# Crystal Nucleation of Polymers Confined to Droplets: Memory Effects

**M. V. MASSA, M. S. M. LEE, K. DALNOKI-VERESS**

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

**ABSTRACT:** We study crystal nucleation within an ensemble of polyethylene droplets created through the dewetting of a thin film on an unfavorable substrate. In particular, we employ standard thermal treatment procedures to induce self-nucleation in samples to gain some insight into the nature of this enhanced crystallization. The novel sample-geometry enables the monitoring of each droplet throughout successive experiments, and hence the changes in their nucleation mechanism for various thermal treatments. We find a consistent self-nucleated crystallization temperature of $\sim 101$ °C under all conditions, suggesting uniformity in the centers which facilitate nucleation. Using correlation plots, we demonstrate that the observed melt-memory effects have a stochastic rather than deterministic nature; self-nucleation is a random process. © 2005 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 43: 3438–3443, 2005

**Keywords:** crystallization; heterogeneous; homogeneous; memory; nucleation; polyethylene (PE); seeding; self-nucleation

## INTRODUCTION

The mechanisms by which a melt of polymer chains of high conformational entropy transform into a low-entropy, semicrystalline state have long been studied.[1] Pioneering works of Vonnegut, Turnbull, and others[2–8] provided a way to decouple the nucleation of the crystal phase from its subsequent growth: By partitioning a material into many small, noninteracting droplets they were able to simultaneously observe the crystallization occurring independently in each domain. Since the crystallization of each droplet often resulted from a single nucleus, it was possible to determine rates of nucleation, crystallization temperatures, and surface energies. Early studies on metals,[2,3] alkanes,[5] and polymers[6–8] lead to

the distinction between different types of nucleation, based upon whether solidification was initiated from impurities within the polymer, at the interface due to droplet coatings, or intrinsically from the polymer itself, corresponding to homogeneous nucleation.

Much of today's research on polymer nucleation is still based upon the same principle; however, advancements in polymer science enable finer control over sample purity, domain sizes, and numbers. Many studies on crystallization within dispersed droplets from immiscible polymer blends,[9–13] mesophases of block copolymers,[14–24] and from the dewetting of thin films[25,26] exist. Reviews can be found in the literature, often focusing on a particular sample-geometry.[12–15]

Among the developments of recent nucleation studies is the demonstration that homogeneous nucleation depends upon the domain size in which the crystallization takes place. This outcome is largely due to the complementary length scales that naturally arise from the various sys-

tems mentioned: Droplets can range in size from micrometres for suspensions and blends, down to nanometres in block copolymer systems. Work on poly(ethylene oxide)[15,26] and polyethylene[14] has shown a straightforward dependence of homogeneous nucleation on domain size and temperature, which is consistent over as much as 30 °C in crystallization temperature, 4 orders of magnitude in domain dimension and 12 orders of magnitude in nucleation rate.

Since the nucleation kinetics can have significant impact upon the bulk properties and processability of polymer materials, methods which control nucleation (i.e., by adding nucleating agents, purifiers, etc.) are of great industrial relevance. One such technique, which can increase both the nucleation density and the crystallization temperature, is the controlled thermal treatment that leads to self-nucleation, or seeding, of the polymer. On the basis of observations that spherulite densities and crystallization temperatures could be affected by the melting temperature and duration prior to crystallization,[27,28] Blundell et al.,[29] conducted experiments in which polyethylene solutions, following a standard crystallization procedure, were dissolved at a self-nucleation temperature $T_s$, then subsequently crystallized. It was found that, depending on the value of $T_s$, the sample could undergo subsequent crystallization, which differed from that of a completely dissolved solution. The study showed that for $T_s > 97.5$ °C, an enhanced crystallization rate was observed, which decreased with increasing $T_s$, up to ~105 °C. At higher temperatures, the crystallization was identical to that of a well-annealed sample. For the lowest $T_s$ values, measurably larger sample volumes were also observed after crystallization (within the resolution of the experiment), indicating a reduction in the crystallinity of the sample.

