

CRYSTALLIZATION AND MELTING OF NYLON 610*

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Abstract Differential scanning calorimetry was used to study the crystallization and melting of nylon 610. For nylon 610 crystallized from the melt state (260°C), the overall rate of bulk crystallization can be described by a simple Avrami equation with Avrami exponent $n \approx 2$, independent of crystallization temperature. With the experimentally obtained T_m^0 (235°C ~ 255°C) of nylon 610, the fold surface free energy σ_e was determined to be 35 ~ 38 erg/cm². The effects of annealing temperature and time on the melting of quenched nylon 610 were also investigated. For nylon 610 quenched at room temperature there is only one DSC endotherm peak. DSC scans on annealed samples exhibited an endotherm peak at approximately 10°C above the annealing temperature. The size and position of the endothermic peak is strongly related to annealing temperature and time. An additional third melting was observed when quenched nylon 610 was annealed at high temperature for a sufficiently long residence time. The existence of the third melting peak suggests that more than one kind of distribution of lamella thickness may occur when quenched nylon 610 is annealed. The implications of these results in terms of crystal thickening mechanism were discussed.

Keywords Nylon 610; Differential scanning calorimetry; Crystallization kinetics; Anneal; Melt

INTRODUCTION

Nylon 610, poly(hexamethylene sebacamide), is one of the important engineering plastics, which has high mechanical strength, low wettability and high abrasion resistance and oil resistance. A remarkable combination of these properties allows the use of nylon 610 in many applications such as automobile parts, chemical appliances and electric elements.

The properties of semicrystalline polymers such as nylon 610 depend on the crystallization behavior of the polymer. Therefore, the study of its morphology

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and crystallization kinetics are of major importance. A few studies have focused on the microstructure of nylon 610^[1,2]. However, only one paper dealt with the crystallization kinetics of this polymer^[3]. The isothermal crystallization behavior of synthetic nylon 610 sample has been analyzed between 185° and 193°C^[3], but no detailed Avrami parameter n and rate constant k were given. Because of the uncertainty of equilibrium melting temperature T_m^0 , no further kinetic analysis has been reported up to date. Similarly, very little information is available on the thermal behavior of nylon 610. The aim of this work is to investigate the isothermal crystallization kinetics and melting behavior of nylon 610 in some detail.

EXPERIMENTAL

The nylon 610 granular samples employed in this study were provided by Shanghai Celluloid Factory. The average molecular weight is known to be of the order of 10^4 . The relative viscosity is 2.6 in 96% H_2SO_4 at 25°C and 0.5 g/100 mL concentration. To improve the reproducibility of DSC experiments, films about 200 μm thick were prepared from molten polymer. DSC specimens with 6 mm diameter were punched out of the films. They were put in aluminium pans with the same internal diameter. Such a geometry ensures a good thermal contact between the specimen and the calorimeter.

The thermal properties of the nylon 610 samples were measured with a Dupont model 910 DSC coupled to a Dupont 2000 data analysis system. The DSC temperature scale was calibrated using the melting temperature of high purity standards. In all cases, polymer samples weighing 5 ~ 7 mg closed in aluminum pans, were used throughout the experiments. All measurements were conducted in a nitrogen atmosphere to prevent the oxidation of the samples. A scanning rate of 20°C/min has been used throughout all the measurements.

For the isothermal crystallization from the melt, the nylon 610 sample was first heated to 260°C and held for 5 min to remove the residual crystal nuclei. Then the sample was rapidly cooled to the pre-selected crystallization temperature. Crystallization from the melt can be analyzed by DSC in the temperature range of 194°C ~ 202°C. Two factors contributed to limit the temperature range. The upper end was set by the long time needed to complete the crystallization at high temperatures. The lower limit was imposed by the high nucleation densities encountered, and accordingly the cooling exotherm of nylon 610 overlaps the initial development of crystallization masking the baseline of the calorimeter and the time at which crystallization develops.

Melting endotherms of the samples crystallized at the chosen temperatures for 30 min were recorded with heating the samples directly from 60°C. The melting temperature was measured at the maximum.

