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Comparison of the Ozawa and modified Avrami models of polymer crystallization under nonisothermal conditions using a computer simulation method

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Abstract

The Ozawa and the modified Avrami models were usually used to describe the nonisothermal crystallization of polymers. A computer simulation approach was adopted to verify the two models. The results show that the Ozawa model is suitable under constant heating and cooling rate conditions, but not the modified Avrami model. Therefore, the Ozawa model was extended to acquiring the linear growth rate of polymer entities. A nonlinear relationship between the logarithm of the rate function and temperature was found. The values of the Avrami exponent are approximate to the designed value and the linear growth rates of the entities obtained are consistent with the designed ones.

Keywords: Nonisothermal crystallization; Ozawa model; Modified Avrami model; Monte Carlo simulation

1. Introduction

The computer simulation of polymer crystallization has been attracting more and more attention because of its bridge effect between theoretical and experimental studies [1]. Since Hay and Przekop [2] evaluated the Avrami equation by computer simulation of crystal growth, the computer simulation has become a powerful technique for assessing models. Galeski [3,4] simulated two-dimensional and three-dimensional spherulite growth and showed the Avrami exponent, the spherulite size distributions and morphology for different nucleation modes. Billon et al. [5] proposed a model derived from Evans' theory for describing the isothermal crystallization of a thin polymer film and developed a computer simulation of the crystallization to test the model. Pineda et al. [6] examined effects of both the reduction in the nucleation and growth rates and the non-randomness in the nucleation protocol on Avrami kinetics. Piorkowska [7] extended the computer simulation to fiber reinforced composite system to verify the derived expressions and to visualize the polymer morphology. Sun et al. [8] simulated isothermal crystallization process of polymers and a primary turning point was found in the Avrami plot at the very beginning of the crystallization in case that the sample thickness is equal or less than a given value. Up to date, the computer simulation of polymer crystallization kinetics has been shown to be an effective means of studying the crystallization.

However, most of the research on simulation of crystallization of polymers has been limited to isothermal process. In current paper, the nonisothermal crystallization was simulated and two of the most popular nonisothermal models were examined.

2. Nonisothermal crystallization kinetics

Several methods have been proposed to obtain the parameters characterizing the kinetics of nonisothermal crystallization, such as Ozawa method [9], Harnisch and Muschik method [10], modified Avrami method [11], Vyazovkin method [12], Mo method [13], Dutta method [14], Caze and co-workers' method [15], Malet method [16], etc. [17–19], wherein the Ozawa and the modified Avrami methods are two of the most popular ones in polymer science.

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2.1. Ozawa method

Based on the basic Evans theory, Ozawa derived a nonisothermal crystallization expression as follows [9]:

$$1-\alpha=\exp\left[\frac{-F(T)}{|\beta|^{n}}\right] \tag{1}$$

where α is the relative degree of crystallinity at temperature T; β, the heating or cooling rate; n, the Avrami exponent depending on the nucleation mode and the growth geometry of the crystals; $F(T)$, the rate function of nonisothermal crystallization, which is related to the nucleation rate and the linear growth rate. For the constant cooling process, $F(T)$ was expressed as

$$F(T)=g\int_{T_0}^{T}\int_{T_0}^{\theta}\upsilon(T)\,\mathrm{d}T\left[\int_{T_0}^{T}G(T)\,\mathrm{d}T-\int_{T_0}^{\theta}G(T)\,\mathrm{d}T\right]^{l}G(\theta)\,\mathrm{d}\theta \tag{2}$$

where $\upsilon(T)$ is the nucleation rate as a function of T; $G(T)$, the linear growth rate as a function of T; T_0, the temperature above which the process cannot proceed; g and l depend on the growth geometry. For the constant heating process, the similar equation holds. If the Ozawa model is valid, the plot of $\ln[-\ln(1-\alpha)]$ versus $\ln|\beta|$ at a given temperature should be a line with a slope of $-n$ and an intercept of $\ln F(T)$. So far, the Ozawa equation has been successfully used for describing the nonisothermal crystallization of poly(ethylene terephthalate) [9], polypropylene [20,21], polyamide 6 [22], poly(*p*-phenylene sulphide) [23], poly(trimethylene terephthalate) [24], poly(trimethylene terephthalate)/poly(butylene terephthalate) blend [25], and some polyethylene [26]. Also, the nonlinearity of the Ozawa plot was found in the case of polyethylene [20], poly(ethylene oxide) and poly(ethylene oxide)/poly(methylmethacrylate) blends [27], poly(ether-ether ketone) [28], etc. In consideration of the fact that contradictory results were reported in literature, it is necessary to test the validity of the Ozawa model and the errors of the parameters obtained in terms of the model.

