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# Isoconversional Analysis of Calorimetric Data on Nonisothermal Crystallization of a Polymer Melt

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The activation energy,  $E$ , of nonisothermal crystallization of polymer melts has been frequently evaluated by the Kissinger equation with positive rates of temperature variation,  $\beta$ . It is demonstrated that reversing the sign for  $\beta$  is a mathematically invalid procedure that generally invalidates the Kissinger method. As an alternative we propose the advanced isoconversional method that can be used for evaluating the effective activation energy of nonisothermal crystallization of the polymer melts. The application of this method to calorimetric data on crystallization of poly(ethylene terephthalate) (PET) yields an activation energy that increases with the extent of crystallization from  $-270$  to  $+20$  kJ mol<sup>-1</sup>. It is demonstrated that this variation is consistent with data on isothermal crystallization of the PET melts and can be interpreted in terms of the accepted crystallization models.

## Introduction

Crystallization of polymer melts is accompanied by significant heat release that can be conveniently measured by differential scanning calorimetry (DSC). The measured rate of heat release is assumed to be proportional to the macroscopic rate of crystallization

$$\frac{dQ}{dt} = Q_c \frac{d\alpha}{dt} \quad (1)$$

where  $Q_c$  is the measured heat of crystallization. The value of  $Q_c$  is determined by integration of a DSC peak. The values of  $Q_c$  can further be used to determine the crystallization rate,  $d\alpha/dt$  as well as the extent of the melt conversion

$$\alpha = \frac{1}{Q_c} \int_0^t \frac{dQ}{dt} dt \quad (2)$$

The value of  $\alpha$  varies from 0 to 1 and represents the relative degree of crystallinity.

The macroscopic kinetics of isothermal crystallization are usually described in terms of the Avrami equation

$$\alpha = 1 - \exp(-kt^n) \quad (3)$$

where  $n$  is the Avrami exponent that is associated with the crystallization mechanism and  $k$  is the overall (macroscopic) rate constant. Note that eq 3 was developed independently by Avrami,<sup>1</sup> Johnson and Mehl,<sup>2</sup> Erofeev,<sup>3</sup> and Kolmogorov<sup>4</sup> and is sometimes referred to as the Johnson–Mehl–Avrami–Erofeev–Kolmogorov (JMAEK) equation. Ozawa<sup>5</sup> extended this equation to nonisothermal conditions. While offering a simple way of estimating the Avrami exponent, Ozawa's

analysis does not suggest a method of determining the activation energy. However, estimating the activation energy for nonisothermal crystallization of melts is not as straightforward as it may seem. The value of  $k$  in eq 3 has the overall nature because the macroscopic crystallization rate is generally determined by the rates of two processes, nucleation and nuclei growth. Because these two processes are likely to have different activation energies, the temperature dependence of the overall rate constant can rarely be fit by a single Arrhenius equation,

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (4)$$

( $R$  is the gas constant,  $A$  is the preexponential factor, and  $E$  is the activation energy) in a wide temperature range. Nevertheless, in this situation eq 4 should hold reasonably well for a relatively narrow temperature interval that permits estimating the effective value of the activation energy,  $E$ . Therefore, by splitting the temperature region of nonisothermal crystallization into smaller regions, it should be possible to determine the temperature dependence of the effective activation energy of nonisothermal crystallization.

DSC is widely used to study various processes in polymers<sup>6</sup> and inorganic solids<sup>7</sup> whose kinetics are almost universally described by the basic rate equation

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (5)$$

where  $f(\alpha)$  is the reaction model related to the mechanism. For nonisothermal conditions of linear heating, eq 5 is modified as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (6)$$

where

$$\beta = \frac{dT}{dt} \quad (7)$$

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$\beta$  is the heating rate. Equation 6 has been employed to develop a great number of methods that make use of either single or multiple heating rate data. The shortcomings of the single heating rate methods have been repeatedly stressed.<sup>6,8</sup> The recent publication<sup>9</sup> summarizing the results of the ICTAC Kinetics Project has recommended the use of multiple heating rate methods such as isoconversional methods.<sup>6</sup>

Perhaps the simplest and most popular representative of multiple heating rate methods is the method of Kissinger<sup>10</sup> that allows the activation energy to be determined from equation

