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Non-isothermal crystallization kinetics of Nylon 10T and Nylon 10T/1010 copolymers: Effect of sebacic acid as a third comonomer☆

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ABSTRACT

Nylon 10T and Nylon 10T/1010 samples were synthesized by direct melt polymerization. The non-isothermal crystallization kinetics of Nylon 10T and Nylon 10T/1010 was investigated by means of differential scanning calorimetry (DSC). Jeziorny equation and Mo equation were applied to describe the non-isothermal crystallization kinetics of the Nylon 10T and the Nylon 10T/1010. The activation energies for non-isothermal crystallization were obtained by Vyazovkin's method and Friedman's method, respectively. These results showed that Jeziorny equation and Mo equation well described the non-isothermal crystallization kinetics of the Nylon 10T and the Nylon 10T/1010. It was found that the values of the activation energy for non-isothermal crystallization of the Nylon 10T/1010 were lower than those of the Nylon 10T at a given temperature or relative crystallinity degree, which revealed that crystallization ability of the Nylon 10T/1010 was higher. The crystal morphology was observed by means of a polarized optical microscope (POM) and X-ray diffraction (XRD). It was found that the addition of sebacic acid comonomer not only did not change the crystal form of the Nylon 10T, but also significantly increased the number and decreased the size of spherulites. Comparing with the Nylon 10T, the crystallization rate was increased with the addition of the sebacic acid comonomer.

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1. Introduction

Nylons, also known as polyamides, are a series of engineering thermoplastics used widely in a variety of applications [1,2]. They can be economically produced by melt processing, but their poor thermal properties, poor dimensional stability and high water absorption impose limitations on successful applications in some industrial and other fields, especially in the LED reflector, the shell of automobile engine and the surface mount technology (SMT) [3]. For improving the thermal properties of nylons, aromatic rings are incorporated into the backbone of them, such as poly(hexamethylene terephthalamide) (Nylon 6T) copolymers [4,5], poly(nonamethylene terephthalamide) (Nylon 9T) [6,7], poly(decamethylene terephthalamide) (Nylon 10T) [8,9], poly(dodecamethylene terephthalamide) (Nylon 12T) [10,11]. Nylon 10T, a condensation type polymer containing 1,10-decanediamine and terephthalic acid, is a good engineering plastic with good thermal durability and low water absorption. However, Nylon 10T has a high

melting point, as high as 315 °C [12], which is close to the decomposition temperature, and hence the melt processing window is narrow so as to limit its industrial processing and application. Sebacic acid comonomer can be used to reduce melting temperature of Nylon 10T and meanwhile mechanical properties of poly(decamethylene terephthalamide/decamethylene decanediamide) (Nylon 10T/1010) are maintained. Furthermore, 1,10-decanediamine and sebacic acid are two types of important raw material to synthesize Nylon 10T/1010 and can be obtained from the product of castor oil, which can be prepared by castor seeds [13]. Therefore Nylon 10T/1010 is a type of biological source material [14].

It is well known that the properties of semi-crystalline polymers, such as nylons, are strongly depending on their crystalline structure, degree of crystallization and morphologies, which are significantly controlled by the crystallization process during the polymer molding process [15]. Furthermore, practical process such as extrusion molding and injection molding usually is performed under dynamic and non-isothermal crystallization conditions [16–20]. In this study, sebacic acid was evaluated as a third comonomer for Nylon 10T/1010. Nylon 10T and Nylon 10T/1010 samples were synthesized by direct melt polymerization. In order to optimize processing conditions of Nylon 10T/1010 in industrial applications and achieve better properties, it is necessary to study the non-isothermal crystallization process quantitatively. Although some studies have synthesized a series of semiaromatic

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polyamides, few of these studies involve the crystallization kinetics of Nylon 10T and Nylon 10T/1010 [2,3,8,9]. For this reason, non-isothermal crystallization kinetics study, from differential scanning calorimetric measurements, was performed.

In this work, Jeziorny and Mo equations were applied to obtain the non-isothermal crystallization kinetics of the Nylon 10T and the Nylon 10T/1010. Moreover, the activation energies for non-isothermal crystallization were calculated as a function of the temperature or the relative crystallinity degree by using Vyazovkin's method or Friedman's method. Finally, the crystal morphology was observed by means of polarized optical microscope (POM) and X-ray diffraction (XRD).

2. Experimental Section

2.1. Materials

Terephthalic acid and benzoic acid were purchased from Beijing Yanshan Lithification Chemical Co. Ltd. (China). 1,10-decanediamine and sebacic acid were provided commercially by Wuxi Xinda Nylons Co. Ltd. (China).

2.2. Synthesis

Nylon 10T/1010 was synthesized via direct melt polymerization which included three reaction processes of prepolymerization, final polycondensation and viscosity increasing reaction, as shown in Fig. 1.

1,10-Decanediamine (172.3 g, 1 mol), terephthalic acid (149.5 g, 0.9 mol), sebacic acid (20.2 g, 0.1 mol) and benzoic acid (6.1 g, 0.05 mol) were added into a polymerization kettle and distilled water (150 g) was added to reduce volatilization of diamine during the polymerization. Benzoic acid was as inhibitor in order to control the molecular weight of Nylon 10T/1010. The polymerization kettle was filled with nitrogen at room temperature and then heated 275 °C in 3 h, meanwhile the pressure was up to 2.0 MPa. After 1.5 h, the pressure of the polymerization kettle was gradually decreased to atmospheric pressure in 1 h by deflating and the reaction temperature of the polymerization kettle was increased to 310 °C. After reaction for another 0.5 h, the pressure of the polymerization kettle was evacuated to -0.099 MPa and the viscosity increasing reaction was kept for 0.3 h. Finally, the polymerization kettle was cooled to room temperature and Nylon 10T/1010 was obtained (327 g, 94%).

