Thermal Degradation Kinetics of Thermotropic Poly(*p*-oxybenzoate-*co-p,p*'-biphenylene terephthalate) Fiber

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ABSTRACT: An advanced heat-resistant fiber (trade name Ekonol) spun from a nematic liquid crystalline melt of thermotropic wholly aromatic poly(p-oxybenzoate-p, p'-biphenylene terephthalate) has been subjected to a dynamic thermogravimetry in nitrogen and air. The thermostability of the Ekonol fiber has been studied in detail. The thermal degradation kinetics have been analyzed using six calculating methods including five single heating rate methods and one multiple heating rate method. The multiple heating-rate method gives activation energy (E), order (n), frequency factor (Z) for the thermal degradation of 314 kJ mol⁻¹, 4.1, 7.02×10^{20} min⁻¹ in nitrogen, and 290 kJ mol⁻¹, 3.0, 1.29×10^{19} min⁻¹ in air, respectively. According to the five single heating rate methods, the average E, n, and Z values for the degradation were 178 kJ mol⁻¹, 2.1, and $1.25 \times 10^{10} \text{ min}^{-1}$ in nitrogen and 138 kJ mol⁻¹, 1.0, and $6.04 \times 10^{7} \text{ min}^{-1}$ in air, respectively. The three kinetic parameters are higher in nitrogen than in air from any of the calculating techniques used. The thermostability of the Ekonol fiber is substantially higher in nitrogen than in air, and the decomposition rate in air is higher because oxidation process is occurring and accelerates thermal degradation. The isothermal weight-loss results predicted based on the nonisothermal kinetic data are in good agreement with those observed experimentally in the literature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1923-1931, 1999

Key words: wholly aromatic polymer; thermotropic liquid crystalline polyester; Ekonol fiber; poly(p-oxybenzoate-co-p,p'-biphenylene terephthalate); thermogravimetry; thermostability; thermal degradation kinetics

INTRODUCTION

There has been an increasing application of thermotropic liquid crystalline wholly aromatic polymer fibers with high heat-resistance, either alone as ropes, cables, and protective apparel, or as reinforcers or matrices for advanced composites. Thermotropic poly(p-oxybenzoate-co-p,p'-biphe-

Contract grant sponsor: Science Technology Development Foundation of Tongji University in Shanghai, China. nylene terephthalate) copolyester fiber, Ekonol fiber, represents one of the most important fully aromatic polymers with high heat resistance and high tensile property.¹ The rigid rod-like aromatic chain structure of the copolyester is responsible for its relatively high glass transition and melting temperature ($\sim 430^{\circ}$ C).² Consequently, the polymer must encounter elevated temperatures at almost every stage in preparing, melt blending, and processing (such as spinning) stages, as well as in service and during repair.^{2,3} It is necessary to assess and predict the thermostability under these conditions.⁴ A few reports have dealt with the synthesis,^{2,5–9} phase transition,² X-ray fiber diagram,^{2,3} three-dimensional diffractogram in

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the temperature range from room temperature to 380° C,² tensile property,¹ and thermal degradation⁴ of the copolyester and its fiber. However, thermal stability and degradation kinetics of the Ekonol fiber have not been studied systematically.

In this article, by performing a detailed constant heating rate thermogravimetry (TG) and a high-resolution TG (High-Res TG) kinetic analysis of the thermal degradation, the thermostability of the Ekonol fiber is clarified. To assess the relative importance of the pyrolytic and thermooxidative processes, the weight-loss curves were measured in nitrogen and air by a dynamic nonisothermal TG technique, and three kinetic parameters of the thermal degradation were calculated.

