Isothermal and Nonisothermal Crystallization Kinetics of Novel Even-Odd Nylon 10 11

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ABSTRACT: Isothermal and nonisothermal crystallization kinetics of even-odd nylon 10 11 were investigated by differential scanning calorimetry (DSC). Equilibrium melting point was determined to be 195.20°C. Avarmi equation was adopted to describe isothermal and nonisothermal crystallization. A new relation suggested by Mo was used to analyze nonisothermal crystallization and gave a good result. The crystallization activation energies have been obtained to be -583.75 and -270.06 KJ/mol for isothermal and nonisothermal crystallization, respectively. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1637–1643, 2005

Key words: even-odd nylon; activation energy; crystallization; differential scanning calorimetry (DSC)

INTRODUCTION

Even-odd nylons are a kind of aliphatic polyamides with different crystal structures from even-even nylons. In the past, a few even-odd nylons were reported about their synthesis and crystal structures.[1–3] In the crystal structures of even-even nylons, all the NH and CO groups can constitute hydrogen bonds in the neighboring molecular chains with all-*trans* conformation.[4–7] However, for even-odd nylons, only a half of NH and CO groups form the hydrogen bonds in the close molecular chains on the base of extended methylene sequences.[8] Kinoshita[1] suggested a different kind of structure for even-odd nylons, in which the methylene segments are permitted to twist to build up the hydrogen bonding network between the adjacent molecular chains and to saturate the interaction between the NH and CO groups. Whichever model is right, the even-odd nylons present a different crystal structure from even-odd nylons. Many special properties are expected to be possessed by even-odd nylons. On the other hand, the preparation conditions of even-odd nylons exert a great effect on their crystal structures, morphology, and properties. The practical procession usually is under isothermal or nonisothermal crystallization conditions.[9,10] The investigation on crystallization kinetics of even-odd nylons can give us many physics parameters that are important for both fundamental study and industrial application. The study of melt behavior reflects the properties of even-odd nylons prepared under different conditions as well. Therefore, it is necessary to investigate crystallization kinetics of even-odd nylons for further application.

Recently, a series of novel even-odd polyamides have been synthesized based on undecanedioic acid.[8] Among them, nylon 10 11 was selected to conduct the study of crystallization kinetics.

EXPERIMENTAL

Materials and preparation

Even-odd nylon 10 11 was synthesized by polycondensation of diaminodecane with undecanedioic acid. The intrinsic viscosity of nylon 10 11 is 0.91 dL/g determined in dichloroacetic acid at 25°C.[8] The obtained nylon was dissolved into the formic acid and precipitated by adding alcohol to remove some impurities. The purified sample was kept in a vacuum oven for 12 h before use.

Differential scanning calorimetry

Isothermal and nonisothermal crystallization kinetics was carried out using a Perkin–Elmer Pyris-1 differential scanning calorimeter under nitrogen condition. Temperature was calibrated with indium. All DSC sample weights were in the range of 5–8 mg.

Melt, isothermal, and nonisothermal crystallization process

Isothermal crystallization process

The samples were heated to 220°C at 20°C/min and stayed for 10 min to completely melt crystals. Then they were cooled to the designated crystallizing temperatures (T_c) at the rate of −100°C/min for isothermal crystallization, which were six different temperatures in the range of 167–177°C (see Figure 3). Finally, the samples were cooled to room temperature and heated to 220°C at the rate of 10°C/min for the collection of melt endotherms (see Figure 1).

