

# Isothermal and Nonisothermal Crystallization Kinetics of Partially Melting Nylon 10 12

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**ABSTRACT:** Nylon 10 12, a newly industrialized engineering plastic, shows a double-melting phenomenon during melting. Partial melts were obtained when the sample was heated to the temperature between the two melting peaks. A differential scanning calorimeter was used to monitor the energies of the isothermal and nonisothermal crystallization from the partially melted samples. During isothermal crystallization, relative crystallinity develops with a time dependence described by the Avrami equation, with the exponent  $n = 1.0$ . For nonisothermal studies, kinetics treatments based on the Avrami and Ozawa equations are presented to describe the crystallization process. It was found that the two treatments can describe the nonisothermal crystallization from the partially melted samples. The

derived Avrami and Ozawa exponents are all about 1.0, which means that the partially melted samples crystallize by one-dimensional growth, which may cause thickening of the lamellae. We calculated the crystallization activation energies for isothermal and nonisothermal crystallization from the partially melted samples. It was found that the activation energy determined by the Kissinger method was not rational, which may be attributed to the free-nucleation process for nonisothermal crystallization from partially melted samples. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1311–1319, 2003

**Key words:** nylon; melt; crystallization; kinetics; differential scanning calorimetry (DSC)

## INTRODUCTION

Nylon 10 12 is a newly industrialized polyamide. It has attracted much attention because of its properties, including a lower melting point, slightly lower density, excellent impact properties, lower dielectric constant, and water affinity. In addition, nylon 10 12 is also special because it has an equal number of methylene units in both the diamine and diacid chain segments. So, it should have a special crystal structure.<sup>1</sup> However, there are few publications about Nylon 10 12 in the past as far as we know.<sup>2,3</sup>

Double-melting peak behavior is a common phenomenon during the thermal analysis of semicrystalline polymers (i.e., nylon, PEEK, etc.).<sup>4–7</sup> There has been interest in the phenomenon for some decades. The interpretations vary from different crystalline lamellar thickness<sup>8,9</sup> to simultaneous melting and recrystallization.<sup>10</sup> In recent years, the recrystallization theory has been favored by many investigators. How-

ever, the recrystallization process during the heating scans of DSC for semicrystalline polymers is still not fully understood.

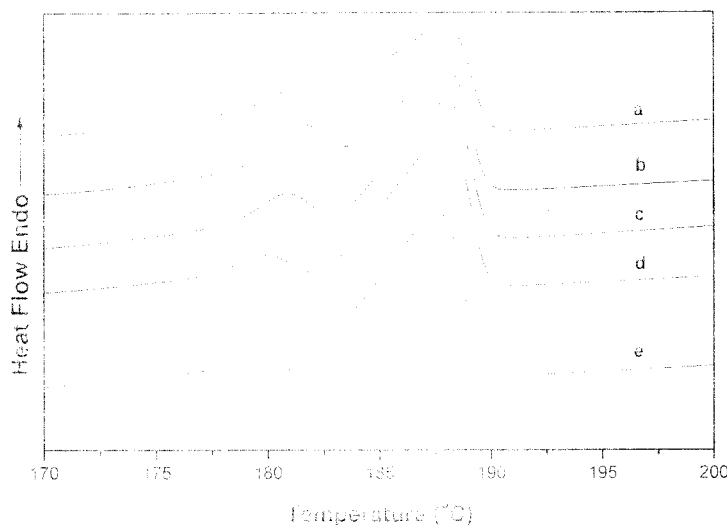
Like most nylons, Nylon 10 12 also shows the double-melting phenomenon. In this article, partially melted samples of Nylon 10 12 were obtained and then isothermal and nonisothermal crystallization of these melts was investigated. The study may be helpful to understand the recrystallization process during thermal analysis of semicrystalline polymers.

