

Kinetics of Isothermal and Nonisothermal Crystallization of Nylon 1313

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ABSTRACT: The crystallization process of a new polyamide, nylon 1313, from the melt has been thoroughly investigated under isothermal and nonisothermal conditions. During isothermal crystallization, relative crystallinity develops in accordance with the Avrami equation with the exponent $n \approx 2$ based on DSC analysis. Under nonisothermal conditions, several different analysis methods were used to elucidate the crystallization process. The Avrami exponent n is greater in the isothermal crystallization process, indicating that the mode of nucleation and the growth of the nonisothermal crystallization for nylon 1313 are more complicated, and that the nucleation mode might include both homogene-

ous and heterogeneous nucleation simultaneously. The calculated activation energy is 214.25 kJ/mol for isothermal crystallization by Arrhenius form and 135.1 kJ/mol for nonisothermal crystallization by Kissinger method, respectively. In addition, the crystallization ability of nylon 1313 was assessed by using the kinetic crystallizability parameters G . Based on this parameter, the crystallizability of many different polymers was compared theoretically. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1415–1422, 2007

Key words: nylon 1313; differential scanning calorimetry; activation energy; kinetic crystallizability

INTRODUCTION

Since the invention of nylon 66 by Carothers in 1934,^{1,2} many different kinds of nylons have been developed and a number of them have been commercialized. Nylons have widely been used as fibers, engineering plastics, coatings, and so on, because of their unique physical and chemical properties.³ Almost all nylons are semicrystalline polymers and usually exhibit good toughness and strength, high modulus, excellent resistance to abrasion, and relatively high temperature resistance. Such attractive matrix of properties primarily originate from the strong hydrogen bonds of amide groups.⁴ As a result, the properties of nylons vary greatly with the concentration of amide groups in the macromolecular chains. Recently, there have been great interests in exploring new nylons, especially short- and long-alkane-segment nylons, since the chemical structure and amide content of short-alkane-segment nylons (e.g., nylon 2,4 and nylon 2,2) are close to those of silk fibroin.⁵ Although many methods have been developed for making these short-alkane-segment nylons,⁶ few practical applications have been found for them mainly

because of their high melting temperatures (T_m s). In contrast, long-alkane-segment polyamides (greater than dodecane) with a higher CH_2/amide ratios exhibit superior properties, including lower T_m s, lower densities, lower dielectric constants, and water affinity and, consequently, have widely been utilized in many areas. Furthermore, because of the unique structure, these long-alkane-segment polyamides bridge the gap between polyamides and polyethylene in terms of both structures and properties.⁷ However, despite expanding interest in the properties of this important class of polymers, its crystallization behaviors remains largely unexplored.^{8–12}

In general, 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. Investigation of the kinetics of polymer crystallization is significant from both theoretical and practical points of view. Regarding the theoretical aspect, the mechanism for the formation of polymer fine structure during crystallization is important. The practical significance arises from the effect of the degree of polymer crystallinity on the physical and chemical properties of polymers. Studies on isothermal and nonisothermal crystallization kinetics have been reported for many semicrystalline polymers in recent years.^{13–23} Of the thermal analysis techniques, differential scanning calorimetry (DSC) has frequently been exploited. It enables calorimetric measurements

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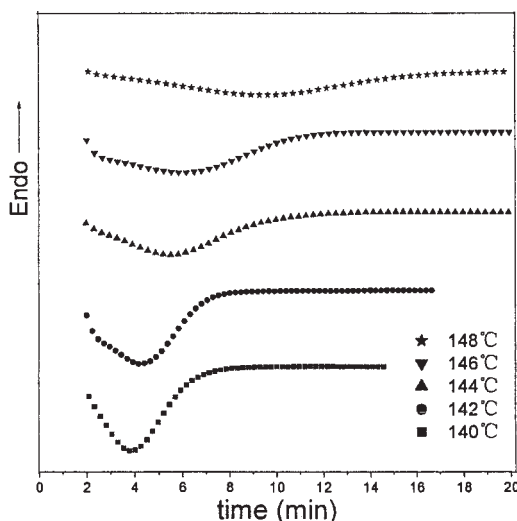


Figure 1 Heat flow versus time during the isothermal crystallization of nylon 1313 at different crystallization temperatures.

to be carried out in a relatively simple, quick, and precise manner. However, since most of the analysis with respect to crystallization is conducted under isothermal conditions instead of the actual nonisothermal conditions, the results are often not very useful. In this context, we report herein the first thorough study on the melt crystallization kinetics of nylon 1313 under both isothermal and nonisothermal conditions.

EXPERIMENTAL

Material and preparation

Nylon 1313 was prepared via a novel “petroleum ferment” technique developed in this laboratory. The nylon 1313 pellets have a relative viscosity of 1.91 as measured in 98% H_2SO_4 at 25°C (1 g/100 mL concentration). A sample film approximately of 0.2 mm thickness was obtained by hot molding of the plastic pellets under 5.0 MPa at 220°C for several minutes, then quenched to room temperature.