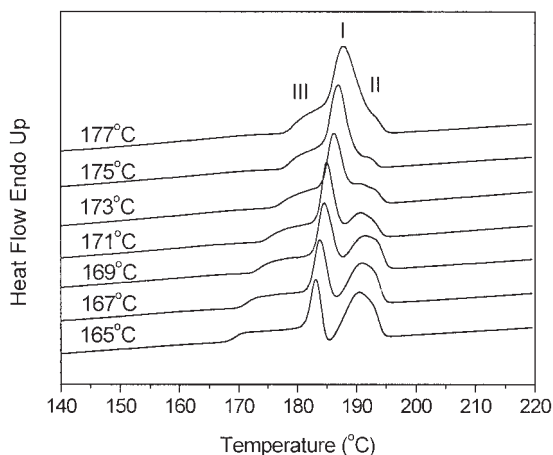Nonisothermal crystallization process

The samples were heated to 220°C at 20°C/min and stayed for 10 min for the full melt of crystals. Then they were cooled to room temperature at different cooling rates, −2.5, −5, −10, −20 and −40°C/min (see Figure 7).
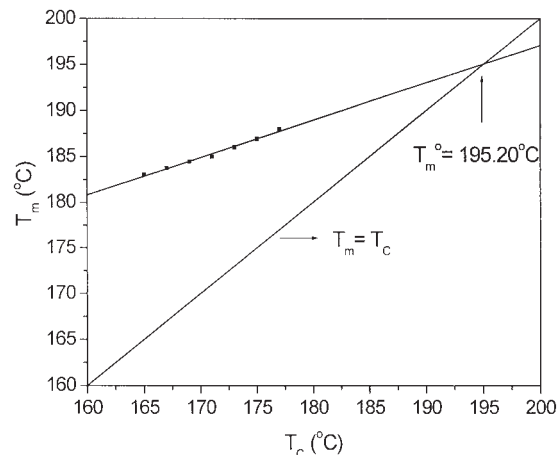
RESULTS AND DISCUSSION

Isothermal crystallization analysis

Melting behavior and equilibrium melting temperature

Figure 1 records the DSC thermograms of nylon 10 11 crystallized at different T_c (165–177°C). All the DSC curves exhibit the double melting peaks at the high temperature side, peak I and peak II. Peak I is found to increase the intensity and approaches a higher temperature as T_c increases. Meanwhile, peak II remains constant at 192°C on the temperature scale and becomes weaker and weaker. The double melting behavior of nylon 9 11 can be attributed to melt and recrys-

Figure 2 The change of the melting temperature taken as a function of the crystallizing temperature for nylon 10 11.

tallization phenomena of crystals upon heating.[11] Peak I originates from the melting of the thinner crystals, while peak II corresponds to the melt of the more perfect crystals recrystallized in the continuous heating process. As T_c increases, crystals grow thicker and more perfect. Therefore, peak I shifts to the high temperature side. Upon heating, the thin crystals melt at the supercooled state. Meanwhile, recrystallization occurs rapidly and more perfect crystals form. Finally, the recrystallized crystals melt at the same temperature despite the various T_cs. In addition, peak III exists in all the samples at 4°C above the corresponding T_c and moves more sharply to high temperature as T_c increases. Peak III is attributed to the annealing effect at T_c.[12] A small part of amorphous polymer between the bundles of lamella forms crystallite and the defective crystals aggregate in the boundary layer, which results to the weak melting endotherms at a few degrees above T_c. Therefore, peak I is associated with the melt of the crystals obtained at the different crystallizing temperatures and appropriate for the acquisition of equilibrium melting temperature (T_m^0).

T_m^0 is an important parameter that records the melting temperature of the fully perfect crystal of the flexible linear polymer and can be determined from the equation suggested by Hoffman–Weeks.[13] According to the theoretical considerations by Hoffman–Weeks, the dependence of melting temperature (T_m) and crystallizing temperature is described as the following form:

$$T_m = \frac{T_C}{2\beta} + T_m^0\left[1 - \frac{1}{2\beta}\right] \qquad (1)$$

where β is the lamella thickness factor, which indicates the ratio of the thickness of the mature crystal L_c to that of the initial crystal L_c^*. Figure 2 shows the plot of T_m versus T_c. The T_m^0 of 195.20°C is determined by

Figure 1 The DSC melting thermograms of even-odd nylon 10 11 after isothermal crystallization at the specified crystallizing temperatures.
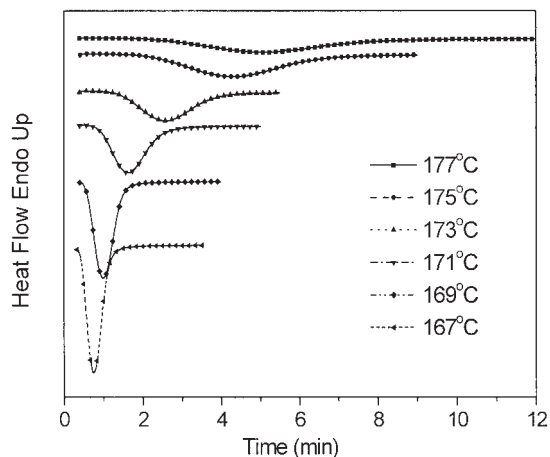
Figure 3 Heat flow versus time during the isothermal crystallization of nylon 10 11 at the specified temperatures.

