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HOFFMAN–LAURITZEN PARAMETERS FOR NON-ISOTHERMAL CRYSTALLIZATION OF POLY(ETHYLENE TEREPHTHALATE) AND POLY(ETHYLENE OXIDE) MELTS

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By applying an advanced isoconversional method to DSC data one can evaluate a dependence of the effective activation energy (the temperature coefficient of the growth rate) on the relative extent of melt crystallization. The conversion dependence can further be converted into a temperature dependence and parameterized in terms of the Hoffman–Lauritzen equation. For poly(ethylene terephthalate) (PET) we observe a transition from regime I to II. Poly(ethylene oxide) (PEO) crystallization appears to begin in regime II and then undergoes 2 consecutive changes that however cannot be clearly interpreted as regime III. The K_g and $\sigma\sigma_e$ parameters obtained for regime I and II (PET) and regime II (PEO) are consistent with the respective parameters reported for isothermal crystallization.

Keywords: *activation energy, crystallization, DSC, isoconversional method, kinetics*

Introduction

Differential scanning calorimetry (DSC) is the most common tool for measuring the overall rates of polymer crystallization [1, 2]. The overall crystallization kinetics are typically described in terms of the Avrami equation [3]:

$$\alpha=1-\exp(-k^m t^m) \tag{1}$$

where α is the extent of conversion from the amorphous to crystalline phase, m is the Avrami exponent that is associated with the crystallization mechanism and k is the overall rate constant. The value of α is readily determined as the partial area of a DSC peak. The typical outcome of the Avrami analysis is the values of k and m. Note that the values of m do not allow for singular mechanistic interpretation [1], and that the Avrami analysis is hardly more than a convenient representation of experimental data [2]. The temperature dependence of k is frequently parameterized via the Arrhenius equation,

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

where R is the gas constant, A is the pre-exponential factor, and E is the activation energy. Equation (2) provides the basis for the majority of kinetic methods, including the Kissinger method [4] that is widely used for evaluating the effective activation energy of non-isothermal polymer crystallization. We have recently demonstrated [5] that this method provides invalid results when applied to the processes that occur on cooling such as melt crystallization. Another limitation is that the method applies only to the processes whose kinetics can be adequately represented by a constant value of E throughout an experimental temperature region. However, the effective activation energy of the melt crystallization varies strongly with temperature [6] that makes the E value estimated by the Kissinger method irrelevant.

The problems associated with the Kissinger treatment can be eliminated [6] when applying an advanced isoconversional method [7, 8] to non-isothermal crystallization of the polymer melt. Isoconversional analysis yields a dependence of the effective activation energy on the relative extent of crystallization. We have recently proposed a method [9] that allows this dependence to be used for obtaining the parameters of the Hoffman–Lauritzen theory of polymer crystallization [10]. In this paper we present results on the application of our novel method to the non-isothermal melt crystallization of poly(ethylene terephthalate) (PET) and poly(ethylene oxide) (PEO).

Experimental

PET (M_W=~$1.8\cdot10^3$) and PEO (M_W=~$5\cdot10^6$) were, respectively, purchased form Aldrich and Scientific Polymer Products Inc. and used as received. The DSC runs

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were performed on PET samples by using Mettler-Toledo DSC821^e and on PEO samples by using Mettler-Toledo DSC822^e. The 5–7 mg samples were heated in Al pans to 10°C above the equilibrium melting point (T_m is 280°C for PET and 69°C for PEO [11]), held for 15 min and then cooled down to 25°C (PET) or –20°C (PEO) at the rates from 2 to 12 K min^{-1}.

