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ISOTHERMAL CRYSTALLIZATION MADE EASY: A SIMPLE MODEL AND MODEST COOLING RATES

By

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ABSTRACT

An understanding of the kinetics of the crystallization process is important for the selection of processing parameters such as mold temperature and hold time during injection molding. Differential scanning calorimetry (DSC), is an excellent tool for following the progress of crystallization. A popular method for obtaining kinetics data known as isothermal crystallization, is based on rapidly cooling the sample from the melt to the crystallization temperature and then measuring the heat evolved while the sample is held isothermal. The model most often applied to isothermal crystallization data is the Avrami model. This model, while possessing physically significant parameters, is somewhat difficult to analyze.

In this study, a simpler kinetic model, the Sestak-Berggren model, is applied to crystallization kinetics. The equivalency of the resultant kinetic parameters to those from the Avrami model is demonstrated. Furthermore, it is shown that modest cooling rates, as low as 5°C/minute, may be used to obtain good kinetic results.

INTRODUCTION AND THEORY

In DSC, heat flow is measured as a function of time and temperature. When a material crystallizes, a measurable amount of heat is evolved, resulting in an exothermic peak in the DSC thermal curve. The shape of this peak is directly related to the kinetics (time and temperature dependency) of crystallization. Two fundamental properties which can be measured in a DSC are the reaction rate ($d\alpha/dt$) which is related to the amount of heat flow at any given time and temperature, and conversion level (α) which is measured as the amount of heat evolved (enthalpy) from the beginning of reaction until the selected time and temperature.

The mathematical equations used to model kinetic reactions generally take the form of $d\alpha/dt = k(T)\, f(\alpha)$ where reaction rate is proportional to the specific rate constant (k) and is some function of the conversion level [$f(\alpha)$]. The specific rate constant itself is a function of temperature (T), the dependence of which is often described by the Arrhenius equation, $k = Z \exp (E/RT)$. [Z is the pre-exponential factor, E the activation energy and R the universal gas constant]. A large number of kinetic methods have been developed which are based on different forms of $f(\alpha)$. For decomposition kinetics (evaluated by TGA) and reaction kinetics (measured by DSC), for example, $f(\alpha)$ is derived from the general rate equation and has the form:

$$f(\alpha) = (1-\alpha)^n \qquad (1)$$

where n is the reaction order. This form of the kinetic equation works well for many simple, single-stage reactions. It is, however, inadequate when applied to more complex reactions such as auto-catalyzed chemical (e.g., thermoset cure) and polymer crystallization reactions. This is due to the multi-stage nature of these more complex reactions. Crystallization, for example, is a two-step process where crystal growth (step 2) takes place at nucleation sites whose appearance (step 1) is controlled by both time and temperature.

The most popular form of $f(\alpha)$ for examination of auto-catalyzed reactions is known as the Sestak-Berggren (SB) equation [1,2]:

$$f(\alpha) = \alpha^m (1-\alpha)^n \qquad (2)$$

where m and n are reaction order constants.

The general rate equation (1) and the SB equation (2) are closely related. The general rate equation may be thought of as a simplified case of the SB equation where m is equal to zero. This is aesthetically satisfying to many practitioners since it has the appearance of reducing the number of applicable concepts which must be considered.

For polymer crystallization, the most popular form of $f(\alpha)$ is:

$$f(\alpha) = r\,(1-\alpha)\,[-1n\,(1-\alpha)]^{1-1/r} \qquad (3)$$

where r is called the Avrami constant. This equation was independently derived by a series of authors [3-7], and is popularly known at the Avrami equation.

Although the Avrami parameters are more difficult to evaluate than those of the general rate or SB equation, equation (3) is derived from first principles and hence, its parameter (r) has physical significance. The value of r depends on the shape of the nuclei and the dimensionality of their growth, as well as on the rate of their formation [8]. When nucleation sites are instantaneously formed, r has the value of 1 for needle-shaped crystals, 2 for plates, and 3 for spheres. If additional nucleation sites sporadically appear with time, the value for r is one integer higher. Most polymer crystals are anticipated to be spherical in nature, so values of r between 3 and 4 are most common.

