

THEORETICAL ANALYSIS OF KINETICS OF NONISOTHERMAL CRYSTALLIZATION OF POLYMERS*

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ABSTRACT

The classical crystallization theories proposed by Avrami, Evans, and Mandelkern were extended to the nonisothermal situation. The expressions derived from the classical equations can be expressed in either the differential form or the integral form. A method was provided so as to obtain the parameters characterizing the crystallization rate and mechanism from DSC curves with several constant heating or cooling rates. The rate constants of crystallization obtained from both isothermal and nonisothermal curves of poly(ethylene terephthalate) were compared.

INTRODUCTION

The Avrami equation, as well-known, is an isothermal equation, which was originally derived for the crystallization of metals and was extended to the crystallization of polymers later on. Because the theory of nonisothermal crystallization of polymers has extensive use in optimizing the technological processes of polymers and in determining the kinetic parameters of crystallization, how the Avrami theory are extended to the nonisothermal crystallization has attracted a more and more great attention. Some papers were presented to describe the nonisothermal crystallization^[1-7]. In these papers, derivation of the equations all were based to some extent on the Avrami or the Evans theory directly or indirectly. However, some shortcomings still exist in the course of applying these equations to calculating the kinetic parameters of crystallization. For example, Avrami exponent n can be obtained through the Ozawa equation, but the rate constant of crystallization can not be calculated from the cooling

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crystallization function because it is very complicated^[1]. Therefore, it has been strongly desired to develop a new equation available to nonisothermal courses.

In this paper, the classical theories, which were proposed by Avrami, Evans, and Mandelkern respectively, were analysed in more detail and were extended to nonisothermal situation. The equations obtained in the present paper can be expressed in either the differential form or the integral form, which all are available under the nonisothermal conditions. The nonisothermal crystallization curves of poly(ethylene terephthalate) with several heating or cooling rates followed by DSC were analysed in terms of the proposed equation.

CLASSICAL THEORIES

1. *Avrami theory*^[8-10]

For the unit volume, if it is assumed that the distribution of crystallite centers is random, the Avrami's exact relation can be expressed as^[9]

$$\frac{dV}{dV_{\text{ex}}} = 1 - V \quad (1)$$

where V represents the real volume of the crystalline phase per unit volume; V_{ex} is the "extended" volume of the crystallite phase. The integral of equation (1) results in

$$1 - V = \exp(-V_{\text{ex}}) \quad (2)$$

Derived equation (1) is not limited to isothermal conditions, neither is equation (2).

2. *Evans theory*^[11]

Evans applied the Poisson's law to the process of crystallization of the materials. For the unit volume, the following equation was obtained

$$1 - V = \exp[-E(t)] \quad (3)$$

where the mathematical expectancy $E(t)$ is equal to the total volume of entities of which appearance and growth are unconstrained. Thus, both the Avrami theory and the Evans theory are equivalent^[12].

3. *Mandelkern theory*^[13]

It is assumed that the crystallized mass of the system during time dt is dM_{ex} in case there are no restraints of any kind to the growth of an entity. Because of the various retardations to growth possible, such as random distribution of nuclei, the real mass crystallized, dM , will be less than dM_{ex} .

Mandelkern assumed that the relationship between dM and dM_{ex} is given by

$$\frac{dM}{dM_{\text{ex}}} = 1 - U(t) \quad (4)$$

where $U(t)$ is the "effective fraction" of the mass crystallized at time t , and is assumed to be equal to

$$U(t) = \frac{M}{X_{\text{em}}M_0} \quad (5)$$

where X_{em} is the maximum mass fraction of crystallized polymer, i. e., the equilibrium mass crystallinity; M_0 the total mass of the material. It can be known from equation(5) that $U(t)$ stands for the relative mass crystallinity.

THEORY OF NONISOTHERMAL CRYSTALLIZATION

1. Differential equation

Avrami theory is suitable for the crystallization of metals. The crystallization of polymers possesses its special characteristic. Especially, when crystallization are completed, the equilibrium crystallinity can not arrive at 100%. Therefore, for the polymeric system, equation(1) should be corrected slightly and rewritten as

$$\frac{dV}{dV_{\text{ex}}} = 1 - \alpha \quad (6)$$

where α is the relative volume crystallinity. Corresponding equation (2) should also be rewritten in the following form

$$1 - \alpha = \exp(-\alpha_{\text{ex}}) \quad (7)$$

where α_{ex} is the "extended" relative volume crystallinity of materials, i. e., assuming that possible overlapping of growing entities is neglected. Equation (6) can be converted into

