Properties and Crystallization Kinetics of Poly(ether ether ketone)-*co*-Poly(ether ether ketone ketone) Block Copolymers

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ABSTRACT: A series of block copolymers composed of poly(ether ether ketone) (PEEK) and poly(ether ether ketone ketone) (PEEKK) components were prepared from their corresponding oligomers via a nucleophllilic aromatic substitution reaction. Various properties of the copolymers were investigated with differential scanning calorimetry (DSC) and a tensile testing machine. The results show that the copolymers exhibited no phase separation and that the relationship between the glass-transition temperature (T_g) and the compositions of the copolymers approximately followed the formula $T_g = T_{g1}X_1 + T_{g2}X_2$, where T_{g1} and T_{g2} are the glass-transition-temperature values of PEEK and PEEKK, respectively, and X_1 and X_2 are the corresponding molar fractions of the PEEK and PEEKK segments in the copolymers, respectively. These copolymers showed good tensile properties. The crystallization kinetics of the copolymers were studied. The Avrami equation was used to describe the isothermal crystallization process. The nonisothermal crystallization was described by modified Avrami analysis by Jeziorny and by a combination of the Avrami and Ozawa equations. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1652–1658, 2005

Key words: block copolymers; crystallization; oligomers; kinetics (polym.); differential scanning calorimetry (DSC)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a semicrystalline polymer. Its excellent mechanical properties, good environmental resistance, and high thermal and thermooxidative stability make it very attractive as a high-performance engineering thermoplastic.

With the development of high technology and the need for materials with comprehensively excellent properties, some new poly(aryl ether ketones), such as poly(ether ether ketone ketone) (PEEKK), poly(ether diphenyl ether ketone) (PEDEK), and poly(ether diphenyl ether ketone ketone) (PEDEKK),[1,2] have been synthesized. With the improvement of the thermal resistance, the processing temperature has been increased, and these polymers proved difficult to process. The incorporation of the aforementioned polymer blocks into PEEK may afford new materials with improved properties,[3] and through the judicious choice of molecular weights of the block, either homogeneous or microphase-separated morphologies should be possible. This could provide another means for the modification of the properties of PEEK. PEEKK possesses a higher thermal resistance and transition temperature than PEEK. To increase the thermal resistance of PEEK and improve the processing conditions of PEEKK, we recently demonstrated a synthetic route of PEEK/PEEKK block copolymers based on the oligomer–oligomer approach. In this study, we dealt in detail with the thermal properties and crystallization behavior of the these kinds of block copolymers [the contents of ether ether ketone (EEK) were 20, 40, 60, and 80 mol %].

EXPERIMENTAL

Materials and preparation

Diphenylsulfone (98%), hydroquinone (98%), and 4,4'-difluorbenzophenone (98.5%) were purchased from Yanbian Chemical Reagent Plant (Yanbian City, Jilin) and were purified before use. Anhydrous sodium carbonate (98%), anhydrous potassium carbonate (99%), and sulfuric acid guarantee reagent (GR) were purchased from Tianjin Chemical Reagent Plant (Tianjin City). 1,4-Bis(4'-fluorobenzoyl)benzene (98.5%) was synthesized in our laboratory.

Synthesis of the PEEK oligomers

Difluoro-terminated PEEK oligomers were prepared by the reaction of 4,4'-difluorbenzophenone and hy-

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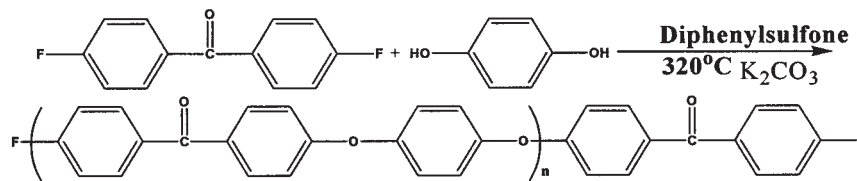
Scheme 1

droquinone in diphenylsulfone in the presence of K_2CO_3 according to procedures published in the literature (Scheme 1).[4,5]

