

Thermal Degradation Kinetics and Lifetime Prediction of Poly(aryl Ether Ketone)s Containing 2,6-Naphthalene Moieties

Si-Jie Liu,^{1,2} Xiang Hou,² Chi-Guang Fang,² Rong-Tang Ma,¹ Zhen-Hua Jiang¹

¹Alan G. MacDiarmid Laboratory, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

²Jilin Provincial Center for Sanitation Inspection and Test Department of Physics and Chemistry Test, Changchun 130062, People's Republic of China

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ABSTRACT: The kinetics of thermal degradation and lifetime of poly(aryl ether ketone) containing 2,6-naphthalene moieties (PANEK) in nitrogen and in air were studied with dynamic thermogravimetry. The results showed that the thermal stability of PANEK in air was substantially less than that in nitrogen. The kinetic parameters for PANEK, including the activation energy, the reaction order, and the frequency factor of the degradation reaction, were analyzed with the Ozawa method. The lifetime of PANEK decreased

gradually from 1.09×10^7 to 0.65×10^2 min as the temperature increased from 200 to 400°C in air and from 2.12×10^8 to 3.30×10^2 min in nitrogen. These lifetime parameters indicated that the service/process temperature had a strong influence on PANEK. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 904–909, 2009

Key words: poly(ether ketones); thermal properties; thermodynamics; thermogravimetric analysis (TGA)

INTRODUCTION

Poly(aryl ether ketone)s are high-performance engineering plastics with outstanding physical, chemical, thermal, and mechanical properties, and they have been extensively applied in aerospace, electronics, automotive, petroleum, and chemical industries and in equipment for medical and food industries. Along with the development of the science and technology, people have attempted to obtain materials with higher temperature classifications and more excellent thermal performances. To improve the performance of poly(aryl ether ketone)s further and fulfill the requirements of some extreme environmental conditions, such as high temperatures, naphthalene rings have been introduced into polymer structures by some researchers because they have a larger volume than benzene rings; they can enlarge the proportion of rigid groups in the main chain, decrease the mobility of the segments, and therefore increase the glass-transition temperature of a polymer.^{1–4}

The thermal stability of a polymeric material is one of the most important properties for both processing and application.^{5–7} Although there have been

several publications concerning the thermal degradation of polymers containing naphthalene moieties by thermogravimetry (TG) at a constant heating rate in nitrogen and air,^{8–10} to date, TG of poly(aryl ether ketone)s containing 2,6-naphthalene moieties (PAN-EEKs) has not been reported. This article mainly presents the thermal degradation kinetics and lifetime prediction of PANEEKs in nitrogen and in air by dynamic thermogravimetry.

EXPERIMENTAL

PANEEK (molar ratio of hydroquinone to 2,6-dihydroxy naphthalene = 0:100) was synthesized with a procedure described elsewhere.¹ The poly(ether ether ketone) (PEEK) used in this study was synthesized by a nucleophilic substitution reaction from hydroquinone and 4,4'-difluorobenzophenone. The inherent viscosities of PANEEK and PEEK were 0.76 and 0.81 dL/g, respectively, when they were measured in 98% H₂SO₄ (at 25°C with a 0.01 g/10 mL concentration). The glass-transition temperatures of PANEEK and PEEK were 173 and 143°C, respectively.

Thermal degradations were performed in a Perkin-Elmer, (Waltham, MA) TGA 7 thermogravimetric analyzer. The temperature calibration of the thermobalance was performed according to the procedure suggested by Mettler and reported in the user manual for the equipment. This procedure is

Correspondence to: Z.-H. Jiang (0928lsj@163.com or jiangzhenhua@mail.jlu.edu.cn).

