Evaluation of Nonisothermal Crystallization Kinetic Models for Linear Poly(phenylene sulfide)

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ABSTRACT: The nonisothermal crystallization kinetics of linear Poly(phenylene sulfide) (PPS) was studied with differential scanning calorimetry. Ozawa theory, Jeziorny model, and Mo equation were applied to describe the crystallization kinetics and to determine the crystallization parameters and mechanism of the linear PPS resin. The crystallization activation energies were also calculated using Kissinger formula and Flynn-Wall-Ozawa equation, respectively. According to the Ozawa model, it is found that instantaneous nucleation takes place during crystallization of PPS; the Ozawa exponent m is 3 in initial stage of crystallization; as the crystallization temperature decreases, the value of m reduces, and the growth rate of crystal almost keeps a constant. The Avrami exponent n obtained from Jeziorny model fluctuate around 1.84. Based on the Jeziorny model, the crystallization rate increases with increasing the cooling rate, but it does not change any longer when the cooling rate rise to a certain value. Mo equation also exhibits great advantages in treating the nonisothermal crystallization kinetics of PPS. The activation energy E of nonisothermal crystallization process of PPS is calculated to be -162.73 kJ/mol by the Kissinger formula, and the mean value of E determined by Flynn-Wall-Ozawa equation is -152.40 kJ/mol. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 14–20, 2011

Key words: poly(phenylene sulfide); nonisothermal crystallization; crystallization activation energy

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a high performance engineering material with an unusual combination of properties such as excellent chemical resistance (no solvent below 200°C) and thermal stability (long-term use at 190°C), high flame retardant (Limited Oxygen Index $\geq$ 35 %) and radiation resistance (Irradiation Dose $\geq 1 \times 10^7$ GY), good electric insulation, and mechanical properties. PPS is widely used in making injection-molded components of complex shapes for engineering application, including pump impellers, ball valves, gears, wear rings, electrical sockets, battery, and telephone components etc.[1] Fiber also can be spun with PPS, which is mainly used in industrial filter bag. With the worldwide increasing attention to environment protection, PPS fibers will develop rapidly.

Crystallization is one of main processes in the structural evolvement during the crystalline poly-mers process. The properties of crystalline polymers are governed by the supermolecular morphology, which in turn is controlled by crystallization behavior. Thus, the study of crystallization kinetics is important for optimizing the process conditions. In the processing of polymers, crystallization usually occurs at nonisothermal conditions, therefore, the research of nonisothermal has more practical signification. In the past few years, much effort has been made to describe the nonisothermal crystallization kinetics of PPS and its blends. Lopez and Wilkes[2] used Ozawa theory to well describe the nonisothermal crystallization process of linear and branched PPS. They found that the values of Ozawa exponent determined by the Ozawa equation ranged from 2.3 to 3, which were in good agreement with the values obtained by isothermal methods. Minkova and Magagnini,[3] Hong et al.[4] and Gopakumar et al.[5] obtained similar values for the Ozawa exponent using Ozawa equation. Blends of PPS with several liquid crystalline polymers (LCPs) and the effect of LCPs on the dynamic solidification process of PPS have been studied by many researchers. Minkova and Magagnini[3] analyzed the nonisothermal crystallization behavior of blends of PPS with the thermotropic LCP Vectra-B950. They considered that the Ozawa theory was valid not only for neat PPS but also for its blends. Hong et al.[4] also studied the

dynamic solidification process of PPS/Vectra-B950 blend. This case suggested that LCP could promote the crystallization of PPS by acting as a nucleating agent. Gopakumar et al.[5] also used Ozawa equation to well describe the nonisothermal crystallization of blends of PPS with the LCP POBET. Much effort has also been made to analyze the effects of various fillers (such as carbon, aramide, graphite, glass, etc.) on the crystallization kinetics of PPS.[6–11] All of these studies only based on the Ozawa model, and they only obtained the mechanism of nucleation and crystal growth of PPS, but the effects of external conditions on the crystallization of PPS, which played very important role in PPS processing, were not discussed.