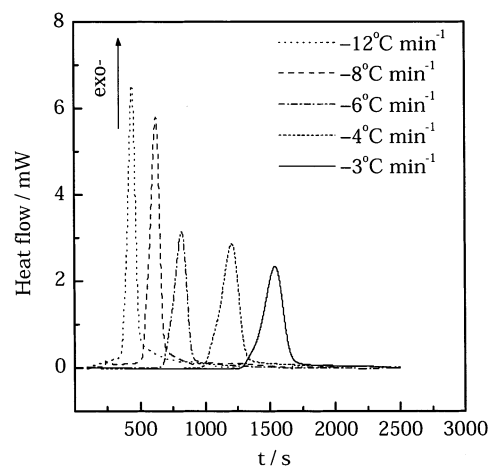
$$\ln\left(\frac{\beta_i}{T_{p,i}^2}\right) = \text{Const} - \frac{E}{RT_{p,i}} \quad (8)$$

where  $T_p$  is the temperature corresponding to the maximum of a differential kinetic curve, and  $i$  is the number of experiment performed at  $\beta_i$ . This method is quite often grouped with isoconversional methods, because the extent of conversion related to  $T_p$  usually shows only minor variations with  $\beta$ . In combination with calorimetry, the Kissinger method has been extensively applied to numerous process that occur on heating, including crystallization of polymeric and metallic<sup>11</sup> glasses as well as nucleation of a new solid phase in an amorphous solid mixture.<sup>12</sup>

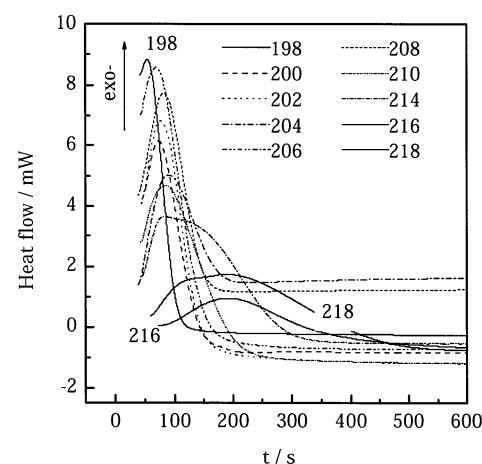
On cooling, the temperature decreases with the time, giving rise to negative values of  $\beta$  (eq 7). Obviously, eq 8 does not permit substitution of negative values for  $\beta$ . In a number of polymer melt crystallization studies<sup>13–29</sup> this problem has been bypassed by simply reversing (dropping) the minus sign for the negative heating rates. In this paper we demonstrate that reversing the sign does not make eq 8 applicable to the conditions of cooling. As an alternative, we consider the advanced isoconversional method.<sup>30,31</sup> This method that has been very helpful in elucidating complex kinetics that occur on heating<sup>8,32–34</sup> may equally be helpful in kinetic analyses of calorimetric data on crystallization of liquid metals<sup>35</sup> and/or polymers. The application of the method is illustrated for nonisothermal crystallization of poly(ethylene terephthalate) (PET). To our knowledge, this paper describes the first application of an isoconversional method for evaluation of the effective activation energy of a process that occurs on continuous cooling.

## Experimental Section

Poly(ethylene terephthalate) (PET) [25038-59-9], average  $M_w$  ca. 18 000 has been purchased from Aldrich and used as received. A Mettler-Toledo DSC 821<sup>e</sup> module was used to follow the kinetics of PET crystallization. A ~6 mg sample was placed in a 40  $\mu$ L Al pan, which was hermetically closed under nitrogen. A closed empty pan was used as a reference. The equilibrium value of  $T_m$  for PET is 280  $^{\circ}\text{C}$ .<sup>36</sup> To secure complete melting, all samples were heated to 290  $^{\circ}\text{C}$  and held at this temperature for 15 min. After that the samples were cooled to 25  $^{\circ}\text{C}$  at the rates 3, 4, 6, 8, and 12  $^{\circ}\text{C}\cdot\text{min}^{-1}$ . The heat release curves are shown in Figure 1. For comparison purposes we have also run a series of isothermal experiments at 10 different temperatures from the region 198–218  $^{\circ}\text{C}$  (Figure 2). A disadvantage of the isothermal runs is that quick cooling from 290  $^{\circ}\text{C}$  to a constant temperature is followed by a period of temperature stabilization of about 45–70 s during which the crystallization kinetics remains inestimable. It seems, therefore, reasonable to treat the activation energies derived from the isothermal runs as rather rough estimates.



**Figure 1.** DSC traces obtained for crystallization of the PET melt at different heating rates. The numbers by the lines represent the heating rate in  $^{\circ}\text{C}\cdot\text{min}^{-1}$ .



**Figure 2.** DSC traces obtained for crystallization of the PET melt at different temperatures. The numbers by the lines represent temperatures in  $^{\circ}\text{C}$ .

