

Nonisothermal Melt and Cold Crystallization Kinetics of Poly(aryl ether ketone ether ketone ketone)

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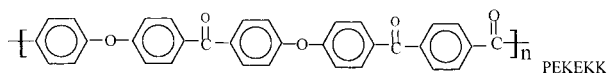
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ABSTRACT: Nonisothermal melt and cold crystallization kinetics of poly(aryl ether ketone ether ketone ketone) (PEKEKK) were investigated by differential scanning calorimetry (DSC). The Avrami equation modified by Jeziorny could only describe the primary stage of nonisothermal crystallization kinetics of PEKEKK. Also, the Ozawa equation could not describe its nonisothermal crystallization behavior. A convenient and reasonable kinetic approach was used to describe the nonisothermal crystallization behavior. The crystallization activation energy were estimated to be -264 and 370 KJ/mol for nonisothermal melt and cold crystallization by the Kissinger method. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2865–2871, 2000

Key words: PEKEKK; nonisothermal; crystallization; kinetics; DSC

INTRODUCTION

Poly(ether ether ketone) (PEEK) is well known as a high-performance engineering thermoplastics possessing excellent mechanical properties, good solvent resistance and high thermal stability.^{1,2} However, its relatively low glass transition temperature (T_g , 143°C) and comparatively high price limit its widespread application. By varying the ratio of ether/ketone groups, one can improve the low T_g of this kind of polymer.^{1–6} Among them, poly(aryl ether ketone ether ketone ketone) (PEKEKK), developed by BASF Co., possesses a higher thermal resistance by improving the ratio of ketone/ether; moreover, its mechanical, physical, and other properties that are comparable with those of PEEK are still maintained. PEKEKK has the following chemical repeating unit:



Up to now, only relatively few articles have reported on this polymer, mainly on its synthesis,⁷ crystal structure,⁸ polymorphism,⁹ and crystallization behavior.¹⁰ Practical processes such as extrusion, molding, and film production are usually performed under dynamic, nonisothermal conditions, so it is of great practical significance to study the nonisothermal crystallization process quantitatively. The present article reported the nonisothermal crystallization behavior of PEKEKK.

EXPERIMENTAL

Materials and Preparation

PEKEKK was prepared by polycondensation of 1,4-diphenoxybenzophenone with terephthaloyl chloride as described by Mikhail G. Zolotukhin and Daniel R. Rueda.⁷ The inherent viscosity of

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the polymer used is 0.96 dL/g (measured at 25°C on a 0.1% solution of the polymer in 98% sulfuric acid). The transparent amorphous glassy film was obtained by quenching the hot-press sheets in ice water from the melt (420°C).

Differential Scanning Calorimetry (DSC)

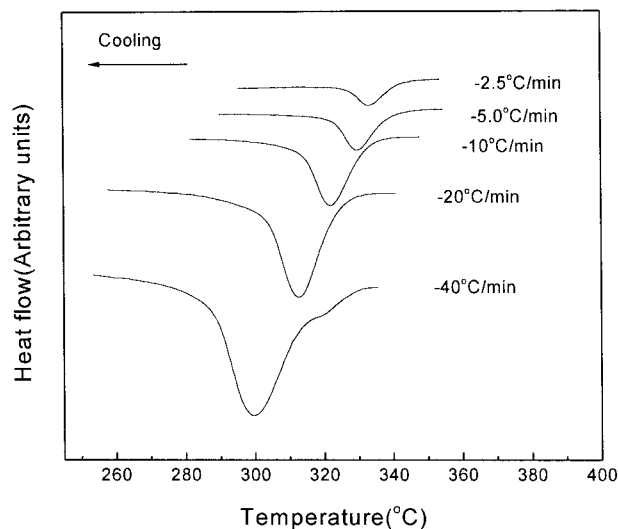
Nonisothermal crystallization kinetics were carried out by using a Perkin-Elmer DSC-7 through two kinds of experiments: melt crystallization and cold crystallization. Melt crystallization: the samples were heated up to 420°C, and held there for 10 min to eliminate small residual nuclei that might act as seed crystals. Then, the melt was cooled to crystallize at selected constant rates Φ (in the range from 2.5 to 40°C/min). Cold crystallization: the amorphous samples were crystallized at the same constant heating rates. All operations were performed under a nitrogen purge. Sample weight varied between 6–8 mg.

