

A STUDY ON THE CRYSTALLIZATION KINETICS OF NYLON 1010*

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ABSTRACT

The kinetic behavior of isothermal and nonisothermal crystallization of nylon-1010 has been studied by means of dilatometry and differential scanning calorimetry, respectively. The isothermal and nonisothermal process can be described by Avrami equation and Ozawa equation, respectively. From the experimental results the kinetic parameters of crystallization and crystalline mechanism for isothermal and nonisothermal measurements are discussed.

INTRODUCTION

The problems of crystallization of polymers are of considerable interest, because the various properties of polymers depend on the size and shape of crystallites and on other morphological characteristics of the crystals. Nylon-1010 is one of the important engineering thermoplastics specifically produced by Chinese chemists and widely used in industry in China due to its excellent properties. In the recent years, the crystalline structure^[1-3], spherulitic morphology^[4,5] and some other properties^[6,7] of nylon-1010 have been reported. However, studies on the crystallization kinetics, whichever isotherms or nonisotherms^[8,9] for this polymer are limited. The crystallization kinetics of various polymers have been studied by many workers using X-ray diffraction, differential scanning calorimetry, dilatometry and polarizing optical microscopy. The present work aims to investigate the crystallization kinetics behavior of nylon-1010 by means of dilatometry for isotherms and differential scanning calorimetry (DSC) measurements for nonisotherms. From the experimental results obtained here, the crystallization parameters and mechanism of nylon-1010 are discussed. The understanding of the nonisothermal melt crystallization behavior of nylon-1010 leads to a better control of the final properties of the polymer, which is generally processed under nonisothermal conditions.

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EXPERIMENTAL

Material

Nylon-1010 polymer used in this work was a granular commercial product of Shanghai Chang Hong Plastic Work. Its inherent viscosity is 2.35 dl/g measured by viscometry in 96% sulfuric acid at 25°C.

Melting characteristics

The change in specific volume with temperature was measured by dilatometer. A weighed quantity of nylon-1010 was placed in a 15 mm diameter tube which formed the reservoir of the dilatometer. The dilatometer was filled under vacuum with clean mercury. The change in volume was measured by noting the change in the height of the mercury in the capillary with the aid of a cathetometer. The temperature of the bath was maintained at a constant temperature within $\pm 0.1^\circ\text{C}$. For each measuring temperature at least 15 min was allowed for the equilibration of temperature before the readings were taken.

Isothermal crystallization

The isothermal crystallization kinetics of nylon-1010 was investigated by measuring specific volume of specimens vs. the time at a constant temperature. In other words, the change of the height of mercury in the capillary during isothermal treatments in the range of 187.5—197.5°C was recorded. A dilatometer was used which has a bulb of 10 mm inner diameter and a length of 60 mm, the diameter of the capillary being 1.5 mm. The granular samples were inserted into the bulb, then a well-purified mercury was added under vacuum. The polymer samples were melted at 240°C for 20 min, under which any crystal nuclei were completely destroyed. This molten polymer was crystallized over the temperature range of 187.5—197.5°C. The temperatures of the crystallization bath were controlled within $\pm 0.05^\circ\text{C}$. Silicone oil was used as a bath liquid.

Nonisothermal crystallization

A Perkin Elmer differential scanning calorimeter, model DSC-7, was employed to study the nonisothermal crystallization kinetics of the polymer. Indium and zinc standards were used for temperature calibration. In the test the specimens were initially heated to 240°C, held 1 min at this temperature and then cooled to 50°C at various predetermined cooling rates. The cooling rates employed were 5, 10, 15, 20, 25 and 30°C/min, respectively.

RESULTS AND DISCUSSION

Melting characteristics

A plot of specific volume and temperature for nylon-1010 is given in Fig.1. The ordinate in this Figure is the changes in specific volume (ΔV) starting from that at 150°C. The temperature at which the last crystalline regions disappear is marked by a inflection point in the specific volume-temperature curve of the sample. We refer to this temperature as the crystalline melting point, T_m . It is obvious that the melting point of the crystalline region for nylon-1010 is 204°C.

Isothermal crystallization

The selection of the melt temperature is an important procedure for the measurement of the isothermal crystallization. Because the apparent overall rates of crystallization depend markedly on the melt temperature of polymers. However, when the crystalline temperature is higher, the effect of melt temperature is rather small^[10].

