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On the nucleation of polyethylene at high supercoolings

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Droplets of polyethylene have been crystallized over a wide temperature range from about 77 to 110°C. The nucleation rates have been measured for a number of samples. It has been found that the nucleation rate remains constant with time for nucleation at temperatures between 80 and 105°C; but that at lower temperatures nucleation accelerates and at higher temperatures decelerates as time passes. © *2000 Kluwer Academic Publishers*

1. Introduction

There was a good deal of interest in the nucleation of polyethylene at high supercoolings in the 1960s and 1970s [1–5]. The main thrust of all that work was to attempt to establish the conditions under which homogeneous nucleation might occur and then, by measuring the variation of the homogeneous nucleation rate, calculate values for the various surface energies of polyethylene crystals that could be used in theories predicting crystallization behaviour at lower supercoolings. Most of this work used the droplet techniques developed by Vonnegut and Turnbull [1, 2] to divide the sample into small enough particles that many should contain no heterogeneities that can cause nucleation.

In fact, although it was claimed in some publications that homogeneous nucleation had been observed, each subsequent publication seemed to find a way of preparing droplets which had to be cooled to ever lower temperatures before nucleation would occur - thus suggesting that the previous works had not in fact seen truly homogeneous nucleation, but rather that the nucleation had been somehow influenced by the surface interactions of the droplets. A variety of useful data was obtained, including estimates of the growth rates and crystal thickness of polyethylene crystals crystallized at temperatures as low as 78°C. However, eventually those of us who had been working in the area decided that enough was enough and the work dried up.

In the last year or two, there has been a sudden reawakening interest in the nucleation behaviour of polymers with the publication of X-ray data which suggests that there may be some ordering in the melt prior to crystallization [6–8]. This work has then led some theorists to speculate on a novel mechanism for nucleation [9] - the spinodal decomposition of supercooled melts into regions rich in those conformations that are more (and less) likely to crystallize. This new model for polymer nucleation, and the experimental evidence on which it is based have been the subject of much debate, with several heated arguments occurring at recent conferences [see e.g. 10, 11].

This debate was of great interest to Andrew Keller, and we had many conversations about the issues. Indeed, it was due to some of Andrew's concerns that I persuaded Simon Hanna to make a detailed simulation of the X-ray scattering experiments at the heart of the issue to see whether it is possible to obtain similar data without the need to invoke a new nucleation mechanism [11, 12]. In fact these simulations provided results that were very similar to the experimental raw data, showing the small angle scattering signal appearing before the wide angle signal. However, the simple model used is not sufficient to make detailed predictions of the growth kinetics and so is not able to explain the experimental observation of apparently spinodal growth of the scattering with time. That work led us to many very interesting discussions with both experimentalists and theorists involved in the original work and started me thinking about other experimental tests of the new model for polymer nucleation.

It occurred to me that there is one very significant difference between a model based on traditional nucleation theory and one that is based on a concept of phase separation. In the traditional nucleation theories a nucleation event occurs when a large enough nucleus is built up from random fluctuations in the melt that further increases in size lead to a reduction, rather than an increase, in the overall free energy. Such nucleation events should occur sporadically in space and time, so that the overall nucleation rate (in events per unit volume, per unit time) should depend only on the temperature and not on the length of time a sample has been held at that temperature. In contrast, in a phase separation based approach one would expect some ripening of the separated phases with time. Such ripening should lead to an increase in the overall nucleation rate with the length of time a sample has been held at a particular temperature.

With this in mind, I decided to revisit the old nucleation work. It is immediately apparent from the data presented in the old papers [2–5] that the nucleation rate does not appear to vary significantly with time.

However, in these papers the possibility of any variation of nucleation rate with time was not considered and no detailed examination of the data for any such effects was performed. Fortunately I was able to find in some old notebooks, previously unpublished detailed measurements of nucleation rates covering a wide temperature range which are suitable for such an analysis. It is these results that are presented in this paper, in the hope that they may shed some new light on current issues.

2. Experimental methods

2.1. Preparation of droplets

The polymer used throughout this work was a sharp fraction obtained from the NBS (now NIST) with weight average molecular weight 31,000 and number average molecular weight 26,000. This is the same material as that labelled 30.6K in the work of Ross and Frolen [3].