2.2. Modified Avrami method

Jeziorny [11] extended the isothermal Avrami equation to the nonisothermal situation, the method in terms of which is referred to as the modified Avrami method here. The Avrami equation can be expressed in a double logarithmic form:

$$\ln[-\ln(1-\alpha)]=n\ln t+\ln Z \tag{3}$$

where α is the relative degree of crystallinity at time t; n, the Avrami exponent, related to the mechanism of crystallization; Z, the parameter for crystallization kinetics. By considering the effect of nonisothermal process, Z should be corrected by the rate of cooling. The final form of this parameter is given by

$$\ln Z_{\mathrm{c}}=\frac{\ln Z}{|\beta|} \tag{4}$$

where β is the linear heating or cooling rate. Many authors [24,29–31] applied the Avrami method to analyze the nonisothermal crystallization of polymers. It is also necessary to evaluate the validity of the modified Avrami equation under nonisothermal conditions.

3. The simulation experiment

In the computer simulation experiments, we assume that the crystallization process is composed of two main steps: nucleation and crystal growth. In the experiments, it is considered that the nucleation process is instantaneous. The nuclei are randomly distributed in a box with a volume of $100\,\mu\mathrm{m}\times100\,\mu\mathrm{m}\times100\,\mu\mathrm{m}$. The growth of spherulites would be limited by each other, that is, the growth would be terminated at the point of the impingement of the growth front. Therefore, the growth geometry of a spherulite would be a polyhedron at the end of the crystallization. The linear growth rate of the crystals is considered to follow the following equation [32–34]:

$$G(T)=G_0\exp\left(-\frac{E_{\mathrm{d}}}{RT}-\frac{\psi T_{\mathrm{m}}^{0^2}}{T^2(T_{\mathrm{m}}^0-T)}\right) \tag{5}$$

where $G(T)$ is the linear growth rate at temperature T; G_0, the pre-exponential factor, a constant for a given polymer; R, the molar gas constant; E_{d}, the activation energy of diffusion of crystallizing segments across the phase boundary; ψ, the nucleation parameter related to the surface-free energy of forming crystals, the melting enthalpy, and the geometry of the crystals; T_{m}^0, the equilibrium melting temperature. Eq. (5) can be transformed into a linear form by logarithmizing it. In the current experiments, we chose poly(ethylene terephthalate) (PET) sample with intrinsic viscosity of 0.67 dL/g. $G(T)$ and the nucleation density was determined using an Olympus BX51 polarizing microscope equipped with a Linkam THMS600 hot stage controlled by a computer program. The nucleation density N is $10^7\,\mathrm{mm}^{-3}$, estimated from the maximum spherulite radius by the expression [35]:

$$\frac{4}{3}\pi\bar{R}_{\max}^{3}=\frac{1}{N} \tag{6}$$

The value of T_{m}^0 for PET was chosen to be 583 K [34]. According to knowledge of $G(T)$ and T_{m}^0, G_0, E_{d}, and ψ can be obtained by the weighted least squares method with the weighted function: $G(T)^2$ [36]. The values of the parameters obtained from fitting are $G_0=1.3393\times10^{22}\,\mu\mathrm{m/min}$, $E_{\mathrm{d}}=106.47\,\mathrm{kJ/mol}$, and $\psi=1634.9\,\mathrm{K}$. At a given time t, the radius of spherulites can be calculated from:

$$r(t)=\frac{1}{\beta}\int_{T_0}^{T}G[T(t)]\,\mathrm{d}T \tag{7}$$

where $T_0=506.91\,\mathrm{K}$ for the constant cooling experiments and 389.90 K for the constant heating experiments, the linearly extrapolated values by using the data determined by using DSC curves with several scanning rates. In computer simulation, the parameters above were adopted. In the case of linear heating or cooling rate, the relationship between temperature and time is given by

$$T = T_0 + \beta t \tag{8}$$

The steps of computation process are as follows:

(a) Yield M nuclei which are randomly distributed in a box. The position of each nucleus is denoted by the coordinates (x_i, y_i, z_i) ($i = 1, 2, \ldots M$). The relative degree of crystallinity is zero at this time since the nuclei are assumed not to occupy any space.