Figure 4 Plots of $\lg\{-\ln[1 - X(t)]\}$ versus $\lg t$ at the indicated temperatures for the isothermal crystallization of nylon 10 11.

means of the extrapolation of the straight line, obtained by the least square fit, with the plot $T_m = T_c$.

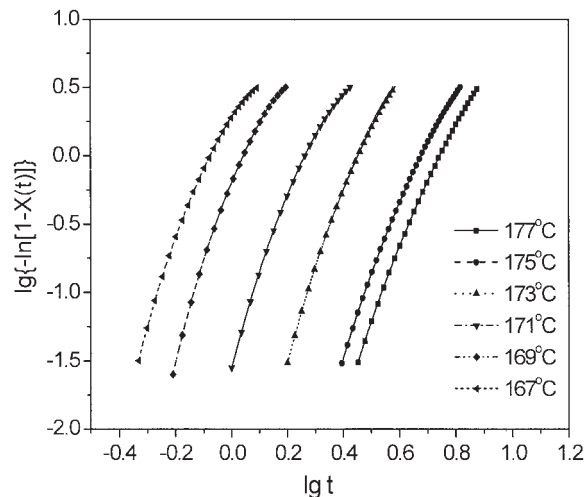### Isothermal crystallization kinetics analysis based on the Avrami equation

The DSC thermograms of the samples in isothermal crystallization process are shown in Figure 3. From the DSC exotherms recorded in Figure 3, it is found that the crystallization exotherm shifts to a higher temperature side and becomes flat as T_c increases. It indicates that as a higher T_c is adopted, longer crystallization time is needed and slower crystallization rate is presented.

The crystallization process is usually treated as a composite of two stages: the primary crystallization stage and the secondary crystallization stage. The Avrami equation [Eq. (2)] is used to describe the isothermal crystallization process:[14]

$$X(t) = 1 - \exp(-K \times t^n)$$

$$\lg\{-\ln[1 - X(t)]\} = n \times \lg t + \lg K \qquad (2)$$

where $X(t)$ is the relative degree of crystallinity at time t, n is the Avrami exponent, and K is the isothermal crystallization rate parameter. The plots of $\lg\{-\ln[1 - X(t)]\}$ versus $\lg t$ are presented in Figure 4. It is observed that each curve is composed of two linear sections, indicating the existence of the secondary crystallization. The spherulite impingement in the secondary stage of the crystallization process results in the deviation of the plots from the straight line.[15] The Avrami exponent n and the crystallization rate parameter K are extracted by performing the least square fit to the plots (Table I). The Avrami exponent n is in the range of 2.47–3.05, relying on T_c. From the results, it is indicated that the spherulite growth mode of nylon 10

11 is primarily in three-dimensional orientation with thermal nucleation. The crystallization rate parameter K decreases as T_c increases (Table I).

The crystallization half-time ($t_{1/2}$) is described as the time at which the relative degree of crystallization is equal to 50% and can be calculated from the measured kinetics parameters.

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/n} \qquad (3)$$

The rate of crystallization G is defined as the reciprocal of $t_{1/2}$, e.g., $G = \tau_{1/2} = (t_{1/2})^{-1}$. It is observed that the rate of crystallization of nylon 10 11 is slightly faster than that of nylon 10 10 ($\tau_{1/2} = 0.1 \sim 1.2$ min^{-1}).[16] However, it is much slower than nylon 6 and nylon 66 ($\tau_{1/2} = 12$ and 144 min^{-1}).[17] The isothermal crystallization parameters n, K, t_{max}, $t_{1/2}$, $\tau_{1/2}$, and $X(t)$ are listed in Table I.

Crystallization activation energy (δE) for isothermal crystallization

Assuming that the isothermal crystallization process of nylon 10 11 is thermally activated, the crystalliza-

TABLE I
The Values of the Parameters for Isothermal Crystallization of Even-Odd Nylon 10 11

T_C (°C)	n	K (min^{-1})	$t_{1/2}$ (min)	$\tau_{1/2}$ (min^{-1})	U^* (J/mol)
167	2.47	1.75	0.77	1.30	42,465.47
169	2.94	4.99×10^{-1}	1.02	0.98	42,185.76
171	2.64	4.87×10^{-2}	1.69	0.59	41,912.18
173	3.05	4.47×10^{-3}	2.62	0.38	41,644.54
175	2.65	6.46×10^{-4}	4.37	0.23	41,382.63
177	2.58	3.55×10^{-4}	5.11	0.20	41,126.28

tion rate parameter K can be described as the following Arrhenius form:[18,19]

