

MELTING CRYSTALLIZATION BEHAVIOR OF NYLON 66*

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Abstract Analysis of isothermal and nonisothermal crystallization kinetics of nylon 66 was carried out using differential scanning calorimetry (DSC). The commonly used Avrami equation and that modified by Jeziorny were used, respectively, to fit the primary stage of isothermal and nonisothermal crystallizations of nylon 66. In the isothermal crystallization process, mechanisms of spherulitic nucleation and growth were discussed. The lateral and folding surface free energies determined from the Lauritzen-Hoffman treatment are $\sigma = 9.77 \text{ erg/cm}^2$ and $\sigma_e = 155.48 \text{ erg/cm}^2$, respectively; and the work of chain folding is $q = 33.14 \text{ kJ/mol}$. The nonisothermal crystallization kinetics of nylon 66 was analyzed by using the Mo method combined with the Avrami and Ozawa equations. The average Avrami exponent $\bar{n}$ was determined to be 3.45. The activation energies (ΔE) were determined to be -485.45 kJ/mol and -331.27 kJ/mol , respectively, for the isothermal and nonisothermal crystallization processes by the Arrhenius and the Kissinger methods.

Keywords Nylon 66, Crystallization kinetics, Activation energy

INTRODUCTION

The crystallization process affects polymer properties through the crystal structure and morphology established during the solidification process. An important aspect of the crystallization process is its kinetics, both from the fundamental view of polymer physics and for the modeling and control of polymer processing operations. Nylon 66, one of the commercially most successful polyamides, is now widely used as an engineering plastic in many fields. The development of crystallization structure and behavior in nylons is a continuing area of technological and scientific studies because it greatly affects the materials properties. The crystallization and melting behavior of nylon 66 mixed with nylon 6 has been studied by differential scanning calorimetry (DSC)^[1]. The crystallization kinetics of nylon 66 under high pressure (200 MPa) has been investigated by using pressure-volume-temperature (PVT) measurements and the Avrami exponents were determined to be between 2 and 3^[2]. X-ray diffraction studies showed that no new crystal structures were formed during pressure crystallization for nylon 66 (up to a pressure of 200 MPa) and DSC measurements showed that the melting point of nylon 66 did not change.

In practical processing, such as extrusion molding and film forming, crystallization usually proceeds under isothermal and nonisothermal conditions. In order to obtain materials with better physical properties, it is important to study the isothermal and nonisothermal crystallization processes. In this paper, the crystallization behavior of nylon 66 was studied under isothermal and nonisothermal conditions. Several kinetic methods were applied to deal with the isothermal and nonisothermal crystallization data.

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EXPERIMENTAL

Sample Preparation

The sample of nylon 66 chosen for this study ($T_m = 253^\circ\text{C}$, $T_g = 50^\circ\text{C}$) was provided by the China Hei Long Jiang Nylon Factory with a molecular weight of 42,000 g/mol determined by viscosimetry in H_2SO_4 (96%) at 25°C . The samples were kept in a vacuum oven at 80°C for 12 h before use.

DSC

Crystallization studies were carried out by using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated with indium. All DSC experiments were performed under nitrogen atmosphere; sample weights were between 10–11 mg.

Isothermal and Nonisothermal Crystallization Processes

The samples were heated to 300°C (at 80 K/min) and kept at this temperature for 10 min in the DSC cell to destroy any nuclei that might act as seed crystals, then cooled (at -80 K/min) to the designated crystallization temperatures, T_c . 5 different temperatures ranging from $229\sim 237^\circ\text{C}$ for the isothermal crystallization process. Nonisothermal crystallization was performed by cooling the above-mentioned melt to crystallize at different cooling rates, ranging from 2.5–40 K/min. The exothermic curves of heat flow as a function of time were recorded and investigated.