## Method of Kissinger

Taking the derivative of eq 5 and setting it to zero, we obtain

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt} \left[ \frac{E}{RT_p^2} \cdot \frac{dT}{dt} + \frac{df(\alpha_p)}{d\alpha} A \exp\left(\frac{-E}{RT_p}\right) \right] = 0 \quad (9)$$

where subscript p denotes the values at the point of the rate maximum (peak). In eq 9 the rate of temperature variation,  $dT/dt$  takes positive values for heating and negative values for cooling. In thermal analysis experiments the temperature is usually varied at a constant rate,  $\beta$ . The value  $\beta$  is traditionally called the heating rate.<sup>10</sup> Regardless of its name, the sign of  $\beta$  is determined by the sign of the respective derivative (7). Substituting into eq 9  $\beta$  for  $dT/dt$  and the reaction order model,  $(1 - \alpha)^n$  for  $f(\alpha)$ , one obtains

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt} \left[ \frac{E}{RT_p^2} \beta - n(1 - \alpha_p)^{n-1} A \exp\left(\frac{-E}{RT_p}\right) \right] = 0 \quad (10)$$

which is the equation that Kissinger originally used to arrive at eq 8. Although Kissinger derived his equation assuming the reaction order kinetics, it can be demonstrated that eq 8 holds for a wide class of the  $f(\alpha)$  models, including the Avrami model that rationalizes its application to crystallization processes. Because in eq 10  $d\alpha/dt$  is not zero, the left-hand side becomes

zero when

$$\frac{E}{RT_p^2} \cdot \beta + \frac{df(\alpha_p)}{d\alpha} A \exp\left(\frac{-E}{RT_p}\right) = 0 \quad (11)$$

Simple rearrangements of eq 11 yield

$$\frac{\beta}{T_p^2} = - \frac{df(\alpha_p)}{d\alpha} \cdot \frac{AR}{E} \exp\left(\frac{-E}{RT_p}\right) \quad (12)$$

that after the logarithmic transformation turns into eq 8 assuming that  $\alpha_p$  is independent of  $\beta$ . Theoretically<sup>37</sup>  $\alpha_p$  should show a minor variation with  $\beta$  that can usually be neglected for practical purposes. Although the value of  $E$  is determined for a single extent of conversion ( $\alpha_p$ ), the method is supposed to yield the effective activation energy of the whole process. Therefore, the basic assumption of the method is that a process occurs as single-step kinetics. This assumption is likely to fail for a complex processes unless its kinetics are limited by a single step.

Let us now analyze eqs 11 and 12 for the conditions of heating and cooling. For heating, the left-hand side in eq 12 is positive. For a regular chemical process  $A$  and  $E$  are positive, and the exponential function is always positive by definition. Subject to all these conditions, eq 11 has a solution for heating when the  $f(\alpha)$  derivative is negative. Therefore the right-hand side in eq 12 is positive. We can apply the logarithmic transformation to both sides of eq 12 and obtain eq 8.

On cooling, the left-hand side of eq 12 is negative and so is the first term in eq 11. Therefore eq 11 has a solution for cooling when the  $f(\alpha)$  derivative is positive. This makes both sides of eq 12 negative and unsuitable for the logarithmic transformation. As mentioned earlier, this problem has been bypassed by dropping the negative sign for  $\beta$ . Mathematically, this procedure is equivalent to reversing the signs of both sides of eq 12 that results in

$$\frac{-\beta}{T_p^2} = \frac{df(\alpha_p)}{d\alpha} \cdot \frac{AR}{E} \exp\left(\frac{-E}{RT_p}\right) \quad (13)$$

both sides of which are positive and suitable for the logarithmic transformation that ultimately leads to the standard Kissinger eq 8.

A similar result is accomplished when the effective activation energy is negative (the situation is discussed later in the present paper). In this situation, the first term in eq 11 is positive and eq 11 has a solution when the  $f(\alpha)$  derivative is negative. Note that for crystallization  $A$  should remain positive because in eq 5  $d\alpha/dt$ ,  $f(\alpha)$ , and the exponent are positive. As a result, both sides of eq 12 are negative. Reversing the signs on both sides of eq 12 gives eq 13 that can further be transformed into the Kissinger eq 8.