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

$$\frac{1}{n} \times \ln K = \ln k_0 - \frac{\Delta E}{R \times T_C} \quad (4)$$
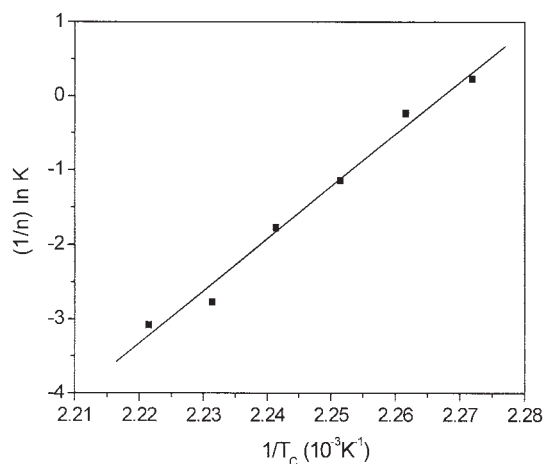
where k_0 is the temperature-independent preexponential factor, R is the gas constant, and ΔE is the crystallization activation energy. The slope of the plot of $(1/n)\ln K$ versus $1/T_c$ is used to calculate the ΔE (Figure 5). The value of the ΔE for isothermal crystallization process is –583.75 KJ/mol. The value of ΔE is negative on the basis of the concept of heat quantity in physics chemistry, indicating that the sample releases energy while it transforms from the molten state into the crystalline state.
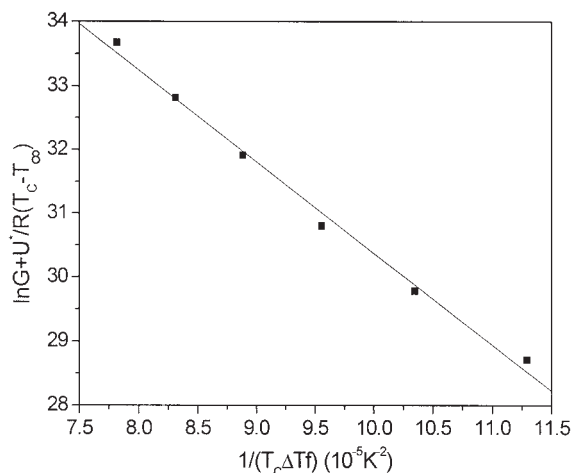
Spherulite growth analysis

The famous Lauritzen-Hoffmann equation is applied to describe the spherulite growth rate in the isothermal crystallization process of nylon 10 11 in the relatively large degree of supercooling.[20,21] That is

$$G = G_0 \times \exp\left[-\frac{U^*}{R \times (T_C - T_\infty)}\right]$$

$$\times \exp\left[-\frac{K_g}{T_C \times \Delta T \times f}\right] \quad (5)$$

where U^* is the transport activation energy, T_∞ is a hypothetical temperature below which all viscous flow ceases ($T_\infty = T_g -30$), K_g is the nucleation parameter, ΔT is the degree of supercooling, and f is the

Figure 6 $\ln G + U^*/R(T_C - T_\infty)$ versus $1/(T_C \Delta Tf)$ for even-odd nylon 10 11.

correction factor accounting for the variation of the fusion enthalpy per unit volume with temperature, $f = 2T_c/(T_m^0 + T_c)$.

The transport activation energy U^* in Eq. (5) can be calculated by using the Williams–Landel–Ferry equation:[22]

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

where C_1 and C_2 are constant, which are generally assumed to be 4,120 cal/mol and 56.1 K, respectively.[15] The calculated results are listed in Table I.

