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Does isothermal crystallization ever occur?

Bruce X. Guan[a], Paul J. Phillips[b,*]

[a]*Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996-2000, USA*
[b]*Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA*

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Abstract

Much of what we think we know about crystallization in polymers is obtained from studies carried out under isothermal conditions. From extrapolations of equilibrium melting temperature to crystallization regimes, interpretations in the literature all assume that the measured temperature of a polymer film is the temperature at which the crystallization occurred.

Recently it has been possible to study crystallization at very high supercoolings, even in rapidly crystallizing polymers, through the use of a rapid cooling technique in which a thin film contains a microthermocouple to measure actual temperature. In adequately thin films an isothermal temperature is set up through a balance between the heat of fusion released and the cooling rate applied. This technique has been applied successfully to polypropylenes, and to polyethylene homopolymers and copolymers. The results have told us much about crystallization at very high supercoolings. Recently, a study of the effect of nucleating agents on quench-crystallization in PET and in nylon 6 was conducted, in which it was discovered that films containing nucleating agents generated the expected temperature plateau when crystallization occurred.

In this paper, we wish to report the results of studies of thin films of nylon 66 and PET which did not contain nucleating agents. The results are totally unexpected and indicate that a steady state condition exists at the growth face of the polymer, which is not reflected in the macroscopic temperature of the thin film, as measured using a microthermocouple. In other words the measured temperature of a film is not the temperature at which crystallization occurs. The consequences of this finding to our general understanding of crystallization in polymers will be discussed.

Keywords: Polyolefins; Polyamides; Polyesters

1. Introduction

Current understanding of polymer crystallization is based on the measurement of temperature and the development of experiments based on studies at what is believed to be a series of isothermal temperatures. Since, the earliest days of crystallization research an important procedure has been the extrapolation of melting points to generate the equilibrium melting temperature using the crystallization temperature as a base. This is the so-called Hoffman Weeks approach [1]. Additionally, our understanding of the mechanism of crystallization has depended on the study of rates of spherulitic, or lamellar, growth measured at a series of isothermal temperatures [2].

It has long been recognized that the free energy of fusion released during the crystallization process must be dispersed. It has generally been assumed that the dispersal process is sufficiently effective for the growth process to be regarded as occurring at an isothermal temperature. In practice, experiments carried out in hot stages on optical microscopes have been the norm. A correction is usually applied to the temperature indicated by the hot stage controller to allow for the difference in temperature between the actual temperature of the film and that of the measurement device. The range of isothermal temperatures achievable on a hot stage was for many years the limiting factor in data acquisition.

The situation changed with the development of a rapid cooling technique by Ding and Spruiell [3] in which a thin film containing a microthermocouple was cooled rapidly

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[*] Corresponding author.
E-mail address: paul.phillips@uc.edu (P.J. Phillips).

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with concurrent measurement of the actual temperature of the film. The objective of the equipment development was to generate a technique for studying polymer crystallization at industrial cooling rates. This approach was first applied to polypropylene and the method checked very thoroughly for that polymer [4] and then to polyethylene by Supaphol and Spruiell [5]. The key to the novelty of the technique was the unexpected discovery that the polymer film developed an isothermal condition when crystallization occurred. Hence, the polymer behaved in a similar way to metals in a classic undergraduate cooling curve experiment [6]. The reason for this occurrence was predicted theoretically by Eder [7], who showed that for a sufficiently thin film an isothermal condition would develop in a quenching experiment. The well-known crystallization range often observed in quench-cooling of polymer films or powders is, hence, a result of a temperature gradient in the sample.

Wagner and Phillips [8,9] then applied the technique to the study of spherulitic growth rates of linear polyethylene and its octene copolymers. The result was an extension of the isothermal crystallization range of linear polyethylene from 120–130 to 90–130 °C, with concomitant increases for the copolymers. This resulted in the generation of the entire crystallization curve for linear polyethylene covering all three regimes of growth, and under conditions achieved during industrial processing of films.

Recently Schreiber and Phillips [10] carried out an extensive study of the isothermal crystallization behavior of nylon 66 and its copolymers. This study was conducted solely with the use of a calibrated hot stage. The conclusion of the study was that the crystallization process was not consistent with secondary nucleation theory and that the polymer was most likely crystallizing through a surface roughening process caused by the presence of hydrogen bonds at the growth face. Lovinger [11] had earlier suggested that the folds in this polymer grow into the melt, rather than along the growth face, because of the direction of hydrogen bonding in the polymer crystal. The results of Schreiber and Phillips were quite consistent with this explanation. Since, nylon 66 is the only known example of a polymer, which does not crystallize by secondary nucleation, a more extensive study was begun using the rapid cooling technique. The objective of this study was to obtain data over a wide range of supercoolings, which would extend into the diffusion controlled region.

An earlier study carried out of PET and nylon 6 containing a variety of nucleating agents had been carried out by Phillips in collaboration with Martinez-Vazquez, Medellin-Rodriguez, et al. [12]. The objective of that study was to obtain some understanding of the effects of physical properties of nucleating agents on their ability to nucleate during a constant cooling rate study, which encompassed rates comparable to those used in industrial processing. It was found that most specimens containing nucleating agents generated an isothermal crystallization condition, but that the polymers without nucleating agents did not develop the isotherm. The purpose of that study was to evaluate the bulk growth rates, not the spherulitic growth rates. So, it was anticipated that the rapid cooling technique, when applied to nylon 66, might not generate the needed data and that full quenching to the amorphous state might result.

As will be reported here, the totally unexpected result was the discovery of linear growth rates in nylon 66 even when an isothermal plateau did not develop during crystallization. In order to determine if the effect was not something unique to polyamides, because of the hydrogen bonding and the surface roughening growth mechanism, the study was extended to poly(ethylene terephthalate), a polymer where all the evidence points to conventional secondary nucleation as the growth mechanism [13].

2. Experimental

An experimental sample of poly(hexamethylene adipamide) was kindly provided in the form of pellets by Monsanto Chemical Company, now Solutia. The number average molecular weight, M_n, of the experimental polymer was less than 18,000 g/mol.

The poly(ethylene terephthalate) (EASTPAK PET polyester 7352) was supplied by Eastman Chemical Company and had M_n 19,278 g/mol and M_w of 50.517 g/mol, respectively.