Nylon 10T has been prepared by the similar procedures only using 1,10-decanediamine (172.3 g, 1 mol), terephthalic acid (166.1 g, 1 mol) and benzoic acid (6.1 g, 0.05 mol). And Nylon 10T was obtained (320 g, 93%). The intrinsic viscosity values ($[\eta]$) of the Nylon 10T and the Nylon 10T/1010 were 83 and 87 $\text{ml} \cdot \text{g}^{-1}$, respectively.

2.3. Characterization

2.3.1. Intrinsic viscosity

The intrinsic viscosities of the Nylon 10T and Nylon 10T/1010 were determined in concentrated sulphuric acid with an Ubbelohde viscometer at $(25 \pm 0.1)^\circ\text{C}$.

2.3.2. FT-IR

FT-IR was recorded on a Japan Shimadzu 8400S spectrometer. The samples were prepared by melting pressed-disk.

2.3.3. Differential scanning calorimetry

The non-isothermal crystallization was carried out by using a Switzerland Mettler Toledo 822e differential scanning calorimeter. All DSC measurements were performed under a nitrogen atmosphere. The weight of the samples was approximately 3 mg. The thermal history of the samples was eliminated by heating the samples at 330 °C for a period of 5 min. In the non-isothermal crystallization process, the cooling scans were conducting at rates of 2.5, 5, 10, 20 and 40 $^\circ\text{C} \cdot \text{min}^{-1}$ from 330 °C to 30 °C.

2.3.4. Polarized optical microscopy

Polarized optical microscopy (POM) images were obtained by using a Shanghai optical instruments factory XPT-7 microscope. Nylon 10T and Nylon 10T/1010 samples were observed in thin films prepared between microscope coverslips by melting the polymer at 315 °C for 2 min and then rapidly cooling to the crystallization temperature in a automatic hot stage. The Nylon 10T and the Nylon 10T/1010 isothermally crystallized for 0.5 h at the temperature of 269 and 260 °C, respectively. The images were recorded after complete crystallization.

2.3.5. X-ray diffraction

The crystal structures of the Nylon 10T and the Nylon 10T/1010 were examined by a Japan Rigaku Industrial Corporation D/max-RB X-ray diffractometer using X-ray tube (40 kV, at 100 mA) and $\text{Cu K}\alpha$ radiation at ambient temperature. The scanning rate was set as 5°min^{-1} in the range from 5° to 50° . The XRD data can be analyzed by using MDI Jade 5.0 software from American Materials Data Corporation.

3. Results and Discussion

3.1. Fourier transform infrared spectra

FT-IR spectra of the Nylon 10T/1010 salt and the Nylon 10T/1010 are shown in Fig. 2. The characteristic peaks of the Nylon 10T/1010 salt are listed as follows: 3392 cm^{-1} (NH_3^+ , N-H stretching vibration),

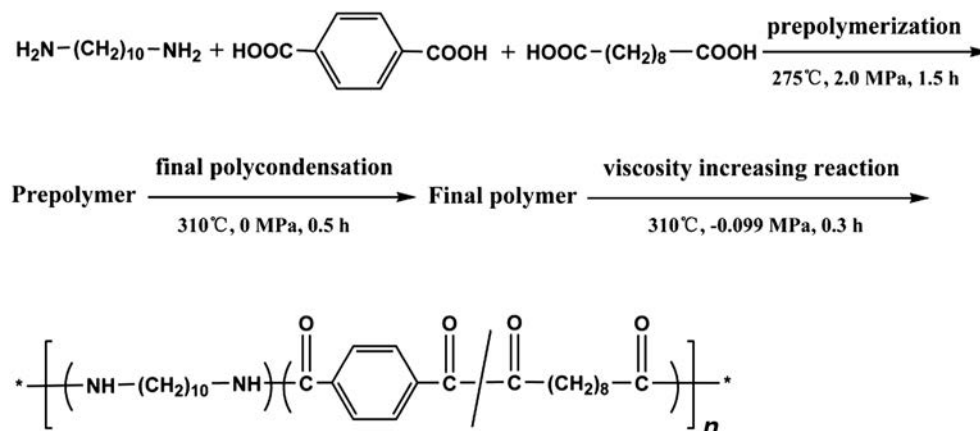


Fig. 1. Schematic representation of the polymerization processes of the Nylon 10T/1010.

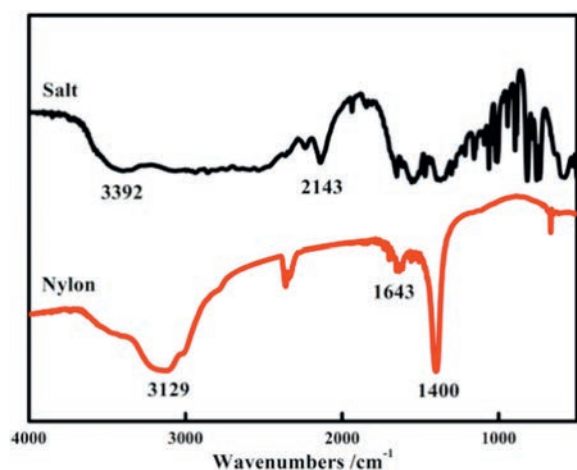


Fig. 2. FT-IR spectra of the Nylon 10T/1010 salt and the Nylon 10T/1010.

