



Prediction of non-isothermal crystallization parameters for isotactic polypropylene

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ABSTRACT

Non-isothermal crystallization kinetics of isotactic polypropylene (iPP) was simulated with the assumption that the non-isothermal crystallization process was composed of some finite isothermal crystallization processes, while each isothermal crystallization process consists of three main steps—induction, nucleation and crystal growth. In the simulation, induction time was taken into account, allowing one to make predictions on the start of the non-isothermal crystallization of iPP; nuclei density was treated as a function of temperature; the Hoffman–Lauritzen theory was employed to describe the spherulite growth rate varied with temperature, and the relative crystallinity was determined by the equation of Kolmogorov. Finally, model prediction was verified by quantitative comparison between the theoretical results with the experimental results.

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1. Introduction

The crystallization of polymer is a complex process, which has been always an attractive topic in polymer physics and process. With most polymers when crystallizing from quiescent melt, some models have been proposed to treat the kinetics of crystallization. Avrami equation [1] has been used universally to describe polymer isothermal crystallization kinetics. Lauritzen and Hoffman [2] developed a rate equation for spherulite growth varied with temperature. Compared with isothermal crystallization, non-isothermal crystallization is of great practical importance to study in terms of approaching more closely the industrial conditions of polymer processing. Therefore, non-isothermal modeling is essential for the understanding of the crystallization behavior of polymer. Ozawa's theory [3] is adopted to describe non-isothermal crystallization process. Nakamura et al. [4] extended the Avrami equation to describe the transformation process occurring in non-isothermal crystallization on the basis of isokinetic conditions. Jeziorny [5] modified Avrami equation with considering the characteristics of non-isothermal crystallization process. According to the research of Liu et al. [6] on non-isothermal crystallization of polymer, an equation describing the non-isothermal crystallization was obtained by combining the Avrami equation and Ozawa equation, which is called Mo method.

Isotactic polypropylene (iPP) is semicrystalline polymer and the properties of iPP in engineering application are critically dependent on the extent of crystallinity. The non-isothermal crystallization

of iPP has been extensively reported in the literature [7–10]. Currently, the main techniques employed to study non-isothermal crystallization are differential scanning calorimetry (DSC), thermal polarizing light microscopy, depolarized light intensity (DLI) and dilatometer. Meanwhile, computer simulation is becoming an effective way to study crystallization kinetics in recent years. Zhang et al. [11] compared the Ozawa and modified Avrami models of polymer crystallization under non-isothermal conditions using a computer simulation method. Lin et al. [12] simulated isothermal crystallization of monomer casting (MC) nylon 6 with a three-dimensional cellular automaton (CA) model applied to predict isothermal crystallization parameters in MC nylon 6. Saraporn and Siripon [13] simulated crystallization kinetics and morphological development during isothermal crystallization of polymers to investigate the effect of number of nuclei and growth rate.

However, few simulation researches on the non-isothermal crystallization of polymer could consider the crystallization induction time. Patel and Spruiell [14] concluded that traditional kinetics models over predict the non-isothermal data can be attributed to not accounting for induction time, which is a certain period between the beginning of crystallization experiment and the emergence of the first crystalline nuclei. Mubarak et al. [15] confirmed with experimental work that some of non-isothermal crystallization kinetic models without considering crystallization induction time could not predict quantitatively the crystallization process.

In this paper, the induction time was incorporated in the simulation model for the prediction on the non-isothermal crystallization kinetics parameters of iPP. It is considered that the nucleation was a progress process and the evolvement of nuclei density with temperature during the crystallization was obtained. The kinetics parameters and activation crystallization energy for the

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non-isothermal crystallization of iPP was acquired based on the simulation, and were compared with those derived from experiment.

2. Theoretical models

2.1. Nuclei density

According to the work of Koscher and Fulchiron [16], the number of activated nuclei varies with temperature under quiescent conditions, and nuclei density N_q of iPP could be empirically described as following equation:

$$\ln N_q(T) = a \Delta T + b \quad (1)$$

where a and b , the material constants independent of temperature, are equal to 1.56×10^{-1} and 1.51×10^1 (with N_q in m^{-3}), respectively. ΔT is undercooling (with $\Delta T = T_m^0 - T$, where T_m^0 is the equilibrium melt temperature which is taken equal to 483 K [17]).

