

## Confinement Effects in Polymer Crystal Nucleation from the Bulk to Few-Chain Systems

Michael V. Massa, Jessica L. Carvalho, and Kari Dalnoki-Veress\*

*Department of Physics and Astronomy and the Brockhouse Institute for Materials Research, McMaster University,  
Hamilton, ON, Canada*

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We have studied crystallization in poly(ethylene oxide) droplets with volumes ranging over several orders of magnitude. In all samples, homogeneous nucleation is observed, scaling with the volume of the droplet, down to systems with as few as  $\sim 10$  polymer chains. Surprisingly, nucleation is unaffected by the high degree of confinement, despite a large surface-to-volume ratio and the restriction of chains to length scales much smaller than the radius of gyration. Nucleation was also found to be independent of chain length for two molecular weights studied, differing by an order of magnitude. The results suggest that, for these highly supercooled systems, the formation of a nucleus is influenced by its immediate surroundings and does not depend on the entire length of the constituent chains.

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The phase transition from a supercooled liquid into a crystalline solid begins with the formation of a nucleus. Spontaneous fluctuations give rise to solidlike regions which remain unstable unless they exceed a critical size, enabling them to overcome the unfavorable interfacial energy. For simple liquids, the nucleus is thought to have a simple shape, and, once the activation barrier is surmounted, the stable crystal phase will continue to grow. In contrast, both the structure and the growth of a nucleus are significantly different when the supercooled liquid is a polymer melt. Kinetic constraints prevent the long-chain molecules from forming extended-chain crystals; rather, the nucleus comprises a region of mutually oriented, short-chain segments which are bounded by surfaces containing chain folds and other crystal defects [1]. Development of this anisotropic nucleus is highly impeded at the fold surfaces and effectively restricts the crystal growth to two dimensions.

Perhaps the most interesting distinction from crystallization of simple liquids is that a single polymer molecule can itself form a crystal. Experimentally, single-chain single crystals have been observed using very dilute solutions [2–5]. Theoretical work has investigated the equilibrium structures of single- and few-chain crystals [6–8], and simulations have demonstrated the ability of single polymer chains to undergo crystallization [6,9]. Muthukumar has shown that a sufficiently long polymer chain can support the initial formation of multiple nuclei [6]. At later stages, the dissolution of some of these nuclei and the aggregation of the remaining crystallites results in single-chain crystals. Nucleation in single-molecule solutions was also studied by Wu *et al.*, as a function of chain length [9]. Their simulation results were supported by a simple free energy model wherein the activation barrier for crystallization was found to be independent of chain length.

While it is known that properties such as chain diffusion, viscosity, and crystal growth rates depend on the size of the

polymer chains, relatively few experiments have investigated the role of molecular weight in crystal nucleation [10,11]. Kraack *et al.* [10] found that homogeneous nucleation in *n*-alkanes exhibited a chain-length dependence which could be extrapolated to data for high molecular weight polyethylene [11]. However, as the molecular weight increased, nucleation became essentially independent of chain length.

In this Letter, we investigate the role of system size on crystal nucleation in polymer melts, as the sample volume is reduced from macroscopic length scales down to droplet sizes approaching that of a single polymer chain. Based on the method developed by Vonnegut and employed by others [10–19], we study the nucleation rate in isolated droplets which are formed by dewetting a thin film on an unfavorable substrate. With this sample geometry, we observe homogeneous nucleation (an intrinsic property of the material) and have previously demonstrated that for bulk samples the homogeneous nucleation rate scales with the volume of the droplets [20]. We extend this study to much smaller droplet sizes in order to investigate finite size effects on nucleation, for a range of molecular weights. As the sample size is reduced, the surface-to-volume ratio increases and chains become confined to droplets smaller than the radius of gyration, both of which may result in deviations from the behavior observed in bulk. Using ellipsometry as a novel probe of crystallization, we are able to observe homogeneous nucleation in droplets which contain as few as  $\sim 10$  polymer chains.

Polystyrene (PS) films were spincoated from toluene solutions onto clean Si substrates ( $M_w = 2100$  kg/mol,  $M_w/M_n = 1.16$ ), providing a reproducible and unfavorable interface from which poly(ethylene oxide) (PEO) dewets. PEO films of two different molecular weights ( $M_w = 370$  kg/mol,  $M_w/M_n = 1.06$  and  $M_w = 27$  kg/mol,  $M_w/M_n = 1.06$ ) were spincoated from acetonitrile solutions directly onto the PS substrates. All polymer was obtained from Polymer Source, Inc. (Dorval, Canada).