Droplets were prepared following a careful cleaning procedure as described in detail elsewhere [5]. Briefly the polymer was dissolved in very pure solvent, crystallized to form uniform single crystals and the resulting suspensions centrifuged to remove the more dense fraction (which was assumed to contain most of the nucleating impurities). The resulting "clean" suspension was then sprayed, using an atomiser, onto preheated glass slides to form the droplets used in the subsequent work. The droplet sizes were reasonably uniform on each slide (but varied from 1 to 5 μ between slides).

The droplets were melted at 160°C for 20 minutes under a vacuum to remove any solvent and then allowed to cool.

A variety of different surface treatments were applied to the glass slides before the application of the droplets. These included coating with lanolin and Anatrox as well as simply cleaning with lens tissue and even smearing the slides with oil taken from the skin of the nose (a procedure found accidentally to lead to the lowest observed nucleation temperatures [5]).

2.2. Measurement of nucleation rates

First, the "nucleation temperature" of each preparation was determined. The droplets were melted at 160°C (using a modified Mettler hot-stage which was capable of maintaining temperature to better than 0.1°C over prolonged periods) and then cooled at 10°/min to 130°C before being cooled at 1°/min. The number of droplets that transformed from the melt was monitored by observing between crossed polars with photographs being taken at appropriate intervals. In all the slides, some 10 to 15% of the droplets always crystallized at temperatures between 125 and 120°C, these normally included any larger droplets present. The remaining droplets then crystallized in a narrow temperature range at some lower temperature. The nucleation temperature was defined as the temperature at which half of this population with the lower crystallization temperature actually had crystallized. As reported previously [5] this nucleation temperature varied widely between different slides. Slides with nucleation temperatures from as low as 75.8°C to as high as 114.5°C were obtained.

The actual nucleation rates were measured following the procedure described by Ross and Frolen. The sample was melted at 160°C and cooled at 1°/minute to the chosen temperature where photographs were taken (between crossed polars) at regular intervals. The number of droplets that crystallized in each time interval was measured subsequently from these micrographs. Typically the total number of droplets in the field of view was between 200 and 300.

For any one slide, measurements of nucleation could be made over a temperature range of about 5° above the nucleation temperature. At lower temperatures nucleation was too fast to permit any detailed observations while at higher temperatures it was too slow. A typical set of data is shown in Fig. 1 in the form of a plot of the proportion of droplets that have crystallized as a function of time at the crystallization temperature for a slide with a nucleation temperature of 87°C.

To examine whether there is any acceleration in the rate of nucleation with time it is better to plot these data in a different form. If all the droplets are of the same size and nucleation is truly sporadic then:

$$\frac{n}{n_0} = \exp(-Ivt)$$

where n_0 is the total number of droplets of volume v, n is the number that remain unfrozen after time, t and I is the nucleation rate. So a plot of $\ln(n/n_0)$ against time should be linear. If there is a variation in droplet size, so that larger droplets nucleate first and smaller droplets nucleate later then such a plot should show the nucleation rate decreasing at longer times. Conversely, if the mechanism of nucleation is due to some form of phase separation, the nucleation rate should increase with time and the data should display the opposite curvature. These different behaviours are illustrated schematically in Fig. 2.

3. Results

In Fig. 3, a selection of plots of $\ln(n/n_0)$ against time are shown for a slide with a nucleation temperature of 91.2°C. These all show a linear nature suggesting that nucleation is sporadic in time and that no acceleration occurs. However, it can be difficult to make comparisons with such a variety of slopes.

A convenient measure of the overall rate is the half time for nucleation, $t_{1/2}$ (the time at which half of the population of droplets with the lower crystallization temperature have crystallized). So, for example, for the data shown in Fig. 1 the crystallization half times vary from 10 minutes at 87.5°C to 300 minutes at 90.8°C. It is then possible to use this half time to normalise the plots of $\ln(n/n_0)$ by plotting against $t/t_{1/2}$, rather than against t.