2.2. Induction time

Between the beginning of a crystallization experiment and the emergence of the first batch of crystalline nucleus, a certain period elapses which is called the induction time. For melt crystallization, the expression for isothermal induction time t_i has been proposed [18], which is as following:

$$t_i = t_m(T_m - T)^{-c} \quad (2)$$

where t_m and c are material constants independent of temperature. According to the work of Mubarak et al. [15], $t_m = 3.0339 \times 10^{22} \text{ min/K}^c$ and $c = 11.965$. T_m is the temperature at which the sample starts to cool during the crystallization experiment.

Based on the approach of Sifleet et al. [19], the non-isothermal crystallization induction time can be obtained by the following equation:

$$\bar{t} = \int_0^{t_i} \frac{dt}{t_i(T)} = 1 \quad (3)$$

where t_i is the isothermal induction time as a function of temperature. When the value of \bar{t} reaches unity, the upper limit of the integration was taken as the non-isothermal induction time.

2.3. Spherulite growth rate

The variation of the spherulite growth rate of iPP with the temperature has been calculated on the basis of the theory of Hoffman–Lauritzen [2]

$$G(T) = G_0 \exp\left(-\frac{U^*}{R(T - T_\infty)}\right) \exp\left(-\frac{K_g}{T \Delta T}\right) \quad (4)$$

where G_0 is the pre-exponential factor; U^* is the activation energy of motion of the macromolecules; R is gas constant; T is the crystallization temperature; T_∞ is the temperature at which no further motions, which was defined by $T_\infty = T_g - 30$, where T_g is glass transition temperature; ΔT , the undercooling, is defined by $\Delta T = T_m^0 - T$; The parameter K_g is the term connected with the nucleation energy. The values of the parameters obtained from literature were $G_0 = 2.83 \times 10^2 \text{ m s}^{-1}$ [16], $U^* = 6270 \text{ J/mol}$ [16], $T_g = 261.2 \text{ K}$ [20] and $K_g = 5.5 \times 10^5 \text{ K}^2$ [16].

2.4. Relative crystallinity

Under quiescent crystallization condition, Kolmogorov [21] adopted the principle of morphology to derive the following equation

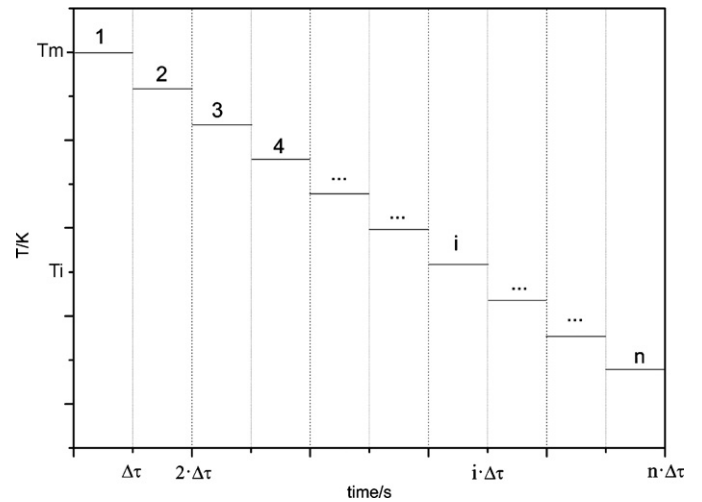


Fig. 1. Temperature versus time in non-isothermal crystallization.

tion for relative crystallinity:

$$\alpha(t) = 1 - \exp[-\alpha_f(t)] \quad (5)$$

where

$$\alpha_f(t) = C_m \int_0^t \dot{N}(s) \left[\int_s^t G(u) du \right]^M ds \quad (6)$$

where M is a constant denoting the dimensionality of the crystallites; in the original form for spherical crystals, $M = 3$ and the constant $C_m = 4\pi/3$; $\dot{N}(t)$ is the rate of increase of nuclei number in the crystallization process; $G(t)$ is the growth rate of the crystals. According to the rule of calculation of Eq. (6), it is obvious that the value of $\alpha_f(t)$ is equal to the total volume of spherulites at the given time t .