Samples were annealed in vacuum for at least 24 hours (thicker films were left for several days to ensure that the films were completely dewetted). PEO film thicknesses ranged from 70 nm down to a few nanometers, which gave a range in droplet volumes from  $10^2 \mu\text{m}^3$  down to less than  $10^{-4} \mu\text{m}^3$ . This means that, for the 370 kg/mol PEO, we are able to compare homogeneous nucleation in systems with  $>10^7$  chains down to  $\sim 10$  chains.

Ellipsometry is a technique which measures changes in the polarization of light upon reflection from (or transmission through) a material. It is typically applied to the study of thin films, where changes in polarization can be related to the film thickness and refractive index. However, the droplet sample geometry precludes the standard use of ellipsometry. We instead employ ellipsometry as a sensitive probe for the crystallization of droplets, where the densification and the anisotropic structure produce a measurable change in the polarization. Measurements were conducted with a homebuilt, single wavelength (632.8 nm) self-nulling ellipsometer, in a dry nitrogen atmosphere. Laser light was reflected off of a  $\approx 3 \text{ mm}^2$  spot on the samples, which was large enough to contain a good statistical representation of the droplet ensemble. Samples were annealed for 20 minutes at  $80^\circ\text{C}$  (well above the observed melting temperature) and subsequently cooled at  $2^\circ\text{C}/\text{min}$  to  $-40^\circ\text{C}$ .

Crystallization was observed through changes in the angles of the ellipsometer's polarizer and analyzer as shown in Fig. 1. Crystallization is identified by a sharp change against the gradual background changes (due to thermal contraction of the PS substrate and the PEO droplets). The crystallization temperature  $T_c$  is assigned to the midpoint of the transition for each sample. Droplet volumes were calculated by measuring their base area, using optical microscopy or noncontact atomic force microscopy (AFM) [Fig. 2(a)], and assuming the droplets to be spherical caps with the measured contact angle ( $25^\circ \pm 3^\circ$ ).

A comparison with optical microscopy cooling experiments showed that the midpoint of the transition observed by ellipsometry coincided with the crystallization of half the total volume of the sample. Direct visualization further enabled the droplet distribution to be binned according to volume (see Ref. [20]), making it possible to identify the

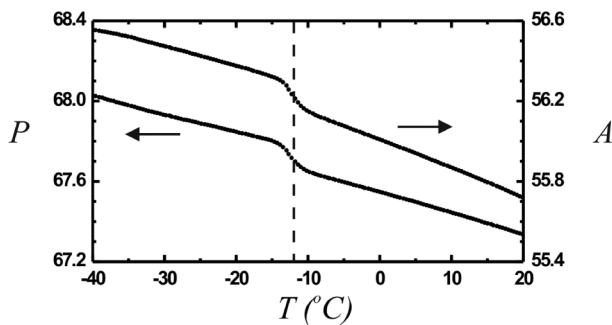


FIG. 1. Polarizer  $P$  and analyzer  $A$  angles as a function of temperature.  $T_c$  is indicated by the vertical dashed line.

ensemble midpoint with that of a specific droplet volume. It was found that a weighted average  $V = (\sum v_i^2/N)^{1/2}$  provided good agreement with all samples that were studied using optical microscopy.

In order to gain some insight into the role of system size on nucleation, the average droplet volume of a sample is plotted against the observed crystallization temperature in Fig. 3(a). We find that  $T_c$  decreases smoothly with  $V$ , indicating a simple dependence of nucleation on the droplet volume.

We have previously shown that the droplets nucleate homogeneously [20]; the data suggest that homogeneous nucleation is observed over more than 6 orders of magnitude in droplet volume. The dewetted droplet sample geometry has the advantage of providing access to a larger range of length scales than that available in block copolymer systems [15–17] or polymer blends [18,19]. Furthermore, the sensitivity of ellipsometry makes it possible to monitor the crystallization in a sample with as little as  $\sim 10^{-9}$  liters of material, which itself is divided into millions of droplets.

Data for both the 27 and the 370 kg/mol PEOs are presented in Fig. 3(a). Over the entire range in droplet volumes, both molecular weights were found to crystallize at the same  $T_c$ , within the scatter of the data. For comparison, crystallization measurements were also made on diblock copolymer films, where PEO is the minority component and forms spheres within a polybutadiene (PB) matrix [21]. Two block lengths were studied (PEO-PB molecular weights: 4.5–26 and 6.8–26 kg/mol), and the results are shown as triangles in Fig. 3(a). These data also fall onto the same curve as the homopolymer data. We emphasize that changing the  $M_w$  from a 370 kg/mol homopolymer to a 4.5 kg/mol diblock segment has no effect on the nucleation rate.