A selection of such plots are shown in Fig. 4. In this figure it becomes apparent that there is in fact a range of behaviour. For nucleation at temperatures above approximately 105°C a curvature can be seen indicating that the nucleation rate of droplets decreases

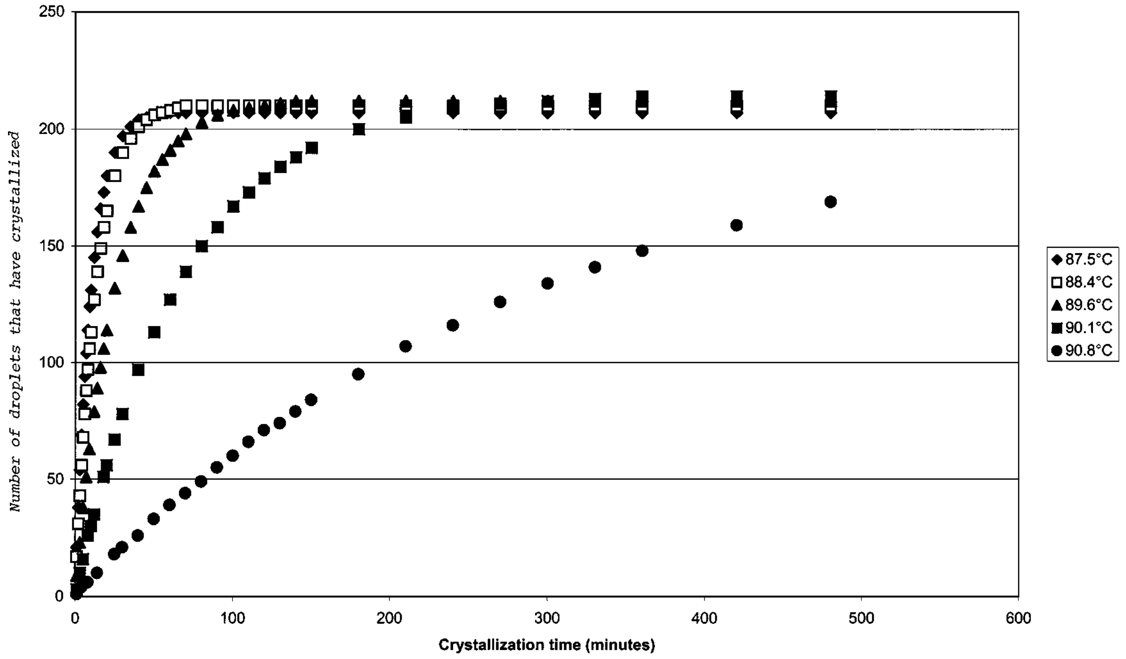


Figure 1 A plot of the proportion of droplets that have crystallized as a function of time at the crystallization temperature for a slide with a nucleation temperature of 87°C.

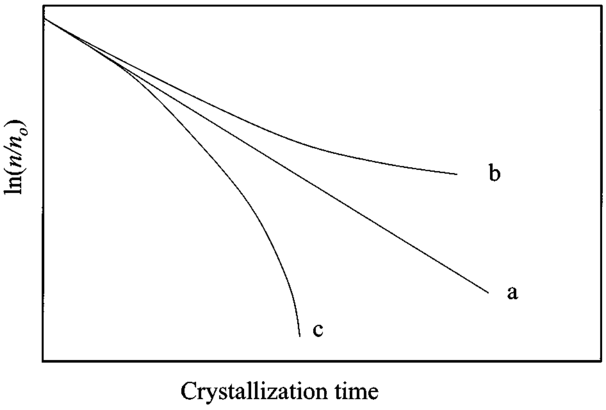


Figure 2 A diagram indicating how the nucleation rate should be expected to vary with time for: (a) Classical nucleation behaviour with droplets of uniform size; (b) Classical nucleation behaviour for droplets with a distributions of sizes; (c) The Olmsted *et al.* "spinodal" nucleation model.

with nucleation time; for nucleation at temperatures between 80 and 100°C almost perfectly linear plots are recorded; while for lower nucleation temperatures there is evidence of acceleration of the nucleation rate with time.

In fact some 35 measurements of nucleation rate as a function of time were made, of these 3 were made at temperatures below 80°C and all showed similar acceleration of the rate as that shown in Fig. 4a. Four measurements were made of samples with nucleation at temperatures above 105°C all show closely similar behaviour as seen in Fig. 4b. All the other samples showed a clear linear relationship between $\ln(n/n_0)$ and $t/t_{1/2}$.