The double logarithmic relation of eq. (5) is presented:

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

The plot of $\ln G + U^*/R(T_c - T_\infty)$ versus $1/T_c \Delta Tf$ yields a good straight line in Figure 6, indicating that the Lauritzen-Hoffmann equation is appropriate for the crystallization process of nylon 10 11. The value of K_g is determined to be 1.4×10^5 K^2 for even-odd nylon 10 11.
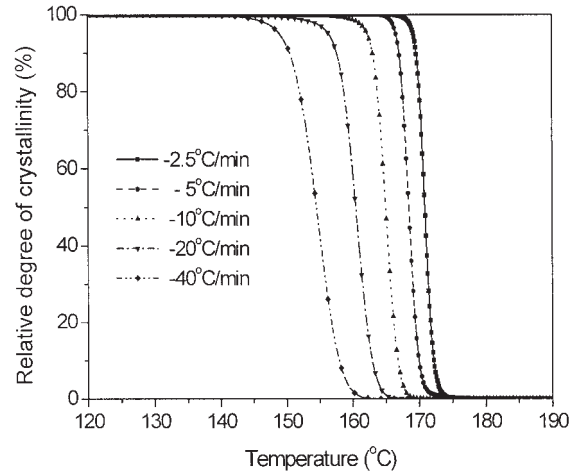
Nonisothermal crystallization analysis

Nonisothermal crystallization kinetics analysis from the Avrami equation modified by Jeziorny

The DSC crystallization exotherms of nylon 10 11 at the various cooling rates, Φ, are shown in Figure 7. The peak temperature, T^*, where the crystallizing rate is maximum, shifts to a lower temperature region as the cooling rate increases. The crystallization enthalp-

Figure 5 $(1/n)\ln K$ versus $1/T_C$ for the Avrami parameters obtained from isothermal crystallization.
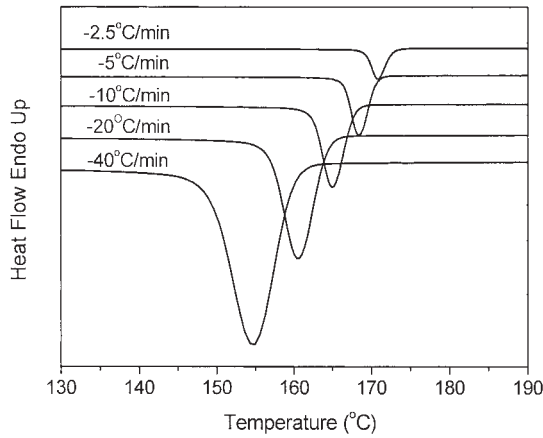
Figure 7 The DSC thermograms of nonisothermal crystallization of nylon 10 11 at the indicated cooling rates.

ies, ΔH_c, and T^* at different cooling rates are recorded in Table II.

Figure 8 presents the temperature dependence of the relative degree of crystallinity of nylon 10 11. A series of reversed S-shaped curves are found. During the nonisothermal crystallization process, the crystallizing temperature, T, has a relationship with the crystallizing time, t, as follows:[9]

$$t = \left| \frac{T_0 - T}{\Phi} \right| \qquad (8)$$

where T_0 is the initial temperature when crystallization starts ($t = 0$). According to Eq. (8), the time-dependence of the relative degree of crystallinity, $X(t)$, can be obtained in Figure 9. The relative degree of crystallinity, $X(t)$, and the corresponding time, t_{max}, at T^* are summarized in Table II.

Assuming the crystallizing temperature is constant, the Avrami relation between the relative degree of crystallinity and the crystallizing time is adopted to analyze nonisothermal crystallization by Mandelken.[23]

$$X(t) = 1 - \exp\lfloor -Z_t \times t^n \rfloor$$

TABLE II
The Values of T^*, t_{max}, ΔH_C, and $X(t_{max})$ during the Nonisothermal Crystallization Process for Even-Odd Nylon 10 11

Φ(°C/min)	T^* (°C)	t_{max} (min)	ΔH_C (J/g)	X (t) (%)
−2.5	170.67	3.38	−57.545	45.44
−5	168.26	2.18	−59.098	52.93
−10	164.82	1.30	−57.572	47.20
−20	160.50	0.72	−54.673	46.50
−40	154.64	0.36	−53.98	47.94

Figure 8 The relative degree of crystallinity of nylon 10 11 in the nonisothermal crystallization taken as a variable of the crystallizing temperatures T.