## EXPERIMENTAL

### Materials and preparation

Nylon 10 12 pellets were kindly provided by the Celulose Co. Ltd. (Shanghai, China) The pellets had a relative viscosity of 1.81 when measured in 96% H<sub>2</sub>SO<sub>4</sub> at 25°C, 1 g/100 mol concentration. A film of Nylon 10 12, approximately 0.2 mm in thickness, was obtained by hot molding at 5.0 MPa and 210°C for several minutes. The samples were first heated from room temperature to 230°C at 20°C/min and held at that temperature for 10 min to eliminate all residual crystallinity, followed by cooling (at 40°C/min) to room temperature.

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**Figure 1** Heating DSC diagram of Nylon 10 12 crystallized from its melt at (a) 2.5°C/min, (b) 5.0°C/min, (c) 10°C/min, (d) 20°C/min, and (e) 100°C/min.

### Differential scanning calorimetry (DSC) measurement

Both isothermal and nonisothermal crystallization kinetics were carried out using a Perkin–Elmer Pyris-1 DSC calibrated with indium. All DSC measurements were performed under a nitrogen purge; the sample weight varied between 3 and 5 mg.

### Isothermal and nonisothermal crystallization processes

For the isothermal crystallization process, the heating scans of samples in the DSC were interrupted at different temperatures (183, 184, 185, and 186°C) and kept in an isothermal state for 5 min. The exothermic curves of the heat flow as a function of time were recorded and examined. For the nonisothermal crystallization process, the samples were heated (at 20°C/min) to 185°C, then cooled at different rates (1, 2, 5, and 8°C/min) to 170°C.

### Polarized optical microscope observation

Morphological observations were performed on a Leica polarized optical microscope, equipped with a temperature-controlled stage.

## RESULTS AND DISCUSSION

### Double-melting phenomenon

As described in the Experimental section, all samples were first subjected to nonisothermal crystallization from the melts with a cooling rate of 40°C/min. The heating DSC scans of the Nylon 10 12 samples crys-

tallized at different cooling rates are shown in Figure 1. Two melting peaks can be seen for all the samples. The positions and heats of fusion of the two peaks are listed in Table I. The shape and position of the main upper peak changed only slightly as a result of the different cooling rates, while the lower minor peak appears as a variable feature with a change in the cooling rate. Thus, the partially melted melts can be obtained by heating samples to a temperature between the upper and lower peaks.

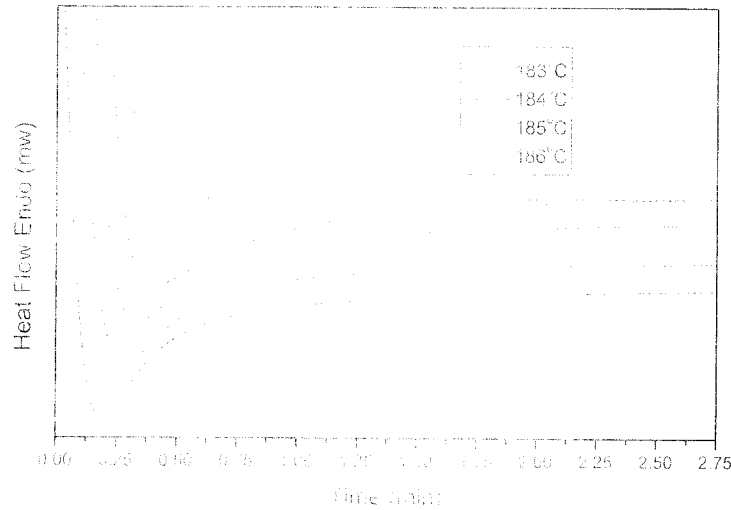
### Isothermal crystallization kinetics analysis

Isothermal crystallization kinetics from Avrami equation

The isothermal crystallization from the partially melting melts was carried out at different temperatures (183, 184, 185, and 186°C) as shown in Figure 2. The starting points can be identified by extrapolating the baselines where no further heat flow is measured. We assumed that the relative crystallinity  $X_t$ , which developed at time  $t$ , is

**TABLE I**  
Thermal Properties of Nonisothermal Crystallized Nylon 10 12 Samples

Sample	$T_m$ (°C)		$\Delta H_f$ (J/g)	
	Lower	Upper	Lower	Upper
Crystallized (2.5°C/min)	182.6	188	7.22	12.29
Crystallized (5.0°C/min)	181.6	188	5.47	15.10
Crystallized (10°C/min)	180.8	188	3.48	20.49
Crystallized (20°C/min)	179.5	188	2.22	23.72
Crystallized (100°C/min)	177.6	187.8	0.70	28.90