4. Discussion

The results presented above raise several distinct issues: why is it that the majority if of the nucleation rate data produce linear plots of $\ln(n/n_0)$ against time, when this should only happen if all the droplets are of strictly uniform size? what are the underlying causes of the deviations from linearity of the plots for nucleation at both higher and lower temperatures? However, there are also some more fundamental questions such as why is there such a wide variation in nucleation temperature between slides and whether homogeneous nucleation can ever be observed which should be addressed.

It seems appropriate first to recap briefly the arguments concerning nucleation mechanisms and how the rate of nucleation may be affected by temperature and environment.

4.1. "Classical nucleation"

In "classical" nucleation theory the free energy balance of a growing crystal is considered. The free energy required to create new surfaces is balanced against that gained from bulk crystallization. The critical nucleus size (the smallest crystal for which the addition of material will lead to a reduction, rather than an increase in free energy) and its corresponding critical free energy is then found by differentiation of the work of formation of the nucleus. The nucleation rate, I, is then governed by this critical free energy $\Delta\phi$ according to:

$$I \propto \exp\left(-\frac{\Delta\phi}{kT}\right)$$

This is a strongly varying function of temperature so it is not surprising that in any preparation the rate of nucleation (as represented by the half time) will vary rapidly from several hours to less than a minute over a temperature range of only a few degrees. At some temperature this half time becomes so short that nucleation becomes more or less instantaneous. This "nucleation

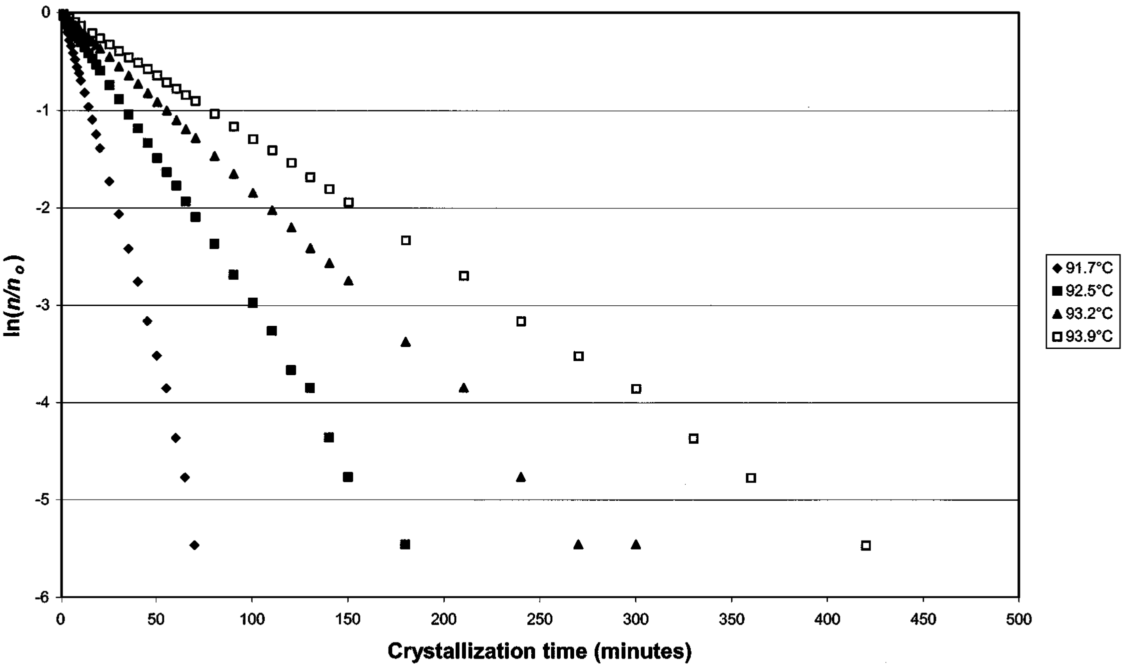


Figure 3 A selection of plots of $\ln(n/n_0)$ against time for nucleation at a variety of temperatures for a slide with a nucleation temperature of 91.2°C.

temperature" will then depend mainly on the critical free energy, $\Delta\phi$. The nucleation temperature will then be higher when $\Delta\phi$ is lower (i.e. when there is a lower barrier to nucleation). $\Delta\phi$ depends on the free energy of the growing crystal with respect to the surface at which it is growing, so if this surface free energy increases, then the nucleation temperature reduces, etc.