$$\lg\{-\ln[1 - X(t)]\} = n \times \lg t + Z_t \qquad (9)$$

Z_t is the rate parameter in the nonisothermal crystallization process. To remove the effect of the cooling or heating rate $\Phi = dT/dt$, the rate parameter typical of the kinetics of nonisothermal crystallization is modified by Jeziorny:[24]

$$\lg Z_c = \frac{\lg Z_t}{\Phi} \qquad (10)$$

With drawing the plot of $\lg\{-\ln[1 - X(t)]\}$ versus $\lg t$ in Figure 10, the values of n and Z_t are determined from the slopes and intercepts, respectively, (Table III). The Z_c is calculated from Eq. (10). With the similar method used as the isothermal crystallization process,
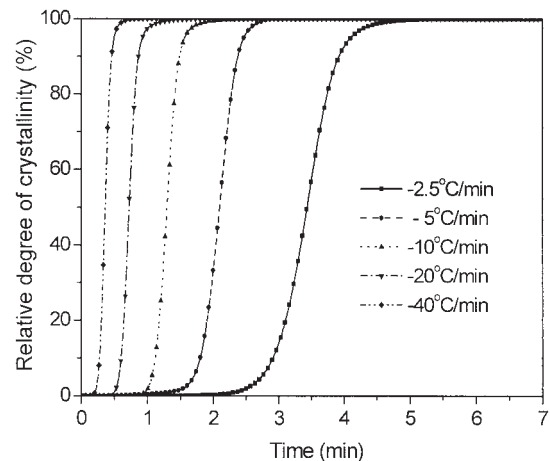
Figure 9 The time dependence of the relative degree of crystallinity of nylon 10 11 in the nonisothermal crystallization.
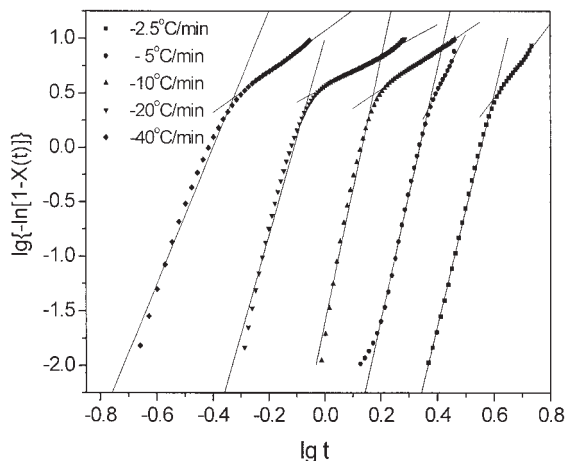
Figure 10 The plots of lg{−ln[1 − X(t)]} taken as a function of lg t in the nonisothermal crystallization process of nylon 10 11.

Figure 11 The plots of lgΦ versus lg t at the different degrees of crystallinity for the nonisothermal crystallization of nylon 10 11.
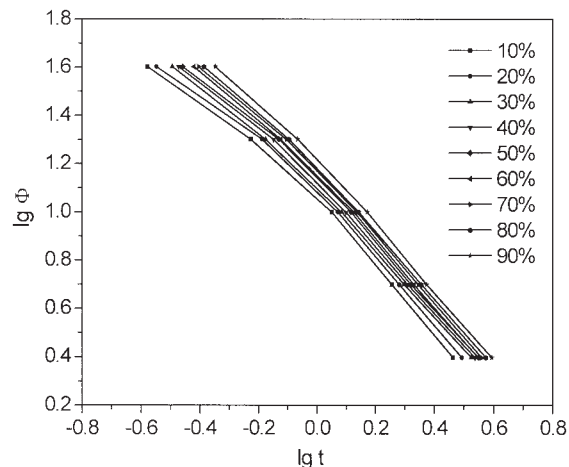
all curves can be divided into two sections: the primary crystallization process and the secondary one. At the first stage, the Avrami exponent n_1 is more than 3, implying that the mode of the nucleation and the growth of even-odd nylon 10 11 is complicated and that the nucleation mode might include the homogenous nucleation and the heterogenous nucleation at the same time. In the secondary crystallization process, the Avrami exponent n_2 is less than 3, indicating that the growth is the two-dimensional mode.

Nonisothermal crystallization kinetics analysis by a new equation

Recently, a new kinetics approach by combining the Avrami eqation with the Ozawa relation is adopted to deal with nonisothermal crystallization by Mo and coworkers[15]

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

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

Assuming $F(T) = [K(T)/Z_t]^{1/m}$, and $a = n/m$, the final form can be obtained:

$$\lg\Phi = \lg F(T) - a \times \lg t \qquad (11)$$

where $F(T)$ is the kinetics parameter referring to the value of the cooling rate chosen at unit crystallizing time when the measured system achieves a certain degree of crystallinity. The parameter a is the ratio of the Avrami exponent, n, to the Ozawa exponent, m. At the given relative degree of crystallinity of nylon 10 11, the plots of lg Φ versus lg t are presented in Figure 11. The least square fit of the data points obtains a series of lines. The parameters $F(T)$ and a in Eq. (11) are determined from the slopes and the intercepts of the obtained straight lines (Table IV). The values of $F(T)$ consecutively increase with the relative crystallinity increased and the value of a maintains approximately constant. Therefore, to achieve the high relative degree of crystallinity at the unit crystallizing time, the relative fast cooling rate should be chosen.