EXPERIMENTAL

The Ekonol fiber is a golden fiber spun from the nematic liquid crystalline melt of thermotropic poly(p-oxybenzoate-co-p,p'-biphenylene terephthalate) was kindly supplied by the Sumitomo Chemical Co., Ltd., in Japan and by Nippon Exlan Co., Japan. Xydar fiber (a trademark of Dartco Manufacturing, Inc., Augusta, GA) and Ekkcel C-1000 (a trade name of Carborundum Co.) have the same nominal macromolecular structure as the Ekonol fiber. The copolyester is prepared by the melt polycondensation of *p*-acetoxybenzoic acid, p,p'-diacetoxy biphenyl, and terephthalic acid in nitrogen and under vacuum at 320°-340°C. Melt polycondensation was continued until its number-average molecular weight reaches 2,000-3,000. The melt was cooled and then ground into powder. Finally, a postpolymerization in the solid state was conducted in a flowing nitrogen until a high molecular weight of 25,000 was obtained. The copolyester has a nominal molecular structure as follows:

TG was done with a TA 2950 high-resolution thermogravimetric analyzer. Conventional constant heating rate TG measurements were run at 1, 5, 10, and 20°C min⁻¹ in both flowing nitrogen and flowing air at 30 mL min⁻¹, with the sample size of 0.6 mg in nitrogen and 0.4 mg in air to provide a control set of values for thermal decomposition parameters. Additionally, a High-Res TG experiment in flowing nitrogen (25 mL min⁻¹), with a sample weight of 2 mg, was conducted. In the high-resolution experiment, the sensitivity was fixed at its default value of 1. Initial heating rate was fixed at 50°C min⁻¹, and resolution was fixed at 3. This High-Res TG technique is a dynamic rate control method. The heating rate of the sample is dynamically and continuously varied in response to changes in the sample's decomposition rate. This method can improve the accuracy of identification and quantification.

There are several techniques for the kinetic evaluation of the TG thermal degradation data, and they have been discussed in several publications.¹⁰ Thermal decomposition kinetics was examined by six evaluating techniques:

Freeman–Carroll Method

$$\Delta \operatorname{Ln}(d\alpha/dt)/\Delta \operatorname{Ln}(1-\alpha)$$

= $n - (E/R) \cdot [\Delta(1/T)/\Delta \operatorname{Ln}(1-\alpha)]$ (1)

where $d\alpha/dt$ and α are the weight-loss rate and weight loss, respectively; *n* and *E* are the order and the activation energy of the thermal decomposition reaction, respectively; and *R* and *T* are the universal gas constant and absolute temperature, respectively. The *n* and *E* values can be determined from the intercept and slope of the plot of $\Delta \text{Ln}(d\alpha/dt)/\Delta \text{Ln}(1 - \alpha)$ versus $\Delta(1/T)/\Delta \text{Ln}(1 - \alpha)$ at a very small and fixed $\Delta(1/T)$ value of 0.00001 from a single nonisothermal TG and single derivative TG (DTG) curves.

Friedman Method

$$\operatorname{Ln}(d\alpha/dt) = \operatorname{Ln} Z + n \cdot \operatorname{Ln}(1 - \alpha) - E/RT \quad (2)$$

where Z is the frequency factor of the thermal degradation. The *E* value can be determined from the slope of the plot of $\text{Ln}(d\alpha/dt) vs. 1/T$ from a single nonisothermal TG and single DTG curves. The plot of $\text{Ln}(1 - \alpha)$ against 1/T will give the *n* value from the maximum slope of the line. Then, Ln Z can be calculated through eq. (2) at a certain temperature.

Chang Method

$$\operatorname{Ln}[(d\alpha/dt)/(1-\alpha)^n] = \operatorname{Ln} Z - E/RT \quad (3)$$

A plot of $\text{Ln}[(d\alpha/dt)/(1 - \alpha)^n]$ versus 1/T will form a straight line if the selected *n* value is



Figure 1 TG (—), DTG (---), and 2DTG (···) curves of the thermotropic liquid crystalline poly(p-oxybenzoate-co-p,p'-biphenylene terephthalate) Ekonol fiber in nitrogen at two heating rates: (a) 1°C min⁻¹ and (b) 10°C min⁻¹.

correct, and the E and Ln Z values can be obtained from the slope and intercept of the straight line, respectively.