Differential scanning calorimetry measurement

Isothermal and nonisothermal crystallization kinetic analysis was carried out using a Perkin–Elmer DSC-7, and the temperature was calibrated using indium. All DSC measurements were performed under nitrogen; the sample weight varies between 5 and 8 mg.

Isothermal and nonisothermal crystallization processes

Isothermal crystallization from the melt was carried out by heating the sample to 220°C for 10 min to eliminate residual crystals, then cooling quickly (at $-100^\circ\text{C}/\text{min}$) to the predetermined crystallization temperature (T_c) in

the range of $140\text{--}148^\circ\text{C}$. The exothermic curves of heat flow as a function of time were recorded. All these procedures were performed on DSC. In the case of nonisothermal crystallization, DSC was used to provide a constant rate of decreasing temperature (2.5, 5, 7.5, 10, 15, and $20^\circ\text{C}/\text{min}$) from the melt to monitor the heat flow as a function of temperature.

RESULTS AND DISCUSSION

Isothermal crystallization kinetic analysis

Isothermal crystallization kinetics from Avrami equation

DSC curves for nylon 1313 in Figure 1 were recorded by heating the samples from room temperature to 30°C above its T_m at a rate of $10^\circ\text{C}/\text{min}$, then holding it at the temperature indicated for 10 min to remove all residues of crystallinity, and cooling ($100^\circ\text{C}/\text{min}$) to various crystallization temperatures (T_c). With increasing crystallization temperature, the crystallization exothermic peak shifts to a longer time and becomes flatter. This result implies that the total crystallization time is lengthened, and crystallization rate decreases with increasing T_c .

The Avrami equation^{24,25} has been widely exploited to analyze the isothermal crystallization process of semi-crystalline polymers [eq. (1)], wherein n is a constant related to the mechanism of nucleation and the form of crystal growth, K is a constant containing the nucleation and growth parameters, and X_t is relative crystallinity of polymers at different crystallization time.

$$X_t = 1 - \exp(-kt^n) \quad \text{or} \\ \log[-\ln(1 - X_t)] = n \log t + \log K \quad (1)$$

The relative amount of crystallization is plotted at different crystallization temperatures (Fig. 2). As ex-

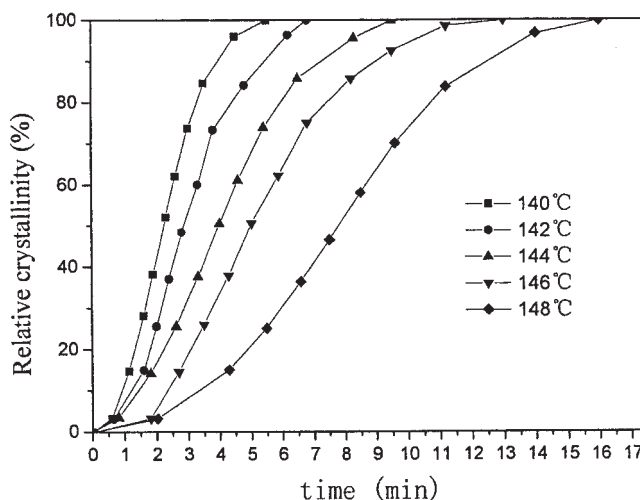


Figure 2 Relative crystallinity at different time in the process of isothermal crystallization on nylon 1313.

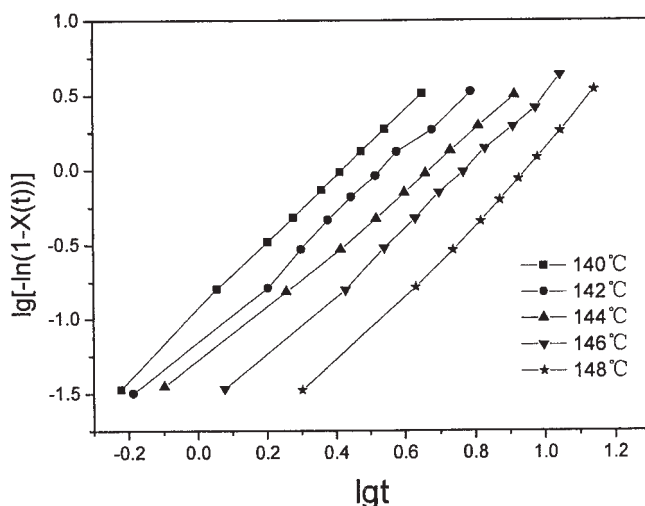


Figure 3 Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for isothermal crystallization at the indicated temperatures.

pected, plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ give a pretty good linear relation for the melt crystallization (Fig. 3). Unlike most semicrystalline polymers, no roll-off at longer times was observed, indicating the secondary crystallization of nylon 1313 does not occur under the experimental conditions. This result demonstrates that the crystallization behavior of nylon 1313 is different from that of nylon 11, which has a secondary crystallization at a longer crystallization time.¹⁸ In contrast, the crystallization process of nylon 1313 is similar to that of nylon 1010²⁰ and nylon 1012²³ with a very good linear relationship between $\log[-\ln(1 - X_t)]$ and $\log t$.

