various aspects of the nucleation of crystallization.

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*Electronic address: dalnoki@mcmaster.ca

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