In this work, the nonisothermal crystallization process of linear PPS was simulated by differential scanning calorimetry. This work evaluated several kinetic models that were used to describe the nonisothermal crystallization process of PPS. Furthermore, the mechanisms of nucleation and crystal growth were described. Meanwhile, the effects of external conditions on the crystallization process of PPS were also discussed. The results obtained from this work have some significance for the processing of PPS.

EXPERIMENTAL

The material used in this study was Fortron® PPS 0203HS resin with melting point of 285°C, density of 1.35 g/cm^3 and melt viscosity (typically) of 30 Pa s, manufactured by Ticona, a business of Celanese AG. Before use, PPS resin was dried in a vacuum oven, at 100°C for 12 h.

Thermal treatment and data gathering were carried out using a NETZSCH DSC 204F1 Differential Scanning Calorimeter (DSC). The temperature and heat enthalpy were calibrated with indium standard before the equipment running. The DSC samples were heated from 30 to 320°C under nitrogen atmosphere at the rate of 30°C/min and held at this temperature for 5 min to destroy any residual nuclei, and then the samples were cooled down until crystallization completed, at a constant cooling rate of 5, 10, 15, 20, 25, and 30°C/min, respectively.

RESULTS AND DISCUSSION

Thermal behavior

It is well known that the crystallization rate of polymer is controlled by both nucleation rate and crystal growth rate.[12] However, nucleation and crystal growth have different temperature dependence. For the nucleation process, if the temperature is too high, it is difficult to form or to stabilize crystal nucleus owing to the violent thermal motion of molecular chain segment. For the rate of crystal growth,
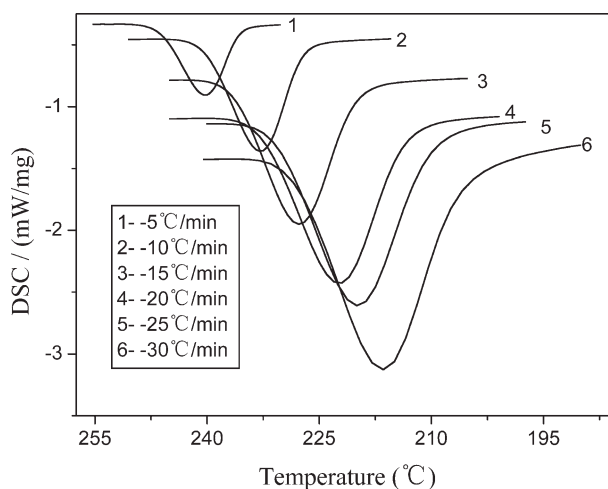

Figure 1 Curves of PPS nonisothermal crystallization.

it depends on the diffusion rate and regular pile rate of chain segment. The higher the temperature is, the more active the chain segment is. Therefore, the crystal growth rate will be faster. DSC curves obtained at different cooling rate for PPS are shown in Figure 1. It is found that the cooling rate has significant effect on the crystallization behavior of PPS. As the cooling rate increases, the crystallization peak temperature, T_p, which corresponds to the maximum crystallization rate, shifts to lower temperature, but it does not affect the degree of crystallinity of PPS. The main reason for that is nucleation occurs at the lower temperature when the PPS sample is cooled at the faster cooling rates because there is not enough time to form the crystal nuclei at higher temperatures. At each cooling rate, crystallization takes place at temperature above the point of maximum crystallization rate (about 180°C). These results suggest the crystallization process is controlled by nucleation. The exothermic crystallization peaks are monomodal and sharp, suggesting that secondary crystallization does not play an important role in PPS.

The S-shaped curves of relative crystallinity α versus crystallization time t at different cooling rates are shown in Figure 2. The relative crystallization fraction of PPS increases slowly at the initial period, and then rapidly, but it tends to slow down in the later crystallization process. For the nonisothermal crystallization of PPS melt, the crystallization time reduces as the cooling rate increases.