(b) Let t increase to $t + \Delta t$. Calculate the temperature from Eq. (8) and the radius of each spherulite from Eq. (7).

(c) Yield a random point with the coordinates (x, y, z) in the box and examine if this point drops into any one of the spherulites in terms of following express:

$$(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2 \leq r^2 \tag{9}$$

(d) Repeat step (c) for N_0 times. If there is N points dropping into any one of the spherulites in N_0 sampling, the relative degree of crystallinity at this moment is written as

$$\alpha(t) = \frac{N}{N_0} \tag{10}$$

(e) Repeat steps (b)–(d) until $\alpha = 1$.

The relative degrees of crystallinity or its increments at different times (or temperatures) are recorded with a sampling number of 10^8 per cubic millimeter for each step.

4. Results and discussion

4.1. Simulated increment curves of the relative degrees of crystallinity

The derivative of degree of crystallinity with respect to time ($\mathrm{d}\alpha/\mathrm{d}t$) is directly proportional to the absolute value of the heat flow under linear heating or cooling rate. The plots of $\mathrm{d}\alpha/\mathrm{d}t$ versus temperature obtained in the simulation experiments are shown in Fig. 1.

4.2. Ozawa model

In terms of Eq. (1), the plots of $\ln[-\ln(1-\alpha)]$ versus $\ln|\beta|$ should be linear at a given temperature, as shown in Fig. 2. A clear linear relationship holds between $\ln[-\ln(1-\alpha)]$ and $\ln|\beta|$ with a slope of $-n$ and an intercept of $\ln F(T)$, suggesting that the Ozawa method appears to be applicable for evaluating non-isothermal crystallization in the ideal crystallization condition.

The values of the Avrami exponent calculated by the slope of the lines by using the least squares method are shown in Fig. 3.

The value of the Avrami exponent is dependent on the nucleation mode and growth geometry of crystals. In current simulation experiments, the nuclei are randomly dispersed in the system, the nucleation process is instantaneous, and every nucleus develops into a spherulite. Theoretically, the Avrami exponent should be equal to 3 in such a case, as represented in the solid line of Fig. 3. The dash line is obtained by fitting the data points using the least squares method. The average value of the Avrami exponent is close to and slightly lower than the theoretical value either in a heating mode or a cooling mode. We infer that this phenomenon is related to random nucleation mode where the distance between some nuclei are close to each other and some are far. Therefore, it is likely that the impingement of spherulites begins to occur at the early stage of the crystallization, which makes the Avrami exponent lower than the ideal value. In the beginning stage of the crystallization, the value of the Avrami exponent is close to the ideal value because the possibility of the impingement of spherulites is small. As the temperature rises under the heating condition or declines under the cooling condition, the value of the Avrami exponent decreases slightly because the spherulites become larger and the possibility of the impingement of spherulites increases.

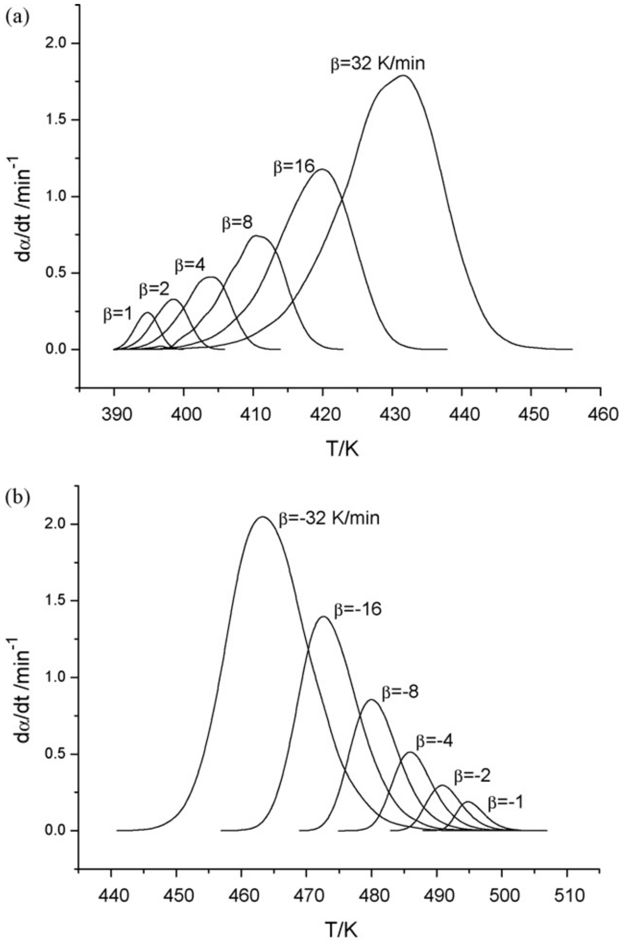

Fig. 1. Plots of derivative of relative degree of crystallinity with respect to time vs. temperature from (a) heating program and (b) cooling program.