**Figure 2** Time dependence of the heat flow for the crystallization of Nylon 10 12 partially melted samples at (a) 183°C, (b) 184°C, (c) 185°C, and (d) 186°C.

$$Xt = \int_{t_0}^t \frac{dHc}{dt} dt / \int_{t_0}^{t_{\infty}} \frac{dHc}{dt} dt \quad (1)$$

All the isothermal curves have a partial sigmoidal shape. There were no typical full sigmoidal shapes of the polymer crystallization behavior for the equilibrium melts. The development of the relative crystallization can also be analyzed using the Avrami equation<sup>11,12</sup>:

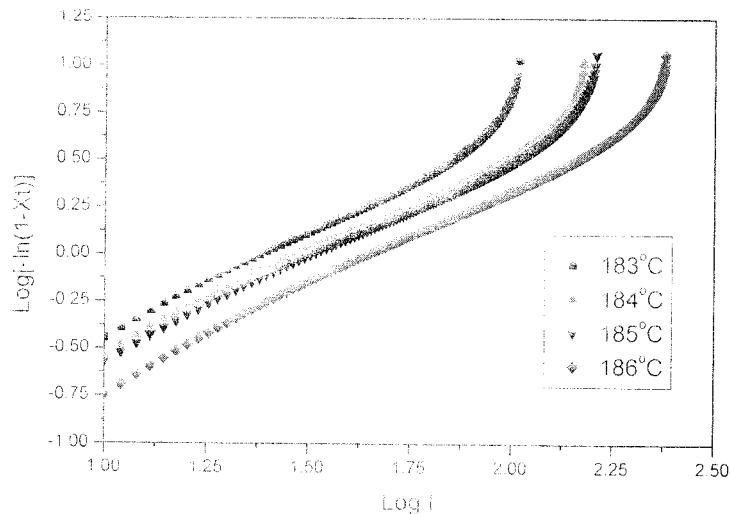
$$Xt = 1 - \exp(-Kt^n) \quad (2)$$

$$\log[-\ln(1 - Xt)] = n \log t + \log K$$

where  $Xt$  is the relative crystallinity at time  $t$ ;  $n$ , a constant, the value depending on the mechanism of

nucleation and on the form of crystal growth; and  $k$ , a constant containing the nucleation and growth parameters.

Plots of  $\log[-\ln(1 - Xt)]$  versus  $\log t$  are shown in Figure 3. Each curve has a linear section followed by a gentle rollover at a longer time; this fact indicates the existence of a secondary crystallization that is caused by the crystals' impingement in the later stage of the crystallization process from the partially melted samples.<sup>13</sup> Fitting the initial linear portion of  $\log[-\ln(1 - Xt)]$  versus  $\log t$ , for the times before rollover, allows us to determine  $k$  and  $n$  from eq. (2). The values are listed in Table II. From the slopes of the Avrami plots, the exponents were found to be 1.15–1.35, varying only slightly with the isothermal crystallization temperature used. These values of  $n$  for isothermal



**Figure 3** Plots of  $\log[-\ln(1 - Xt)]$  versus  $\log t$  for isothermal crystallization from partially melted samples at the temperatures indicated.

**TABLE II**  
Parameters for Isothermal Crystallization  
from the Partially Melted Samples

Parameter	$T_c$ (°C)			
	183	184	185	186
$n$	1.35	1.22	1.24	1.15
$\log k$	-2.09	-1.99	-2.05	-2.04
$t_{1/2}$ (min)	0.285	0.342	0.375	0.508
$\tau_{1/2}$ (min <sup>-1</sup> )	3.51	2.92	2.67	1.97
$t_{\max}$ (min)	0.093	0.115	0.118	0.127
$t_c$ (min)	1.75	2.52	2.70	4.0
$\Delta H_c$ (J/g)	-7.82	-8.66	-8.68	-13.01

