

ORIGINAL ARTICLE

Estimation of polymer nucleation and growth rates by overall DSC crystallization rates

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Isothermal crystallization of a polyoxymethylene copolymer in the temperature range of 423–429 K (150–156 °C) was performed using a differential scanning calorimeter (DSC) and data of crystalline development processed within the framework of a nucleation and growth model. Morphological investigations on DSC crystallized specimens were performed by scanning electron microscopy (SEM) and correlated to DSC data to obtain good estimations of spherulite growth rates in the explored temperature range. The accuracy of the growth rate has been enhanced by Hoffman regime analysis using reliable values of input parameters. Moreover, the function describing the number of growing spherulites as a function of time at constant temperature has been obtained. *Polymer Journal* (2011) 43, 78–83; doi:10.1038/pj.2010.111; published online 10 November 2010

Keywords: crystallization; differential scanning calorimetry; microscopy; microstructure; phase transformation kinetics; polymers

INTRODUCTION

Spherulites are the main morphological form of polymers crystallized from melts. The phase transformation kinetics is of primary importance for technological profit, as the crystallization mechanism controls the spherulitic texture, which in turn affects the mechanical properties. For instance, stochastic models consider crystallization a random spatial process leading to uniform spherulite density, whereas deterministic models account for nonhomogeneous temperature fields¹ and predict different spherulite densities in different parts of a sample. Temperature gradients acting along the thickness of polymer specimens lead to the formation of layers of approximately bi-dimensional spherulites² with a change of structure and, hence, of the mechanical behavior of the material.

Generally, growth rates of polymers are evaluated by visually following the growth of spherulites developing at constant temperature. The radii of spherulites are usually found to be a linear function of time; that is, the growth rate seems to remain constant during isothermal crystallization. This procedure gives accurate growth rate values, but takes a long time and is not useful for polymers with high-nucleation densities in which spherulites achieve sizes too small to be continuously monitored during crystallization through an optical microscope.³ It may also happen that additives with high refractive indices hinder the observation of polymer samples under light-transmission microscopes, making the use of the classic method for growth rate measurements impossible.⁴ Furthermore, if spherulites with different growth rates arise in various concentrations during solidification (as for polymorphs and polymer blends), the conventional measure of growth rates may not be easy, especially for less abundant spherulite types. Usually, to measure growth rates of different crystalline forms, it is necessary to add specific nucleating

agents, although these foreign substances could affect the crystallization kinetics of the polymer. The visual observation of solids by means of high-resolution microscopes, as opposed to monitoring during solidification, has already been proved to be very useful in obtaining information on the crystallization mechanism.⁵ Indeed, the shape of the interface between spherulites gives an indication of the relative instances of nucleation and growth rates of the spherulites.⁵ Growth parameters have also been obtained from the overall crystallization rate of previously self-nucleated samples at an ideal temperature.^{3,6} This method requires preliminary differential scanning calorimeter (DSC) scans to identify the self-nucleation temperatures of polymers. For two-phases polymeric materials with close melting points, the determination of the self-nucleation ranges could be very complicate. Moreover, a large number of copolymers do not show self-nucleation temperatures.⁶ A new method to determine the growth rate of polymer spherulites is described herein. It is on the basis of measuring both the time required for a specimen to entirely crystallize by DSC and the maximum radial dimension of coalesced spherulites in the crystallized sample by microscopy. Indeed, the final size of coalesced spherulites grown at the same rate depends on the distance between the centers of the spherulites and on their nucleation events; therefore, the fraction of spherulites with maximum radial sizes is representative of spherulites nucleated early, which ultimately impinge at the end of the crystallization because of their long distance from neighbors.

THEORETICAL BACKGROUND

The present method has been conceived in the context of the classic crystallization theory, based on the mechanism of nucleation, crystal growth and cessation, which is explained in the following section.

At a constant temperature, the overall crystallization rate ν of a polymer sample may be defined as:

$$\nu = G \cdot N(t) \quad (1)$$

where G is the growth rate (the change of the radius of a spherulite per unit time) and $N(t)$ is the time function describing the number of growing spherulites in the sample. $N(t)$ accounts for both the birth of spherulites and the end of their growth due to impingement. Impingement begins when adjacent spherulites touch each other at a point and causes the cessation of the growth at the contact region between spherulites with a progressive reduction of the length of the growth fronts relative to separate spherulites.⁵ Therefore, the function $N(t)$ has values in the range of rational numbers and accounts for the decrease of the fraction of the growth front of coalescing spherulites. For instance, the contribution to $N(t)$ of z spherulites is z until they remain separate, but once they begin to coalesce, their contribution to $N(t)$ is a fractional number that becomes progressively smaller than z , according to the increasing fraction of the contour that ceases to grow.