Coats-Redfern Method

$$\ln[1 - (1 - \alpha)^{1 - n}]/T^{2}(1 - n)] = \ln[(ZR/qE) + (1 - 2RT/E)] - E/RT \quad (n \neq 1) \quad (4)$$

where q represents the heating rate (°C min⁻¹). Plotting of $\text{Ln}[1 - (1 - \alpha)^{1-n}]/T^2(1 - n)]$ against 1/T will give a straight line only if the decomposition order is selected correctly.

Kissinger Method

$$\operatorname{Ln}(q/T_{dm}^2) = \operatorname{Ln}[n(1 - \alpha_{dm})^{n-1} \cdot Z \cdot R/E] - E/RT_{dm} \quad (5)$$

where the T_{dm} and α_{dm} are the temperature and weight loss at the maximum weight-loss rate $(d\alpha/dt)_m$. The *E* value can be calculated from the slope of the plotting of ${\rm Ln}(q/T_{dm}^2)$ as a function of $1/T_{dm}$ at the maximum weight-loss rate. The intercept of the plot of ${\rm Ln}(q/T_{dm}^2)$ vs. $1/T_{dm}$ is

$$\mathbf{I} = \operatorname{Ln}[n(1 - \alpha_{dm})^{n-1} \cdot Z \cdot R/E]$$
(6)

Solving for n and substituting it into the following equation

$$d\alpha/dT = Z \cdot (1 - \alpha_{dm})^n [\exp(-E/RT_{dm})]/q \quad (7)$$

giving an expression for n

$$n = (1 - \alpha_{dm}) \cdot E \cdot [\exp(\mathbf{I})]$$
$$\cdot [\exp(-E/RT_{dm})]/[q \cdot R \cdot (d\alpha/dT)] \quad (8)$$

The *n* value can be easily obtained from eq. (8) by using *E* and the intercept determined from eq. (5). Finally, the Ln *Z* value can be calculated from eq. (6) after the *n* value is known.

The n value can be also obtained directly from the symmetrical index of a single DTG peak:



Figure 2 TG (—), DTG (—–), and 2DTG (···) curves of the Ekonol fiber in air at two heating rates: (a) 5° C min⁻¹ and (b) 20° C min⁻¹.

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

where indices L and R correspond the maximum and minimum $d^2\alpha/dt^2$ values on the second derivative TG (2DTG) curve.

Kim–Park Method¹¹

$$Ln q = Ln(ZE/R) + Ln(1 - n + n/0.944) - 5.331 - 1.052E/RT_{dm}$$
(10)

$$n = E(1 - \alpha_{dm}) / [RT_{dm}^2 (d\alpha/dT)_m]$$
(11)

$$Z = [q \exp(E/RT_{dm})]/(1 - \alpha_{dm})^n$$
(12)

A linear relationship between Ln q and $1/T_{dm}$ from eq. (10) will form from the DTG and TG curves obtained at two or more heating rates, and the E can be calculated from its slope. Then, the n and Z values can be calculated based on eqs. (11) and (12), respectively.

Table I Characteristics of Thermal Decomposition of the Ekonol Fiber by TG Methods

Heating Rate (°C min ⁻¹)	Test Atmosphere	T_d (°C)	$\begin{array}{c} T_{dm} \\ (^{\circ}\mathrm{C}) \end{array}$	$\mathop{T_{dm1}}_{(°\mathrm{C})}$	Char Yield at 600°C (wt %)	$\frac{(d\alpha/dt)_m}{(\% \min^{-1})}$	$(dlpha/dT)_m \ (\%/^{\circ}\mathrm{C})$
1	Nitrogen	455	484	573	46	0.7	0.7
2^{a}	Nitrogen	470	490	631	52	1.3	0.7
5	Nitrogen	465	506	567	43	6.0	1.2
10	Nitrogen	475	517	583	11	9.3	0.9
Variable ^b	Nitrogen	460	496	557	45	10.5	2.0
2^{a}	Air	468	518	_	0	8.8	4.4
5	Air	460	535	_	48	4.6	0.9
10	Air	475	547	_	5.3	14.0	1.4
20	Air	483	558	—	2.1	14.5	0.7

^a Its TG and DTG were obtained from ref. 4.