The question arises whether the procedure of reversing the sign is valid. At the first sight it looks perfectly valid as it does not violate eq 9. However eq 9 is not the sufficient condition of maximum. The sufficient condition of maximum requires the first derivative be zero (eq 9) and the second derivative be negative

$$\frac{d}{dt} \left\{ \frac{d\alpha}{dt} \left[ \frac{E}{RT_p^2} \cdot \beta + \frac{df(\alpha_p)}{d\alpha} A \exp\left(\frac{-E}{RT_p}\right) \right] \right\} < 0 \quad (14)$$

This rather complicated inequality has a very simple meaning

that if at  $T_p$  the rate peak points upward, then eq 9 satisfies the condition of maximum. The upward rate peaks obviously represent the most common experimental situation regardless of whether the process rate passes through a maximum on heating (e.g., decomposition) or on cooling (e.g., crystallization). As a matter of fact, eq 5 cannot give rise to any downward peaks as long as  $A$  and  $f(\alpha)$  remain positive (i.e., physically meaningful). For this reason eq 9 as well as, derived from it, eq 12 are equations of maximum.

On the other hand, eq 13 is obtained by reversing the signs in eq 12, which is equivalent to reversing the signs in eq 9 as follows

$$\frac{d}{dt} \left( \frac{d\alpha}{dt} \right) = \frac{d\alpha}{dt} \left[ - \frac{E}{RT_p^2} \cdot \beta - \frac{df(\alpha_p)}{d\alpha} A \exp\left(\frac{-E}{RT_p}\right) \right] = 0 \quad (15)$$

Because the function in the brackets of eq 15 is a mirror image of the respective function in eq 9, eq 15 is an equation of minimum and so is eq 13. This means that eq 13 requires the process rate to pass through a minimum, i.e., to yield a downward rate peak. This requirement contradicts the basic rate eq 5. It can be shown that to arrive at eq 15, one needs to reverse the sign of the right-hand side of eq 5. This requirement also contradicts experimental observations for crystallization of polymer melts, whose rate passes through a maximum and gives rise to an upward peak. Therefore, dropping the negative sign for  $\beta$  to make the Kissinger equation applicable to cooling processes is an invalid procedure. In general, the requirements for the use of the method are that the process should be describable as single-step kinetics and that it should occur on heating.

### Advanced Isoconversional Method

The problem of negative  $\beta$  can be resolved with the help of the advanced isoconversional method that has been developed by Vyazovkin<sup>30</sup> by using the basic eq 5 with time dependent temperature

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT(t)}\right) dt = AJ[E_\alpha, T(t_\alpha)] \quad (16)$$

where  $g(\alpha)$  is the integral form of the reaction model,  $T(t)$  is the temperature program of an experiment, and the subscript  $\alpha$  denotes the values related to a given extent of conversion. By the virtue of the basic assumption of the isoconversional methods that at a given  $\alpha$  the value of  $g(\alpha)$  is independent of the heating program, the  $J$  integrals (eq 16) for any particular segment ( $0-t_\alpha$ ) should be equal for all experiments, regardless of differences in the heating programs. That is, for a series of  $n$  experiments carried out under different temperature programs,  $T_i(t)$  eq 17 holds true

$$J[E_\alpha, T_1(t_\alpha)] = \dots = J[E_\alpha, T_i(t_\alpha)] = \dots = J[E_\alpha, T_n(t_\alpha)] \quad (17)$$

Obviously, the ratio of any two of the  $J$  integrals should ideally be unity. Equation 17 is equivalent<sup>30</sup> to the condition of minimum

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (18)$$

Because the value of  $E_\alpha$  is the only unknown parameter in eq 18, this equation can be used to determine the activation energy at any particular value of  $\alpha$  by finding  $E_\alpha$ , which

minimizes the function  $\Phi(E_\alpha)$ . The method has recently been modified to account for a strong variation of  $E_\alpha$  with  $\alpha$  that is accomplished by performing integration over small time segments

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (19)$$

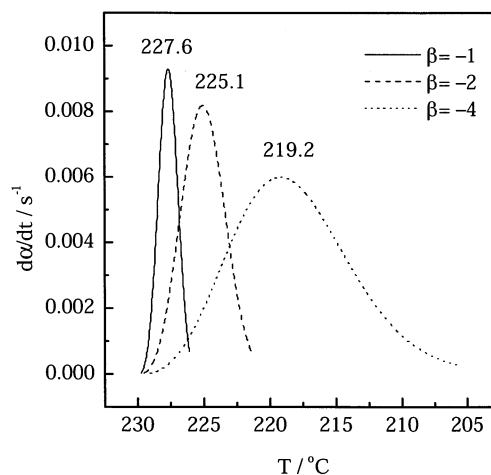
In eq 19  $\alpha$  varies from  $\Delta\alpha$  to  $1 - \Delta\alpha$  with a step  $\Delta\alpha = m^{-1}$ , where  $m$  is the number of intervals chosen for analysis. We usually set  $m = 50$  that gives  $\Delta\alpha = 0.02$ . The integral  $J$  in eq 19 is evaluated numerically by using the trapezoid rule. The minimization procedure is repeated for each value of  $\alpha$  to find the dependence of the activation energy on the extent of conversion.