2143 cm^{-1} (NH_3^+ , the absorption peaks of frequency doubling and combination band). The characteristic peaks of amide groups of the Nylon 10T/1010 are listed as follows: 3129 cm^{-1} (hydrogen-bonded and N–H stretching vibration), 1643 cm^{-1} (C=O stretching vibration), 1400 cm^{-1} (C–N stretching and CO–N–H bending vibration). Comparing with the FT-IR spectra of the Nylon 10T/1010 salt, the characteristic absorption peaks of the Nylon 10T/1010 around 2143 cm^{-1} (NH_3^+) have disappeared. The results indicate that Nylon 10T/1010 can be synthesized via direct melt polymerization, which are in accordance with the description of Fig. 1.

3.2. Non-isothermal crystallization behaviors

The non-isothermal crystallization curves of the Nylon 10T and the Nylon 10T/1010 at various cooling rates are shown in Fig. 3. From Fig. 3, it is evident that by increasing cooling rate the crystallization peak temperature is decreased and the peak becomes broader. The result indicates that at lower cooling rate the polymer chains have sufficient time to move from polymer melt to crystallization, and meanwhile the crystallization can occur at higher temperature [21]. The motion of polymer chains cannot follow the cooling rate, when the cooling rate becomes high. Thus, more super-cooling degree is needed in order to crystallize and the crystallization peak becomes broader at higher cooling rate [22].

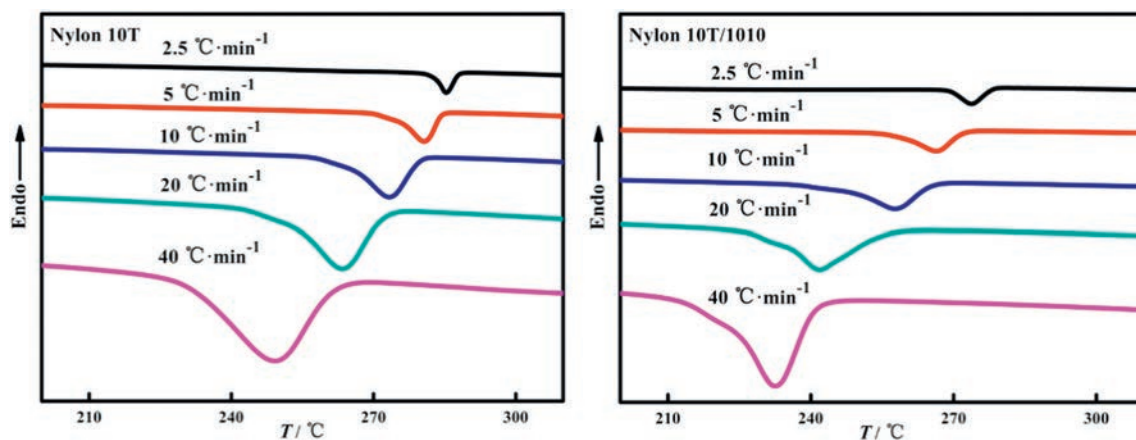


Fig. 3. Heat flow versus temperature during non-isothermal crystallization of the Nylon 10T and the Nylon 10T/1010 at different cooling rates by DSC.

At various cooling rates, the values of the relative crystallinity can be calculated on the basis of the DSC curves. The relative crystallinity as a function of temperature can be defined as [23]:

$$X(t) = \frac{\int_{T_0}^T \frac{dH_c(T)}{dT} dT}{\int_{T_0}^{T_\infty} \frac{dH_c(T)}{dT} dT} \quad (1)$$

where dH_c denotes measured enthalpy of crystallization, T_0 is the initial crystallization temperature and T_∞ is the end crystallization temperature. The instantaneous crystallization temperature T can be converted to crystallization time t by using the relationship for non-isothermal crystallization process at a constant cooling rate [24], as below:

$$t = \frac{|T_0 - T|}{\phi} \quad (2)$$

where ϕ is the cooling rate. The relative crystallinity $X(t)$ of the Nylon 10T and the Nylon 10T/1010 is plotted in Fig. 4 with respect to crystallization time t at different cooling rates, and the curves of plots have similar sigmoidal shapes. The curvatures of the lower and upper parts of the curves are caused by the formation of nuclei and the spherulitic impingement in the later stages of crystallization, respectively. Meanwhile, through Fig. 4, we can get the half-time of non-isothermal crystallization $t_{1/2}$, when the $X(t)$ is equal to 50%. The crystallization peak temperature T_p , the crystallization enthalpies ΔH and the half-time of crystallization $t_{1/2}$ at different cooling rates are shown in Table 1. The $t_{1/2}$ suggests that the higher the cooling rate, the shorter the time of crystallization completion.