Nucleation is considered to be caused by temperature fluctuations in the melt. If all spherulites grow at the same rate, are equally distanced and the nucleation does not depend on time, all spherulites appear simultaneously (instantaneous nucleation), and their growth will also stop simultaneously; consequently, the overall crystallization rate will be constant at constant temperature, except during the final stage of crystallization when spherulites begin to impinge one another causing a decrease in $N(t)$. However, if the nucleation is not instantaneous and/or the space position of spherulites is not random but deterministic (so that new growth fronts originate while other fronts collide and gradually their growth stops), the number of growing spherulites will be time dependent and, consequently, the overall crystallization rate will also be a function of time. For bi-dimensional growth in a thin polymer film, assuming as zero time t_0 the time at which the early spherulites begin to grow, the solid area developed per spherulite during the time interval $[t, t']$ is:

$$\pi(r'^2 - r^2) \quad (2)$$

where r and r' represent the spherulite radius at the instants t and t' . Substituting $r+(t'-t)G$ for r' in Equation (2), and assuming $(t'-t)=1$, the increase in the area of each spherulite in a time unit is given by:

$$\pi[2r(t'-t)G+(t'-t)^2G^2] \quad (3)$$

As $r = tG$, the solid surface that develops in a time unit per a growing spherulite is:

$$\begin{aligned} \pi(2r(t'-t)G+(t'-t)^2G^2) &= \pi[2t(t'-t)G^2+(t'-t)^2G^2] \\ &= \pi[2t(t'-t)+(t'-t)^2]G^2 \end{aligned} \quad (4)$$

whereas the solid surface that develops per unit of time in the whole sample is:

$$\pi[2t(t'-t)+(t'-t)^2]G^2N(t) \quad (5)$$

Dividing Equation (5) for the total surface of the polymer sample A , the increase of the solid fraction in a time unit $dX(t)/dt$ is obtained as a function of the crystallization time:

$$\frac{dX(t)}{dt} = \pi[2t(t'-t)+(t'-t)^2]G^2N(t)/A \quad T = \text{constant}; \quad t' - t = 1 \quad (6)$$

From Equation (6), it results that

$$A(dX(t)/dt)/\{\pi[2t(t'-t)+(t'-t)^2]\} = G^2N(t) \quad (7)$$

Hence, the function $A(dX(t)/dt)/\{\pi[2t(t'-t)+(t'-t)^2]\}$ shows the same trend as $N(t)$, with G^2 being constant. The degree of phase transformation $X(t)$ from the DSC crystallization peak (time zero at the onset of the exothermal peak) can be obtained using the formula:

$$X(t) = \frac{\int_0^t (dH/dt) dt}{\int_0^\infty (dH/dt) dt} \quad (8)$$

and dX/dt can be obtained from the data from Equation (8) by applying the well-known Taylor formula:

$$\frac{dX(t)}{dt} = \lim_{h \rightarrow 0} \frac{X(t+h) - X(t)}{h} \quad (9)$$

When the crystallinity development follows the Avrami equation, the derivative dX/dt can also be obtained by the formula:⁷

$$\frac{dX(t)}{dt} = -\frac{n(1-X(t)) \ln(1-X(t))}{t} \quad (10)$$

where n is the Avrami index⁸ that according to the original phase transformation theory should be an integer from 1 to 4, depending on the geometry of the crystals and on the nucleation dependence on time. Actually, the Avrami index n has mostly a fractional value.^{1,9}

It is worth noting that Equations (6) and (7), obtained for a bi-dimensional growth of spherulites in thin films, remain valid for three-dimensional specimens consisting of layers of bi-dimensional spherulites.