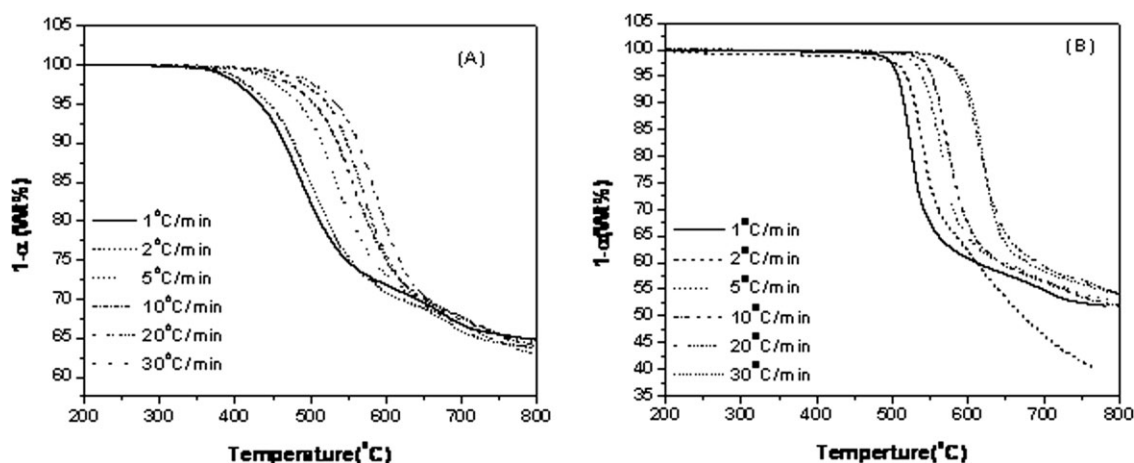


Figure 1 TG curves of (A) PANEK and (B) PEEK in nitrogen at heating rates of 1, 2, 5, 10, 20, and 30°C/min.

based on the change in the magnetic properties of three metal samples (aluminum, nickel, and iron) at their Curie points (154.2, 355.3, and 780.0°C, respectively). Degradation experiments were performed under both isothermal and dynamic heating conditions with 4–8-mg samples placed in alumina open crucibles under either nitrogen or air at a flow rate of 20 mL/min. Degradation experiments for PANEK and PEEK under dynamic conditions were performed at heating rates of 1, 2, 5, 10, 20, and 30°C/min from 200 to 800°C in nitrogen and in air, respectively. For the experiments under isothermal conditions, the samples were quickly heated from 35°C up to the selected temperature and then maintained at that temperature for 90 min.

RESULTS AND DISCUSSION

Thermogravimetric analysis

TG is the most widely used technique for characterizing the thermal degradation of polymer materials.

The TG and derivative thermogravimetry (DTG) curves of PANEK in nitrogen at heating rates of 1, 2, 5, 10, 20, and 30°C/min from 200 to 800°C are shown in Figures 1 and 2, respectively. In each case, a thermally stable residue was formed in nitrogen. From Figure 1, it can be seen that the thermal degradation temperatures increased with the heating rate. Below 450°C, PANEK was stable, and it showed a noticeable weight loss only above 450°C. The weight loss of PANEK at all heating rates gradually decreased to about 62% at a temperature of about 750°C, but the weight loss of PEEK at all heating rates gradually decreased to about 53% at the same temperature. As the temperature increased up to about 800°C, only a slight additional reduction in the weight could be observed. The temperature of 5% weight loss increased with the heating rate increasing. The corresponding DTG curves of PANEK and PEEK degraded in nitrogen at different heating rates indicated that the weight loss occurred in one stage.

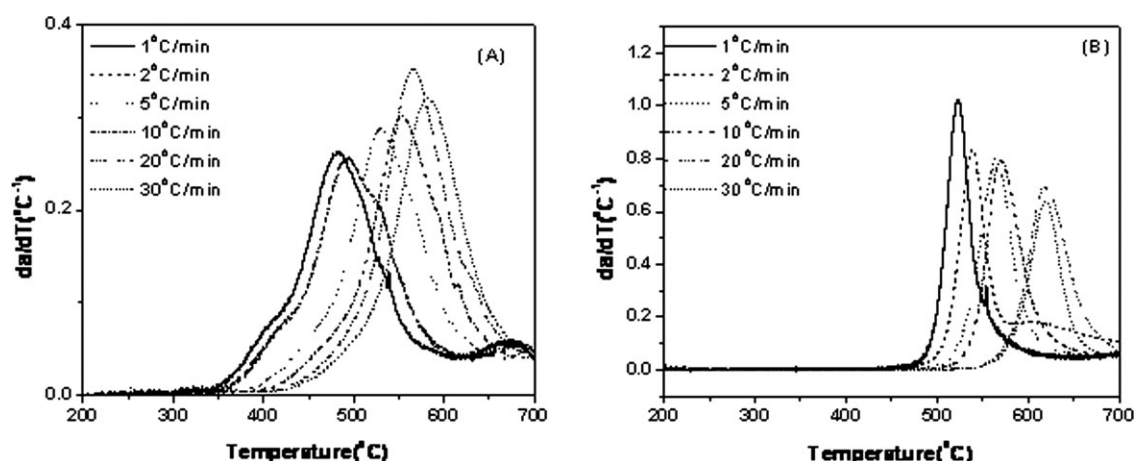


Figure 2 DTG curves of (A) PANEK and (B) PEEK in nitrogen at heating rates of 1, 2, 5, 10, 20, and 30°C/min.