Synthesis of the PEEKK oligomers

Dihydroxyl-terminated PEEKK oligomers were prepared by the reaction of hydroquinone and 1,4-bis(4′-fluorobenzoyl)benzene in diphenylsulfone in the presence of Na_2CO_3, K_2CO_3 according to procedures presented in the literature (Scheme 2).[1]

Synthesis of the PEEK/PEEKK block copolymers

PEEK/PEEKK block copolymers were prepared from the previously mentioned two oligomers via a nucleophilic aromatic substitution reaction (Scheme 3).[6] The typical reaction condition for the copolymer synthesis were as follows: PEEKK oligomer (0.2 mol) was prepared first but was not isolated from the reaction mixture. PEEK oligomer (0.5 mol, solid powder), which had been isolated and characterized, was added to the diphenylsulfone solution of the PEEKK oligomer, and the two oligomers were reacted at 260–310°C for 2–4 h. The copolymer solution was then poured into water. After it was cooled, the precipitate was crushed, repeatedly washed with acetone and water for a total of 10 times, and dried.

Sample preparation

The copolymer samples were molded into films with a thickness of 0.5 mm at a pressure of 10 MPa at 370–380°C for 10 min and were quenched by placement in an ice and water mixture. We prepared crystalline film samples by annealing the quenched film at various temperatures for a predetermined period of time and then cooling the samples slowly to room temperature.

Measurements

The inherent viscosities of the copolymers were measured in a 0.1 wt % H_2SO_4 solution at 25°C. The thermal analysis and crystallization behavior analysis were carried out with a Mettler Toledo DSC821[e] instrument (Switzerland) under a N_2 atmosphere at a scanning rate of 20°C/min, ranging from 50 to 420°C. We measured the tensile properties of the polymeric films with an Instron 1121 tensile testing machine (UK) by recording the uniaxial stress–strain curves with a crosshead speed of 10 mm/min at room temperature.

RESULTS AND DISCUSSION

Properties of the block copolymers

Differential scanning calorimetry (DSC) curves for the quenched samples are shown in Figure 1. The copolymers with different EEK contents showed a single glass-transition temperature (T_g). T_g increased with decreasing EEK content. The plot of T_g against the copolymers is shown in Figure 2. In this figure, the straight line indicates the calculated values according to the following equation:

$$T_g = T_{g1}X_1 + T_{g2}X_2 \qquad (1)$$

where T_{g1} and T_{g2} denote the glass-transition-temperature values of PEEK and PEEKK, and X_1 and X_2 are the corresponding molar fractions of the PEEK and PEEKK segment in the copolymers, respectively. As shown in Figure 2, the relationship between T_g and EEK content approximately followed that of eq. (1).

The results of the tensile tests of the crystallization samples of the copolymers are listed Table I. The tensile moduli of the copolymers were a little lower than those of the pure components. The tensile
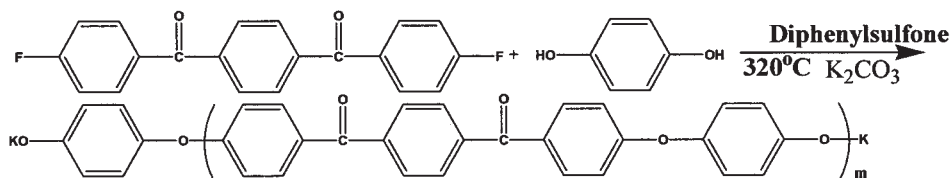
Scheme 2
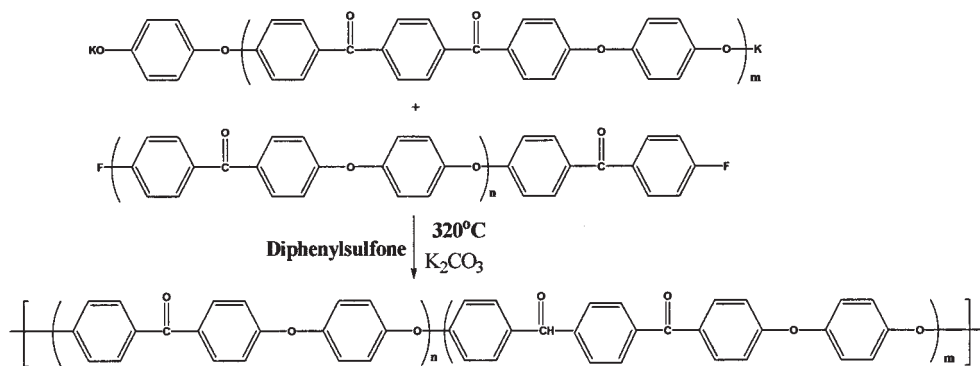
Scheme 3

strength decreased with increasing EEK molar fractions. The elongation at break of the block copolymers decreased with increasing EEK molar fractions.