RESULTS AND DISCUSSION

Isothermal Crystallization Kinetics Analysis

Analysis based on the Avrami equation

The crystallization process is usually treated as a composite of 2 stages: the primary crystallization stage and the secondary crystallization stage. The crystallization process is very marked in its temperature dependency. The Avrami equation (Eq. (1))^[3, 4] can be used to analyze the isothermal crystallization process:

$$\begin{aligned} X(t) &= 1 - \exp[-Kt^n] \\ \lg(-\ln(1-X(t))) &= n\lg t + \lg K \end{aligned} \quad (1)$$

where $X(t)$ is the weight fraction of crystallized material at time t , n is the Avrami exponent and K the crystallization rate parameter. The plots of $\lg(-\ln[1-X(t)])$ versus $\lg t$ for nylon 66 are shown in Fig. 1. Each curve shows an initial linear portion and subsequently tends to level off. These phenomena indicate the existence of a secondary crystallization stage with deviation from linearity caused by the spherulite impingement in that stage of the crystallization process^[4]. The values of n and K are determined from the initial linear portion shown in Fig. 1. The Avrami parameter n ranges from 4.9 to 3.5 depending upon the crystallization temperature (T_c). These results indicate that the spherulites nucleate and grow freely at the primary crystallization stage. The values of the crystallization rate parameter K increases with decreasing the crystallization temperature (Table 1), exhibit very different temperature dependence of nucleation-controlled and thermal-activated crystallization associated with the proximity to the melting temperature (T_m).

The crystallization half-time $t_{1/2}$ is defined as the time at which the extent of crystallization is 50% and can be determined from the measured kinetic parameters.

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

Usually, the rate of crystallization G is described as the reciprocal of $t_{1/2}$; that is to say, $G = \tau_{1/2} = t_{1/2}^{-1}$. The values of $\tau_{1/2}$ and $t_{1/2}$ are listed in Table 1. Lin^[5] used Eq. (1) to calculate the necessary time for maximum crystallization $t_{\max}$ since this time corresponds to the point where $dQ(t)/dt = 0$, $Q(t)$ is the heat-flow rate, and this is obtained as:

$$t_{\max} = \left(\frac{n-1}{nK} \right)^{1/n}$$

(3)

The results of $t_{\max}$ are listed in Table 1 and the cyclic diagram of thermal analysis for nylon 66 is shown in Fig. 2. With the increase of crystallization temperature, the crystallization exothermal peaks shift to longer times and become flat (Fig. 2) which implies that the total crystallization time is lengthened (Table 1).

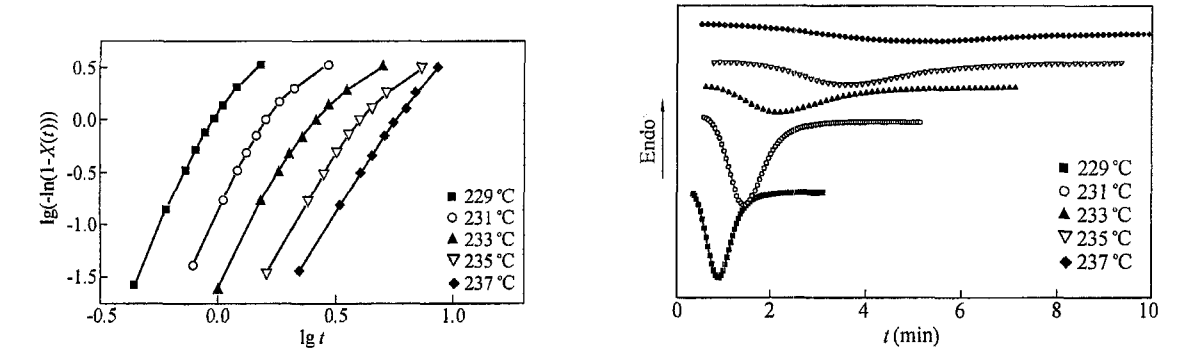


Fig. 1 Plots of $\lg(-\ln(1-X(t)))$ versus $\lg t$ for isothermal crystallization of nylon 66 at the indicated temperatures

Fig. 2 Heat flow versus time during isothermal crystallization of nylon 66 at different crystallization temperatures

Table 1. Collection of kinetic parameters for isothermal crystallization of nylon 66