The relationship between $\ln F(T)$ and temperature from the intercepts of the plots of $\ln[-\ln(1-\alpha)]$ versus $\ln|\beta|$, is shown in Fig. 4.

A linear empirical relationship between logarithm of $F(T)$ and temperature was found by some researchers [15,20,37,38]. Differently, the plots in Fig. 4 are hardly precisely described by a linear function, which perhaps origins from the wider range of temperatures in current research. Additionally, it is nearly

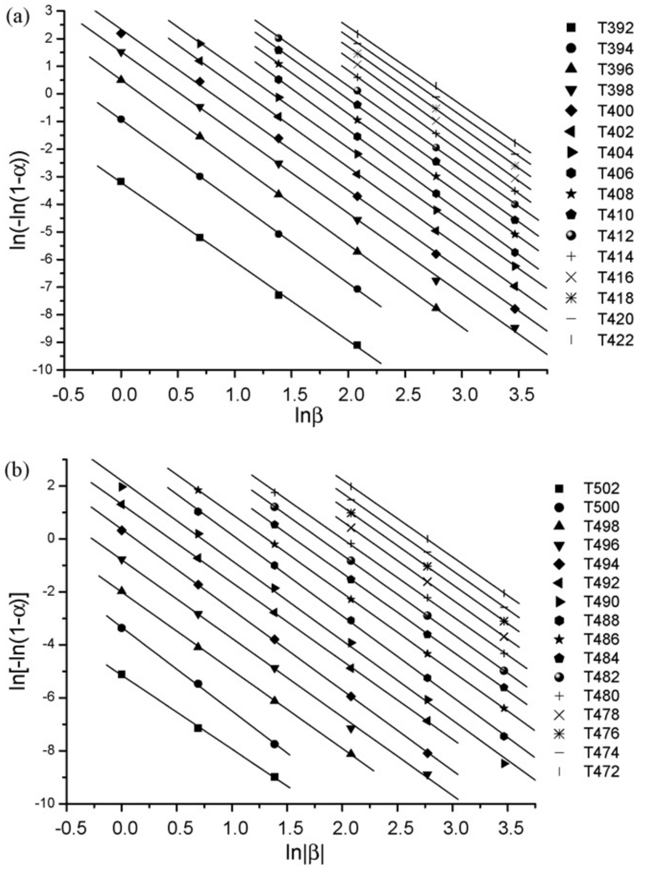

Fig. 2. Plots of ln[−ln(1−α)] vs. ln |β| for nonisothermal crystallization at different temperatures from (a) linear heating curves and (b) linear cooling curves.

impossible to obtain the parameter of linear growth rate by using Eq. (2) because of its complexity. Here, a new rate function was proposed and a newly developed method was used to obtain the parameter characterizing the crystallization rate.

From the results above, we can conclude that the Ozawa model is suitable for describing the behavior nonisothermal crystallization in these ideal simulation experiments. As for the finding that the Ozawa model could not describe the behavior of nonisothermal crystallization of some polymers [20,27,28,39,40], the possible reason is that the secondary crystallization of these polymers should not be neglected. In current simulation experiments, we did not take the contribution of secondary crystallization to degree of crystallinity into account, such as the further crystallization within spherulites.

4.3. Obtaining the parameter characterizing crystallization rate

In terms of the Avrami theory, the relationship between the real volume of crystalline phase per unit volume V and the ‘extended’ volume of the crystalline phase V_{ex} can be expressed in following form without isothermal limit [41]:

$$\frac{\mathrm{d}V}{\mathrm{d}V_{\mathrm{ex}}} = 1-\alpha \tag{11}$$

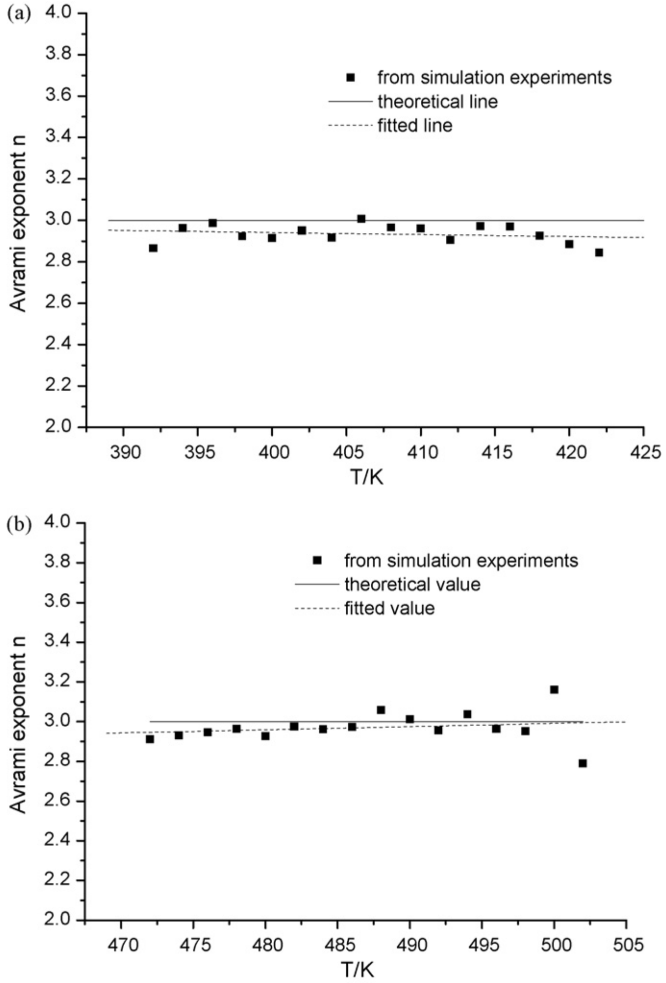

Fig. 3. Temperature dependence of the Avrami exponent obtained from (a) linear heating curves and (b) linear cooling curves.

where α is the relative volume degree of crystallinity. Because V_{ex} neglects possible overlapping of growing entities, Eq. (11) can be rewritten by

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\mathrm{d}V_{\mathrm{ex}}}{\mathrm{d}r}\frac{\mathrm{d}r}{\mathrm{d}t}(1-\alpha) \tag{12}$$

where r is the radius of ‘extended’ spherulites; dr/dt is the linear grown rate of crystalline entities, only depending on temperature for a given polymer. By taking relationships between dV_{ex}/dr and α into account, the differential equation for describing the nonisothermal crystallization is given by [18,42]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K(T)[-\ln(1-\alpha)]^m(1-\alpha) \tag{13}$$

where α is the relative volume degree of crystallinity at time t; m, the parameter characterizing the mechanism of crystallization, which is related to the Avrami exponent n in the following expression:

$$m = \frac{n-1}{n} \tag{14}$$

$K(T)$ is the crystallization rate which is a constant at a given temperature T for a given polymer and proportional to the linear