Accordingly, n and k can be obtained from the linear line of $\log[-\ln(1 - X_t)]$ versus $\log t$ (Fig. 3). As shown in Table I, the Avrami parameter n varies from 1.93 to 2.38, depending on the crystallization temperature. The result indicates that the crystallization mode of nylon 1313 under the isothermal conditions may not be three-dimensional. The narrow spread of n value centered 2.0 means that the nucleation process is simultaneous and the growth of crystals in nylon 1313 is most likely two-dimensional under the experimental conditions.

The value of the crystallization half-time, $t_{1/2}$, defined as the time at which the extent of crystallization is 50%, can be derived directly from Figure 2. It can also be determined from the kinetics parameters [eq. (2)]. Usually the rate of crystallization G is described as the reciprocal of $t_{1/2}$, i.e., $G = \tau_{1/2}$. The values of $t_{1/2}$ derived from the two methods and $\tau_{1/2}$ are listed in Table I.

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

Comparably, the crystallization rate of nylon 1313 is faster than that of nylon 1010 ($\tau_{1/2} = 0.1\text{--}0.2 \text{ min}^{-1}$)²¹

and slower than that of nylon 6 and nylon 66 ($\tau_{1/2} = 12$ and 144 min^{-1} , respectively).²² In addition, t_{\max} and t_c can also be used to describe the rate of crystallization. Crystallization continues till time t_c when no further heat flow is observed. The time t_{\max} represents the time to reach the maximum rate of heat flow, and corresponds to the change-over to a slower kinetics process.²⁶ It is very easy to find t_{\max} from Figure 1. In the meantime, since t_{\max} is the solution of $dH/dt = 0$, eq. (1) can be used to derive t_{\max} in terms of n and k [eq. (3)]. The calculated values of t_{\max} are listed in Table I. Data of t_{\max} can also be obtained from the heat-flow curves in Figure 1.

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

Crystallization activation energy

The Avrami parameter K , assuming to be thermally activated, can be used to determine the activation energy for crystallization. Thus, the crystallization rate parameter can be described in an Arrhenius form,²⁷ wherein K_0 is a temperature independent pre-exponential factor, ΔE is the crystallization activation energy, R is the gas constant, and T is the absolute temperature. The plot of $\ln k^{1/n}$ against $1/T_c$ yields a straight line, from which $\Delta E/R$ is determined (Fig. 4). The activation energy is found to be 214.25 kJ/mol from the melt, which is lower than the value of nylon 11 (394.56 kJ/mol) for isothermal crystallization from its melts.¹⁸

$$K^{1/n} = K_0 \exp(-\Delta E/RT_c) \quad \frac{\ln K}{n} = \ln K_0 - \frac{\Delta E}{RT_c} \quad (4)$$

It can be deduced from Turnbull–Fisher expression [eq. (5)],²⁸ wherein G is the spherulitic growth rate, G_0 is a preexponential factor, k is the Boltzmann constant, T_c is the crystallization temperature, ΔE^* is the free energy of activation for transporting a chain segment from the supercooled to the crystalline phase, and ΔF^* is the free energy of formation of a nucleus of critical size, the transportation term, $-\Delta E^*/kT_c$, decreased rapidly at low temperature and becomes dominant

TABLE I
Collection of Kinetic Parameters for the Isothermal Crystallization of Nylon 1313

	T_c (°C)				
	140	142	144	146	148
n	2.25	2.10	1.93	2.17	2.38
t_{\max} (min)	2.20	3.45	5.01	11.94	44.43
$\tau_{1/2}$ (min ⁻¹)	0.37	0.22	0.14	0.065	0.019
K (min ⁻¹)	0.11	0.072	0.050	0.021	0.0055
$t_{1/2}$ (min)	2.74	4.56	7.19	15.36	53.05