T_c (°C)	229	231	233	235	237
n	4.90	4.66	4.11	3.79	3.56
K (min ⁻¹)	1.541	0.133	0.0268	5.862×10^{-3}	2.122×10^{-3}
$T_{\max}$ (min)	0.874	1.464	2.254	3.579	5.134
$t_{1/2}$ (min)	0.850	1.425	2.206	3.523	5.084
$\tau_{1/2}$ (min ⁻¹)	1.176	0.702	0.453	0.284	0.197
U^* (J/mol)	37680.85	37505.62	37333.42	37164.12	36997.63

Crystallization activation energy (ΔE)

The crystallization process for bulk nylon 66 is assumed to be thermally activated, then the crystallization rate parameter K can be approximately described by the following Arrhenius form^[6]:

$$K^{1/n} = k_0 \exp\left(-\frac{\Delta E}{RT_c}\right)$$
$$\frac{\ln K}{n} = \ln k_0 - \frac{\Delta E}{RT_c}$$

(4)

where k_0 is a temperature-independent preexponential factor, R is the gas constant, and ΔE is the crystallization activation energy. ΔE can be determined from the slope of plots of $\ln K/n$ versus $1/T_c$ (Fig. 3).

The value of the activation energy for the primary crystallization process is determined to be -485.45 kJ/mol, which is negative on the basis of the concept of heat quantity in physical chemistry, because energy has to be released while transforming the molten fluid into the crystalline state.

Spherulitic growth analysis

Lauritzen and Hoffman analyzed the spherulitic growth rate G and obtained the Lauritzen-Hoffman equation^[7]

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

(5)

where R is the gas constant, U^* is the transport activation energy, T_∞ is a hypothetical temperature below which all viscous flow ceases, K_g is a nucleation parameter, ΔT is the degree of supercooling, and f is a correction factor

to account for the variation in the bulk enthalpy of fusion per unit volume with temperature, $f = 2T_c/(T_m^0 + T_c)$. $T_\infty = T_g - 30\text{K}$ and $T_m^0 = 280^\circ\text{C}^{[8]}$ are used in the present study.

The transport term U^* in Eq. (5) may be calculated by using the WLF relation^[9, 10]:

$$U^* = \frac{C_1 T_c}{C_2 + T_c - T_g} \quad (6)$$

where C_1 and C_2 are constants (generally assumed as 17304 J/mol and 51.6 K, respectively) and T_g is the glass-transition temperature. The respective values of U^* are listed in Table 1.

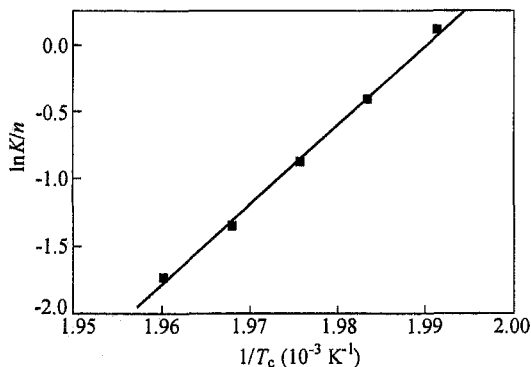


Fig. 3 $\ln K/n$ versus $1/T_c$ for Avrami parameter K deduced from isothermal crystallization

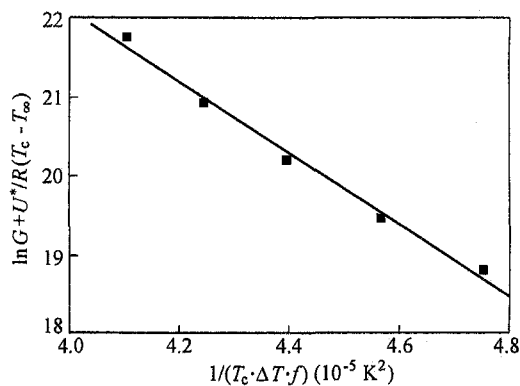


Fig. 4 Plot of $\ln G + \frac{U^*}{R(T_c - T_\infty)}$ versus $1/(T_c \cdot \Delta T \cdot f)$

It is convenient to rearrange Eq. (5) into:

$$\ln G + \frac{U^*}{R(T_c - T_\infty)} = \ln G_0 - \frac{K_g}{T_c \cdot \Delta T \cdot f} \quad (7)$$

By drawing a plot of $\ln G + U^*/R(T_c - T_\infty)$ versus $1/(T_c \cdot \Delta T \cdot f)$ (Fig. 4), K_g is determined to be $4.56 \times 10^5 \text{ K}^2$ for isothermal crystallization of nylon 66.