Ozawa theory

Based on the Evans theory, Ozawa[13] assumed that the nonisothermal crystallization was composed of innumerable isothermal solidification process. From the nucleation and crystal growth of polymer, he derived the crystallization kinetics equation at a constant cooling rate, which was called Ozawa equation[14–17]:
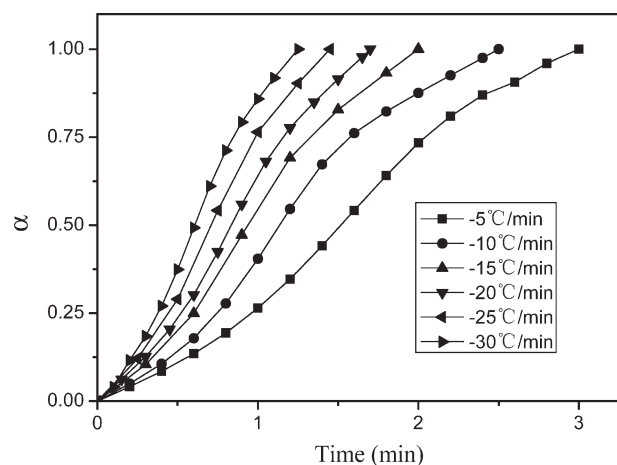
Figure 2 Fraction of relative crystallinity versus crystallization time.

$$1 - \alpha = \exp\left[\frac{-K(T)}{|\beta|^m}\right] \quad (1)$$

where α represents the relative crystallization fraction at temperature T; β is cooling rate; m is Ozawa exponent, which depends on the nucleation model and dimension of crystal growth; and $K(T)$ is cooling crystallization function, which is related to the nucleation rate and crystal growth rate etc. Equation (1) can be written as:

$$\ln[-\ln(1 - \alpha)] = \ln K(T) - m \ln \beta \quad (2)$$

If this model can correctly describe the nonisothermal crystallization kinetics of PPS, at a certain temperature the diagram of $\ln[-\ln(1-\alpha)]$ as a function of $\ln\beta$ will be a straight line, from which the m and $K(T)$ can be obtained.
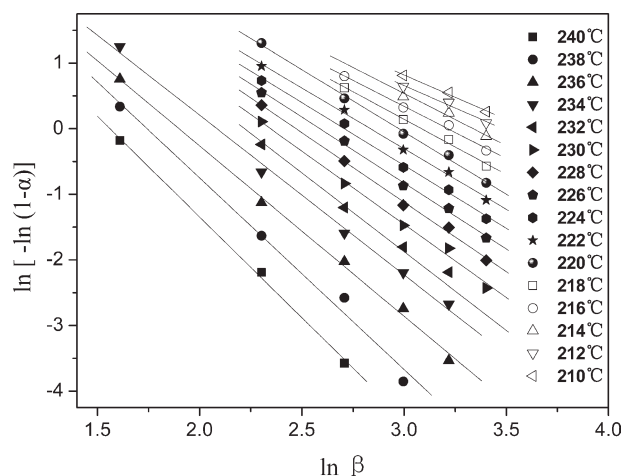

Figure 3 The plot of $\ln[-\ln(1-\alpha)]$ versus $\ln \beta$ for nonthermal crystallization at different temperatures.
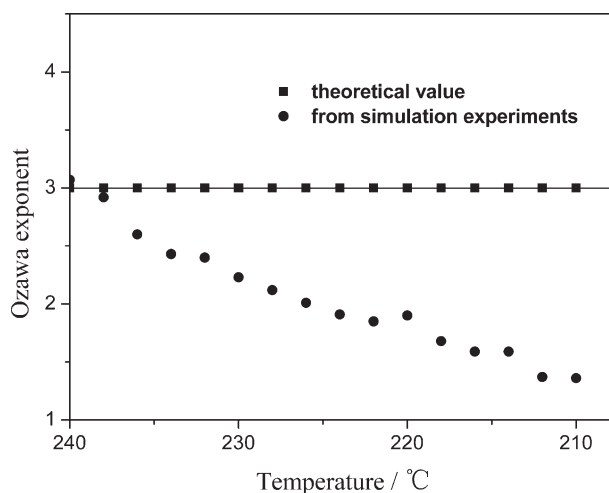
Figure 4 The temperature dependence of Ozawa exponent.