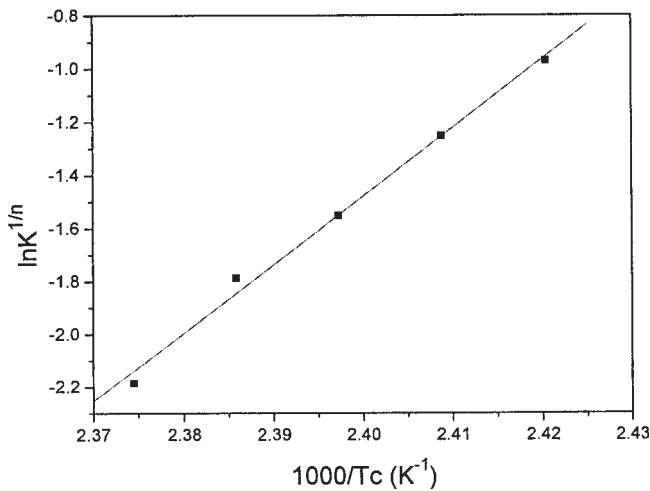


Figure 4 Plot of $\ln k^{1/n}$ versus $1/T_c$ for the Avrami parameter K deduced from isothermal crystallization.

for the crystallization rate when T_c approached to T_g . On the other hand, the nucleation term, $-\Delta F^*/kT_c$, decreased rapidly at high temperature (i.e., the melt crystallization T_c approaches T_m), and becomes 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.^{22,29}

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

In the current experiment, the value of T_c is in the range of 140–148°C, which approached $T_m = 174^\circ\text{C}$ (measured by DSC at a heating rate of 10 K/min), so $-\Delta E^*/kT_c$ is negligible in the isothermal crystallization process for nylon 1313. This leads to eq. (6), wherein the crystallization rate is controlled by a single nucleation term. The term for $-\Delta F^*/kT_c$ is de-

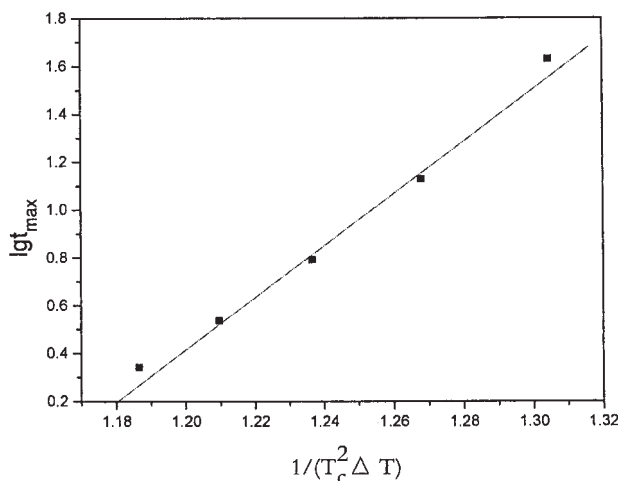


Figure 5 Plot of $\log t_{\max}$ versus $1/(T_c^2 \Delta T)$ of nylon 1313.

scribed as in eq. (6b) (derived by Hoffmann), wherein T_m^0 is the equilibrium melting point ($T_m^0 = 183^\circ\text{C}$),¹⁰ and χ is a parameter concerned with the heat of fusion and the interfacial free energy.

$$\ln G = \ln G_0 - \frac{\Delta F^*}{kT_c} \quad (6a)$$

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

From eqs. (1), (3), and (6b), Lin obtained eq. (7),³⁰ wherein B and C are constants, and ΔT is the degree of supercooling ($\Delta T = T_m^0 - T_c$). Equation (7) can be used to verify the possibility if nylon 1313 could be described by the Avrami equation during the isothermal crystallization. This means if the plot of $\log t_{\max}$ versus $1/(T_c^2 \Delta T)$ gives a linear line, it is very likely that nylon 1313 can be described as undergoing primary crystallization at t_{\max} . Indeed, a good linear relationship is observed (Fig. 5).

$$\log t_{\max} = B - \frac{C}{2.303 T_c^2 \Delta T} \quad (7)$$

Nonisothermal crystallization kinetic analysis

Nonisothermal crystallization kinetics from the Avrami equation modified by Jeziorny

The nonisothermal crystallization of nylon 1313 was studied under different cooling rates. The results are shown in Figure 6. The exothermic peak shifts to a lower temperature and becomes broader as the cooling rate increases. At a cooling rate of 2.5°C/min, the peak temperature is about 135°C, which decreases to

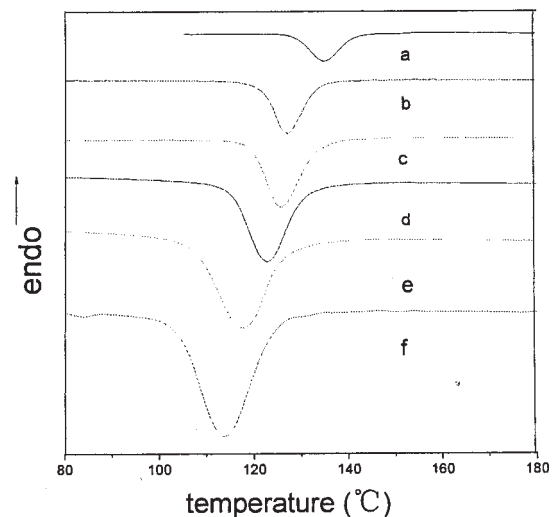


Figure 6 Heat flow versus temperature during nonisothermal crystallization of nylon 1313 at different cooling rates: (a) 2.5°C/min; (b) 5°C/min; (c) 7.5°C/min; (d) 10°C/min; (e) 15°C/min; (f) 20°C/min.