Computation method

According to the Hoffman–Lauritzen theory [10], a dependence of the linear growth rate, G on temperature, T can be described as:

$$G = G_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right]\exp\left(-\frac{K_g}{T\Delta T f}\right) \tag{3}$$

where G_0 is the preexponential factor, U^* is the activation energy of the segmental jump, $\Delta T=T_m-T$ is the undercooling, $f=2T/(T_m+T)$ is the correction factor, T_∞ is a hypothetical temperature where motion associated with viscous flow ceases that is usually [10] taken 30 K below the glass transition temperature, T_g. The kinetic parameter K_g has the following form:

$$K_g = \frac{nb\sigma\sigma_e T_m}{\Delta h_f k_B} \tag{4}$$

where b is the surface nucleus thickness, σ is the lateral surface free energy, σ_e is the fold surface free energy, T_m is the equilibrium melting temperature, Δh_f is the heat of fusion per unit volume of crystal, k_B is the Boltzmann constant, and n takes the value 4 for crystallization regime I and III, and 2 for regime II. Because Eq. (3) has two exponents, the temperature dependence of the growth rate is obviously non-Arrheniusian. That is a single Arrhenius equation cannot be used to describe the temperature dependence of the growth rate over the wide range of ΔT. Nevertheless, this temperature dependence can be approximated by a sequence of the Arrhenius equations each of which holds over a relatively narrow temperature region and has its own effective activation energy, E. The resulting E value is temperature dependent and has a meaning of the temperature coefficient of the crystallization rate. An explicit dependence of E on T can be derived from Eq. (3) as:

$$\begin{aligned} E &= -R\frac{\mathrm{d}\ln G}{\mathrm{d}T^{-1}} = \\ &= U^*\frac{T^2}{(T-T_\infty)^2} + K_g R\frac{T_m^2 - T^2 - T_m T}{(T_m - T)^2 T} \end{aligned} \tag{5}$$

It has been demonstrated [9] that an experimental E_α dependence estimated by using an advanced isoconversional method can serve as an estimate for E in Eq. (5). Since E_α is unavoidably evaluated for some non-infinitesimal temperature interval, we can conventionally relate this value to an average temperature, T for this interval so that Eq. (5) takes the following form:

$$E_\alpha(T) = U^*\frac{T^2}{(T-T_\infty)^2} + K_g R\frac{T_m^2 - T^2 - T_m T}{(T_m - T)^2 T} \tag{6}$$

The first step in evaluation of the $E_\alpha(T)$ is the application of an isoconversional method to the overall crystallization data in order to obtain a dependence of E_α on α. An advanced isoconversional method [7, 8] is capable of treating the kinetics occurring under arbitrary temperature program, $T(t)$. The method can be applied to the processes that occur on heating as well as on cooling. It also allows one to account for self-heating/cooling detectable by the thermal sensor of the instrument. Depending on the cooling rate, the same value of α is accomplished at different temperatures that have been used to evaluate an average temperature associated with the α value. This dependence is used to correlate the E_α values with temperature as required by Eq. (6).

Results and discussion

Figures 1 and 2 display the $E_\alpha(T)$ dependencies. The values of E_α are negative that indicates that the crystallization rate increases with decreasing temperature. This should invariably occur [6] in the temperature from T_m down to the temperature of the maximum crystallization rate, T_{max}.

As seen in Fig. 1, the $E_\alpha(T)$ dependence demonstrates a breakpoint at ~475 K (i.e., ~202°C) that may be due to a change in crystallization mechanism. For isothermal PET crystallization, similar changes have been detected [12, 13] as a break point in the Hoffman–Lauritzen plot at the temperatures 217 and 236°C. Okamoto *et al*. [14] have reported a change in the crystallization regime at 202°C which is the same temperature as found by us. Because of the change in the mechanism that occurs at ~475 K, it makes sense to parameterize the A (T>475 K) and B (T<475 K) portions of the $E_\alpha(T)$ dependence separately. The graphics software Origin 6.0 (Microcal Software, Inc.) has been employed to fit segments A and B to Eq. (6) (T_g=342 K [11]). The fits yield the values of K_g and U^* shown in Table 1. The values of K_g for A and B regions are 3.2 and $1.9\cdot10^5$ K^2, respectively. It is noteworthy, that the higher temperature fit gives the K_g value that is 1.7 times larger than the lower temperature value. This ratio is very close to the theoretical ratio 2 that corresponds to the change in the crystallization mechanism from regime I to regime II [10]. The value of K_g can be used to evaluate the product