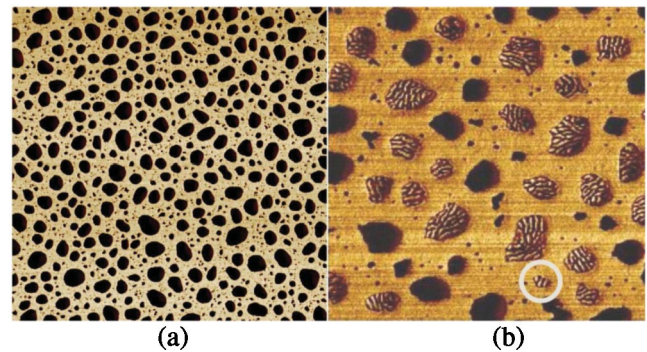


FIG. 2 (color). Typical AFM phase images of PEO droplets. (a) The difference in the damping associated with the molten PEO and the glassy PS makes it possible to clearly measure the base area of each droplet, in order to obtain the droplet volume ( $8 \mu\text{m} \times 8 \mu\text{m}$ ). (b) The partially crystallized sample clearly shows the lamellar structure within the droplets. Even in droplets which contain  $\sim 10$  chains (shown in the white circle), ordered lamellae are observed ( $1.25 \mu\text{m} \times 1.25 \mu\text{m}$ ).

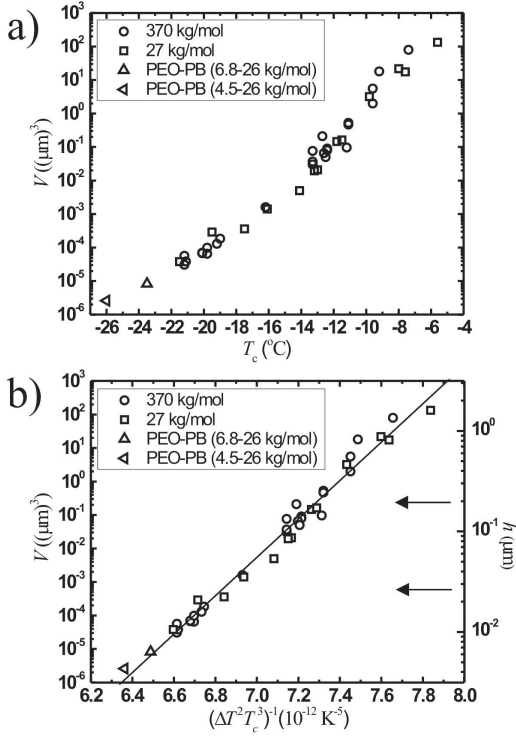


FIG. 3. (a) Relationship between droplet volume and crystallization temperature. (b) Droplet volume as a function of  $[\Delta T^2 T_c^3]^{-1}$ . The average droplet height is indicated on the right axis, with arrows identifying the length scale  $2R_G$  for the two homopolymers investigated.

From classical nucleation theory, the homogeneous nucleation rate has a complex relationship with the crystallization temperature. The activation barrier to nucleation is expressed in terms of the degree of supercooling below the melting temperature:  $\Delta F \propto \Delta T^{-2} = (T_m^0 - T_c)^{-2}$ . Furthermore, corrections for the enthalpy of fusion far below  $T_m^0$  give an additional temperature dependence of  $(T_c/T_m^0)^{-2}$  to the activation barrier [22]. The homogeneous nucleation rate for an ensemble of droplets of volume  $V$  is

$$I = VI_0 \exp\left(-\frac{C}{\Delta T^2 T_c^3}\right), \quad (1)$$

where  $C$  is related to the activation barrier.

The droplet volume has been plotted as a function of  $[\Delta T^2 T_c^3]^{-1}$  in Fig. 3(b). Here it is assumed that at the crystallization midpoint, where  $T_c$  is assigned, the nucleation rate  $I$  is approximately the same for all samples. The data for all samples fits a single straight line over the entire range in droplet volumes, in agreement with Eq. (1). This result implies that the nucleation process is the same throughout all of the droplet sizes and for all molecular weights studied. AFM images of crystallized droplets further support this finding. Remarkably, the droplets in Fig. 2(b) clearly show a lamellar morphology, as is observed in bulk crystallization, even when the system contains only  $\sim 10$  chains.