3. Method of simulation

The simulation was conducted by supposing that the non-isothermal crystallization process consist of some finite isothermal crystallization processes, and each isothermal crystallization process contained three steps: induction, nucleation and crystal growth. The simulation was dealt with discrete time and, in the case of linear cooling rate, the expression to describe the relationship between temperature and time is showed as follows:

$$T_i = T_m - \phi(i - 1)\Delta\tau \quad (7)$$

where $i = 1, 2, 3 \dots n$ and T_m is the temperature at which sample starts to cool from melt; $T_m = 473 \text{ K}$ for iPP sample starts to cool at the crystallization experiment, while ϕ is the cooling rate; the step length of time $\Delta\tau$ in our simulation was 1 s.

The relation of temperature with time in non-isothermal crystallization was showed in Fig. 1. Crystallization, during the i isothermal stage that the duration was $\Delta\tau$, was treated as isothermal process, and it was denoted by isothermal crystallization i , of which the crystallization temperature was T_i and the initial time was $(i - 1)\Delta\tau$ ($i = 1, 2, 3 \dots n$).

At the first isothermal stage, of which the temperature was T_1 , the nuclei activated N_1 was given by

$$N_1 = \exp(a \Delta T_1 + b) \quad (8)$$

whereas, because of the induction, these nuclei N_1 did not appeared immediately until the induction finished, which was equal to the difference of the upper and lower limit of the integration of the equation $\int_0^{t_1} dt/t_i(T) = 1$, where the time t_1 was that the nuclei

N_1 appeared and started growth. Therefore, the radius R_1 of these nuclei N_1 was calculated by the equation

$$R_1 = \sum_{t_{i1}}^{n \times \Delta t} G(T_i) \cdot \Delta t \quad (9)$$

where $G(T_i)$ was the Spherulite growth rate at the temperature T_i , which was determined by the theory of Hoffman–Lauritzen.

At the second isothermal stage, of which the temperature T_2 was, the nuclei activated N_2 was given by

$$N_2 = \exp(a \Delta T_2 + b) - \exp(a \Delta T_1 + b) \quad (10)$$

Likewise, the new nuclei N_2 did not appeared immediately until the time t_{i2} , where $\int_{\Delta t}^{t_{i2}} dt/t_i(T) = 1$. The radius of these nuclei N_2 was given by

$$R_2 = \sum_{t_{i2}}^{n \times \Delta t} G(T_i) \cdot \Delta t \quad (11)$$

while, at the i isothermal stage, of which the temperature was T_i , the nuclei activated N_i was given by

$$N_i = \exp(a \Delta T_i + b) - \exp(a \Delta T_{i-1} + b) \quad (12)$$

and appeared at the time t_{ii} , where $\int_{(i-1)\Delta t}^{t_{ii}} dt/t_i(T) = 1$. The radius of the nuclei at N_i was given by

$$R_i = \sum_{t_{ii}}^{n \times \Delta t} G(T_i) \cdot \Delta t \quad (13)$$

while, based on the physical meaning of Eq. (6), at the time $n \times \Delta t$ the relative crystallinity was calculated by Eq. (5), and Eq. (6) could be described by that

$$\alpha_f(t) = \sum_1^j N_i \cdot \frac{4}{3} (R_i)^3 \quad (14)$$

whereas at the j isothermal stage the activated nuclei N_j appeared until the time $(n - 1) \times \Delta t$, therefore, the j isothermal stage was the last isothermal stage whose nuclei appeared before the time $n \times \Delta t$.

4. Experimental work

Isotactic polypropylene (iPP, T30s) with a melt flow rate (MFR) of $3.881 \text{ g} \times 10 \text{ min}^{-1}$ ($503 \text{ K} \times 2.16 \text{ kg}^{-1}$) used in this study was purchased from Fujian Petrochemical Co., Ltd., Quanzhou, China.

DSC data of iPP were measured on a Diamond DSC under nitrogen atmosphere to compare the theoretical results with the experimental results. The samples were quickly heated to 473 K and maintained for 5 min to eliminate the thermal history, and then were cooled down to room temperature at the rates of 2.5, 5, 10, 20 and 40 K/min. the crystallization exotherms of iPP at different cooling rate were presented in Fig. 2. To characterize the beginning of crystallization, the temperature corresponding to the beginning of deviating from the baseline of DSC curves has been selected as the onset temperature of crystallization.