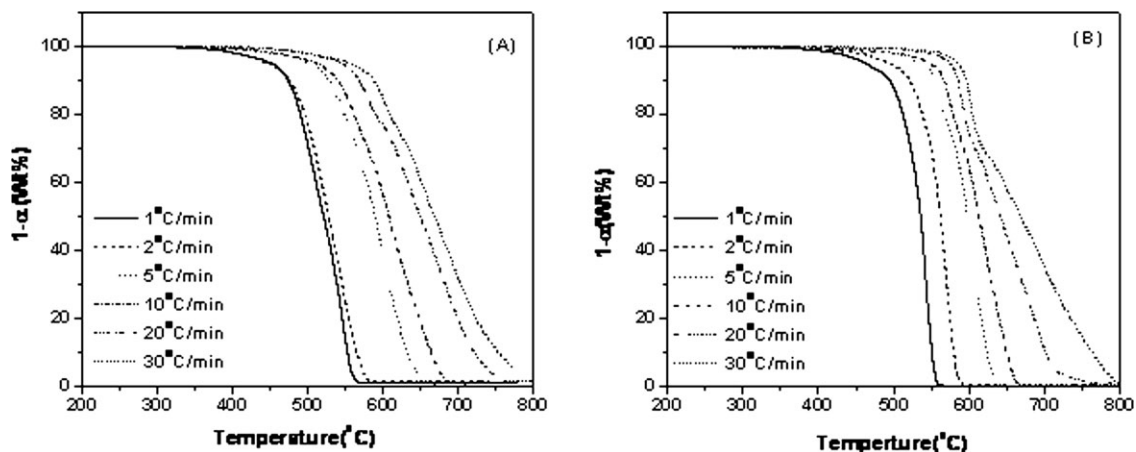


Figure 3 TG curves of (A) PANEK and (B) PEEK in air at heating rates of 1, 2, 5, 10, 20, and 30°C/min.

The TG and DTG curves of PANEK heated in air are shown in Figures 3 and 4, respectively. Figure 3 shows that the influence of the heating rate on the initial temperature of degradation was similar to the influence in nitrogen; at the end of degradation, there was no residue at all. The initial temperature of degradation in air increased with the heating rate increasing, and the degradation was complete at a temperature of about 550°C, depending on the heating rate. In Figure 4, two peaks can be observed for PANEK at all heating rates investigated. This indicates that the degradation took place in two stages. The initial reaction stage was similar to that observed in nitrogen, although the temperatures of the initial weight loss in air were lower than those in nitrogen. The subsequent degradation that appeared was oxidative in nature.

From these experimental data, we can see that the thermal stability of PANEK was better than that of PEEK and that the speed of thermal oxidative degradation was slower than that of PEEK.