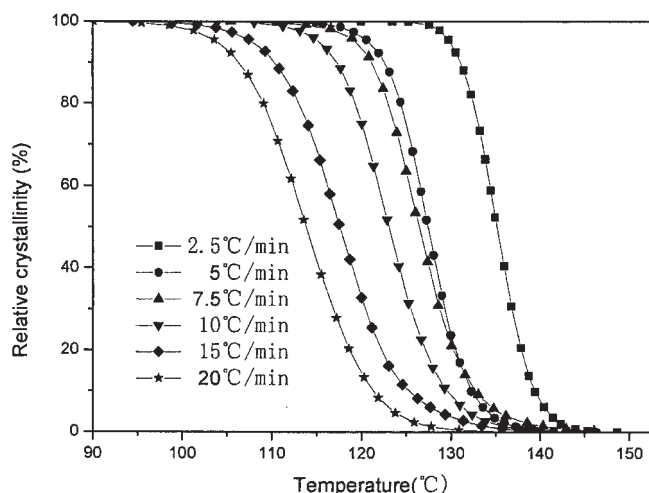


Figure 7 Relative crystallinity (X_t) at different crystallization temperatures in the process of nonisothermal crystallization for nylon 1313.

113°C at a cooling rate of 20°C/min. Integration of the exothermic peak during the nonisothermal scan gives the relative degree of crystallization as a function of temperature (shown in Fig. 7).

It is worth noting that the abscissa for curves in Figure 7 is temperature instead of time as in the isothermal crystallization (Fig. 2). The curves in Figure 7 horizontally shift to a higher temperature because of the rate-dependent induction time preceding the initiation of crystallization. The value of T_p , and the corresponding peak times t_{max} , the relative degree of crystallinity at T_p , and the crystallization enthalpies ΔH_c are listed in Table II. The crystallization enthalpy varied slightly with increasing cooling rate, which may be due to the differences in nucleation densities when using different cooling rates.³¹

A relationship between crystallization temperature (T_c) and time (t) during the nonisothermal crystallization process can be described by eq. (8), wherein T_0 is the initial temperature when crystallization begins ($t = 0$). The value of T of X-axis in Figure 7 could be transformed into crystallization time t (shown in Fig. 8).

The curves tend to S-shaped (or reversed S-shaped) because of the spherulite impingement at the later stage. The higher the cooling rate is, the shorter the time is of crystallization completion.

TABLE II
Values of T_p , t_{max} , ΔH_c and $X(t)$ during the Nonisothermal Crystallization of Nylon 1313

π (°C/min)	2.5	5	7.5	10	15	20
T_p (°C)	135.1	127.3	126.1	122.8	117.5	113.6
t_{max} (min)	5.44	3.82	2.67	2.12	1.77	1.31
ΔH_c (J/g)	40.52	39.71	40.87	40.1	38.84	39.11
$X(t)$ (%)	47.69	48.33	46.57	48.21	49.31	48.26

$$t = \frac{T_0 - T}{\Phi} \quad (8)$$

There are several methods that can be used to describe the nonisothermal crystallization kinetics. As for the isothermal analysis, the nonisothermal crystallization can be also analyzed by Avrami equation, wherein Z_t is the rate constant in the nonisothermal crystallization process.

$$X_t = 1 - \exp(-Z_t t^n) \\ \log[-\ln(1 - X_t)] = n \log t + \log Z_t \quad (9)$$

Considering an influence on the cooling or heating rate ($\Phi = dT/dt$), Φ can be assumed to be constant or approximately constant.³² The final form of the rate parameter (Z_c) characterizing the nonisothermal crystallization kinetics is given as follows [eq. (10)]. The plot of $\log[-\ln(1 - X_t)]$ versus $\log t$ at each cooling rate results a straight line, from which values of n and Z_t or Z_c could be determined from the slopes and intercepts, respectively (as shown in Fig. 9 and Table III). It must be taken into account that in nonisothermal crystallization, the values of Z_t and n do not have the same respective physical meaning as in the isothermal crystallization, because under nonisothermal conditions, the temperature changes constantly, but the Z_t and n still provide a good measure to get insight into the kinetics of nonisothermal crystallization for the nonisothermal data of nylon 1313, because there is a good linearity by plotting $\log[-\ln(1 - X_t)]$ versus $\log t$ during the defined range of nonisothermal crystallization process.