The advanced isoconversional method holds for a wide class of the  $g(\alpha)$  models, including the Avrami model that justifies its application to crystallization kinetics. As shown above, the Kissinger method accounts for the temperature program in the form of the  $\beta$  value, which for obvious mathematical reasons must be positive. Conversely, the advanced isoconversional method accounts for the temperature program in its most general mathematical form,  $T(t)$ , and imposes no limitations on it. For this reason the method can be used for heating as well as for cooling. Another advantage of applying this method to crystallizations is that it permits estimating the effective activation energies for a complex process whose temperature dependence of the overall rate cannot be fit by a single Arrhenius equation over a wide temperature range. It should be stressed that evaluation of  $E_\alpha$  by eq 18 assumes that the Arrhenius equation holds only within the region of the temperatures related to a given value of  $\alpha$ . Each of these regions is much smaller than the entire temperature region of nonisothermal crystallization.

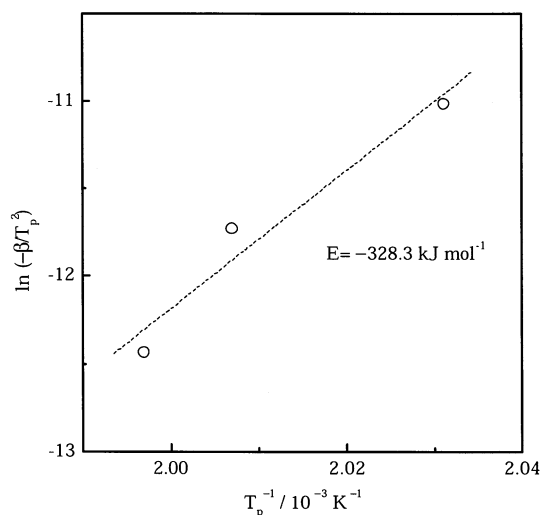
### Simulated Example

Let us test the advanced isoconversional method and the Kissinger method (with reversed sign for  $\beta$ ) on some cooling data. Because the only process whose kinetic parameters are known precisely is a simulated process, we have simulated a simple process whose rate obeys eq 5 with the following parameters:  $E = 100 \text{ kJ mol}^{-1}$ ,  $A = 10^{10} \text{ min}^{-1}$ , and  $f(\alpha) = 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$  (the differential form of the Avrami eq 3 with  $n = 4$ ). The resulting rate equation has been integrated by using the Runge–Kutta method of fourth order<sup>38</sup> to calculate the  $\alpha$  vs  $t$  and  $d\alpha/dt$  vs  $t$  dependencies. Integration was performed at three rates of temperature variation,  $\beta$ , which were  $-1$ ,  $-2$ , and  $-4 \text{ }^\circ\text{C min}^{-1}$ . The obtained rate peaks and the respective peak temperatures are shown in Figure 3. For the Kissinger method, the values of  $T_p$  and the values of  $-\beta$  were substituted into eq 8. The resulting Kissinger plot is shown in Figure 4. It is seen that the plot has a positive slope, which means that the activation energy is negative. Its value is  $-328.3 \text{ kJ mol}^{-1}$ . Apparently, the use of positive cooling rates in the Kissinger equation may result in the  $E$  values that differ drastically from the actual values. It would, therefore, be highly advisable to recalculate the values of  $E$  reported in numerous papers that apply the Kissinger equation to the processes that occur on cooling.

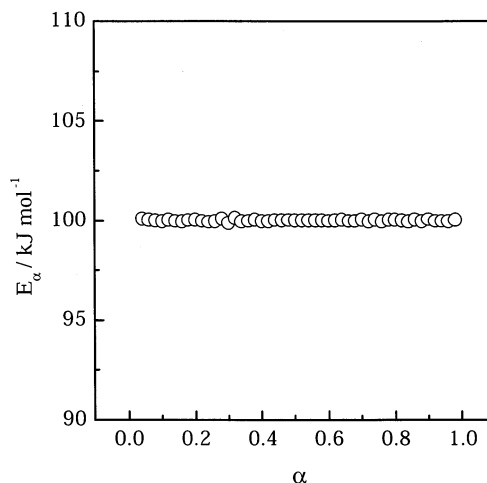
On the contrary, the use of the simulated data in the advanced isoconversional method (eqs 18 and 19) has resulted in obtaining  $E_\alpha$  values (Figure 5) that are practically identical with the actual value of  $E$  used for simulations. This method can, therefore, be used for evaluation of the effective activation energies of the processes that occur on cooling.



