

Kinetics of Thermal Degradation of Poly(*p*-phenylene benzobisoxazole)

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ABSTRACT: The kinetics of thermal degradation of poly(*p*-phenylene benzobisoxazole) (PBO) were studied by thermogravimetric analysis (TG) in dynamic nitrogen gas at four different heating rates: 5, 10, 15, 20°C/min. The activation energy calculated by Kissinger Method was 352.19 kJ/mol, and the mean value of activation energies evaluated by Flynn-Wall-Ozawa Method was 338.32 kJ/mol. The degradation kinetic model of PBO followed the mechanism of random scission of weak bonds of PBO molecule and impact of the active

groups obtained from the broken bonds, Mampel Power equation with integral form $G(\alpha) = \alpha^{3/2}$ and differential form $f(\alpha) = \frac{2}{3}\alpha^{-1/2}$. And the mathematical equation of kinetic compensation effect was $\ln A = 0.1365 E_a - 1.4102$. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3675–3679, 2007

Key words: thermal degradation; kinetics; poly(*p*-phenylene benzobisoxazole); thermogravimetric analysis; mechanism function

INTRODUCTION

Poly(*p*-phenylene benzobisoxazole) (PBO) (Fig. 1) is one of the most widely studied PBZ-type heterocyclic aromatic polymers, which is a family of high-performance materials with excellent chemical performance and thermal stability, and its commercial production started in 1998. During the past two decades, extensive reports have been published on its synthesis, fiber spinning, and ultra-high performances.^{1–4}

In addition to its advantageous mechanical properties, PBO also reveals an outstanding thermal stability. Because the thermal stability is one of the most important properties for polymer, the thermal stability and degradation kinetics of PBO may be vital to its production and application.

In some Refs. 5–9 the pyrolysis reaction of PBO has been reported using thermogravimetric analysis (TG), differential thermal analysis (DTA), mass spectrometry (MS), and other experiments. The results showed that the components evolved from TG at elevated temperature were CO₂, H₂O, benzonitrile, dicyanobenzene, and so on, and the dominating reactions of PBO degradation were homolytic scission of a single bond and decomposition of a heterocyclic ring to produce an aromatic nitrile. Also the thermal degradation mechanism and kinetic parameters of PBO have been reported in some articles,^{6,8} but there have not

been advanced that which mechanism function is the most probable one.

In this article, the thermal degradation kinetics of PBO was studied by TG/DTG measurements under dynamic nitrogen at different heating rates. The apparent activation energies were evaluated by Kissinger Method¹⁰ and Flynn-Wall-Ozawa (F-W-O) Method,¹¹ and the most probable mechanism function was determined using Coat-Redfern Method.¹²

KINETICS METHOD

Calculation of activation energy E_a

In nonisothermal kinetics theory, thermal degradation of PBO can be expressed by the following function:

$$\frac{d\alpha}{dt} = Ae^{E_a/RT}f(\alpha) \quad (1)$$

where α is the conversion degree, A is the pre-exponential factor, E_a is the activation energy, R is the general gas constant, and $f(\alpha)$ is the differential expression of a kinetic mechanism function. If β is the constant heating rate: $dT = \beta dt$, the eq. (1) can be deduced as follows:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (2)$$

Furthermore, the integral expression of a kinetic model function $G(\alpha)$ can be derived from eq. (2):

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E_a/RT} dT \quad (3)$$

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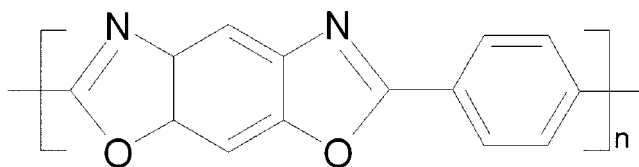


Figure 1 Repeat unit of PBO molecule.

Kissinger method

The activation energy can be calculated by the Kissinger method without precise knowledge of the reaction mechanism using following equation deduced from taking logarithms of the differentiation of eq. (2):¹⁰

$$\ln \frac{\beta}{T_p^2} = \ln \left(\frac{RA}{E_a} \right) - \frac{E_a}{RT_p} \quad (4)$$

where T_p is the temperature of the peak point of the DTG curve, which corresponds to the maximum reaction rate. The activation energy can be determined from the slope obtained by linear regression of the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$.

Flynn-Wall-Ozawa method

The eq. (3) was integrated by the Doyle approximation, and the result taken logarithms:¹¹

$$\lg \beta = \lg \frac{AE_a}{RG(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT} \quad (5)$$

The activation energies for different conversion values can be calculated from the slopes of $\lg \beta$ versus $1/T$ plots. This method is one of the integral methods that can estimate the activation energy without the knowledge of reaction order and mechanism; hence, it has been widely used for validating other methods.

