# Isothermal and Nonisothermal Crystallization Kinetics of Nylon-11

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**ABSTRACT:** Analysis of the isothermal, and nonisothermal crystallization kinetics of Nylon-11 is carried out using differential scanning calorimetry. The Avrami equation and that modified by Jeziorny can describe the primary stage of isothermal and nonisothermal crystallization of Nylon-11. In the isothermal crystallization process, the mechanism of spherulitic nucleation and growth are discussed; the lateral and folding surface free energies determined from the Lauritzen–Hoffman equation are $\sigma = 10.68$ erg/cm$^2$ and $\sigma_e = 110.62$ erg/cm$^2$; and the work of chain folding $q = 7.61$ Kcal/mol. In the nonisothermal crystallization process, Ozawa analysis failed to describe the crystallization behavior of Nylon-11. Combining the Avrami and Ozawa equations, we obtain a new and convenient method to analyze the nonisothermal crystallization kinetics of Nylon-11; in the meantime, the activation energies are determined to be $-394.56$ and $328.37$ KJ/mol in isothermal and nonisothermal crystallization process from the Arrhonius form and the Kissinger method. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2371–2380, 1998

**Key words:** nylon-11; isothermal and nonisothermal crystallization kinetics; activation energy; differential scanning calorimetry

## INTRODUCTION

The crystal structure of Nylon-11, a high-performance semicrystalline polymer, was studied by Aelion,[1] Slichter,[2] and Little[3] and a few crystal modifications, that is, $\alpha$, $\alpha'$, $\beta$, $\gamma$, $\delta$, and $\delta'$ were found.[4,5] In room temperature, the stable $\alpha$ form has a triclinic unit cell. Unit cell dimensions are as follows[2]: $a = 0.49$ nm, $b = 0.54$ nm, $c = 1.49$ nm (fiber axis), $\alpha = 49°$, $\beta = 77°$, and $\gamma = 63°$. The glass transition temperature ($T_g$) of purified Nylon-11 is 41.96°C, and the melting temperature ($T_m$) is 184°C (heated at 10°C/min by DSC).[6–8]

In our previous work, the structure and morphology of Nylon-11 was investigated by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and density method.[9] The isothermal and nonisothermal crystallization kinetics of Nylon-11 was studied by DSC in this article.

## EXPERIMENTAL
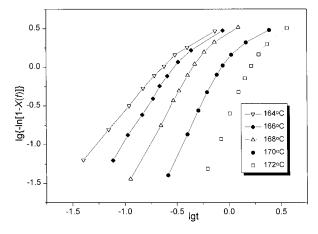
### Materials and Preparation

The samples of Nylon-11 were obtained from Aldrich Chemical Company, Inc. (USA), and have a density of 1.026 g/cm$^3$. The samples need be purified to remove addition agents. Nylon-11 was dissolved in concentrated formic acid solution at 80–100°C and filtered to remove impurities. Distilled water was put into the solution to separate

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**Figure 1** Plots of lg{−ln[1 − $X(t)$]} versus lg$t$ for isothermal crystallization at the indicated temperature.

Nylon-11. The sample was hot-filtered with filter paper and rinsed with distilled water, and then placed in a vacuum oven for 48 h.

### Differential Scanning Calorimetry

Isothermal and nonisothermal crystallization kinetics was carried out using a Perkin–Elmer DSC-7 differential scanning calorimeter calibrated the temperature with indium. All DSC were performed under a nitrogen purge; sample weights were between 8–10 mg.

### Isothermal and Nonisothermal Crystallization Process

The samples were heated quickly (at 80°C/min) to 20–30°C above the melting temperature ($T_m$), stayed there for 10 min to eliminate residual crystals, then cooled (at −80°C/min) to the designated crystallization temperatures ($T_c$), which were 5 different temperatures in the range of 164 to 172°C for the isothermal crystallization process (Fig. 2) and 5 different speed rates of cooling in 2.5, 5, 10, 20, and 40°C/min for the nonisothermal crystallization process (Fig. 6). The exothermic curves of heat flow as a function of time were recorded and investigated.