5. Results and discussion

Usually the crystallization kinetics is mainly investigated based on the experimental observation or measurements, and one of the most important measurements was differential scanning calorimetry (DSC). However, the limitation of DSC as a main method to measure the crystallization of polymer is that it could not provide the parameters such as nuclei number, nuclei size, etc. Furthermore, DSC has more error in the research of non-isothermal

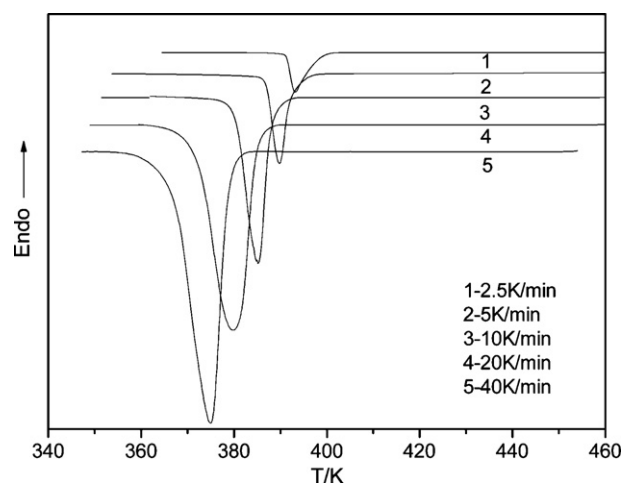


Fig. 2. DSC thermograms of iPP at different cooling rates.

crystallization at high cooling rate because of the serious thermal lag between sample and the calorimeter furnace. Computer simulation is becoming one of the most important supplementary techniques to study the crystallization kinetics due to that it could examine lots of influence factors of crystallization and then finding out how the factors affect the crystallization process.

5.1. Crystallization kinetics parameters

In our current work, the relationship between the relative crystallinity and temperature could be gotten according to Eq. (14). Fig. 3 shows the comparison between the experimental and predicted non-isothermal crystallinity data for iPP, it was found that while the cooling rates was 2.5, 5 and 10 K/min, the predicted data were very good fit to the experimental data, however, when the cooling rate was higher than or equal to 20 K/min, the development of the relative crystallinity for the experimental work lagged behind that for the simulation work at the late stage of crystallization. This phenomenon may be attributed to that there existed thermal lag between the sample and the calorimeter furnace, and the higher cooling rate, the more serious thermal lag. It is well known that the reciprocal of crystallization half-time ($t_{1/2}$) represents the overall crystallization rate and it was a very important parameter to describe the crystallization rate. Half-time ($t_{1/2}$) obtained from simulation was presented in Table 1, while the results agreed

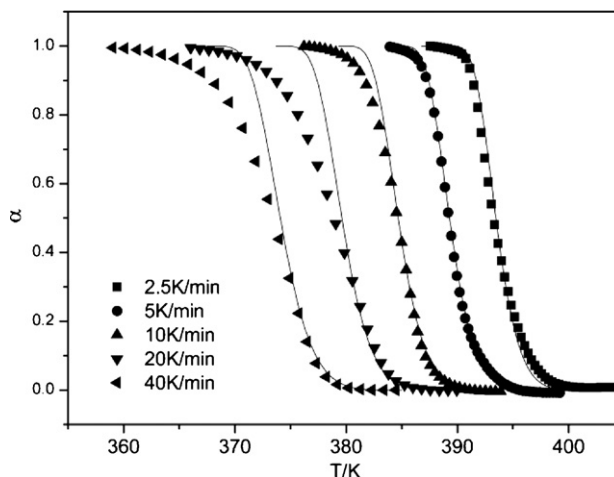


Fig. 3. Plots of the relative crystallinity as a function of temperature for iPP at different cooling rates. Solid lines are predicted data.

Table 1

Kinetics parameters for the non-isothermal crystallization obtained from experimental and simulation work.

Cooling rate (K/min)	Experimental work	Simulation work
2.5		
$t_{1/2}$ (min)	4.22	3.86
T_p (K)	393.2	393.0
T_0 (K)	402.5	402.1
t_{id} (s)	1692	1701
5		
$t_{1/2}$ (min)	1.89	1.77
T_p (K)	389.1	388.8
T_0 (K)	399.2	398.2
t_{id} (s)	885	898
10		
$t_{1/2}$ (min)	0.93	0.94
T_p (K)	385.2	384.2
T_0 (K)	393.9	394.0
t_{id} (s)	475	474
20		
$t_{1/2}$ (min)	0.55	0.50
T_p (K)	379.8	379.2
T_0 (K)	389.9	389.7
t_{id} (s)	249	250
40		
$t_{1/2}$ (min)	0.29	0.27
T_p (K)	375.0	373.7
T_0 (K)	384.5	385.0
t_{id} (s)	133	132

with the experiment well no matter which cooling rate the process crystallize at.