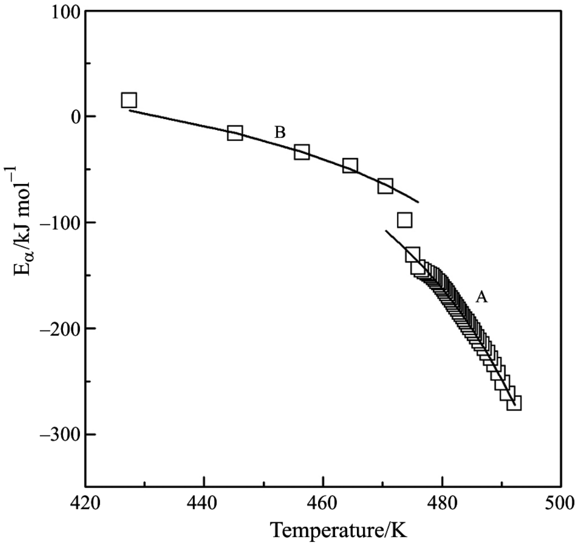

Fig. 1 Dependence of the effective activation energy on average temperature for PET. Solid lines represent fits of Eq. (6)

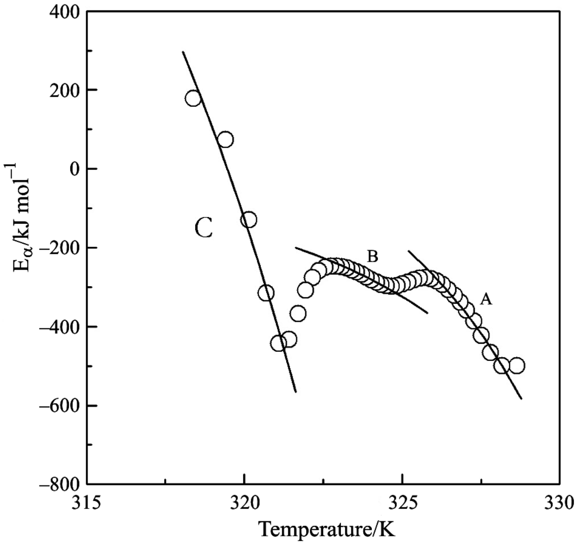

Fig. 2 Dependence of the effective activation energy on average temperature for PEO. Solid lines represent fits of Eq. (6)

$\sigma\sigma_e$ from Eq. (4). The volumetric heat of fusion (Δh_f=2.1·10^8 J m^{-3}) is determined as the mass heat of fusion (140 J g^{-1}) [11] times the density (1.5 g cm^{-3}) [15]. The monomolecular layer thickness, b is 5.53·10^{-10} m [16]. The values of $\sigma\sigma_e$ evaluated from K_g equal to 3.2·10^5 K^2 (n=4 in Eq. (4)) and 1.9·10^5 K^2 (n=2 in Eq. (4)), respectively, are 7.6 and 9.0·10^{-4} J^2 m^{-4}. Table 1 collects the values of K_g and $\sigma\sigma_e$ reported in [12–14, 16–21] for isothermal crystallization of PET. Our numbers appear to be reasonably consistent with the reported values, although tend to be on the low side.