3.3. Jeziorny equation

Based on the assumption that the crystallization temperature was constant, Mandelkern [25] considered that the primary stage of non-isothermal crystallization could be described by the Avrami equation. Jeziorny [26] modified the crystallization rate Z_t in Avrami equation via dividing by cooling rate ϕ to incorporate the temperature change during the non-isothermal crystallization process, as follows:

$$\lg[-\ln(1-X(t))] = n \lg t + \lg Z_t \quad (3)$$

$$\lg Z_c = \frac{\lg Z_t}{\phi} \quad (4)$$

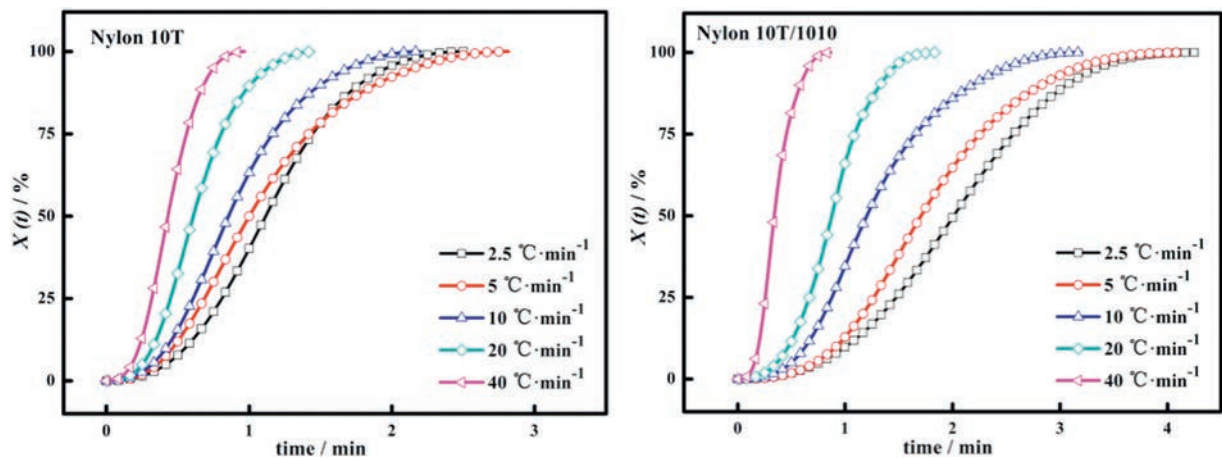


Fig. 4. Development of relative crystallinity with crystallization time of the Nylon 10T and the Nylon 10T/1010.

Table 1
The values of T_p , ΔH and $t_{1/2}$ in non-isothermal crystallization for the Nylon 10T and the Nylon 10T/1010

Sample	$\phi/^\circ\text{C}\cdot\text{min}^{-1}$	$T_p/^\circ\text{C}$	$\Delta H/\text{J}\cdot\text{g}^{-1}$	$t_{1/2}/\text{min}$
Nylon 10T	2.5	285.34	−24.45	1.11
	5	280.63	−39.10	1.00
	10	273.25	−43.16	0.86
	20	263.31	−41.12	0.61
	40	249.49	−41.57	0.43
Nylon 10T/1010	2.5	273.77	−38.48	2.01
	5	266.38	−43.12	1.70
	10	257.68	−41.21	1.20
	20	241.79	−37.56	0.88
	40	232.27	−36.73	0.34

Table 2
The values of n_1 , Z_{t1} , Z_{c1} , n_2 , Z_{t2} and Z_{c2} for the Nylon 10T and the Nylon 10T/1010 during non-isothermal crystallization

Sample	$\phi/^\circ\text{C}\cdot\text{min}^{-1}$	Primary crystallization stage			Secondary crystallization stage		
		n_1	Z_{t1}	Z_{c1}	n_2	Z_{t2}	Z_{c2}
Nylon 10T	2.5	2.48	0.46	0.73	2.58	0.53	0.78
	5	2.64	0.78	0.95	1.83	0.72	0.94
	10	2.63	1.05	1.00	2.14	0.98	1.00
	20	2.88	2.85	1.05	2.32	2.28	1.04
	40	2.88	7.62	1.05	2.80	6.84	1.05
Nylon 10T/1010	2.5	2.52	0.10	0.40	2.86	0.09	0.39
	5	2.86	0.14	0.67	2.42	0.19	0.72
	10	2.93	0.41	0.91	2.01	0.50	0.93
	20	2.64	0.77	0.99	2.79	1.08	1.00
	40	3.27	24.14	1.08	2.20	7.70	1.05

where Z_t and Z_c are the rate constant in the non-isothermal crystallization process. According to Eq. (3), plots of $\lg[-\ln(1 - X(t))]$ versus $\lg t$ are shown in Fig. 5. The values of n and Z_t are determined from the slope and intercept of the plots, respectively, which are listed in Table 2. As shown in Fig. 5, all curves are divided into the following 2 sections the primary crystallization stage and the secondary crystallization stage. At the primary crystallization stage, the n_1 values for the Nylon 10T and the Nylon 10T/1010 range from 2.48 to 2.88 and 2.52 to 3.27, respectively, which mean the addition of the sebacic acid comonomer slightly influenced the mechanism of nucleation and the growth of the Nylon 10T crystallites. These results also indicate that the mode of

the nucleation and growth at the primary crystallization stage of the non-isothermal crystallization for the Nylon 10T and the Nylon 10T/1010 may be two-dimensional, circular, diffusion controlled growth with thermal nucleation. At the secondary crystallization stage, the n_2 values are in the range of 1.83–2.80 for the Nylon 10T and 2.01–2.86 for the Nylon 10T/1010. These results reveal that the nucleation and growth at the secondary crystallization stage of the non-isothermal crystallization for the Nylon 10T and the Nylon 10T/1010 may transform into a mixture mode of one-dimensional and two-dimensional space extension because of the spherulitic impingement

