True Sample Temperatures in Isothermal Differential Scanning Calorimetry Scans and Their Effect on the Overall Polymer Crystallization Kinetics

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ABSTRACT: The true temperature of a sample during isothermal crystallization is higher than the recorded differential scanning calorimetry program temperature because of two combined effects: the thermal resistance of the sample, which is mainly dependent on the thickness of the sample, and the release of the heat of crystallization. This is especially true for a low crystallization temperature, at which the heat of crystallization is released within a relatively short time. Isothermal crystallization is treated here as a nonisothermal process, and the values of the parameters obtained with single-mechanism equations (Avrami and Nakamura's) used in their description are compared. The validity of the procedure used for evaluating the temperature increase of a sample is analyzed and discussed (i.e., the evaluation of the thermal resistance of a sample as a function of its thickness). Some isothermal crystallization data obtained at relatively high supercoolings may be affected by errors if temperature corrections are not carried out. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 125–131, 2004

Key words: differential scanning calorimetry (DSC); crystallization; thermal properties

INTRODUCTION

The effects of heat transfer on the isothermal crystallization of polymers have recently interested several researchers. Piorkowska and Galeski[1] analyzed the influence of the release of the heat of crystallization on the temperature near the crystallization front during the isothermal crystallization of polymers. They recognized that the old assumption that the crystallization of polymers is not governed by the dissipation of the heat of fusion, based on the premise that the spherulite growth rate is constant in time, is not necessarily true. Because of the release of the heat of crystallization, the temperature at the crystallization front is, of course, below the thermodynamic melting temperature but above the temperature of the supercooled liquid phase. They predicted, for the isothermal crystallization of isotactic polypropylene (iPP) at 121.5°C, a temperature increase of 1°C at the growth front after 10 min of crystallization.

In a subsequent work, Piorkowska[2] predicted a temperature increase in the middle of iPP samples during their isothermal crystallization. The prediction was based on a solution of the heat-transfer problem in a plate of thickness d, initially at temperature T_0, bounded by two parallel planes at $x = 0$ and $x = d$. The planes were kept at T_0 for $t > 0$, and the bulk heat production rate was dependent on the time and x coordinates. The predicted temperature increase, for a 2-mm-thick iPP sample crystallized at 122.5°C, under the assumption of instantaneous nucleation, was around 2°C for a time corresponding to half of the overall crystallization. Experimental measurements were carried out in a special device in which sample disks with a radius of 10 mm and a thickness of 2 mm were used. A maximum temperature increase of 2°C was, in fact, observed for a sample crystallized around 120.5°C, that is, two degrees lower than that of the simulation. For a simulation carried out at 120°C, the maximum temperature increase was around 3.5°C.

If the heat transfer to and from the samples used in ref. 2, as in differential scanning calorimetry (DSC) samples, is mainly by conduction, the thermal resistance of a sample for conduction (R_s) is the ratio between its thickness (L) and the product of its area (A) by its thermal conductivity (k). Samples used in regular DSC experiments have higher R_s values than those used in the work of Piorkowska.[1,2] A regular DSC sample has a thickness of 0.3 mm and a radius of

3 mm. Its R_s value is 1.6 times higher than that of the sample used in ref. 2. It is expected that, for thin DSC samples, because of their relatively high R_s values, the heat generated during the solidification will contribute to the development of a temperature profile within the samples and that this profile will be more significant for lower crystallization temperatures, for which temperature increases similar to and even higher than those measured by Piorkowska should occur.

Other authors have analyzed the effects of the temperature profile in quasi-isothermal temperature-modulated different scanning calorimetry (TMDSC) measurements as a function of the sample thickness.[3] The results obtained for two-dimensional conduction through DSC samples (along the thickness and in the radial direction) yielded for poly(ethylene terephthalate) samples with $r/L = 1.5$ (sample radius = 3.3 mm and thickness = 0.74 mm) a thermal gradient along the sample thickness of 0.14°C under typical TMDSC conditions. On the basis of these results, and to avoid thermal gradients, the use of thin samples, roughly 33 μm thick, was suggested.

Previous works have not, to our knowledge, provided any evaluation of the temperature increase during isothermal DSC crystallization or analyzed its effect on the description of the overall crystallization kinetics. Part of this work was carried out previously,[4] but it is presented here with an additional detailed analysis of the effect of the temperature increase on the definition of the sample temperature corresponding to the half-crystallization time ($t_{50\%}$), together with a kinetic description of the nominally isothermal crystallization formulated as a nonisothermal process (particularly at low crystallization temperatures) with Nakamura's equation.