TABLE III
The Parameters of n, Z_t, and Z_C from the Avrami Equation at the Two Stages of Nonisothermal Crystallization of Even-Odd Polyamide 10 11

Φ (°C/min)	Primary crystallization stage			Secondary Crystallization Stage		
	n_1	Z_{t1}	Z_{c1}	n_2	Z_{t2}	Z_{c2}
2.5	4.65	1.21×10^{-6}	4.30×10^{-3}	2.44	2.45×10^{-2}	0.23
5	4.54	2.50×10^{-4}	1.90×10^{-1}	2.76	2.84×10^{-2}	0.49
10	4.86	2.41×10^{-2}	0.69	1.76	1.51	1.04
20	4.03	9.56	1.12	1.43	3.61	1.07
40	3.26	3.13×10^2	1.15	1.88	11.69	1.09

Crystallization active energy (δE) for nonisothermal crystallization

The crystallization active energy of the nonisothermal crystallization process is given by Kissinger, which takes the effect of the different cooling rate Φ in nonisothermal crystallization into account.[25]

$$\frac{d[\ln (\Phi/T^{*2})]}{d(1/T^*)} = -\frac{\Delta E}{R} \qquad (12)$$

where R is the gas constant and T^* is the peak temperature of the exotherms in Figure 7. The plot of ln (Φ/T^{*2}) versus $1/T^*$ is presented in Figure 12 and the crystallization activation energy is obtained from the slope of the least square fit line to be -270.06 KJ/mol.

CONCLUSIONS

The isothermal and nonisothermal crystallization kinetics of even-odd nylon 10 11 has been studied in this work. The equilibrium melting point of nylon 10 11 is 195.20°C measured by the Hoffmann–Weeks method. Isothermal crystallization of nylon 10 11 is described by the Avrami equation, which slightly tends to leave off from the straight line, indicating the existence of the secondary crystallization. Nonisothermal crystallization of this nylon is analyzed by the Avrami equation modified by Jeziorny and the new relation suggested by Mo. Both of them can describe isothermal crystallization and obtain the good results. In the nonisothermal crystallization process of nylon 10 11, the mode of the nucleation and the growth is complicated at the first stage while the growth at the secondary stage is mainly in two-dimensional mode. The crystallization activation energies for the isothermal crystallization and the nonisothermal crystallization are -582.75 and -274.06 KJ/mol, respectively, which are much smaller than those of even-even nylons such as nylons 66 and 1010.

TABLE IV
The Values of a and $F(T)$ from the Equation Suggested by Mo at a Certain Degree of Crystallinity for Even-Odd Nylon 10 11

$X(t)$ (%)	a	$F(T)$
10	1.16	9.82
20	1.16	10.62
30	1.19	11.40
40	1.21	12.00
50	1.21	12.47
60	1.25	13.06
70	1.26	13.61
80	1.26	14.12
90	1.29	15.41

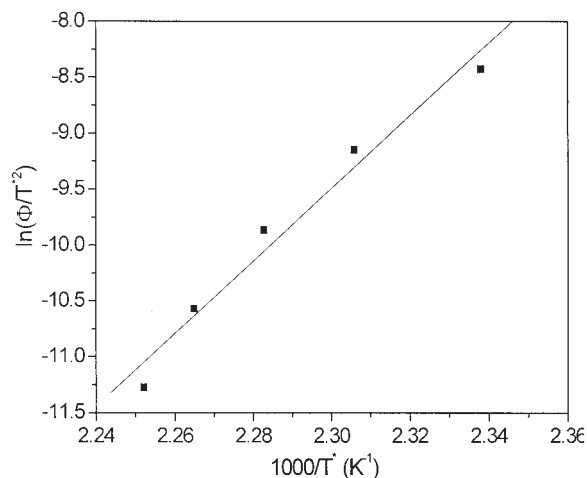**Figure 12** The variation of $\ln(\Phi/T^{*2})$ taken as a function of $1/T^*$ for nonisothermal active energy of nylon 10 11.

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