Thin nylon 66 film samples (50 μm) were prepared by solution casting on a 150 °C hot plate from 2 (w/v)% solution of nylon 66 in formic acid (88%). A thermocouple (0.002 in. in diameter) was embedded in the film sample to monitor the temperature change inside the sample during the rapid crystallization process. The pherulites growth rates were measured by using an automated version of the Ding-Spruiell hot stage—polarized optical microscope system with a high speed camera attached to a computer for image recording and data analysis.

3. Results

Fig. 1 shows the typical relationship of temperature to time during the crystallization process of PE in a rapid cooling experiment using an embedded microthermocouple. There is horizontal plateau on the *T*–*t* curve, which is due to the release of latent heat of fusion balancing the heat transfer to the cooling medium [3,8]. It was found that before spherulite growth rate remains constant as long as the temperature plateau exists, and that the growth rate increases rapidly when the temperature begins to drop again.

In the case of nylon 66 (PA66) there was no horizontal plateau ever observed in the rapid cooling curves (Fig. 2). It is believed that this is due to the low crystallinity of PA66 and to its low crystallization rate. As was mentioned earlier, when effective nucleating agents are present in the polymer the horizontal plateau can be seen.

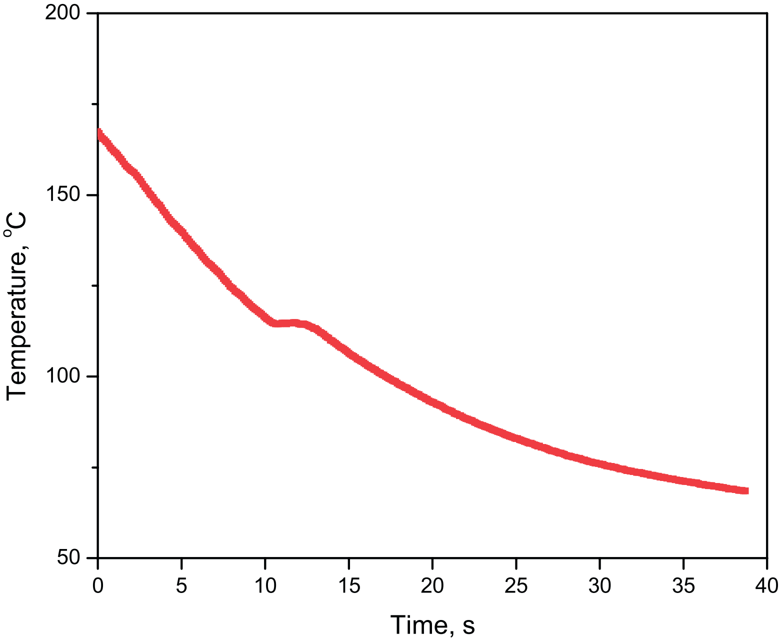

Fig. 1. Typical cooling curve of polyethylene shows a horizontal plateau.

Instead, however, there was a plateau or a point of inflexion in the temperature derivative versus time curve over the time span in which an increase of light intensity occurred (Fig. 3). The temperature corresponding to the beginning of the temperature derivative–time curve disturbance was taken as the crystallization onset temperature. Studies of spherulitic growth rate showed that the growth rate was linear over much of the temperature drop measured by the embedded microthermocouple (Fig. 4). This observation clearly requires a constant crystallization temperature at the growth face. The measured temperature change in the film over the time period that spherulitic growth is measured is as much as 30 °C. Such a change in crystallization temperature would normally give rise to a change in spherulitic growth rate of an order of magnitude. The light intensity kept increasing after the impingement of the spherulites, from which it is possible to infer the presence of a significant secondary crystallization process.

In order to understand the phenomenon further a more in-depth analysis of the data is warranted. In Fig. 4 it is clear

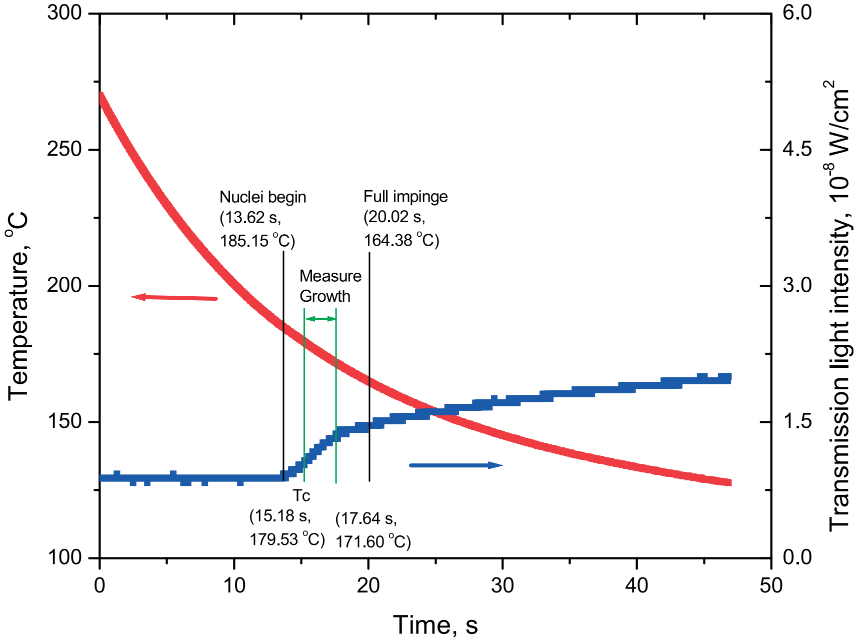

Fig. 2. Temperature and light intensity vs. time during the rapid cooling of PA66.