The calculation of the average true sample temperature from the experimental isothermal DSC crystallization curve requires a preliminary evaluation of the R_s value of the sample. This evaluation is usually obtained from the difference between the reciprocal of the slopes of the ascending section of the melting peaks of indium and indium over a polymer sample.[5] The reasonableness of the method for evaluating the R_s value was assessed by a series of experiments carried out over polymer samples of controlled thickness, together with simulations of the temperature profile in lower thermal conductivity samples, with appropriate boundary conditions.[6] The results shown in ref. 6 and others from subsequent work have shown that acceptable values for R_s may be obtained with the aforementioned procedure, as long as the sample thickness is not close to the depth or height of the sample pan.

A reasonable first estimate of the average sample temperature (any temperature gradients within the sample being neglected or averaged out) may then be obtained from the experimental DSC curve by the application of a heat-transfer balance, by which the

TABLE I
R_s Values of MDPE and POM

	Mass (mg)	Thickness (mm)	Area (mm²)	R_s (K/W)
MDPE	10.313	0.39	34.10	26.30
POM	4.328	0.21	17.60	36.52

sensible heat flux received by the sample equals the heat flux released within the sample because of the ongoing crystallization process minus the instrument-sensed net heat loss from the sample to the corresponding temperature sensor:[7,8]

$$mc_p \frac{dT_t}{dt} = |\Delta\dot{Q}| - \frac{1}{R_s}(T_t - T_m) \tag{1}$$

where m is the sample mass; c_p is the specific heat capacity; dT_t/dt is the rate of the sample temperature variation; T_t and T_m are the true sample temperature and the temperature measured by the temperature sensor, respectively; and R_s is equal to L/Ak. The heat flux released within the sample is $|\Delta\dot{Q}|$ $= m|\Delta h_c|dX/dt$, where Δh_c is the specific heat of crystallization and X is the mass fraction transformed at time t. According to Kriegl et al.,[7] the additional effect of the specific heat capacity and mass of the aluminum pan should also be considered. Although more correct from a physical point of view, the sample temperature profile obtained with this procedure is the same as that obtained with eq. (1) because of the negligible R_s value of the aluminum pans.

EXPERIMENTAL

The experiments were carried out in a PerkinElmer (Norwalk, CT) DSC-7 upgraded for dynamic DSC (DDSC) experiments. The calibrations were carried out according to standard procedures.[9] The temperature calibration for isothermal experiments was performed at the slowest scanning rate allowed by the instrument (0.1°C/min). The materials used in this work were poly(oxymethylene) (POM) (Delrin 150) and a medium density poly(ethylene) (MDPE) (Enichem RP264H). The m values for POM and MDPE sample were 4.328 and 10.313 mg, respectively. The thermal conductivities, obtained with a Moldflow software package (Victoria, Australia), were 0.42 and 0.29 W K^{-1} m^{-1} for MDPE and POM, respectively. Further experimental details related to the samples used in this work can be found in Table I.

The isothermal crystallization of these materials was studied at temperatures ranging from 109 to 115°C for MDPE and from 149 to 157°C for POM. Aluminum pans (25 μL) with holes were used for MDPE, and hand-crimped pans were used for POM. Further de-
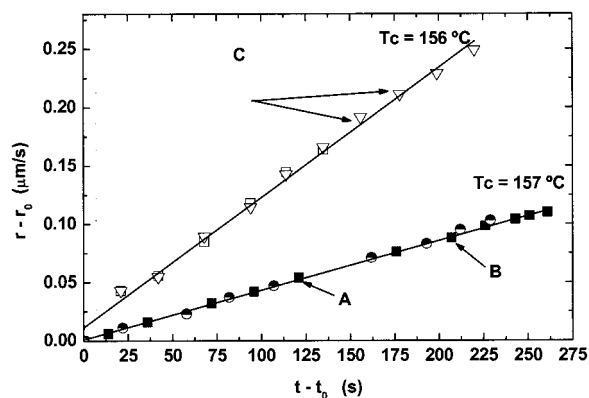
Figure 1 Isothermal crystallization of POM recorded in a hot stage at the indicated crystallization temperatures: (A,C) the times at which the indicated spherulites impinged with neighboring spherulites and (B) the time at which the spherulite symbolized by black squares impinged on the one symbolized by half-filled circles.

tails related to the materials characterization and the experimental procedures used in the isothermal experiments may be found in ref. 10. For analyzing the time dependence of the spherulite growth rate for the materials under study, that rate was measured for several crystallization temperatures and relatively long time intervals. A Mettler Toledo (Switzerland) hot stage, coupled to an optical microscope, was used for this purpose.