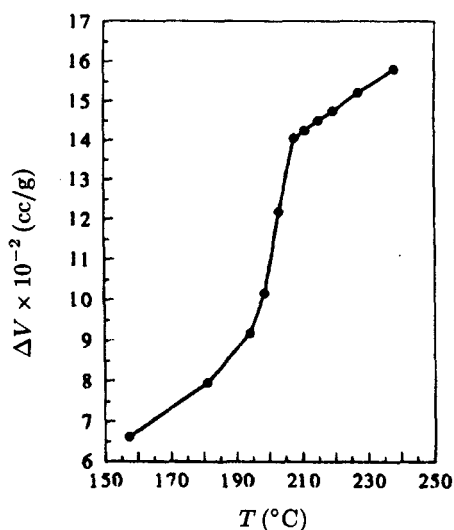


Fig.1 Relationship between specific volume and temperature for nylon-1010

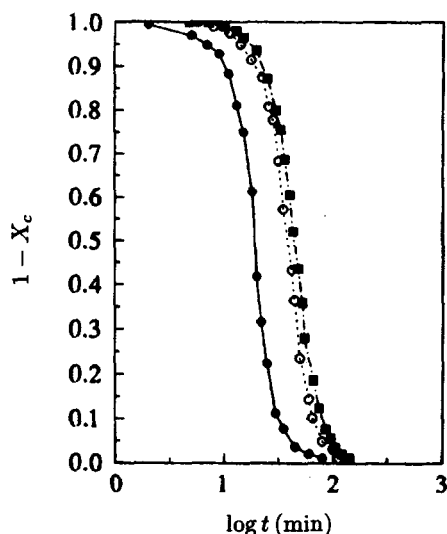


Fig.2 Crystallization isotherms of nylon-1010 at various melt temperatures, $T_c = 189.5^\circ\text{C}$
 • 200°C; ○ 220°C; ■ 240°C

Fig.2 shows the crystallization isotherms at various melt temperatures, the crystallization temperature is 189.5°C. It can be clearly seen that the effect of melt temperature decreases with increasing the melt temperature. In this case the effect of melt temperature above 220°C on the rate of crystallization can be neglected.

It implies that nylon-1010 is melted at 240°C for 20 min, under which any crystal nuclei are completely destroyed.

Almost ideal isothermal crystallization would be expected to occur for cases in which the melting temperature is about 240°C. Fig.3 shows the typical crystallization isotherm of nylon-1010 at different crystallization temperatures obtained from dilatometric measurement. The crystallization isotherm can be analyzed in terms of the Avrami equation^[11,12]

$$1 - X_t = (V_\infty - V_t)/(V_\infty - V_0) = \exp(-kt^n) \quad (1)$$

where X_t is the fraction of material crystallized after time t , V_t is the specific volume of the specimen at time t , V_0 and V_∞ are the values of specific volume of the specimen at $t = 0$ and $t = \infty$, respectively. The parameters k and n are related to the rate and mechanism of crystallization.

Fig.3 shows the plot of $(1 - X_t)$ vs. $\log t$ of the nylon-1010 specimen at various crystallization temperatures (T_c). It is apparent from this Fig.3 that the fraction of untransformed (amorphous) material has an inverted 'S' shape dependence on the logarithm of time as with the isothermal crystallization of other crystalline polymers. The curves can be superimposed on each other by an appropriate shift along the time axis. The Avrami exponent n can be obtained from the double logarithmic form of the Avrami equation

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

Fig.4 shows the plot of $\log[-\ln(1 - X_t)]$ vs. $\log t$ for the nylon-1010 specimen at various T_c . Obviously, such plot yield several straight lines with a slope of 3 for the crystalline temperature below 195°C and a slope of 4 for the crystalline temperature higher than 195°C of T_c . The parameter k can be determined from equation (1):

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

where $t_{1/2}$ is the half-time of crystallization, i.e., the time at which the various values of the specific volume of nylon-1010 specimen reaches one half of its final value. The value of $1/t_{1/2}$ are plotted against the crystallization temperature in Fig.5. These values change continuously as a function of the crystallization temperatures. The kinetic parameters of isothermal crystallization for nylon-1010 are listed in Table 1.