Determination of the most probable mechanism function

Coats-Redfern method

By rearranging eq. (2) and integrating both sides of it,¹² the following equation will be obtained:

$$\ln \left[\frac{G(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \quad (6)$$

The value of E_a and $\ln A$ can be calculated from the slope and intercept of the linear least-square plots of $\ln[G(\alpha)/T^2]$ versus $1/T$ respectively.

Estimation of the most probable mechanism function

By substituting the basic values of α obtained by TG curves, the 41 mechanism functions¹³ and the corresponding values of T are put into eq. (6) respectively.

The kinetic parameters E_a and $\ln A$ will be calculated. Finally, we can determine the most probable mechanism function when the mean value of kinetics parameter above is most similar to the mean value of F-W-O Method.

EXPERIMENTAL

The PBO polymers with high molecular weight used for the study were prepared from 4,6-diaminoresorcinol salts and terephthalic acid in polyphosphoric acid by a solution polycondensation under inert gas. The samples were washed with water in a Soxhlet extractor for 12 h to remove residual polyphosphoric acid and dried in a high vacuum oven before further analysis. The TG/DTG measurements were carried out on a DuPont 1090B Thermalgravimetric Analyzer in dynamic nitrogen environment from 30 to 900°C. Flow rate was fixed at 50 mL/min and the size of purified PBO granule sample was about 10 mg. The kinetics experiments were performed at several heating rates of 5, 10, 15, and 20°C/min respectively.

RESULTS AND DISCUSSION

Thermal degradation of PBO

Figure 2 shows the TG and DTG curves of PBO degradation in nitrogen at different heating rates. And the TG characteristic temperatures of PBO degradation at different heating rates are illustrated in Table I.

The Figure 2 and Table I showed that PBO polymers stabled up 600°C approximately and the characteristic temperatures increased with increase of heating rate, at the end of the degradation almost 65–70% residual remained. The results revealed that PBO polymers had very excellent thermal stability.

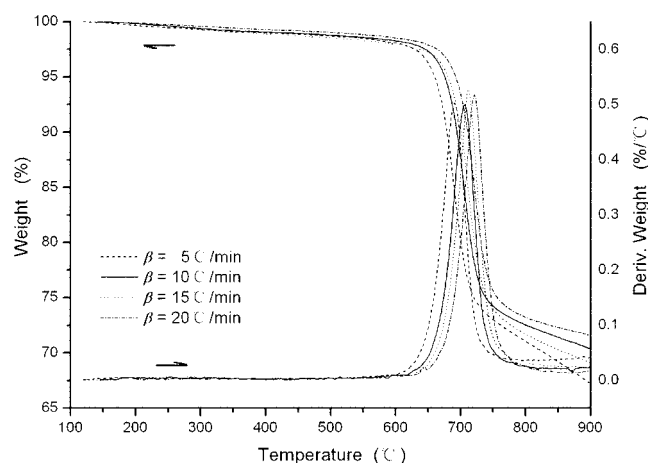


Figure 2 The TG and DTG curves of PBO degradation in nitrogen.

TABLE I
The Characteristic Temperatures of PBO Degradation at Different Heating Rates

β ($^{\circ}\text{C}/\text{min}$)	T_i ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_d , 5% ($^{\circ}\text{C}$)	T_d , 10% ($^{\circ}\text{C}$)
5	596	690	661	679
10	617	706	676	694
15	620	712	681	701
20	628	721	693	711

T_i , onset temperature of TG; T_p , peak temperature of DTG; T_d , decomposition temperature of loss 5% or 10% of the sample weight.

Kinetics of thermal degradation of PBO

Calculation of activation energy E_a

As shown in Figure 3, the Kissinger plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ of PBO degradation fitted linearly. The value of activation energy $E_{a(K)}$ of PBO degradation calculated from the slope, which corresponding to the maximum degradation rate, is 352.19 kJ/mol. The pre-exponential factor $\ln A_{(K)}$ obtained from the intercept is 42.49, and the correlation coefficient R is 0.9945.

By using F-W-O Method, the basic parameters β and the temperature of TG curve corresponding to the difference conversions were introduced into eq. (5), the plots of $\lg \beta$ versus $1/T$ are illustrated in Figure 4. The values of $E_{a(O)}$ of PBO degradation at different conversions are shown in Table II, all correlation coefficients R are more than 0.98. From the table, the highest $E_{a(O)}$ (356.55 kJ/mol) appears at the conversion of 20%, which closes to the value of $E_{a(K)}$, and the mean value of $\bar{E}_{a(O)}$ is 338.32 kJ/mol.

