

ESTIMATING THE ACTIVATION ENERGY FOR NON-ISOTHERMAL CRYSTALLIZATION OF POLYMER MELTS

S. Vyazovkin^{1*} and *N. Sbirrazzuoli*²

¹Department of Chemistry, University of Alabama at Birmingham, 901S 14th Street Birmingham, AL 35294, USA

²Chemistry of Organic and Metallic Materials C.M.O.M., Thermokinetic group, University of Nice, Sophia Antipolis, 06108 Nice, cedex 2, France

Abstract

The advanced isoconversional method can be used to determine the effective activation energy of non-isothermal crystallization of the polymer melts. The method has been applied to DSC data on crystallization of poly(ethylene terephthalate) (PET). The resulting activation energy increases with the extent of crystallization from –270 to 20 kJ mol⁻¹. The variation is interpreted in terms of the Turnbull and Fisher crystallization theory.

Keywords: crystallization, effective activation energy, isoconversional kinetics, poly(ethylene terephthalate)

Introduction

DSC is widely used to study crystallization of polymer melts. The measured rate of heat release, dQ/dt is assumed to be proportional to the macroscopic rate of crystallization, $d\alpha/dt$

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

where Q_c is the measured heat of crystallization.

Integration of DSC peaks yields the values of Q_c as well as the extent of the melt conversion, α . The value of α varies from 0 to 1, where $\alpha=1$ corresponds to the degree of crystallinity, which is attained after completion of the heat release.

The macroscopic kinetics of isothermal crystallization are usually described by the Avrami model. Ozawa [1] extended the Avrami equation to non-isothermal conditions. While offering a way of estimating the Avrami exponent, Ozawa's analysis does not suggest a method of determining the activation energy. Estimating the activation energy for non-isothermal crystallization encounters several problems. Be-

* Author for correspondence: E-mail: Vyazovkin@uab.edu

cause the macroscopic crystallization rate is generally determined by the respective rates of nucleation and nuclei growth which are likely to have different activation energies, the temperature dependence of the overall rate can rarely be fit by a single Arrhenius equation,

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (2)$$

in a wide temperature range. Nevertheless, Eq. (2) should hold reasonably well for a relatively narrow temperature interval that permits estimating the effective value of the activation energy, E .

The rate measured by DSC is customarily described by the basic rate equation [2]:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (3)$$

where R is the gas constant, A is the preexponential factor, and $f(\alpha)$ is the reaction model related to the mechanism.

For non-isothermal conditions of linear heating, Eq. (3) is modified as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (4)$$

where β is the heating rate.

The results of the ICTAC Kinetics Project suggest [3] that the most reliable way of evaluating non-isothermal kinetics is the use of multiple heating rate methods. The more popular representatives of the multiple heating rate methods are the methods of Flynn and Wall [4], Ozawa [5], and Kissinger [6]. Because these methods require taking the logarithm of β , they cannot be directly applied to crystallization of polymer melts that occurs on cooling ($\beta < 0$).

The problem of negative β can be avoided by using the basic rate Eq. (3) with time dependent temperature. Vyazovkin [7, 8] has used the integral form of Eq. (3) to develop an advanced isoconversional method. This method has been designed to treat the kinetics that occur under arbitrary variation in temperature. For a series of n experiments carried out under different temperature programs, $T_i(t)$, the activation energy is determined at any particular value of α by finding E_α , which minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (5)$$

where

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (6)$$

Henceforth the subscript α indicates the values related to a given extent of conversion. In Eq. (6) α varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha = m^{-1}$, where m is the num-

ber of intervals chosen for analysis. The integral, J in Eq. (6) is evaluated numerically. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion.

It should be stressed that evaluation of E_α assumes that the Arrhenius equation holds only within a region of the temperatures related to a given value of α . Each of these regions is much smaller than the entire temperature region of non-isothermal crystallization and usually not greater than 10°C. For this reason the isoconversional method can be applied to non-isothermal crystallizations for evaluating the dependence of the effective activation energy on conversion and temperature. Such dependencies have been quite helpful in detecting and elucidating complex kinetics in polymeric systems [9–12]. Although we have successfully used the isoconversional method to study the kinetics of various processes that occur in polymers on heating, the method has never been applied to treat the kinetics occurring on cooling. This paper presents the application of the method to non-isothermal crystallization of a polymer melt.

Experimental

Poly(ethylene terephthalate) (PET) ($M_w \sim 18,000$) has been purchased from Aldrich and used as received. A Mettler-Toledo DSC 821° module was used to follow the kinetics of PET crystallization. A ~6 mg sample was placed in a 40 μL Al pan, which was hermetically closed under nitrogen. The equilibrium value of T_m for PET is 280°C [13]. In order to secure complete melting, all samples were heated to 290°C and held at this temperature for 15 min. In non-isothermal runs, the samples were cooled down to 25°C at the rates 3, 4, 6, 8, and 12°C min^{-1} . For isothermal runs the temperature was dropped quickly from 280°C to the present constant values. The isothermal runs were carried out at eleven temperatures varying from 198 to 218°C with a step 2°C.

Results and discussion

Integration of the DSC peaks 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 $140 \pm 20 \text{ J g}^{-1}$ [13]. Therefore crystallization of the PET melt results in semicrystalline samples having about 46% of the crystalline phase.