The effects of annealing temperature and time on the melting of quenched nylon 610 sample were studied by employing the following procedure: each sample was heated to 260°C and held for 5 min. The sample was then rapidly removed from the DSC cell and quenched at room temperature. The sample was designated as quenched RT one. The DSC endotherm in this rerun was taken as the standard for comparing the annealing effects. Nylon 610 RT sample was held at various annealing temperatures for some time and then cooled at room temperature before rescanning. Subsequently, the melting behavior related to the annealing temperature and time was recorded and analyzed.

RESULTS AND DISCUSSION

Isothermal crystallization kinetics

Some typical exotherms of crystallization at some temperatures for nylon 610 are presented in Fig. 1. The relative crystallinity of nylon 610 was plotted in Fig. 2 for the six crystallization temperatures. The crystallization rate becomes slower with increasing crystallization temperature T_c . Development of the relative crystallinity can be analyzed using the well known Avrami equation^[4~6]:

$$X_c(t) = 1 - e^{-kt^n} \quad (1)$$

where $X_c(t)$ is the volume fraction of crystals at time t , k is a rate constant containing information regarding nucleation and diffusion rates, n is an Avrami constant which depends on the mechanism of nucleation and growth geometry of the crystals. Accordingly:

$$\lg[-\ln(1 - X_c(t))] = \lg k + n \lg t \quad (2)$$

If the crystallization kinetics of a semicrystalline polymer follows the Avrami model, a plot of $\lg[-\ln(1 - X_c(t))]$ as a function of $\lg t$ should be linear with slope n . Plots of $\lg[-\ln(1 - X_c(t))]$ versus $\lg t$ of nylon 610 are shown in Fig. 3. Avrami's plots at different T_c show a linear trend with no change in the slope up to high degree of conversion. Fitting the straight line of $\lg[-\ln(1 - X_c(t))]$ versus $\lg t$ allows us to determine n and k from equation (2). These values are listed in Table 1. The value of n is about 2 for the crystallization temperature range (194°C ~ 202°C). For crystallizations of many flexible, linear polymers from a melt, heterogeneous

nucleation was found, followed by spherulites, chain-folded crystal growth^[5,7]. For athermal nucleation, the Avrami exponent is 3 and for thermal nucleation n is 4. The value of $n = 2$ obtained for nylon 610 may be attributed to crystal growth that is not three-dimensional, which lowers the value of the Avrami exponent. Avrami equation is generally applied to such kinetics that crystallization species, e.g. spherulites, are growing from the liquid phase without any restriction in volume. However, the DSC measurements are performed with small amount of material, which implies that small dimensions of the specimens are concerned. J.M. Esclein^[8] theoretically discussed the influence of specimen thickness on isothermal crystallization kinetics including Avrami exponent. The influence of thickness becomes important when thickness is in the order of or smaller than the average spherulite radius. The decreasing sample thickness will lead to a decrease in the Avrami exponent. According to the theory, for relatively thin sample (about 0.2 mm thick) the resulting crystallinity develop-

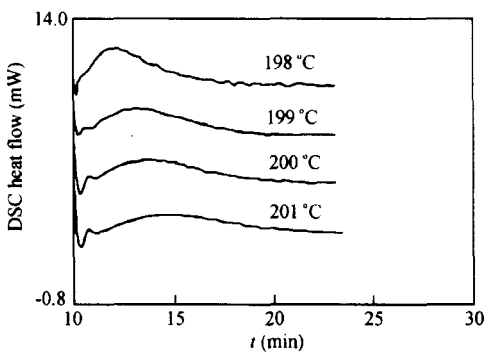


Fig. 1 Isothermal crystallization curves of Nylon 610 obtained by DSC

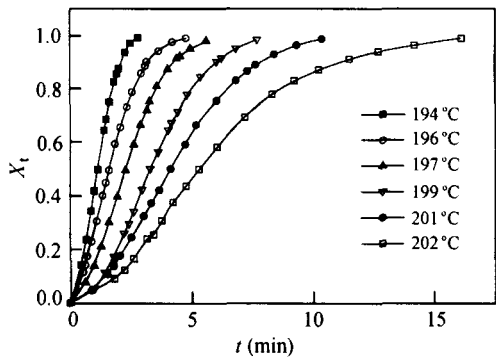


Fig. 2 Plot of the relative crystallinity of Nylon 610 versus crystallization time at different crystallization temperatures T_c