According to the Avrami theory, the exponent n depends on the geometry of crystal growth and on the type of nucleation. A thermal nucleation and spherulitic

growth lead to an Avrami exponent of 3, while thermal nucleation and spherulitic growth to a value of 4. Based on the experimental results as tabulated in the above tables, it is obvious that nylon-1010 exhibits an Avrami exponent of 4 in the region of higher crystallization temperatures. It may imply that the nylon-1010 shows homogeneous nucleation, followed by three dimensional spherulitic growth.

Table 1 Kinetic parameters of isothermal crystallization for nylon-1010

T ($^{\circ}\text{C}$)	t_i (min)*	$t_{1/2}$ (min)	n	k (min^{-n})
187.5	3	32	3	2.12×10^{-5}
189.5	6	44	3	8.14×10^{-6}
191.5	12	59	3	3.37×10^{-6}
193.4	18	82	3	1.25×10^{-6}
195.5	55	145	4	1.57×10^{-9}
197.8	120	331	4	5.78×10^{-11}

* t_i is crystallization induction time

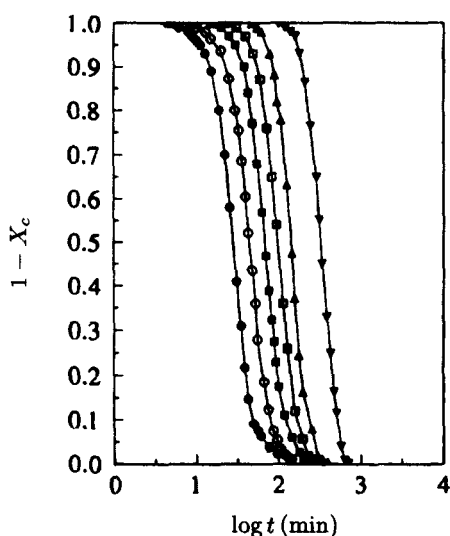


Fig.3 Plot of $(1 - X_t)$ vs. $\log t$ of nylon-1010 during isothermal crystallization at different temperatures

● 187.5 $^{\circ}\text{C}$; ○ 189.3 $^{\circ}\text{C}$; ■ 191.5 $^{\circ}\text{C}$;
□ 193.4 $^{\circ}\text{C}$; ▲ 195.5 $^{\circ}\text{C}$; ▼ 197.8 $^{\circ}\text{C}$

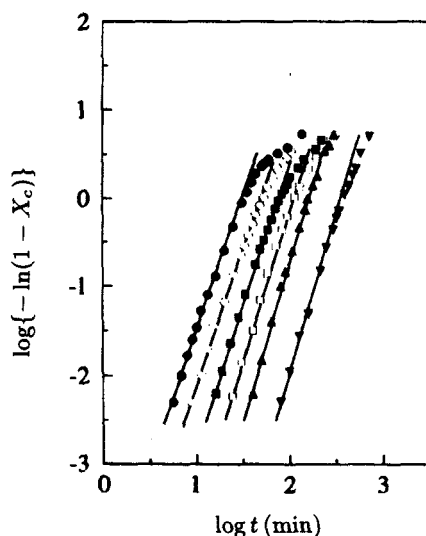


Fig.4 Plot of $\log\{-\ln(1 - X_t)\}$ vs. $\log t$ of nylon-1010 during isothermal crystallization at different temperatures

● 187.5 $^{\circ}\text{C}$; ○ 189.3 $^{\circ}\text{C}$; ■ 191.5 $^{\circ}\text{C}$;
□ 193.4 $^{\circ}\text{C}$; ▲ 195.5 $^{\circ}\text{C}$; ▼ 197.8 $^{\circ}\text{C}$

The influence of temperature on the rate of crystallization composed of nucleation and growth has been discussed by many authors^[13,14], and the overall crystallization rate expressed as $1/t_{1/2}$ can be correlated with temperature through a general

equation

$$\ln(1/t_{1/2}) = A - B_k(T_m^0)^k/T_c(\Delta T)^k \quad (4)$$

T_m^0 is the equilibrium temperature and $k = 1$ and 2 for different nucleation models. B_k is a parameter characterizing the difficulty of nucleation of crystallization process. In all cases the experimental data can fall into a straight lines for plots of $\ln(t_{1/2})$ vs. $T_m^0/T_c(\Delta T)$ and $T_m^0/T_c(\Delta T)^2$ as shown in Fig.6 by proper selection of the T_m^0 value. The slope B_k value of nylon-1010 is 23 for B_1 and 0.5 for B_2 , respectively. It is indicated to be consistent with those reported for conventional crystalline polymers^[13,14].