Figure 3 presents the plots of $\ln[-\ln(1-\alpha)]$ as a function of $\ln\beta$. The plots show excellent linear relationship at each temperature, suggesting the Ozawa model can describe the nonisothermal crystallization of PPS at least in the form.

Here, we carry out the following assumptions: (1) Nucleation of PPS is instantaneous, that is, the nuclei has been pre-existing before the start of crystal growth, and the number of nuclei does not change with the time in the unit volume; (2) Spherulites grow with a constant rate. If this is the case, the theoretical value of Ozawa exponent is 3 in the whole crystallization process of PPS. The relationship between the experimental value of m and temperature is shown in Figure 4. We find the experimental value of m is near theoretical value 3 in initial stage of crystallization, suggesting the assumption of instantaneous is tenable. However, the Ozawa exponent decreases as the decreasing temperature. The main factors lowering the Ozawa exponent m, such as growth site impingement and truncation of spherulites may reduce the crystallization dimension as the spherulites growing.[2,4,5] The crystals will grow to the direction of two-dimension or one-dimension, corresponding to forming the sheet-like or rod-like crystals. And the intercollision is less probable in the early stage of PPS crystallization, so the crystals grow to the direction of three-dimension, and the Ozawa exponent is 3. By calculating, we know the mean value of m is 2.06.

The cooling crystallization function, $\ln K(T)$, which can be determined by the intercept of each straight line in Figure 3, represents the crystallization rate including nucleation rate and crystal growth rate. We know PPS will undergo instantaneous nucleation, so $\ln K(T)$ only depends on the crystal growth rate. The relationship between the cooling crystallization rate and temperature is shown in Figure 5. It is found that $\ln K(T)$ is nearly a constant,
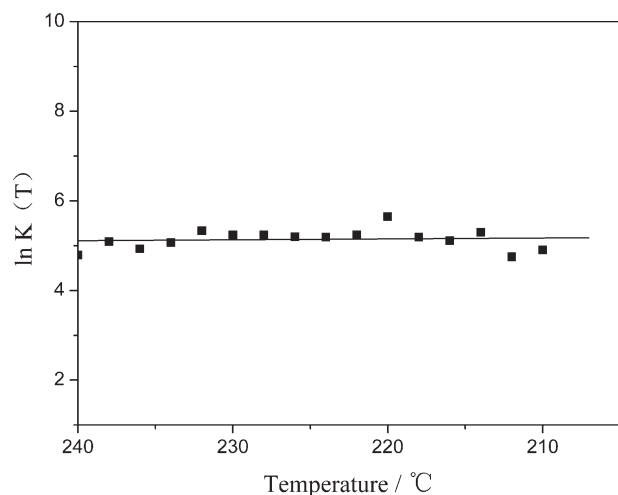
Figure 5 Plot of cooling crystallization function versus temperature.

Figure 6 Plot of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ at different cooling rates.

illuminating the crystal growth rate of PPS does not change as the relative crystallization fraction increases. The main reason for that is growth site impingement and truncation of spherulites and the decreasing temperature have negative and positive effects on the crystal growth rate, respectively.