It will be shown below that by measuring the development of the crystallinity with time at various temperatures and estimating the maximum radial dimension of impinging spherulites in DSC crystallized samples, it is possible to obtain information on the nucleation and growth processes of a polymer. Here, a polyoxymethylene copolymer (POMC) has been chosen to validate the method because clear correlations between kinetics, microstructure and crystallization conditions have already been established for this polymer.² However, the method is applicable to any linear polymer to gather information on crystallization and microstructure, even in cases of thick specimens for which nucleation is deterministic. The only important requirement is that the thickness of the specimens be relatively low (about 1 mm) in order to favor the development of an appreciable number of spherulites on the surface at the beginning of the crystallization. Indeed, the number of these spherulites on the top surface (the surface submitted to scanning electron microscopy (SEM) investigations) is much lower than that of the spherulites simultaneously originating in the lower layers because of the proximity of the cooling source. In other words, there is a decrease in the nucleation density in DSC crystallized specimens if nucleation is not stochastic but deterministic.

EXPERIMENTAL PROCEDURE

A POMC containing a small amount of randomly distributed oxyethylene units was provided by Goodfellow (Huntingdon, UK). It had a melt flow index (MFI) of 3 g per 10 min. The weight average molecular weight $M_w=94\,000$ was calculated by the formula:¹⁰

$$\text{MFI} = 1.30 \times 10^{18} M_w^{-3.55}$$

Thermal analysis was performed under nitrogen using a Mettler TA-3000 differential scanning calorimeter (Mettler Toledo S.p.A., Novate Milanese, MI, Italy) equipped with a control and programming unit and a calorimetric cell. The apparatus was calibrated with pure indium, lead and zinc at various

scanning rates. The isothermal crystallization of samples was carried out in 40- μ l pans, with the following thermal protocol:

- Heating to 473 K at a scan rate of 20 K min⁻¹ (I RUN).
- Cooling to the selected temperatures at a scan rate of -50 K min⁻¹ (II RUN).
- Holding at the selected temperature until the time necessary to complete the crystallization (III RUN).

Isothermal crystallization was explored in the temperature range 423–429 K.

It is worth specifying that the time required to start crystallization in the III RUN (the so-called induction time) is longer than the time required to obtain a stable baseline. Moreover, the DSC baseline after the crystallization peak falls to the same level as the onset of the crystallization peak.

To ensure that crystallization does not occur during the cooling at the selected isothermal temperature, the following protocol was also performed:

- Heating to 473 K at a scan rate of 20 K min⁻¹.
- Cooling to the selected temperatures at a scan rate of -50 K min⁻¹.
- Re-heating to 473 K at a scan rate of 20 K min⁻¹.

Indeed, the absence of a melting peak in the third run demonstrated that crystallization does not occur during the second run.

SEM was performed with a Philips 501 SEM after vacuum metallization of the samples by means of a Polaron sputtering apparatus with a Au-Pd alloy. The whole surface of the DSC crystallized specimens was analyzed by SEM to obtain results representative of the polymer sample.

RESULTS AND DISCUSSION

Early crystallization theories of polymers considered the rate of heat transfer infinite. This assumption leads to the instantaneous cooling and heating of a mass of substances, which ignores the fact that heat developed during solidification cannot be removed instantaneously for the establishment of a constant and uniform temperature.¹¹ The assumption of an infinite propagation rate of heat leads, in turn, to the adoption of stochastic nucleation. This kind of nucleation entails the random appearance of nuclei in space, without any connection to the distance from cooling or heating sources, which is likely to occur only in very thin and small samples. The existence of temperature gradients over the thickness of crystallizing specimens results in nonhomogeneity of crystallite size over the thickness.^{12,13} Deterministic nucleation has been observed even in thin specimens,^{9,14} and it has been proved that thicker samples crystallized in DSC pans consist of superimposed layers of bi-dimensional spherulites.^{2,4} Despite the dependence of the nucleation modality on the thickness, the method herein proposed is applicable not only to thin, but also to thick samples provided that spherulites nucleated at the beginning of the solidification on the top surface of the DSC crystallized specimens are present.

This method consists of carrying out isothermal crystallization with DSC to appreciate the time t_{tot} needed to entirely crystallize the polymer samples. This quantity is given by the difference between the time at which the development of the latent heat of solidification stops and the time t_0 at which the latent heat begins to develop. The reciprocal of the overall crystallization time t_{tot} may be considered an estimation of the overall crystallization rate.² The top surfaces of the DSC crystallized samples are then submitted to SEM analysis to estimate the maximum radial dimension of coalesced spherulites. This length is a good approximation of the radius, at the time t_{tot} of the unique spherulite that would have developed if a single-nucleation event had occurred in the melt at the time t_0 (although, at the time t_{tot} not all of the melt would have been transformed in the

case of the growth of a monocrystal) and the ratio between the size of the crystal and the time t_{tot} required to achieve that size would give the crystal growth rate. Therefore, the growth rate at a certain temperature may be obtained by the ratio of the maximum 'radius' of the spherulites and the overall crystallization time t_{tot} of a polycrystalline sample. This procedure can be iterated to obtain the growth rate at different temperatures. Furthermore, the accuracy of the growth rates can be improved by exploiting the Hoffman regime analysis, provided that accurate input parameters are available.