In addition to $t_{1/2}$, the onset temperature (T_0) and induction time (t_{id}) of crystallization at different cooling rates were obtained from the simulation as was listed in Table 1. In our case, the simulation starts at the same temperature ($T_m = 473$ K), however, the onset temperature of crystallization vary with the cooling rate, which was attributed to that the time elapsing from the temperature T_m until appearing of the first batch nuclei, called induction time, was various with cooling rate. According to the calculation results, the nuclei activated at the first several isothermal stage were emergent at the same time and therefore, the induction time of the whole process of non-isothermal crystallization, reflecting the rate of nucleation of the first batch of nuclei, was equal to that of the isothermal crystallization at the first few isothermal stage. Based on the principle of our simulation, the non-isothermal crystallization process was divided to a group of finite isothermal crystallization process, and each one had its own induction stage, whereas the induction time for the isothermal crystallization decreased as the temperature decreased, indicating that the nuclei activated at the lower temperature emerged within a shorter time. The reason was that a higher cooling rate made it possible to reach a lower crystallization temperature, which produced a higher driving force to produce nuclei, and the greater driving force produced nuclei in shorter time [22].

The value of T_0 and t_{id} for the non-isothermal crystallization at various cooling rates coincided well with the experiment results, verifying that the model described the induction stage of crystallization was reasonable.

5.2. Effective activation energy

Kissinger [23] method was one of the most popular approach for evaluating the effective activation energy of non-isothermal crystallization, however, Vyazovkin [24] has demonstrated that this method provide invalid results when applied to the process occurred on cooling and proposed that the correct values can be determined by the differential isoconversional method of Friedman [25] or by the integral isoconversional method of Vyazovkin

Table 2 d_{max} and \bar{d} of the spherulites at different cooling rates.

Cooling rate (K/min)	d_{max} (μm)	\bar{d} (μm)
2.5	237.75	111.90
5	195.82	87.52
10	157.91	66.27
20	124.67	48.85
40	94.38	34.31

[26,27]. To obtain the dependence of the effective activation energy on conversion, the method of Friedman was used in the present study and the equation is expressed as follows:

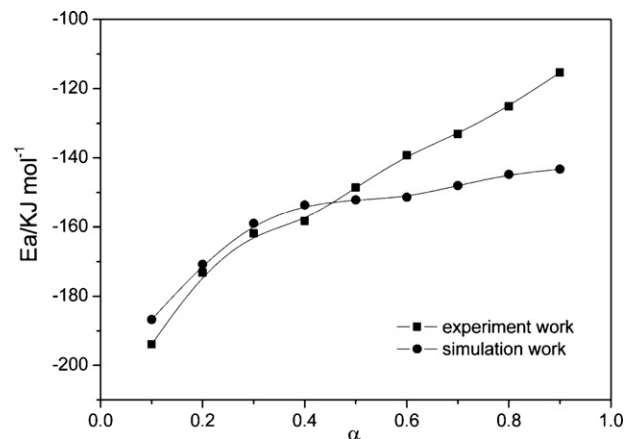
$$\ln\left(\frac{da}{dt}\right)_{a,i} = \text{constant} - \frac{E_a}{RT_{a,i}} \quad (15)$$

where $\ln(da/dt)_{a,i}$ is the instantaneous crystallization rate at a given relative crystallinity, and i is the ordinal number of the experiment carried out at the cooling rate, ϕ_i . E_a is the effective energy barrier of the process at the given value of a . Karayannidis and co-workers [7] also used this method to derive the effective energy barrier of iPP, the dependence of the effective activation energy on conversion was shown in Fig. 4.

The activation energy (E_a), whether being derived from experiment or simulation, increased with the increases in the relative crystallinity. It can be observed that for the crystallization at the low degree of relative crystallinity, the value of E_a derived from the simulation closed to the experiment results, whereas at the high degree of relative crystallinity, iPP crystallization had higher activation energy as was compared with the theoretical results, which indicated that in the actual situation, the crystallization of iPP need to accept more energy at the late crystallization stage and suggested that the crystallization of iPP at the high degree of relative crystallinity was a more complicate process than the models described.