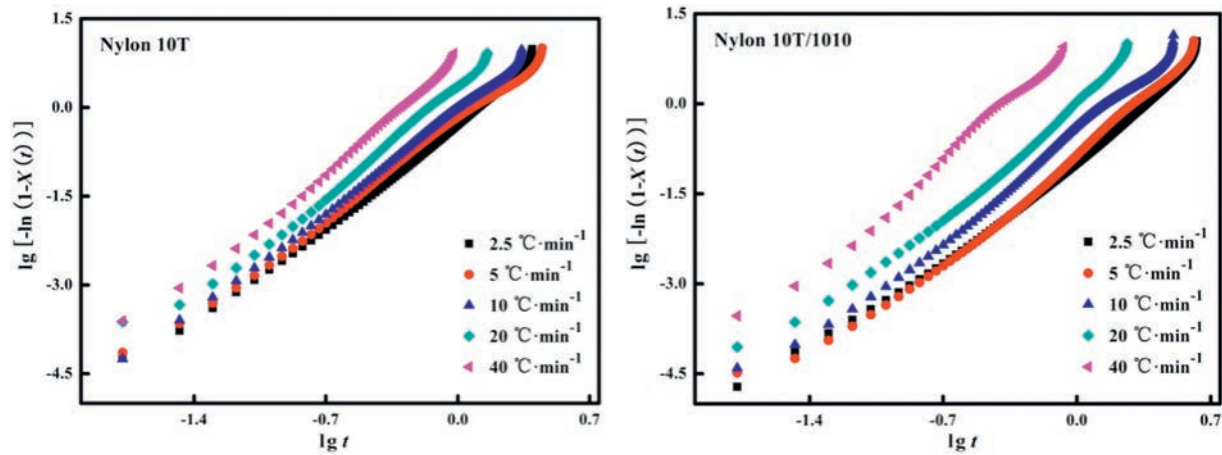


Fig. 5. Plots of $\lg[-\ln(1 - X(t))]$ versus $\lg t$ for non-isothermal crystallization process of the Nylon 10T and the Nylon 10T/1010.

and crowding. Besides, the larger the Z_c value was, the higher the crystallization rate became. At a given cooling rate (excepting $40^\circ\text{C}\cdot\text{min}^{-1}$), the higher Z_c of the Nylon 10T than that of the Nylon 10T/1010 indicated that the sebacic acid comonomer might hinder the crystallization of the Nylon 10T.

3.4. Mo equation

Mo *et al.* [27,28] proposed a new method to analyze the non-isothermal crystallization kinetics of polymers by combining the Avrami and Ozawa equations together, as follows [29–32]:

$$\lg \Phi = \lg F(T) - a \lg t \quad (5)$$

where the parameter $F(T) = [K_T / Z_c]^{1/m}$ refers to the value of the cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity [33]. And a is equal to the Avrami exponent n divided by the Ozawa exponent m . The plots of $\lg \Phi$ versus $\lg t$ for the Nylon 10T and the Nylon 10T/1010 are shown in Fig. 6. Good linear relationship between $\lg \Phi$ and $\lg t$ can be obtained from Fig. 6, indicating that the Mo equation can describe well the non-isothermal crystallization for the Nylon 10T and the Nylon 10T/1010. Values of α and $\lg F(T)$ are obtained from the slope and intercept of these lines, respectively, which are presented in Table 3. For each sample, the a values changed slightly with the relative crystallinity degree, and the $F(T)$ values increased as the relative crystallinity degree increased. The smaller the value of $F(T)$ was, the higher the crystallization rate became. Thus, at a given relative crystallinity degree, the $F(T)$ values of the Nylon 10T/1010 were higher than those of the Nylon 10T, which meant that the sebacic acid comonomer might hinder the crystallization of the Nylon 10T. The results were consistent with those obtained from Jeziorny equation.

3.5. Non-isothermal crystallization activation energy

Usually, the activation energy of non-isothermal crystallization could be calculated by the Kissinger equation [34]. Recently, Vyazovkin [35] has demonstrated that the Kissinger equation provides invalid results when applied to the processes of non-isothermal crystallization. Another disadvantage of Kissinger equation was that it was applicable only to single-step processes, and meanwhile the non-isothermal crystallization kinetics might be adequately represented by a single value for activation energy. However, the rate of crystallization was generally determined by the rates of nucleation and crystal growth, whose

Table 3

The values of a and $F(T)$ versus degree of crystallinity based on Mo equation for the Nylon 10T and the Nylon 10T/1010

Sample	$X(t)/\%$	20	40	50	60	80
Nylon 10T	α	2.95	2.74	2.73	2.68	2.54
	$F(T)$	1.27	3.37	4.68	6.53	12.47
Nylon 10T/1010	α	1.51	1.49	1.50	1.48	1.48
	$F(T)$	6.02	9.15	10.79	12.39	17.42

activation energy was likely to be different with the change of temperature [36]. That was because the temperature of non-isothermal crystallization had great influence on the activation energy. Based on their experimental analysis, Vyazovkin *et al.* [37] modified the Lauritzen–Hoffman equation, thus the activation energy of non-isothermal crystallization could be calculated using the following equation:

$$E_a(T) = U^* \frac{T^2}{(T - T_\infty)^2} + K_g R \frac{T_m^{0^2} - T^2 - T_m^0 T}{(T_m^0 - T)^2 T} \quad (6)$$