RESULTS AND DISCUSSION

Optical microscopy experiments

The modeling of the isothermal crystallization kinetics assumes a constant growth rate of the spherulites at a constant crystallization temperature. For the materials studied in this work, the growth rate of the spherulites, as measured in a hot stage, at constant temperature, is constant during the crystallization. The growth rate remains constant even after the impingement of spherulites; this can be checked by the results shown in Figure 1. However, it is known that for highly heterogeneous polymers, or for polymers with a large amount of atactic components, the growth rate is not constant. At a constant temperature, it decreases with the crystallization time. According to the theory of secondary nucleation, the spherulite growth rate should be constant in time at a constant crystallization temperature. In a hot stage, because thin films are used and the sample area is large, the crystallization temperature may be assumed to be constant during the entire crystallization process. Thus, the R_s value of the sample is small, facilitating the dissipation of the heat of crystallization generated.

DSC experiments

When thicker samples (with respect to those used in the hot-stage experiments), with higher weights, are used in isothermal DSC experiments, the sample temperature is surely different from the temperature measured by the temperature sensor. The reasons for this difference are twofold. The first is the R_s value of the sample, which is related to its thermal conductivity (a temperature-dependent property) and to its thickness and area. The second is the release of the heat of crystallization, which, because of the relatively low sample thermal conductivity, will inevitably contribute to the sample temperature increase. Thus, in nominally isothermal DSC experiments, and contrary to hot-stage isothermal experiments, because of the sample temperature increase due to the two aforementioned effects, the spherulite growth rate may change locally with time during the crystallization process.

Before proceeding to evaluations of the R_s value of the sample and the temperature increase during isothermal crystallization, we should discuss the physical meaning of the temperature usually recorded in isothermal DSC experiments. This temperature is usually the program temperature, and one may argue that the meaningful temperature for recording those scans should be the sensor temperature. A direct recording of the sample temperature is impossible because of the complicated set of thermal resistances existing between the temperature sensor and the sample. Among them are the R_s values of the oven, the aluminum pan, and the sample itself.

The results shown in Figure 2 are scans carried out over an indium sample, with a mass of 4 mg, at the scanning rates of 0.1 and 1°C/min. One scan was recorded with the sensor temperature, and another was recorded with the program temperature. Independent temperature calibrations were carried out for both recording modes and scanning rates. The results
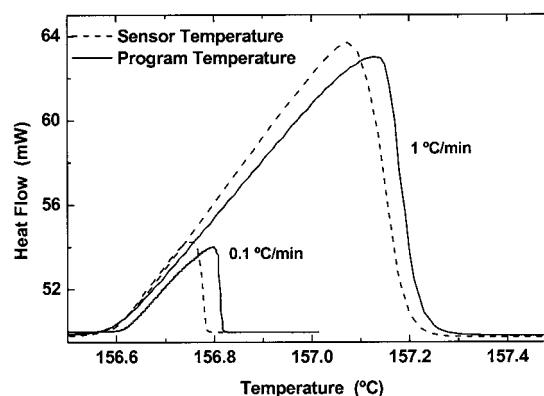

Figure 2 Effect of the recording mode (sensor temperature and program temperature) during the melting of indium at the scanning rates indicated. An independent temperature calibration was carried out for each recording mode.

clearly show that it is irrelevant which mode is chosen to record the data, as long as a specific temperature calibration is performed for each mode and the thermal gradient between the oven and the cooling block is high enough to guarantee proper temperature control (the average temperature of the sample and reference ovens following the program temperature).

Scans consistent with the ones shown in Figure 2 were obtained for the isothermal crystallization experiments reported in this work and also for nonisothermal experiments at accurately controlled cooling rates.