Thus, as there was no correlation between droplet size on the slides and the nucleation temperature of the slides, it is possible to argue that the range of different nucleation temperatures seen in the different preparations results from chemical differences in the surfaces of the slides which affect the surface free energy of the growing crystals.

4.2. "Spinodal Induced" Nucleation

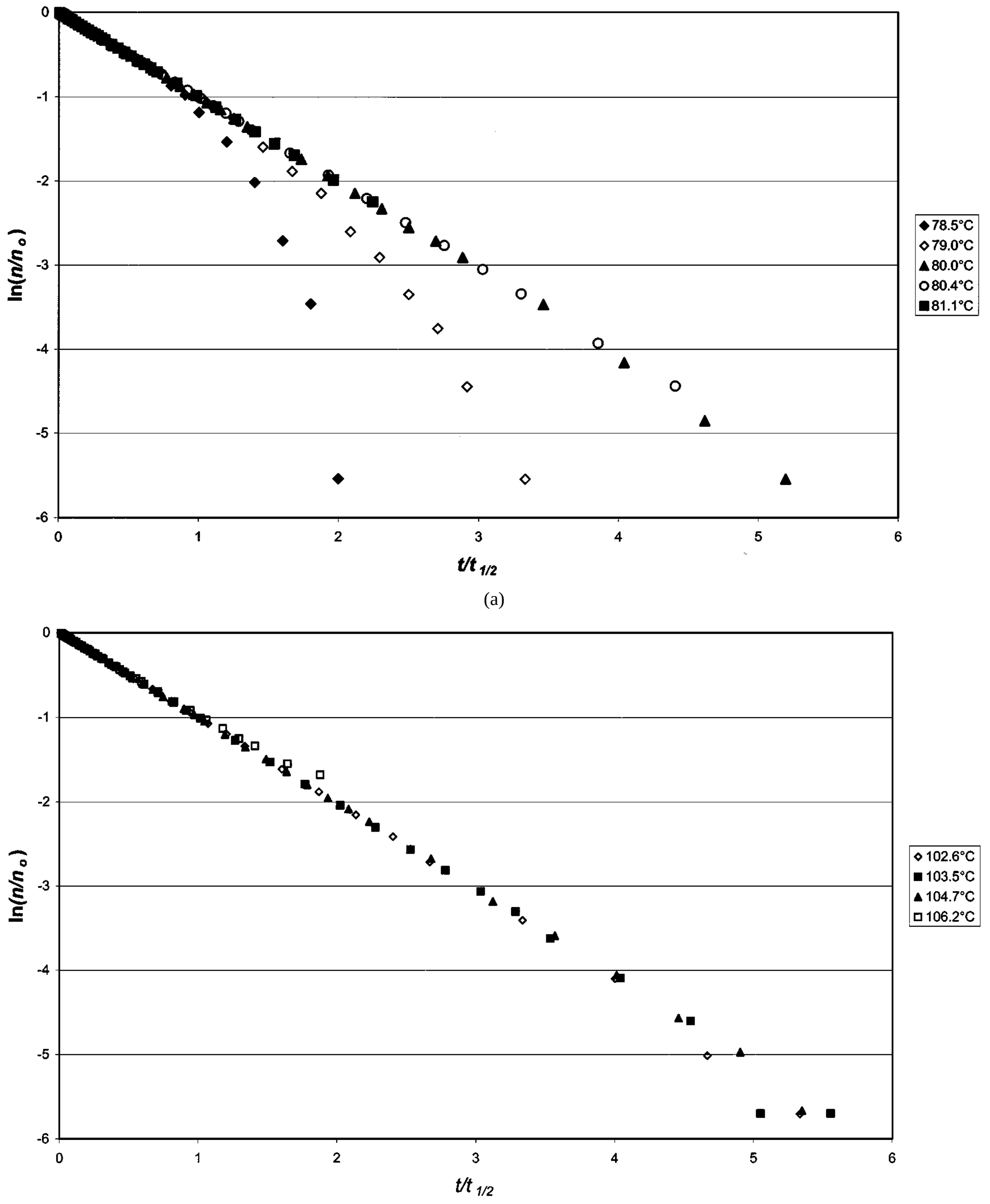
In their new model, Olmsted *et al.* [9] propose that at some temperature, below the equilibrium melting temperature, a supercooled polymer melt will separate into two distinct liquid phases where one phase is richer, and the other poorer, in those conformations that are found in the crystalline polymer. For example, in polyethylene one phase would be rich in trans conformations and the other in gauche conformations. The authors approach the modelling of such a buried phase separation by consideration of the density of the phases and are able to calculate phase diagrams for polyethylene and polypropylene using literature values for all except one parameter, the spinodal temperature. By choosing a value for the spinodal temperature (based on some experimental data [7]) they argue that melts of polyethylene and polypropylene cooled into the range where they normally crystallize will undergo liquid-liquid phase separation as a precursor to crystallization. The authors further suggest that this phase separation will be spinodal in nature and will, in some instances, form the basis of the initial nucleation step.