Jeziorny model

Jeziorny[18] used Avrami equation to treat the nonisothermal crystallization process, and then corrected the crystallization rate constant. The equation can be written as follows[14–17]:

$$\ln[-\ln(1-\alpha)] = \ln k + n \ln t \qquad (3)$$

$$\ln K_c = \frac{\ln k}{|\beta|} \qquad (4)$$

where α is relative crystallization fraction at time t, k is crystallization rate constant, while K_c and n present corrected rate constant and Avrami exponent, respectively, which depend on the mechanism of crystallization. A plot of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ will give a straight line, and n and k can be derived from the slope and the intercept, respectively, and then correct k using eq. (4).
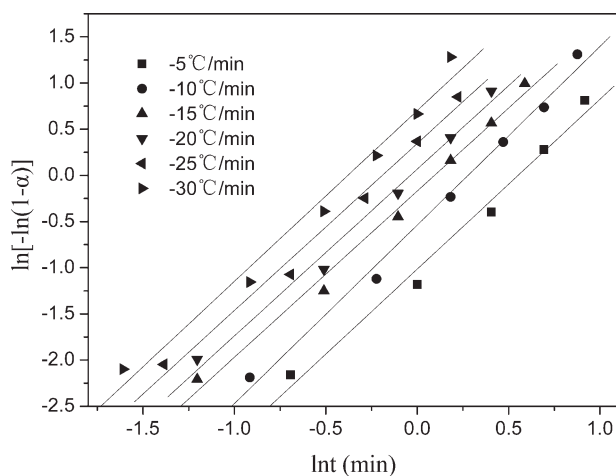
By plotting $\ln[-\ln(1-\alpha)]$ versus $\ln t$ at different cooling rates shown in Figure 6, some straight lines are obtained, which indicates Jeziorny model can well describe the nonisothermal crystallization process in the form. The kinetic parameters n, K_c and half crystallization time $t_{1/2}$ are also listed in Table I. Although the Avrami exponent n obtained from Jeziorny model lost the physical meaning derived for isothermal conditions,[15] it also depends on the nucleation model and dimension of crystal growth. It is found that the value of n fluctuate around 1.84 at different cooling rates, which approximates the mean value of Ozawa exponent m determined by Ozawa theory. This demonstrates the nonisothermal crystallization process of PPS consists of numerous isothermal processes, and n is the mean value of numerous isothermal Avrami exponents. The value of n nearly keeps a constant, indicating the crystallization mechanism of PPS does not change as the cooling rate increases.

The parameters K_c and $t_{1/2}$ are related to the rate of crystallization. The value of K_c increases, but $t_{1/2}$ decreases as the cooling rate elevated, presenting that the higher cooling rate is, the faster crystallization rate is obtained. However, the changes of K_c and $t_{1/2}$ are gradually slow as the increasing of the cooling rate, indicating when the cooling rate reach to a certain value, the crystallization rate will not increase with increasing the cooling rate.

TABLE I
Nonisothermal Crystallization Kinetics Parameters from Jeziorny Model

Cooling rate (°C/min)	r	n	ln K	ln K_c	K_c	$t_{1/2}$ (min)
−5	0.993	1.84	−1.015	−0.203	0.816	0.9151
−10	0.996	1.93	−0.537	−0.0537	0.948	0.8502
−15	0.996	1.80	−0.170	−0.0113	0.989	0.8208
−20	0.995	1.81	0.068	0.0034	1.004	0.8149
−25	0.995	1.81	0.346	0.0138	1.014	0.8104
−30	0.990	1.85	0.702	0.0234	1.024	0.8098
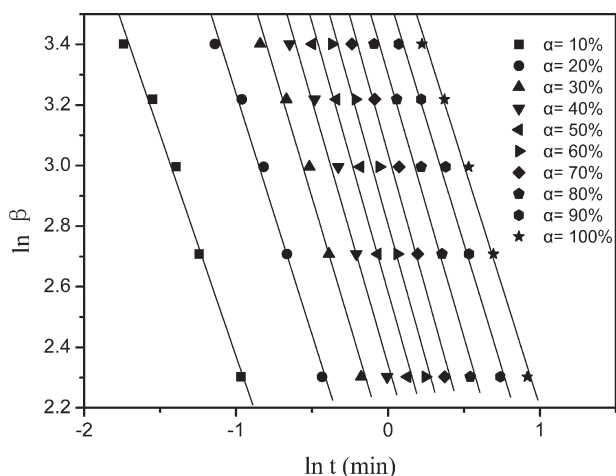
Figure 7 Plot of ln β versus ln t for nonisothermal crystallization at different relative crystallinity.