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

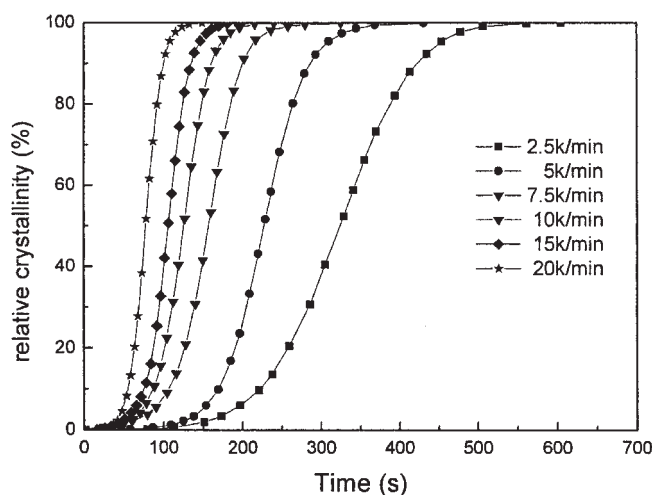


Figure 8 Relative crystallinity (X_t) at different crystallization times in the process of nonisothermal crystallization for nylon 1313.

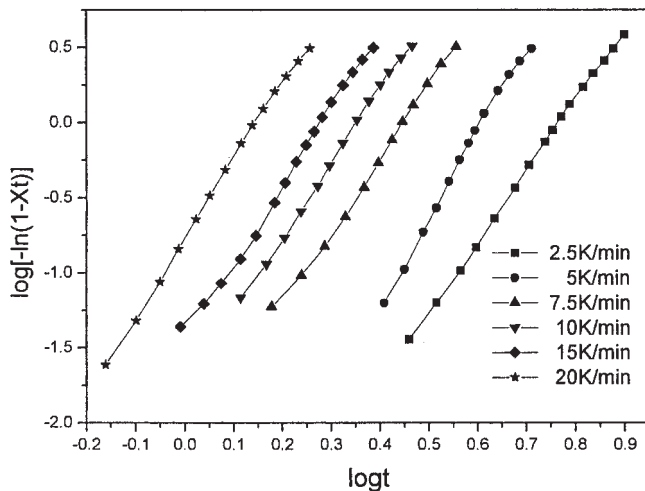


Figure 9 Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for the nonisothermal crystallization process of nylon 1313.

From the slopes and the intercepts of the lines in Figure 9, the Avrami exponent n and rate constant Z_t can be determined. Meanwhile, the half-time $t_{1/2}$ for the crystallization can also be obtained from eq. (2). The data are presented in Table III. Results in Table III show that in the case of the Avrami exponent n is greater than that in the isothermal crystallization process (Table I), which indicates that the mode of nucleation and the growth of the nonisothermal crystallization for nylon 1313 are complicated and that the nucleation mode might include homogeneous and heterogeneous nucleation at the same time. The more rapid the cooling, the larger the value of n is. It seems that this dependence is directly related to the increasing effect of the athermal nucleation process, which is connected with the increase in the cooling rate. Thus the morphology of crystallization, i.e., the amounts of the individual forms, is dependent on the processing conditions. The decisive factor is the cooling rate, the polymer morphology can be determined in a specific manner.

Combined Avrami equation and Ozawa equation

Considering the effect of Φ , Ozawa³³ shifted the Avrami equation into all of the process of nonisothermal crystallization, as described in eq. (11), wherein

TABLE III
Values of n , $\log Z_t$, $\log Z_c$ and $t_{1/2}$ Determined by Avrami Equation During the Nonisothermal Crystallization of Nylon 1313

Φ ($^{\circ}\text{C}/\text{min}$)	2.5	5	7.5	10	15	20
n	4.70	5.78	4.78	4.93	5.02	5.20
$\log Z_t$	-3.62	-3.54	-2.15	-1.75	-1.41	-0.77
$\log Z_c$	-1.45	-0.71	-0.29	-0.18	-0.094	-0.039
$t_{1/2}$	5.44	3.84	2.61	2.10	1.78	1.31

$C(T)$ is the relative crystallinity, m is Ozawa exponent, and $K(T)$ is kinetics crystallization rate constant.