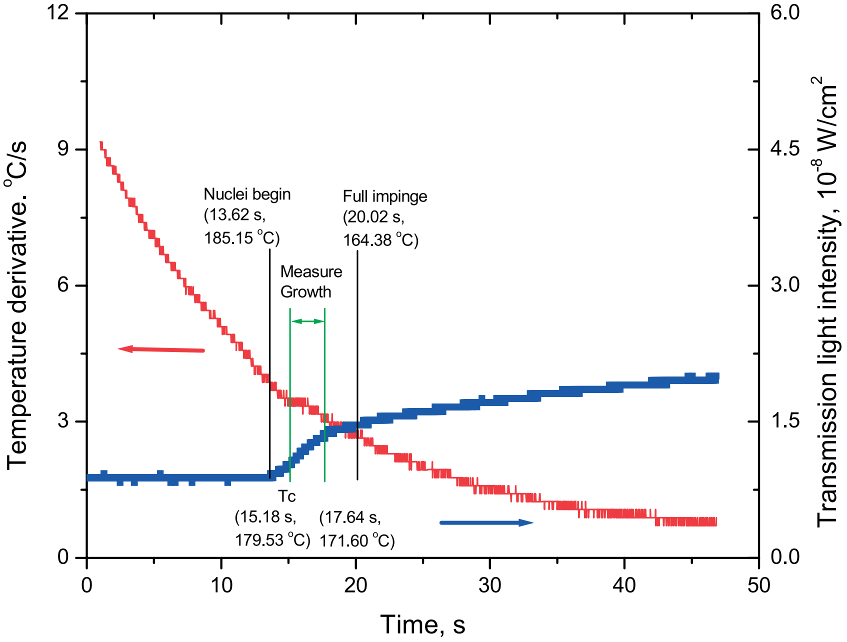

Fig. 3. Temperature derivative and light intensity vs. time during the rapid cooling of PA66.

that some curves show deviations from linearity. This is not unexpected, as the rate of release of heat of fusion by the crystallization process would not be expected to maintain a constant temperature at the growth face regardless of the temperature of the surrounding melt. In practice, there must be a temperature gradient at the growth face. In order to explore this point further, first the instantaneous growth rate of a spherulite has been plotted as a function of crystallization time. In Fig. 5 is shown the behavior of linear polyethylene. Shown is a plot of temperature measured by the embedded thermocouple as a function of time along with a plot of the point-to-point slope of the spherulite radius versus time curve, as a function of the same time range. Clearly, for this material there is a direct correlation between measured temperature and time. When the temperature begins to drop the spherulite growth rate begins to increase.

When PA66 is considered from the same point of view a somewhat different phenomenology is observed. In Fig. 6 it can be seen that, although the temperature measured using

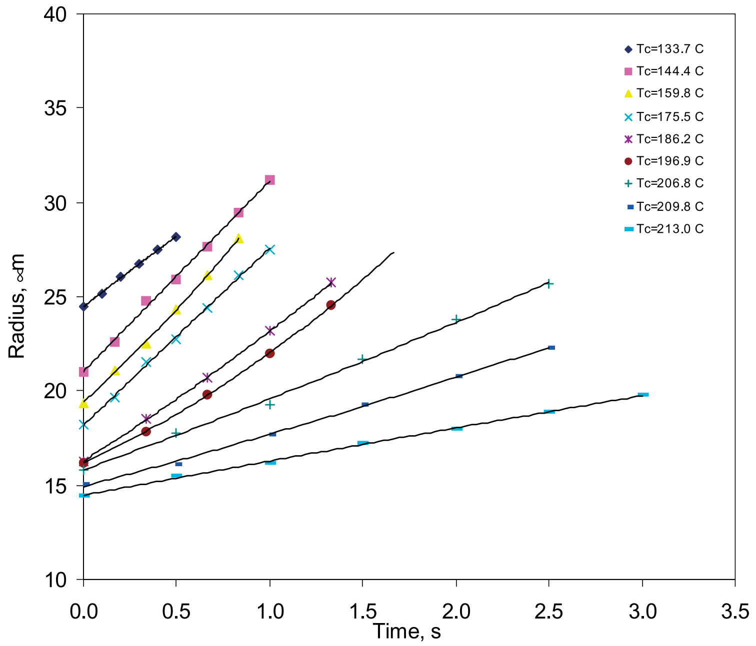

Fig. 4. Linear relationship between radius of spherulites and crystallization time during crystallization of PA66.

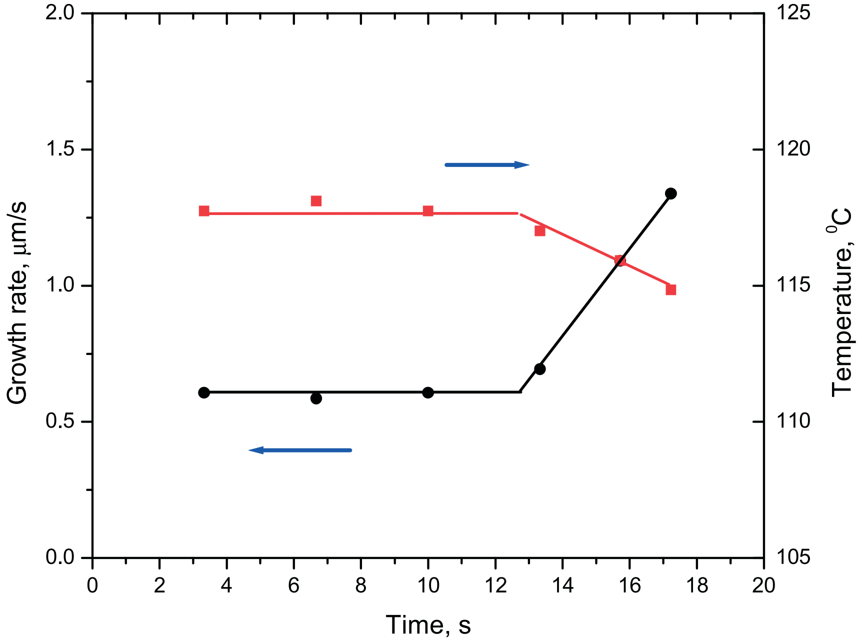

Fig. 5. Growth rate and temperature change with time in the rapid crystallization of polyethylene.

the embedded thermocouple is decreasing at a constant rate of 5 °C/s, the growth rate stays linear within the error bounds. This phenomenon is explored further in Fig. 7, where the instantaneous point-to-point growth rate has been plotted for several spherulites as a function of time for several cooling rates, all of which display the type of behavior shown in Figs. 2 and 3. This figure demonstrates convincingly the phenomenon of linear growth rates in these thin films of PA66 despite the measurement of continuously decreasing internal film temperatures as measured by an embedded microthermocouple close to the spherulites being studied.