Isothermal crystallization of the block copolymers

For the isothermal crystallization process, quenched films of the block copolymers were melted at 400°C for 5 min and then scanned by DSC at an appointed temperature.

For the isothermal crystallization process, the Avrami equation[7,8] is often used to described the crystallization dynamics of the polymers as shown:

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

where t is the time, k is a constant of the crystallization dynamics rate, n is the Avrami exponent, and X_t is the relative crystallization degree. Equation (2) can be changed into the following form:

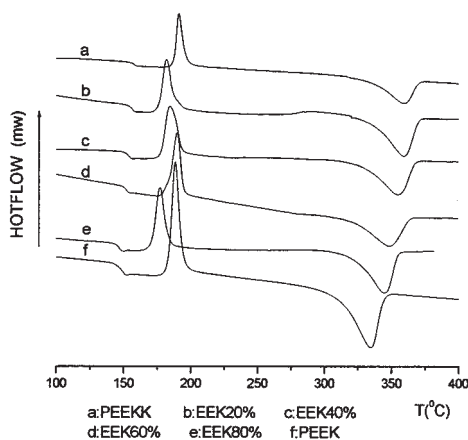$$\log[-\ln(1 - X_t)] = \log k + n \log t \quad (3)$$

In the isothermal crystallization process from the melt, the block copolymers at different crystallization temperatures were recorded to obtain the Avrami plot of $\log[-\ln(1 - X_t)]$ versus $\log t$, as shown in Figure 3. All of the plots were close to a straight line. From these plots' intercepts and their slopes, the values of $\log k$ and n were obtained; the results of these parameters are listed in Table II. The half-crystallization time ($t_{1/2}$) increased with the temperature of isothermal crystallization for the same block copolymer, and the crystallization rate ($1/t_{1/2}$) slowed as the crystallization temperature increased. $t_{1/2}$ was given by the following equation:

$$t_{1/2} = (\ln 2/k)^{1/n} \quad (4)$$

From this crystallization process, we found $n \approx 1$ or 2, which corresponded to one-dimensional linear drown athermal nucleation in the crystallization stage.

Nonisothermal crystallization of the block copolymers from the melt

For the nonisothermal crystallization process, quenched films of the block copolymers were melted
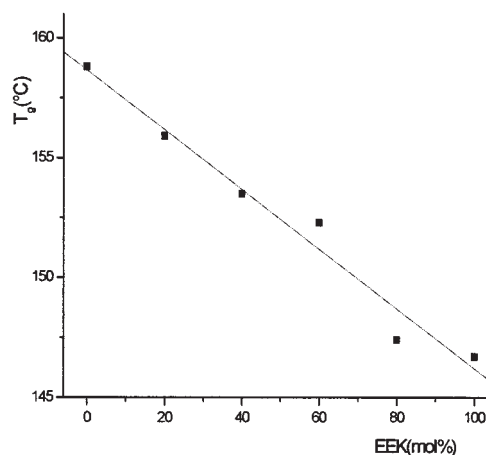

Figure 1 DSC curves of the amorphous PEEK/PEEKK copolymers.

Figure 2 Relationship between T_g and EEK content of the PEEK/PEEK copolymers.