^b Variable means a variable heating rate during the High-Res TG measurement.



Figure 3 High-Res TG (—), DTG (---), 2DTG (···), and heating rate $(- \cdot - \cdot)$ curves of the Ekonol fiber in nitrogen with resolution 3 at an initial heating rate of 50°C min⁻¹.

Calculation of Lifetime Estimates (t_f)

The lifetime t_f of polymers to failure can be defined when the weight loss reaches 5 wt %,

$$\mathbf{t_f} = (1 - 0.95^{1-n}) \\ \cdot \exp(E/RT) / [Z(1-n)] \quad (n \neq 1) \quad (13)$$

The general form of this equation is:

$$\mathbf{t_f} = [1 - (1 - \alpha)^{1 - n}] \\ \cdot \exp(E/RT) / [Z(1 - n)] \quad (n \neq 1) \quad (14)$$

RESULTS AND DISCUSSION

Thermal Stability

The representative TG, DTG, and 2DTG curves of the Ekonol fiber in nitrogen and air at heat-



Figure 4 Freeman–Carroll plots of $-\Delta \text{Ln}(d\alpha/dt)/\Delta \text{Ln}(1 - \alpha)$ against $\Delta(1/T)/\Delta \text{Ln}(1 - \alpha)$ for the thermal degradation of the Ekonol fiber: (a) in nitrogen at three heating rates of 1°C min⁻¹(\bigcirc); 10°C min⁻¹(\triangle); a variable heating rate in a High-Res TG (\bigtriangledown). (b) In air at three heating rates of 5°C min⁻¹(\bigcirc); 10°C min⁻¹(\triangle); 20°C min⁻¹(\bigtriangledown).



Figure 5 Friedman plots of $\operatorname{Ln}(d\alpha/dt) vs. 1/T$ for the thermal degradation of the Ekonol fiber at the following conditions: (\Box) 1°C min⁻¹ in nitrogen; (\bigcirc) 10°C min⁻¹ in nitrogen; (\bigtriangleup) a variable heating rate in a High-Res TG in nitrogen; (\bigtriangledown) 5°C min⁻¹ in air; (\diamondsuit) 10°C min⁻¹ in air; (+) 20°C min⁻¹ in air.



Figure 6 Chang plots of $\operatorname{Ln}[(d\alpha/dt)/(1 - \alpha)^n]$ vs. 1/T for the thermal degradation of the Ekonol fiber at the following conditions: (\Box) 1°C min⁻¹ in nitrogen; (\bigcirc) 10°C min⁻¹ in nitrogen; (\triangle) a variable heating rate in a High-Res TG in nitrogen; (\bigtriangledown) 5°C min⁻¹ in air; (\diamond) 10°C min⁻¹ in air; (+) 20°C min⁻¹ in air.

ing rates of 1°, 5°, 10°, and 20°C min⁻¹ are shown in Figures 1 and 2. The DTG curves in both nitrogen and air indicate that two weightloss stages occur during degradation. The DTG peaks of the first-stage in nitrogen is much stronger than those of the second stage. Quite the contrary, the DTG peaks of the first stage in air are only shoulder peaks and much weaker



Figure 7 Coats–Redfern plots of $\text{Ln}[1 - (1 - \alpha)^{1-n}]/T^2(1 - n)]$ against 1/T for the thermal degradation of the Ekonol fiber at the following conditions: (\Box) 1°C min⁻¹ in nitrogen; (\bigcirc) 10°C min⁻¹ in nitrogen; (\bigtriangleup) a variable heating rate in a High-Res TG in nitrogen; (\bigtriangledown) 5°C min⁻¹ in air; (\diamondsuit) 10°C min⁻¹ in air; (+) 20°C min⁻¹ in air.