RESULTS AND DISCUSSION

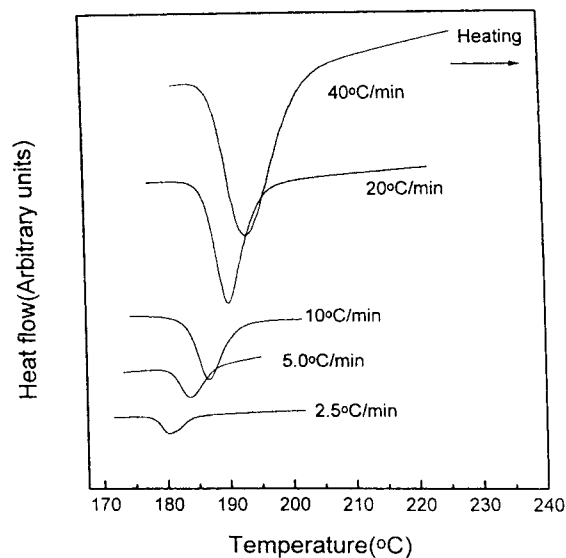
The results of heating and cooling crystallization of PEKEKK were shown in Figure 1. For melt crystallization, the exothermic peak temperature (T_p) on cooling, shown in Figure 1(A), shifted to lower temperature as the cooling rate increased, and became more broad. At $-2.5^\circ\text{C}/\text{min}$, the peak temperature was measured at 333.2°C, decreasing to 303.2°C at the highest cooling rate of $-40^\circ\text{C}/\text{min}$. But for cold crystallization, the opposite was seen, as the heating rate increased [Fig. 1(B)]. The values of T_p , their corresponding peak times t_{max} , the crystallization enthalpies ΔH_c , and the relative crystallinity X_t of the nonisothermal melt and cold crystallization for PEKEKK under different cooling and heating rates were collected in Table I.

Because it is not necessary to determinate the absolute degree of crystallinity during the data treatment of crystallization kinetics, the relative crystallinity X_t as a function of crystallization temperature is defined as¹⁶

$$X_t = \frac{\int_{T_0}^T \left(\frac{dH_c}{dT} \right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH_c}{dT} \right) dT} \quad (1)$$



(a)



(b)

Figure 1 Heat flow vs. temperature during nonisothermal melt (A) and cold (B) crystallization at different rates.

where T_0 and T_∞ represent the onset and end temperatures of crystallization, respectively. Integration of the exothermic peaks during the nonisothermal scan gave the relative degree of crystallinity as a function of temperature. These results were shown in Figure 2(A) and 2(B) for the heating and cooling, respectively. Generally, all these curves had the same sigmoid shape, implying that only the lag effect of cooling or heating rate on crystallization were observed for these curves.

Table I Peak Temperature (T_p), Peak Time (t_{\max}), Crystallization Enthalpy (ΔH_c), and Relative Crystallinity (X_t) at Maximum Rate of Heat Flow during Nonisothermal Crystallization of PEKEKK

Φ ($^{\circ}\text{C}/\text{min}$)	T_p ($^{\circ}\text{C}$)	t_{\max} (min)	ΔH_c (J/g)	X_t (%)
Melt Crystallization				
-2.5	333.2	8.26	53.3	45
-5.0	329.7	4.98	53.1	49
-10	322.0	2.59	54.9	47
-20	312.7	1.41	53.4	45
-40	303.2	0.81	51.0	53
Cold Crystallization				
2.5	180.4	3.51	27.1	38
5.0	183.8	2.13	26.4	42
10	186.8	1.24	24.2	42
20	190.1	0.63	30.3	37
40	193.1	0.28	28.6	37