TABLE I
Properties of the PEEK/PEEKK Block Copolymers

Sample	EEK (mol %)	η_{iv} (dL/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ε (%)	σ (MPa)	E (GPa)
1	0	0.90	158.8	360.4	41.1	12.3	108.8	2.39
2	20	1.16	155.9	359.3	37.1	27.5	106.7	2.27
3	40	1.17	153.5	355.2	27.7	16.6	104.5	2.27
4	60	0.95	152.6	348.8	31.3	10.8	102.4	2.27
5	80	0.88	147.4	345.2	38.4	10.8	100.2	2.47
6	100	0.84	146.7	333.8	33.3	8.3	98.1	2.51

ΔH_m, melting thermal enthalpy; η_{iv}, inherent viscosity; ε, elongation at break; σ, tensile strength; E, tensile moduli.

at 400°C for 5 min and then scanned by DSC at constant cooling rates of 2, 5, 10, 20 ,and 50°C/min.

Nonisothermal crystallization kinetic analysis by a modified Avrami equation

Most methods for describing the nonisothermal crystallization are also based on the Avrami equation,[7,8] which assumes that the relative degree of crystallinity (X_t) development with crystallization time is described by the following equation:

$$\log[-\ln(1 - X_t)] = \log Z_t + n \log t \tag{5}$$

where n is still the Avrami exponent, X_t is the relative crystallization degree, and Z_t is a composite constant involving both nucleation and growth rate parameters. Although eq. (5) is reasonable to some extent for many systems, a number of researchers have tried to use it to fit experimental results obtained from crystallization polymers and have proposed some modified forms.[9,10] Considering the nonisothermal character of the process investigated, Jeziorny[11] pointed out that the parameter for the value of rate,0 Z_t, should be properly corrected. The factor that should be considered was the cooling/heating rate (Φ) of the polymer. If Φ is assumed to be constant or approximately constant, the final form of the parameter characterizing

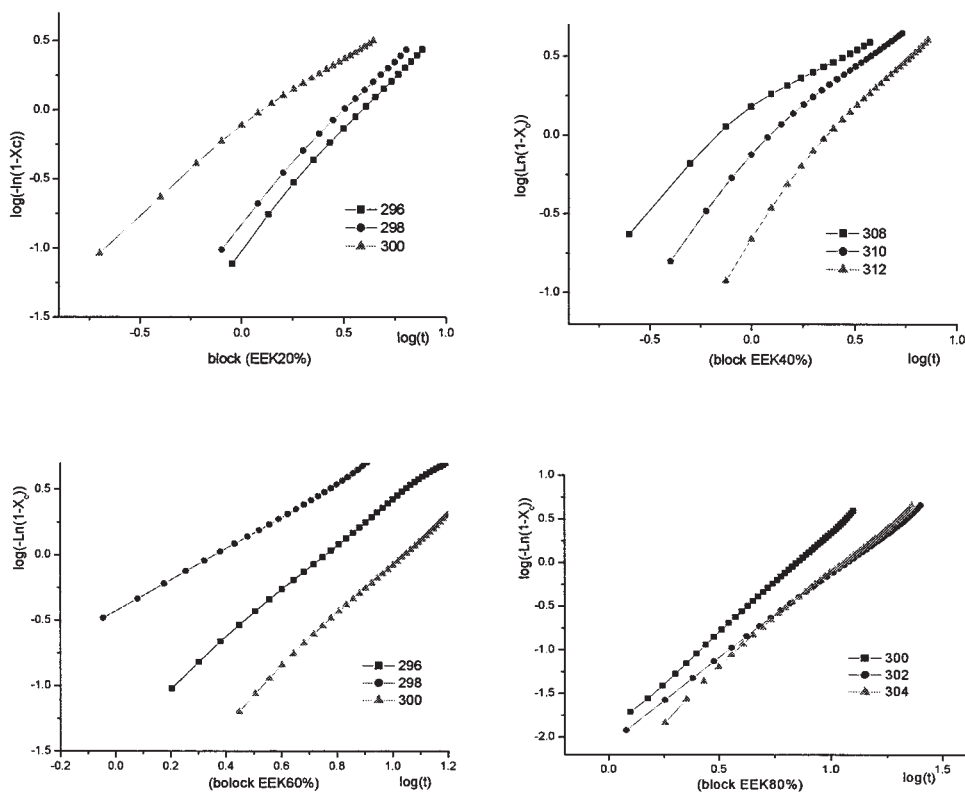**Figure 3** Avrami plots for the isothermal crystallization of the block copolymers at different temperatures.