Because of its widespread availability to an easy-to-use data analysis software form, the SB equation is often used to model polymer crystallization processes with surprisingly good fit. The empirical observation that the SB equation may be applied to polymer crystallization, is supported in theory by the work of Sestak, Satava and Wendlandt who have shown that the SB equation is equivalent to the Avrami equation, to a first approximation [9]. Further, the relationship between the values of m, n and r may be obtained by equating α's from the two equations at the peak of the reaction curve where $d(d\alpha/dt)/dt = 0$ [10]. This results in the relationship:

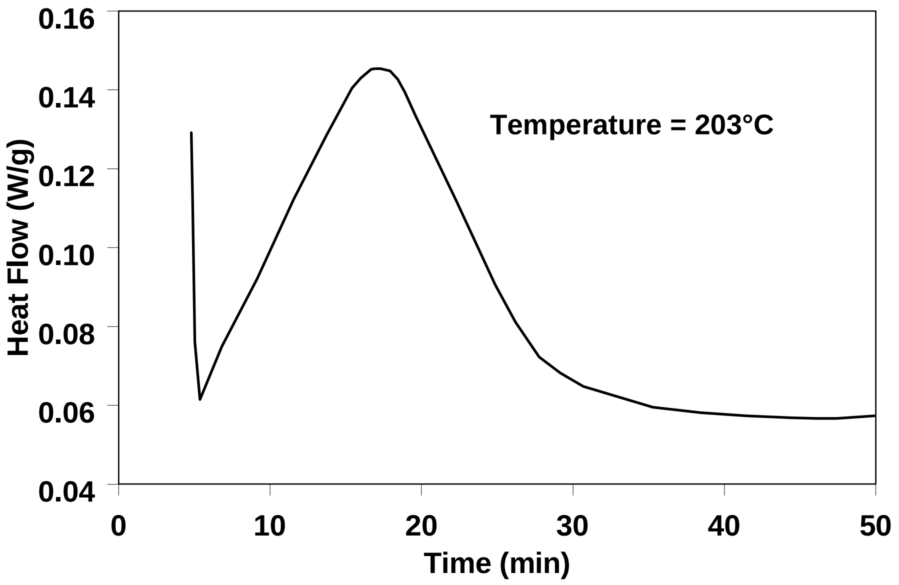
$$r = 1 / [1 + \ln(n) - \ln(n + m)] \qquad (4)$$

EXPERIMENTAL

Isothermal polymer crystallization kinetic studies were carried out using a TA Instruments Differential Scanning Calorimeter. Test specimens, typically 5 mg, were heated to temperatures about 10°C above the end of the polymer melting and held there for several minutes to remove order in the liquid phase. Specimens were then cooled (typically at 8°C/min) to temperatures below the melting temperature and held isothermal until the crystallization reaction exotherm reached completion. The polymers studied included polyethylene (PE), polyethylene terephthalate (PET), polycaprolactam (Nylon 6), and polyetheretherketone (PEEK). For each material, a minimum of 6 crystallization experiments were performed over a range of temperatures. Figure 1 illustrates a typical DSC thermal curve obtained.

The auto-catalyzed (i.e., SB) kinetics option of the TA Instruments Isothermal Kinetics software package was used to analyze the resultant DSC thermal curves and the kinetic parameters obtained were compared to literature values.

Figure 1: DSC thermal curve (raw data) for isothermal crystallization of polycaprolactam (Nylon 6)



RESULTS AND DISCUSSION

Figure 2 shows the results of the SB analysis for the crystallization of polycaprolactam (Nylon 6) plotted as the log of reaction rate ($d\alpha/dt$) versus the Sestak-Berggren log conversion term. The triangles indicate individual data points taken from 5 to 75% conversion across the crystallization exotherm. These results demonstrate that the SB model may appropriately be used for Nylon 6 since the experimental data points fall close to the line. The SB model is also appropriate for the other materials tested.

Figure 2: Reaction rate of Nylon 6 crystallization plotted as a function of the Sestak-Berggren conversion term.