The self-nucleation procedure was revisited by Fillon et al.,[30] who examined the crystallization kinetics and morphology of isotactic polypropylene. In addition to the changes in crystallization temperature brought on by self-nucleation, a corresponding increase in the nucleation density was observed. The authors also divided the range of temperatures into three domains: Self-nucleation was achievable over a narrow range of $T_s$ (about 4 °C). For higher $T_s$, samples retained no memory of prior crystallization, and the regular kinetics and morphology was observed. For lower $T_s$, residual crystal structure was annealed, as evidenced from a shift to higher melting temperature

and spherulite structure that coincided with the previous morphology.

Experiments controlling the thermal history of samples have since been applied to study nucleation in immiscible polymer blends,[9,10] block copolymer systems,[15,22,23] and bulk samples of neat polymer.[31] In the block copolymer systems, it was noted that the intermediate $T_s$ range, yielding self-nucleation, was not observed. This absence was attributed to the very small domain volumes in block copolymer systems, which hindered the memory from being retained and the detection of self-nucleation within an appreciable fraction of the domains.

In the present study we investigate the melt memory effects on crystal nucleation in an ensemble of dewetted droplets of polyethylene. Using our previous sample-geometry[25,26] we can readily observe the crystallization of each individual droplet, over successive experiments. With the use of a correlation plot (described below) we are able to demonstrate the statistical nature of self-nucleation, as revealed from variations in thermal history of the sample. By examining the effects of thermal history on the occurrence and the distribution of induced crystallization, we hope to gain some insight into the processes governing nucleation in polymer systems.

## EXPERIMENTAL

Moderate molecular weight ($M_w = 33$ kg/mol), monodisperse ($M_w/M_n = 1.04$) polyethylene (PE) was dissolved in hot toluene (~85 °C) for several hours to ensure that chains were melted (polymer was obtained from Polymer Source, Canada and prepared by hydrogenation of polybutadiene). Solutions were then filtered (0.2 $\mu$m pore size) to remove residual catalyst, and subsequently heated for at least one additional hour prior to spincasting. PE films were spincast onto freshly cleaved mica, and were transferred onto substrates using a water transfer technique. Films of polystyrene ($M_w = 2.12 \times 10^6$ g/mol) on Si were used as substrates in this study. The polystyrene film provides a reproducible and unfavorable substrate from which the polyethylene dewets. The trilayer samples (PE on PS on Si) were annealed in vacuum at 160 °C for at least 48 h, after which the samples consisted of an ensemble of droplets (spherical caps) of PE on PS. Although the annealing temperature is above the glass transition temperature for the polystyrene substrate,

the high molecular weight ensures a minimal deformation of the film under the PE droplets.

Measurements were conducted using a commercial hot stage (Linkam THMS-600) and monitored using an optical microscope with a CCD camera. Upon cooling, images were taken at regular intervals, with ~1300 droplets in the field of view. Using crossed polarizers, crystallization of a specific droplet was readily identified as the droplet brightened; consequently the time (and temperature) at which nucleation occurred in each droplet was obtained. At all times, samples were heated in an inert nitrogen atmosphere to minimize degradation of the polymer. The procedure to induce self-nucleation in PE droplets was performed as follows:

a. Erasure of prior thermal history by heating the sample at 160 °C for 20 min.
b. Creation of a standard thermal history by cooling down to 60 °C at 20 °C/min and holding for 1 min, which results in semicrystalline samples
c. Heating rapidly (20 °C/min) up to a self-nucleation temperature, $T_s$, where the sample is held for 20 min.
d. To minimize the variation in melting times between different $T_s$ runs, samples are quickly cooled to a well-defined starting temperature of 122 °C, at which point the cooling rate is reduced to 1 °C/min.
e. Allowing the system to thermally stabilize at the new cooling rate, data is acquired over the range of temperature from 120 °C to 60 °C.

The polyethylene used in this study was prepared by hydrogenation of polybutadiene, and it is expected that chains will contain ~8% 1,2- units along the PE backbone. While this leads to a slight reduction in the melting temperature from true linear polyethylene, several studies of crystal nucleation have been conducted on both hydrogenated polybutadiene[14,18] and linear polyethylenes[7,8] and thus provide a good comparison for our results.