## RESULTS AND DISCUSSION

### Isothermal Crystallization Kinetic Analysis

#### *Isothermal Crystallization Kinetics from Avrami Equation*
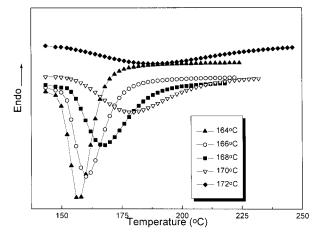
The crystallization process is usually treated as a composite of 2 stages: the primary crystallization stage and the secondary crystallization stage. The crystallization process is very marked by temperature dependence. Assuming that the relative degree of crystallinity increases with an increase in the crystallization time $t$, then the Avrami equation [eq. (1)][10,11] can be used to analyze the isothermal crystallization process of Nylon-11, as follows:

$$X(t) = 1 - \exp[-Kt^n]$$

$$\lg\{-\ln[1 - X(t)]\} = n\,\lg t + \lg K \qquad (1)$$

The double logarithmic plot of lg{−ln[1 − $X(t)$]} versus lg $t$ is shown in Figure 1. Each curve shows an initial linear portion, then subsequently tends to level off; this fact indicates the existence of a secondary crystallization of Nylon-11, with the deviation due to the secondary crystallization that is caused by the spherulite impingement in the later stage of crystallization process.[12,13] The values of $n$ and $K$ are determined from the initial linear portion in Figure 1 and Table I. The Avrami parameter $n$ is range from 1.6 to 3.2, depending upon the crystallization temperature $T_c$. The result indicates that the spherulites nucleate and grow freely at the primary crystallization stage; the crystallization mode of Nylon-11 might be the mixture with one-dimensional, needle-like and two-dimensional, circular, diffusion-controlled growth with thermal nucleation.[12] The values of the crystallization rate parameters $K$ increase with a decrease in the crystallization temperature $T_c$ (Table I), and the values of $K$



**Figure 2** Heat flow versus time during isothermal crystallization of Nylon-11 at the different crystallization temperatures by DSC.

**Table I   Avrami Parameters *n*, *K*, $t_{max}$, $t_{1/2}$, $\tau_{1/2}$, and $X(t_{max})$ from the Avrami Equation for Nylon-11**

| $T_c$ (°C) | 164 | 166 | 168 | 170 | 172 |
|---|---|---|---|---|---|
| $n$ | 1.6 | 2.1 | 2.4 | 2.7 | 3.2 |
| $K$ (min$^{-1}$) | 12.30 | 10.00 | 6.92 | 1.62 | 0.22 |
| $t_{max}$ (min) | 0.1220 | 0.2390 | 0.3588 | 0.7047 | 1.4268 |
| $t_{1/2}$ (min) | 0.173 | 0.275 | 0.385 | 0.730 | 1.430 |
| $\tau_{1/2}$ (min$^{-1}$) | 5.87 | 3.63 | 2.60 | 1.37 | 0.70 |
| $X(t_{max})$ (%) | 32.31 | 40.36 | 44.29 | 46.72 | 49.77 |

exhibit very different temperature dependency characteristic of nucleation-controlled and thermal-activated crystallization associated with the proximity of the $T_m$ and the $T_g$, respectively.

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

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

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 I. Compared with other polyamides, the crystallization rate of Nylon-11 is faster than that of Nylon-1010 ($\tau_{1/2} = 0.1 \sim 0.2$ min$^{-1}$)[13] and slower than Nylon-6 and Nylon-66 ($\tau_{1/2} = 12$ min$^{-1}$ and 144 min$^{-1}$).[14] C. C. Lin[15] 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, obtaining

$$t_{max} = \left(\frac{n-1}{nK}\right)^{1/n} \tag{3}$$

The calculated values of $t_{max}$ are listed in Table I. Data of $t_{max}$ can be obtained from the heat-flow curves in Figure 2.

The cyclic diagram of thermal analysis for Nylon-11 in Figure 2 is recorded by heating the amorphous film from room temperature to 20–30°C above the melting temperature ($T_m$) at 10°C/min, holding it there for 10 min in order to remove all residues of crystallinity, and then cooling down (at −80°C/min) to various crystallization temperatures, $T_c$. With the crystallization temperature increases, the crystallization exo-

therms shifted to higher temperatures and became flat (Fig. 2); it implies that the total crystallization time is lengthened, and the crystallization rate decreases with the increased $T_c$ (Table I).

