Crystallization Kinetics of Novel Poly(aryl ether ketone) Copolymers Containing 2,7-Naphthalene Moieties

Si-Jie Liu,[1,2] Xiao-Bo Sun,[1] Xiang Hou,[2] Gui-Bin Wang,[1] Zhen-Hua Jiang[1]

[1]Alan G. MacDiarmid Lab, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
[2]Jilin Provincial Center for Sanitation Inspection and Test Department of Physics and Chemistry Test, Changchun 130062, People's Republic of China

ABSTRACT: To increase the glass transition temperature (T_g) of poly(aryl ether ketone), and to decrease the melting temperature (T_m) and temperature of processing, a series of novel poly(aryl ether ketone)s with different contents of 2,7-naphthalene moieties (PANEK) was synthesized. We focused on the influence of the naphthalene contents to the copolymer's crystallization. The crystallization kinetics of the copolymers was studied isothermally and nonisothermally by differential scanning calorimetry. In the study of isothermal crystallization kinetics, the Avrami equation was used to analyze the primary process of the crystallization. The study results of the crystallization of PANEK at cooling/heating rates ranging from 5 to 60°C/min under nonisothermal conditions are also reported. Both the Avrami equation and the modified Avrami–Ozawa equation were used to describe the nonisothermal crystallization kinetics of PANEK. The results show that the increase in the crystallization temperature and the content of 2,7-naphthalene moieties will make the crystallization rate decrease, while the nucleation mechanism and the crystal growth of PANEK are not influenced by the increasing of the content of 2,7-naphthalene moieties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2527–2536, 2006

Key words: poly(aryl ether ketone); naphthalene moiety; crystallization kinetics; differential scanning calorimetry (DSC)

INTRODUCTION

Poly(aryl ether ketone)s are high performance engineering plastics with outstanding physical, chemical, thermal, and mechanical properties, and have been applied to aerospace, electronics, automobile, petroleum, chemical, medical, and food industry extensively.[1–4] Poly (ether ether ketone) (PEEK), being one of the most important one of poly(aryl ether ketone)s, has been successfully developed for its excellent performance. Along with the development of the science and technology, people hope to get materials with higher temperature classification and more excellent mechanical performances. To develop these performances, structural modifications, such as introduction of crosslinkable lateral groups or functional groups onto the main chain, and synthesis of copolymers have been attempted.[5,6] Naphthalene rings have been introduced into polymer structures by some authors as they have a larger volume than benzene rings, which can enlarge the proportion of the rigid groups in the main chain, decrease the mobility of segments, and therefore increase T_g of a polymer.[7–14]

In this work, a series of novel poly(aryl ether ketone)s with different contents of 2,7-naphthalene moieties (PANEK) was synthesized by the nucleophilic substitution reaction from hydroquinone (HQ), 2,7-dihydroxynaphthalene (2,7-DHN), and 4,4'-difluorobenzophenone (DFB). In our previous work,[14] the wide-angle X-ray diffraction (WAXD) data of PANEK showed that the molar fraction of 2,7-DHN is over 30%, while the clear cold-crystallization temperature (T_c) and T_m were not detected. The result proves that the copolymers become amorphous. For the copolymer samples with 2,7-DHN molar fraction less than 30%, the T_m decreases with increasing contents of 2,7-naphthalene moieties, while the T_g shows a reverse tendency. The crystal structures of the copolymers are a rhombic system in the same manner as PEEK. Therefore, introducing of 2,7-naphthalene moieties into PEEK not only decreases the temperature of processing, but also retains the copolymer's higher usage temperature and excellent thermal stability. It is an ideal method for improving polymer's properties. It is well known that the properties of semicrystalline polymers are strongly dependent on their crystalline structures formed during processing. To search for the optimum processing conditions in an industrial process and to obtain products with better properties, it is necessary to study the crystallization process quantitatively. The crystallization kinetics of such polymers were investigated by means of DSC to reveal the influence of the contents of 2,7-naphthalene moieties on the crystallization behavior of poly(aryl ether ketone)s.
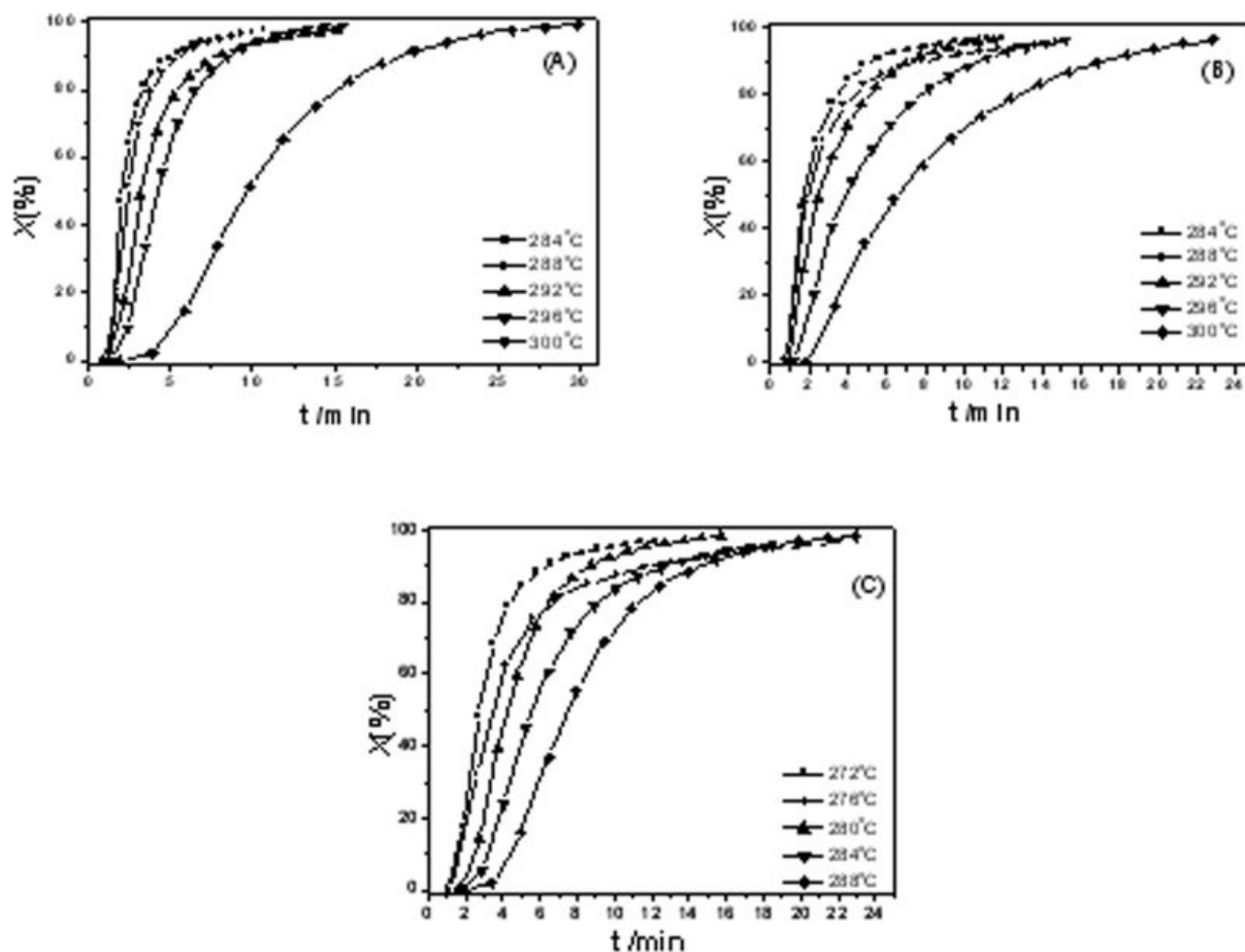
Figure 1 The plots of X versus t for the PANEK at different crystallized temperatures. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%.