## RESULTS AND DISCUSSION

In Figure 1 we show the results for two cooling runs where the sample was held at $T_s = 160$ °C for 20 min. It should be noted that steps (b) and (c) of our thermal treatment were omitted for



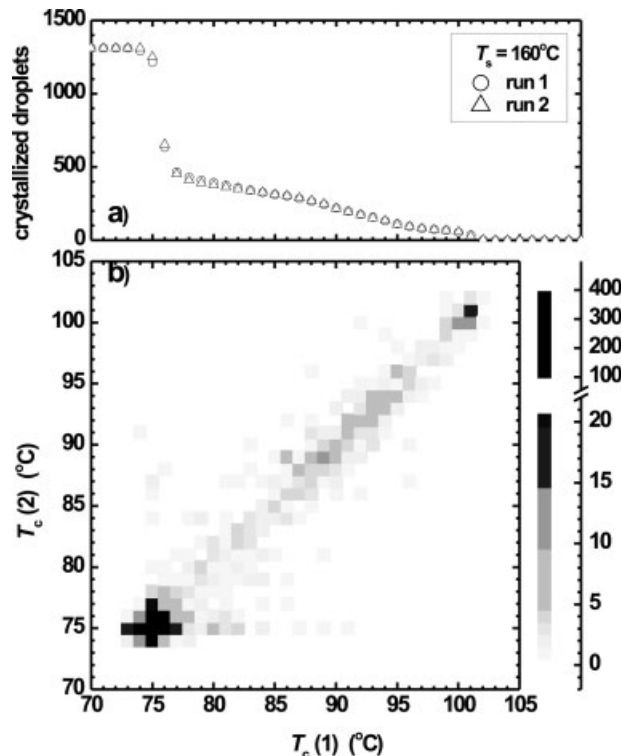**Figure 1.** Results for two cooling experiments for well-annealed sample conditions (160 °C for 20 min). (a) Crystallization upon cooling follows same profile in both experiments. (b) Correlation plot indicates that each droplet crystallizes at roughly the same temperature in both runs. Scale on right indicates number of droplets that crystallized at specific temperature coordinates ($T_c(1)$ and $T_c(2)$). The large number of droplets crystallizing at ~75 °C is consistent with homogeneous nucleation observed in other nucleation studies of polyethylene [7].

these two runs, to demonstrate that we do in fact erase prior thermal history in step (a). It is immediately clear from the overlap of the two data sets that the crystallization proceeds in the same fashion for both runs, indicating that there is no effect from prior thermal history. The sharp increase in crystallization at ~75 °C is consistent with homogeneous nucleation in polyethylene domains of similar volume found by Barham et al.,[8] which has since been related to the homogeneous nucleation observed in much smaller block copolymer systems.[14] Figure 1(b) shows a correlation plot for the two runs. Here, each data point corresponds to a specific single droplet in the sample, where we have plotted the temperature at which the droplet crystallized in the first experiment ($T_c^{(1)}$) against the crystallization temperature of the same droplet

in the following run ($T_c^{(2)}$). Correlation plots allow us to distinguish between homogeneous and heterogeneous (or self-) nucleation within each droplet[25,26]: For well-annealed samples, droplet crystallization, whether homogeneously or heterogeneously nucleated, generally results in small variation of $T_c$ over successive cooling experiments. The corresponding correlation plot would then show data concentrated along the diagonal (see Fig. 1b), with homogeneously nucleated droplets distributed over a narrow range of the lowest observed $T_c$, and heterogeneously nucleated droplets spread across higher temperatures according to the effectiveness of the nucleating agent or defect. Additionally, by observing the consistency of $T_c$ for each droplet subject to different thermal histories (i.e., changing $T_s$), we can gain insight into the nature of the self-nucleation process. From Figure 1 we can identify those droplets which nucleated homogeneously. In the following we exclude all heterogeneous droplets, thus ensuring that all the self-nucleation studies are performed on droplets with identical nucleation properties.