$$\frac{dV}{dt} = \frac{dV_{\text{ex}}}{dt}(1 - \alpha) \quad (8)$$

Supposing entities of given shape grow in the direction of $\vec{r}$ (r is the radius of a spherulite or the length of a rodlike entity), dV_{ex}/dt in the right side of equation(8) can be expressed in the following form

$$\frac{dV_{\text{ex}}}{dt} = \frac{dV_{\text{ex}}}{dr} \frac{dr}{dt} \quad (9)$$

dr/dt represents the linear growth rate of the entities,. Many experiment facts have demonstrated that dr/dt is only dependent on temperature for a given polymer, as well symbolized by $G(T)$. For a given shape crystalline entity (such as a sphere, disk, or rod), whether the process of nucleation is

instantaneous or sporadic, dV_{ex}/dr is equal to the "extended" surface area, symbolized as S_{ex} . Therefore, equation (8) can be rewritten as

$$\frac{d\alpha}{dt} = K'(T)S_{ex}(1 - \alpha) \quad (10)$$

where $K' = G/X_e$, X_e the equilibrium volume crystallinity. From this, it can be known that the Avrami classical equation can be expressed in the same form as the modified first-order kinetic model which was adopted in our previous paper^[14]. The difference between the two is that the S_{ex} stands for the "extended" surface area other than the real one. For the system per unit volume, the relationship between the "extended" relative volume crystallinity α_{ex} and the total volume of the entities is

$$V_{ex} = X_e \alpha_{ex} \quad (11)$$

the relationship between S_{ex} and V_{ex} can be derived in terms of the method adopted in the previous paper^[14]. Taking equation (11) into account, one can obtain the relationship between S_{ex} and α_{ex} .

In case that the nuclei are pre-determined, then for the sphere entities, one attains

$$S_{ex} = 4\pi N_0 (3X_e/4\pi N_0)^{2/3} \cdot \alpha_{ex}^{2/3} \quad (12)$$

for the disk-shaped entities

$$S_{ex} = 2(\pi d_0 N_0 X_e)^{1/2} \cdot \alpha_{ex}^{1/2} \quad (13)$$

for the rodlike entities

$$S_{ex} = N_0 S' \cdot \alpha_{ex}^0 \quad (14)$$

where N_0 is the number of nuclei per unit volume; d_0 the thickness of a disk-shape entity; S' the surface area of the cross-section of a rodlike entity.

In case that nucleation is sporadic, the following equations are derived for the sphere entities

$$S_{ex} = (4/3)\pi k (3X_e/\pi k)^{3/4} \cdot \alpha_{ex}^{3/4} \quad (15)$$

for the disk-shaped entities

$$S_{ex} = \pi d_0 k (3X_e/\pi d_0 k)^{2/3} \cdot \alpha_{ex}^{2/3} \quad (16)$$

for the rodlike entities

$$S_{ex} = (2X_e S' k)^{1/2} \cdot \alpha_{ex}^{1/2} \quad (17)$$

where $k = I(T)/G(T)$; $I(T)$ is the nucleation rate. According to the assumption about "isokinetic conditions", k is independent of the temperature^[2]. Inserting expressions about S_{ex} into equation (10) leads to

$$\frac{d\alpha}{dt} = K(T)\alpha_{ex}^m(1 - \alpha) \quad (18)$$

Considering the relationship between ideal crystallinity and actual one

(equation(7)), one can rewrite equation (18) as

$$\frac{d\alpha}{dt} = K(T)[- \ln(1 - \alpha)]^m(1 - \alpha) \quad (19)$$

This is the differential equation that was derived in terms of the classical Avrami theory. The derived processes did not concern the isothermal limitation, therefore equation(19) should be able to use under nonisothermal conditions.

When the Mandelkern theory is used, an equation can be derived in the same form as equation(19). In the equation, m has the same content as that obtained from the Avrami theory, but the relative volume crystallinity α in equation(19) should be replaced by the relative mass crystallinity α_m . Because the relationship between the total volume and the relative mass crystallinity is $V_{ex} = X_{em} \alpha_m / \rho_c$ ^[14] for the system per unit mass (X_{em} stands for the equilibrium mass crystallinity and ρ_c the density of the crystallized entities.), the contents represented by $K(T)$ are not perfect equivalent to that obtained from the Avrami theory. In the case of different nucleation mechanism and crystalline morphology(geometry), the contents of K and m were shown in Table 1.