The application of the advanced isoconversional method (Eqs (5) and (6)) to the obtained data has resulted in estimating the activation energy that increases with the extent of the melt conversion (Fig. 1) from around -270 to 20 kJ mol^{-1} . The experimental activation energy takes greater negative values at low extents of conversion that correspond to the temperatures closer to the melting point. The value of E_α increases as the extent of conversion rises and the temperature decreases. A physical meaning of this phenomenon can be understood in terms of the nucleation theory proposed by Turnbull and Fisher [14]. Wunderlich [15] has comprehensively discussed the application of this theory to crystallization of polymers. According to this theory the temperature dependence of the nucleation rate is given by Eq. (7)

$$r = r_0 \exp\left(\frac{-E_D}{k_B T}\right) \exp\left(\frac{-\Delta F^*}{k_B T}\right) \quad (7)$$

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 ΔF^* is the maximum free energy necessary for nucleus formation.

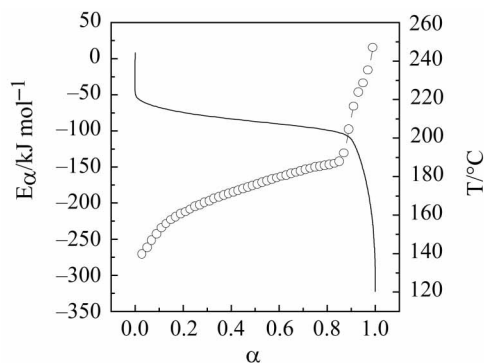


Fig. 1 Dependence of the activation energy on the extent of PET conversion under non-isothermal conditions. Solid line represents a kinetic curve obtained via integration of the DSC trace corresponding to the average cooling rate 6°C min^{-1}

The ΔF^* and E_D exponential terms of Eq. (7) have opposing effects on the rate. If the value of E_D is considered to be approximately constant, the value of ΔF^* is inversely proportional to the degree of supercooling [16].

$$\Delta F^* \sim \frac{1}{(T_m - T)^2} \quad (8)$$

Obviously, the value ΔF^* can be very large in the close proximity to the melting point. For this reason the overall crystallization rate in that area is determined primarily by the nucleation rate, and its temperature dependence is determined by the temperature variation of ΔF^* (Eq. (8)). Since ΔF^* decreases with decreasing the temperature, the ΔF^* exponential term (Eq. (7)) increases giving rise to increasing the crystallization rate. This anti-Arrheniusian behavior gives rise to a negative value of the experimental (effective) activation energy.

Once ΔF^* 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. (7)). The rate of the transport process decreases with decreasing the temperature in accord with the regular Arrhenius law (Eq. (2)). Because of the opposing effects of the ΔF^* and E_D exponential terms, their product (i.e., the rate of nucleation) demonstrates a maximum at some temperature, T_{max} . Isothermal crystallization performed at this temperature accomplishes a maximum rate. This temperature is a dividing line between the anti-Arrheniusian and regular Arrheniusian behavior. In the

region $T_{\max}-T_m$, crystallization demonstrates the anti-Arrheniusian crystallization behavior that is characterized by negative values of the effective activation energy. Below T_{\max} , one should observe the regular Arrheniusian behavior which is described by positive values of the experimental activation energy.

For PET the experimentally found values of T_{\max} fall into the region 170–190°C [17]. Because in our experiments crystallization of PET practically stops in this region (Fig. 1), we predominantly observe the negative values of the activation energy. Only the effective activation energy, $E_{0.99}$ corresponding to the highest temperature has a positive value of $\sim 20 \text{ kJ mol}^{-1}$. The continuous increase in E_α is consistent with the decrease in the value of ΔF^* that occurs on cooling (Eq. (8)). Also, the E_α dependence shows a break-point at $\alpha=0.85$ that corresponds to the average temperature $\sim 205^\circ\text{C}$. The change in the shape of the dependence is indicative of a change in the crystallization mechanism. Lu and Hay [18] have recently applied the Hoffman–Lauritzen equation [19] to the isothermal crystallization of PET melts and found that at temperatures below 217°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. Because the rates of these two regimes usually have different temperature dependencies [19], a transition between the regimes is detected as a change in the slope of the Hoffman–Lauritzen plot. In our situation, the change between these regimes should be reflected in an abrupt change of the effective activation energy as that we observed at $\alpha=0.85$.

The isoconversional method (Eqs (5) and (6)) has also been applied to the isothermal crystallization data. The E_α dependencies have been evaluated for two temperature regions, 198–206 and 208–218°C (Fig. 2). In both cases the effective activation energy demonstrates some decrease with the extent of conversion. The average values of E_α for these temperature regions appear to agree with the E_α values found in respective temperature regions of non-isothermal crystallization (Fig. 1). Another remarkable fact is that the minor temperature difference of $\sim 10^\circ\text{C}$ between the temperature regions 198–206 and 208–218°C is associated with a significant change ($>100 \text{ kJ mol}^{-1}$) in the values of E_α (Fig. 2). This change is consistent with the abrupt change in E_α that we observe for

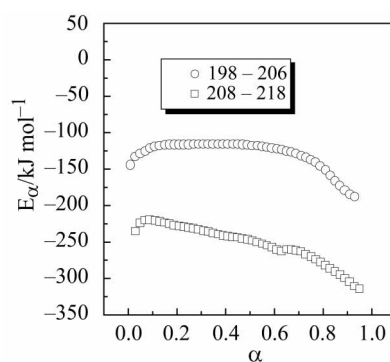


Fig. 2 Dependence of the activation energy on the extent of PET conversion under isothermal conditions for two temperature regions: 198–206°C (circles) and 208–218°C (squares)

non-isothermal crystallization around 205°C (Fig. 1) and appears to be associated with the aforementioned change in crystallization mechanism from regime I to regime II.

Conclusions

The advanced isoconversional method provides a sound way of estimating the effective activation energy, E_{α} for non-isothermal crystallization of the polymer melts. The experimentally obtained E_{α} -dependence adequately reflects the changes in the crystallization kinetics that occur with changing the temperature of the process. The method can be used as a tool for extracting from DSC data information on the dynamics of non-isothermal crystallization of polymer melts.

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