TABLE II
Avrami Parameters for the Block Copolymers Isothermally Crystallized from the Melt

EEK (mol %)	T_c (°C)	n	k	$T_{1/2(ob)}$ (min)	$T_{1/2(cal)}$ (min)	$\tau_{1/2(ob)}$ (min^{-1})
20	296	1.60	0.105	0.85	0.89	1.18
	298	1.55	0.160	2.39	2.25	0.42
	300	1.09	0.684	3.03	2.67	0.33
40	308	1.53	0.784	0.54	0.52	1.85
	310	1.17	0.682	0.93	0.92	1.08
	312	1.14	0.411	1.83	1.91	0.55
60	296	1.69	0.0507	1.75	1.71	0.57
	298	1.24	0.359	4.66	4.68	0.21
	300	1.97	9.10E-3	9.03	9.01	0.08
80	300	2.30	0.0111	5.93	5.96	0.17
	302	1.90	9.08E-3	9.45	9.74	0.12
	304	2.13	5.59E-3	9.56	9.64	0.10

$T_{1/2(ob)}$, observation value; $T_{1/2(cal)}$, calculation value; $\tau_{1/2(ob)}$, crystallization velocity; T_c, crystallization temperature.

the kinetics of nonisothermal crystallization is given by the following equation:

$$\log Z_c = \log Z_t / \Phi \qquad (6)$$

Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for the PEEK/PEEKK block copolymer nonisothermal crystallization are shown in Figure 4. Each curve showed an initial linear portion, with a subsequent tendency to level off

slightly. Usually, this deviation was considered to be due to secondary crystallization, which was caused by spherulite impingement in the later stage. The linear portions were almost parallel to each other, shifting to longer times with decreasing Φ. This indicated that the nucleation mechanism and crystal growth geometries were similar for the primary crystallization at all of the cooling rates. The values of n and the rate parameter (Z_c, corrected by Z_t), as determined from the slope and
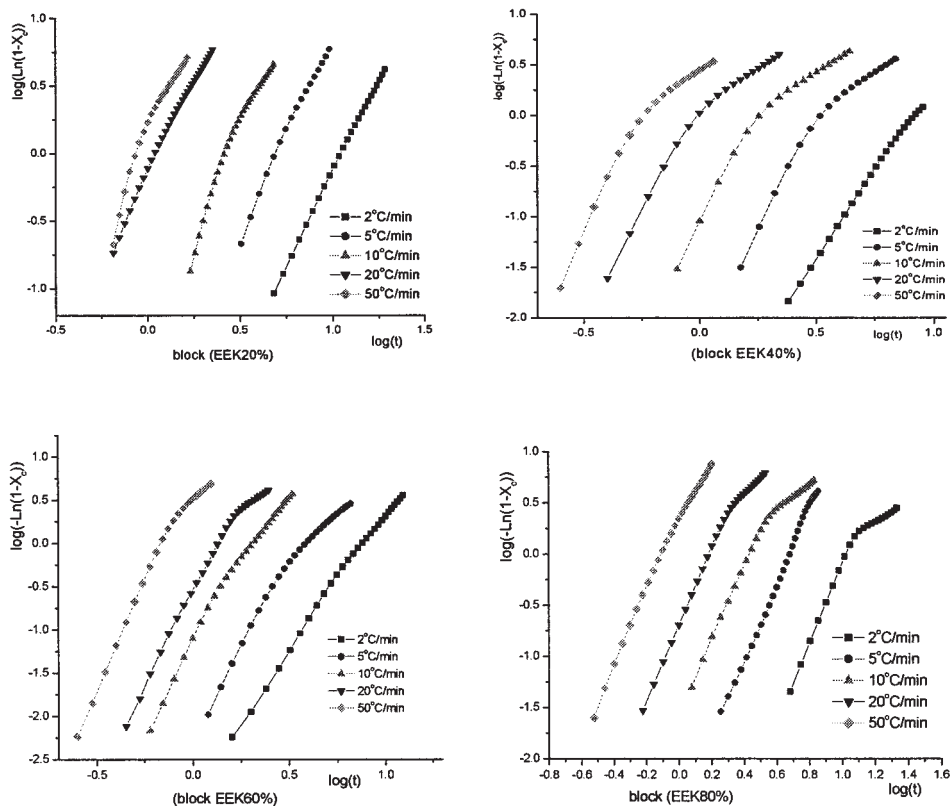

Figure 4 Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for nonisothermal crystallization.