Once assured of the conditions mentioned previously, one may proceed to evaluate the R_s values of the sample. The values obtained, from the difference between the reciprocal of the slopes of the ascending part of the melting peaks of indium alone and indium over a polymer sample of known area and thickness, are listed in Table I, along with the values of the dimensions of the sample. From the R_s values in Table I, the thermal conductivities evaluated for MDPE and POM are 0.43 and 0.33 W K^{-1} m^{-1}, respectively. The values found for these two materials, taken from the material database of the Moldflow software package, are 0.42 and 0.29 W K^{-1} m^{-1}, respectively. Presumably, those values are for a temperature range in the molten state, in which the thermal conductivity of the material does not change significantly, and they are also coincident with values found in other references for the same materials that do not specify the measurement temperature.

R_s is, in principle, dependent on the mass (or thickness) for the same contact area. The sample dimensions (area and thickness) were measured before and after a series of experiments. With this procedure, mistakes were avoided that could occur because of the eventual shrinkage in area and the increase in the thickness of samples of small weights, having at the end a higher R_s value than other thicker and larger samples. Thus, samples of higher weight will not always have higher R_s values.

For samples with an equal contact area and different thicknesses, the true temperature should be dependent on the weight. Samples of MDPE of different weights (and thicknesses) were used, and the corresponding temperature increases at the same crystallization temperatures were analyzed. Figure 3 shows the effect of m on the temperature increase during the isothermal crystallization of MDPE at 109, 111, and 115°C. The temperature increase was evaluated according to eq. (1). This equation is a first-order differential equation, which can be numerically solved to find the true temperature of a sample as a function of time simultaneously with the extent of the liquid-to-solid conversion. The equation is general and applicable to both isothermal and nonisothermal experiments. For that, the previous equation may be directly
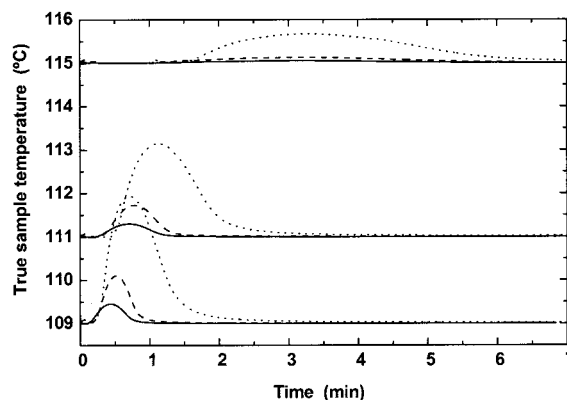

Figure 3 Effect of m (or sample thickness) on the temperature increase during the isothermal crystallization of MDPE at the temperatures indicated: (—) $m = 5.968$ mg, $R = 10.82$ K/W, and thickness = 0.14 mm; (- - -) $m = 10.313$ mg, $R = 26.30$ K/W, and thickness = 0.39 mm; and (· · ·) $m = 32.03$ mg, $R = 40.53$ K/W, and thickness = 0.55 mm. The sample/pan contact area was approximately the same for all the samples.

applied to the raw data obtained from DSC ($\Delta\dot{Q}(t)$, with respect to the appropriate crystallization peak baseline, or to the integrated transformed mass fraction data [$X(t)$ or $X(T)$].

The effect of the sample weight on the overall crystallization kinetics may be evaluated through the measurement of $t_{50\%}$. If there is instantaneous nucleation, the reciprocal of $t_{50\%}$ is proportional to the spherulite growth rate (the proportionality factor being a function of the average density of nuclei at each crystallization temperature), and their temperature dependence should be similar.

The temperature dependence of the spherulite growth rate may be derived from Lauritzen and Hoffman's theory of secondary nucleation.[11] For coherent secondary surface nucleation, the linear spherulite growth rate is

$$G = \beta \exp\left(-\frac{k_g}{T\Delta Tf}\right) \qquad (2)$$

where T is the absolute crystallization temperature, ΔT is the supercooling (the difference between the thermodynamic melting temperature and the crystallization temperature), and K_g is proportional to the folding and lateral surface energies of the growing lamellae, the proportionality factor being dependent on the crystalline growth regime. In recent versions of Lauritzen and Hoffman's theory, the transport factor (β) is derived from the reptation model:

$$\beta = \left(\frac{k_B T}{h}\right)\left(\frac{1}{\overline{M}_z}\right)\exp\left(-\frac{\Delta G_t}{k_B T}\right) \qquad (3)$$