**Figure 3.** Simulated rate data for several cooling rates. The numbers by the peaks are the peak temperatures in  $^\circ\text{C}$ .



**Figure 4.** Kissinger plot for simulated data.

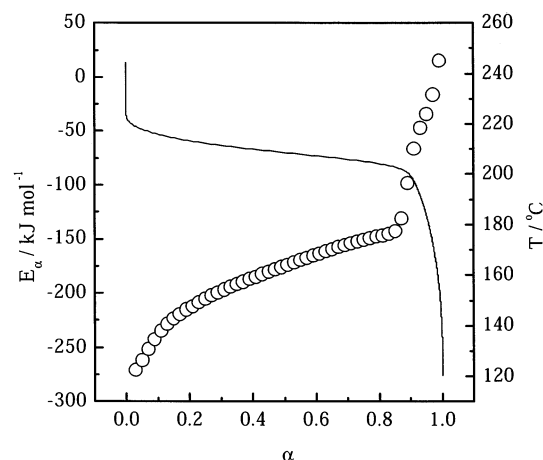


**Figure 5.**  $E_\alpha$  dependence obtained from simulated data by using the advanced isoconversional method.

### Results and Discussion

Integration of the DSC peaks (Figure 1) gives consistent values of the heats of crystallization having the average of  $64 \pm 2 \text{ J g}^{-1}$ . For purely crystalline PET the heat of fusion is  $140 \pm 20 \text{ J g}^{-1}$ .<sup>36</sup> Therefore crystallization of the PET melt results in semicrystalline samples whose absolute degree of crystallinity is  $\sim 0.46$  (i.e., they contain  $\sim 46\%$  of the crystalline phase).





**Figure 6.** Dependence of the activation energy on the extent of PET conversion. The solid line represents a kinetic curve obtained via integration of the DSC trace corresponding to the average cooling rate  $6\text{ }^{\circ}\text{C min}^{-1}$ .

The use of the advanced isoconversional method (eqs 18 and 19) requires evaluating the  $\alpha$  against  $t$  and  $T$  against  $t$  data. The kinetic curves  $\alpha$  against  $t$  have been evaluated from the DSC data (Figure 1) by using eq 2. The function  $T(t)$  has been determined experimentally as a variation of the sample temperature measured by DSC. The application of the advanced isoconversional method to the obtained data has resulted in estimating the activation energy that increases with the extent of the melt conversion (Figure 6) from around  $-270$  to  $+20\text{ kJ mol}^{-1}$ . Because after crystallization our samples contain about 46% of the crystalline phase, the extent of conversion 1 (i.e., the relative degree of crystallinity) corresponds to the absolute degree of crystallinity 0.46. With regard to this relationship, one can easily recast the obtained dependence (Figure 6) as a function of the absolute degree of crystallinity.

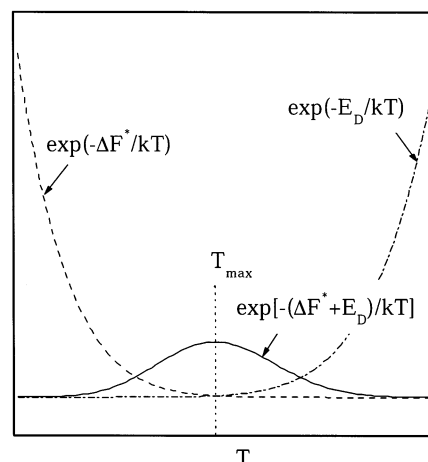
It is seen in Figure 6 that the experimental activation energy takes greater negative values at low extents of conversion that correspond to the temperatures closer to the melting point. The effective activation energy increases as the extent of conversion rises and the temperature decreases. A physical meaning of this phenomenon can be elucidated in terms of the nucleation theory proposed by Turnbull and Fisher.<sup>39</sup> The application of this theory to crystallization of polymers is discussed comprehensively by Wunderlich.<sup>40</sup> According to this theory the temperature dependence of the nucleation rate is given by

$$r = r_0 \exp\left(\frac{-E_D}{k_B T}\right) \exp\left(\frac{-\Delta F^*}{k_B T}\right) \quad (20)$$

where  $r$  is the rate,  $r_0$  is the preexponential factor,  $k_B$  is the Boltzmann constant,  $E_D$  is the activation energy for diffusion across the phase boundary, and  $\Delta F^*$  is the maximum free energy necessary for nucleus formation. The  $\Delta F^*$  and  $E_D$  exponential terms of eq 20 have opposing effects on the rate. The value of  $\Delta F^*$  is inversely proportional to the degree of supercooling as follows

$$\Delta F^* \sim \frac{1}{(T_m - T)^2} \quad (21)$$

whereas  $E_D$  is considered to be approximately constant at temperatures close to  $T_m$ .<sup>40</sup> According to eq 21, the value  $\Delta F^*$  can be very large in the close proximity to the melting point. For this reason the overall crystallization rate is determined by