Table 1 The physical significance of $K(T)$ and m in equation(19)

Shape		m	$K(T)$	
			Avrami theory	Mandelkern theory
Inst.*	Sphere	2/3	$4\pi N_0 G(3X_e/4\pi N_0)^{2/3}/X_e$	$4\pi N_0 G\rho_c(3X_{em}/4\pi N_0\rho_c)^{2/3}/X_{em}$
	Disk	1/2	$2G(\pi d_0 N_0 X_e)^{1/2}/X_e$	$2G(\pi d_0 N_0 X_{em}\rho_c)^{1/2}/X_{em}$
	Rod	0	$N_0 S'G/X_e$	$N_0 S'G\rho_c/X_{em}$
Sporadic	Sphere	3/4	$(4/3)\pi kG(3X_e/\pi k)^{3/4}/X_e$	$(4/3)\pi kG\rho_c(3X_{em}/\pi k\rho_c)^{3/4}/X_{em}$
	Disk	2/3	$\pi d_0 Gk(3X_e/\pi d_0 k)^{2/3}/X_e$	$\pi d_0 G\rho_c k(3X_{em}/\pi d_0 k\rho_c)^{2/3}/X_{em}$
	Rod	1/2	$G(2X_e S'k)^{1/2}/X_e$	$G(2X_{em} S'k\rho_c)^{1/2}/X_{em}$

* Inst. = Instantaneous

It can be known from Table 1 that $K(T)$ is proportional to the linear growth rate of crystals and can be used as a parameter that characterize the crystallization rate.

2. Integral equation

Rearranging and integrating equation(19), one obtains

$$- \ln(1 - \alpha) = [(1 - m) \int_0^t K(T) dt]^{1/(1-m)} \quad (20)$$

In order to employ the known parameters to express this equation, firstly, one should determine that the relationships between the parameters such as m and $K(T)$ and the ones in the Avrami equation. In isothermal condition, integrating equation(20) results in

$$-\ln(1 - \alpha) = [(1 - m)Kt]^{1/(1-m)} \quad (21)$$

The general form of the Avrami equation is^[15]

$$1 - \alpha = \exp[-Zt^n] \quad (22)$$

where n is referred as to the Avrami exponent and related to the type of nucleation; Z the composite crystallization rate constant; t the elapsed time. Comparing equation(21) with (22), one obtains

$$n = \frac{1}{(1 - m)} \quad (23)$$

$$Z = [(1 - m)K]^{1/(1-m)} = \left(\frac{K}{n}\right)^n \quad (24)$$

Because K varies with the linear growth rate, i. e., $K \propto dr/dt$, using K to characterize the rate of crystallization is preferred. Combining this with $Z = \ln 2/t_{1/2}^n$ the relationship between K and the known half time of crystallization $t_{1/2}$ can be derived as

$$K = n(\ln 2)^{1/n}/t_{1/2} \quad (25)$$

Then, equation(20) can also be rewritten in the following several forms

$$-\ln(1 - \alpha) = \left[(1/n) \int_0^t K(T) dt \right]^n \quad (26a)$$

$$-\ln(1 - \alpha) = \left[\int_0^t Z(T)^{1/n} dt \right]^n \quad (26b)$$

$$-\ln(1 - \alpha) = (\ln 2) \left[\int_0^t [1/t(T)_{1/2}] dt \right]^n$$

3. Ozawa form of integral equation

The form of the Ozawa equation is one of the most common ones if the parameters characterizing the kinetics of crystallization are determined by using nonisothermal differential scanning calorimetry. The Ozawa equation has proved to be applicable for poly (ethylene terephthalate)^[1,16], polypropylene^[17], and poly(p-phenylene sulfide)^[18]. The Ozawa equation can be expressed as

$$1 - \alpha = \exp[-F(T)/\beta^n] \quad (27)$$

where α is the relative crystallinity at temperature T ; β the cooling rate; n the Avrami exponent; and $F(T)$ the cooling crystallization function, which is given by

$$F(T) = g \int_{T_m}^T N_c(\theta) [R_c(T) - R_c(\theta)]^{n-2} V(\theta) d\theta \quad (28)$$

where

$$N_c(\theta) = \int_{T_m}^{\theta} U(T) dT$$

$$R_c(\theta) = \int_{T_m}^{\theta} V(T) dT$$

where $U(T)$ and $V(T)$ stand for the nucleation rate and the linear growth rate respectively; T_m is the temperature above which the crystallization can not proceed. According to equation (27), a plot of $\ln[-\ln(1-\alpha)]$ against $\ln\beta$ at a given temperature should yield a straight line with a slope of $(-n)$ and an intercept $F(T)$. But more information about crystallization can not be obtained from knowledge of the intercept because the content of $F(T)$ is very complicated. This shortcoming can be overcome in the present paper. Hereinafter, taking equation (26a) as an example, we will illustrate the use of the integration equation under the nonisothermal condition.