EXPERIMENTAL

Materials

We used 2,7-dihydroxynaphalene (2,7-DHN), hydroquinone (HQ), and 4,4'-difluorobenzophenone as starting materials to synthesize the new poly(ether ether ketone)s random copolymers containing 2,7-naphthalene moieties. To the solution were added HQ and 2,7-DHN (total amount of 0.20 mol) at molar ratios of 95 : 5, 90 : 10, and 85 : 15. The inherent viscosity of the copolymers are 0.86, 0.82, 0.85 dL/g when measured in 98% H_2SO_4 (at 25°C and 0.01 g/10 mL concentration).

Crystallization behavior investigation

The crystallization behavior of PANEK was investigated by means of a Mellter Toledo differential scanning calorimeter (DSC821^e) in two manners: cold crystallization and melt crystallization.

For isothermal crystallization, the samples were heated up to 380°C and held at that temperature for 5 min to remove small nuclei that might act as seed crystals, and then cooled at a cooling rate of 120°C/min to the crystallization temperatures. In the process of cold crystallization of nonisothermal crystallization, the amorphous samples (obtained by rapidly
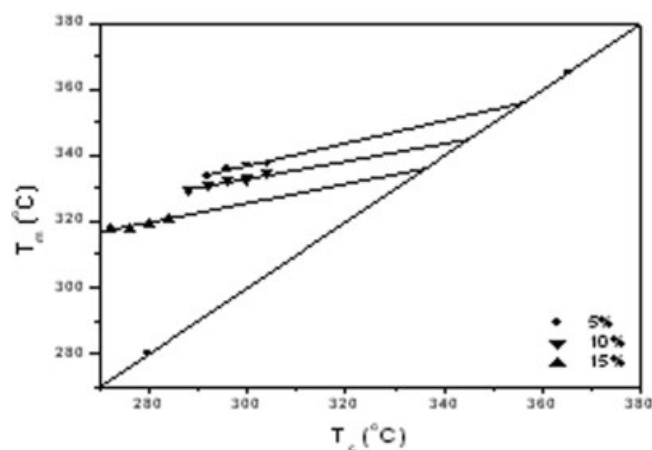

Figure 2 Hoffman–Weeks plots for the estimation of the equilibrium melting point of PANEK.

TABLE I
Avrami Parameter n, k, $t_{1/2(exp)}$, $t_{1/2(cal)}$, G, $t_{i(exp)}$, $t_{i(cal)}$ of PANEK

2,7-Naphthalene moieties content (mol %)	T_c (°C)	N	k (min^{-1})	$t_{1/2(exp)}$ (min)	$t_{1/2(cal)}$ (min)	G	$t_{i(exp)}$ (min)	$t_{i(cal)}$ (min)
5	284	3.2	0.15	1.64	1.63	0.61	1.22	1.60
	288	2.7	0.16	1.75	1.62	0.57	1.52	1.66
	292	3.0	0.07	2.38	1.72	0.42	1.81	2.10
	296	3.7	0.01	3.18	2.56	0.31	2.35	2.66
	300	3.1	0.005	4.03	3.76	0.25	3.23	3.18
10	284	3.1	0.24	1.72	1.41	0.58	1.02	1.39
	288	3.8	0.13	1.85	1.55	0.54	1.09	1.57
	292	3.0	0.11	2.46	1.85	0.41	1.48	1.82
	296	3.3	0.04	3.86	2.85	0.26	2.13	2.37
	300	3.3	0.01	4.42	3.61	0.23	3.38	3.61
15	272	3.0	0.09	3.38	2.76	0.30	2.43	1.95
	276	3.1	0.05	4.22	4.11	0.24	3.25	2.83
	280	3.5	0.02	5.47	4.67	0.18	4.17	3.77
	284	3.2	0.02	7.45	6.23	0.13	5.84	5.02
	288	3.7	0.003	8.26	7.72	0.12	6.66	6.36

quenching the melts in liquid nitrogen) were heated at constant rates and the exothermal curves of heat flow, as a function of temperature, were recorded.

The melt crystallization was carried out as follows: the samples were heated up to 380°C and held for 5 min; Then, the samples were crystallized at a con-
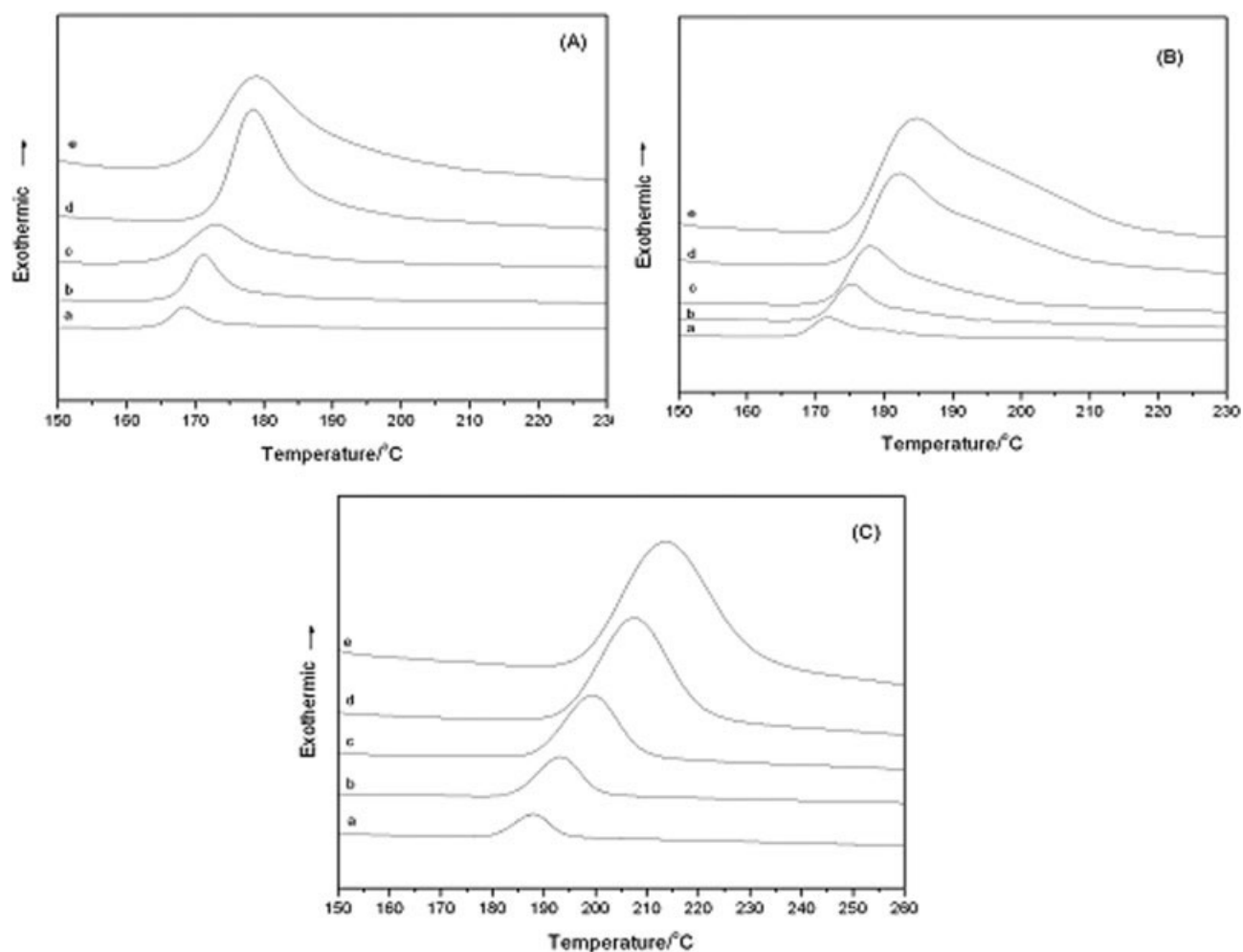