### *Crystallization Activation Energy* (ΔE)

The crystallization process for bulk Nylon-11 is assumed to be thermally activated, then the crystallization rate parameter $K$ can be approximately described by the following Arrhenius form[16]:
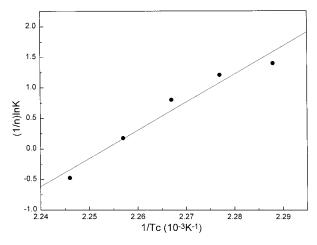
$$K^{1/n} = k_0 \exp(-\Delta E/RT_c)$$

$$\frac{1}{n}\ln K = \ln k_0 - \frac{\Delta E}{RT_c} \tag{4}$$

where $k_0$ is a temperature-independent preexponential factor, R is the gas constant, and $\Delta E$ is the crystallization activation energy. $\Delta E$ can be determined by the slope coefficient of plots of $(1/n)\ln K$ vs. $1/T_c$ (Fig. 3). The value of the activation energy for the primary crystallization process is found to be −394.56 kJ/mol. Because it has to release energy while transforming the molten fluid into the crystalline state, the value of $\Delta E$ is negative on the basis of the concept of heat quantity in physical chemistry.

From Turnbull–Fisher expression [eq. (5)],[17]

$$\ln G = \ln G_0 - \frac{\Delta E^*}{kT_c} - \frac{\Delta F^*}{kT_c} \tag{5}$$

where $G$ is the spherulitic growth rate, $G_0$ is a preexponential factor, k is the Boltzmann constant, $T_c$ is the crystallization temperature, $\Delta E^*$ is the free energy of activation for transporting a chain segment from the supercooled to the crystalline phase, and $\Delta F^*$ is the free energy of for-

**Figure 3** $(1/n)\ln K$ versus $1/T_c$ for Avrami parameter $K$ deduced from isothermal crystallization.

mation of a nucleus of critical size. At low temperature, the transportation term, $-\Delta E^*/kT_c$, decreased rapidly; when $T_c$ is approached to $T_g$, the transportation term should be dominant for the crystallization rate. At high temperature (that is, the melt crystallization $T_c$ approached $T_m$), the nucleation term, $-\Delta F^*/kT_c$, decreased rapidly, and it should be dominant for the crystallization rate in the melt crystallization process; the result can be explained as the presence of a maximum in the behavior of the growth rate.[14,18] In our experiment, the values of $T_c$ are 164–172°C, which approached $T_m = 184°C$, so $\Delta E^*/kT_c$ is negligible in the isothermal crystallization process for Nylon-11. This leads to

$$\ln G = \ln G_o - \Delta F^*/kT_c \tag{6a}$$

where the crystallization rate is controlled by a single nucleation term, and the term for $\Delta F^*/kT_c$ is adapted as derived by Hoffmann, as follows:

$$\ln G = \ln G_0 - \frac{\chi T_m^0}{T_c^2(T_m^0 - T_c)} \tag{6b}$$

where $T_m^0$ is the equilibrium melting point ($T_m^0 = 202.85°C$),[9] and $\chi$ is a parameter concerned with the heat of fusion and the interfacial free energy.

From eqs. (1), (3), and (6b), C. C. Lin obtained[15]

$$\lg t_{\max} = B - \frac{C}{2.303 \cdot T_c^2 \cdot \Delta T} \tag{7}$$

where B and C are constants, and $\Delta T$ is the degree of supercooling ($\Delta T = T_m^0 - T_c$). Equation (7) can be used to verify the possibility that Nylon-11 could be described by the Avrami equation at the primary stage of the isothermal crystallization. This means that drawing a plot of $\lg t_{\max}$ versus $1/(T_c^2 \Delta T)$, if the plot is a straight line, it is very likely that Nylon-11 can be described as undergoing primary crystallization at $t_{\max}$. The plot is shown in Figure 4, and it has a good linear relation.
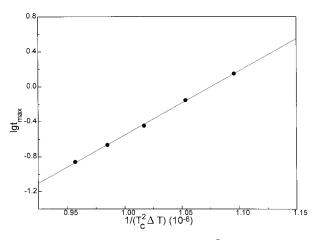
### Spherulitic Growth Analysis