The calculation of F-W-O Method is applicable to all points on the TG curve, and Kissinger Method uses only one point, which is the primary different between these two methods. Comparing values of E_a obtained from the above two methods, a relative error valued 3.9% indicates that it is reasonable to calculate

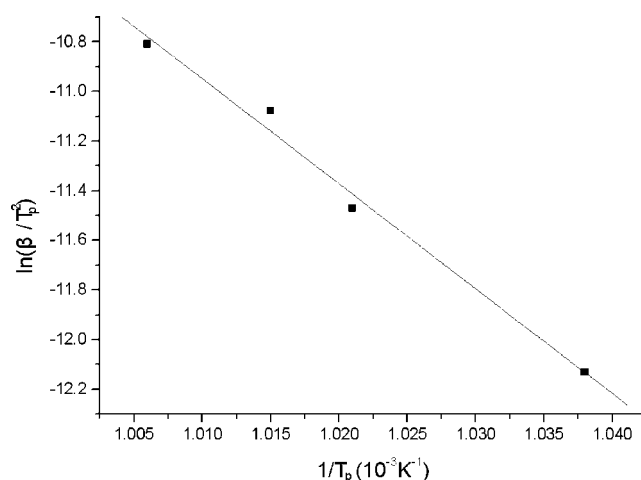


Figure 3 The Kissinger plot of PBO degradation.

activation energy of PBO degradation using these two methods. And it is obviously that the actual values of activation energy are dependent not only on the mathematical measurements used to evaluate the data, but also upon such factors as sample mass, sample size, flow rate, and so on.

Determination of the most probable mechanism function

Combined with 41 types of mechanism functions,¹³ the corresponding values of E_a , $\ln A$, and the correlation coefficient R obtained by Coats-Redfern Method were calculated (Table III), meanwhile the values of $\bar{E}_{a(O)}$ determined by F-W-O Method was used to restrict the results given above. When the kinetic parameters of Coats-Redfern Method was similar to that defined by F-W-O Method, at the same time the correlation coefficient R was better, the most probable mechanism function could be determined.

Comparing with the values of $\bar{E}_{a(O)}$ provided by F-W-O Method, it is obviously that the values of kinetic parameters of Model No. 26 is most similar to the apparent value. Consequently, the most probable mechanism function of PBO degradation follows Mampel Power function, which obeys the models that are random scission of weak bonds of PBO molecule and impact of the active groups obtained from the broken bonds. The integral form of the above mechanism is $G(\alpha) = \alpha^{3/2}$ ($n = 3/2$), and the differential form is $f(\alpha) = \frac{2}{3}\alpha^{-1/2}$. The mechanism of this function means that PBO degradation happens at some parts of the backbone of the PBO chains, and the active groups generate randomly, some of these active groups goes on decomposition or losses activity, others generates new active groups. This conclusion reveals an extraordinary similarity to the report of So et al.,⁶ which showed that there were two path-

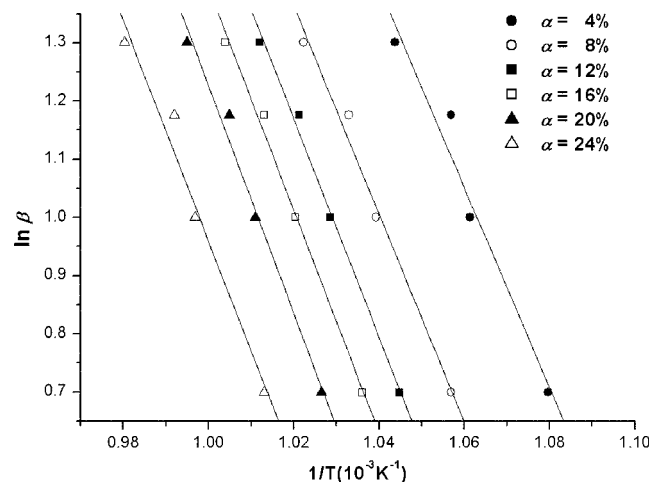


Figure 4 The Flynn-Wall-Ozawa plots of PBO degradation at different conversions.

TABLE II
The Values of E_a of PBO Degradation Obtained from F-W-O Method

α (%)	4	8	12	16	20	24
E_a (kJ/mol)	313.82	325.47	341.68	347.88	356.55	344.49
R	0.9828	0.9934	0.9966	0.9967	0.9929	0.9861

ways for the thermal degradation of PBO polymers. One is the homolytic bond scission to generate a benzoxazole radical and a phenyl radical, and the other is decomposition of a heterocyclic ring to give a nitrile, which generates benzonitrile, dicyanobenzene, and an unstable diradical. Both these two modes are all predicated to the random scission of weak bonds. And then, the follow steps of first pathway are that