Table II Kin	etic Parameter	s for the Thermal Degrad	ation of the Ekonol Fibe	er Obtained by Five Sing	le Heating Rate Methods	
		Freeman–Carroll	Friedman	Chang	Coats-Redfern	
Heating Rate (°C min ⁻¹)	Test Atmosphere	$E/n/{\rm Ln} Z/r$ (kJ mol ⁻¹ /-/min ⁻¹ /)	E/n/Ln Z/r (kJ mol ⁻¹ /—/min ⁻¹ /—)	$E/n/{ m Ln}~Z/r$ (kJ mol ⁻¹ /-/min ⁻¹ /)	$E/n/{ m Ln}~Z/r$ (kJ mol ⁻¹ /-/min ⁻¹ /)	Kissinger n
1	N_{2}	184/2.4/22/0.999	163/2.9/19/0.999	180/2.0/22/0.999	217/2.0/27/0.996	1.5
10	N_2	179/1.6/22/0.999	161/1.9/19/0.998	176/1.5/21/0.999	159/1.6/19/0.999	1.4
Variable	N_2	172/3.0/22/0.989	159/1.8/20/0.999	172/2.9/22/0.988	239/2.9/32/0.999	2.2
Average	\mathbf{N}_2	196/2.7/24				
5	Air	149/1.5/17/0.997	150/2.0/18/0.995	148/1.5/18/0.996	169/1.5/23/0.995	2.0
10	Air	171/0.6/24/0.999	160/1.0/22/0.999	170/0.5/24/0.999	152/0.5/18/0.999	
20	Air	148/0.5/20/0.999	142/0.6/17/0.997	147/0.5/20/0.999	143/0.5/18/0.999	0.7
Average	Air	162/1.0/20				

r = linear correlation coefficient.

		Kissir	iger Method			Kim–Park Method		
Atmosphere	$E \over ({\rm kJ\ mol}^{-1})$	n	${\rm Ln} Z \over ({\rm min}^{-1})$	Correlation Coefficient	$E \ ({\rm kJ\ mol}^{-1})$	n	${\rm Ln} Z \over ({\rm min}^{-1})$	Correlation Coefficient
Nitrogen Air	$\frac{314}{290}$	$\begin{array}{c} 4.1\\ 3.0\end{array}$	48 44	$0.995 \\ 0.999$	314 291	$4.3 \\ 2.8$	51 46	$0.994 \\ 0.998$

Table IIIKinetic Parameters for the Thermal Degradation of the Ekonol Fiber by ConventionalConstant Heating Rate TG Measurements Obtained by Multiple Heating Rate Methods

than those of the second stage. The two characteristic temperatures, including T_d and T_{dm} , all increase as the heating rate increases. At the same heating rate, the T_d is higher, but T_{dm} is lower in nitrogen than in air. A very similar variation of T_d and T_{dm} with heating rate was observed for the thermal degradation of another thermotropic liquid crystalline poly(p-oxybenzoate-co-2,6-oxynaphthoate) Vectra copolyester.¹⁰ The char yield at 600°C exclusive of the data in ref. 4, decreases significantly in both nitrogen and air with increasing heating rate. At 2°C min⁻¹ in ref. 4, 0% residue at 550°C in air appears to be completely thermo-oxidative in nature. This is different from the results in this study. Possibly, its experimental condition is different from that in this study. Note that the char yield is an additive parameter and then could be estimated on the basis of polymer structure. It is known the molecular weight of the repeating unit is 435 and the contributive values of $-\bigcirc$ -COO-, \bigcirc - \bigcirc -, and $-\bigcirc$ -COO- to char formation are 2.7, 8.0, and $1.\overline{25}$, respectively.¹² Thus, the estimated char residue is $(2.7 + 8.0 + 1.25) \times 12 \times 100$ \div 435 = 33 wt %, which is only a little bit lower than the char yield (35%) observed at 800°C in nitrogen at 1° C min⁻¹ and variable heating rate. It is found that this estimated char residue is the same as the extrapolated char yield at 950°C in nitrogen in the High-Res TG curve. Additionally, as shown in Table I, the $(d\alpha/dt)_m$ value increased significantly, but the $(d\alpha/dT)_m$ value varied slightly as the heating rate increased.