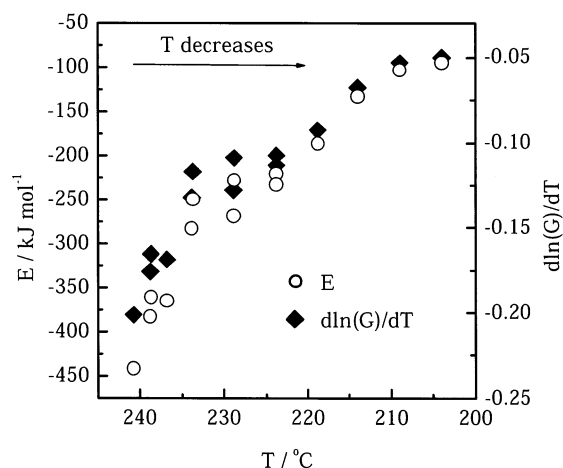


**Figure 7.** Schematic representation of the exponential terms contributing to the temperature dependence of nucleation rate (eq 20).

the nucleation rate, and its temperature dependence is determined by the temperature variation of  $\Delta F^*$  (eq 21). Because  $\Delta F^*$  decreases with decreasing the temperature, the  $\Delta F^*$  exponential term (eq 20) increases (Figure 7), giving rise to increasing the crystallization rate in the region from  $T_m$  to  $T_{\max}$ . This anti-Arrhenius behavior should definitely yield a negative value of the experimental (effective) activation energy.

Once  $\Delta F^*$  drops below a certain value, the nucleation rate becomes controlled by the transport process whose temperature dependence is determined by the  $E_D$  exponential term (eq 20). The rate of the transport process decreases with decreasing the temperature in accord with the Arrhenius law (Figure 7) that results in decreasing crystallization rate in the region  $T < T_{\max}$ . Because of the opposing effects of the  $\Delta F^*$  and  $E_D$  exponential terms, their product (i.e., the rate of nucleation) demonstrates a maximum at some temperature,  $T_{\max}$  (Figure 7). If carried out at this temperature, crystallization occurs with a maximum rate. This temperature is a dividing line between the anti-Arrhenius and regular Arrhenius behavior. Within the region  $T_{\max} - T_m$ , one encounters the anti-Arrhenius crystallization behavior that is characterized by negative values of the effective activation energy. Below  $T_{\max}$ , one should observe the regular Arrhenius behavior that is described by positive values of the experimental activation energy.

For PET the value of  $T_{\max}$  is experimentally found in the region  $170\text{--}190\text{ }^{\circ}\text{C}$ .<sup>41</sup> Because in our experiments crystallization of PET practically stops in this region (Figure 6), we predominantly observe the negative values of the activation energy. Only the effective activation energy,  $E_{0.99}$  corresponding to the lowest temperature has a positive value of  $\sim 20\text{ kJ mol}^{-1}$ . The  $E_{\alpha}$  dependence is continuously increasing, which is consistent with the decrease in the value of  $\Delta F^*$  as the temperature decreases. Also, the  $E_{\alpha}$  dependence shows a breakpoint at  $\alpha = 0.85$  that corresponds to the average temperature  $\sim 205\text{ }^{\circ}\text{C}$ . The change in the shape of the dependence is likely to be associated with a change in the crystallization mechanism. Lu and Hay<sup>42</sup> have recently applied the Hoffman–Lauritzen equation<sup>43</sup> to the isothermal crystallization of PET melts and found that at temperatures below  $217\text{ }^{\circ}\text{C}$  the crystallization mechanism changes from regime I to regime II. In regime I the rate of the formation of a surface nucleus is slower than the rate of crystal growth, whereas in regime II the rate of nucleation becomes larger than the rate of growth. The rates of these two regimes usually have different temperature dependencies.<sup>43</sup> A transition between the regimes is recognized by a change in the slope of the Hoffman–Lauritzen plot. In our situation, a change between



**Figure 8.** Data reported by Toda et al.<sup>45</sup> for crystallization of the PET melt (diamonds) and activation energies estimated by eq 22 (circles).