At the rate of constant heating or cooling, $dT/dt = \beta$, inserting it into equation (26a) yields

$$-\ln(1-\alpha) = [(1/n) \int_{T_0}^T K(T) dT / \beta]^n \quad (29)$$

For a test of the constant heating, this equation can be expressed as

$$1-\alpha = \exp[-F_h(T)/\beta^n] \quad (30)$$

$$F_h(T) = [\frac{1}{n} \int_{T_0}^T K(T) dT]^n \quad (31)$$

where T_0 is the temperature at which the crystallization begins to occur. For test of the constant cooling, equation (29) can be expressed as

$$1-\alpha = \exp[-F_c(T)/|\beta|^n] \quad (32)$$

$$F_c(T) = [-\frac{1}{n} \int_{T_0}^T K(T) dT]^n \quad (33)$$

In terms of equations (30) and (32), the kinetic parameters can be obtained from DSC curves at different rates of cooling or heating. Plotting $\ln[-\ln(1-\alpha)]$ versus $\ln|\beta|$ at a given temperature, one can obtain a straight line, the slope being $(-n)$ and the intercept $\ln F(T)$. From knowledge of $F(T)$ and n at various temperatures, the rate constant of crystallization $K(T)$ can be calculated from the following method.

A METHOD OF CALCULATION OF THE RATE CONSTANT

For the heating DSC method, equation (31) is differentiated with respect to the temperature, leading to

$$K_h(T) = \frac{d[n F_h(T)^{1/n}]}{dT} \quad (34)$$

For the cooling DSC method, equation (33) becomes

$$K_c(T) = \frac{d[-n F_c(T)^{1/n}]}{dT} \quad (35)$$

where $K_h(T)$ and $K_c(T)$ stand for the rate constant of crystallization obtained from the heating and cooling DSC curves respectively.

The previous studies have proved that the following empirical relationship between $\ln F(T)$ and the temperature holds^[6,7,12,17]

$$\ln F(T) = aT + b \quad (36)$$

$$\text{or} \quad F(T) = \exp(aT + b) \quad (37)$$

where a and b is an empirical constant. Inserting this equation into (34) and (35), we obtain

$$K_h(T) = a \exp[(aT + b)/n] \quad (38)$$

$$K_c(T) = -a \exp[(aT + b)/n] \quad (39)$$

In our previous paper, poly(ethylene terephthalate) sample was subjected to DSC test. From the several rates of constant heating experiment, the following parameters were obtained in the range of 400 to 435K, i. e., $a = 0.1839$, $b = -69.60$, and $n = 3.3$ (average value)^[6]. Inserting the values of a , b , and n into equation (38), one gets

$$K_h(T) = 0.1839 \exp(5.573 \times 10^{-2}T - 21.09) \quad (40)$$

From the several rates of constant cooling experiment, in the range of 476–490K, we obtain $a = -0.2727$, $b = 134.29$, $n = 3.1$ (average value)^[7], then equation (39) becomes

$$K_c(T) = 0.2727 \exp(-8.797 \times 10^{-2}T + 43.32) \quad (41)$$

In order to compare the nonisothermal results with the isothermal one, we treat the isothermal data with equation (19) which can be rewritten as

$$\ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{dt}\right) = \ln K + m \ln[-\ln(1-\alpha)] \quad (42)$$

According to this equation, a plot of $\ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{dt}\right)$ versus $\ln[-\ln(1-\alpha)]$ should yield a straight line with a slope of m and an intercept of $\ln K$. The isothermal crystallization plots obtained from the glassy state and from the melt are shown in Fig. 1 and Fig. 2 respectively. For the process crystallized from the glassy state, the rate constant of crystallization under nonisothermal condition was calculated from equation (40). Both isothermal and nonisothermal results were illustrated in Fig. 3. For the process crystallized from the melt, the rate constant obtained from the constant cooling method was calculated from equation (41) and was shown in Fig. 4 with the isothermal one. It can be seen that the nonisothermal results are in

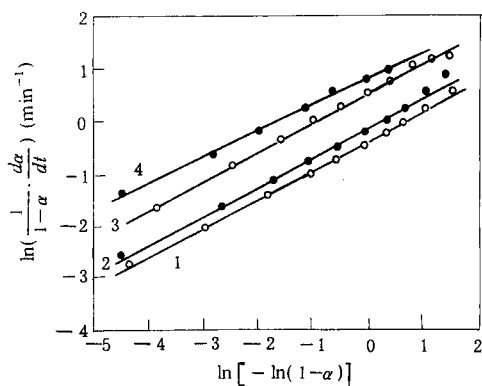


Fig. 1 The analysis of isothermal crystallization curves of PET crystallized from the glassy state
(1) 400K; (2) 405K; (3) 410K; (4) 415K