It is well known that the nucleation density (the number of spherulites per unit surface area or volume in fully crystallized polymer sample) is a function of the crystallization temperature; namely, it decreases with the temperature.

It is worth noting that if nucleation is instantaneous and nucleation density uniform in the whole polymer sample, the overall crystallization rate at a certain temperature, and hence the reciprocal overall crystallization time $1/t_{\text{tot}}$ will be proportional to the growth rate G . If there was a single nucleation site, referring to r as the radius of the unique spherulite at the time t_{tot} , the growth rate would be given by $G=r/t_{\text{tot}}$, and the proportionality constant h between $1/t_{\text{tot}}$ and G would be given by the reciprocal of the radius r of the spherulite. Hence, the dimensions of $h=1/r$ are length⁻¹. Because it is difficult to obtain monocrystals from polycrystalline materials like polymers, accurate values of h cannot be determined by visual observations of separate spherulites. However, the growth rate of polymers is generally found to follow the Lauritzen–Hoffman equation:¹⁵

$$G = G_0 \exp\{-U^*/[R(T - T_\infty)]\} \exp\{-K_g/[T(T_m^0 - T)]\} \quad (11)$$

(valid for $T < T_g + 100$)¹⁶

where U^* is a 'universal' constant characteristic of the activation energy for transport of macromolecules through the melt onto the substrate, R is the gas constant, T_∞ is the theoretical temperature at which all motion associated with viscous flow ceases, T_m^0 is the equilibrium melting temperature and T is the crystallization temperature. Generally, the values assumed for U^* and T_∞ are 1500 cal mol⁻¹ and $T_g - 30$, respectively, where T_g is the glass transition temperature.

Substituting the quantity $1/(ht_{\text{tot}})$ for G in the logarithmic form of Equation (11) results in the following:

$$\ln(1/t_{\text{tot}}) - \ln h + U^*[R(T - T_\infty)] = \ln G_0 - K_g/[T(T_m^0 - T)] \quad (12)$$

Therefore, for crystallization in a temperature range where nucleation is stochastic and instantaneous, the plot obtained for $\ln(1/t_{\text{tot}}) + U^*/[R(T - T_\infty)]$ vs $1/[T(T_m^0 - T)]$ will be linear such that the slope of the line is the negative of the nucleation constant $-K_g$ and the intercept is $\ln G_0 + \ln h = \ln(hG_0)$. Knowing $1/t_{\text{tot}}$, it is necessary to know h to obtain G_0 or, vice versa, to know G_0 to obtain h . The value of h cannot be accurately estimated by measuring the radius of spherulites in actual polymer samples because crystallization occurs from multiple nucleation sites; the collision between spherulites, according to their distance and growth rates,⁵ causes the cessation of their growth and the generation of a tessellated structure with polyhedral tessellations. However, because the impingement between a number of spherulites nucleated far from the cooling source can be considered to occur only during the final stage of crystallization, a good approximation of h is obtained by using in $h=1/r$ the maximum radial dimension of spherulites visible on the top surface of a crystallized sample. Then, G_0 may be obtained from the value of the intercept $\ln(hG_0)$ (that is, $G_0 = e^{(\text{intercept} - \ln h)}$) and $G(T)$ may be estimated from $G=r/t_{\text{tot}}$ or by Equation (11). This latter procedure is applicable only when

Equation (12) leads to a linear plot because of instantaneous and stochastic nucleation in the whole specimen; for example, in very thin films such as those used for observations through an optical microscope. However, very thin films generate crystallization heat well below the sensitivity of the DSC. Therefore, thicker specimens characterized by non-instantaneous nucleation are required for DSC analysis.

For not very thin samples with low-thermal conductivity, nucleation is generally deterministic (that is, the nucleation density is variable inside a specimen) and time-dependent. Therefore, the number of growing spherulites $N(t)$ and, hence, the overall crystallization rate, depend on time and the plot of $\ln(1/t_{\text{tot}}) + U^*/[R(T - T_{\infty})]$ as the function of $1/[T(T_m^0 - T)]$ is not linear.