When the growth rates measured are plotted against the point of inflexion temperatures a conventional bell-shaped growth rate curve is observed (Fig. 8). The solid symbols represent the rapid cooling data, whereas the open symbols are conventional hot stage data, but using embedded microthermocouples. Analysis of these kinetic data in the conventional manner will be the subject of a separate publication. It will be shown, that even though PA66 data

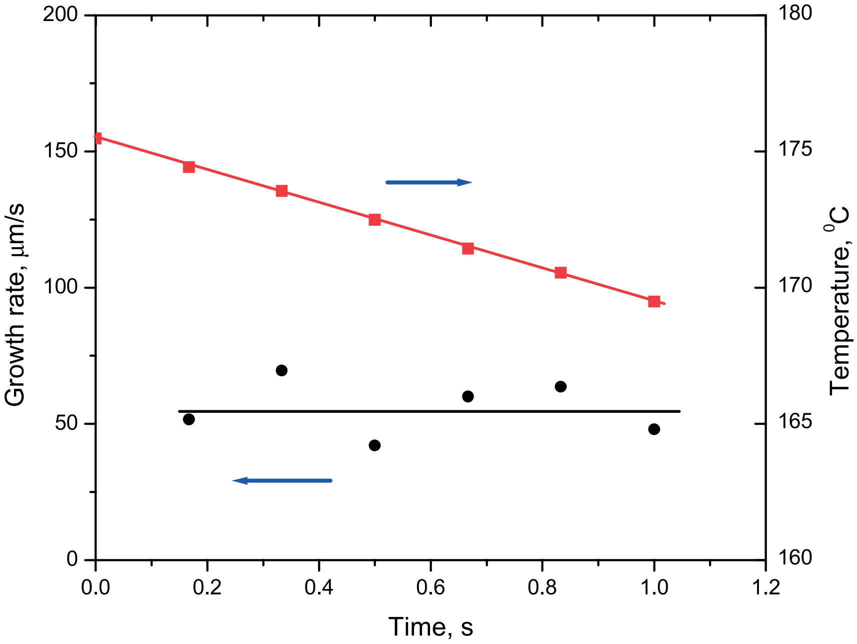

Fig. 6. Growth rate and temperature change with time in the rapid crystallization of PA66.

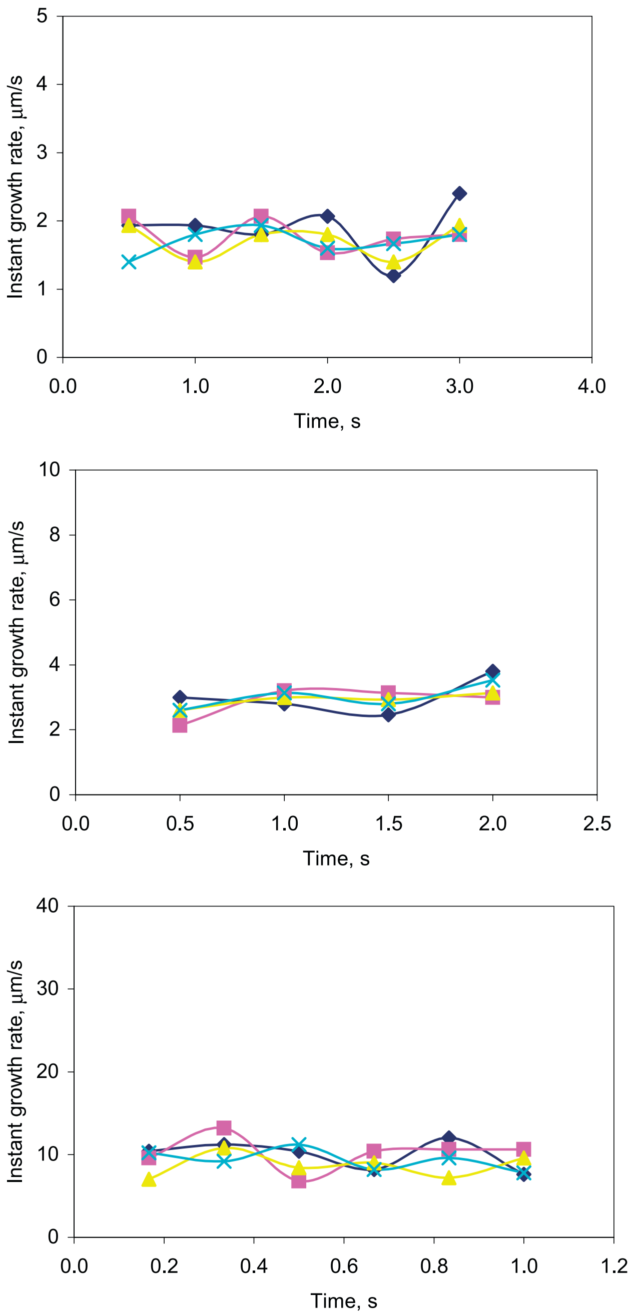

Fig. 7. Instantaneous growth rates of PA66 at increasing cooling rates.

are characteristic of growth by surface roughening, regimes of growth are observed.

In order to explore the possibility of the data being generally characteristic of polymers, and not simply characteristic of a surface-roughening system, poly(ethylene terephthalate) has been studied. The reason for this choice for material was simply that earlier bulk growth rate studies of the polymer using the rapid cooling equipment had discovered that samples containing nucleating agents showed a plateau region, but that plain samples did not. In addition, PET is a well-studied polymer and its growth rate dependence on crystallization temperature is well-known.