The value of K_g for nylon 66 allows the apparent lateral and end surface energies, σ and σ_e , to be calculated from the following formulas^[11]:

$$K_g(I) = \frac{4b_0(\sigma\sigma_e)T_m^0}{\Delta h_f^0 \cdot k} \text{ or } K_g(II) = \frac{2b_0(\sigma\sigma_e)T_m^0}{\Delta h_f^0 \cdot k} \quad (8)$$

where b_0 is the thickness of a monomolecular layer in the crystal, k is the Boltzmann constant, and Δh_f^0 is the bulk enthalpy of fusion per unit volume for a fully crystalline polymer, $\Delta h_f^0 = \Delta H_m^0 \times \rho_c = 188.1 \times 1.2376 = 232.8 \text{ J/cm}^3$ (ΔH_m^0 was given by Dole and Wunderlich^[12]). $K_g = K_g(I)$, if the formation of a surface nucleus is followed by rapid completion of the substrate (regime I kinetics), and $K_g = K_g(II)$, if the surface nuclei form in large number on the substrate and spread slowly (regime II kinetics). In order to investigate the regime in the selected temperature region (that is, from 229 to 237°C), the Z-test of Lauritzen^[11] is used. Z is defined by:

$$Z \cong 10^3 \left(\frac{L}{2a_0} \right)^2 \exp \left[-\frac{X}{T_c \cdot \Delta T} \right] \quad (9)$$

where L is the effective lamella width, and a_0 is the width of the molecular chain in the crystal. If substitution of $X = K_g$ into Z-test results in $Z \leq 0.01$, then crystallization conforms to regime I; on the other hand, if $X = 2K_g$ into Z-test yields $Z \geq 1.0$, regime II kinetics is obeyed. It is convenient, as pointed out by Lauritzen and Hoffman^[7], to

use the known value of K_g and the inequalities for Z to estimate the range of values of L in regime I or regime II and determine if these values of L are realistic in each regime. According to the lattice parameters of nylon 66^[13] its crystals are of α form with triclinic unit cells, with the lattice parameters being $a = 0.49$ nm, $b = 0.54$ nm, $c = 1.72$ nm, $\alpha = 48.5^\circ$, $\beta = 77^\circ$ and $\gamma = 63.5^\circ$. The preferred growth plane will be (100), where the thickness of a monomolecular layer, b_0 , in the (100) plane is 0.436 nm and the chain width, a_0 , is 0.404 nm. Assuming $Z \geq 1$ and $X = 2K_g$, $L \geq 10^7$ nm. This is clearly unrealistic. Assuming $Z \leq 0.01$ and substituting $X = K_g$ into Z -test, we obtain $L \leq 80$ nm. This conclusion is reasonable for nylon 66, so $Z \leq 0.01$ can be used to explain experimental results. With all the above-mentioned results, the regime of crystallization is easily determined to be regime I; that is, numerous surface nuclei are involved in the formation of the substrate; thus, $K_g(I) = \frac{4b_0(\sigma\sigma_e)T_m^0}{\Delta h_f^0 \cdot k}$.

Surface-free energy (σ , σ_e) and work of chain folding (q)

Following the procedure of Hoffman *et al.*^[11] σ and σ_e are determined from the value of $\sigma\sigma_e$, as follows:

$$\sigma = \alpha \Delta h_f^0 (a_0 b_0)^{1/2} = \alpha \Delta h_f^0 (A_0^{1/2}) \quad (10)$$

where A_0 is the cross-sectional area of a chain in the crystal, and α is an empirical constant which usually ranges between 0.1 and 0.3. In general, $\alpha = 0.1$ for hydrocarbons, e.g., polyolefins; $\alpha = 0.24$ for polyesters; and $\alpha = 0.3$ for most organics. However, it is not possible to predict the appropriate α value of nylon 66. Therefore, the task we undertook was to calculate σ , σ_e and q using these three α values, respectively, and to find out which one (if any) may produce more reasonable results. The values of q calculated with $\alpha = 0.24$ and $\alpha = 0.3$ are unrealistically small; therefore, we shall only discuss the values derived with $\alpha = 0.1$. Thus σ was estimated to be 9.77 erg/cm² and $\sigma_e = 155.48$ erg/cm².