TABLE III
The Mean Values of Kinetics Parameters of PBO Degradation

No.	E_a (kJ/mol)	$\ln A$ (A, s^{-1})	R
1	463.42	52.42	0.9883
2	473.34	53.02	0.9889
3	107.49	9.96	0.9866
4	478.49	53	0.9893
5	108.77	9.93	0.987
6	483.6	52.85	0.9896
7	476.76	51.96	0.9892
8	447.15	48.09	0.9873
9	504.49	55.57	0.9907
10	47.59	2.64	0.9832
11	68.85	5.46	0.9858
12	85.85	7.64	0.9869
13	111.36	10.84	0.9878
14	153.87	16.06	0.9887
15	175.12	18.63	0.989
16	238.89	26.29	0.9895
17	366.42	41.41	0.9899
18	493.96	56.4	0.9902
19	749.03	86.2	0.9904
20	1004.09	115.87	0.9905
21	ve	ve	ve
22	43.77	2.07	0.9793
23	63.76	4.73	0.9827
24	103.72	9.79	0.9853
25	223.62	24.27	0.9874
26	343.52	38.41	0.988
27	463.42	52.42	0.9883
28	235	24.39	0.989
29	233.71	24.51	0.9888
30	233.71	25.6	0.9888
31	231.16	24.57	0.9885
32	231.16	25.27	0.9885
33	209.15	23.04	0.9849
34	195.47	21.62	0.9821
35	182.55	20.18	0.9787
36	15.15	ve	0.9244
37	254.95	28.41	0.9912
38	ve	ve	ve
39	ve	ve	ve
40	ve	ve	ve
41	46.48	3.3	0.965

ve means negative.

the benzoxazole radical decomposes to produce aromatic nitrile along with H_2O , CO_2 , and other carbon compounds, and the phenyl radical grafts onto another PBO molecule or abstracts hydrogen to generate phenylbenzobisoxazole, which produces benzonitrile and benzene. And the follow step of second pathway is the decomposition of diradical fragments to produce aromatic nitrile along with H_2O , CO_2 , and other carbon compounds. All these steps are predicated to the impact of the active groups obtained from the broken bonds.

Kinetic compensation effect of the nonisothermal degradation

To investigate the correlation between E_a and $\ln A$, the kinetic compensation effect needs to be advanced as follow:

$$\ln A = aE_a + b \quad (7)$$

where a and b are compensation coefficients. By putting $G(\alpha) = \alpha^{3/2}$ into F-W-O equation [eq. (5)], the plot of $\ln A_{(O)}$ versus $E_{a(O)}$ of F-W-O Method showed in Figure 5 was fitted linearly. The expression of kinetic compensation effect of PBO degradation was provided that $\ln A = 0.1365 E_a - 1.4102$, and the correlation coefficient R is 0.9989. Thus it can be seen that, there is an interdependent and coordinated relationship between $\ln A$ and E_a . On the other hand, because the situations of experiment are effectless to them, the compensation coefficients used to describe the charac-

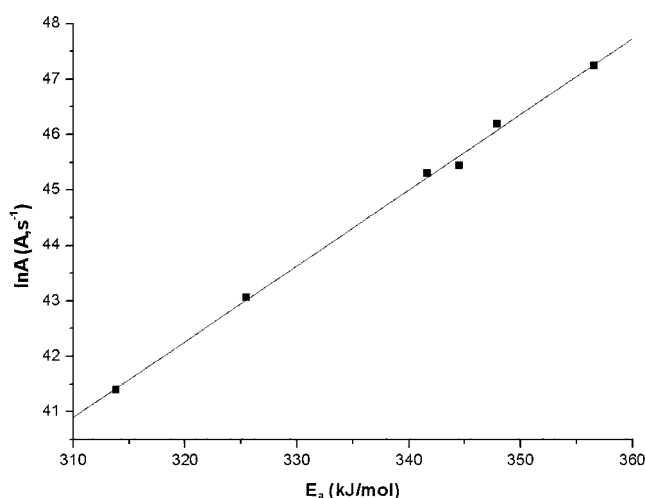


Figure 5 The kinetic compensation effect of PBO degradation.

terization of degradation are more effective on demonstrating the interrelation between the kinetic parameters $\ln A$ and E_a of thermal degradation.

CONCLUSIONS

TG/DTG measurements were used to investigate the kinetics of PBO thermal degradation. The activation energy calculated by Kissinger Method was 352.19 kJ/mol, and the mean value of activation energies evaluated by Flynn-Wall-Ozawa Method was 338.32 kJ/mol. The degradation kinetic model of PBO followed the mechanism of random scission of weak bonds of PBO molecule and impact of the active groups obtained from the broken bonds, Mampel Power equation with integral form $G(\alpha) = \alpha^{3/2}$ and differential form $f(\alpha) = \frac{2}{3}\alpha^{-1/2}$. And the mathematical equation of kinetic compensation effect was $\ln A = 0.1365 E_a - 1.4102$.

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