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

$$\log\{-\ln[1 - C(T)]\} = -m \log \Phi + \lg K(T) \quad (11)$$

To describe the nonisothermal crystallization process exactly, a new technique³⁴ by associating the Avrami equation and Ozawa equation was used here.

$$\log Z_t + n \log t = \lg K(T) - m \log \Phi \quad (12)$$

$$\log \Phi = \frac{1}{m} \log[K(T)/Z_t] - \frac{n}{m} \log t \quad (13)$$

Let $F(T) = [K(T)/Z_t]^{1/m}$, and $a = n/m$, the parameter $F(T)$ then becomes the value of cooling rate, which has to be chosen at unit crystallization time when the measured system reaches a certain degree of crystallinity. By means of front assumptions, we obtain the final form [eq. (14)].

$$\log \Phi = \log F(T) - a \log t \quad (14)$$

At a given degree of crystallinity, the plots of $\log \Phi$ versus $\log t$ according to eq. (10) were given in Figure 10, from which the values of a and $F(T)$ were obtained, respectively (see Table IV). The values of $F(T)$ systematically increase with raising relative crystallization time. A higher cooling rate is required for obtaining a higher degree of crystallinity. Meanwhile, the value of a remains constant approximately throughout the crystallization process.

Kinetic crystallizability

The kinetics of nonisothermal crystallization was first investigated in 1967 by Ziabiki.^{22,35} A theory was

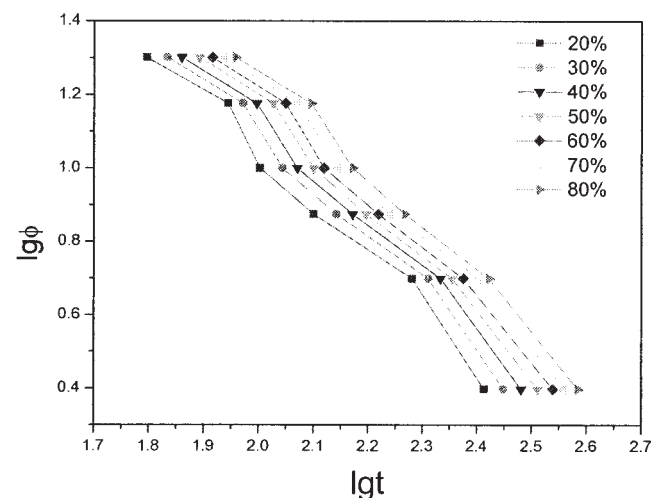


Figure 10 The plot of $\lg \phi$ versus $\lg t$ from the combined Avrami and Ozawa equation.

TABLE IV
Nonisothermal Crystallization Kinetics Parameters of Nylon 1313 at Different Degree of Crystallinity

X_t (%)	20	30	40	50	60	70	80
a	1.43	1.44	1.44	1.45	1.44	1.44	1.44
$F(T)$	3.91	3.97	4.00	4.07	4.09	4.11	4.15

developed based on the assumption that crystallization can be presented by means of the equation for first order kinetics [eq. (15)], where the rate constant $K(T)$ is only temperature-dependent.

$$dX/dt = [1 - X]K(T) \quad (15)$$

The change of rate constant as a function of temperature is illustrated by a curve resembling a Gaussian. The curve is described by eq. (16), where K_{\max} is the maximum value of the rate constant corresponding to the temperature T_{\max} ; D is the half-width of the crystallization curve; and T_m is the melting temperature of the polymer. The kinetic crystallizability (G) [eq. (17)] can be obtained from eq. (13), where T_g is the glass transition temperature of the polymer.

$$K(T) \approx K_{\max} \exp[-4 \ln 2(T - T_m)^2/D^2] \quad (16)$$

$$G = \int_{T_g}^{T_m} K(T)dT = (\pi/\ln 2)^{1/2} K_{\max} D/2 \quad (17)$$

The kinetic crystallizability (G) characterizes the degree of transformation obtained over the entire crystallization range ($T_g - T_m$) with unit cooling rate. Considering the influence of cooling rate during nonisothermal crystallization, the final corrected form of this parameter will thus be described as follows:

$$G_c = \frac{G}{dT/dt} \quad (18)$$

Calculation of G_c parameter was made possible by knowing the values of K_{\max} and D appearing in eq. (14). The half-width D can be easily determined from the crystallization thermogram. The K_{\max} value, corresponding to temperature T_{\max} , at which the crystallization rate is maximum, can be calculated. It

TABLE V
Parameters Characterizing the Kinetic Crystallizability of Nonisothermal Crystallization of Nylon 1313

Φ ($^{\circ}\text{C}/\text{min}$)	2.5	5	7.5	10	15	20
D (K)	6.5	6.7	7.7	9.1	11.7	11.8
K_{\max}	0.21	0.23	0.50	0.54	0.55	0.88
G	1.44	1.62	4.13	5.20	6.89	11.04
G_c	0.58	0.32	0.55	0.52	0.46	0.55

can be shown, using eq. (12) as a starting point, that the formula required is as follows:

$$K_{\max} = C_k(t_{\max})^{-1} \quad (19)$$

wherein

$$C_k = \frac{\int_{t_0}^{t_{\max}} v_c(t)dt}{\int_{t_{\max}}^{t_E} v_c(t)dt} \quad (20)$$

wherein t_0 and t_E are the initial and final time, respectively. t_{\max} is the time taken from the start of crystallization until reaching the maximum rate of reaction.