It should be noted that the model of Olmsted *et al.* is consistent with the concept of nucleation at a heterogeneity, provided the scale of the spinodal structure is smaller than the size of the heterogeneous nuclei - then where the dense phase, rich in the more crystallizable conformations, is close to the heterogeneous surface, nucleation is promoted. In this case, one can consider the free energy penalty of forming a nucleus to be significantly reduced due to the trans conformation rich melt. However, as phase separation is, of itself, a dynamic process the composition and size of the trans rich regions should be expected to be a function of time - making the effective reduction in free energy barrier greater as time passes.

4.3. Linearity of $\ln(n/n_0)$ *v.* $t/t_{1/2}$ plots

At first sight, and as argued by Ross and Frolen in their paper [4], a linear plot of $\ln(n/n_0)$ against $t/t_{1/2}$ is strong evidence that nucleation is proceeding by the "classical" mechanism with nucleation occurring sporadically in both space and time. However, this relies on making the assumption that all the droplets have the same volume (and surface area). Indeed Ross and Frolen argue that all the droplets in their preparations are of closely similar size - although the electron micrograph of their Fig. 1 suggests a variation of more than 10% in diameters. Certainly, in the preparations used in this work, the droplets did have a range of diameters within any one preparation, making the assumption of uniformity incorrect.

There is however, a simple argument which may be used to explain why the droplet size does not greatly affect the results and at the same time account for the wide variation in observed "nucleation temperatures". First it should be noted that a criterion for selecting a slide as being suitable for nucleation rate measurements was that it actually showed a clear nucleation



(a)

(b)

Figure 4 A selection of plots of $\ln(n/n_0)$ against $t/t_{1/2}$, for samples with different nucleation temperatures from two different slides. (a) Data from slide with a nucleation temperature of 78°C; (b) Data from a slide with nucleation temperature of 102°C.

temperature - that is that a graph of the proportion of droplets that had crystallized on cooling as a function of temperature in a constant cooling rate experiment showed a sigmoidal shape (as shown schematically in Fig. 5). In practice many slides showed several different "nucleation temperatures" (again noted schematically on Fig. 5) these were rejected as unsuitable for further study.

If we assume that the surface of the slides is not itself uniform, but that there are small regions where nucleation is more probable (for example due to variations in surface composition, or topography) then the probability of a nucleation event occurring will depend on the number of such sites that are in contact with a droplet (as well as the temperature). So those slides where the distribution of these surface hetreogenities is such that droplets are in contact with only one such region are most likely to show a single "nucleation temperature". While those where droplets are in contact with differing numbers of these regions are more likely to show multiple "nucleation temperatures". Further, different surface treatments will affect the interaction between the polymer and these regions of high nucleation probability differently so leading to differences in their effectiveness and hence to different "nucleation temperatures".