There are a number of other important implications to note from the results in Fig. 3(b). (i) The volume dependence of homogeneous nucleation persists throughout all samples: This reflects the fact that the probability of having a homogeneous nucleation event scales with the volume. Although the surface-to-volume ratio increases by more than 4 orders of magnitude, crystallization in even the smallest block copolymer system is initiated by homogeneous nucleation in the bulk of the domains. If a transition to predominantly surface-nucleated crystallization occurred below some critical size, the data would show a crossover to scale with the droplet surface, leading to a reduction in the slope by a factor of  $2/3$ . Therefore, even in samples where the average droplet contains only  $\sim 10$  chains, the probability of nucleation depends on the amount of material available and is not influenced by the interface. (ii) No chain confinement effects are observed: When a polymer chain is restricted to length scales that are comparable to, or less than, the space pervaded by a molecule in the bulk ( $\sim 2R_G$ ), the confinement can lead to anomalous behavior. Chain confinement could then lead to a change in the nucleation rate, the onset of which would occur when the size of the droplet becomes comparable to the pervaded volume of the chain. The right axis in Fig. 3(b) indicates the height of the droplets ( $h$ ), with arrows identifying the point at which  $h \approx 2R_G$ , for each of the homopolymers [23]. The data show no deviation from the straight line trend, indicating that chain confinement has no discernible effect on nucleation. (iii) Nucleation exhibits no molecular weight dependence: The data fall onto a single straight line for all molecular weights, indicating that the nucleation rate does not depend on the chain length. Even for the block copolymer samples, no difference in nucleation rate is observed over almost 2 orders of magnitude in  $M$ . This implies that both the activation barrier for nucleation (related to  $C$ ) and the kinetic prefactor ( $I_0$ ) which accounts for the polymer mobility do not depend on the molecular weight for the homogeneous nucleation observed in this study. This is perhaps surprising given that the viscosity changes by more than 6 orders of magnitude for this range of molecular weight.

An important point in comparing nucleation data between different molecular weights is the choice of the melting temperature in determining the degree of supercooling. The driving force for crystallization depends on how far below the melting temperature the system is cooled. The equilibrium melting temperature of fully extended-chain crystals  $T_m$  is often used to define the supercooling [11]. However, a melting point depression arises due to the finite thickness of the crystal, which leads to a molecular-weight-dependent melting temperature. For the two homopolymers in this study,  $T_m$  would differ by  $4\text{--}5^\circ\text{C}$  [24]. The data presented in Fig. 3(b) use instead a single melting temperature to define the supercooling among the different molecular weights. The equilibrium melting temperature for a perfect crystal of infinite molecular weight  $T_m^0$  is the appropriate parameter [1]. The use

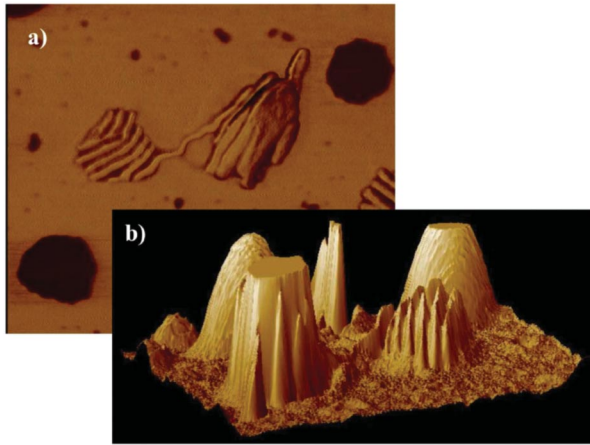


FIG. 4 (color). AFM image showing the rare event where the crystallization of a droplet induces the crystallization of a nearby neighbor. (a) The phase image clearly shows stacked lamellae (image width  $1 \mu\text{m}$ ). (b) 3D rendering of the topography image. Note that the two droplets in the background [black in (a)] are still molten and, hence, rounded.

of  $T_m^0$  in the supercooling makes intuitive sense:  $T_m^0$  reflects the strength of the monomer-monomer interactions that drive the spontaneous formation of a nucleus, which is common to all molecular weights of a polymer species.