Figure 3 DSC traces of nonisothermal cold crystallization for PANEK. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%. Heating rate: (a) 5°C/min; (b) 10°C/min; (c) 20°C/min; (d) 40°C/min; (e) 60°C/min.

TABLE II
The Equilibrium Melting Point T_m^0

PANEK	T_m^0 (°C)
$n = 0$	384[19]
$n = 5\%$	355
$n = 10\%$	345
$n = 15\%$	338

stant cooling rate. For nonisothermal crystallization, samples were cooled/heated at various cooling/heating rates, i.e., 5, 10, 20, 40, and 60°C/min. All operations were carried out in nitrogen. It is important to minimize the thermal lag, so samples of less than or equal to 4 mg were used in the DSC tests.

RESULTS AND DISCUSSION

Isothermal crystallization

The isothermal crystallization kinetics of PANEK were studied in a temperature range from 284 to 300°C. The result was analyzed by means of the Avrami equation[15]:

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

Equation (1) is often written in the logarithmic form:

$$\ln(1 - X_t) = -k\,t^n \qquad (2)$$

where k is the crystallization rate constant and n is the Avrami exponent, which can be related to the type of nucleation and the geometry of crystal growth. The plots of X_t versus t for PANEK copolymers with different contents of 2,7-naphthalene moieties at different crystallized temperatures are shown in Figure 1. From such curves, the half-time of crystallization, $t_{1/2(\exp)}$, defined as the time taken for half of the crystals to develop, can be derived. The crystallization rate (G) values can be calculated based on the inverse of the half-time of crystallization. The time to reach the maximum rate of heat flow, $t_{i(\text{cal})}$, and $t_{1/2(\text{cal})}$ can be calculated using the following equations:

$$t_i = [(n-1)/nk]^{1/n} \qquad (3)$$

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

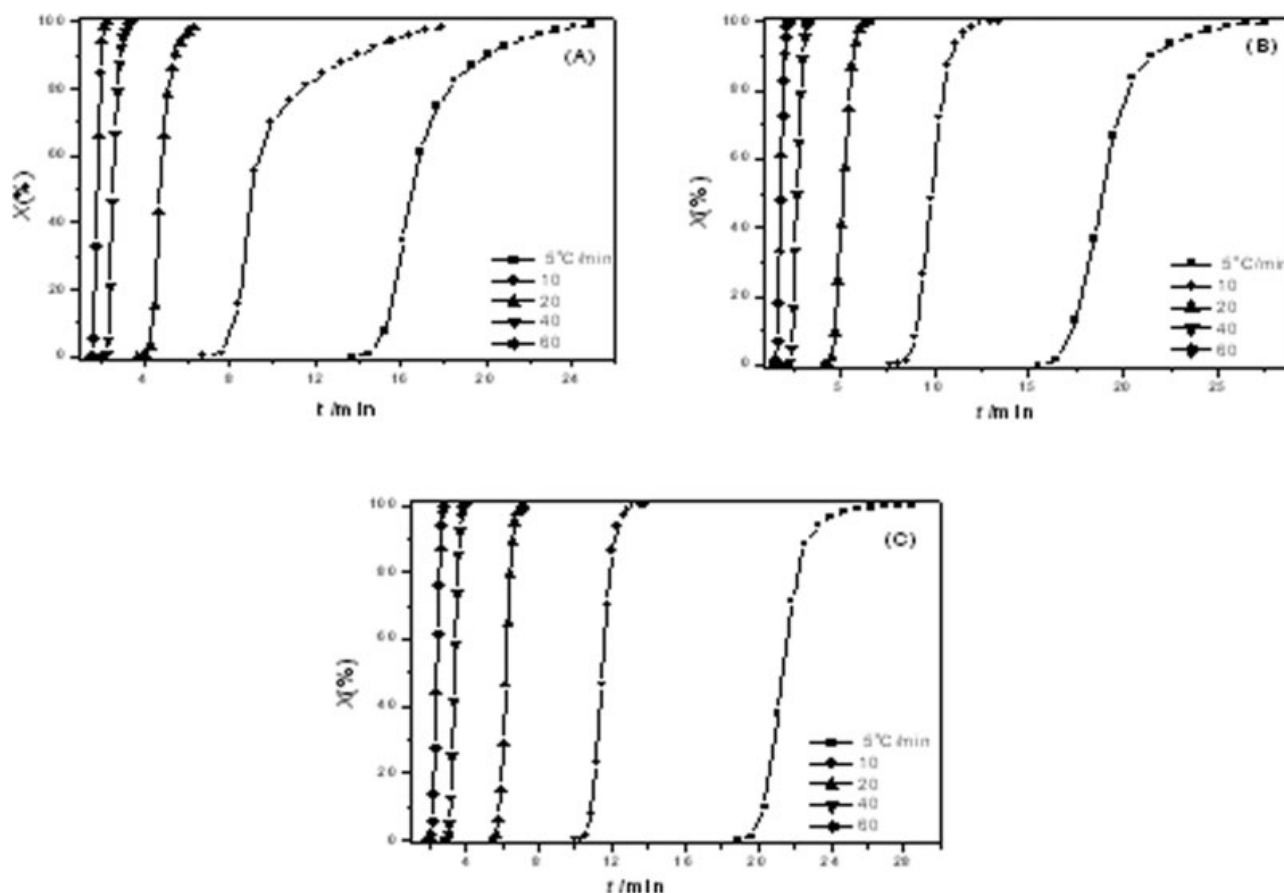The plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ are shown in Figure 2. It can be seen that, from the change of