According to the above arguments, the linear plots of $\ln(n/n_0)$ against $t/t_{1/2}$ arise from a combination of

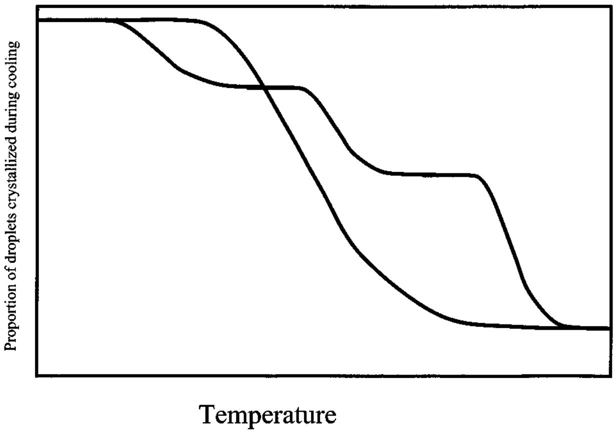


Figure 5 A diagram showing schematically how the proportion of droplets crystallized on cooling increases as the temperature decreases temperature in a constant cooling rate experiment. (a) The sigmoidal shape curved data from a slide with a single well defined "nucleation temperature"; (b) An example of a sample that shows multiple "nucleation temperatures" - such samples were not used for nucleation rate studies.

"classical" nucleation behaviour with a particular distribution of droplets and imperfections on the slides.

However, this argument apparently cannot explain the observations made of nucleation at higher temperatures, where the nucleation rate appears to decrease as time goes by. These data, are at first sight most easily explained in terms of the size distribution of droplets. However, an alternative explanation may be seen when one considers the shape of the graph of the proportion of droplets that had crystallized on cooling as a function of temperature in a constant cooling rate experiment. For those samples with a high nucleation temperature the tail of this curve (the number of droplets remaining un-crystallized at a temperature) is rather long - indicating that there are some droplets that are not as easily nucleated as the majority. This may, using the arguments of the previous paragraph, be due to a poorer contact with the imperfections in the slide surface.

The observations of an increase in the nucleation rate with time at the crystallization temperature cannot, as far as I can see, be explained by any "classical" nucleation theory.

4.4. "Spinodal" v. "classical" nucleation

One may adopt one of two views concerning the relevance of the results presented here to the arguments concerning the mechanisms of nucleation in polyethylene.

On one hand the data for nucleation at all temperatures above 80°C show no increase in nucleation rates with time at the crystallization temperature - even in experiments which have lasted for many hours. This lack of any time dependence suggests that phase separation is not playing a significant role in nucleation. The model as proposed by Olmsted *et al.* [9] for polyethylene suggests (based on experimental evidence from elsewhere [6]) that the spinodal temperature is above 125°C. However, the data presented would suggest the spinodal temperature can be no higher than about 80°C.

On the other hand one may argue that the data are consistent with the model of phase separation in the melt prior to crystallization, but that the phase separation proceeds quickly compared to the cooling rate of the samples. In that case, all the droplets would contain two fully developed phases before they reach their actual crystallization temperatures and it is the interaction of the trans-rich phase with the surface imperfections that leads to nucleation, in the same "classical" fashion. In their model Olmsted *et al.* have noted that there should be some temperature where the density of the trans rich phase equals that of the crystal phase so that at that temperature all barriers to crystallization disappear. It could be argued that the increase in nucleation rate with time at temperatures below 80°C might be related to the onset of such behaviour. However, any time dependence would seemingly run counter to the suggestion that the phase separation is fast compared to the cooling rate allowing the molten droplets to remain in a sort of equilibrium state.

An interesting further suggestion (from a referee of this paper) is that the linearity of the plots arises from a competition between the effects of size polydispersity (reducing the nucleation rate with time) and that of the phase separation (increasing the nucleation rate with time).

It is unfortunate that the data presented here are, of themselves, unable to distinguish unambiguously between the possible nucleation mechanisms. Further work, especially at higher temperatures is needed before any firm conclusions can be reached. However, on balance, it is this author's opinion that it is more likely that "classical" nucleation operates at most supercoolings with the new "spinodal" mechanism only setting in at very high supercoolings, if at all.

5. Conclusions

The nucleation rate of polyethylene droplets has been found to remain constant with time over a wide temperature range. The data are consistent with nucleation occurring randomly in time at locations where droplets interact with heterogeneous nuclei in the surface of the glass slides. Different surface treatments can affect the effectiveness of these nuclei and thus the temperature at which they become effective.

The data are not clear enough to distinguish between "classical" and "spinodal" models for nucleation of polymers, but suggest that the "spinodal temperature" in polyethylene is much lower than previously thought.

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