In typical self-nucleation experiments, crystallization will occur at higher temperatures if $T_s$ is decreased below some maximum self-nucleating temperature.[9,10,15,23,24,29,30] Figure 2 shows the fraction of crystallized droplets as a function of temperature for a series of cooling experiments with various $T_s$. For $T_s$ above 150 °C, no influence of thermal history is observed, and crystallization occurs as in a well-melted sample (Fig. 1). Enhanced nucleation is observed for $T_s$ between 140 °C and 150 °C, where a population of droplets is found to crystallize from 100 °C to 102 °C. The number of droplets containing self-nucleation centers is found to increase with decreasing $T_s$, and for $T_s = 140$ °C the entire sample crystallizes above 100 °C.

The enhanced crystallization exhibits qualitatively different behavior than what has been found in previous studies. The three $T_s$ domains first described by Fillon et al.[30] (melting, self-nucleation, and annealing) have been related to DSC melting endotherms, with self-nucleation occurring for $T_s$ just above the peak melting temperature—a result that is consistent with self-nucleation studies in block copolymer systems. However, DSC measurements of PE in the current investigation exhibited a melting peak at $T_m \sim 109$ °C, indicating that memory effects persist in the melt to temperatures as much as
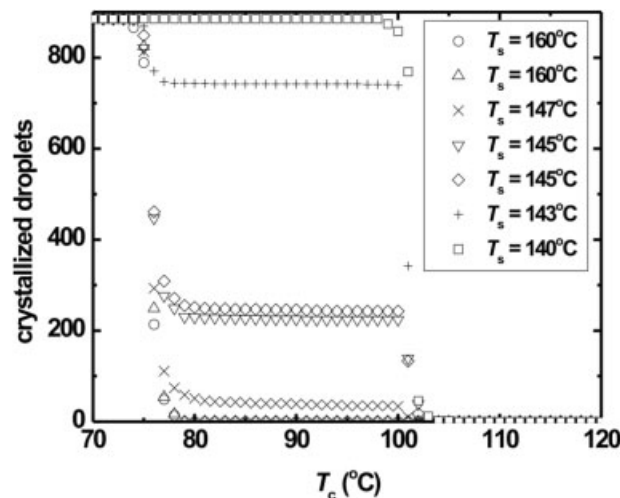


**Figure 2.** Cooling experiments for samples held for 20 min at various values of $T_s$. Homogeneous population is shown exclusively for clarity. Self-nucleation is observed at ~101 °C for $T_s < 150$ °C. The relative fraction of self-nucleated droplets is found to increase with decreasing $T_s$, until 140 °C, where all droplets crystallize at elevated temperatures.

40 °C above $T_m$. The much larger $\Delta T = T_s - T_m$ for which self-nucleation can be observed might be accounted for by differences in molecular weight, polydispersity, or confinement of the polymer chains, all of which could affect the chain mobility and hence the erasure of crystal memory.

Additionally, in contrast to previous experiments that show a continuous increase in $T_c$ as $T_s$ decreases,[9,10,15,23,24,29,30] we observed an enhanced crystallization that occurs consistently at ~101 °C for all values of $T_s$. This disparity is likely due to a difference in the cooling rates between experiments. In DSC measurements, high cooling rates (typically from 5 to 20 °C/min) can shift slow crystallization processes to lower apparent temperatures. The self-nucleated crystallization illustrated in Figure 2 is found to occur over a spread of 2–3 °C, or 2–3 min. Nucleation and growth rates with these time scales will result in temperature shifts of several degrees, with larger shifts occurring when fewer nucleation centers are available. The shifts in $T_c$ would correspond to changes in the number density of equally effective self-nucleation sites, rather than a fixed density of sites of varying strengths. Thus, the slow cooling rates used in our experiment enable us to separate nucleation events arising from different activation energies.

It has been suggested that self-nucleation centers result from small crystallites[15,30] or residual,

locally ordered regions[31] of a partially melted sample. It is not unreasonable to assume that these nucleation centers might form preferentially in regions where chains are more slowly reverted to isotropic melt. An alternative behavior for self-nucleation is that of a stochastic process. For an ensemble of identical droplets (same volume, interfacial area with substrate, and even number density of heterogeneities of equal effectiveness), there should be an equal probability for a self-nucleation process to occur within any particular domain in a particular experiment. Furthermore, between different experiments of identical thermal conditioning (same $T_s$ and time held at $T_s$), one expects the same fraction of active nucleation centers to be present, but their distribution throughout the ensemble should be random.