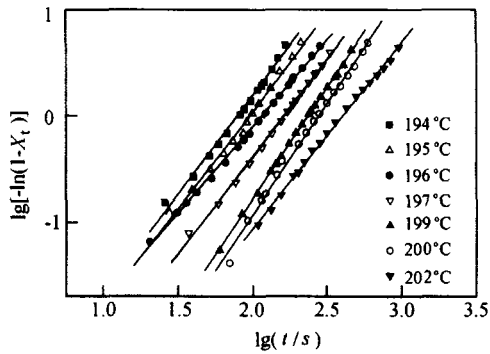


Fig. 3 Avrami plots for Nylon 610 at various crystallization temperatures T_c

Table 1 Avrami exponent n , k and half time of crystallization $t_{0.5}$ of nylon 610 as function of crystallization temperature T_c

$T_c(^{\circ}\text{C})$	n	k	$t_{0.5}(\text{min})$
194	1.9	2.88×10^{-4}	1.13
195	1.9	1.55×10^{-4}	1.35
196	1.7	3.55×10^{-4}	1.6
197	1.8	8.91×10^{-5}	2.27
198	1.6	3.09×10^{-4}	2.34
199	2.1	1.07×10^{-5}	3.28
200	2.1	7.59×10^{-6}	3.85
201	1.9	2.82×10^{-6}	4.12
202	1.8	2.75×10^{-6}	5.29

ment should thus change from the true three-dimensional cases to the two-dimensional truncated spherulites. For athermal nucleation and two-dimensional spherulites, the Avrami exponent should be 2.

Determination of the equilibrium melting temperature of nylon 610

We scanned the samples melt-crystallized at different crystallization temperatures (T_c) for 30 min, as shown in Fig. 4. Multiple DSC endotherms arise for most melt crystallized nylon 610 samples. A typical example of the change of the melting peak temperatures with T_c is given in Fig. 5. Peak III is found in all samples at about 221°C and corresponds to the melting of the ultimate metastable crystals in given condition. Peak I is present in all samples at about 10°C above T_c . It moves with increasing crystallization temperature and time more sharply to higher temperatures than peak II. Peaks I and II mainly refer to the melting of the original crystals with different crystal perfection. According to similar explanations of multiple endotherms of nylon 6^[9], the cause of peak I is assumed to be microcrystallite formation in the boundary layer between the larger crystallites. It can be seen from Figs. 4 and 5 that peak III remains almost constant and independent of T_c . Although T_m (I) varies linearly with T_c , it is parallel with the $T_m - T_c$ line. Therefore, both peak I and III are useless in the determination of the equilibrium melting temperature of nylon 610 (T_m^0). Only T_m (II) varies linearly with T_c , and not parallel with the $T_m - T_c$ line. However, only the high part of peak II is valid to be extrapolated the equilibrium melting temperature of nylon 610, but it is difficult to exactly determine T_m^0 of nylon 610. Therefore, it is better to give a scope of T_m of nylon 610. According to Hoffman-Weeks equation, the value of T_m^0 ranging from 235°C to 255°C was obtained by extrapolation of the $T_m = f(T_c)$ curve. For poly-

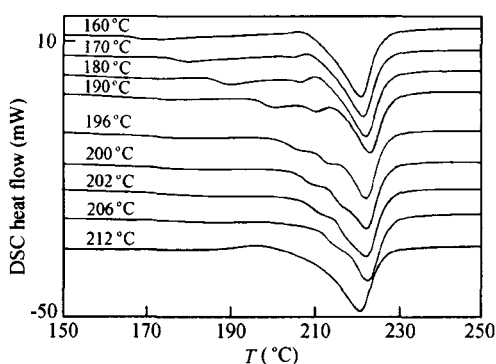


Fig. 4 DSC heating curves of isothermally melt crystallized Nylon 610

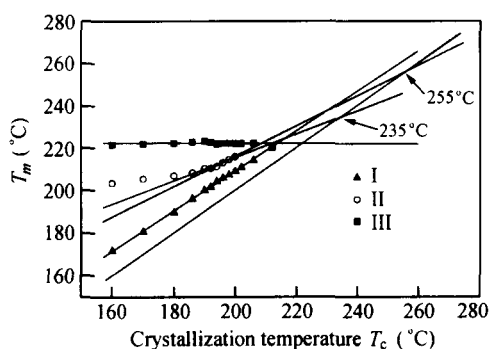


Fig. 5 Plot of the peak temperature versus crystallization temperature for Nylon 610

amides, there is a trend that the longer the hydrocarbon segment in the repeating unit, the lower the value of T_m^0 . Therefore, the scope can be said to be reasonable compared with nylon 66 (280°C)^[9] and nylon 1010^[10] (214°C).