To make the Turnbull–Fisher expression [eq. (5)] be suitable for the crystallization process of homopolymers in large degree of supercooling, J. I. Lauritzen and J. D. Hoffman analyzed the spherulitic growth rate $G$ and obtained the famous Lauritzen–Hoffman equation, as follows[19–22]:
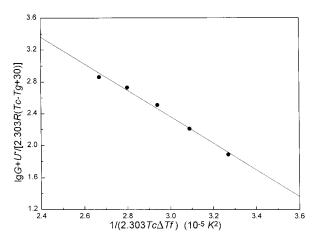
$$G = G_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right]$$

$$\times \exp\left[-\frac{K_g}{T_c \cdot \Delta T \cdot f}\right] \tag{8a}$$

where $R$ is the gas constant, $U^*$ is the transport activation energy, $T_\infty$ is a hypothetical temperature below which all viscous flow ceases, $K_g$ is a nucleation parameter, $\Delta T$ 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, $f = 2T_c/(T_m^0 + T_c)$. The universal values of $U^* = 1500$ cal/mol and $T_\infty = T_g$



**Figure 4** Plot of $\lg t_{\max}$ versus $1/(T_c^2 \Delta T)$ of Nylon-11.

**Figure 5** Plot of lg $G$ + $U*/[2.303R(T_c - T_g + 30)]$ versus $1/(2.303\,T_c\Delta T \cdot f)$ for Nylon-11.

$- 30K$ are used here in all calculations.[20] It is often most convenient to rearrange eq. (8a) as

$$\lg G + \frac{U*}{2.303R(T_c - T_\infty)}$$

$$= \lg G_0 - \frac{K_g}{2.303T_c \cdot \Delta T \cdot f} \quad (8b)$$

drawing a plot of lg $G$ + $U*/2.303R(T_c - T_\infty)$ versus $1/(2.303T_c \cdot \Delta T \cdot f)$, with the slope $= -K_g$ (Fig. 5). Hence, the values of $K_g$ are 1.66 $\times 10^5 K^2$.
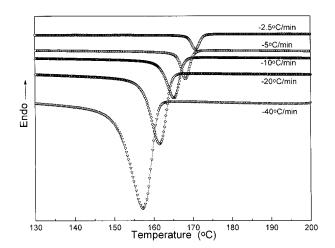
The value of $K_g$ for Nylon-11 allows the apparent lateral and end surface free energies, $\sigma$ and $\sigma_e$, to be calculated from the following formulas.[19,20]

$$K_g(I) = \frac{4b_0(\sigma\sigma_e)T_m^0}{\Delta h_f^0 \cdot k} \text{ or } K_g(II) = \frac{2b_0(\sigma\sigma_e)T_m^0}{\Delta h_f^0 \cdot k} \quad (9)$$

where $b_0$ is the thickness of a monomolecular layer in the crystal, $k$ is the Boltzmann constant, and $\Delta h_f^0$ is the bulk enthalpy of fusion per unit volume for fully crystalline polymer, $\Delta h_f^0 = \Delta H_m^o \times \rho_c = 189.05 \times 1.153 = 217.97$ J/cm$^3$, $K_g = K_g(I)$, 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 surface nuclei form in large number on the substrate and spread slowly (regime II kinetics). In order to investigate which regime the data in the selected temperature region (that is, from 164 to 172°C), the $Z$-test of Lauritzen[20,21] is used. $Z$ is defined by

$$Z \cong 10^3(L/2a_0)^2 \exp[-X/T_c(\Delta T)] \quad (10)$$

where $L$ is the effective lamellar width, and $a_0$ is the width of the molecular chain in the crystal. If substitution of $X = K_g$ into $Z$-test (10) results in $Z \leq 0.01$, then crystallization conforms to regime I; on the other hand, with $X = 2K_g$ into $Z$-test (10) yields $Z \geq 1$, regime II kinetics is obeyed. It is more convenient, as pointed out by Lauritzen and Hoffman,[21] 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. Since we do not yet know which crystallographic plane represents the preferred growth face, we have followed the standards of the Bavais–Friedel law, which states that the preferred face will be the crystal plane with the largest spacing. Therefore, according to the lattice parameters of Nylon-11 given in our previous article,[9] Nylon-11 crystals are of $\alpha$-form with triclinic unit cells, with the lattice parameters being $a = 0.49$ nm, $b = 0.54$ nm, $c = 1.49$ nm (fiber axis), $\alpha = 49°$, $\beta = 77°$, and $\gamma = 63°$. This preferred growth plane will be (100), where the thickness of a monomolecular layer, $b_0$, in the (100) plane is 0.444 nm and the chain width, $a_0$, is 0.54 nm. Assuming $Z \leq 0.01$ and substituting $X = K_g$ into $Z$-test (10), we obtain $L \leq 0.004$ nm. This conclusion does not conform experimental results, so $Z \leq 0.01$ is not correct; in the meantime, assuming $Z \geq 1$ and $X = 2K_g$, we obtain $L \geq 1.05$ nm from eq. (10), so $Z \geq 1$ can be used to explain experimental results. With all the