crystallization of partially melted melts are different from those of the equilibrium melts of Nylon 10 12, which are about 2.0.<sup>2</sup> The  $n$  values of approximately 2.0 for the equilibrium melt crystallization of Nylon 10 12 suggests that the crystallization process is simultaneous and the growth of the crystals is probably two-dimensional. However, the narrow spread in the  $n$  value centered around 1.0 for the partially melted samples indicates that the mechanism of the crystallization is completely altered, with the initiation process being of heterogeneous nucleation and probably of linear crystal growth, which may cause the thickening of the lamellae.<sup>14</sup> The likely reason for this alteration in the mechanism lies in the existing crystals in the partially melted state serving as nuclei. Thus, the chains in the partially melted samples crystallize from the edge or surface of the original crystals.

The value of the crystallization half-time  $t_{1/2}$  is defined as the time at which the extent of crystallization is 50% completed and it can be determined from the measured kinetic parameter, as follows:

$$t_{1/2} = (\ln 2/K)^{1/n} \quad (3)$$

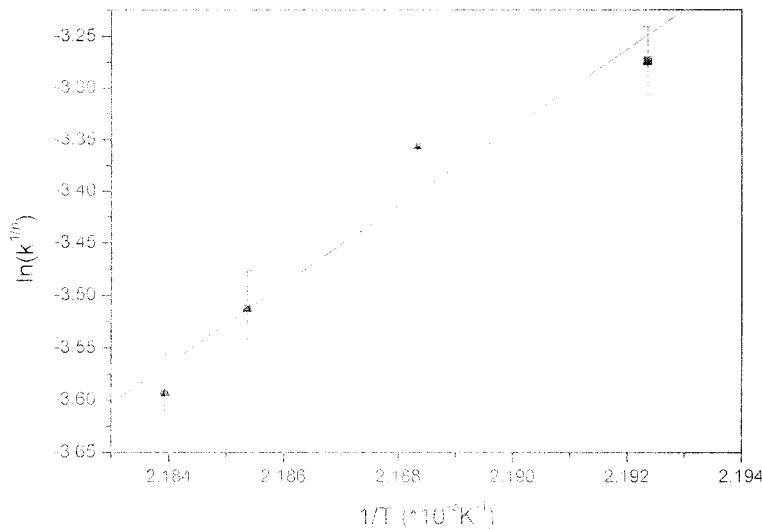
Usually, the rate of crystallization  $G$  is described as the reciprocal of  $t_{1/2}$ , that is,  $G = \tau_{1/2} = t_{1/2}^{-1}$ . The values of  $\tau_{1/2}$  and  $t_{1/2}$  are listed in Table II. It was found that the crystallization rate of the partially melted samples is faster than that of the Nylon 10 12 equilibrium melts ( $\tau_{1/2} = 0.1\text{--}0.8 \text{ min}^{-1}$ ).<sup>2</sup> In addition,  $t_{\max}$  (the time to reach the maximum rate of heat flow) and  $t_c$  (the time at which there is no further heat flow) can also be used to describe the crystallization rate. They can be obtained directly from the plots of heat flow versus  $t$  and the results are listed also in Table II.

#### Crystallization activation energy ( $\Delta E$ )

The Avrami parameter  $k$  is assumed to be thermally activated and can be used to determine an activation energy for crystallization. Thus, the crystallization rate parameter can be described by the Arrhenius form as follows<sup>15</sup>:

$$K^{1/n} = k_0 \exp(-\Delta E/RT_c) \quad (4)$$

where  $k_0$  is a temperature-independent preexponential factor;  $\Delta E$ , the activation energy;  $R$ , the gas constant; and  $T_c$ , the absolute temperature.  $\Delta E$  can be determined by the slope coefficient of plot of  $1/n \ln k$  versus  $1/T$  (Fig. 4). The value of the activation energy crystallizing from the partial melts was found to be 240 kJ/mol. This activation energy is a little lower than the value of 264.4 kJ/mol derived from the equilibrium melt crystallization.<sup>2</sup> It is clear that the activation energy is strongly dependent on the type of nucleation in the crystallization process. In the partially melted system, the existing principal lamellae play an important role in the crystallization process, so the