Temperature dependence of the overall crystallization rate constant

Assuming that for nylon 610 samples the process of crystal growth during the primary crystallization is controlled by a surface coherent two dimensional secondary nucleation process, then in accordance with the kinetic theory of polymer crystallization^[11,12], the temperature dependence of the overall kinetic rate constant may be expressed with the relation:

$$\frac{1}{n} \lg k + \frac{\Delta F^*}{2.3RT_c} = A_n - \frac{\Delta G^*}{2.3KT_c} \quad (3)$$

where K is Boltzman constant, R is gas constant, k is the rate constant in the Avrami equation, A_n is a constant (in the hypothesis that the density of primary nucleation does not vary with time at the T_c examined) and ΔF^* is the activation energy for the transport process at interface, which can be obtained by the WLF equation^[13]:

$$\Delta F^* = \frac{C_1 T_c}{C_2 + T_c - T_g} \quad (4)$$

where C_1 and C_2 are constants generally assumed to be 17.22 kJ/mol, 51.6 K respectively. The free energy of formation of a nucleus of critical size ΔG^* may be expressed by^[5]:

$$\Delta G^* = 4b_0\sigma\sigma_e/\Delta g_f \quad (5)$$

σ, σ_e are the surface free energies per unit area of the surface parallel and perpendicular, respectively, to the molecular chain direction, b_0 is the distance between two adjacent fold planes, and Δg_f is the Gibbs free energy difference between the liquid and the crystal. The Δg_f is given by:

$$\Delta g_f = \Delta H_f \Delta T / T_m^0 \quad (6)$$

To calculate σ and σ_e , the following parameter values of nylon 610 were adopted^[10]: $T_g = 40^\circ\text{C}$, $\rho_a = 1.041 \text{ g/cm}^3$, $\rho_c = 1.160 \text{ g/cm}^3$; $\Delta H_f = 211.7 \text{ J/g}$; $T_m^0 = 235^\circ\text{C} \sim 255^\circ\text{C}$. The results of infrared absorption and X-ray analyses turn out that the lattice parameters of nylon 610 vary with crystallization temperature^[14]. Therefore, we chose the unit-cell parameters of nylon 610 crystallized at 200°C : $a_0 = 0.493 \text{ nm}$, $b_0 = 0.550 \text{ nm}$.

In Fig. 6 both plots of $\frac{1}{n} \lg k + \frac{\Delta F^*}{2.3RT_c}$ versus $T_m^0/T_c \Delta T$ ($T_m^0 = 235^\circ\text{C}$, $T_m^0 = 255^\circ\text{C}$) are straight lines for the chosen crystallization temperatures. From the

value of the slope and $\sigma = 0.1\Delta H_f(a_0b_0)^{1/2[15]}$, σ and σ_e were calculated to be 13 erg/cm², 35 erg/cm² ($T_m^0 = 235^\circ\text{C}$) $\sim$ 38 erg/cm² ($T_m^0 = 255^\circ\text{C}$) respectively.

Effect of annealing temperature and time on the melting behaviors of quenched nylon 610