where h and k_B are Planck's and Boltzmann's constants, respectively; M_z is the z-average molecular
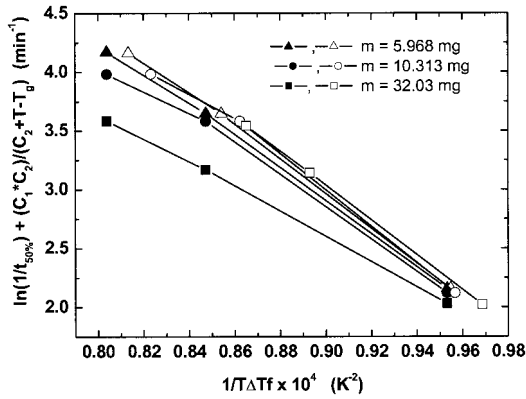
Figure 4 Variation of $1/t_{50\%}$ with $1/(T\ \Delta Tf)$ for MDPE samples of different weights. The full symbols refer to the values of $t_{50\%}$ at different crystallization temperatures, as recorded by DSC. The corresponding open symbols refer to the shifts of the curves due to the crystallization-induced sample temperature increase.

mass; and ΔG_t is the activation energy for the transport of a molecule across the phase boundary by reptation. The argument of the exponential in eq. (3) may be written with a Williams–Landel–Ferry functionality, $\Delta G_t/k_B T = C_1 C_2/(C_2 + T - T_g)$, where C_1 and C_2 are universal constants ($C_1 = 25$ K and $C_2 = 30$ K) and T_g is the material's glass-transition temperature. Plots of $\ln(G)$ (where G is the spherulite growth rate), or $\ln(1/t_{50\%})$, should yield straight lines with slope K_g, which may change with the temperature, depending on the presence of regime transitions.

Figure 4 shows the variation of $\ln(1/t_{50\%})$ against $1/(T\Delta Tf)$ for the samples whose temperature increases are plotted in Figure 3. The full symbols represent the reciprocal of $t_{50\%}$ measured after the integration of the isothermal DSC curve at 109, 111, and 115°C. Because, as shown by the results of Figure 3, the estimated temperature increase is dependent on m (or thickness), it is expected that the slope of the curves shown in Figure 4 ($K_g^{1/t_{50\%}}$) will be affected by R_s of the sample and by the release of the heat of crystallization. In fact, the slope of the lines joining the full symbols decreases with the sample weight, indicating relatively lower crystallization kinetics for the heavier samples. The open symbols represent the same values of the reciprocal of $t_{50\%}$ corrected for the estimated sample temperature at that time [$T(t_{50\%})$], instead of the nominal crystallization temperature (T_c) recorded by the DSC calibrated temperature program. The observed shift in the results, and their approximate superposition into a single line, are indications of the validity of the approach used for estimating the average true temperature of a sample during isothermal crystallization experiments.

The isothermal crystallization kinetic data, obtained by DSC, were fitted with Avrami's equation:

$$X(t) = 1 - \exp(-kt^n) \qquad (4)$$

where $X(t)$ is the degree of conversion from the liquid phase to the solid phase and k is a kinetic constant proportional to the average density of nuclei and to G^n (instantaneous nucleation being assumed), G being the spherulite growth rate and n the Avrami exponent. Figure 5 and Table II show the fittings obtained for two and three crystallization temperatures, respectively. The results show that, for the same crystallization temperature, the k values of a sample with a higher mass are lower, and this is consistent with a higher temperature increase. Also, the n values for a thicker sample have relatively lower values, all of them being near 3. The spherulite size in MDPE is small (ca. 33 μm for $T_c = 111$°C[10]), and the role played by the upper and lower columnar and cornrow structures is even more diluted in thicker samples. Thus, we may assume that predominant geometry is spherulitic for both thin and thick samples.

The results of Figures 3–5 clearly show that truly isothermal crystallization processes do not occur unless ΔT is small and the time for the development of the solid-to-liquid transformation is long. Often, for a comprehensive description of the overall crystallization kinetics, it is imperative to record reliable crystallization data at lower crystallization temperatures and to use samples of higher weights. These data may be affected by large errors, as shown by the results of Figures 3–5.