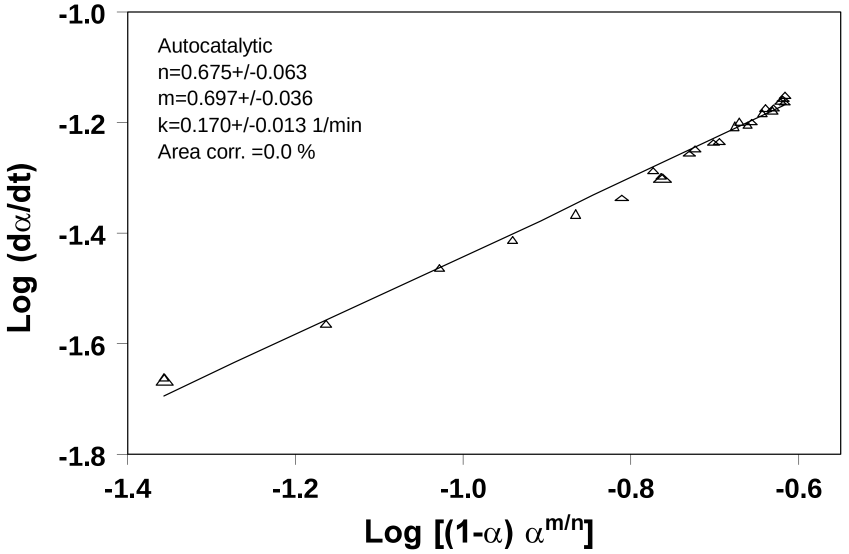


Table 1 compares the values for the reaction orders m and n derived from the SB analysis of the respective polymer systems along with the corresponding values of r calculated using equation (4). Values of r taken from the literature are presented for comparison. Overall, the agreement between the experimental and literature values for the Avrami constant is good.

Table 1: COMPARISON OF SESTAK-BERGGREN AND AVRAMI REACTION ORDERS

	Experimental			Literature	
Polymer	m	n	r	r	Ref
PET	0.38	0.76	1.7	1.7	11
PE	0.33	0.65	1.7	2.2	11
Nylon 6	0.65	0.64	3.4	2.1	11
PEEK	0.77	0.82	2.9	3.6	12

Isothermal kinetic experiments were carried out over a series of temperatures in order to obtain the temperature dependence of the specific rate constant. These experiments were limited at short time periods (low crystallization temperatures) by the ability of the sample to achieve temperature equilibrium (i.e., return to baseline) prior to the onset of crystallization. At higher crystallization temperatures (long time scales), the experiments were limited by the sensitivity and experimental noise. In general, 100 minutes is about the upper practical limit of most isothermal crystallization experiments. Due to the exponential nature of the specific rate constant temperature dependence, crystallization temperature ranges are typically on the order of 10°C. For polymers, known as "fast" crystallizers, this range may be only a few degrees. For "slow" crystallizing polymers, the range may be 20-30 degrees wide.

Table 2 provides the specific rate constants (k, in logarithmic form), activation energies (E) and pre-exponential constants (Z) derived from the SB model for the polymers studied. Comparison between the SB results obtained, and Avrami model data from the literature is not easy. The Avrami kinetic equation (and therefore E and Z) is expressed as a pseudo rate constant k* since it contains the constant r term of equation (3) as well. The easiest comparison of the Avrami and SB approaches is through a comparison of their respective reaction order constants, as discussed previously.

Table 2: SESTAK-BERGGREN KINETIC CONSTANTS

Polymer	Temperature (°C)	Log k (sec^{-1})	E (kJ/mol)	Log Z (min^{-1})
PET	217	-2.88	1080	142
PE	129	-2.97	88	10
Nylon 6	205	-2.59	357	40
PEEK	322	-2.36	472	42

The purpose in gathering kinetic information, regardless of whether it is obtained via the Avrami or the SB equation, is to estimate sample behavior under conditions not tested. Commercial kinetic software packages like TA Instruments DSC Isothermal Kinetics software meet that purpose. Figure 3, for example, illustrates the conversion versus time profiles for Nylon 6. The solid lines represent actual experimental data and the dashed traces reflect conditions beyond the experimental. Figure 4 presents conversion time information as a function of sample temperature for a family of curves ranging from 10 to 90% conversion. Again, the solid portions of the curves represent ranges covered by experimental data and the dashed portions are outside of actual experimental conditions.

Figure 3: Percent conversion versus time for Nylon 6.

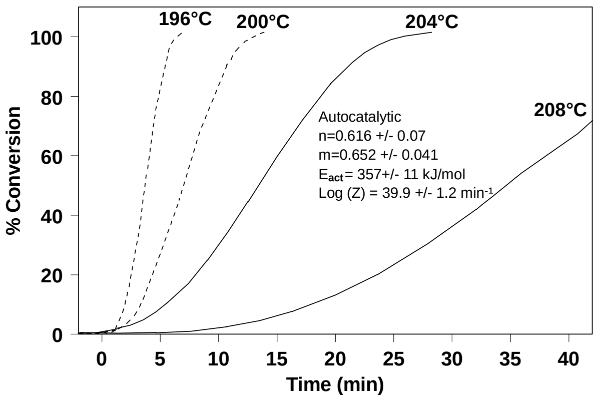
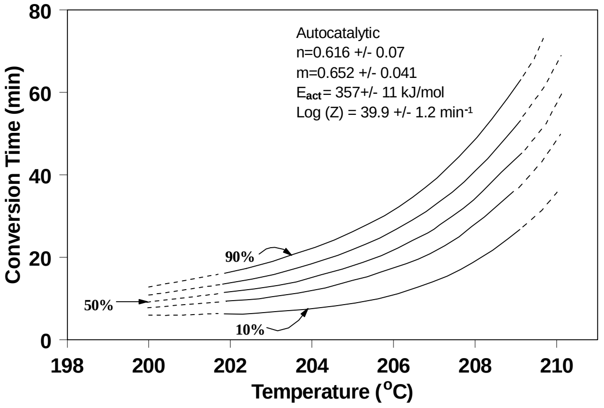