The collective DSC melting endotherms of nylon 610 quenched at room temperature, annealing from 120°C to 220°C for 10 min, are shown in Fig. 7 and 8. The dual endothermic peak has been observed on most of the melting endotherms. Plots of two melting peak temperatures of nylon 610 versus the annealing temperature (T_a) are given in Fig. 9. The data of Fig. 6 show that there is only one DSC endotherm for quenched nylon 610. The ratio of the heat fusion of this endotherm to equilibrium melting heat fusion of nylon 610^[16] indicates about 40% crystallinity. There were no glass transition and crystallization exothermic peak as expected from a typical DSC thermogram from an amorphous sample. This turns out that an amorphous nylon 610 sample can't be obtained after quenched at room temperature from a melt, due to the fast crystallization rate of nylon 610. Polarizing optical microscopy verified that many small spherulites formed for the quenched nylon 610 solid. These small spherulites will melt and show a melting endotherm on the DSC scan. After annealing, an additional melting peak is observed at 10°C above the annealing temperature. This is called the "annealing peak" and is attributed to the much poorer crystals growing between original crystals. As the annealing temperature is increased, the low-temperature-peak crystals perfect themselves and melt at increasingly higher temperatures. The main melting peak, corresponding to the original crystals of quenched nylon 610, is completely independent of T_a and has a constant value of 217°C. With increasing T_a , the lower temperature melting peak moves toward the main endotherm and eventually merges with it. The overlapped single melting peak then increases to high temperatures when T_a is increased. Meanwhile, a new broad low peak is found at lower temperature. The two peaks are described as peak 1 and 2 from low temperature to high temperature successively. The occurrence of peak 1 is because T_a have risen to the melting range, and some of the original crystals melted out below T_a fail to recrystallize in the time available and solidify on cooling. The crystals formed are more imperfect, with a lower melting point than before. They become more perfect with increasing T_a until T_a exceeds the higher end of the initial melting range, and quenching restores the original behavior. At this stage for 10 min anneal, the melting temperature of peak 2 can be raised to approximately 227°C, about 10° higher than the unannealed samples as T_a was increased to 216°C. The area underneath peak 2 reduces with increased T_a . The shape and position of

this peak are also dependent upon the total time of anneal, as shown below.

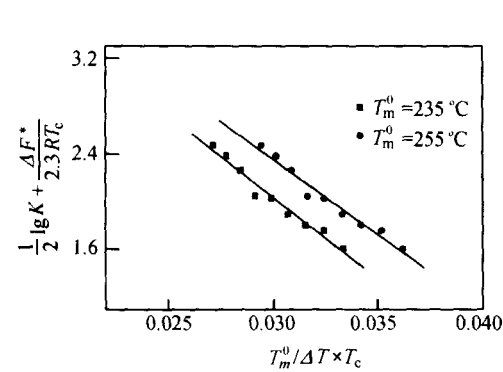


Fig. 6 Plot of $\frac{1}{2} \lg k + \frac{\Delta F^*}{2.3RT_c}$ versus $T_m^0/\Delta T \cdot T_c$ for Nylon 610

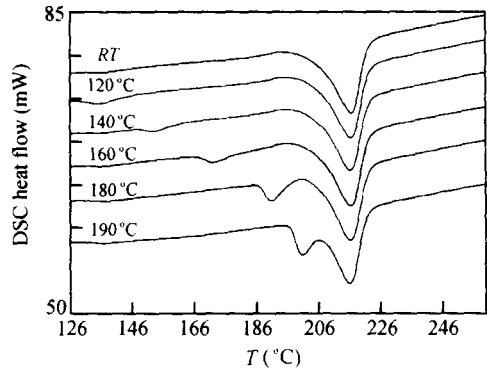


Fig. 7 Selected DSC scans of Nylon 610 RT sample after annealing for 10 min at the temperature indicated

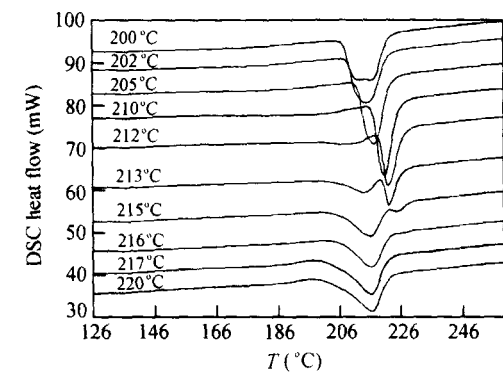


Fig. 8 Selected DSC scans of Nylon 610 RT sample after annealing for 10 min at the temperatures indicated

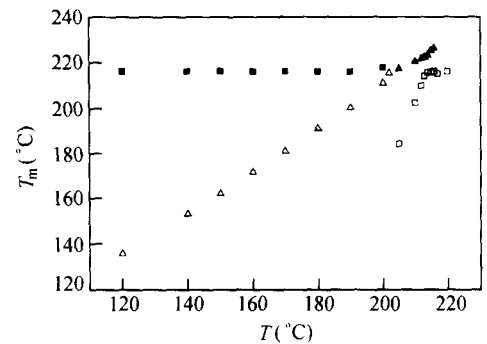


Fig. 9 Plots of the melting peak temperatures of nylon 610 versus annealing temperature T_a for 10 min anneal; $\blacksquare$ and $\triangle$ are the lower and upper melting peak temperature for low temperature anneal range, $\blacktriangle$ and $\square$ are the lower and upper melting peak temperature for high temperature anneal range