A typical plot of temperature versus time, as measured using an embedded microthermocouple, during a rapid cooling experiment on PET is shown in Fig. 9. Characteristic data of spherulite size versus crystallization time are shown in Fig. 10, where it can be seen that approximately linear growth is observed, similar to what was seen for the PA66. The temperatures shown in the legend of Fig. 10, as for the PA66, are the observed points of inflexion in the temperature–time curves. In some cases the growth curves are linear with time and in other cases the spherulite growth rate decreases slowly with time, presumably because the slower growth rate of the PET versus that of PA66 does not release enough thermal energy per unit time to maintain the isothermal state at the growth face. An example of this behavior is shown in Fig. 11 where although the temperature, as measured by the embedded microthermocouple decreases in a linear fashion, the size growth rate of the spherulite, although linear at first, begins to decrease slowly with time. The rate of decrease of growth rate is not of the order of magnitude that would be expected for a drop of 10 °C in growth temperature, based on the known behavior of PET. The behavior is explored further in Fig. 12, where the instantaneous point-to-point growth rates of several spherulites are plotted as a function of time for several cooling rates. When the growth rates are plotted against the inflexion temperature, it is seen that the temperatures correspond to the diffusion-controlled side of the characteristic bell-shaped curve of PET (Fig. 13).

4. Discussion

From the results presented above it is apparent that both PA66 and PET exhibit linear growth rates during rapid cooling and that the film temperature, as represented by an embedded microthermocouple, does not represent the actual crystallization temperature at the crystal growth face. It is also apparent that the behavior cannot be sustained indefinitely and that there is a limit to the externally applied temperature that can be balanced by the released heat of fusion. It is also clear that the phenomenon can be sustained better by a more rapidly crystallizing polymer, such as PA66, than the more slowly crystallizing PET.

The results of this study have profound implications for our understanding of polymer crystallization. If the temperature at the growth face is different for a relatively slow crystallizer such as PA66, then it must be significantly different for fast crystallizers, such as linear polyethylene and isotactic polypropylene. In the case of these two polymers the heat of fusion released during crystallization is large enough to maintain a constant temperature in the entire film, as measured by the embedded microthermocouple. Hence, the temperature at the growth face must be significantly higher than the measured value.

It is a general law of physics that crystals conduct better than amorphous materials because of phonons. The

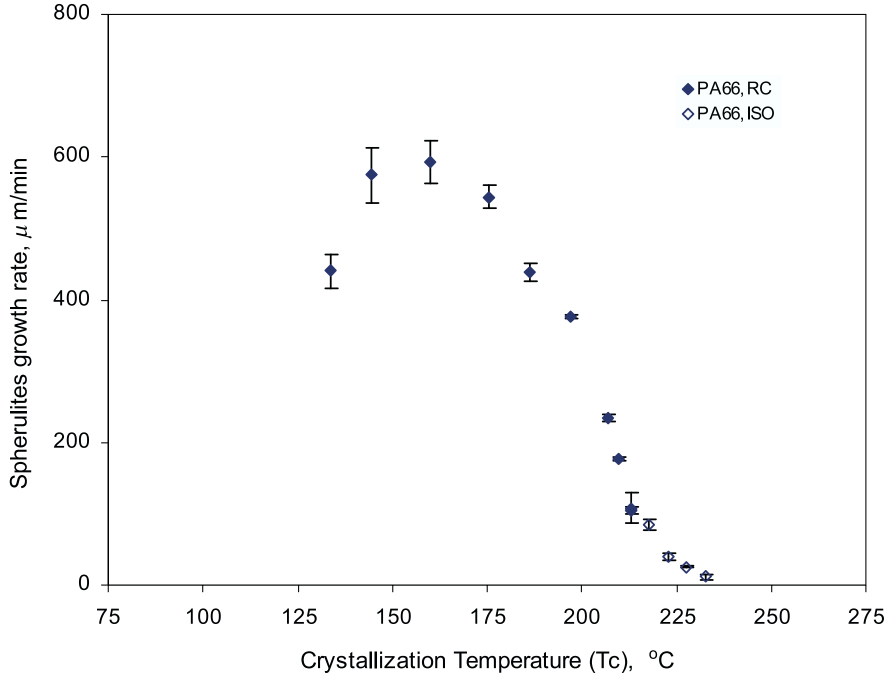

Fig. 8. PA66 growth rates determined from the slope of radius–time curves.

phenomenon is observed in polymers, although the data are sparse. For instance polyethylene [14,15] has a conductivity which varies with crystallinity (54%, 0.33; 67%, 0.42; 76%, 0.52), which leads estimates of the conductivity of the pure crystal in the neighborhood of 0.80, and of the amorphous phase of about 0.20, at ambient.

Since, the thermal conductivity of a crystal is higher than that of an amorphous material, the thermal energy released by crystallization would be expected to be conducted into the lamella more rapidly than into the melt. There should, therefore, be a temperature gradient at the growth face, which penetrates into the crystal. This case has already been considered theoretically for metals during splat cooling. It is based [16] on a heat balance equation of the form:

$$\rho_c \Delta H_f(G) = k_c \left(\frac{\partial T}{\partial x}\right)_c - k_l \left(\frac{\partial T}{\partial x}\right)_l$$

where ρ_c is the density of the crystal, ΔH_f is the heat of

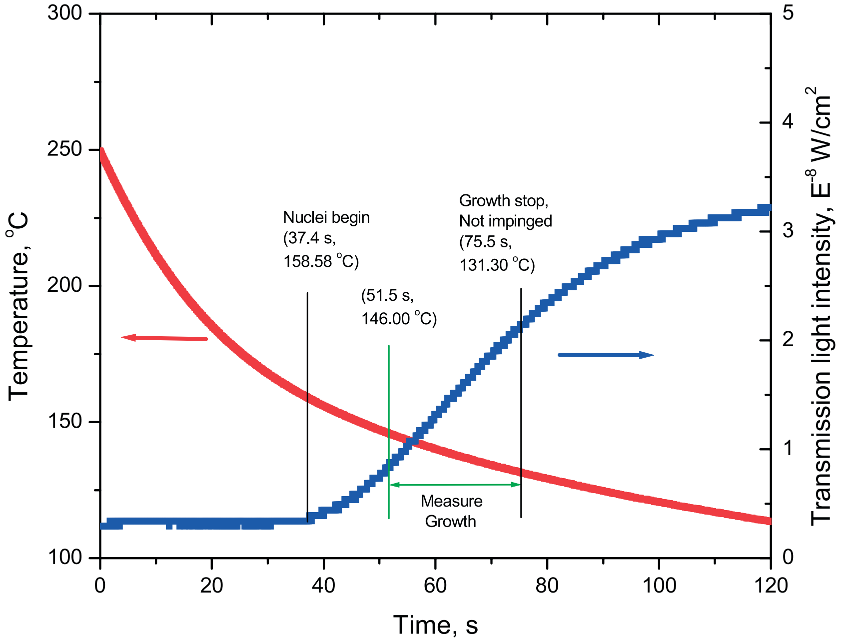

Fig. 9. Plot of temperature vs. time during the rapid cooling of PET.