The well-known Avrami equation¹¹ is used to analyze the crystallization kinetics, which assumed that the relative degree of crystallinity developed with crystallization time t ,

$$1 - X_t = \exp(-Z_t t^n) \quad (2)$$

where n is the Avrami crystallization exponent, depending on the nature of nucleation and growth geometry of the crystals; Z_t is a composite rate constant involving both nucleation and growth rate parameters. While eq. (2) is reasonable for many systems, some modified forms^{12,13} have been proposed to be fitted the experimental results obtained from crystallizing polymers. Considering the nonisothermal character of the process investigated, Jeziorny¹⁴ suggested that the value of rate parameter Z_t should be adequately corrected. The factor that should be considered was the cooling rate, Φ . Assuming constant or approximately constant Φ , the final form of the parameter characterizing the kinetics of nonisothermal crystallization was given as below:

$$\log Z_c = \frac{\log Z_t}{\Phi} \quad (3)$$

By using eq. (2), plots of $\log[-\ln(1 - X_t)]$ vs. $\log t$ are shown in Figure 3. Each curve has a linear portion followed by a gentle deviation at longer times. Usually, this deviation is considered to be due to the secondary crystallization, which

is caused by the spherulite impingement in the later stage. The linear portions are almost parallel to each other, shifting to shorter time with increasing Φ , indicating that the nucleation mechanism and crystal growth geometries are similar for the primary and secondary crystallization at all cooling or heating rates. Each region give different values for n (n_1 and n_2) and Z_c (Z_{c1} and Z_{c2}), (Table II). For nonisothermal melt crystallization, the average value of Avrami exponent were $n_1 \approx 5$ and $n_2 \approx 2$. This suggested that the primary crystallization stage for nonisothermal melt crystallization might correspond to a three-dimensional solid-sheaf growth with athermal nucleation, and in the secondary crystallization

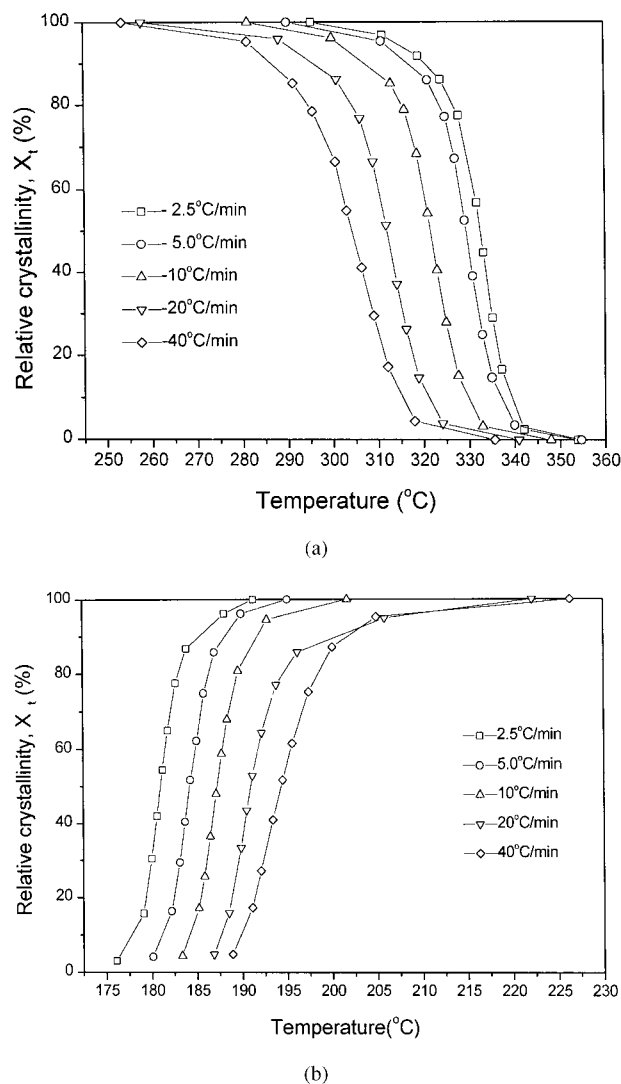


Figure 2 Development of relative crystallinity with temperature for nonisothermal melt (A) and cold (B) crystallization.