For instance, the plot of $\ln(1/t_{\text{tot}}) + U^*/[R(T - T_{\infty})]$ against $1/[T(T_m^0 - T)]$ for POMC, obtained using the values of $1500 \text{ cal mol}^{-1}$, 192.5 K^{17} and 455 K^{18} for U^* , T_{∞} and T_m^0 , respectively, is shown in Figure 1. This demonstrates that the nucleation is not uniform in the whole specimen because the data seem to follow a second-order polynomial equation rather than a linear equation.

Even if nucleation is neither stochastic nor instantaneous, the functions $G(T)$ and $N(t)$ at a constant temperature can be obtained as explained in the following section follows.

The method to evaluate the growth rate through DSC and SEM evaluations, described in the above paragraph, is shown for POMC in the temperature range of 423–429 K. In Table 1, the time required to complete the isothermal crystallization of DSC specimens of POMC is reported. The SEM micrographs of the top surfaces of POMC crystallized at 423 and 428 K are shown in Figure 2. The SEM analysis

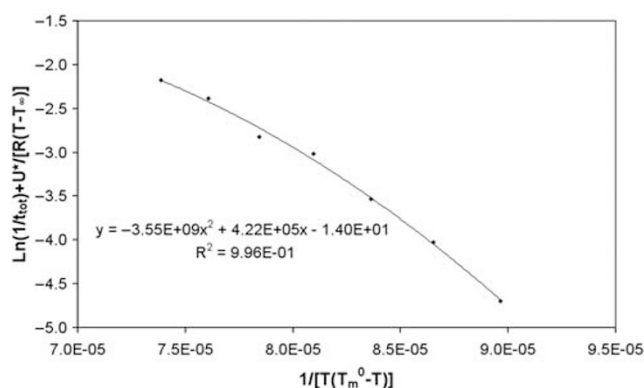


Figure 1 Plot of $\ln(1/t_{\text{tot}}) + U^*/[R(T - T_{\infty})]$ against $1/[T(T_m^0 - T)]$ for polyoxymethylene copolymer with $T_m^0 = 455 \text{ K}$,¹⁸ $T_{\infty} = 192.5 \text{ K}$ ¹⁷ and $U^* = 1500 \text{ cal mol}^{-1}$.

Table 1 Overall crystallization time t_{tot} of POMC specimens isothermally crystallized and calculated growth rate G

T(K)	t_{tot} (s)	G ($\mu\text{m s}^{-1}$) estimated from SEM analysis	G ($\mu\text{m s}^{-1}$) calculated by Equation (13)
423	233	0.1071	0.1172
424	283	0.0885	0.0789
425	434	0.0576	0.0521
426	518	0.0482	0.0338
427	860	0.0291	0.0215
428	1383	0.0181	0.0133
429	2672	0.0094	0.0081

Abbreviations: POMC, polyoxymethylene copolymer; SEM, scanning electron microscopy.

of the superior surfaces of the specimens evidences that in the explored temperature range no significant differences in the average size of spherulites exists, and a unique value of $25 \pm 1 \mu\text{m}$ was also estimated for the maximum radial size of spherulites in all specimens, regardless of the crystallization temperature. Dividing the maximum radial extension of spherulites by the time t_{tot} , reliable values for the growth rate of spherulites are obtained and shown in Table 1. Taking into account the differences in structure and molecular weight between poly(oxymethylene) homopolymer and POMC, it can be stated that there is a very good agreement between the growth rate calculated and the values given for growth rates of poly(oxymethylene) homopolymer with $M_n = 70\,000$ (Delrin 150) by Hoffman.¹⁹ This author found for the growth rate of Delrin 150 experimentally determined by Pelzbauer and Galeski²⁰ the following expression in regime III:

$$G_{\text{III}}(\text{cm s}^{-1}) = 2.83 \times 10^8 e^{-7,000/RT} e^{-4.576 \times 10^5/T(\Delta T)} \quad (13)$$

where R is the gas constant and ΔT the undercooling. The melting point $T_m^0 = 471.5 \text{ K}$ has been used in Equation (13) to measure the undercooling, according to the original analysis.¹⁹

The uncertainty of the calculated growth rates for POMC can be reduced by applying the Lauritzen–Hoffman equation on the following bases.