Figure 4 The plots of X versus t for PANEK at different cooling rates. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%.
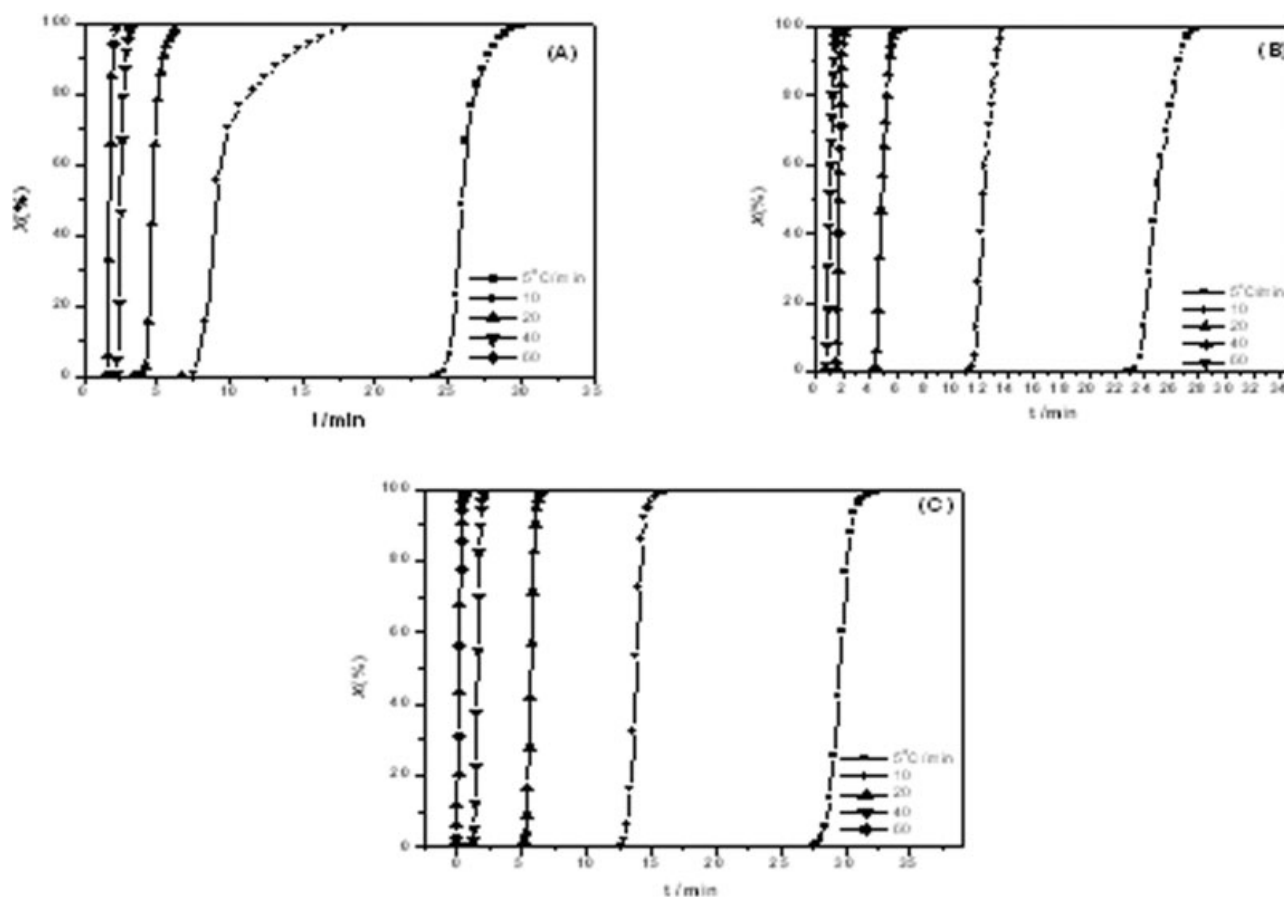
Figure 5 The plots of X versus t for the PANEK at different heating rates. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%.

slope, two regions could be divided for each curve, i.e., an initial linear part (usually called the primary crystallization stage) and the leveling off part (the secondary crystallization stage). The linear part of each curve is almost parallel to each other. Such a deviation of Avrami plots at the secondary stage of crystallization has also been found by Cebe and Hong[16] and Lee and Porter[17] in the isothermal crystallization of PEEK. From the intercept and slope of the linear part, the values of k and n were calculated, respectively.

The values of n, k, $t_{i(exp)}$, $t_{i(cal)}$, G, $t_{1/2(exp)}$, and $t_{1/2(cal)}$ are listed in Table I. From Table I, it can be seen that the G value of the samples increases, while the crystallization temperature decreases. At the same crystallization temperature, along with the increment of the content of 2,7-naphthalene moieties, the G value descends, but with the same content of 2,7-naphthalene moieties, the G value will decrease with the increase of the crystallization temperature, which shows that the increment in crystallization temperature and the content of 2,7-naphthalene moieties will cause the crystallization rate to descend. This phenomenon can be explained by the fact that a higher crystallization temperature will make the

nucleation more difficult. The higher the content of 2,7-naphthalene moieties in a polymer is, the more difficult it is for the segments to move. According to the polymer crystallization theories, a crystallization process consists of nucleation and growth stages. A crystallization rate is a result of these two stages. Therefore, the more difficult the nucleation is or the more difficult it is for segments to move, the lower a crystallization rate will be.