TABLE III
Effect of Φ on the Crystallization Kinetics of the Block Copolymers

EEK (mol %)		ϕ (°C/min)				
		-2	-5	-10	-20	-50
n	20	3.01	3.87	4.64	3.55	4.46
	40	3.39	4.62	4.32	4.57	4.55
	60	3.34	4.75	4.75	4.54	4.89
	80	3.98	3.22	4.07	3.87	4.31
Z_c	20	1.52	0.22	0.19	3.63×10^{-2}	5.93×10^{-3}
	40	1.75	0.45	0.10	1.04×10^{-2}	1.55×10^{-3}
	60	1.28	0.39	0.11	2.72×10^{-2}	1.42×10^{-3}
	80	2.35	0.38	0.16	3.36×10^{-2}	1.30×10^{-3}
$t_{1/2}$	20	9.47	4.28	1.59	1.18	0.75
	40	7.34	2.99	1.49	0.87	0.51
	60	6.6	3.39	1.79	1.24	0.62
	80	7.85	4.38	2.46	1.38	0.7

intercept of the initial linear portion in Figure 4, respectively, are listed Table III. For nonisothermal melt crystallization, the average value of n was 4; however, Z_c decreased, and $t_{1/2}$ decreased with increasing Φ.

Similarly, the secondary stage was considered to be due to the effect of slower crystallization or further perfection of the crystals, which was caused by spherulite impingement in the later stage of crystallization or to the reorganization of initially poorly crystallized macromolecules or small and metastable crys-

tals. It is well known that if the secondary crystallization is not competed in a longer period, the product will continue crystallizing in the course of the application. This leads to a continuous change in the properties of the product. Therefore, to obtain materials with more stable and better properties, the annealing technique is usually used in the treatment that was always performed to accelerate the secondary crystallization process under the temperature of the maximum crystallization rate.
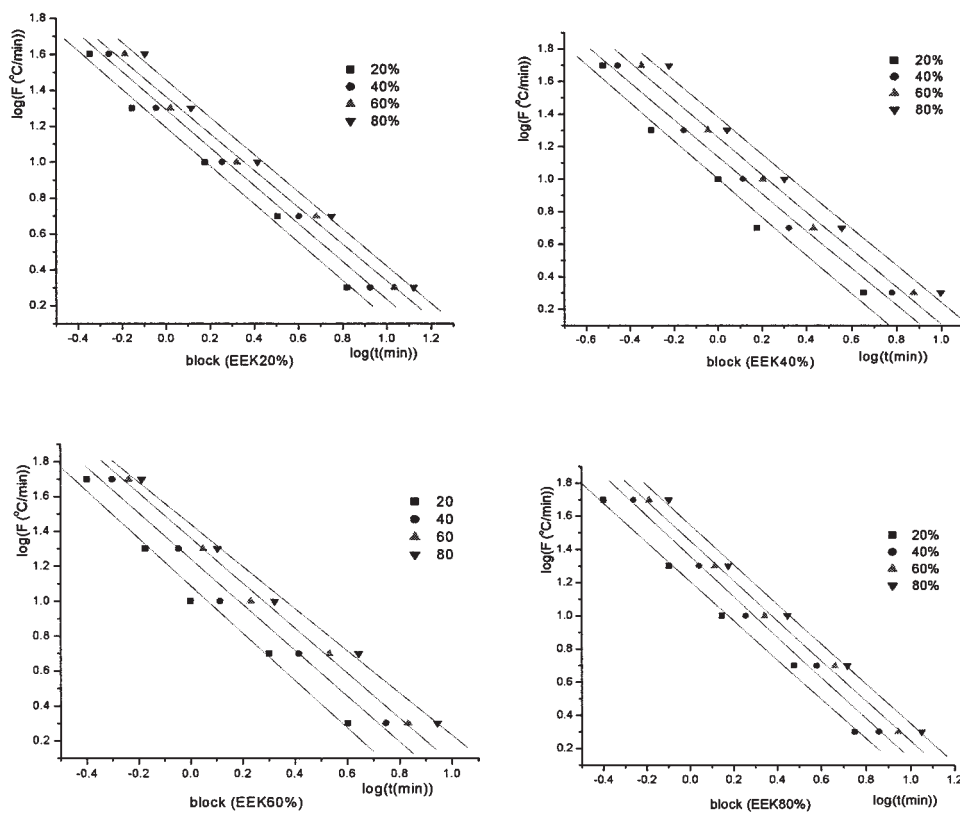