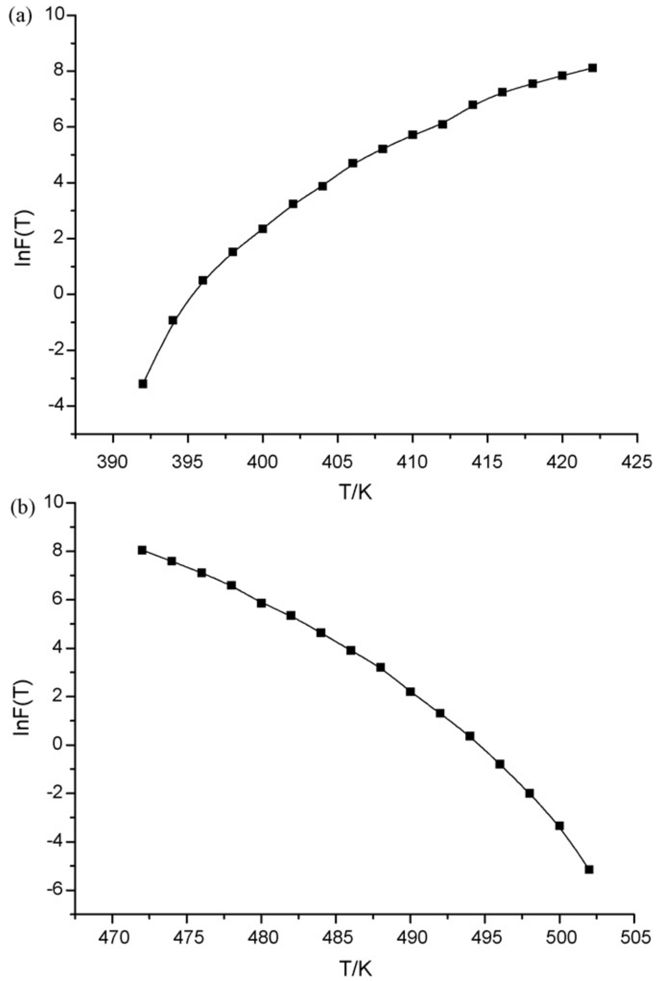

Fig. 4. Plot of $\ln F(T)$ vs. temperature obtained from (a) linear heating curves and (b) linear cooling curves.

growth rate of the crystals, the physical significance of which is listed in Table 1.

In Table 1, N_0 is the number of nuclei per unit volume; d_0, the thickness of a disk-shape entity; S', the surface area of the cross-section of a rod-like entity; k, the ratio of the nucleation rate to linear growth rate of crystalline entities; $G(T)$, the linear growth rate of the entities at temperature T; X_e, the volume fraction occupied by crystalline entities at the end of crystallization. Eq. (13) can be converted into an integrate form:

$$-\ln(1-\alpha) = \left[(1-m)\int_0^t K[T(t)]\,\mathrm{d}t\right]^{1/(1-m)} \tag{15}$$

By taking Eqs. (8) and (14) into account, Eq. (15) becomes

$$-\ln(1-\alpha) = \left[\frac{1}{n\beta}\int_{T_0}^{T} K(T)\,\mathrm{d}T\right]^{n} \tag{16}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$, the constant heating or cooling rate; T_0, the temperature at which the crystallization begins to occur. Eq. (16) can be expressed in the same form as Eq. (1), where $F(T)$ is different from that given by Ozawa [9] and here it is

$$F(T) = \begin{cases} \left[\dfrac{1}{n}\displaystyle\int_{T_0}^{T} K(T)\,\mathrm{d}T\right]^{n} & (\beta > 0) \\ \left[-\dfrac{1}{n}\displaystyle\int_{T_0}^{T} K(T)\,\mathrm{d}T\right]^{n} & (\beta < 0) \end{cases} \tag{17}$$

The parameter characterizing crystallization rate can be calculated by differentiating Eq. (17) with respect to T

$$K(T) = \begin{cases} \dfrac{\mathrm{d}[nF(T)^{1/n}]}{\mathrm{d}T} & (\beta > 0) \\ -\dfrac{\mathrm{d}[nF(T)^{1/n}]}{\mathrm{d}T} & (\beta < 0) \end{cases} \tag{18}$$

From knowledge of $F(T)$ and n obtained by plotting $\ln[-\ln(1-\alpha)]$ versus $\ln|\beta|$ at different temperatures, the crystallization rate parameter, $K(T)$, can be calculated from Eq. (18). Furthermore, the linear growth rate, $G(T)$, can be obtained from the expression of predetermined nucleation and spherical geometry listed in Table 1.

$$G(T) = K(T)\left(\frac{X_e}{36\pi N_0}\right)^{1/3} \tag{19}$$

In terms of the values of $\ln F(T)$ and n at different temperatures, a curve of $nF(T)^{1/n}$ versus T can be fitted by a cubic spline function and then $K(T)$ can be obtained by a number differential of the function, as described by Eq. (18). Then $G(T)$ can be estimated according to $K(T)$ and Eq. (19) with $X_e = 1$ and $N_0 = 10^{-2}\ \mu\mathrm{m}^{-3}$, as shown in Fig. 5. The solid line is the designed linear growth rate calculated according to Eq. (5) where $G_0 = 1.3393 \times 10^{22}$ μm/min, $E_d = 106.47$ kJ/mol, and

Table 1
The physical significance of $K(T)$ and m in Eq. (13)

Shape	Predetermined nucleation		Sporadic nucleation	
	$K(T)$	m	$K(T)$	m
Sphere	$4\pi N_0 G(T)\dfrac{(3X_e/4\pi N_0)^{2/3}}{X_e}$	2/3	$\dfrac{4}{3}\pi k G(T)\dfrac{(3X_e/\pi k)^{3/4}}{X_e}$	3/4
Disk	$\dfrac{2G(T)(\pi d_0 N_0 X_e)^{1/2}}{X_e}$	1/2	$\pi d_0 k G(T)\dfrac{(3X_e/\pi d_0 k)^{2/3}}{X_e}$	2/3
Rod	$\dfrac{N_0 S' G(T)}{X_e}$	0	$\dfrac{G(T)(2X_e S' k)^{1/2}}{X_e}$	1/2