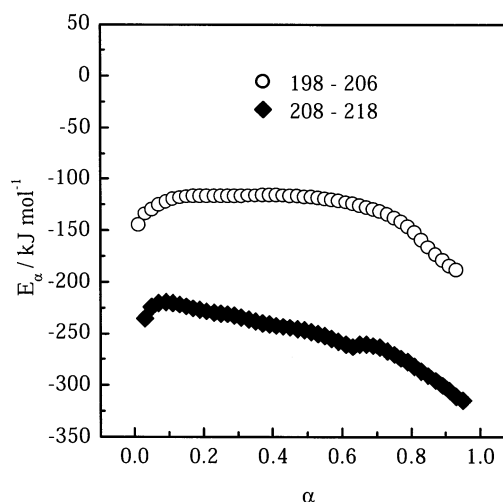
these regimes should be reflected in an abrupt change of the effective activation energy as that observed at  $\alpha = 0.85$ .

How does this dependence compare with the results of isothermal crystallization? A temperature variation of the effective activation energy can be derived from the data by Toda et al.,<sup>44,45</sup> who used temperature modulated DSC to determine the crystal growth rate,  $G$ , in the PET melt under quasi-isothermal conditions (0.2 °C oscillations around a constant temperature). Toda et al. report the values of  $d(\ln G)/dT$  at different temperatures (Figure 8) that can be used to estimate the effective activation energy. By assuming that over a temperature range of 0.4 °C (double amplitude of temperature oscillations in experiments of Toda et al.) the crystallization rate,  $G$ , obeys the rate eq 5 and that the  $\alpha$  value does not change significantly over the modulation period, one can easily determine the  $E$  value as follows

$$E = RT^2 \frac{d(\ln G)}{dT} \quad (22)$$

We used eq 22 to convert the  $d(\ln G)/dT$  values into the values of the effective activation energy. In agreement with our data (Figure 6), the estimated activation energies (Figure 8) are negative and increase with decreasing crystallization temperature. Toda et al. have collected their data in the temperature region 240–204 °C (Figure 8). Our values of  $E_\alpha$  (Figure 6) have been determined for the region of average temperatures 220–160 °C. In the common temperature region 220–204 °C, the  $E$  values derived by eq 22 from the data of Toda et al. demonstrate (Figure 8) an increase from around –190 to –90 kJ mol<sup>–1</sup>. According to our data (Figure 6) in the similar temperature region, the  $E_\alpha$  values increase from around –270 to –150 kJ mol<sup>–1</sup>. Therefore, the numerical values of the effective activation energies derived from the two different experiments appear to be fairly consistent, especially given the difference in crystallization conditions as well as in samples.

The advanced isoconversional method (eqs 18 and 19) has also been applied to the isothermal crystallization data (Figure 2). The  $E_\alpha$  dependencies have been evaluated for two temperature regions, 198–206 and 208–218 °C (Figure 9). In both cases the effective activation energy demonstrates some decrease with the extent of conversion. The average values of  $E_\alpha$  for these temperature regions appear to agree with the  $E_\alpha$  values found in respective temperature regions of nonisothermal crystallization (Figure 6). Another remarkable fact is that the minor temperature difference of ~10 °C between the temper-



**Figure 9.** Dependence of the activation energy on the extent of PET conversion estimated for two temperature regions (circles, 198–206 °C; diamonds, 208–218 °C).

ature regions 198–206 and 208–218 °C is associated with a significant change (>100 kJ mol<sup>–1</sup>) in the values of  $E_\alpha$  (Figure 9). This change is consistent with the abrupt change in  $E_\alpha$  that we observe for nonisothermal crystallization around 205 °C (Figure 6) and appears to be associated with the aforementioned change in the crystallization mechanism from regime I to regime II.

## Conclusions

The widely used Kissinger method appears to be generally inapplicable for evaluating the activation energy of the processes that occur on continuous cooling. Such evaluations can be accomplished by using the advanced isoconversional method. The application of the method to nonisothermal crystallization of the PET melt has resulted in obtaining negative values of the effective activation energy that increases with the extent of the melt conversion. The effect is explained by a decrease in the free energy of nucleation with the increasing degree of supercooling. The observed abrupt increase in the effective activation energy at ~205 °C can be assigned to a change in the crystallization mechanism. In general, the application of the isoconversional analysis to calorimetric data can be recommended as a means of obtaining important clues about the dynamics of nonisothermal crystallization of polymer melts.

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