**Figure 6** Heat flow versus temperature during nonisothermal crystallization of Nylon-11 at different cooling rates by DSC.

above-mentioned results, the regime of crystallization is easily determined to be regime II; that is, numerous surface nuclei involved in formation of substrate; thereby, $K_g = 2b_0\sigma\sigma_e T_m^0/\Delta h_f^0 k$.

### Surface-Free Energy ($\sigma$,$\sigma_e$) and Work of Chain Folding (q)

Following the procedure of Hoffman et al.[20] $\sigma$ and $\sigma_e$ are determined from the value of $\sigma\sigma_e$, as follows:

$$\sigma = 0.1\Delta h_f^0(a_0 b_0)^{1/2}$$

$$\sigma_e = \sigma\sigma e/\sigma \tag{11}$$

In eq. (9), using $\Delta h_f^0 = 217.97$ J/cm$^3$ and $T_m^0 = 202.85°$C, the value of $\sigma\sigma_e$ is derived. From eq. (11), we obtain $\sigma = 10.68$ erg/cm$^2$ and $\sigma_e = 110.62$ erg/cm$^2$.
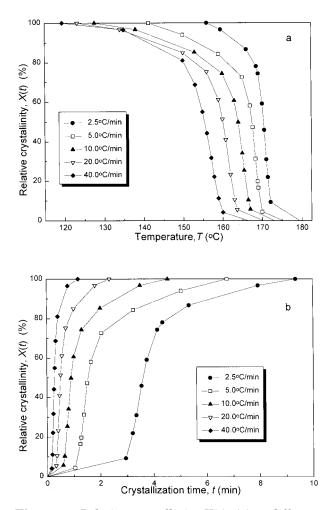
The work of chain folding per molecular fold can be obtained as[20,24]

$$\sigma_e = \sigma_e^0 + q/2a_0 b_0 \approx \sigma + q/2a_0 b_0 \tag{12a}$$

where $\sigma_e^0$ is the value that $\sigma_e$ would assume if no work were 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, $\sigma_e^0$ may be taken as being roughly equal to the lateral surface energy, $\sigma$. It is expected, therefore, that $\sigma_e^0$ will be significantly less than $q/2a_0 b_0$ and, consequently, may be set equal to zero as the second approximation. Accordingly, eq. (12a) is usually written as follows:

$$q = 2a_0 b_0 \sigma_e \tag{12b}$$

For any single polymer, $\sigma_e$ is considered to be inversely proportional relationship to the chain area ($a_0 b_0$), with the proportionality constant being $q/2$; therefore, the value of $q$ is $5.31 \times 10^{-20}$ J per molecular chain fold, that is, 7.61 kcal/mol for Nylon-11. Compared with Nylon-1010, the values of $\sigma$ and $\sigma_e$ are 10.36 and 68.0 erg/cm$^2$, and the work of chain folding $q = 3.96$ Kcal/mol; the result indicates that the chains of Nylon-11 are stiffer than those of Nylon-1010.



**Figure 7** Relative crystallinity $X(t)$: (a) at different crystallization temperatures $T$ and (b) at different crystallization times $t$ in the process of nonisothermal crystallization for Nylon-11.

### Nonisothermal Crystallization Kinetic Analysis

#### Avrami Equation by Jeziorny Modified

We have discussed isothermal crystallization kinetics for Nylon-11. Now nonisothermal crystallization kinetics will be discussed. The crystallization exothermic peaks of Nylon-11 at various cooling rates, $\Phi$, are shown in Figure 6. $T^*$ is the peak temperature where the crystallization rate is maximum, and $T^*$ is shifted to a low temperature region with the cooling rate increased (Fig. 6). The values of the corresponding peak times $t_{max}$ and $T^*$ at different cooling rates are listed in Table II; at the in the meantime, the crystallization enthalpies are also listed in Table II. The data indicate that for the maximum crystallization temperature (or time), very different rate

**Table II   The Values of $T^*$, $t_{max}$, ΔHc, and $X(t)$ in Nonisothermal Crystallization for Nylon-11**

| Φ (°C/min) | 2.5 | 5 | 10 | 20 | 40 |
|---|---|---|---|---|---|
| $T^*$ (°C) | 170.80 | 168.20 | 165.23 | 161.54 | 157.20 |
| $t_{max}$ (min) | 3.44 | 1.39 | 0.77 | 0.43 | 0.23 |
| $\Delta H_c$ (J/g) | 46.27 | 53.35 | 55.20 | 55.41 | 52.08 |
| $X(t)$ (%) | 41.51 | 34.50 | 31.39 | 29.42 | 29.40 |

dependencies existed in the melt crystallization for Nylon-11.