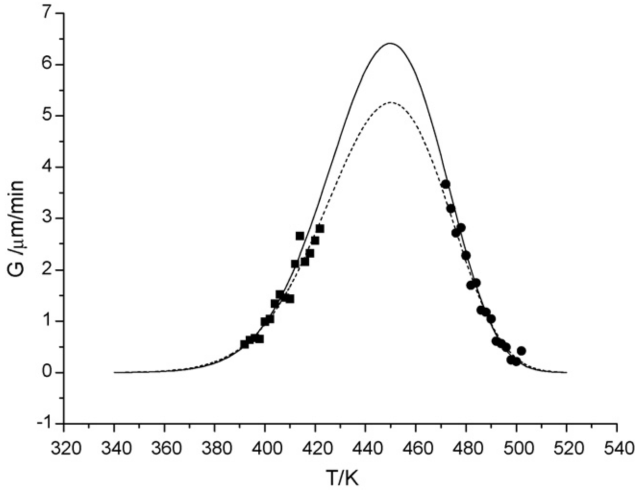

Fig. 5. Temperature dependence of the linear growth rate. Symbol squares: obtained from the heating experiments; symbol circles: obtained from cooling experiments; solid line: original data adopted in simulation experiments; dashed line: the fitting values in terms of those obtained from the heating and cooling experiments.

$\psi = 1634.9$ K, adopted in the simulation experiments. The calculated values, which are denoted as squares for the linear heating program and circles for the linear cooling program, were obtained based on the simulation results. The calculated values are quite consistent with the designed ones, suggesting that the Ozawa model and the current method to obtain the kinetic parameters are suitable for such a system. The dashed line was fitted using the least squares method based on both the calculated values and Eq. (5) with $G_0 = 7.99 \times 10^{19}$ μm/min, $E_d = 96.11$ kJ/mol, and $\psi = 1464.3$ K. In range of lower and higher temperature, the crystallization is in the beginning stage because of the heating and the cooling method. The crystallization reaches gradually its end stage near the maximum growth rate. The difference increases slightly in the end stage of the crystallization, perhaps resulting from the increase of the impingement of spherulites.

4.4. Modified Avrami model

According to Eq. (3), the plot of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ should be a line with an intercept of $\ln Z$ and a slope of n, as shown in Fig. 6(a) and (b). The parameters obtained from the plots are listed in Table 2.

As seen in Fig. 6, the plots of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ maintain linear, showing that the modified Avrami method could formally be suitable for describing the nonisothermal crystallization. But the kinetic parameter Z_c does not keep a constant as suggested by Jeziorny [11] at different scanning rates. The half time of crystallization is also calculated from:

$$t_{1/2} = \left(\frac{\ln 2}{Z}\right)^{1/n} \tag{20}$$

The values of $t_{1/2}$, as listed in Table 2, decrease as increasing $|\beta|$, indicating that the rate of crystallization is faster at a higher