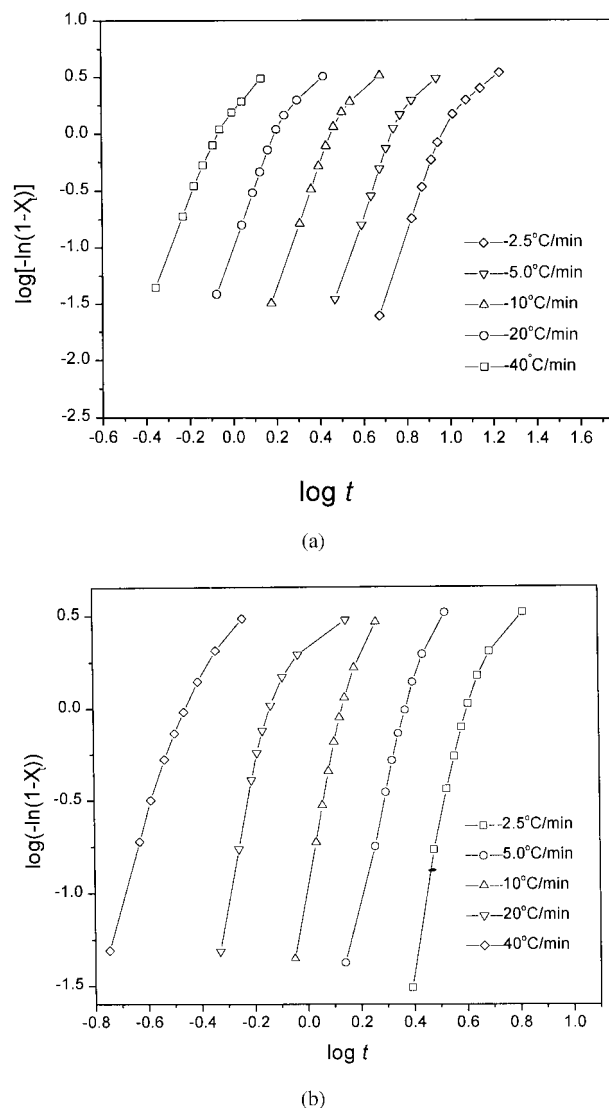


Figure 3 Plots of $\log[-\ln(1 - X_t)]$ vs. $\log t$ for nonisothermal melt (A) and cold (B) crystallization.

$n_2 \approx 2$ probably corresponds to the one-dimensional linear growth and thermal nucleation. For nonisothermal cold crystallization, the average value of Avrami exponent were $n_1 \approx 7$ and $n_2 \approx 2$. This suggested that the primary crystallization stage for nonisothermal cold crystallization might correspond to a three-dimensional solid sheaf growth with thermal nucleation, and in the secondary crystallization $n_2 \approx 2$ probably corresponds to the one-dimensional linear growth and thermal nucleation.¹³ The secondary stage was considered to be due to the effect of the slower crystallization or further perfection of crystal, which was caused by the spherulite impingement in the later stage of crystallization, or due to the

reorganization of initially poorly crystallized macromolecules or small and metastable crystals. It was well known that, if the secondary crystallization was not completed at longer period, the product would continue crystallizing in the course of application. This would lead to a continuous change in the properties of the product. Therefore, to obtain the materials with more stable and better properties, an annealing technique was usually used in practical production, where the heat treatment was always performed to accelerate the secondary crystallization process at the temperature of the maximum crystallization rate.