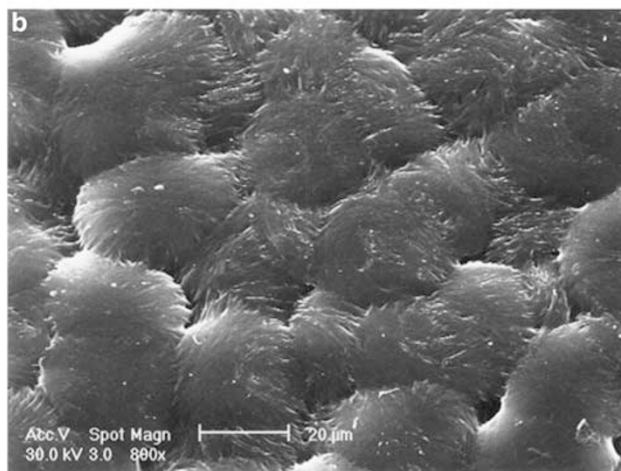
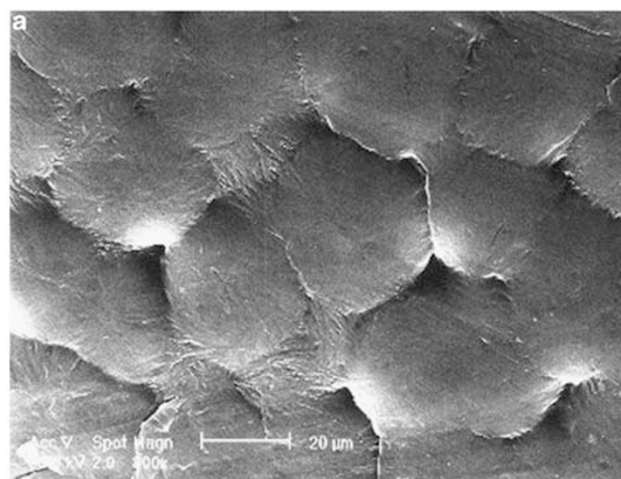


Figure 2 Scanning electron microscopy micrographs of the surfaces of polyoxymethylene copolymer specimens crystallized at 423 K (a) and 428 K (b).

It can be demonstrated that a systematic error in the growth rate function $G(T)$ of polymer spherulites biases the outcomes of the regime analysis.²¹ Indeed, assuming that G follows the Equation (11), the measured growth rate $G+\delta G$ biased by a systematic error δG is given by the following:

$$G+\delta G = G_0 \exp\{-U^*/[R(T-T_\infty)]\} \times \exp\{-K_g/[T(T_m^0-T)]\} + \delta G \quad (14)$$

Taking the logarithm produces the following:

$$\ln(G+\delta G) = \ln\{G_0 \exp\{-U^*/[R(T-T_\infty)]\} \times \exp\{-K_g/[T(T_m^0-T)]\} + \delta G\} \quad (15)$$

Therefore, the plot constructed using $\ln(G+\delta G)+U^*/[R(T-T_\infty)]$ and the measured values of $G+\delta G$ and T against $1/[T(T_m^0-T)]$ results in a linear relation in each regime only for $\delta G \rightarrow 0$, when Equation (15) reduces to:

$$\ln(G+\delta G) \cong \ln G_0 - U^*/[R(T-T_\infty)] - K_g/[T(T_m^0-T)] \quad (16)$$

Otherwise, the observed growth rate follows Equation (14) and, thus, the plot of $\ln(G+\delta G)+U^*/[R(T-T_\infty)]$ as a function of $1/[T(T_m^0-T)]$ is non-linear. A linear plot can be obtained only by the addition of the negative of the systematic error $-\delta G$ to the measured growth rate $G+\delta G$ such that 'true' values of G are used; under these conditions, Equation (15) gives:

$$\ln G + U^*/[R(T-T_\infty)] = \ln G_0 - K_g/[T(T_m^0-T)] \quad (17)$$

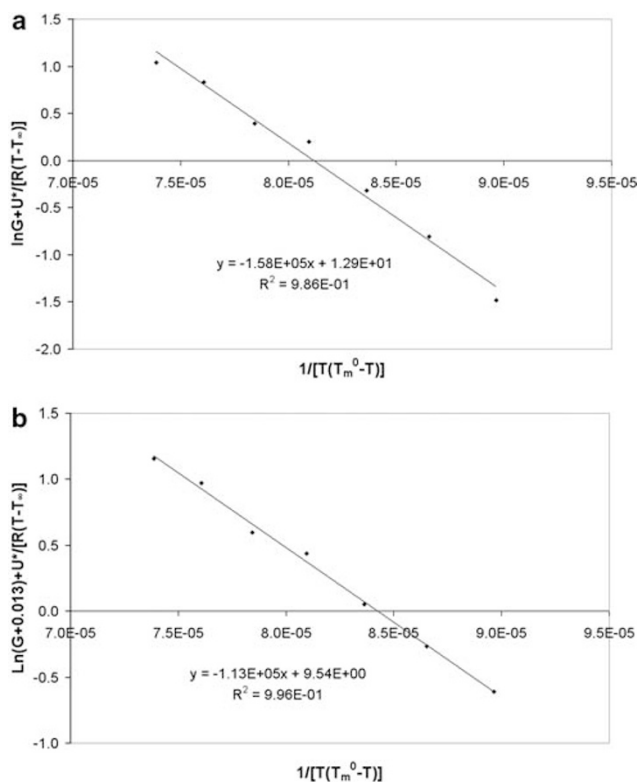


Figure 3 Plot of $\ln G+U^*/[R(T-T_\infty)]$ as a function of $1/[T(T_m^0-T)]$ (a) and of $\ln(G+0.013)+U^*/[R(T-T_\infty)]$ as a function of $1/[T(T_m^0-T)]$ (b) obtained using for U^* , T_∞ and T_m^0 the same input values used in Figure 1 and G values reported in Table 1.

Briefly, given a function $F(T)$ that differs by a constant c from the growth rate $G(T)$, the growth rate can be obtained by searching for the value of the constant c for which the plot of $\ln(F-c)+U^*/[R(T-T_\infty)]$ as a function of $1/[T(T_m^0-T)]$ is linear. This procedure is rigorously valid if reliable values of U^* , T_∞ and T_m^0 are used.

Figure 3 shows the Hoffman plot for POMC obtained using the G values from SEM analysis reported in Table 1 and the values of $1500 \text{ cal mol}^{-1}$, 192.5 K^{17} and 455 K^{18} for U^* , T_∞ and T_m^0 , respectively. The data points seem to follow a curve rather than a line, and, indeed, the correlation coefficient of the linear regression is far from 1. However, adding 0.013 to the calculated growth rate increases the correlation coefficient, indicating that an error of -0.013 in the approximate growth rates exists.

Finally, the function describing the nucleation process for POMC was derived as follows. The derivative dX/dt was obtained from the DSC crystallinity data at constant temperature by Equation (9). Then, the quantity $N(t) = (AdX/dt)/(\pi G^2[2t(t'-t)+(t'-t)^2])$ (with $A=\pi 2000^2 \mu\text{m}^2$, $t'-t=1$ and corrected G values) was calculated for each temperature and plotted against time. Figure 4 shows the functions $N(t)$ at the temperatures 423–429 K, proving that at higher temperatures a smaller number of spherulites arises in the bulk at the onset of crystallization (that is, at time zero). Furthermore, at higher temperatures, the function $N(t)$ first increases with increasing time, reaches a maximum and finally decreases. The trend of $N(t)$ indicates that there is first a massive development of spherulites, and there after the crystallization slows down because impingement begins to prevail on nucleation. The ascending stretch of $N(t)$ at the beginning of