Using correlation plots we can test the nature of the observed self-nucleation, to determine which of these two behaviors best describes the memory effect. In Figure 2 there are two runs with $T_s = 145$ °C. Figure 3 shows a correlation plot of these two cooling experiments. The data separates into four distinct domains, where A corresponds to the population of droplets that have crystallized homogeneously in both cooling experiments; B and C indicate those droplets that nucleated homogeneously in the first (second) experiment, but were self-nucleated in the second (first); domain D corresponds to droplets that were self-nucleated in both cooling runs.

Consider first the situation where self-nucleation is facilitated at specific regions in the melt, perhaps local to an impurity within a droplet. Since there is a preference to the formation of a nucleation center, repeated experiments should show that the droplet containing this impurity consistently crystallizes at a higher temperature. Hence, the correlation plot would contain two populations: domain D, containing those droplets that crystallize via self-nucleation, and domain A, containing the remaining droplets, which lack such a preference. However, if the thermal treatment gives rise to nucleation centers in a random fashion, it is expected that between successive experiments some droplets will self-nucleate only at some of the time. In terms of the correlation plot, this implies that domains B and C should also be populated, as is the case in Figure 3.

Further evidence of the stochastic nature of self-nucleation can be found from the relative fraction of droplets in domains, $f_A$–$f_D$. Figure 2 indicates that a fraction of 0.26 and 0.28 of the droplets
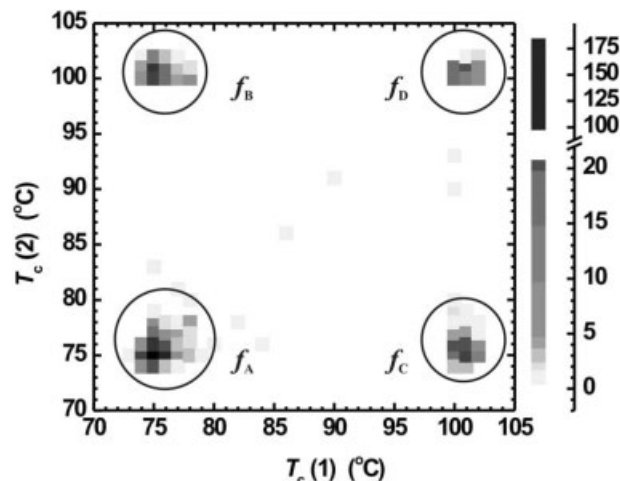


**Figure 3.** Correlation plot for two $T_s = 145$ °C experiments. The crystallization of each droplet in the two experiments follows one of four behaviors, as indicated by the four populations. $f_A$, regular nucleation in both experiments; $f_B/f_C$, regular nucleation in one experiment and self-nucleation in the other; $f_D$, self-nucleated in both experiments.

crystallize via self-nucleation in each of the $T_s = 145$ °C experiments. One would then expect that a fraction of $0.26 \times 0.28 = 0.073$ of the droplets to be found in domain D. We find that $f_D = 0.1$. Similarly, we find reasonable agreement with the expected population fractions of the other domains: 0.57, 0.18, and 0.15 for $f_A$, $f_B$, and $f_C$ (expected fractions are 0.54, 0.21, and 0.18 respectively).

## CONCLUSIONS

The novel sample-geometry of droplets formed through the dewetting of a thin film can provide new insight into crystal nucleation processes by enabling the monitoring of each individual domain over successive experiments. Subject to a controlled thermal treatment resulting in crystallization at elevated temperatures, we have observed self-nucleation. While the relative fraction of droplets that undergo self-nucleation depends on the value of $T_s$, such crystallization was consistently found to occur at ~101 °C. Using correlation plots it has been shown that self-nucleation in polyethylene occurs randomly throughout an ensemble of droplets, indicating that the crystal memory effects observed in this study arise from a stochastic process within the polymer, rather than from specific preferential sites.

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