From the DSC digital information, we calculate the values of relative crystallinity $X(t)$ at different crystallization temperatures $T$, shown in Figure 7(a). We obtain a series of reversed $S$-shaped curves. A relationship between crystallization temperature $T$ and time $t$ is given by eq. (13) during the nonisothermal crystallization process, as follows:

$$t = \frac{|T_0 - T|}{\Phi} \qquad (13)$$

$T_0$ is the initial temperature when crystallization begins ($t = 0$). The values of $T$ of X-axis in Fig. 7(a) could be transformed into crystallization time $t$ [shown in Fig. 7(b)]. Because of the spherulite impingement in the later stage, the curves tend to flat and became $S$-shaped (or reversed $S$-shaped). We can obtain the values of $T$ or $t$ at the various cooling rate from Figure 7 at a random relative crystallinity $X(t)$. The values of $X(t)$ are shown in Table II at the peak temperature $T^*$.

Mandelkern[25] considered that the primary stage of nonisothermal crystallization can be described by the Avrami equation, based on the assumption that the crystallization temperature is constant. Mandelkern obtained the following:
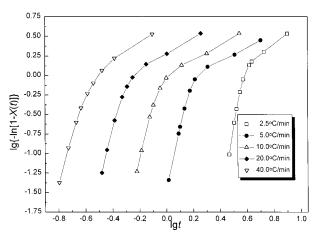
$$1 - X(t) = \exp[-Z_t t^n]$$

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

where $Z_t$ is the rate constant in the nonisothermal crystallization process. Jeziorny[26] considered the values of $Z_t$ determined by Avrami eq. (14) should be adequate. Considered to be an influence on the cooling or heating rate $\Phi = dT/dt$, Jeziorny assumed that $\Phi$ was constant or approximately constant. The final form of the rate parameter

characterizing the kinetics of nonisothermal crystallization is given as follows:

$$\lg Z_c = \frac{\lg Z_t}{\Phi} \qquad (15)$$

Drawing the straight line corresponding to $\lg[-\ln(1 - X_t)]$ versus $\lg t$ by using eq. (14), we can determine the values of Avrami exponent $n$ and the rate parameter $Z_t$ or $Z_c$ from the slope and intercept (Fig. 8). The values of $n$, $Z_t$, $Z_c$, and $t_{1/2}$ are shown in Table III. Like the process of isothermal crystallization (Fig. 1), all curves are divided into the following 2 sections: the primary crystallization stage, and the secondary crystallization stage. At the secondary stage, the straight line tends to level off at 55–60% relative crystallinity. The result also indicates the existence of a secondary crystallization in the process of nonisothermal crystallization for Nylon-11. At the primary stage, the Avrami exponent, $n_1 > 5$, indicates that the mode of the nucleation and growth at primary stage of the nonisothermal crystallization for Nylon-11 is more complicated than those of the isothermal crys-



**Figure 8**   The plot of $\lg\{-\ln[1 - X(t)]\}$ versus $\lg t$ for the nonisothermal crystallization process of Nylon-11.

**Table III   The Values of $n$, $Z_t$, $Z_c$ and $t_{1/2}$ from the Avrami Equation at the Two Stages of Nonisothermal Crystallization for Nylon-11**