**Figure 4**  $\ln(k)^{1/n}$  versus  $1/T_c$  for Avrami parameter  $k$  deduced from isothermal crystallization data.



(a)



(b)

**Figure 5** Electron micrographs for Nylon 10 12 samples: (a) crystallized at 167°C for 30 min, quenched to room temperature, heated to 183°C for 5 min, and then cooled to room temperature; (b) crystallized at 167°C for 30 min, quenched to room temperature, heated to 230°C for 5 min, and then cooled to room temperature.

crystallization activation energy is lower and the crystallization rate is faster.

#### Crystal morphology of the crystals from partially melted samples

The crystalline morphologies of the partially melted samples and the equilibrium melts are shown in Figure 5. It can be observed that the samples that partially melt at 183°C [Fig. 5(a)] display larger and fewer spherulites compared with those of the equilibrium melt at 210°C [Fig. 5(b)]. From a comparison of the two, it is seen that the unmelted crystals in the partially melted state play a strong nucleation role

in the crystallization of the partially melted samples.

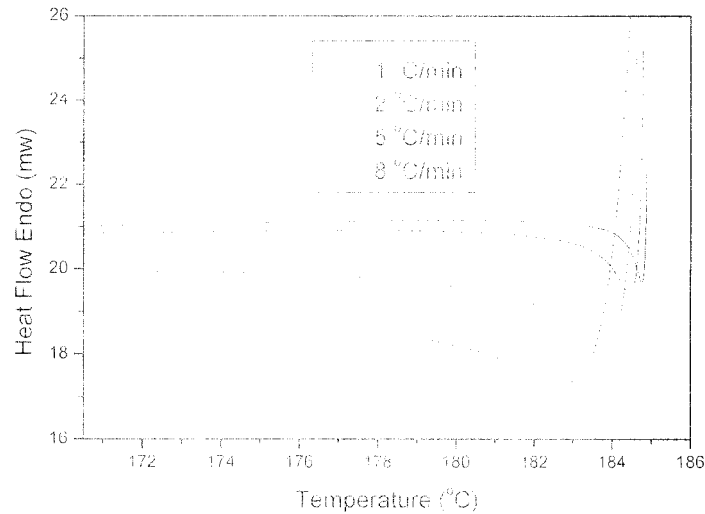
#### Nonisothermal crystallization kinetics analysis

Nonisothermal crystallization kinetics from Avrami and Ozawa equation

Recrystallization theory predicts that the processes of melting and recrystallizing happen simultaneously during the melting of the sample. So, the nonisothermal crystallization of the partially melted state with different cooling rates was carried out in a small temperature range between 185 and 170°C. The lower temperature limit was selected to be 170°C because it is just lower than the melting onset temperature of Nylon 10 12.

The crystallization exotherms of the partially melted samples at various cooling rates are presented in Figure 6. The exothermic peak temperature  $T_p$  shifts to a lower temperature as the cooling rate increases. Integration of the exothermic peak during the nonisothermal scan gives the relative degree of crystallinity as function of the temperature. According to the relation between the crystallization time and the temperature, the temperature axis can be transformed into a time scale. It can be found that, similar to isothermal crystallization, nonisothermal crystallization of the partially melted state is also fast and there are almost no retardation effects, which can also be attributed to the effects of the unmelted crystals in the system; therefore, there is no nucleation process and, hence, no induction period. The values of  $T_p$ , the corresponding peak time  $t_{max}$ , the relative degree of crystallinity at  $T_p$ , and the crystallization enthalpies are shown in Table III. The crystallization enthalpies decrease as the cooling rate increases. A possible explanation lies in the more perfect crystal structure crystallized at a lower cooling rate.