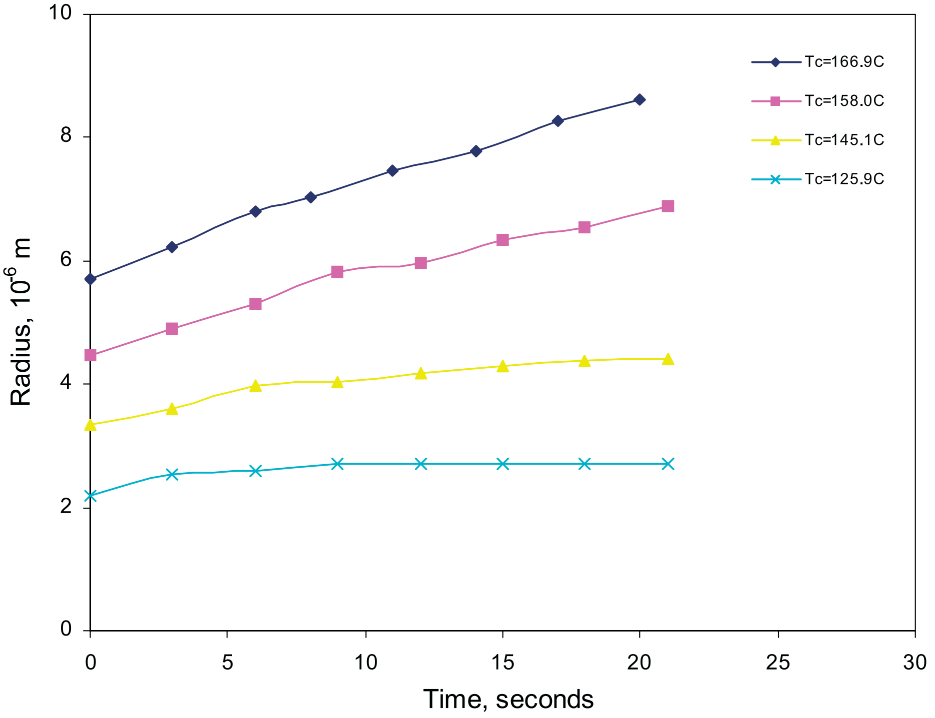

Fig. 10. Plots of spherulite radii vs. crystallization time during the rapid cooling of PET.

fusion, $G = dX_c/dt$, the growth rate of the crystal, k is the thermal conductivity, the temperature T is a function of time t and position x, and the subscripts ‘c’ and ‘l’ represent the crystal and the melt, respectively. It should be noted that the bulk crystallization of a polymer is very different for that from solution crystallization, on which most polymer crystallization theories are based [17]. The small mobile solvent molecules are no longer there to ensure that the heat of fusion is carried away from the growth front and the crystal.

The modeling of the metal process results in a curve similar to that of curve (a) of Fig. 14. The important features are (i) the prediction of a temperature gradient, and (ii) the existence of a temperature plateau, at T_1, which corresponds to $T_m = T_c$, where T_c is the actual crystallization temperature. The environmental, or measured, temperature is given

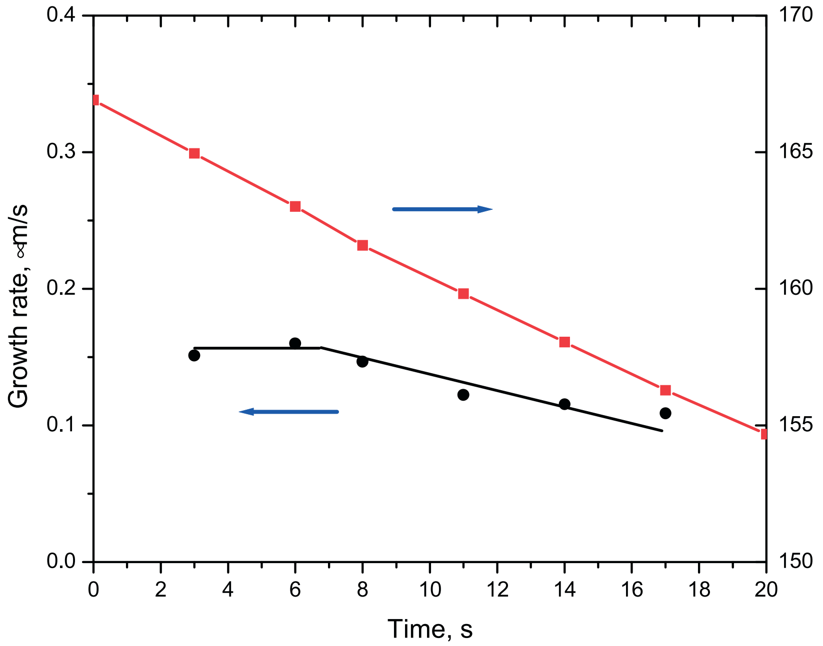

Fig. 11. Growth rate and temperature change with time in the rapid crystallization of PET.