| $\Phi$ (°C/min) | Primary Crystallization Stage | | | | Secondary Crystallization Stage | | | |
|---|---|---|---|---|---|---|---|---|
| | $n_1$ | $Z_{t1}$ | $Z_{c1}$ | $\tau_{1/2}$ (min$^{-1}$) | $n_2$ | $Z_{t2}$ | $Z_{c2}$ | $\tau_{1/2}$ (min$^{-1}$) |
| 2.5 | 7.71 | $3.02 \times 10^{-5}$ | 0.0156 | 0.61 | 1.34 | 0.21 | 0.540 | 0.83 |
| 5.0 | 6.54 | $4.27 \times 10^{-2}$ | 0.532 | 0.96 | 0.85 | 0.69 | 0.929 | 1.41 |
| 10.0 | 5.50 | 1.17 | 1.016 | 1.08 | 0.94 | 1.05 | 1.005 | 1.49 |
| 20.0 | 5.38 | 26.30 | 1.178 | 1.10 | 0.96 | 1.91 | 1.033 | 1.52 |
| 40.0 | 5.05 | 524.81 | 1.169 | 1.11 | 1.20 | 4.47 | 1.038 | 1.41 |

tallization process. At the secondary stage, the Avrami exponent, $n_2 \approx 1$ (Table III), because of the spherulites' impingement and crowding, and the form of spherulites' growth transform into the one-dimensional space extension, the crystallization mode becomes simpler; in the meantime, the crystallization rate $\tau_{1/2}$ increases with increased the cooling rate $\Phi$ and tends to constant.

### Ozawa Analysis in Nonisothermal Crystallization Kinetics

Considering the effect of $\Phi$, Ozawa[27] shifted the Avrami equation [eq. (14)] into all of the process of nonisothermal crystallization, as follows:

$$1 - C(T) = \exp[-K(T)/\Phi^m]$$

$$\lg\{-\ln[1 - C(T)]\} = -m \lg \Phi + \lg K(T) \quad (16)$$

where $C(T)$ is the relative crystallinity, $m$ is Ozawa exponent, and K(T) is kinetics crystallization rate constant. Drawing the plot of $\lg\{-\ln[1 - C(T)]\}$ versus $\lg\Phi$ according to eq. (16), we should obtain a series of straight lines, but we do not obtain straight lines in Figure 9. The experimental facts indicate that eq. (16) is limited to describe the kinetics in the nonisothermal crystallization process.
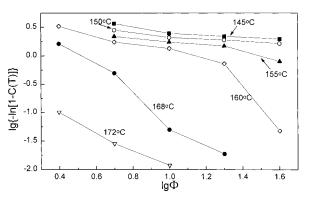
### Combined Avrami Equation and Ozawa Equation

In order to find a method to describe exactly the nonisothermal crystallization process, we obtain the following by associating eqs. (14) and (16)[28,29]:

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

$$\lg \Phi = \frac{1}{m} \lg[K(T)/Z_t] - \frac{n}{m} \lg t$$
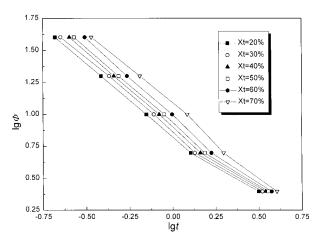
Let $F(T) = [K(T)/Z_t]^{1/m}$, and $a = n/m$; the parameter $F(T)$ is the value of cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity. $F(T)$ has a definite physical and practical meaning. By means of front assumptions, we obtain

$$\lg \Phi = \lg F(T) - a \lg t \quad (17)$$

At a certain degree of crystallinity of Nylon-11, drawing the plot of $\lg \Phi$ versus $\lg t$ according to eq. (17) is shown in Figure 10. When the cooling rate is very small ($\Phi = 2.5$°C/min), the crystallization time $t$ is extended and caused the spherulites impingement in the later stage, the lines tend to level off. Using straight line to fit these data points, one can obtain a series of lines with slope $= -a$ and intercept $= \lg F(T)$. The values of $a$ and $F(T)$ are listed in Table IV, the values of $F(T)$ increase with an increase in the cooling rate $\Phi$, and the values of $a$ are constant approximately.



**Figure 9**   The plot of $\lg\{-\ln[1 - C(T)]\}$ versus $\lg\Phi$ from the Ozawa equation for Nylon-11.

**Figure 10**   The plot of lg $\Phi$ versus lg $t$ from the combined Avrami and Ozawa equation for Nylon-11.



**Figure 11**   The plot of lg$(\Phi/T^{*2})$ versus $1/T^*$ from the Kissinger method for Nylon-11.

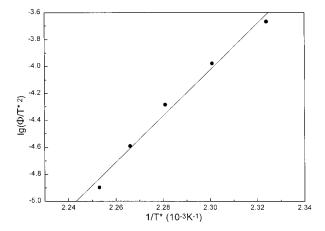### *Crystallization Activation Energy* $\Delta$E