The work of chain folding per molecular fold can be obtained by^[11]:

$$\sigma_e = \sigma_e^0 + \frac{q}{2a_0 b_0} \quad (11)$$

where σ_e^0 is the value of σ_e assumed if no work is required to form the fold, and q is the work required to bend a polymer chain back upon itself, taking into account the conformational constraints imposed on the fold by the crystal structure. As a first approximation, σ_e^0 may be taken as being roughly equal to the lateral surface energy, σ . It is expected, therefore, that σ_e^0 will be significantly less than $q/2a_0 b_0$, and, consequently, maybe set equal to zero as the second approximation. Accordingly, Eq. (11) is usually written as

$$q = 2a_0 b_0 \sigma_e \quad (12)$$

For any single polymer, σ_e is considered to be inversely proportional to the chain area ($a_0 b_0$), with the proportionality constant being $q/2$; therefore, $q = 5.477 \times 10^{-20}$ J per molecular chain fold or is 33.14 kJ/mol for nylon 66. By comparing with the data of nylon 11 ($q = 31.96$ kJ/mol) and nylon 1010 ($q = 16.63$ kJ/mol) it is concluded that the chains of nylon 66 are stiffer than those of nylon 1010, but they are nearly as stiff as those of nylon 11.

Nonisothermal Crystallization Kinetics Analysis

Analysis based on the Avrami equation modified by Jeziorny

The nonisothermal crystallization exothermic peaks of nylon 66 at various cooling rates, Φ , are shown in Fig. 5. T^* is the peak temperature where the crystallization rate was maximum, and T^* shifts to a lower temperature region with increasing the cooling rate. The values of the corresponding peak time $t_{\max}$, T^* and the crystallization enthalpies at different cooling rates are listed in Table 2. The data indicate that for the maximum crystallization temperature (or time), very different rate dependencies exist in the melt crystallization for nylon 66.

From the DSC digital information, the values of relative crystallinity $X(t)$ at different crystallization temperatures T are determined and plotted in Fig. 6(a). We obtain a series of reversed S-shaped curves. During

the nonisothermal crystallization process, a relationship between crystallization temperature T and time t is given by:

$$t = \frac{|T_0 - T|}{\Phi} \tag{13}$$

where T_0 is the initial temperature when crystallization begins ($t = 0$), Φ is the cooling rate. The values of t in Fig. 6 (a) could be transformed into crystallization time t (shown in Fig. 6b). The values of T or t at the various cooling rates could be obtained from Fig. 6(a) or (b) at a random $X(t)$. It indicates the higher the cooling rate, the shorter the time of crystallization completion.

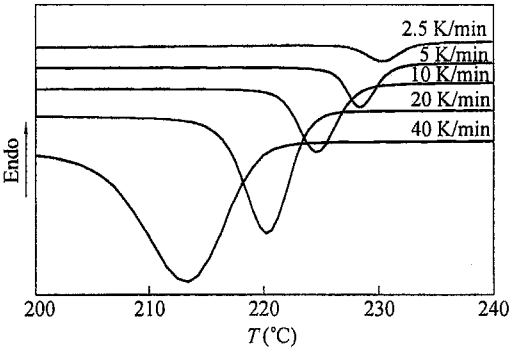


Fig. 5 Heat flow versus temperature during nonisothermal crystallization at different cooling rates by DSC