The n value was found to be about 3 (it is the same as that of PEEK[16]), which indicates that the nucleation mechanism and the crystal growth will not be influenced by the increase of crystallization temperature. The value of parameter k decreases with increasing of crystallization temperature and increasing of the content of 2,7-naphthalene moieties. The crystallization temperature and the content of 2,7-naphthalene moieties do not influence the manner of nucleation and growth of PANEK, as well as the fact that there is not much difference between the values calculated with eqs. (3) and (4) and those experimentally measured. The agreement in the values of $t_{i(exp)}$, $t_{i(cal)}$, $t_{1/2(exp)}$, and $t_{1/2(cal)}$ suggests that the Avrami equation works well in describing the initial crystallization process of PANEK.
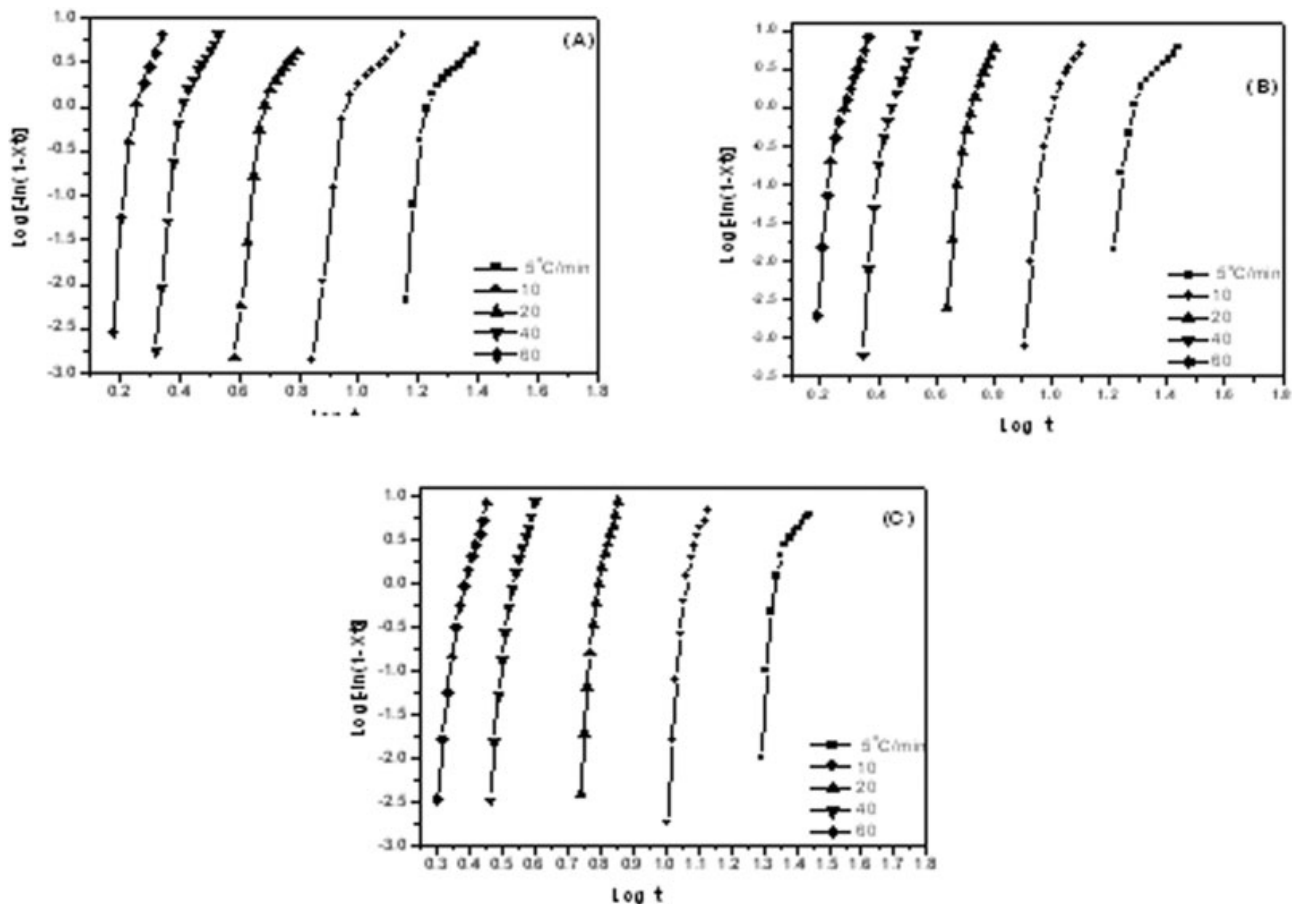
Figure 6 The Avrami curves for the PANEK at different cooling rates. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%.

The equilibrium melting point can be evaluated from extrapolation using the well-known Hoffman–Weeks theory,[18] which is based on eq. (5):

$$T_m = T_m^0 (1 - 1/\gamma) + T_c/\gamma \qquad (5)$$

where γ is the lamellar thickening factor signifying the ratio of the final lamellar thickness to the critical lamellar thickness. T_m^0 is obtained by the intersection of the experimental T_m versus T_c line and the $T_m = T_c$ line (Fig. 3). From Table II, it can be seen that the equilibrium melting points of PANEK are lower than that of PEEK[19] and decrease with increase in the content of 2,7-naphthalene moieties. This implies that the 2,7-naphthalene moieties inhibit the crystallization of PANEK.

Nonisothermal crystallization

Crystallization of PANEK was also studied under nonisothermal conditions of cooling/heating rates from 5 to 60°C/min. The results are shown in Figures 4 and 5. From Figure 4, it can be seen that as the cooling rate increases, the exothermic peak becomes wider and shifts to a lower temperature.

However, for the cold crystallization, an opposite situation can be found, that is, with the increase of the heating rate the exothermic peak becomes wider and shifts to a higher temperature (see Fig. 5). At the same heating rate, the peak temperature (T_p) of the PANEK copolymer with the 2,7-DHN molar fraction of 15% is higher than those of the PANEK copolymer with the 2,7-DHN molar fractions of 5 and 10%.

Integration of the exothermic peaks during the nonisothermal scan gives plots of the relative crystallinity versus time, which are shown in Figures 6 and 7. From Figures 6 and 7, the similar sigmoid curve can be seen for all the compositions and cooling/heating rates mentioned above. To a certain extent, the nonisothermal crystallization process is similar to the isothermal crystallization process. It shows that the higher the cooling or heating rate, the shorter the time for the completion of crystallization.