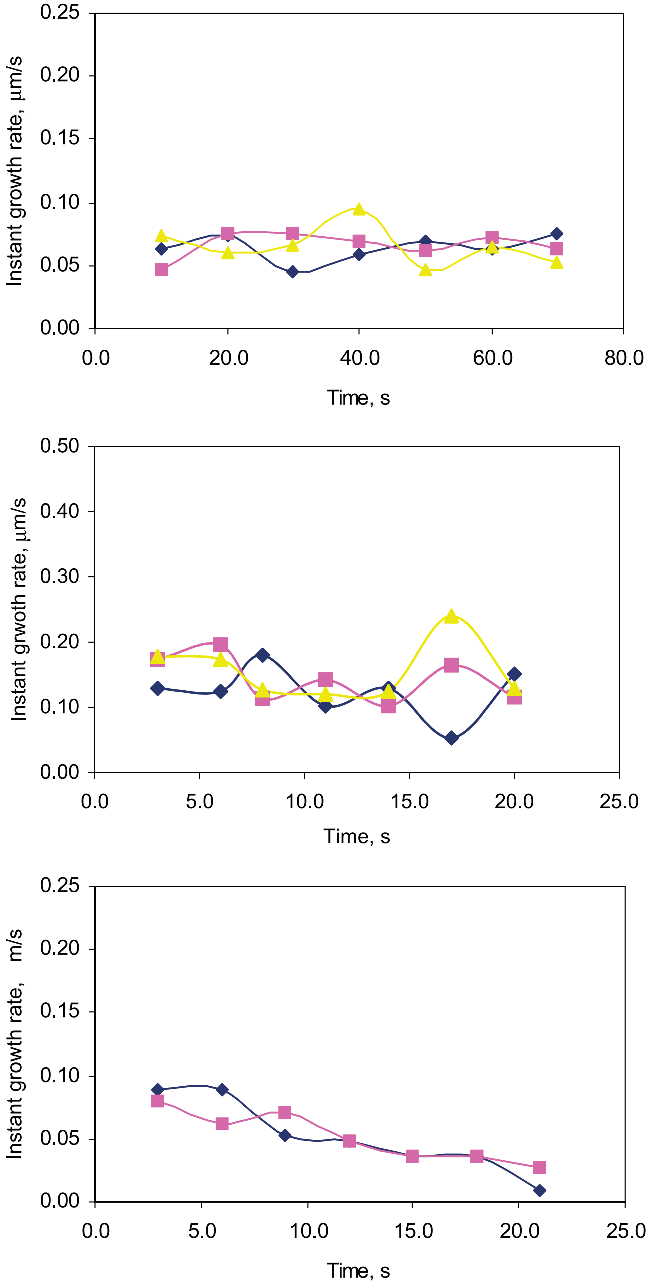

Fig. 12. Instantaneous growth rates of PET measured at increasing cooling rates.

in Fig. 14 by T_{ENV}. In the metal case the upward slope in the melt approaches the plateau in an almost vertical manner.

For a polymer the condition of the (equilibrium) melting point being equal to the crystallization temperature cannot occur, however, a reasonable assumption would be that $T_1 = T_m(l^*)$, corresponding the actual melting temperature of the critical nucleus, i.e. the initial lamellar thickness. Of course, this would not negate the incentive for crystallization as the driving force for crystallization comes from the supercooling relative to the equilibrium melting point. Also, it is generally believed that a distribution of initial lamellar thicknesses exists, a condition, which is an integral part of secondary nucleation theory [17]. Because of this, the region in curve (a) where the temperature gradient intersects the plateau has been rounded, unlike the situation in metals where there is a single well-defined melting point [16].

Since, a polymer crystal can transmit its excess energy through longitudinal vibrations and chain oscillations to cilia and tie-molecules (i.e. processes unique to polymers, which are in addition to the normal mechanisms of heat dispersion available to all materials), it is possible that the temperature decreases within the crystal, away from the growth front. This condition would result in curve (b) of Fig. 14.

However, it is well-known that most polymers are capable of lamellar thickening, and that such a process is recognized as being generally present. Hence, as the heat of fusion is conducted into the crystal it will result in thickening, and an increase in the melting point. Therefore, it is expected that a second plateau temperature will be reached, gradually, represented by T_2 and that it will likely be equal to $T_m(l)$, the melting point of the thickened crystal. The value achieved will, of course, be dependent on heat flow into the crystal. Hence, a crystal capable of thickening will have a temperature profile represented by curve (c) of Fig. 14. As for the earlier case with no thickening, there remains the possibility of cooling by cilia and tie-molecule conduction, resulting in curve (d) of Fig. 14.

Calculations of the temperature gradient at a crystal surface, ignoring conduction into the crystal result in the equation

$$\rho_c \Delta H_f \frac{\partial R}{\partial t} = -k_l \left(\frac{\partial T}{\partial r}\right)_R$$

where R is the spherulite radius and $\partial T/\partial r$ the temperature gradient at the interface, results in estimates of the temperature gradients of the order of 10 K/mm.

The temperature profile of Fig. 14 implies that the crystal will be annealed at temperatures significantly higher than the crystallization temperature for a considerable amount of time after its formation. The consequence of this will be a rapid thickening and perfection process, which has been long recognized as occurring immediately after crystallization, but for which there has been no acceptable mechanism postulated, due to the assumption of an isothermal crystallization process.

It needs to be recognized that the model proposed in Fig. 14 is for a single lamellar crystal. In practice, the result will be modified for agglomerations of crystals by the lamellar environment, typified by the orientation and proximity of other lamellae. For instance, the situation in a spherulite would be different from that in a row-nucleated morphology. A high crystallinity spherulite with close lamellae would be different from an open low-crystallinity spherulite such as *cis*-polyisoprene. The generation of branches, their frequency and orientation relative to the 'mother' lamella would also be important. This overall