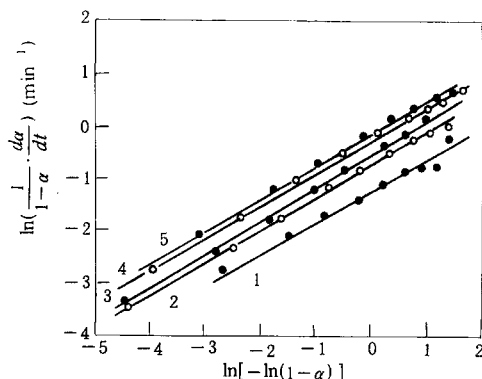


Fig. 2 The analysis of isothermal crystallization curves of PET crystallized from the melt
(1) 490K; (2) 487.5K; (3) 485K; (4) 482.5K; (5) 480K

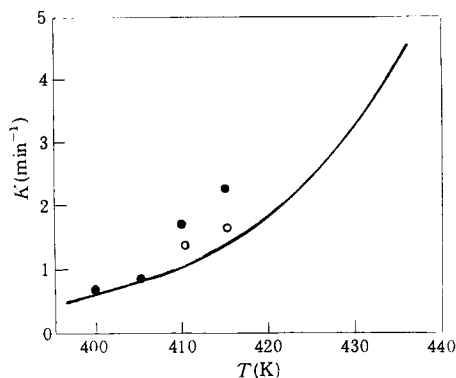


Fig. 3 The temperature dependence of the rate constant of crystallization of PET from the glassy state; (point) isothermal crystallization, (●) the t_0 was chosen as the onset point, (○) t'_0 as the onset point (see Fig. 5); (solid line) calculated in terms of eqn(39)

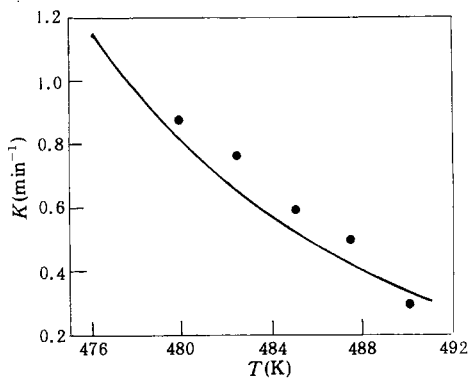


Fig. 4 The temperature dependence of the rate constant of crystallization from the melt;
(●) isothermal crystallization; (solid line) calculated in terms of eqn(40)

good accordance with the isothermal one with the exception of the two points crystallized from the glassy state in higher temperatures.

The discrepancy in the values of K for isothermal and nonisothermal crystallization from the glassy state properly stems from that the rate of

crystallization is fast in the range of higher temperature and the crystallization begins to occur before system reaches the desired temperature. As shown in Fig. 5, the solid line stands for the curve determined by DSC, t_0 is the onset point in the calculation of K , but the real onset point may be t_0' shown by dotted line. substituting for t_0' with t_0 may be the cause of the discrepancy in the values of K . So we use t_0' as the onset point of crystallization, and the calculated results are also illustrated in Fig. 3, symbolized by $\bigcirc$. It could be seen that the values of K obtained by the nonisothermal method are much closer to that calculated according to the onset point of t_0' than to t_0 .

Keywords:

Crystallization kinetics; Nonisothermal crystallization; Avrami theory; Poly(ethylene terephthalate)

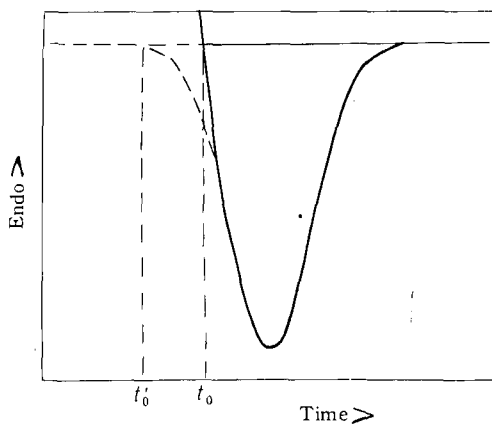


Fig. 5 Schematic representation of DSC curve of isothermal crystallization from the glassy state;
dotted line: a hypothetical curve

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