Considering the influence of the various cooling rate $\Phi$ in the nonisothermal crystallization process, Kissinger[30] thought the activation energy $\Delta E$ could be determined as follows:

$$\frac{d[\ln(\Phi/T^{*2})]}{d(1/T^*)} = -\frac{\Delta E}{R} \tag{18}$$

where $R$ is the gas constant and $T^*$ is the peak temperature. Drawing a plot of lg $\Phi/T^*$ versus $1/T^*$, we obtain a line with good linear relation in Figure 11; the slope $= d[\text{lg}(\Phi/T^{*}2)]/d(1/T^*) = -\Delta E/2.303R$, *and* $\Delta E = -328.37$ KJ/mol for Nylon-11. Compared with $\Delta E$ in the isothermal crystallization process, the values of $\Delta E$ are equal approximately, and the experimental result indicates that the research method is correct in the isothermal and nonisothermal crystallization process for Nylon-11.

## CONCLUSIONS

The study of the isothermal and nonisothermal crystallization kinetics of Nylon-11 was carried out by DSC. The Avrami analysis indicates that the crystallization process is composed of the primary stage and the secondary stage. At the primary stage, the Avrami exponent $n = 2 \sim 3$ in the isothermal crystallization process for Nylon-11, and the process of crystal nucleation and growth is a mixture of a one-dimensional, needle-like process and a two-dimensional, circular, diffusion-controlled process. The spherulitic nucleation and growth kinetics were discussed, are the results listed in Table V. The result of $q > 7$ kcal/mol indicates that the chains of Nylon-11 is stiffer than another polyamide (that is, Nylon-1010).

At the primary stage in the nonisothermal crystallization process, the Avrami exponent, $n_1 > 5$, indicates that the mode of spherulitic nucleation and growth is more complicated than that in the isothermal crystallization process for Nylon-11. But at the lateral stage, the crystallization time is lengthened, the spherulites are impinged and crowded, the crystallization rate decreases, and the mode of spherulitic nucleation and growth becomes simple (Avrami exponent, $n_2 \approx 1$). The Ozawa equation failed to describe singly the nonisothermal crystallization process. But with a combined Avrami and Ozawa equation, we can obtain a new method to describe it.

**Table IV   The Values of $a$ and $F(T)$ at a Certain Degree of Crystallinity from Equation (17) of Nylon-11**

| $X(t)$ (%) | 20 | 30 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|---|
| $a$ | 1.039 | 1.055 | 1.078 | 1.089 | 1.129 | 1.140 |
| $F(T)$ | 7.36 | 7.95 | 8.56 | 9.09 | 10.15 | 11.88 |

**Table V   The Results of the Isothermal Crystallization Kinetics for Nylon-11**

| Quantity | Value | Remarks |
|---|---|---|
| Equilibrium melting point, $T_m^0$ | 202.85°C | Liu et al.[9] |
| Heat of fusion, $\Delta h_f^0$ | 217.97 J/cm$^3$ | $\Delta h_f^0 = \Delta H_m^0 \times \rho_c$ |
| The chain width, $a_0$ | 0.54 nm | Liu et al.[9] |
| The thickness of a monomolecular layer, $b_0$ | 0.444 nm | Liu et al.[9] |
| The lateral surface free energy, $\sigma$ | 10.68 erg/cm$^2$ | $\sigma = 0.1\Delta h_f^0 (a_0 b_0)^{1/2}$ |
| The arithmetic product, $\sigma\sigma_e$ | 1181.42 erg$^2$/cm$^4$ | $K_g = 2b_0\sigma\sigma_e T_m^0/\Delta h_f^0 k$ |
| The end surface energy, $\sigma_e$ | 110.62 erg/cm$^2$ | $\sigma_e = \sigma\sigma_e/\sigma$ |
| The work of chain folding, $q$ | 7.61 Kcal/mol | $q = 2a_0 b_0 \sigma_e$ |
| The nucleation parameter, $K_g$ | $1.66 \times 10^5$ K$^2$ | Collier and Carter[18] and Hoffman[19,20] |

The crystallization activation energy $\Delta E$ is determined by the Arrhonius form and the Kissinger method in the isothermal and nonisothermal crystallization process of Nylon-11, and the values of $\Delta E$ are approximately equal.

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