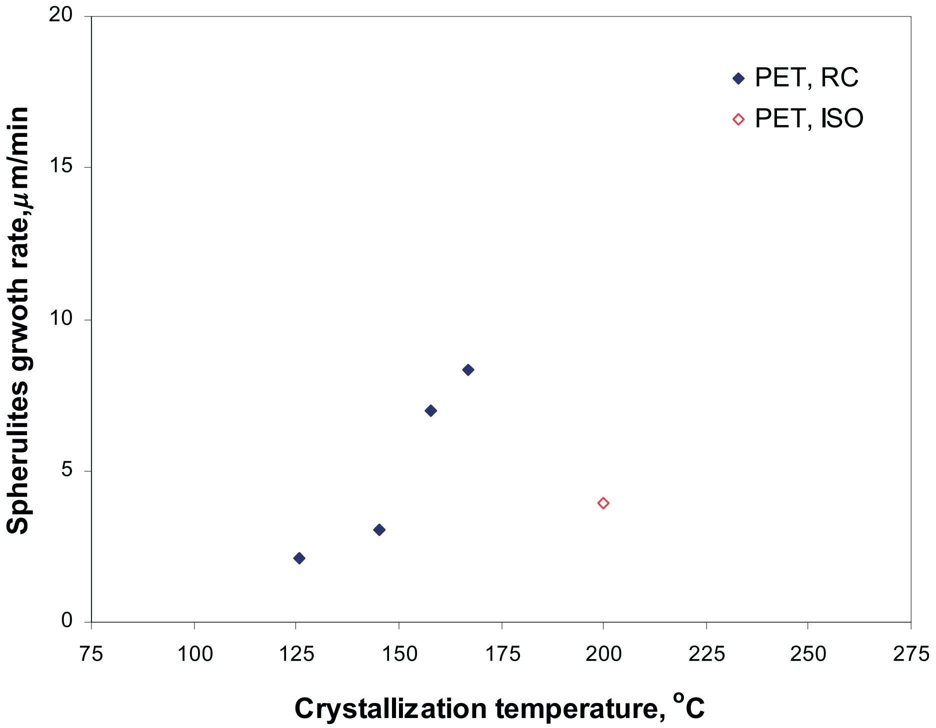

Fig. 13. PET growth rates determined from the slope of radius-time curves.

situation and its effects on morphology has been discussed amply in the past by Schultz and others, and summarized in Schultz's book [18].

It is important to recognize that in our earlier studies of polyethylenes using rapid cooling that the data for linear spherulitic growth rates and lamellar thickness, when combined with studies from conventional isothermal experiments, formed continuous curves as a function of measured temperature [8,9]. Since, it is highly likely that the situation reported here for nylon and PET is a common occurrence at the growth face of all polymers, there has to be a fairly simple relation between the actual temperature distribution within the lamellae and the environmental temperature. Previous analyses have suggested that the temperature T_1 is simply determined by heat fluxes. Such analyses do not lead to the known relations between environmental temperature (i.e. 'normal' crystallization temperature), melting point, lamellar thickness etc. The model being suggested here explicitly involves measurable morphological parameters, such as initial lamellar thickness and final lamellar thickness, and should lead directly to the traditional experimentally determined relations. In addition, the suggestion being made here that lamellar thickening is a direct result of heat of fusion being conducted into the

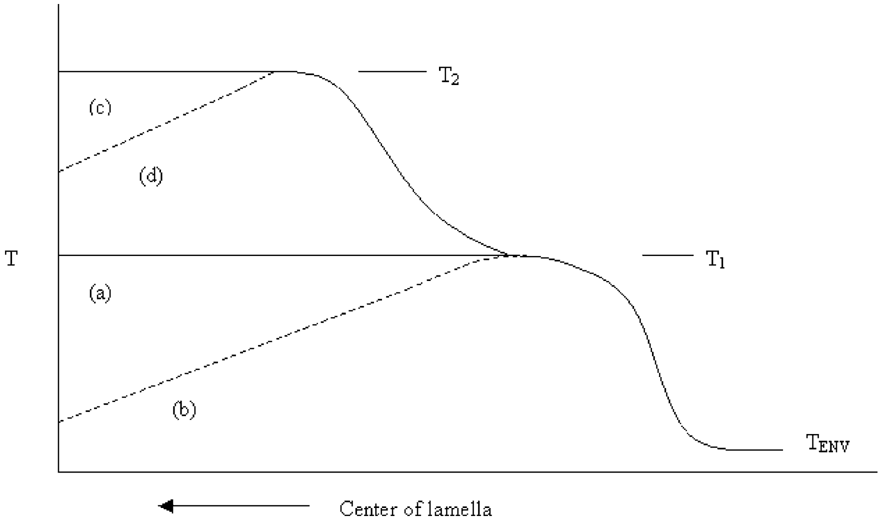

Fig. 14. Schematic of temperature profile around the growth face of a growing lamella.

crystal has not been made before, to the best of our knowledge.

The assumptions used in the suggested model above, that the plateaux temperatures correspond approximately to the melting points of the initial and thickened crystals, if proved correct, should make it possible to generate consistency between this phenomenology and currently established relations, such as the Hoffman Weeks equation and the Hoffman Lauritzen expressions for crystal growth. The simplest approach would be to replace T_c in those expressions by $T_m(l^*)$.

The presence of a temperature gradient, similar to that shown in Fig. 14, but not recognized as such, could also give rise to many false interpretations of experimental data, such as the presence of a mesophase or an adsorbed phase on the crystal surface. A temperature greater than that of the crystallization temperature, in the crystal behind the growth front, could also lead to unnecessary assumptions about the internal mobility of the chains in the crystal. These are just a few of the potential consequences of this finding and remain to be explored in detail. Indeed, it will be necessary to re-evaluate all of our current beliefs about the crystallization process and the mechanisms of crystallization.

It should also be apparent that for conditions of growth at low supercooling the temperature gradient at the crystal-amorphous interface would be quite low and might be consistent with an isothermal assumption. The conditions under which an isothermal or pseudo-isothermal condition would occur remain to be seen. It is quite possible that the ranges will vary significantly from one polymer to another, as one of the important parameters in the expressions is the actual rate of growth.

To the best of our knowledge the results presented here are the first clear evidence that the rate of growth of a crystal is constant during rapid cooling, even when no temperature plateau is observed. This means that there is a microenvironment at the growth face of the crystals, which cannot be inferred from measurements of film temperature, even when an embedded microthermocouple is used. The simple fact remains that we can no longer assume that any measured temperature, whether in 'isothermal' or rapid cooling experiments, is indicative of the actual crystallization temperature at the growth front. Indeed, no method exists for the measurement of the actual temperature at which crystallization is occurring at the growth front. Additionally, the fact that the scale on which deposition of stems occurs is truly nanoscale, further complicates the elucidation of physical measurement. Currently, there are no simulations of the deposition of a polymer stem on a crystal, which handle the elimination and dispersion of the free energy of fusion. Clearly, the most likely route for elimination of the excess energy is along the crystallizing polymer chain itself, either into the still-amorphous section of chain or into the previously crystallized section of the polymer chain. This would result in both sections of the chain being hotter than the crystallizing stem. However, it should be self-evident that a considerable amount of modeling of the temperature distribution and evolution during the crystallization process on a molecular level is necessary, before any real understanding of the situation can be obtained. This would be a very different level of modeling from that of the past, ably summarized in Schultz [18], and used in our own discussions above.

Acknowledgements

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