There are several methods to describe nonisothermal crystallization kinetics: The Avrami equation can also be used to analyze the nonisothermal crystallization process.<sup>16,17</sup> As mentioned, in plotting  $\log[-\ln(1 - Xt)]$  versus  $\log t$  (shown in Fig. 7), the linearity that was maintained from the initial stages of crystallization until a high degree of relative conversion indicates that the Avrami equation correctly describes the nonisothermal crystallization process of the partially melted melts. Similar to isothermal crystallization, a gentle rollover at a longer time can also be observed, which may be caused by crystal-crystal impingement. From the slopes and intercepts of Figure 7, the Avrami exponent  $n$  and rate constant  $k$  can be determined (also listed in Table III). The Avrami exponent increases with an increase of the cooling rate. The values of the exponent are around 1.0, which is equal to that of the



**Figure 6** Heat flow versus temperature curves for nonisothermal crystallization of Nylon 10 12 partially melted samples at different cooling rates by DSC.

isothermal crystallization. This fact means that the partially melted state crystallizes also nearly by one-dimensional growth under nonisothermal crystallization conditions.

Ozawa<sup>18</sup> extended the Avrami equation to the nonisothermal condition. Assuming that the nonisothermal crystallization process may be composed of infinitesimally small isothermal crystallization steps,<sup>18</sup> the following equation was derived:

$$1 - X_t = \exp[-K(T)/\phi^m] \quad (5)$$

where  $K(t)$  is the cooling function;  $\phi$ , the cooling rate; and  $m$ , the Ozawa exponent that depends on the dimension of the crystal growth. By studying the process at different cooling rates and plotting  $\log[-\ln(1 - X_t)]$  against  $\log \phi$  at a given temperature, if the Ozawa method is valid, a straight line should be obtained. The Ozawa plot for different crystallization temperatures is shown in Figure 8. It is different from the nonisothermal crystallization from the equilibrium melts<sup>2</sup>; good linearity can be obtained in the process of

the nonisothermal crystallization of partially melted samples, which means that the Ozawa analysis can be used to analyze the nonisothermal crystallization process.  $K(T)$  and  $m$  are also determined from the intercept and slope of the straight lines. The data are shown in Table IV. A value of about 1.0 for the Ozawa exponent is in agreement with the results from the isothermal crystallization at 183 and 184°C, reported in Table II.

Crystallization activation energy ( $\Delta E$ )

For nonisothermal crystallization, the Kissinger method is usually used to determine the activation energy as follows<sup>19</sup>:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = -\Delta E/R \quad (6)$$

where  $R$  is the gas constant, and  $T_p$ , the peak temperature. In the graphs of  $\ln(\phi/T_p^2)$  versus  $1/T_p$  (shown in Fig. 9), according to the slope of the line, the activation energy was determined to be 2000 kJ/mol. In comparing the calculated activation energy value of the nonisothermal crystallization with that of the isothermal crystallization, the value was found to be too large, that is, the method cannot be used to determine the  $\Delta E$  from the partially melted state. A possible explanation lies in the fact that the Kissinger method is used mainly in nonisothermal crystallization for the equilibrium melt, from which crystallization is composed in two stages, that is, the nucleation stage and the growth stage. However, there was no nucleation stage in the process of the nonisothermal crystallization from the partially

**TABLE III**  
Parameters of Nylon 10 12 Partially Melted Samples During Nonisothermal Crystallization and  $k$  and  $n$  determined by Avrami Equation

Parameter	$\phi$ (°C/min)			
	1	2	5	8
$T_p$ (K)	457.9	457.6	456.9	455.9
$n$	1.04	1.11	1.26	1.32
$\log k$	-1.62	-1.69	-1.83	-1.88
$t_{\max}$ (min)	0.26	0.28	0.23	0.25
$X_{tp}$ (%)	14.31	14.96	17.71	22.46
$\Delta H_c$ (J/g)	16.15	14.36	13.63	12.39