The time corresponding to the maximum crystallization rate (t_{max}), the peak temperature (T_p), and relative crystallinity (X_c) at the maximum rate of heat flow during nonisothermal crystallization at different cooling/heating rates are listed in Tables III and IV. From Tables III and IV, we can see that t_{max} and X_c will decrease with the increase of the cooling/heat-
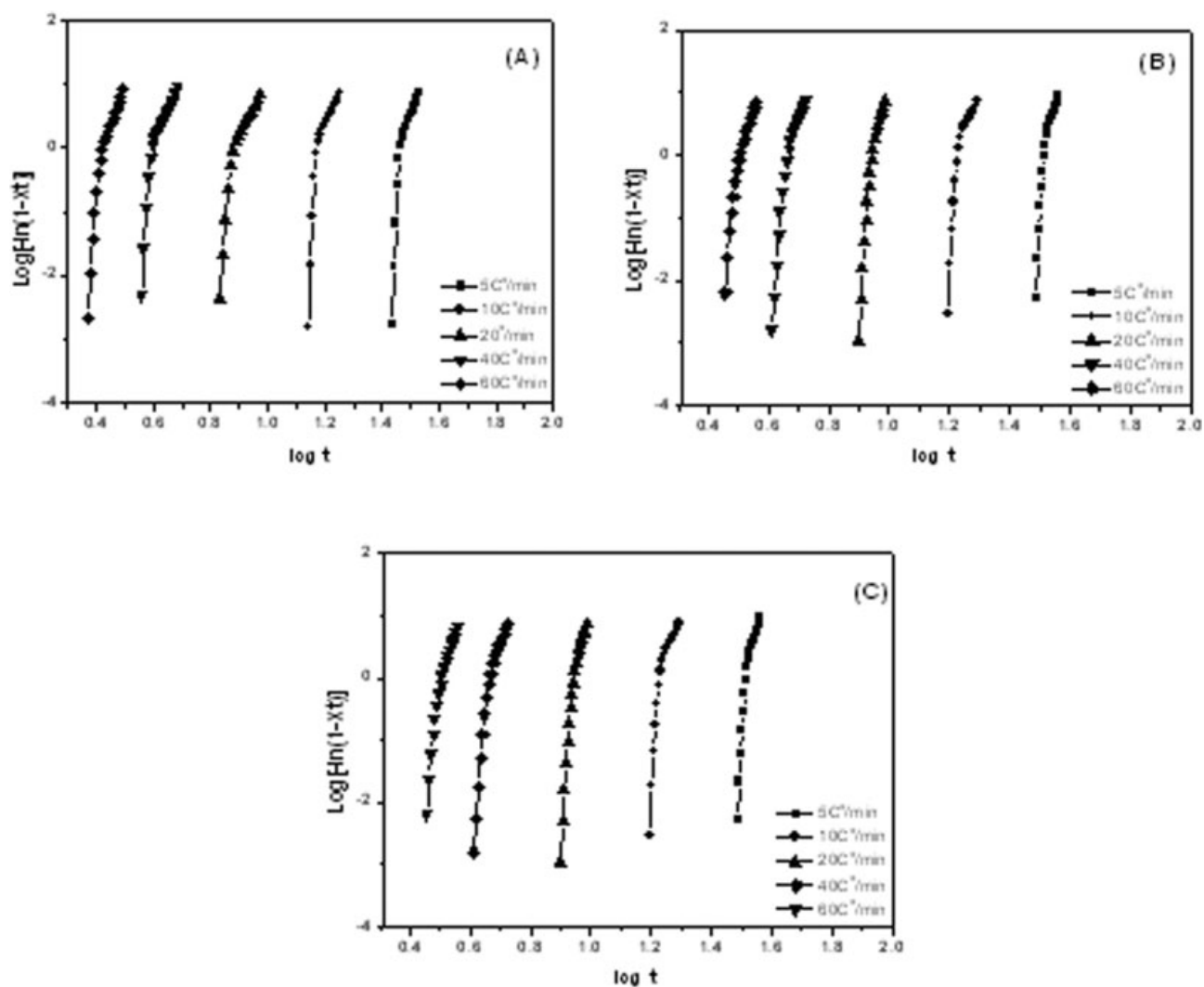
Figure 7 The Avrami curves for the PANEK at different heating rates. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%.

<table>
<tr><td colspan="5" align="center">TABLE III
Time of the Maximum Crystallization Rate(t_{max}), Peak Temperature (T_p), and Relative crystallinity (X_c) at the Maximum Rate of Heat Flow During Nonisothermal Crystallization at Constant Cooling Rate</td></tr>
</table>

2,7-Naphthalene moieties content (mol%)	Cooling rate ϕ (°C/min)	t_{max} (min)	T_p (°C)	X_c (%)
5	−5	16.02	300.2	34
	−10	8.55	294.7	32
	−20	4.06	288.3	31
	−40	2.47	281.5	32
	−60	1.72	276.9	29
10	−5	15.49	285.7	32
	−10	9.98	284.4	30
	−20	5.30	281.5	29
	−40	2.58	277.4	29
	−60	1.77	273.4	27
15	−5	20.23	274.0	33
	−10	11.47	265.7	31
	−20	6.18	256.8	30
	−40	3.38	245.5	28
	−60	2.38	238.1	28

<table>
<tr><td colspan="5" align="center">TABLE IV
Time of the Maximum Crystallization Rate (t_{max}), Peak Temperature (T_p), and Relative crystallinity (X_c) at the Maximum Rate of Heat Flow During Nonisothermal Crystallization at Constant Heating Rate</td></tr>
</table>

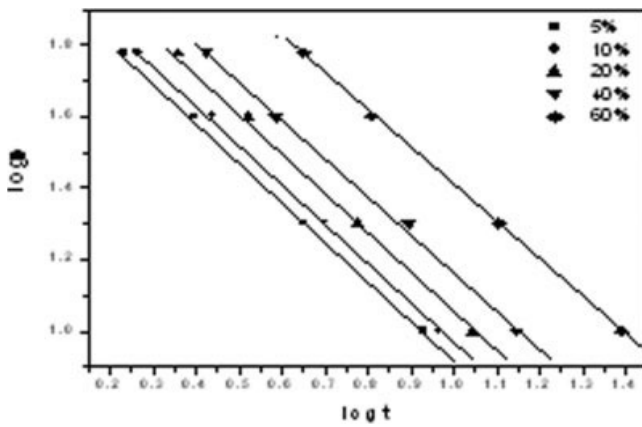| 2,7-Naphthalene moieties content (mol%)	Heating rate ϕ (°C/min)	t_{max} (min)	T_p (°C)	X_c (%)
5	5	23.80	168.4	38
	10	6.82	171.2	35
	20	3.69	173.0	36
	40	2.21	178.7	35
	60	1.28	179.9	31
10	5	23.88	171.8	30
	10	11.19	175.1	28
	20	4.20	177.9	26
	40	1.59	182.2	25
	60	0.70	183.8	24
15	5	27.50	187.8	52
	10	12.57	193.2	48
	20	5.00	199.3	48
	40	1.05	207.7	48
	60	0.15	213.8	46

Figure 8 Plot of log Φ versus log t for PANEK during nonisothermal melt crystallization at the 2,7-naphthalene content of 5%.

ing rates. At the same cooling/heating rate, the t_{max} of PANEK is longer than that of PEEK,[16] which suggests that the crystallization rate of PEEK is faster than that of PANEK in the nonisothermal crystallization condition.

The plots of log $[-\ln (1 - X_t)]$ versus log t are shown in Figures 8 and 9. In Figures 8 and 9, two regions of crystallization exist, and the slopes of the log $[-\ln (1 - X_t)]$ versus log t curves are varied, which suggests that the nucleation mechanism and crystal geometrical growth are similar for the primary and secondary crystallization processes at all cooling or heating rates. Such results have also been reported by Liu and Mo.[20]