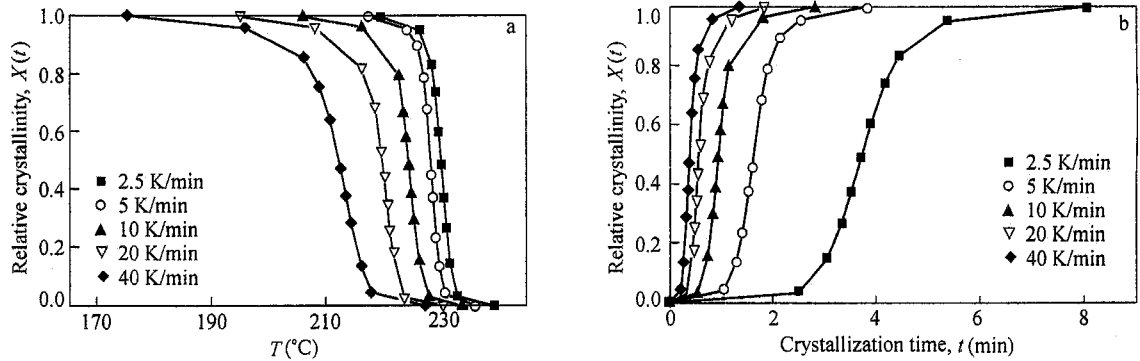


Fig. 6 Relative crystallinity $X(t)$
a) At different crystallization temperatures T
b) At different crystallization times t in the process of nonisothermal crystallization

Mandelkern^[14] considered that the primary stage of nonisothermal crystallization could be described by the Avrami equation based on the assumption that the crystallization temperature is constant and we could obtain

$$X(t) = 1 - \exp[-Z_t t^n]$$
$$\lg(-\ln(1-X(t))) = n \lg t + \lg Z_t \tag{14}$$

where Z_t is the rate constant in the nonisothermal crystallization process. Considering an influence of the cooling or heating rate $\Phi = dT/dt$, Jeziorny^[15] assumed Φ to be constant or approximately constant. The final form of the rate parameter characterizing the nonisothermal crystallization kinetics is given by:

$$\lg Z_c = \frac{\lg Z_t}{\phi} \tag{15}$$

By drawing straight lines corresponding to $\lg(-\ln[1-X(t)])$ versus $\lg t$, the values of the Avrami exponent n and the rate parameter Z_t or Z_c could be determined from the slopes and intercepts respectively (Fig. 7), and the results are shown in Table 3. Similar to the process of isothermal crystallization, all curves could be divided into two sections: the primary crystallization stage and the secondary crystallization stage. In the secondary stage, the straight lines tend to level off at 80% relative crystallinity. The results also indicate the existence of a secondary crystallization in the process of nonisothermal crystallization for nylon 66. In the primary stage, the Avrami exponent, $n_1 > 5$, which indicates the mode of nucleation and growth at primary stage of the nonisothermal crystallization for nylon 66 are complicated, and the mode of the nucleation might include the homogeneous nucleation and heterogeneous nucleation at the same time. In the secondary stage, the Avrami exponent, $n_2 < 3$ (Table 3) because of the spherulites' impingement and crowding, and the growth form of spherulites transformed into one- or two-dimensional space extension and the crystallization mode becomes simple.

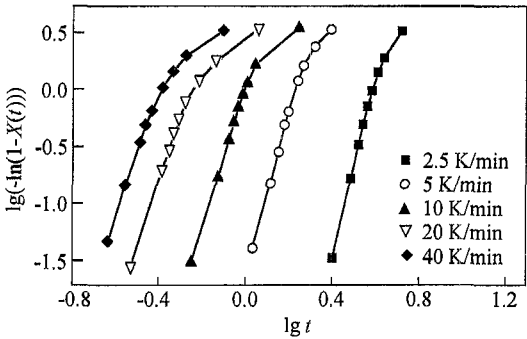


Fig. 7 Plots of $\lg(-\ln(1-X(t)))$ versus $\lg t$ for the nonisothermal crystallization process

Table 3 Values of n , Z_t and Z_c in the two stages of nonisothermal crystallization of nylon 66

Φ (K/min)	Primary Crystallization Stage			Secondary Crystallization Stage		
	n_1	Z_{t1}	Z_{c1}	n_2	Z_{t2}	Z_{c2}
2.5	7.89	2.215×10^{-5}	0.0137	2.95	0.0138	0.180
5	6.94	0.0237	0.473	2.44	0.353	0.812
10	6.10	0.999	0.999	1.62	1.334	1.029
20	5.74	48.159	1.214	1.61	2.673	1.050
40	5.37	124.902	1.128	1.47	4.550	1.039