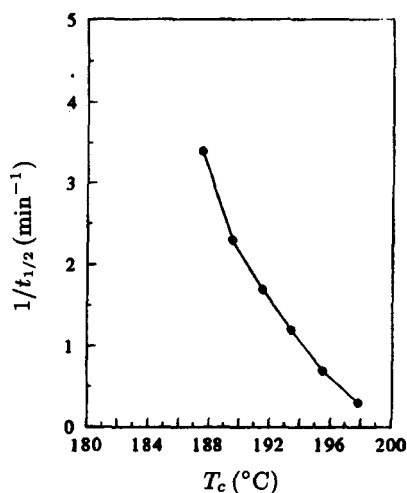


Fig.5 Half-time of crystallization vs. crystalline temperatures for nylon-1010

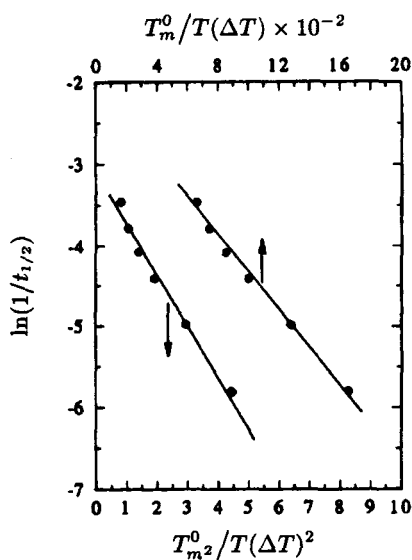


Fig.6 Plot of $\ln(t_{1/2})$ vs. $T_m^0/T_c(\Delta T)$ and $T_m^0/T_c(\Delta T)^2$ of nylon-1010 specimens

Non-isothermal crystallization

The nonisothermal crystallization of nylon-1010 was studied by DSC measurements. Ozawa^[15] has extended the isothermal kinetic crystallization to the non-isothermal case of controlled cooling rate. From the Evans model^[16], Ozawa has derived the following relationship:

$$X(T)/X_\infty = 1 - \exp[-k(T)/\lambda^n] \quad (5)$$

where $X(T)$ is the crystallinity attained at temperature T , X_∞ is the crystallinity at termination of the crystallization process, $k(T)$ is a constant for a given cooling rate, λ is the cooling rate and n is the Ozawa index. This index is somewhat similar

to the Avrami exponent, and it is depended on the type of nucleation and the growth dimensions. The double logarithmic form of the Ozawa equation exhibits the following relationship:

$$\log\{-\ln[1 - X(T)/X_\infty]\} = \log k(T) + m \log(1/\lambda) \quad (6)$$

Similarly, the plot of $\log\{-\ln[1 - X(T)/X_\infty]\}$ vs $\log(1/\lambda)$ at a fixed temperature should yield a straight line. The parameters n and $k(T)$ can be determined from the slope and the intercept of the line, respectively.

Fig.7 shows the typical DSC traces for the crystallization of nylon-1010 at various cooling rates. From the DSC profiles, the transformed fraction, $X(T)/X_\infty$, is calculated as a function of temperature. The variation of $X(T)/X_\infty$ vs. T for the nylon-1010 specimen at various cooling rates is shown in Fig.8. These curves are similar to that of crystallization isotherms as shown in Fig.3, namely, all these curves of relative crystallinity vs. temperature have essentially the same shape and they can be super-

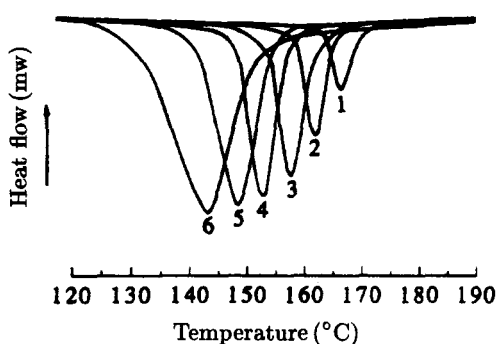


Fig.7 DSC cooling traces of nylon-1010 during nonisothermal crystallization at different cooling rates