The parameters characterizing the nonisothermal kinetic crystallizability of nylon 1313 examined are listed in Table V. The results show that G_c can be successfully used for characterizing the kinetics of nonisothermal crystallization. This arises from the fact that the value of G_c is not dependent on the conditions of the crystallization process, and particularly on the cooling rate of the polymer.

Crystallization activation energy (ΔE)

Considering the influence of the various cooling rate Φ on the nonisothermal crystallization process, the activation energy can be determined by eq. (18) as proposed by Kissinger,³⁶ wherein R is the gas constant and T_p is the peak temperature. The plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$ are shown in Figure 11, from which $\Delta E/R$ can be derived. The activation energy was found to be 135.1 kJ/mol. The n and k obtained from the nonisothermal Avrami equation at low crystallinity can be used to calculate the activation energy of crystallization under nonisothermal conditions.²⁷ For nonisothermal crystallization of nylon 1313, the activation

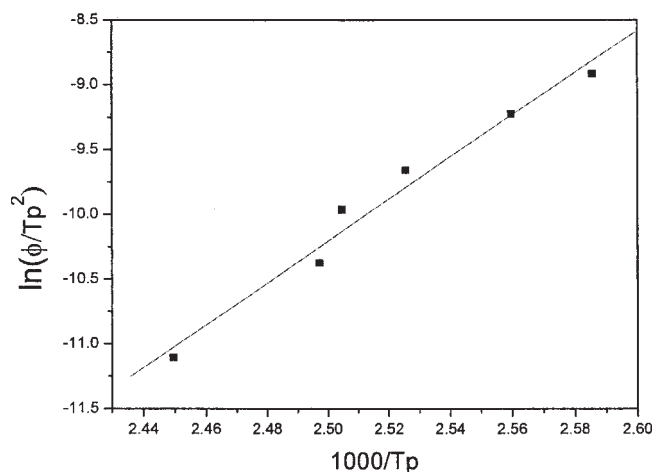


Figure 11 Plot of $\ln(\Phi/T_p^2)$ versus $1/T_p$ from the Kissinger method.

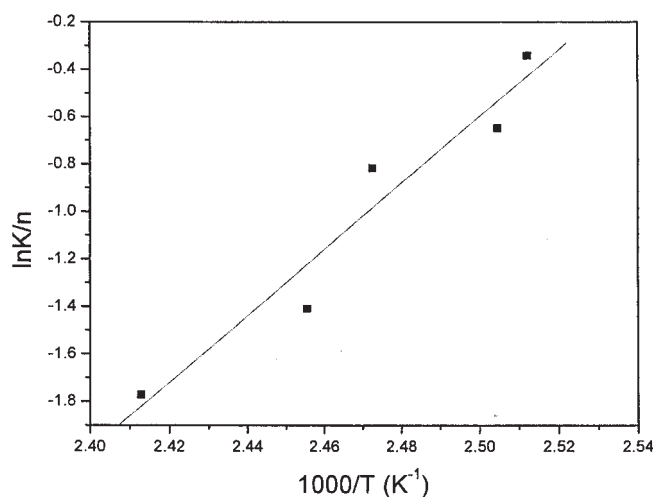


Figure 12 Arrhenius plots for evaluating nonisothermal crystallization activation energy of nylon 1313.

energy can also be determined by the Avrami equation [eq. (4)], where T is the onset temperature of crystallization. From the slope of Figure 12, $\Delta E/R$ can be obtained. Consequently, the crystallization energy was determined to be 116.5 kJ/mol.

$$\frac{d[\ln(\Phi/T_p^2)]}{d(1/T_p)} = \frac{-\Delta E}{R} \quad (21)$$

CONCLUSIONS

A systematic study of the isothermal and nonisothermal melt crystallization kinetics of nylon 1313 was carried out with DSC. The results indicate that the Avrami equation can be successfully used to describe the kinetics of isothermal crystallization processes. The Avrami exponent was found to be around 2.0 for nylon 1313 under isothermal conditions, indicating that the crystallization of nylon 1313 during isothermal conditions is of two-dimensional growth. The nonisothermal crystallization process of nylon 1313 was analyzed by a modified Avrami equation and a novel equation combining the Avrami and Ozawa equation. The calculated activation energy is 214.25 kJ/mol for isothermal crystallization by Arrhenius form, and 135.1 kJ/mol for nonisothermal crystallization by Kissinger method, respectively. The activation energy determined by Arrhenius forms for nonisothermal crystallization was 116.5 kJ/mol. In addition, the ability of the nylon 1313 samples to crystallize was determined by the kinetic crystallizability parameters

G . Its crystallizability was then compared theoretically with other polymers based on the values of G .

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