Many of the approaches for describing the crystallization kinetics are based on the Avrami equation (see earlier). Considering the nonisothermal charac-
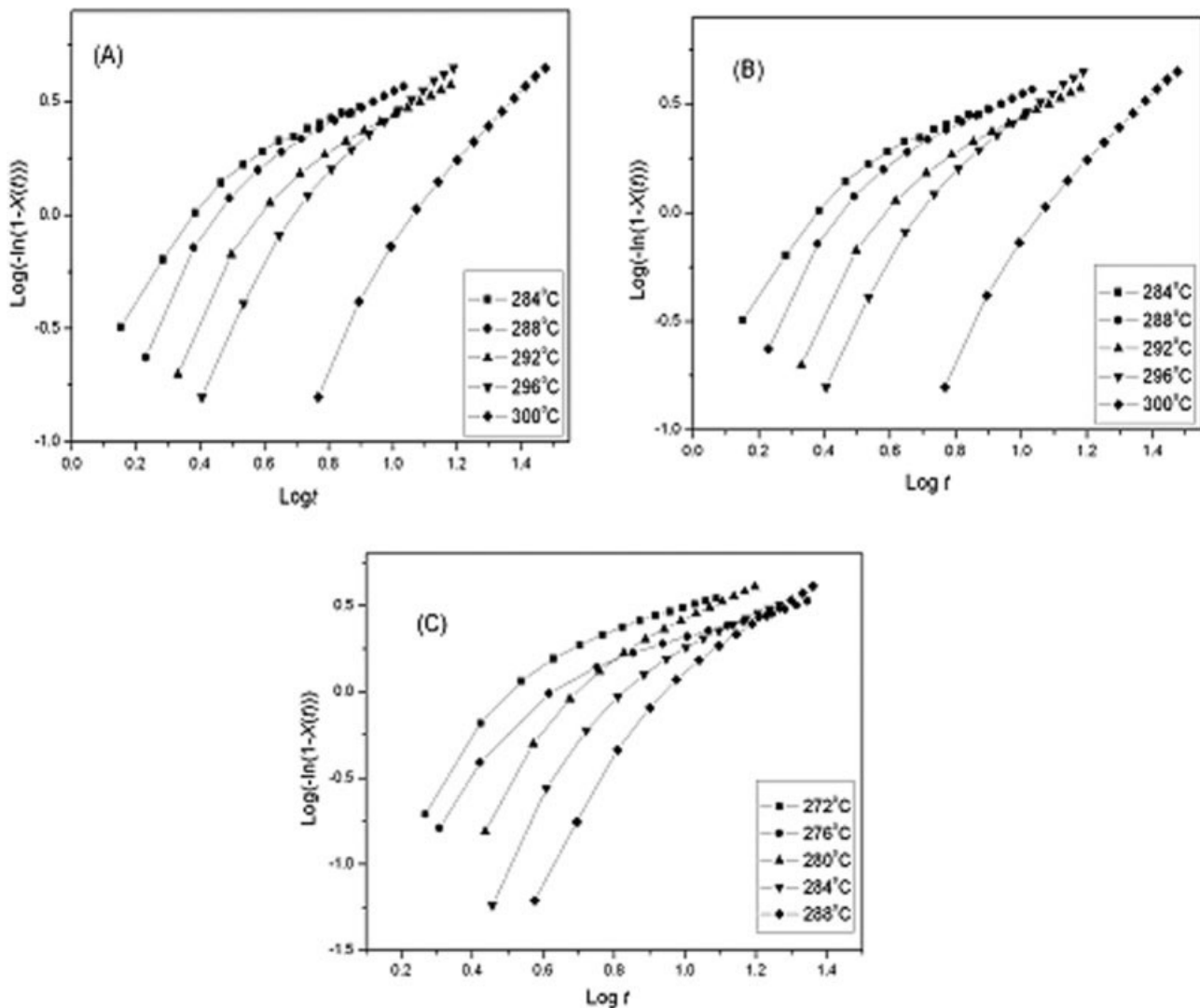

Figure 9 The Avrami curves for the PANEK at different crystallized temperatures. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%.
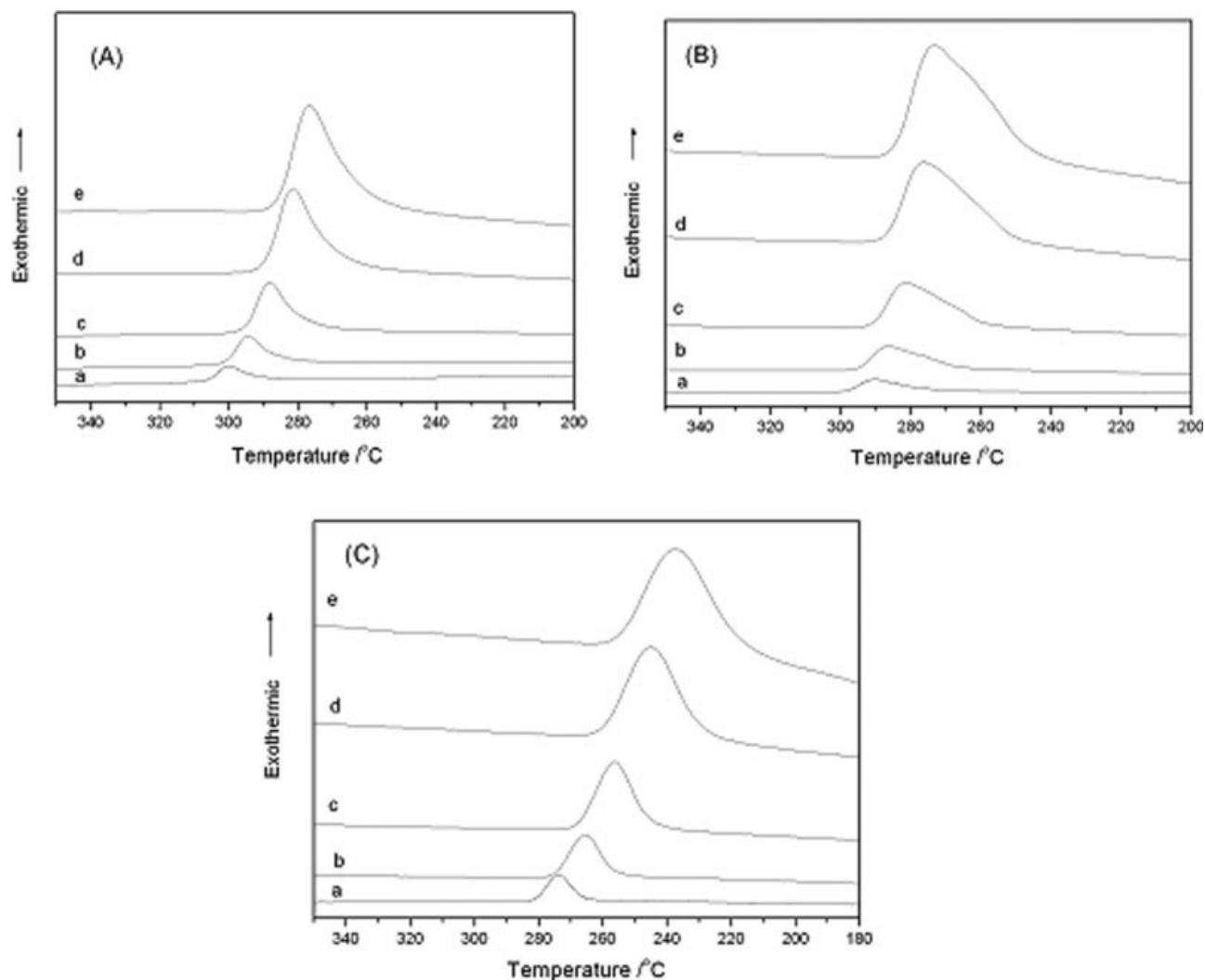
Figure 10 DSC traces of nonisothermalmelt crystallization for PANEK. 2,7-Naphthalene content: (A) 5%; (B) 10%; (C) 15%. Cooling rate: (a) 5°C/min; (b) 10°C/min; (c) 20°C/min; (d) 40°C/min; (e) 60°C/min.