To compare the thermal decomposition temperatures and kinetics from a conventional constant heating rate TG with a High-Res TG at variable heating rates, Figure 3 shows TG, DTG, 2DTG, and heating rate curves of the Ekonol fiber in nitrogen. Clearly, the DTG peak is sharper, and characteristic degradation temperatures are easier to determine than conventional TG/DTG curves shown in Figure 1. An additional small shoulder peak on the DTG curve before the major DTG peak was observed. The thermal decomposition results determined by High-Res TG are also listed in Table I. It is seen that the $(d\alpha/dt)_m$, $(d\alpha/dT)_m$, and char yield at 600°C determined by High-Res TG were higher than those by the constant heating rate TG in nitrogen, probably due to the highest resolution produced by the variable heating rate experiment in High-Res TG.

Kinetics of Thermal Degradation

The Freeman–Carroll, Friedman, Chang, Coats– Redfern, and Kissinger methods can all determine the kinetic parameters for the thermal degradation of the Ekonol fiber by using only one heating rate. Figures 4–7 show the relationships given by eqs. (1)–(4) in the same weight-loss and temperature ranges for a certain heating rate measurement. Good linear relationships for each heating rate in nitrogen and air were obtained. First-stage kinetic parameters calculated by the four methods for the Ekonol fiber at different heating rates in different environments were compared and summarized in Table II.

From Table II, it can be concluded that the kinetic parameters changes with heating rate, and the E value in nitrogen decreases slightly with heating rate. This indicates that the changes in the thermal decomposition kinetics are taking place. But there is no regular variation of the E value with heating rate in air. The three kinetic parameters are larger in nitrogen than in air. The same phenomenon was shown in the thermal degradation kinetics of the Vectra copolyester.¹⁰

Equations (3)–(5) from the Kissinger technique that requires at least two TG curves obtained at various heating rates give larger parameters comparable with those of the Freeman–Carroll, Friedman, Chang, and Coats–Redfern techniques



Figure 8 Kissinger plots of Ln(heating rate/ T_{dm}^2) vs. $1/T_{dm}$ for the thermal degradation of the Ekonol fiber in nitrogen (\bigcirc) and in air (\triangle).

at a single run measurement (as shown in Table III). The Kissinger plots obtained for the Ekonol fiber decomposed in nitrogen and air are shown in Figure 8. Reasonable straight lines were obtained for the experiments. Respective E, n, and Ln Zvalues of 314 kJ mol⁻¹, 4.1, and 48 min⁻¹ in nitrogen, and 290 kJ mol⁻¹, 3.0, and 44 min⁻¹ in air were obtained from the slope and intercept of the straight lines. Kinetic parameters obtained by the Kim-Park method are also listed in Table III. The three parameters in nitrogen are higher than those measured in air, just like the degradation kinetics of the Vectra copolyester.¹⁰ The higher Eand n values clearly indicate the higher thermostability and slower degradation rate of the Ekonol in nitrogen than in air.

Compared with the parameters in Table III with those in Table II, it is found that the three kinetic parameters calculated by the Kissinger and Kim–Park methods (multiple heating rate method) at a higher weight loss are much larger than those by other five single heating rate methods in a wide weight-loss range. This difference might be attributed to a difference between the



Figure 9 A comparison of thermal stability observed experimentally with that calculated according to the kinetic parameters obtained nonisothermally for poly(p-oxybenzoate-p,p'-biphenylene terephthalate).

weight losses and also to the different mathematical approaches used to calculate the parameters. A similar difference has been found in other studies on the thermal degradation of the polymer. But, at a fixed heating rate, there are only a few differences in the three kinetic parameters between four calculating methods of Freeman-Carroll, Friedman, Chang, and Coats-Redfern (as shown in Table II). The average E, n, and $\ln Z$ values determined by the single heating rate methods are 196 kJ mol^{-1} , 2.7, and 24 min^{-1} in nitrogen, and 162 kJ mol⁻¹, 1.0, 20 min⁻¹ in air. Note that the average E, n, and $\operatorname{Ln} Z$ in nitrogen and E in air were obtained from the six larger values in Table II, because the parameters in Table II are much smaller than those in Table III.