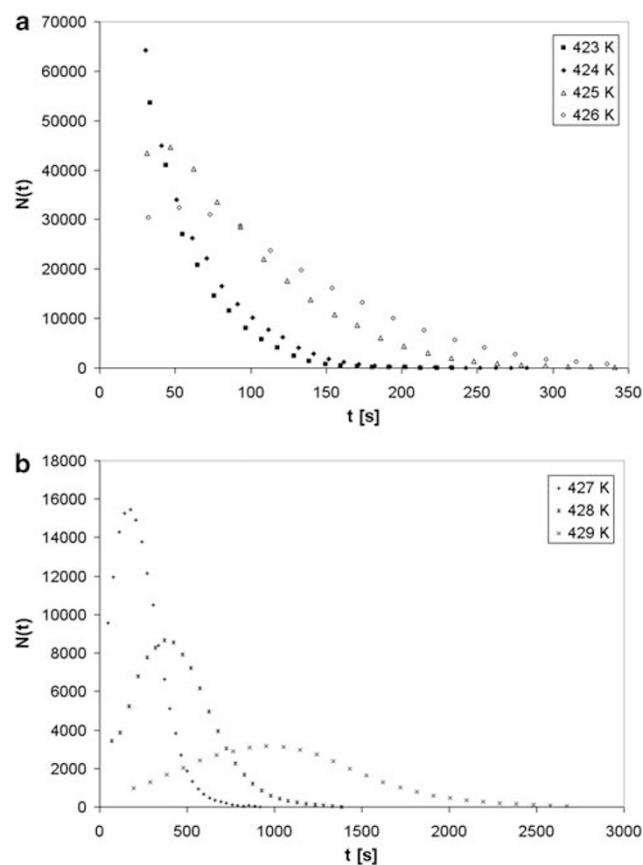


Figure 4 The functions $N(t)$ over the time interval $[0, t_{\text{tot}}]$ at the temperatures 423–426 K (a) and 427–429 K (b).

crystallization is not observable at low temperatures (423–424 K), because of very high nucleation densities, especially, in the bottom layers of the specimens. High growth rates at low temperatures soon lead to the impingement of a number of spherulites overcoming the nucleation process. Indeed, there is a variation of the nucleation density along the thickness of a crystallizing polymer sample as a consequence of the different distance from the cooling source and of the finite rate of heat propagation.²

The overall crystallization rate ν as function of time at various temperatures can finally be obtained by the product of the growth rate G and the function $N(t)$.

The present method can be easily extended to materials with high-thermal conductivity for which stochastic nucleation, leading to a uniform nucleation density along the thickness, could be observed. In fact, besides polymers, several substances form spherulites.²² Moreover, three-dimensional spherulites can be observed by crystallizing polymers from a solution.²³ In the case of three-dimensional spherulites, it is only necessary to consider the volume

$$\frac{3}{4}\pi(r'^3 - r^3)N(t) \quad (18)$$

instead of the surface, which develops per unit of time in the whole sample in order to obtain the increase of the solid fraction over unit time. Considering the equality $r' = r + (t' - t)G$ for $t' - t = 1$, taking the radius r as the product of the growth rate G for the respective time t and dividing by the final volume of the solid V , the following formula is obtained from Equation (18):

$$\frac{dX(t)}{dt} = \frac{\frac{3}{4}G^3[(t' - t)^3 + 3t(t' - t)^2 + 3t^2(t' - t)]}{V}N(t) \quad (19)$$

The Equation (19) can be rewritten as follows:

$$V(dX(t)/dT) / \left\{ \frac{3}{4}\pi[(t' - t)^3 + 3t(t' - t)^2 + 3t^2(t' - t)] \right\} = G^3N(t); t' - t = 1 \quad (20)$$

Therefore, G and $N(t)$ for DSC crystallized samples may be obtained as for the bi-dimensional case; although, in the three-dimensional case, the top surface of the sample will show sections of spherulites nucleated on different planes in the bulk.

CONCLUSIONS

A quick but accurate method to calculate the growth rates of polymer spherulites has been described. It consists of measuring the maximum size of spherulites in the top layer of DSC crystallized samples and the overall crystallization time at constant temperature. The growth rates can then be calculated at various temperatures by the ratios of these two quantities. A formula is also given to obtain, from data of crystallinity development and growth rates, a measure of the effective growth front during crystallization.

The method shown herein is reliable for both stochastic and deterministic nucleation. Both thick samples and thin polymer films, with an appreciable overall crystallization rate, may be used. In the case of deterministic nucleation, the only important requirement is that the thickness be not so high as to hinder the development of an appreciable number of spherulites at the top surface at the beginning of crystallization. This method can also be used to calculate the growth rate of crystalline forms that occasionally nucleate in polymorphic samples when the traditional method is not easy. For instance, in the absence of β -nucleating substances, it is very

difficult to follow the growth of β -polypropylene spherulites by means of an optical microscope because of their high growth rate and the predominance of α -spherulites in isothermally crystallized samples. It is worth noting that conventional growth rate measurements require the presence of β -nucleating substances, which could affect the growth rate measurements, whereas the present method allows for growth rate measurements in the absence of foreign substances provided that a few β -spherulites are visible on the surface of DSC crystallized specimens. Polypropylene spherulites of different phases are clearly distinguishable by atomic force microscopy.²⁴

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