where U^* is the diffusional activation energy for the transport of segments to the crystallizable site at the liquid–solid interface taken as $6280 \text{ J}\cdot\text{mol}^{-1}$ [38]. T_∞ is the hypothetical temperature where all motion associated with viscous flow ceases, which is usually assumed to be equal to $(T_g - 30) \text{ K}$. T_m^0 is the equilibrium melting point. The values of T_m^0 for the Nylon 10T and the Nylon 10T/1010 are 589.33 and 595.48 K, respectively. R is the universal gas constant. K_g is the nucleation parameter that reflects the regime behavior. The values of K_g for the Nylon 10T and the Nylon 10T/1010 are 85,322 and 127,871 K^2 , respectively. The curves of $E_a(T)$ versus T for the Nylon 10T and the Nylon 10T/1010 are presented in Fig. 7. $E_a(T)$ is the sum of the activation energy for the nucleation and crystal growth in the non-isothermal crystallization process. The lower $E_a(T)$ was, the faster the crystallization rate became. As shown in Fig. 7, the rate of crystallization decreased with decreasing temperature. At a given temperature, the values of $E_a(T)$ for the Nylon 10T/1010 were lower than those of the Nylon 10T, which revealed that crystallization ability of the Nylon 10T/1010 is higher, since the sebacic acid comonomer may improve the mobility of polymer chains. Such a result is different from the results of the Jeziorny and Mo equations. This also shows that the non-isothermal crystallization process of the Nylon 10T/1010 is more complicated than that of the Nylon 10T.

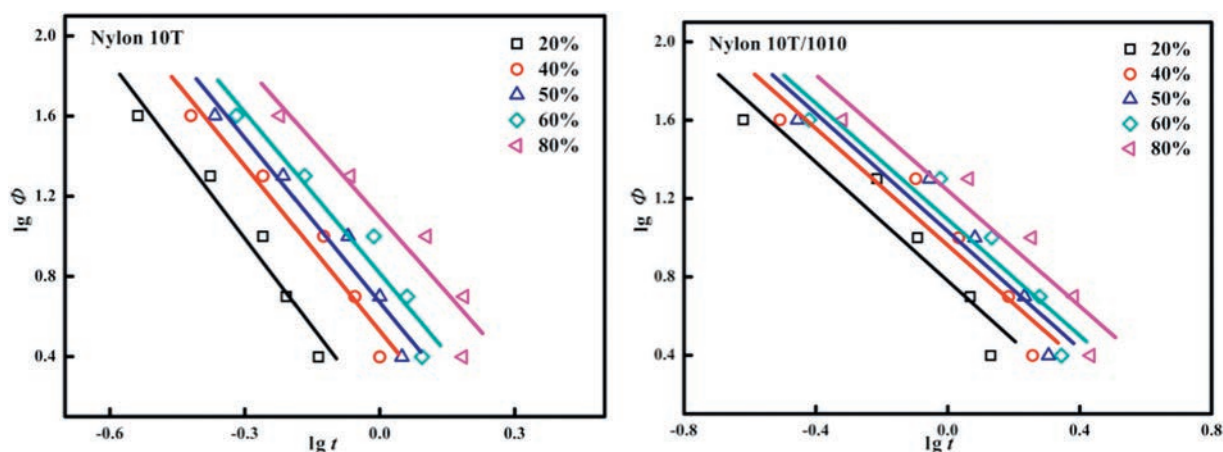


Fig. 6. Plots of $\lg \Phi$ versus $\lg t$ from the Mo equation for non-isothermal crystallization of the Nylon 10T and the Nylon 10T/1010.

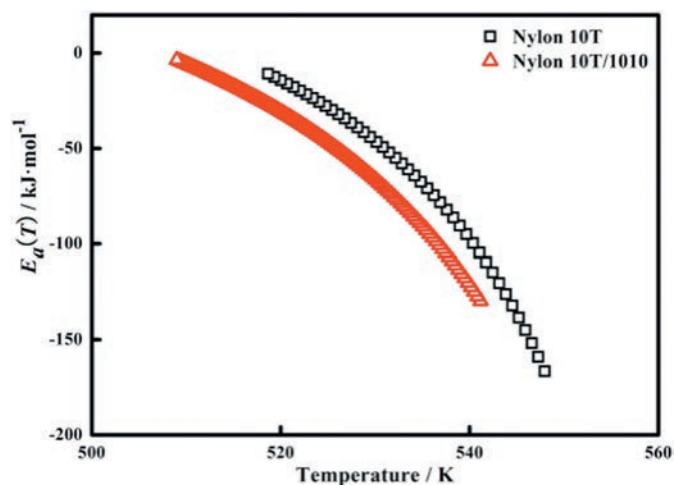


Fig. 7. Plots of $E_a(T)$ versus T for the Nylon 10T and the Nylon 10T/1010 during non-isothermal crystallization.

Apart from Vyazovkin's method, the differential isoconversional method of Friedman [39] is one of the most appropriate methods for evaluating the effective activation energy, which bases on the differentiation of Arrhenius equation [40]. In this work, the Friedman's method was used, largely because of the simplicity and reliability of the method. The Friedman equation can be expressed as follows [41,42]:

$$\ln \left(\frac{dX}{dt} \right)_{X,i} = \text{constant} - \frac{\Delta E_X}{RT_{X,i}} \quad (7)$$

where dX/dt is the instantaneous crystallization rate as a function of time at a given conversion X and ΔE_X is the activation energy in the non-isothermal crystallization process. R is the gas constant. $T_{X,i}$ is the set of temperatures related to a given conversion X at different cooling rates ϕ and the subscript i refers to every individual cooling rate used [43]. Furthermore, by selecting appropriate degrees of crystallinity (i.e. from 10% to 90%, each step increased by 20%) the values of dX/dt at a specific X are correlated to the corresponding crystallization temperature at this X , that is T_X [44]. The plots of $\ln(dX/dt)$ versus $1/T_X$ are illustrated in Fig. 8. ΔE_X can be calculated from the slopes of these lines of Fig. 8, which are shown in Fig. 9. Generally, the values of ΔE_X for the Nylon 10T and the Nylon 10T/1010 increased with an increase in relative crystallinity degree, which meant that as the crystallization progresses it was more difficult from