As the nonisothermal crystallization is a rate-dependent crystallization process, it can be analyzed using the Ozawa analysis.¹⁵ Ozawa accounted for the effect of cooling (or heating) rate, Φ , on crystallization from the melt (or the glassy state), and modified the Avrami equation by replacing t [in eq. (2)] with T/Φ . The Ozawa equation is:

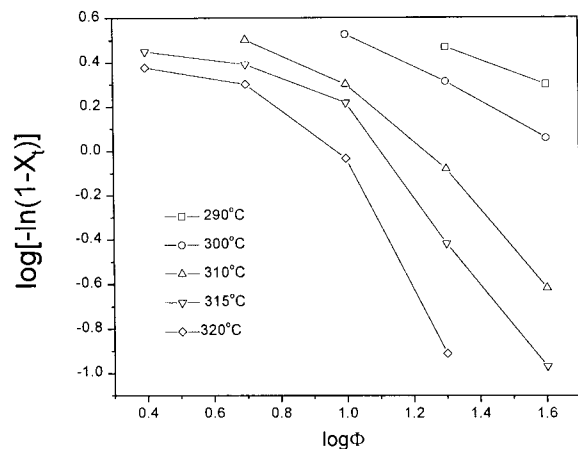
$$1 - X_t = \exp\left[-\frac{K(T)}{\Phi^m}\right] \quad (4)$$

where $K(T)$ was heating or cooling function; m was Ozawa exponent that depended on the crystal growth and nucleation mechanism. Results of the Ozawa analysis are shown in Figure 4(A) and 4(B), plotted as $\log[-\ln(1 - X_t)]$ vs. $\log(\Phi)$, for temperatures from 290 to 320°C for the nonisothermal melt

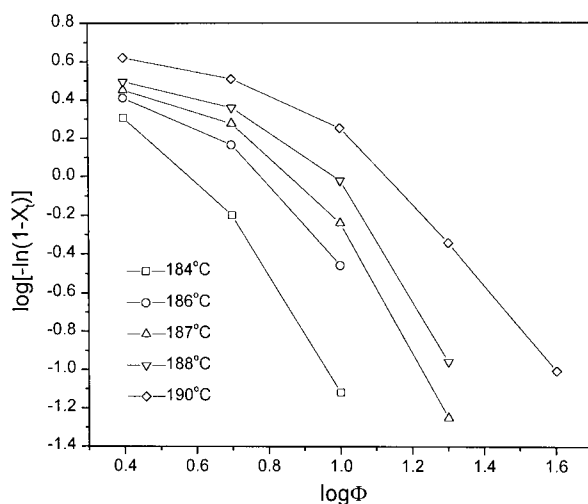
Table II Effect of Cooling/Heating Rates on Crystallization Kinetics of PEKEKK

Φ (°C/min)	Primary Stage			Secondary Stage	
	n_1	Z_{c1}	$t_{1/2}$ (min) ^a	n_2	Z_{c2}
Melt Crystallization					
-2.5	5.6	0.007	2.272	1.6	0.273
-5.0	5.5	0.155	1.313	1.9	0.557
-10	5.5	0.568	1.037	1.8	0.850
-20	5.3	0.890	0.954	1.9	0.969
-40	4.8	1.021	0.922	2.2	1.011
Cold Crystallization					
2.5	7.3	0.018	1.644	1.9	0.387
5.0	6.0	0.357	1.117	2.9	0.624
10	7.6	0.799	0.981	3.3	0.909
20	7.3	1.136	0.935	1.8	1.035
40	5.1	1.154	0.905	2.0	1.057

^a Here, the parameter $t_{1/2}$ is given by $t_{1/2} = (\ln 2/Z_{c1})^{1/n_1}$.



(a)



(b)

Figure 4 Ozawa plots of nonisothermal melt (A) and cold (B) crystallization of PEKEKK.

crystallization, and from 184 to 190°C for the nonisothermal cold crystallization. If the Ozawa treatment correctly models the nonisothermal crystallization process of PEKEKK, the plot of $\log[-\ln(1 - X_t)]$ vs. $\log(\Phi)$ would result in a series of parallel lines of slope m and intercept $K(T)$. But, in fact, Figure 4 shows some nonparallel lines, which is similar to that observed in PEEK¹⁶ and PEEKK.¹⁷ The changing slopes indicate that m is not constant with temperature during the primary crystallization process. The general curvature seen in Figure 4 makes it impossible to determine the cooling or heating function $K(T)$ by the Ozawa method. The reason why the nonisothermal crystallization of PEKEKK does not follow the Ozawa equation is probably due to secondary crystallization, but may,

in fact, be also due to the inaccurate assumption of a constant cooling or heating function over the entire crystallization process.