ter of the process investigated, Ozawa[21] had extended the Avrami equation to the nonisothermal condition. According to the Ozawa theory, the degree of conversion at temperature T amounts to:

$$1 - X_t = \exp\left[-K(T)/\phi^m\right] \quad (6)$$

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

During the nonisothermal crystallization process, the relationship between crystallization time t and temperature T is given by

$$t = |T_0 - T|/\phi \quad (7)$$

where T is the temperature at time t; T_0 is the initial temperature when crystallization begins ($t = 0$). As the degree of crystallinity is related to the cooling/heating rate ϕ and the crystallization time t (or tem-

perature T), the relationship between ϕ and t can be built up at a given degree of crystallinity. Liu et al.[22] pointed out that parameters, such as the cooling/heating rate ϕ and k, should be adequately corrected. By assuming ϕ to be constant or approximately constant, the final form of the parameter characterizing the kinetics of nonisothermal crystallization is given as follows:

$$\log \phi = \log F(T) - a \log t \quad (8)$$

where the parameter $F(T)$ $\{F(T) = [K(T)/k]^{1/m}\}$ refers to the value of the cooling/heating rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity; α is the ratio of the Avrami exponent n to the Ozawa exponent m. It can be seen that $F(T)$ has a definite physical and practical meaning. In this article, the nonisothermal result was analyzed by means of the modified Avrami–Ozawa equation

TABLE V
Nonisothermal Crystallization Kinetic Parameters of PANEK at Different Crystallinities by the Combination of Avrami–Ozawa Equation

$X(t)$ (%)	5% DHN		10% DHN		15% DHN	
	$F(T)$	a	$F(T)$	a	$F(T)$	a
5	7.6	1.1	8.0	1.2	8.6	1.2
10	7.9	1.1	8.4	1.2	9.2	1.2
20	8.9	1.1	9.7	1.1	10.3	1.2
40	9.5	1.1	10.1	1.1	11.2	1.2
60	11.7	1.0	12.2	1.1	12.8	1.2

[eq. (8)]. The kinetic parameter $F(T)$ and values of α (n/m) can be estimated by the intercepts and the slopes of the lines in Figure 10, respectively, which are listed in Table V. It shows that $F(T)$ increases with raising the relative degree of crystallinity, but the values of α are almost constant, which is about 1.0 and 1.2 for nonisothermal crystallization.

If the secondary crystallization is not completed, the product will continue crystallizing in the course of use. This will lead to a change in the properties of products. Therefore, to obtain more stable materials with better properties and to accelerate secondary crystallization under the temperature of the maximum crystallization rate, the annealing technique is usually used in the practical production.

CONCLUSIONS

In this article, experiments conducted using DSC indicate that both the nucleation stage and the crystal growth stage are influenced by the temperature at which PANEK is heated and the duration it is kept for. At the same crystallization temperature, along with the increment of the content of 2,7-naphthalene moieties, the G value descends; but with the same content of 2,7-naphthalene moieties, the G value will decrease with the increase of the crystallization temperature, which shows that the increment in crystallization temperature and the content of 2,7-naphthalene moieties will cause the crystallization rate to descend. The Avrami analysis indicates that both the isothermal and nonisothermal processes of PANEK can be distinctly divided into the primary region and the secondary crystallization region. The processes of nucleation and growth of the primary and secondary crystallization for both isothermal and nonisothermal are very different from each other. It is shown that the increment of the crystallization temperature and the content of 2,7-naphthalene moi-

eties will make the crystallization rate descend. At the same cooling/heating rate, the t_{max} of PANEK is longer than that of PEEK, which suggests that the crystallization rate of PEEK is faster than that of PANEK in the nonisothermal crystallization condition. The n value was found to be about 3, which indicates that the nucleation mechanism and the crystal growth will not be influenced by the increase in crystallization temperature. The value of parameter k decreases with the increase in crystallization temperature and the content of 2,7-naphthalene moieties, while the nucleation mechanism and crystal growth of PANEK are not influenced by the increase in the content of 2,7-naphthalene moieties.

The modified Avrami–Ozawa equation has been used to deal with nonisothermal data. We found that $F(T)$ increases with raising the relative degree of crystallinity, but the values of α are almost constant.

References

1. Lakshmana, R. V. J Macromol Sci Rev Macromol Chem Phys 1995, 35C, 661.
2. Hamciuc, C.; Bruma, M.; Klapper, M. J Macromol Sci Pure Appl Chem 2001, 38A, 659.
3. Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. Polymer 1988, 29, 358.
4. Gao, Y.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. Macromolecules 2004, 37, 6748.
5. Wang, J. Z.; Cao, J. K.; Chen, Y.; Ke, Y. C.; Wu, Z. W.; Mo, Z. S. J Appl Polym Sci 1996, 61, 1999.
6. Bottino, F. A.; Pasquale, G. Di.; Pollicino, A. Eur Polym J 1995, 31, 35.
7. Őzarslan, Ő.; Yildiz, E.; Yilmaz, T.; Güngör, A.; Kuyulu, A. Macromol Chem Phys 1998, 199, 1887.
8. Wang, Z. Y.; Guen, A. L. Macromolecules 1995, 28, 3728.
9. Ohno, M.; Takata, T.; Endo, T. J Polym Sci Part A: Polym Chem 1995, 33, 2647.
10. Matsumura, S.; Kihara, N.; Yakata, T. Macromolecules 2001, 34, 2848.
11. Bottino, F. A.; Pasquale, G. Di.; Leonardi, N.; Pollicino, A. J Macromol Sci Pure Appl Chem 1997, 32A, 1947.
12. Yoshida, S.; Hay, A. S. J Macromol Sci Pure Appl Chem 1997, 34A, 1299.
13. Kenn Corwin, H. G.; Benjamin, S. H.; Katherine, L. F. Polymer 1994, 35, 2290.
14. Liu, S. J.; Niu, Y. M.; Zhu, X. L.; Wang, G. B.; Jiang, Z. H. Chem J Chin Univ 2006, 22, 114.
15. Avrami, M. J Chem Phys 1940, 8, 812.
16. Cebe, P.; Hong, S. D. Polymer 1986, 27, 1183.
17. Lee, Y.; Porter, R. S. Macromolecules 1988, 21, 2770.
18. Hoffman, J. D.; Weeks, J. J. J Chem Phys 1962, 37, 1723.
19. Chen, H.; Porter, R. S. J Polym Sci Part B: Polym Phys 1993, 31, 1845.
20. Liu, T. X.; Mo, Z. S. Polym Eng Sci 1997, 37, 568.
21. Ozawa, T. Polymer 1971, 12, 150.
22. Liu, T. X.; Mo, Z. S.; Zhang, H. F. J Appl Polym Sci 1998, 67, 815.