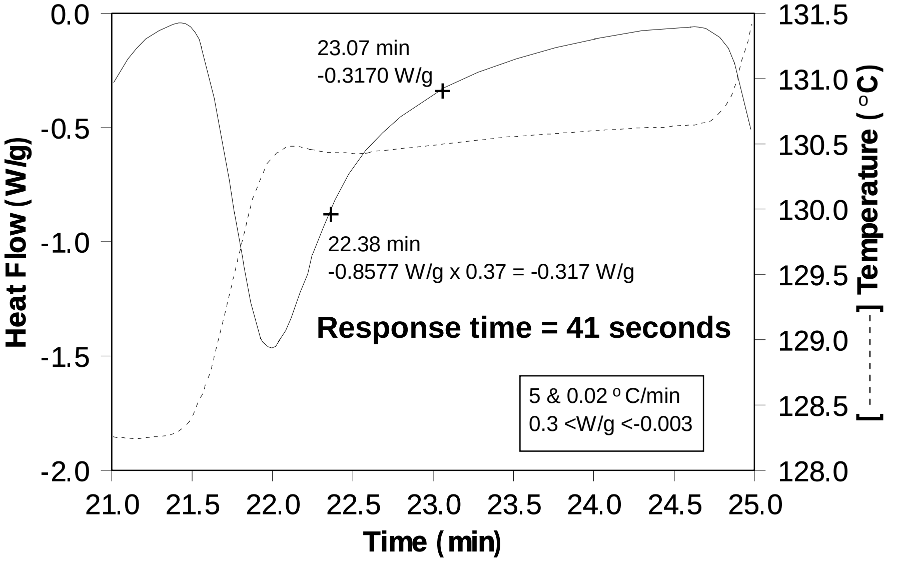
Figure 4: Conversion time curves for Nylon 6.



It is often (erroneously) thought that cooling from the annealing temperature to the test temperature in isothermal crystallization studies needs to take place very rapidly. In fact, cooling can take place at very modest rates, as low as 5°C/minute, provided that : (1) there is no overshoot of the test temperature, (2) sample temperature equilibrium at the test temperature is rapidly established, and (3) the actual sample temperature is accurately measured. In a practical sense, this means that crystallization studies may be successfully carried out without resorting to elaborate cooling devices or procedures.

Two tests can be used to demonstrate that slow heating rates are acceptable. First, as previously shown, crystallization and melting do not occur instantaneously. Rather, there is a distinct dependence on time. To further illustrate this point, a stepwise quasi-isothermal DSC experiment was performed in which the heating rate was varied between 5°C/min and 0.02°C/min depending on the heat flow. The higher heating rate was used until the heat flow reached 1 mW (endothermic), at which point the heating rate was reduced. When the heat flow returned to the baseline (dropping below 0.1 mW), the higher heating rate was resumed. The resultant curve (Figure 5) obtained for polyethylene, which is generally considered to be a "fast" crystallizer, shows that the return to baseline takes over two minutes.

Figure 5: Stepwise isothermal melting of polyethylene



Second, the kinetic results themselves show that cooling rate is a less significant factor than the amount of undershoot. A crystallization of Nylon 6 at 201°C, can be performed with a cooling rate on the order of 5-10°C/min. These slow cooling rates give the sample a thermal history that can be approximated by sitting at temperatures 3-5°C above crystallization isotherm for about 5 minutes. In Figure 3, it can be seen that after 5 minutes at 204°C, Nylon has crystallized on the order of 6%. On the other hand, if there is even so much as 1°C undershoot, the sample will crystallize to over 25% in 5 minutes.

CONCLUSIONS

In summary the Sestak-Berggren equation is shown to be an effective tool for the evaluation of crystallization kinetic parameters for polymers of widely varying crystallization rates. The reaction order thus derived may be converted to forms comparable with those derived from the Avrami equation and good agreement is obtained between the SB-derived reaction orders and those in the literature derived from the Avrami equation. The SB equation provides the user with the advantage of using commercially available software packages, with their associated plotting flexibility for the evaluation of the kinetic process.

In addition, the myth is dispelled that isothermal crystallization requires rapid cooling rates to achieve accurate and easily-used kinetic parameters even for "fast" crystallizing polymers such as polyamides (Nylon) or polyolefin.

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