The independence of nucleation on molecular weight suggests that the formation of a nucleus is sensitive only to its local environment, which does not extend over length scales comparable to entire chains. A critical molecular weight  $M^*$  could be assigned, whose pervaded volume corresponds to the range of the surrounding melt which affects the formation of a nucleus. For polymers larger than  $M^*$ , no chain-length dependence would be exhibited, while for smaller chains the molecular weight would become important. The size of the local environment should depend on the size of the nucleus, which, in turn, depends on the degree of supercooling. It is possible that for moderate supercoolings (heterogeneous nucleation), where the nucleus is expected to be large, the kinetics could depend on the chain size [10,11]. However, for the low crystallization temperatures observed in this study ( $\Delta T > 80^\circ\text{C}$ ), homogeneous nucleation is unaffected by changes in the molecular weight. This suggests that the local neighborhood is smaller than the pervaded volume of the smallest chain size investigated.

It should be noted that the results of this study provide some insight into the nucleation process, which may differ significantly from the growth kinetics in confined systems [25]. However, it is clear from Fig. 4 that, at the very least, lamellae are the prevailing crystalline structure in these confined systems.

The results presented in this Letter are the first to show the length scale dependence of homogeneous nucleation in

droplets ranging over 6 orders of magnitude in volume. We find that the nucleation rate scales with the volume of the droplets for all samples. No deviations in behavior were observed, despite a large change in the surface-to-volume ratio and the confinement of chains to length scales smaller than  $R_G$ . Finally, the nucleation rate was independent of molecular weight over almost 2 orders of magnitude and even chain architecture (homopolymer or diblock).

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\*Electronic address: dalnoki@mcmaster.ca

- [1] L. Mandelkern, *Crystallization of Polymers* (Cambridge University, New York, 2002).
- [2] H. Bittiger and E. Husemann, *Makromol. Chem.* **96**, 92 (1966).
- [3] H. Bu *et al.*, *J. Polym. Sci., Part B: Polym. Phys.* **29**, 139 (1991); **32**, 1351 (1994).
- [4] J. Cao *et al.*, *Macromol. Symp.* **124**, 89 (1997).
- [5] F. Y. Su *et al.*, *Polymer* **22**, 5379 (1998).
- [6] M. Muthukumar, *Phil. Trans. R. Soc. A* **361**, 539 (2003).
- [7] J.-U. Sommer, *Eur. Phys. J. E* **19**, 413 (2006).
- [8] B. Crist, *Macromolecules* **39**, 1971 (2006).
- [9] W. Hu, D. Frenkel, and V.B.F. Mathot, *Macromolecules* **36**, 8178 (2003).
- [10] H. Kraack, M. Deutsch, and E. B. Sirota, *Macromolecules* **33**, 6174 (2000).
- [11] G.S. Ross and L.J. Frolen, *J. Res. Natl. Bur. Stand. Sect. A* **79**, 701 (1975).
- [12] B. Vonnegut, *J. Colloid Sci.* **3**, 563 (1948).
- [13] D. Turnbull and R.L. Cormia, *J. Chem. Phys.* **34**, 820 (1961); R.L. Cormia, F.P. Price, and D. Turnbull, *J. Chem. Phys.* **37**, 1333 (1962).
- [14] J. A. Koutsky *et al.*, *J. Appl. Phys.* **38**, 1832 (1967).
- [15] Y.-L. Loo, R. A. Register, and A. J. Ryan, *Phys. Rev. Lett.* **84**, 4120 (2000).
- [16] G. Reiter *et al.*, *Phys. Rev. Lett.* **87**, 226101 (2001).
- [17] H.-L. Chen *et al.*, *Macromolecules* **34**, 6936 (2001).
- [18] M.L. Arnal *et al.*, *Macromol. Chem. Phys.* **201**, 2493 (2000).
- [19] A. Taden and K. Landfester, *Macromolecules* **36**, 4037 (2003).
- [20] M. V. Massa and K. Dalnoki-Veress, *Phys. Rev. Lett.* **92**, 255509 (2004).
- [21] J. Carvalho, M.V. Massa, and K. Dalnoki-Veress, *J. Polym. Sci., Part B: Polym. Phys.* (to be published).
- [22] J.D. Hoffman, *J. Chem. Phys.* **29**, 1192 (1958).
- [23] *Physical Properties of Polymers Handbook*, edited by J.E. Mark (American Institute of Physics, New York, 1996).
- [24] G. C. Alfonso and T. P. Russell, *Macromolecules* **19**, 1143 (1986).
- [25] G. Reiter and J.-U. Sommer, *Phys. Rev. Lett.* **80**, 3771 (1998).