Average Avrami parameter

A new method was reported to determine the average Avrami exponent^[16] $\bar{n}$ from experimental crystallization exotherms with peak maximum (T^*) and two inflexion points (T_1 , T_2) for different cooling rates. Firstly, in determination of $\bar{n}$ at a constant cooling rate, the following equation proposed by Ozawa^[17] is used:

$$[X_v(T)]_\phi = 1 - \exp\left(-\frac{K(T)}{\Phi^n}\right) \tag{16}$$

where $X_v(T)$ is the volume fraction of the transformed polymer at a temperature T , Φ is the cooling rate, and $K(T)$ is the so-called cooling function. Assuming linear dependence between $\ln K(T)$ versus temperature as suggested by the theory:

$$\begin{aligned} \ln K(T) &= aT + b \\ \Rightarrow K(T) &= \exp(aT + b) \end{aligned} \tag{17}$$

So, T^* , T_1 , and T_2 as a function of $\ln \Phi$ can be expressed as:

$$T^* = \frac{\bar{n}}{a} \ln \Phi - \frac{b}{a} \tag{18}$$

$$T_1 = \frac{\bar{n}}{a} \ln \Phi + \frac{\ln\left(\frac{3-\sqrt{5}}{2}\right)}{a} - \frac{b}{a} \tag{19}$$

$$T_2 = \frac{\bar{n}}{a} \ln \Phi + \frac{\ln\left(\frac{3+\sqrt{5}}{2}\right)}{a} - \frac{b}{a} \tag{20}$$

From the different crystallization peaks for cooling rates between 2.5 and 40 K/min, the values of the temperature T_1 (first inflexion point), T^* (maximum of the peak), and T_2 (second inflexion point) were determined. According to the theory, these temperatures vary linearly with the cooling rate logarithm (Fig. 8) when the latter stays low (< 10 K/min). Above this cooling rate, the values of T_1 , T^* , and T_2 decrease considerably when $\ln \Phi$ increases, because of the superposition of several crystallization regimes. It was established that under these conditions the slopes of the three straight lines are identical for the low cooling rates. Moreover, the symmetry of the crystallization exotherms implies the equal distance between the straight lines. Therefore, in a general manner, T_1 , T^* , and T_2 may be expressed as $T_i = A \ln \Phi + B_i$. So, the following simple system was resolved:

$$\begin{cases} \frac{\bar{n}}{a} = A \\ \frac{\ln\left(\frac{3-\sqrt{5}}{2}\right)}{a} - \frac{b}{a} = B_1 \\ \frac{\ln\left(\frac{3+\sqrt{5}}{2}\right)}{a} - \frac{b}{a} = B_2 \end{cases} \Rightarrow \bar{n} = A \cdot \frac{\ln\left(\frac{3-\sqrt{5}}{3+\sqrt{5}}\right)}{B_1 - B_2} \tag{21}$$

From the experimental results presented in Fig. 8, the coefficients A , B_1 , and B_2 are respectively calculated to be:

$$A = -4.12; B_1 = 233.48; B_2 = 231.18$$

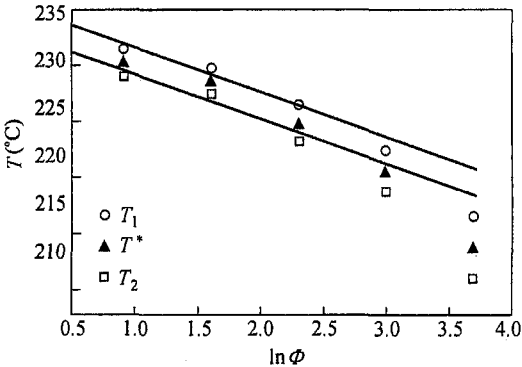


Fig. 8 The plots of evolution of T_1 , T^* and T_2 of nylon 66 as a function of $\ln \Phi$

Under these conditions, $\bar{n}$ is 3.45. Indeed, a value of about 3 is characteristic of a heterogeneous nucleation followed by three-dimensional spherulitic growth for the whole nonisothermal crystallization process.