Figure 8 Kissinger plot for evaluating the nonisothermal crystallization activation energy.

Mo model

Mo and coworkers[19] proposed a combined Ozawa equation and Avrami equation to describe the nonisothermal crystallization kinetics of polymers namely,

$$\ln k + n \ln t = \ln K(T) - m \ln |\beta| \tag{5}$$

$$\ln |\beta| = \ln F(T) - a \ln t \tag{6}$$

where $a = n/m$, $F(T) = [K(T)/k]^{1/m}$. $F(T)$ is related to the cooling rate, it represents the speed of the crystallization, and describes the necessary value of cooling rate when approaching a certain degree of crystallization at unit crystallization time; the higher $F(T)$ is, the faster crystallization rate is. Based on eq. (6), at a certain relative crystallization fraction, the plots of $\ln |\beta|$ as a function of $\ln t$ are shown in Figure 7. The parameters $F(T)$ and the value of a at each relative crystallization fraction are listed in Table II, which can be derived by the slopes and the intercepts of the straight lines.

As shown in Figure 7, Mo plots have excellent linear relationship, indicating Mo model can also well depict the nonisothermal crystallization kinetics in the form. As can be seen in Table II, the value of $F(T)$ increases with increasing relative crystallization fraction. The higher the degree of crystallization is, the higher cooling rate is needed with the unit

crystallization time. It means that the activity ability of molecular chain declines with the formation of the crystals, and lead to being more difficult to form the crystals. Nevertheless, the values of a are almost constant, which fluctuate around 1.68 at different relative crystallization fractions. This is similar to the conclusions of nylon 6/foliated graphite nanocomposites and Maleic Anhydride-Modified iPP studied by Weng et al.[14] and Bogoeva-Gaceva,[20] respectively.

Crystallization activation energy

Based on the n-order kinetic model, Kissinger[21] proposed that the activation energy could be determined as follows:

$$\ln \frac{|\beta|}{T_p^2} = \ln \frac{AR}{E} - \ln[G(a)] - \frac{E}{RT_p} \tag{7}$$

where β is the cooling rate, T_p is the crystallization peak temperature, A is the pre-exponential factor, R is the universal gas constant, E is the activation energy, and $G(\alpha)$ is the conversion function. The values of $\ln[\beta/(T_p*T_p)]$ are plotted as a function of $1/T_p$ in Figure 8 and a good linear relations is obtained. Accordingly, the crystallization activation energy E could be determined from the slope of the line. The value of the crystallization activation energy is found to be -162.73 kJ/mol.

In nonisothermal kinetics theory, the conversion rate α will satisfy the following relationship[21]:

$$\frac{d\alpha}{dT} = \frac{A}{|\beta|} \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha) \tag{8}$$

where $f(\alpha)$ is the kinetic mechanism function. Flynn-Wall-Ozawa method[21] used the approximation of

TABLE II
Nonisothermal Crystallization Kinetics Parameters from Mo Model

α (%)	ln F(T)	a	α	ln K(T)	a
10	0.907	1.46	60	2.805	1.80
20	1.645	1.59	70	3.038	1.80
30	2.051	1.68	80	3.300	1.74
40	2.343	1.74	90	3.564	1.65
50	2.582	1.78	100	3.798	1.60
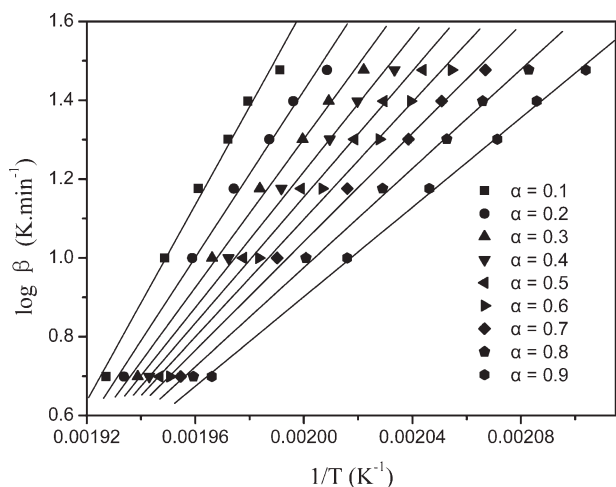
Figure 9 Plots of log β versus 1/T at different relative crystallinity.