- (1) 5°C/min; (2) 10°C/min;
(3) 15°C/min; (4) 20°C/min;
(5) 25°C/min; (6) 30°C/min

Table 2 Kinetic parameters of nonisothermal crystallization for nylon-1010

T_c (°C)	m	k (min ^{-m})
145.0	3.6	8.1×10^{-3}
147.5	3.5	2.2×10^{-3}
150.0	3.7	6.1×10^{-4}
152.5	3.9	1.3×10^{-4}
155.0	3.8	5.0×10^{-5}
157.5	3.1	2.5×10^{-5}
160.0	2.8	8.2×10^{-6}

imposed by an appropriate shift along the time axis. This result indicates that the kinetics of the nonisothermal crystallization of nylon-1010 is in good agreement with the Ozawa equation. At a given temperature, it appears that only three cooling rates are used in the plots of double logarithmic form of the Ozawa equation. The plot of $\log\{-\ln[1 - X(T)/X_\infty]\}$ vs. $\log(1/\lambda)$

for the nylon-1010 specimen at various temperatures is shown in Fig.9. Similarly, these plots yield several straight lines with the slopes m and k value. The kinetic

parameters of nonisothermal crystallization of nylon-1010 are listed in Table 2.

On the basis of nonisothermal crystallization measurements, the Ozawa exponent m of nylon-1010 specimens have values between 2.8 and 3.9 at the range of the crystallization temperatures in this work. It is noted that the m value of nylon-1010 is 3.4 on average. This value of m is in very good agreement with that determined isothermally. Therefore, the Ozawa's theory has shown to be a good method to analyse data corresponding to non-isothermally crystallized nylon-1010. Although this method presents some possible limitations yet, it is a simple method to describe the non-isothermal crystallization of the polymers.

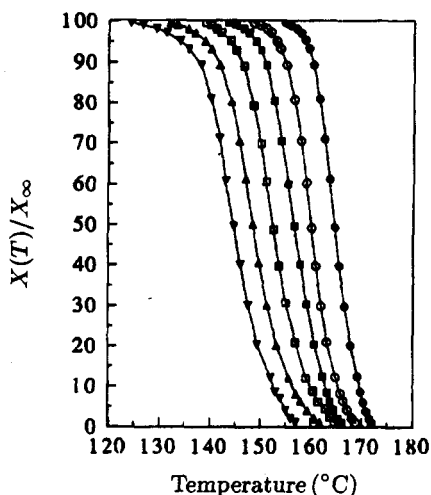


Fig.8 Plot of $[X(T)/X_\infty]$ vs. T of nylon-1010 during nonisothermal crystallization at different cooling rates

- 5°C/min; ○ 10°C/min;
- 15°C/min;
- 20°C/min; ▲ 25°C/min;
- ▼ 30°C/min

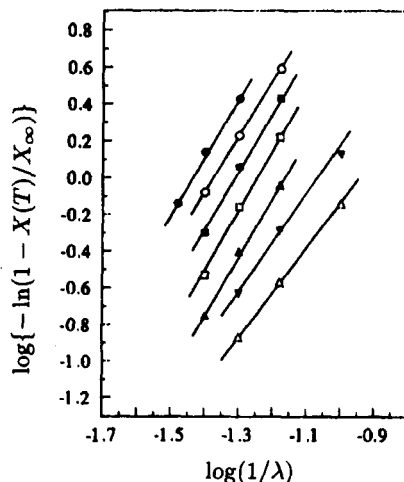


Fig.9 Plot of $\log\{-\ln[1 - (X(T)/X_\infty)]\}$ vs. $\log(1/\lambda)$ of nylon-1010 specimen during nonisothermal crystallization at various temperatures

- 145.0°C; ○ 147.5°C; ■ 150.0°C;
- 152.5°C; ▲ 155.0°C; ▼ 157.5°C;
- △ 160.0°C

Keywords:

Crystallization kinetics; Nylon-1010; Dilatometry; Differential scanning calorimetry

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