5.3. Spherulite size

For most semicrystalline polymer, the crystallization temperature has a great influence on the spherulite size. Higher temperature or lower cooling rate was favorable to the formation of large size spherulites. Therefore, cooling rate had a profound effect on the morphology that developed in semicrystalline polymers during processing [28]. The computation of spherulite radius was conducted in the simulation, and the relationship of the number average diameter (\bar{d}) as well as the maximum diameter (d_{max}) of spherulites with cooling rates were investigated, which were presented in Table 2. It can be seen that both \bar{d} and d_{max} decreased with

**Fig. 4.** Dependence of the effective energy barrier on the relative crystallinity.

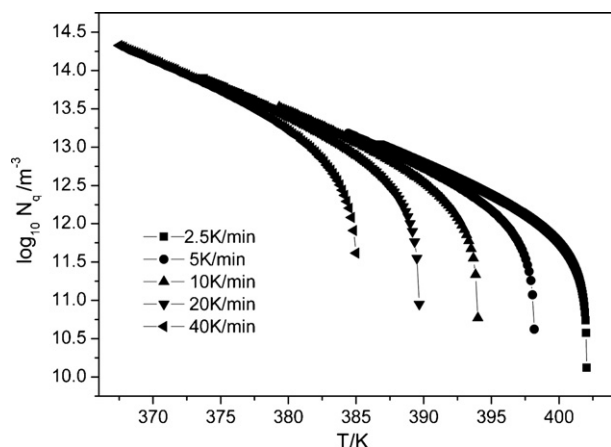


Fig. 5. Trend of nuclei density varying with temperature for iPP at different cooling rate.

the increasing of the cooling rate ϕ , which has also been observed by Sun et al. [29] and Tai et al. [30]. It is indicated that the size of spherulites of polypropylene would decreased when the crystallization occurred at higher cooling rate. Moreover, It could also be observed that the ratio of \bar{d} to d_{\max} decreased with the increasing of cooling rate, implying that the spherulite size distribution was more uniform as iPP crystallized at lower cooling rate.

5.4. Nuclei density

Compared with that of isothermal crystallization, nucleation process of non-isothermal crystallization was much more difficult to observe directly with experiments. Combined the simulation model with the experimental data of the nuclei density of isothermal crystallization at various temperatures measured by Koscher and Fulchiron [16], we could obtain the evolvement of nuclei density with the time during the non-isothermal crystallization. Here the nuclei density of non-isothermal crystallization was treated as a function of time, and the number of nuclei at a certain time was the sum of those which had been activated and finished their induction stage. Fig. 5 shows the details for nuclei density evolvement during non-isothermal crystallization at different cooling rates. The increasing rate of nuclei density increased as crystallization carried through because with the crystallization temperature decreasing the supercool degree becomes lower, which produced a higher driving force to make nucleation more quickly. The nuclei density after the completion of crystallization at 2.5, 5, 10, 20 and 40 K/min were 7.655×10^{12} , 1.515×10^{13} , 3.3481×10^{13} , 8.1043×10^{13} and $2.1208 \times 10^{14} \text{ m}^{-3}$, respectively. As was illustrated above, a higher cooling rate make it possible to reach lower crystallization temperature, meaning the crystallization processes with higher supercool degree, therefore, the rate of nucleation rise. Thus nuclei density increases as cooling rate increased.

6. Conclusions

The calculated results of the simulation model are in good agreement with non-isothermal crystallization kinetics at low cooling rate for iPP, whereas due to the thermal lag between the sample and calorimeter furnace, the predicted data deviate from the experiment data at the late stage of crystallization at high cooling rate. With the incorporation of the crystallization induction time which is ignored in most crystallization models, the simulation well predict the kinetics parameters for the non-isothermal crystallization of iPP at various cooling rates. With the increase in the relative

crystallinity, the value of E_a obtained from the simulation has a more smooth increasing trend than the experiment results. According to our simulation, the size of number average diameter (\bar{d}) as well as the maximum diameter (d_{\max}) of spherulites after finishing the crystallization was obtained, and the results showed that the spherulite size distribution is more uniform as iPP crystallize at lower cooling rate; the development of the nuclei density during the crystallization at various cooling rates was acquired and the nuclei density was increased with the increasing of cooling rate. Generally the simulation is reasonable for the non-isothermal crystallization of iPP.

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