Nonisothermal crystallization kinetics from Mo equation analysis

It is evident that the Avrami analysis and its Jeziorny modification could describe only the primary stage of nonisothermal melt crystallization of nylon 66. In order to find a method to describe exactly the nonisothermal crystallization process, we adopted a novel kinetic approach by combining the Avrami equation with the Ozawa equation^[17] and successfully dealt with the nonisothermal crystallization behavior of nylon 11^[18], PEDEKK^[19] and polyalkylthiophenes^[20]:

$$\lg Z_t + n \lg t = \lg K(T) - m \lg \Phi$$

$$\lg \Phi = \frac{1}{m} \lg \left[\frac{K(T)}{Z_t} \right] - \frac{n}{m} \lg t$$

Its final form is:

$$\lg \Phi = \lg F(T) - a \lg t \tag{22}$$

where the kinetic parameter, $F(T)=[K(T)/Z_t]^{1/m}$, refers to the value of the cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity; the Mo exponent a is the ratio of the Avrami exponent n to the Ozawa exponent, m , i.e., $a = n/m$. It could be seen that $F(T)$ had a definite physical and practical meaning. At a given degree of crystallinity, the plots of $\lg \Phi - \lg t$ are given in Fig. 9, from which the values of a and $F(T)$ could be obtained from the slopes and the intercepts of these lines, respectively (Table 4). The values of $F(T)$ systematically increase with rising relative crystallinity, indicating that at unit crystallization time, a higher cooling rate should be used in order to obtain a higher degree of crystallinity; nevertheless, the values of a are almost constant.

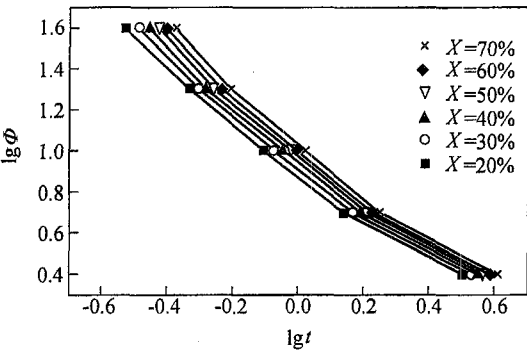


Fig. 9 The plots of $\lg \Phi$ versus $\lg t$ from the Mo equation

Table 4. Nonisothermal crystallization kinetic parameters of nylon 66 at different degrees of crystallinity

$X(t)$ (%)	20	30	40	50	60	70
a	0.845	0.836	0.830	0.818	0.816	0.810
$F(T)$	6.01	6.33	6.61	6.80	7.08	7.39

Crystallization activation energy (ΔE)

Considering the influence of cooling rate Φ on the nonisothermal crystallization process, Kissinger^[21] reported that the activation energy ΔE could be determined by:

$$\frac{d[\ln(\Phi/T^{*2})]}{d(1/T^*)} = -\frac{\Delta E}{R} \quad (23)$$

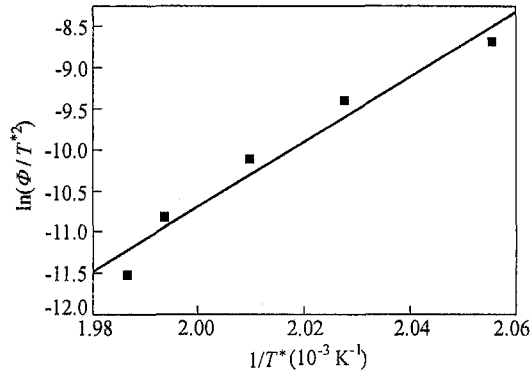


Fig. 10 The plot of $\ln(\Phi/T^{*2})$ versus $1/T^*$ from the Kissinger method

where R is the gas constant and T^* is the peak temperature. The good linear relation plots of $\ln(\Phi/T^{*2})$ versus $1/T^*$ is shown in Fig. 10. The slope $d[\ln(\Phi/T^{*2})]/d(1/T^*) = -\Delta E/R$, and ΔE was determined to be -331.27 kJ/mol for nylon 66.

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