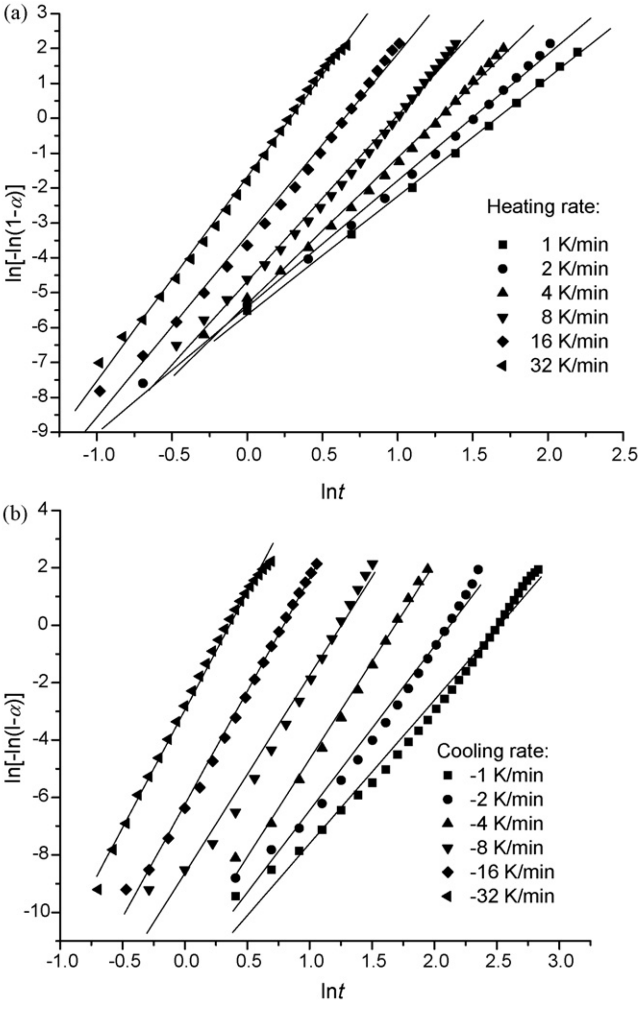

Fig. 6. Plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ from (a) linear heating curves and (b) linear cooling curves.

$|\beta|$. The values of the Avrami exponent deviate significantly from the theoretical value of 3 in the predetermined nucleation and spherulite growth condition, as shown in Fig. 7, which suggests that the value of the Avrami exponent obtained from the modi-

Table 2
The Avrami parameters from nonisothermal crystallization

Scanning rate	n	$\ln Z$/min^{-n}	Z_c	$t_{1/2}$/min
Heating				
1	3.40	−5.63	3.59×10^{-3}	4.70
2	3.62	−5.41	6.69×10^{-2}	4.03
4	4.19	−5.33	2.64×10^{-1}	3.27
8	4.77	−4.68	5.57×10^{-1}	2.47
16	5.21	−3.36	8.11×10^{-1}	1.78
32	5.85	−1.68	9.49×10^{-1}	1.25
Cooling				
−1	5.00	−12.6	3.37×10^{-6}	11.6
−2	5.72	−12.2	2.24×10^{-3}	7.92
−4	6.81	−11.5	5.64×10^{-2}	5.13
−8	6.89	−8.64	3.40×10^{-2}	3.32
−16	7.88	−6.23	6.77×10^{-1}	2.10
−32	8.20	−2.95	9.12×10^{-1}	1.37

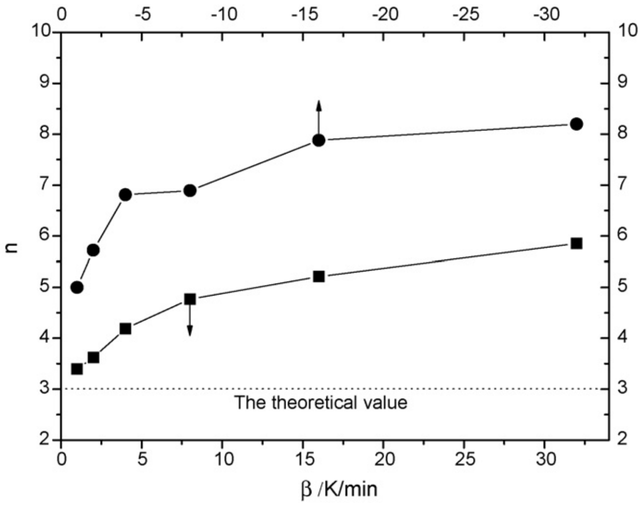

Fig. 7. Changes of the Avrami exponents with scanning rates. Squares: obtained from the heating experiments; circles: obtained from cooling experiments. The dotted line stands for the theoretical value.

fied Avrami method is not reasonable. The values of the Avrami exponent approach to the theoretical value of 3 only if that the scanning rate is close to zero. Also, some higher values of the Avrami exponent were found by some researchers [31,43–47] in the nonisothermal crystallization of many polymers in terms of the method, which is in agreement with the results in current paper. Therefore, it is not reasonable to explain the nucleation mechanism and growth geometry of entities based on the values of the Avrami exponent derived using the modified Avrami method.

5. Conclusion

The Ozawa model is suitable for describing the nonisothermal crystallization under these ideal simulation experiments and was extended to acquiring the linear grown rate of polymer entities. The results show there is a nonlinear relationship between the logarithm of the rate function and temperature. The values of the Avrami exponent are slightly lower than the designed value and the linear growth rates of the entities obtained are consistent with the designed ones.

The modified Avrami method is not reasonable for obtaining the parameters characterizing the kinetics of the nonisothermal crystallization of polymers. The values of the Avrami exponent obtained are higher than the theoretical one, which could not reflect the nucleation mechanism and the growth geometry of the entities.

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