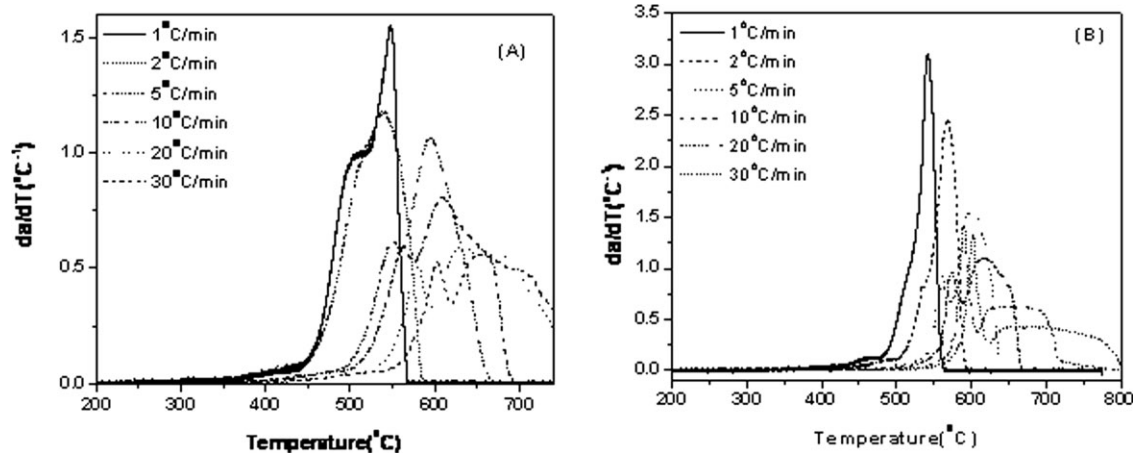


Figure 4 DTG curves of (A) PANEK and (B) PEEK in air at heating rates of 1, 2, 5, 10, 20, and 30°C/min.

Degradation kinetics

In thermogravimetric analysis, the conversion rate of a reaction (α) can be defined as the ratio of actual weight loss to the total weight loss corresponding to the degradation process:

$$\alpha = \frac{M_0 - M}{M_0 - M_f} \quad (1)$$

where M , M_0 , and M_f are the actual, initial, and final weights of the sample, respectively.

The rate of degradation ($d\alpha/dt$) can be expressed as functions of the temperature and weight of the sample:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1 - \alpha)^n \quad (2)$$

where A is the frequency factor, n is the reaction order, E is the apparent activation energy of the degradation reaction, R is the gas constant, and T is the

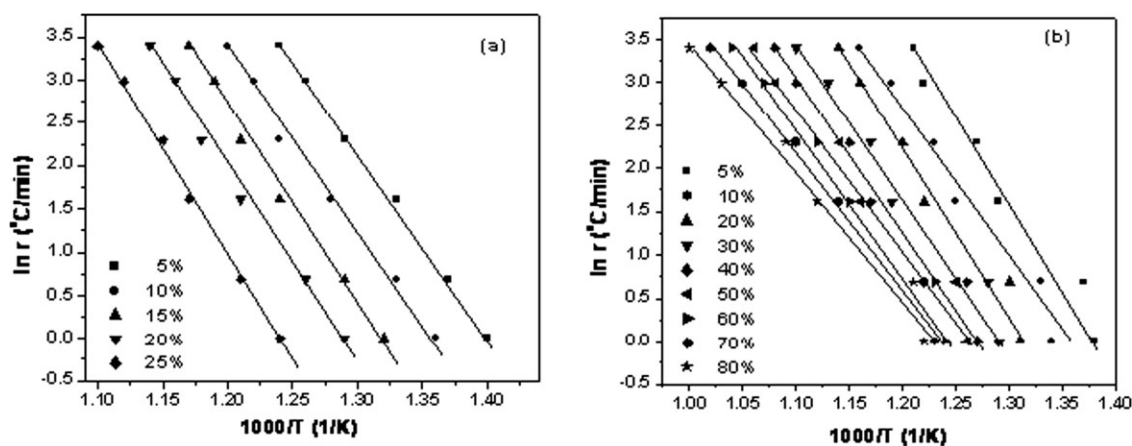


Figure 5 Temperature dependence of the heating rate ($\ln r$) versus $1/T$ for various weight losses in (a) nitrogen and (b) air.

absolute temperature. Upon the introduction of the heating rate ($r = dT/dt$), eq. (2) can be modified to

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{r} \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

Therefore, eq. (3) is the fundamental relationship for determining the kinetic parameters on the basis of TG data. The integral form of eq. (3) can be written as follows:

$$g(\alpha) = \frac{A}{r} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{rR} p(x) \quad (4)$$

where $x = \frac{E}{RT}$ and $p(x) = -\int_{\infty}^x \frac{\exp(-x)}{x^2} dx$.

To describe the thermal degradation kinetics, Ozawa assumed $\log p(x) \approx -2.315 - 0.457x$ or $\ln p(x) \approx -5.330 - 1.052x$ for $20 < x < 60$ for the non-plateau region of the curves.¹⁰ Equation (4) can be written as follows:

$$\ln g(\alpha) = \ln \frac{AE}{rR} - 5.330 - 1.052 \frac{E}{RT} \quad (5)$$

where A and R are constants and, for a particular value of α or weight-loss percentage, $g(\alpha)$ is a constant. Then, eq. (5) becomes

$$\ln r = C - 1.052 \frac{E}{RT} \quad (6)$$

where the constant C is given by

$$C = \ln \frac{AE}{g(\alpha)R} - 5.330$$

Hence, the value of E can be computed by Ozawa's method for any particular weight loss, being determined from the linear dependence of the $\ln r$ versus $1/T$ plot at different heating rates for the nonplateau region of the curves.