Figure 5 Plots of log Φ versus log t for the PEEK/PEEKK block copolymers during nonisothermal crystallization.

Nonisothermal crystallization kinetic analysis by a combination of the Avrami equation with the Ozawa equation

Ozawa extended the Avrami equation to nonisothermal conditions, with the assumption that the quenched polymer is heated or the polymer melt is cooled at a constant rate and that the mathematical derivation of Evans was valid. According to Ozawa theory, the degree of conversion at temperature (T) amounts to[12]

$$1 - X_t = \exp[-K(T)/\Phi^m] \quad (7)$$

where $K(T)$ is the cooling or heating function and m is the Ozawa exponent, which depends on the dimensions of crystal growth.

For the PEEK/PEEKK block copolymers, a large portion of the crystallization was attributed to the secondary process. In addition, the crystallinity was related to Φ and crystallization time (or temperature), so eq. (7) failed to adequately describe the nonisothermal crystallization kinetics for these block copolymers. Here, we adopted a convenient kinetic method to deal with the nonisothermal data by combining the Avrami equation [eq. (2)] with the Ozawa equation [eq. (7)] as follows:[13–15]

$$\log \Phi = \log F(T) + a \log t \quad (8)$$

where the parameter $F(T) = [K(T)/Z_t]^{1/m}$ and to the value of the cooling rate, which has to be chosen at a unit crystallization time when the measured system amounts to a certain degree of crystallinity, and a is the ratio of n to m (i.e., $a = n/m$). According to eq. (8), the plot of $\log \Phi$ versus $\log t$ gave a series of straight lines at a given X_t (Fig. 5). The kinetic parameter $F(T)$ and the exponent a were estimated with the intercepts and slopes of these lines, respectively (Table IV). $F(T)$ systematically increased with increasing relative crystallinity, but the values of a were almost constant at about 1.2. This indicated that this kinetic approach was a reasonable application for the nonisothermal crystallization process of these PEEK/PEEKK block copolymers.

CONCLUSIONS

PEEK/PEEKK block copolymers were prepared from PEEK and PEEKK oligomers in the presence of K_2CO_3. No phase separation was observed for these block copolymers. These copolymers were a compatible sys-

TABLE IV
Nonisothermal Crystallization Kinetic Parameters of the Copolymer at Different Degrees of Crystallization by the Modified Ozawa Equation and Activation Energies for the PEEK/PEEKK Copolymer by Kissinger Equation

X_c (%)	EEK (mol %)			
	20	40	60	80
$F(T)$				
20	10.03	13.73	18.10	24.05
40	12.30	17.54	23.09	27.67
60	15.61	19.03	23.17	28.74
80	16.13	22.94	28.38	35.45
a				
20	1.06	1.06	1.03	1.04
40	1.18	1.14	1.15	1.14
60	1.16	1.31	1.29	1.21
80	1.16	1.22	1.21	1.20

X_c, crystallization degree.

tem. With increasing PEEK content, both T_g and the melting temperature (T_m) decreased. These block copolymers showed good tensile properties.

A systematic study of the melt crystallization kinetics of these block copolymers was performed by several methods through DSC experiments. The Avrami analysis modified by Jeziorny indicated that the crystallization processes of these block copolymers were divided into primary and secondary crystallization stages. It was suitable to combine the Avrami and Ozawa equations to handle the nonisothermal crystallization of these block copolymers.

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