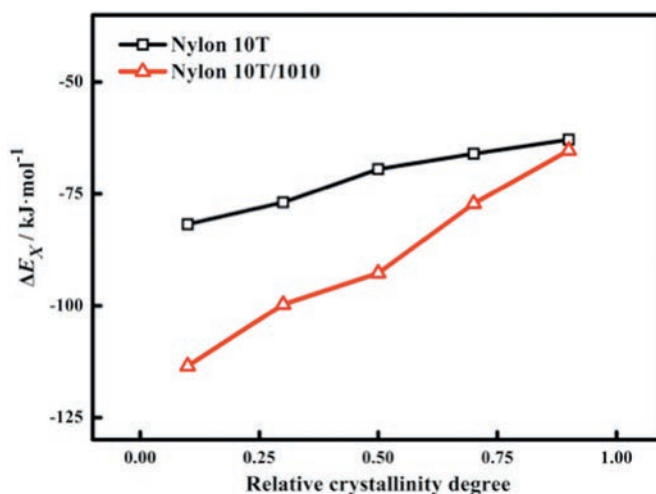


Fig. 9. Non-isothermal crystallization activation energy as a function of the relative crystallinity for the Nylon 10T and the Nylon 10T/1010.

polymer melt to crystallization. Also similar to the results of Vyazovkin's method, at a given relative crystallinity, the values of ΔE_X for the Nylon 10T/1010 were lower than those of the Nylon 10T, suggesting that crystallization ability of the Nylon 10T/1010 is higher with the addition of the sebacic acid comonomer.

3.6. Crystal morphology

Polarization microscope images of the Nylon 10T and the Nylon 10T/1010 are shown in Fig. 10. In order to observe and compare with the crystal morphology of samples clearly during the isothermal crystallization process, we chose the middle temperature of the range of isothermal crystallization experiment to observe by means of POM. The Nylon 10T and the Nylon 10T/1010 isothermally crystallized for 0.5 h at the temperature of 269 and 260 °C, respectively. It was found that typical spherulitic structure could hardly be observed by the Maltese cross in the images. From a comparison of the two photographs, the Nylon 10T contains relatively large crystalline grains, whereas a dense granular texture of crystals is formed for the Nylon 10T/1010 and the size of crystalline grains becomes smaller. It is clear that the number of crystal nuclei is increased and the growth rate of crystalline grains is decreased by the addition of the sebacic acid comonomer, considering the results of Fig. 10. Because the symmetry and regularity of the polymer chains are destroyed by the sebacic acid comonomer for

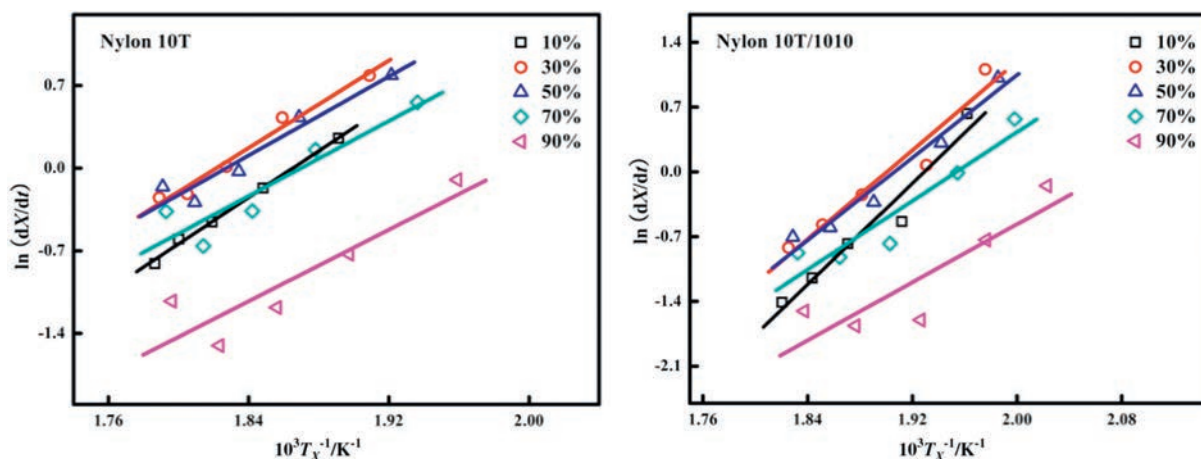


Fig. 8. Friedman-plots of $\ln(dX/dt)$ versus $1/T_X$ for the Nylon 10T and the Nylon 10T/1010 at different relative degrees of crystallinity during non-isothermal crystallization.