On the basis of eq. (6), the relationships between $\ln r$ and $1/T$ for different weight losses during the thermal degradation of PANEK in nitrogen and air are shown in Figure 5. The isoconversional plots are almost parallel straight lines in nitrogen but not in air, and this indicates that the double-stage

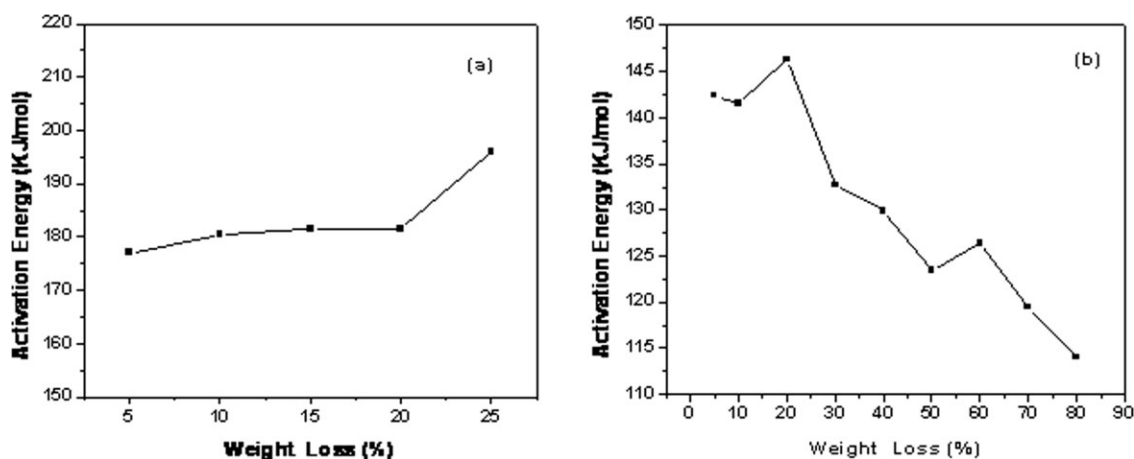


Figure 6 Dependence of the activation energy on the weight loss percentage for the degradation of PANEK in (a) nitrogen and (b) air.

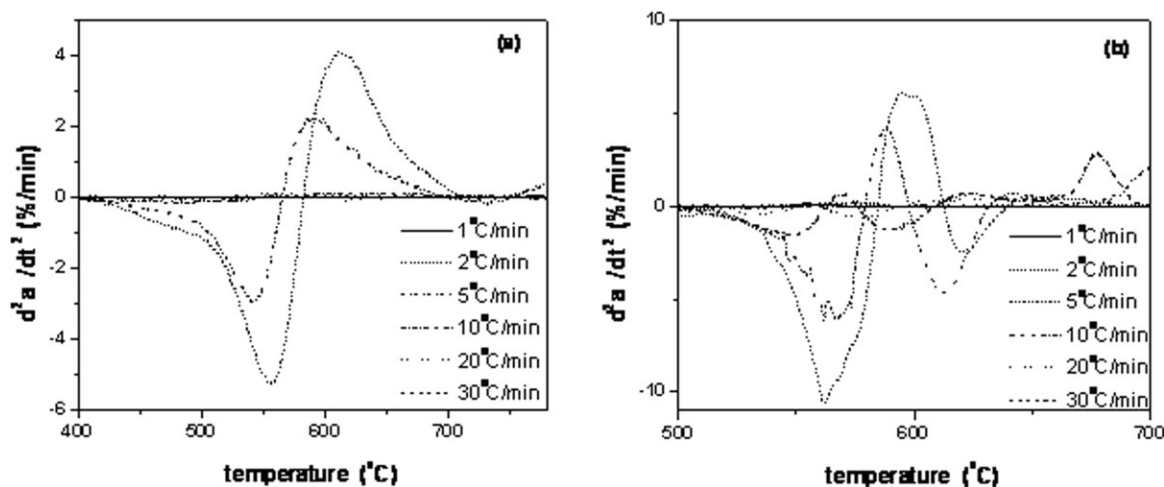


Figure 7 2DTG curves of PANEK at various heating rates in (a) nitrogen and (b) air.