Fig.10 shows the melting endotherm of the annealed nylon 610 sample which has been annealed at 214°C for various times ranging from 3 to 500 min. Three endothermic peaks are observed when annealing time reaches 60 min. As the time of anneal is increased, the temperature of peak 1 decreases in magnitude and shifts to lower temperatures while the temperature of peak 2 increases in magnitude and shifts to higher temperatures. The temperature of peak 2 can rise to be about 240°C with increased time.

When T_a exceeds the original crystal melting range, as shown in Fig. 8 and 9, the annealing temperature and time dependence of peak 2 can be explained by the melt-recrystallization mechanism proposed by Bassett^[17], that is, at high T_a annealing behavior is indeed of a consequence of the melting followed by recrystallization around residual crystallites acting as seeds.

If the quenched nylon 610 *RT* sample is annealed at a temperature closer to its melting point, the chain mobility will be high enough and it is easier for molten samples to recrystallize at T_a . Therefore more thickened crystals are formed through annealing process and have a higher melting point. On the other hand, the reduction of crystal nuclei presented by original crystals brings about the decrease of the area underneath peak 2. When T_a is increased too high, 216°C or higher, most of the original crystals are melted and the resulting thermogram is similar to that of unannealed sample. With increased annealing time, more of the molten samples have the opportunity to participate in the recrystallization process at T_a and the crystal lamellae appreciably thicken. On the other hand, the amount of molten crystals keeps constant for a given annealing temperature and accordingly fewer molten samples recrystallize on cooling, which leads to the decrease of size of peak 1. The drop in temperature of peak 1 may be the result of increased vacancy concentration. Therefore, we can observe the drop in temperature and in size of the lower temperature peak with increasing annealing time.

It is worthwhile to point out that as the annealing time is increased to 60 min, a new small endothermic melting peak (peak 3) appears at about 240°C. Its peak temperature slightly increases with annealing time, as can be seen from Table 2. The occurrence of the new melting peak signifies that for quenched nylon 610 annealed at high temperature for a long time, a small population of more perfect crystals are formed. The melting point of these crystals is about 12°C above that of the normal-thickening crystals (peak 2), independent of annealing time, which suggests that the mechanism of peak 3 is different from that of peak 2.

For solution-crystallized nylon 66 and 612, observations of the preferred doubling

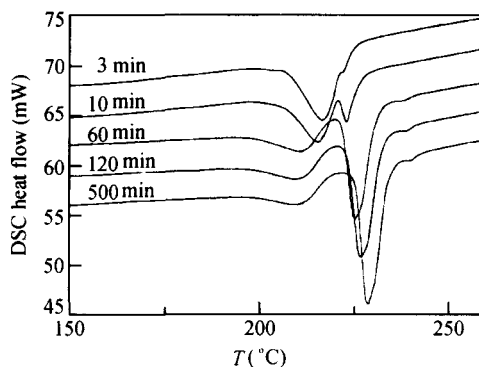


Fig. 10 Selected DSC scans of Nylon 610 *RT* sample annealing at 214°C for the times indicated.

For solution-crystallized nylon 66 and 612, observations of the preferred doubling

of the initial fold-length bring about the following mechanism proposed by Drefuss and Keller^[18] and Burmester^[19]. Fig. 11 is a schematic picture for the development of fold-length. Fold a is consumed by folds b and c in their drive to a larger fold length, which is called fold dislocation. The double initial fold length is given after the climb of the dislocation. A new fold dislocation will result in further double-thickening process. It is proposed that the lamellae thickening mechanism is a possible reason for the occurrence of the new melting peak of nylon 610.