Lifetime Prediction

On the basis of the kinetic data derived from the nonisothermal TG, the average E, n, and Ln Z values from the average parameters from Tables II and III are listed in Table IV; two average E values in nitrogen and air from ref. 4 are also

Table IV Average Values of the Kinetic Parameters of the Thermal Degradation for Thermotropic Liquid Crystalline Poly(*p*-oxybenzoate-*co-p*,*p*'-biphenylene terephthalate)

Parameter Atmosphere	$E \ (kJ \ mol^{-1})$		Order	n	$\operatorname{Ln} Z (\min^{-1})$	
	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air
Average	255	226	3.4	2.0	36	32
Average ⁴	234	185	—	—	_	_



Figure 10 Estimated lifetime of thermotropic poly(*p*-oxybenzoate-*p*,*p'*-biphenylene terephthalate) Ekonol fiber based on the weight loss $\alpha = 5\%$ in nitrogen (\bigcirc) and in air (\triangle).

listed. It is clear that the average E values in this study are slightly higher than those from ref. 4. The isothermal stability in 2 h calculated through eq. (14), based on the average three kinetic parameters (E, n, and Ln Z), was compared with the results obtained experimentally (as shown in Fig. 9).⁴ It is seen that the predicted stability is in good agreement with the experimental stability at the temperature below 465°C in nitrogen or below 440°C in air. Using these kinetic data listed in Table IV, the lifetime estimates for the Ekonol fiber generated from weight loss of 5% are constructed by eq. (13) and are shown in Figure 10. It is apparent that the lifetime of the Ekonol fiber decreases dramatically from 2.51×10^{16} min (in nitrogen) or 2.19 $imes 10^{14}$ min (in air) to 2.16 min (in nitrogen) or 1.25 min (in air) as the temperature increases from 127°C to 500°C. The lifetime of the Ekonol fiber at 300° C is ~ 4.3 years (in nitrogen) or 0.47 years (in air). Obviously, the lifetime is longer in nitrogen than in air. Similar results have been observed for high heat resistance Vectra copolyester¹⁰ and poly(aryl-ether-ether-ketone).¹³ These lifetime parameters indeed suggest the thermostability of the Ekonol fiber appears to be lower than those of the Vectra copolyester and poly(ether-ether-ketone), because the longest lifetimes of the Vectra copolyester and poly(ether-ether-ketone) at 300°C in nitrogen is higher than 1718 years¹⁰ and 45 years,¹² respectively. It seems to be concluded from Figure 10 that the Ekonol fiber can resist 427°C for 135 min, indicative that the melt processing time at 427°C should be shorter than 135 min to avoid any significant thermal degradation.

CONCLUSIONS

The thermal degradation temperature and kinetic data for a thermotropic liquid crystalline wholly aromatic poly(p-oxybenzoate-co-p,p'-biphenylene terephthalate) Ekonol fiber heated in nitrogen and air suggest that the Ekonol fiber exhibits an excellent thermostability. The activation energy (E) and frequency factor (Z) of the thermal decomposition for the Ekonol fiber obtained by various techniques have some difference at the same experimental condition. Degradation temperatures usually increase with increasing heating rate. The three kinetic parameters decrease slightly with an increase of heating rate from 1°C min⁻¹ to 10°C min⁻¹ in nitrogen, but the effect of the heating rate on the three kinetic parameters is not apparently regular in air. The thermal stability of the Ekonol fiber is reduced in air. The isothermal stability of the Ekonol fiber below 440°C could be predicted correctly on the basis of the nonisothermal kinetic parameters obtained in this study.

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