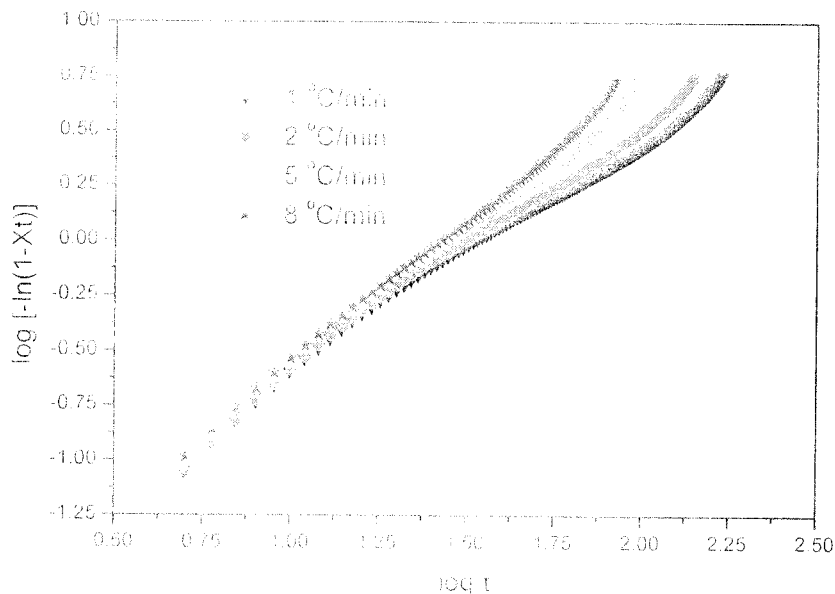


Figure 7 Plots of  $\log[-\ln(1 - Xt)]$  versus  $\log t$  for partially melted samples; nonisothermal crystallization.

melted samples. The crystallization from the partially melted state is involved mainly in the transport of the chains in the partially melted state to the edge or surface to the existing crystals. So, the process is mainly thermally activated.

The Avrami parameter  $k$  is assumed to be thermally activated and can also be used to determine the activation energy for nonisothermal crystallization. Cebe<sup>17</sup> also used  $k$  and  $n$  obtained from the Avrami equation for the nonisothermal crystallization to determine the activation energy for crystallization during nonisothermal crystallization at a low degree of conversion. The nonisothermal crystallization for the Nylon 10 12 partially melted state can be described well using the Avrami equation, so the activation energy can also be determined by applying eq. (4). It should be noted that here  $T_c$  is the onset temperature of the nonisothermal crystallization. From the slope of Figure 10,  $\Delta E/R$  can be obtained.  $\Delta E$  was determined as 290 kJ/mol, which is comparable to the value reported in the Isothermal Crystallization section.

TABLE IV  
Parameters  $K(T)$  and  $m$  Determined by Ozawa Equation for Nonisothermal Crystallization from Nylon 10 12 Partially Melted Samples

Parameter	$T_c$ (°C)				
	182	182.5	183	183.5	184
$m$	1.15	1.19	1.29	1.50	1.77
$K(T)$	0.705	0.602	0.501	0.399	0.22

## CONCLUSIONS

Nylon 10 12 shows a typical double-melting phenomenon during heating of the samples. The study of isothermal and nonisothermal crystallization kinetics from its partially melted state was carried out by DSC. It was found that the Avrami equation can be used to analyze the isothermal crystallization, with the exponent  $n = 1.0$ . For the nonisothermal crystallization, both the Avrami and Ozawa equations can describe the crystallization process correctly. The values of the Avrami and Ozawa exponents are all about 1.0 when the cooling rate is low. The Avrami exponent,  $n = 1.0$ , under isothermal and nonisothermal crystallization conditions, implies that the one-dimensional growth of the crystals occurs through heterogeneous nucleation from the partially melted state, which may cause thickening of the lamellae.

An Arrhenius plot can be applied to determine the activation energy of the isothermal crystallization for the Nylon 10 12 partially melted state. The obtained activation energy, 240 kJ/mol, is lower than that for the isothermal crystallization of the equilibrium melts. The activation energy for nonisothermal crystallization from the partial melting obtained by the Kissinger method is not rational, which may be attributed to the function of the existing lamellae. However, the Arrhenius form can be used to determine the activation energy for the system, which is based on the fact that the crystallization process from the partially melted state is thermally activated. The obtained value, 290 kJ/mol, is