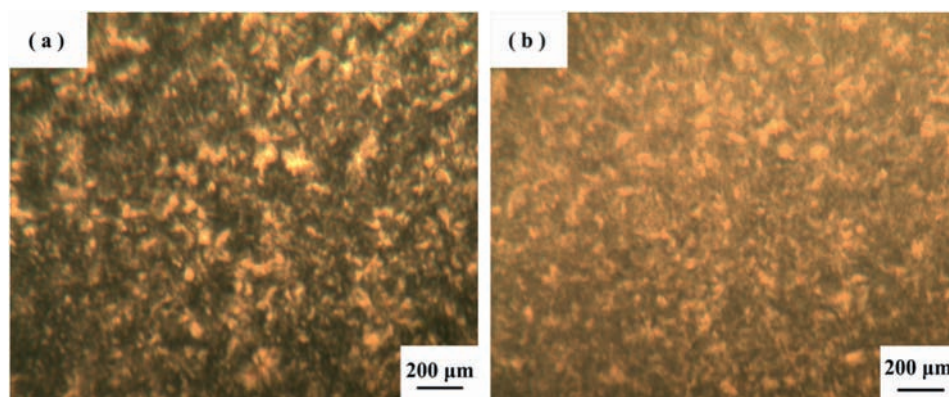


Fig. 10. Crystal morphology of samples by POM: (a) the Nylon 10T, observed at 269 °C; (b) the Nylon 10T/1010, observed at 260 °C.

the Nylon 10T/1010, its intracrystalline flaw is increased and crystal growth is restricted.

XRD patterns of the Nylon 10T and the Nylon 10T/1010 are presented in Fig. 11. According to the Bragg equation, the typical diffraction peaks of the Nylon 10T and the Nylon 10T/1010 are at 20.96 and 20.65°, which correspond to interplanar spacing of about 0.423 and 0.430 nm, respectively. Comparing with the Nylon 10T, the characteristic peaks of the Nylon 10T/1010 are almost unchanged. This indicates that the addition of sebacic acid comonomer into the Nylon 10T does not change its crystalline form. All XRD data is listed in Table 4. The absolute crystallinity is calculated by the area of the crystalline peaks divided by total area under the diffraction curve using MDI Jade 5.0 software from American Materials Data Corporation. From Table 4, compared with the Nylon 10T, it was observed that the size of crystalline grains of the Nylon 10T/1010 decreased, which was consistent with the results of POM. Meanwhile, the absolute crystallinity of the Nylon 10T/1010 increased, that was to say that the crystallization rate increased. The results suggest that even though the crystal growth of the Nylon 10T/1010 is restricted,

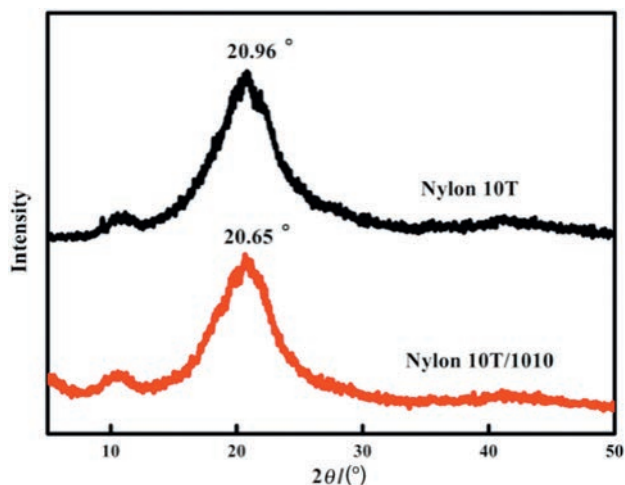


Fig. 11. XRD patterns of the Nylon 10T and the Nylon 10T/1010.

Table 4

The XRD data of the Nylon 10T and the Nylon 10T/1010 by the MDI Jade 5.0

Sample	2θ/(°)	Interplanar spacing/nm	Intensity	Spherulitic size/nm	Absolute crystallinity/%
Nylon 10T	20.96	0.423	2196	15.2	9.59
Nylon 10T/1010	20.65	0.430	1995	13.1	16.45

as shown previously, the nucleation rate is increased more fastly, increasing the overall crystallization rate. These results are in accordance with those obtained from Vyazovkin's method and Friedman's method.

4. Conclusions

A systematic investigation of the crystallization kinetics and morphology of the Nylon 10T and the Nylon 10T/1010 prepared by direct melt polymerization has been carried out. The intrinsic viscosity values ($[\eta]$) of the Nylon 10T and the Nylon 10T/1010 were 83 and 87 ml·g⁻¹, respectively. The study of the non-isothermal crystallization kinetics of the Nylon 10T and the Nylon 10T/1010 was carried out by DSC.

For the non-isothermal crystallization of the Nylon 10T and the Nylon 10T/1010, the crystallization peak of polymer shifted to a lower temperature and the peak became wider with the increasing cooling rate. Jeziorny equation analysis reveals that the non-isothermal crystallization can be divided into two distinct stages: primary and secondary crystallization stages. At the primary stage, the n_1 values for the Nylon 10T and the Nylon 10T/1010 range from 2.48 to 2.88 and 2.52 to 3.27, respectively, which mean the addition of the sebacic acid comonomer slightly influences the mechanism of nucleation and the growth of the Nylon 10T crystallites. These results also indicate that the mode of the nucleation and growth at primary stage of the non-isothermal crystallization for the Nylon 10T and the Nylon 10T/1010 may be two-dimensional, circular, diffusion controlled growth with thermal nucleation. The Mo equation successfully describes the non-isothermal crystallization process of the Nylon 10T and the Nylon 10T/1010. The values of $E_a(T)$ and ΔE_x are calculated by Vyazovkin's method and Friedman's method, respectively. It is found that the values of the $E_a(T)$ and ΔE_x for the Nylon 10T/1010 are lower than those of the Nylon 10T at a given temperature or relative crystallinity, which reveal that crystallization ability of the Nylon 10T/1010 is higher.

POM and XRD observation showed that the addition of the sebacic acid comonomer not only did not change the crystal form of the Nylon 10T, but also significantly decreased the size and increased the number of spherulites. Comparing with the Nylon 10T, the crystallization rate was increased with the addition of the sebacic acid comonomer.

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