degradation process in air was a complex weight loss process with several mechanisms. Figure 6 presents the variation of the apparent activation energies with the percentage of weight loss for the degradation of PANEK in nitrogen and air. The apparent activation energy of degradation in nitrogen was much higher than that in air and almost independent of the percentage of weight loss; it increased obviously around a 35% weight loss. The variation of the activation energies with the weight loss in air was quite different from that in nitrogen; the activation energy decreased with increasing weight loss. This shows that the reaction was autoaccelerated as the degradation reaction was initiated.

Lifetime prediction

The estimated lifetime of a polymer to failure can be defined as the time when the weight loss reaches 5 wt %, $\alpha = 0.05$. From the integration of eq. (2), the lifetime (t_f) can be estimated by

$$t_f = \frac{(1 - 0.95^{1-n})}{A(1-n)} \exp \frac{E}{RT} \quad (n \neq 1) \quad (7)$$

or

$$t_f = \frac{(0.0513)}{A} \exp \frac{E}{RT} \quad (n = 1) \quad (8)$$

n can be obtained directly from the symmetrical index of a DTG peak based on the second Kissinger technique:⁶

$$n = 1.88 |(d^2\alpha/dt^2)_L| / |(d^2\alpha/dt^2)_R| \quad (9)$$

where the subscripts L and R correspond to the left and right peak ($d^2\alpha/dt^2$) values on the second deriv-

ative thermogravimetry (2DTG) curves. If we assume that PANEK occurs at $\alpha = 0.05$, the lifetime can be estimated with eq. (7).

Figure 7 shows the 2DTG curves of PANEK at various heating rates in nitrogen and air. The n values at various heating rates in nitrogen and air, as well as the frequency factor ($\ln A$) values calculated from eq. (2) based on the activation energies at a weight loss of 5%, are listed in Table I. The average n and $\ln A$ values were 1.59 and 22.89 min^{-1} in nitrogen, respectively, whereas the respective average n and $\ln A$ values were 1.37 and 21.34 min^{-1} in air. Based on these kinetic data and eq. (7), the estimated results for the lifetime values for PANEK in nitrogen and air at a weight loss of 5% and at various temperatures are listed in Table II. The lifetime of PANEK decreased gradually from 1.09×10^7 to

TABLE I
Thermal Degradation Kinetic Parameters of PANEK
at a Weight Loss of 5%

Heating rate (°C/min)	Atmosphere	Activation energy (kJ/mol)	n	$\ln A$ (min^{-1})
1	Nitrogen	177.0	1.79	22.38
2			1.52	22.79
5			1.70	22.75
10			1.61	22.83
20			1.45	23.36
30			1.47	23.25
Average			1.59	22.89
1	Air	159.2	1.28	20.49
2			1.10	21.72
5			1.70	21.40
10			1.55	21.61
20			1.45	21.49
30			1.16	21.36
Average			1.37	21.34

TABLE II
Estimated Values of the Lifetime of PANEK Based on a Weight Loss of 5% at Various Temperatures

Atmosphere	Lifetime (min)				
	200°C	250°C	300°C	350°C	400°C
Nitrogen	2.12×10^8	2.87×10^6	8.20×10^4	4.17×10^3	3.30×10^2
Air	1.09×10^7	2.27×10^5	9.31×10^3	6.37×10^2	0.65×10^2

0.65×10^2 min as the temperature increased from 200 to 400°C in air and from 2.12×10^8 to 3.30×10^2 min in nitrogen. Obviously, the lifetime was longer in nitrogen than in air. These lifetime parameters clearly suggest that the service temperature had a strong influence on PANEK.

CONCLUSIONS

1. The thermal stability of PANEK containing 2,6-naphthalene moieties was better than that of PEEK.
2. PANEK containing 2,6-naphthalene moieties showed a one-stage thermal degradation process in nitrogen but a double stage in air.
3. The apparent activation energy of PANEK in air was lower than that in nitrogen and decreased with the percentage of weight loss increasing.
4. The lifetime of PANEK decreased dramatically with increasing temperature both in air and in

nitrogen. The lifetime was much longer in nitrogen than in air.

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