Table 2 Effect of annealing time on the melting peaks of annealed nylon 610

Annealing time (min)	$T_{m1}(^{\circ}\text{C})$	$T_{m2}(^{\circ}\text{C})$	$T_{m3}(^{\circ}\text{C})$
3	216.6	221.2	
10	215.6	223.4	
60	211.3	225.5	238.5
180	211.4	227.0	239.4
500	210.5	228.6	240.3

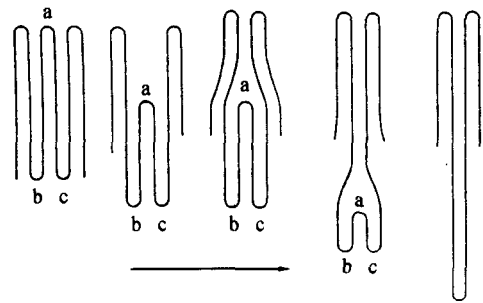


Fig. 11 Schemic representation of succes-
sive stages of the fold increase on
annealing

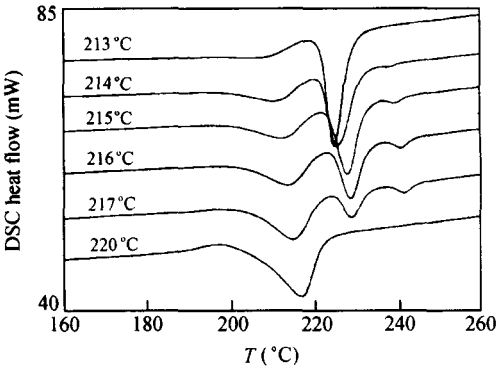


Fig. 12 Selected DSC scans of Nylon 610
RT sample after annealing for 60
min at the temperature indicated

To test the annealing temperature effect on peak 3, the nylon 610 samples were selected and undergone a 60 min anneal at specific temperatures varying from 213°C to 220°C. The resulting thermograms are shown in Fig. 12. It can be seen that peak 3 only appears for a certain temperature range (for the 60 min anneal, $214^{\circ}\text{C} \leq T_a < 220^{\circ}\text{C}$). When the annealing temperature is low, the molecular chain mobility is relatively low and the fold dislocation can't be formed. When T_a exceeds the higher end of melting range, peak 3 also disappears due to the melting of most original crystals. Therefore, the appearance of peak 3 requires annealing at the specific

temperatures, which must be high enough to give sufficient molecular mobility to allow the doubling or quadrupling of initial lamellae but not so high as to produce a considerable amount of melting of a major portion of the sample.

CONCLUSION

Nylon 610 has been shown to follow an Avrami behavior during isothermal crystallization from the melt. The Avrami exponent n was about 2. The equilibrium melting temperature of nylon 610 was determined to be $235^{\circ}\text{C} \sim 255^{\circ}\text{C}$. With the determined value of T_m° , the temperature dependence of the overall kinetic rate constant can be analyzed and the lateral and fold surface free energy were obtained to be 13 erg/cm^2 , $35 \sim 38 \text{ erg/cm}^2$ successively. Moreover, we have investigated melting behaviors of nylon 610 by changing heat treatment conditions. There exists only one endothermic peak in the DSC thermograms of nylon 610 quenched at room temperature, implying the existence of preexisting crystals before scanning. When quenched nylon 610 was annealed at temperatures between the glass temperature and melting point for 10 min, most of the DSC thermograms show two peaks. For low temperature anneal, the main endotherm remains almost constant, but a small endotherm 10°C above the annealing temperature arises. As the annealing temperature increases to the melting range, the low peak 1 can be explained that some of the original crystals melt and recrystallizes on cooling. The temperature of peak 2 can be raised to 227°C for 10 min anneal and further increases with increased annealing time. The increase of the melting point of annealed nylon 610 implies the reorganization of original crystals at high annealing temperatures. This organization can be explained by melt-recrystallization mechanism, which has been well applied to many crystalline polymers such as polyethylene. In addition, for quenched nylon 610 annealed for 1h above 213°C , an additional third melting peak 3 appears at about 240°C higher than peaks 1 and 2. This suggests the appearance of the more thickened crystals during annealing. Peak 3 is always about 12°C higher than the melting temperature of peak 2, independent of annealing temperature and time. The experimental results imply another lamellae thickening mechanism exists in quenched nylon 610 annealed at high temperature for relatively long time. The mechanism for fold increase of lamellae proposed by Keller and Burmester may be appropriate for the appearance of peak 3.

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