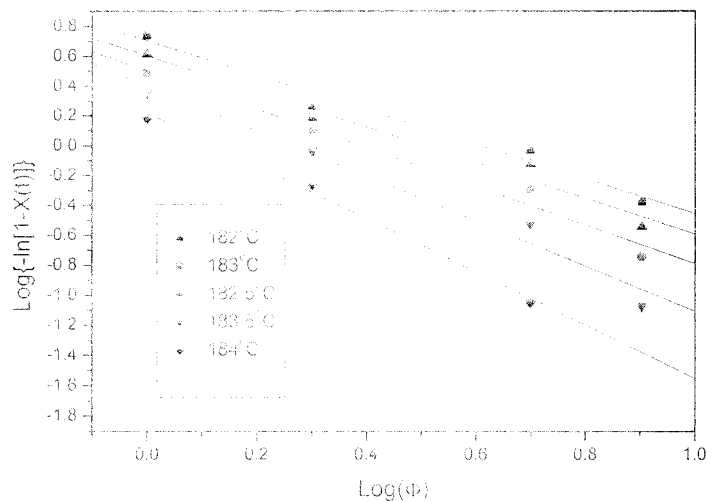


Figure 8 Ozawa Plots of  $\log\{-\ln(1 - X(t))\}$  against  $\log \phi$  for partially melted samples; nonisothermal crystallization.

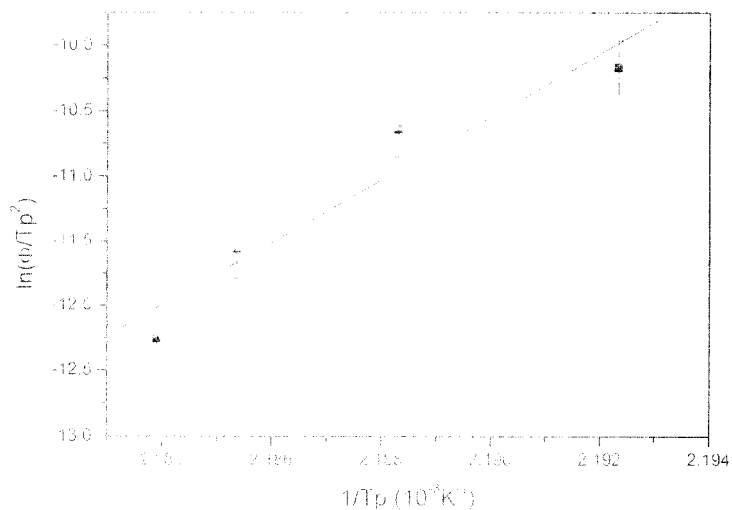


Figure 9 Kissinger plots for evaluating nonisothermal crystallization activation energy of Nylon 10 12 from the partially melted samples.

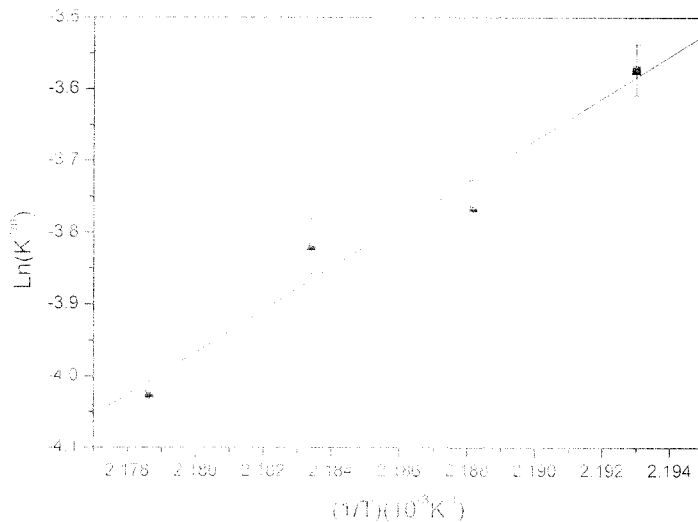


Figure 10  $\ln(k)^{1/n}$  versus  $1/T$  for Avrami parameter  $k$  deduced from partially melted samples; nonisothermal crystallization data.



comparable to that of the isothermal crystallization from the partially melted state.

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