It is apparent that the Ozawa analysis does not adequately describe the nonisothermal crystallization kinetics of many polymers, such as PEEK¹⁶ and PEEKK,¹⁷ in which a large portion of the crystallization is attributed to secondary processes. Recently, we have adopted a convenient kinetic approach by combining the Avrami equation with the Ozawa equation and successfully deal with the nonisothermal crystallization behavior of PEEKK,¹⁷ its final form is given as below:

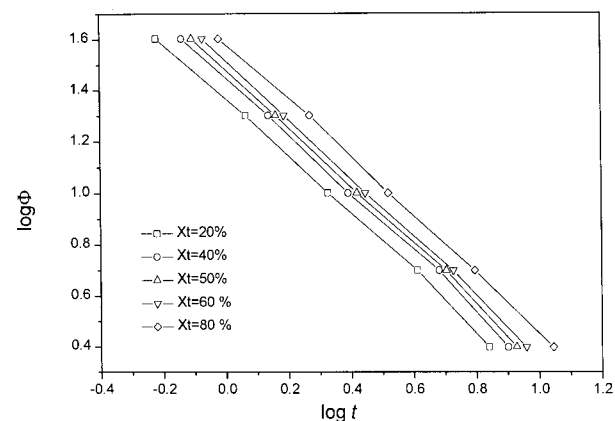
$$\log \Phi = \log F(T) - a \log t \quad (5)$$

where, the kinetic parameter $F(T) = [K(T)/Z_t]^{1/m}$, refers to the value of cooling rate that has to be chosen at the unit crystallization time when the measured system amounts to a certain degree of crystallinity; a is the ratio of the Avrami exponent n to the Ozawa exponent m , i.e., $a = n/m$. It can be seen that $F(T)$ has a definite physical and practical meaning. In this article, the nonisothermal crystallization kinetics of PEKEKK can be conveniently analyzed by using this method. At a given degree of crystallinity, the plots of $\log(\Phi)$ vs. $\log(t)$ were given in Figure 5(A) and 5(B), from which the values of a and $F(T)$ could be obtained by the slopes and the intercepts of these lines, respectively (Table III). The values of $F(T)$ systematically increases with raising the relative crystallinity, indicating that at unit crystallization time, a higher cooling (or heating) rate should be used to obtain a higher degree of crystallinity; but the values of a are almost constant, which is about 1.2 and 1.1 for nonisothermal melt and cold crystallization, respectively. In addition, this combination method has successfully described the nonisothermal crystallization process of many polymers, such as PEEKK,¹⁷ PEDEKK,¹⁸ PEDEK m K,¹⁹ PHB,²⁰ and Nylon-11.²¹

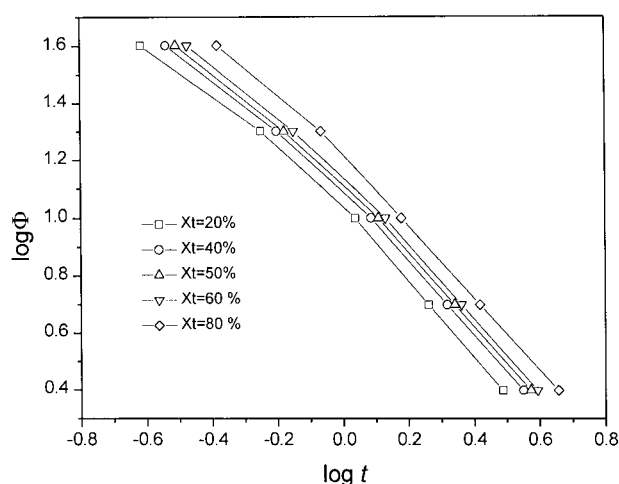
The activation energy of crystallization is derived by Kissinger equation in the following form:²²

$$\frac{d\left(\ln \frac{\Phi}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{\Delta E}{R} \quad (6)$$

where R is the universal gas constant, the rest parameters have as above-mentioned meanings.