Figure 10 The effect of relative crystallization fraction and the average crystallization temperature on the activation energy.

Doyle to evaluate the integrated form of eqs. (8) and (9) as an approximation solution can be obtained:

$$\log |\beta| = \log\left[\frac{AE}{RG(\alpha)}\right] - 2.315 - 0.4567\frac{E}{RT} \quad (9)$$

where $G(\alpha)$ is the integrated form of the kinetic mechanism function, which is related to the reaction mechanism. At a certain conversion, the diagram of $\log|\beta|$ as a function of $1/T$ will be a straight line, from which the value of E can be obtained. This method is mainly used to treat the kinetic of thermal degradation. In this work, we attempt to describe the nonisothermal crystallization kinetic of PPS using the Flynn-Wall-Ozawa method, to calculate the crystallization activation energy of PPS.

As shown in Figure 9, the plots exhibit good linear relationship at different relative crystallization fraction, and the values of E derived from the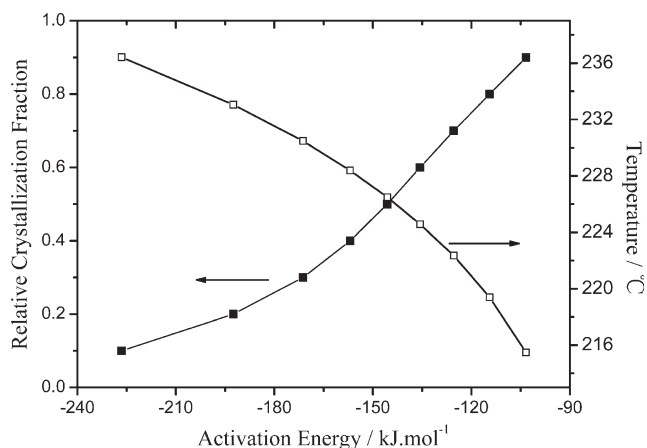 slopes of these lines are listed in Table III. Figure 10 represents the effect of relative crystallization fraction and the average crystallization temperature on the activation energy. It is found that the values of E are negative as expected. The activation energy sign indicates that crystallization gradually becomes easy with the decreasing crystallization temperature. It also can be

seen that the average value of E is -152.40kJ/mol, which is near the value calculated from the Kissinger method.

CONCLUSIONS

A systematic study of the nonisothermal crystallization kinetics of linear PPS is performed by the DSC technique. The availabilities of several kinetic models that were used to describe the nonisothermal crystallization process of PPS were evaluated. Three different kinetics models, namely, the Ozawa, the Jeziorny, and the Mo model, can describe the mechanism of nucleation and crystal growth, and the effects of external conditions on the crystallization process of PPS very well at different angles. The crystallization activation energy can also be derived by the Kissinger and F-W-O method, respectively.

TABLE III
Crystallization Activation Energy of PPS from Flynn–Wall–Ozawa Method

α	r	E (kJ/mol)	α	r	E (kJ/mol)
0.1	0.995	−226.56	0.6	0.996	−135.62
0.2	0.996	−192.5	0.7	0.997	−125.34
0.3	0.997	−171.3	0.8	0.998	−114.46
0.4	0.996	−156.92	0.9	0.999	−103.33
0.5	0.996	−145.61	Average	–	−152.40

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