Crystallization of PEO is a very complex process that shows multiple rate maxima [22], a change in crystallographic orientation of the growth front around 50°C [23], and an increase in $\sigma\sigma_e$ with increasing M_W [24]. Kovács *et al*. [22] have found that crystallization of PEO (M_W=1.5·10^5) is consistent with regime II in the whole temperature range (ca., 30–60°C). Cheng *et al*. [25] has reported that at ΔT>10°C crystallization occurs in regime II that is followed by a change to regime III at ΔT>17.5°C (i.e., below 50°C). The change in the temperature dependence of the rate has been alternatively explained [23] by the aforementioned change in crystallographic orientation of the growth front. Wu *et al*. [26] suggest the process to occur in regime II in the temperature region 43–60°C, whereas Marentette and Brown [27] propose regime III for the temperature region 45–56°C. According to our data (Fig. 2), the effective activation energy shows 3 distinct regions (A–C) whose behavior is consistent with Eq. (6). The respective segments have been fitted separately to Eq. (6) (T_g=206 K [11]). For the region A (ΔT<16°C, T>53°C), the value of K_g is 0.62·10^5 K^2 that falls in the middle of the region of the K_g values reported in the literature (Table 2). Assuming regime II crystallization (n=2 in Eq. (6)) we can estimate $\sigma\sigma_e$. The value of Δh_f= 2.67·10^8 J m^{-3} is determined as the mass heat of fusion (203 J g^{-1}) [11] times the density (1.33 g cm^{-3}) [15]. The b value is 4.65·10^{-10} m [24]. The resulting value of $\sigma\sigma_e$ is 6.8·10^{-4} J^2 m^{-4} that is in good agreement with values of other workers (Table 2). The region B (T=50–53°C,

Table 1 Crystallization parameters of PET

K_g·10^{-5}/K^2		T_m/°C	U*/kJ mol^{-1}	$\sigma\sigma_e$·10^4/J^2 m^{-4}	Reference
regime I/III	regime II				
5.0	2.5	289	6.3	11.6	12
8.7	6.1	305	6.3	18.9–26.5	13
		279	5.8	5.0	14
		280	8.4	14.3	16
^{2}12.80		278	12.8	31.6	17
	2.8	280	6.3	15.1	18
	3.0	280	6.3	13.6	19
^{3}3.7		280	6.3		20
	2.3	251	6.3	9.97–9.55	21
3.2	1.9	280	4.3/2.3	7.6–9.0	this work

^{2}identified as regime III, ^{3}regime is not identified

Table 2 Crystallization parameters of PEO

$K_g \cdot 10^{-5}$/K^2		T_m/°C	U*/kJ mol^{-1}	$\sigma\sigma_e \cdot 10^4$/J^2 m^{-4}	$M_W \cdot 10^{-5}$	Reference
regime II	regime III					
		69	29.3	4.5	1.5	22
		76	12.0	7.2[4]	9.9	24
0.12–0.13	0.23	69	29.3	2.9–3.0	1.05	25
		69	29.3	2.7	1.05	25
0.38		69	6.3	4.0	1.44	26
	1.22	76	29.3	7.0	1.8	
0.62		69	74.0	6.8	50	this work

[4]regime is not identified

ΔT>17°C) appears to be in the same temperature region that was identified by Cheng *et al*. [25] as regime III crystallization. According to our data, the value of K_g for the region B is $0.40 \cdot 10^5$ K^2 whereas by the theory it should be 2 times larger than that for the region A, if we actually have a change from regime II to III. Therefore the change cannot be assigned to this transition and may be due to the aforementioned change in crystallographic orientation of the growth front. The value of K_g increases to $4.5 \cdot 10^5$ K^2 in the region C (ΔT>21°C, T<48°C). Unlike the K_g values for the regions A and B whose standard error less than 5%, the error for K_g in region A is 0.5. Given only 5 points involved in the estimate, this standard error translates into a relatively large 95% confidence region, 1.5. However, even with regard of this confidence interval, the K_g value for the C region is more than 2 times larger than that for A and B regions so that the respective transition is not consistent with the typical transition from regime II to III.

Conclusions

The application of the advanced isoconversional method to the overall crystallization rate data allows for estimating the temperature dependence of the temperature coefficient (i.e., the effective activation energy) of the growth rate. The obtained dependence can be used to determine the parameters of the Hoffman–Lauritzen equation from DSC data on non-isothermal crystallization. The parameters determined for non-isothermal crystallization of the PET and PEO melts compare favorably with the literature values for isothermal crystallization.

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