(a)



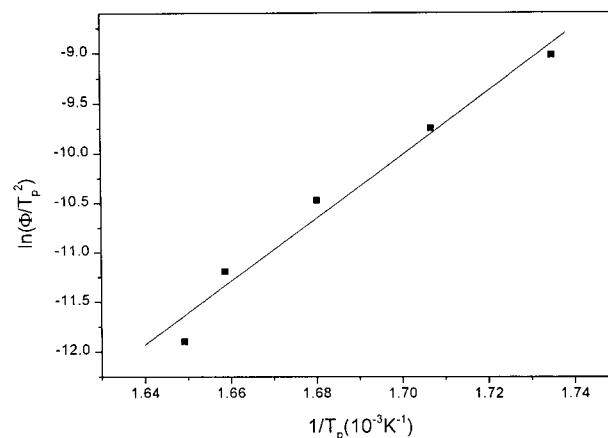
(b)

Figure 5 Plots of $\log \Phi$ vs. $\log t$ for nonisothermal melt (A) and cold (B) crystallization of PEKEKK.

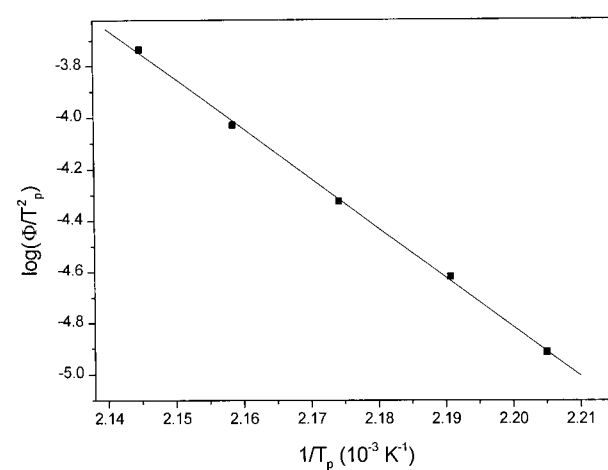
Accordingly, in the light of the results in Table I, the slopes of $\ln(\Phi/T_p^2)$ vs. $1/T_p$ will give $\Delta E/R$ (Fig. 6). The slope of $\log(\Phi/T_p^2)$ vs. $1/T_p$ plot (Fig.

Table III Nonisothermal Crystallization Kinetic Parameters of PEKEKK at Different Degrees of Crystallinities by the Combination of Avrami-Ozawa Equation

X_t (%)	20	40	50	60	80
Melt Crystallization					
$F(T)$	1.38	1.48	1.52	1.54	1.68
a	1.2	1.2	1.2	1.2	1.2
Cold Crystallization					
$F(T)$	0.99	1.05	1.08	1.11	1.19
a	1.1	1.1	1.1	1.1	1.2



(a)



(b)

Figure 6 Kissinger plots for estimating the energy of nonisothermal melt (A) and cold (B) crystallization of PEKEKK.

6) will give the crystallization activation energy, i.e., $\Delta E = -R \times \text{slope}$. The activation energies of nonisothermal melt and cold crystallization can be determined as -264 kJ/mol and 370 kJ/mol, respectively. These values of activation energies for nonisothermal crystallization are rather smaller than those of isothermal melt (923 kJ/mol) and cold (459 kJ/mol) crystallization.²³

CONCLUSIONS

A systematic study of the nonisothermal melt and cold crystallization kinetics of PEKEKK has been performed by the DSC technique. This indicates that the Avrami analysis can gratifyingly describe the primary stage of both crystallization

processes, and the deviation of linearity at the "tails" of lines may be ascribed to the occurrence of the spherulite impingement in the secondary stage as in the cases of the other members of PAEKs. A convenient method is applied to characterize the nonisothermal crystallization of PE-KEKK by combining the Avrami equation with the Ozawa equation.

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