These statements may also be confirmed by the evaluation of the temperature increase during the isothermal crystallization of POM at 149 and 157°C, as shown in Figure 6(a,b). The temperature increase for 157°C is small, around 0.08°C, and for even higher crystallization temperatures, for which crystallization times of around 1 h are needed, the crystallization
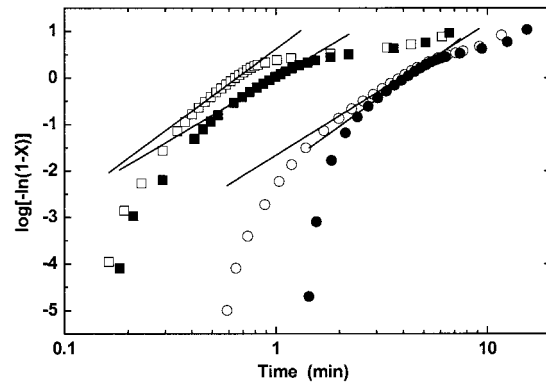

Figure 5 Effect of the sample weight on the isothermal crystallization kinetics of MDPE at the crystallization temperatures of 109 [(■) $m = 32.03$ mg and (□) $m = 10.313$ mg] and 115°C [(●) $m = 32.03$ mg and (○) $m = 10.313$ mg]. The full lines represent the fits of Avrami's equation to the experimental data.

TABLE II
Values of k, n, and the Sum of Least Squares (SLS) Obtained After the
Fitting of Avrami's Equation to the Experimental Data for the
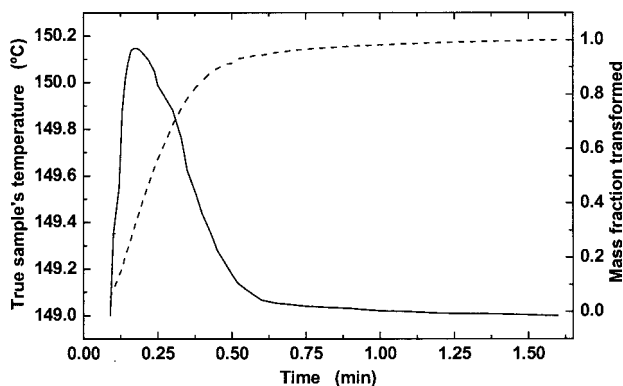**Isothermal Crystallization of MDPE**

	$m = 10.313$ mg			$m = 32.03$ mg		
	109°C	111°C	115°C	109°C	111°C	115°C
$k \times 10^4$ (min^{-n})	2.67	6.60×10^{-1}	1.22×10^{-1}	1.65	1.85×10^{-1}	1.45×10^{-4}
n	3.36	3.39	2.83	2.69	2.95	3.27
$k^{(1/n)} \times 10^2$ (min)	8.64	5.85	1.84	1.67	1.14	0.40
SLS $\times 10^2$	7.56	4.76	1.90	5.52	5.72	4.56

process may be assumed, with reasonable approximation, to be truly isothermal.

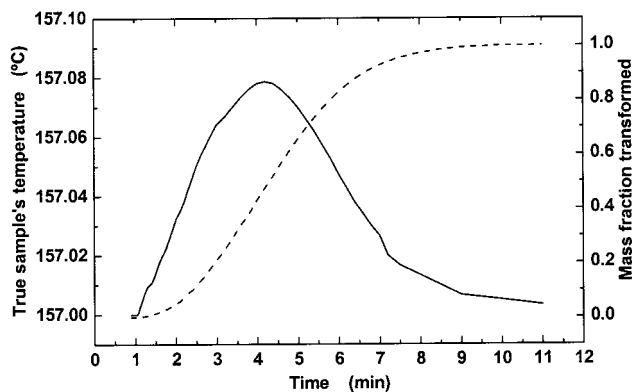For other situations, however (e.g., $T = 149°C$ in POM), it is worthwhile to analyze the differences obtained when the isothermal crystallization is treated as a nonisothermal process, with an evaluation of the effect that the temperature increase of the sample may have on the development of the overall crystallization kinetics through the values obtained for the relevant kinetic parameters. The result of this exercise is shown in Figure 7 for the isothermal crystallization of POM. After the time-dependent temperature increase was evaluated for each crystallization temperature according to eq. (1), the isothermal crystallization was treated as a nonisothermal process, and Nakamura's equation was applied to the experimental data of the conversion versus time:

$$-\ln[1 - X(T)] = \left[\int_{T_m^o}^{T} Z(T') \frac{1}{\dot{T}} dT' \right]^n \quad (5)$$

where $\dot{T}$ is dT_t/dt [eq. (1)], T_m^o is the thermodynamic melting temperature, and $Z(T)$ is related to k of the Avrami equation [eq. (4)] by $Z(T) = [k(t)]^{1/n}$. The results of parameters k and n obtained with eq. (4) when the process is treated as truly isothermal, and the results of k' and n' when Nakamura's equation [eq. (5)] is fitted to the experimental data, are shown in Table III for the crystallization of POM recorded by DSC at several crystallization temperatures.

The values of the kinetic parameters obtained after the fitting of Nakamaura's equation to the experimen-
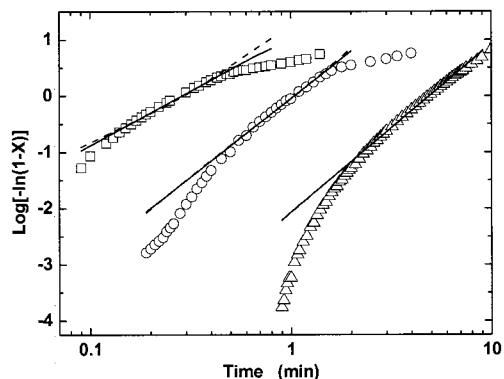

(a)

(b)

Figure 6 Isothermal crystallization of POM ($m = 4.328$ mg) at (a) 149 and (b) 157°C. The full lines represent the temperature increase during the isothermal crystallization. The dashed lines represent the degree of conversion from the liquid phase to the solid phase.

Figure 7 Isothermal crystallization of POM at (□) 149, (○) 153, and (△) 157°C. The full line is the fit to the experimental data with Avrami's equation, and the dashed line is the fit to the same experimental data with Nakamura's equation, after the evaluation of the temperature increase at each crystallization temperature according to eq. (1).

TABLE III
Values of the Kinetic Parameters Obtained After the Fitting of Avrami's and Nakamura's Equations to Experimental, Nominally Isothermal Crystallization Data for POM

T_c (°C)	k (Avrami) $\times 10^6$ (s^{-n})	n (Avrami)	$T(t_{50\%};$ °C)	k' (Nakamura) $\times 10^6$ (s^{-n})	n (Nakamura)
149	4075.75	1.93	150.11	3312.52	2.14
150	1291.72	2.20	151.02	710.09	2.53
151	319.98	2.45	151.80	192.36	2.72
152	82.02	2.58	152.53	52.94	2.78
153	9.89	2.79	153.35	6.77	2.93
154	0.95	3.03	154.24	0.62	3.16
155	0.33	3.04	155.17	0.23	3.14
156	0.11	3.07	156.12	0.08	3.13
157	0.04	2.99	157.08	0.03	3.03

The sample temperature increases evaluated for $t_{50\%}$ are also shown

tal data are lower, and this agrees with the evaluated increase of the sample temperature. Despite the non-integer values obtained for n, the relatively lower values obtained for k', especially evident for lower crystallization temperatures, indicate that the nonisothermal treatment of the isothermal crystallization data potentially provides more realistic information when DSC data are correlated to the spherulite growth rate and average nucleation density.[10] Because both are single-mechanism equations, the quality of the fitting obtained with them is the same. Also, similar values of n have been obtained for both situations. Moreover, this improved treatment does not eliminate (and, in fact, reinforces) the need for improved quantitative descriptions of the crystallization process for both short and long times.

CONCLUSIONS

This work shows that it is possible to evaluate the temperature increase during the isothermal crystallization of polymers. The temperature increase is dependent on the crystallization temperatures, being especially higher for lower crystallization temperatures and heavier samples. The effect of the sample thickness on the temperature increase is also an important specific parameter because it will determine R_s of a sample.

The description of the nominally isothermal process when it is treated as truly nonisothermal has yielded, as expected, similar values for n and lower values for k. An evaluation of these constants that is as accurate as possible is important for a more precise description of the overall crystallization and for the evaluation of the average density of nuclei (or average spherulite size) from global crystallization parameters ($t_{50\%}$ and the average true sample crystallization temperature) and the spherulite growth rate.

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