

# A Kinetic Analysis on Thermal Degradation of Poly(phenylene sulfide ether)

Aiqun Gu, Zili Yu, Yubao Li

*Institute of Materials Science and Technology, Analytic and Testing Center, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China*

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**ABSTRACT:** Thermal degradation of poly(phenylene sulfide ether) (PPSE) was investigated by using thermogravimetry (TG) under air and nitrogen atmosphere. It was found that the existence of oxygen depressed the thermal stability of PPSE and changed the mechanism of thermal degradation. The influences of molecular weight and heating rate on the decomposition of PPSE were also investigated under N<sub>2</sub> atmosphere. The results showed that the thermal stability of PPSE was excellent and can be further enhanced by increasing molecular weight. A simple kinetic model concerning two parallel reactions in overall temperature range was proposed to describe the thermal degra-

ation process of PPSE in nitrogen. Kinetic analysis of the dynamic TG curves for PPSE was carried out by using Kissinger, Flynn–Wall–Ozawa, and Coats–Redfern methods. The kinetics of PPSE degradation displayed that the two parallel reactions were in accordance with the first-order equation. The kinetic model was further validated by comparing the experimental and calculated results. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 911–918, 2009

**Key words:** kinetics (polymer); poly(phenylene sulfide ether); thermal properties; thermogravimetric analysis; reaction mechanism

## INTRODUCTION

Poly(aryl sulfide)s (PASs) and poly(aryl ether)s (PAEs) have found many applications in electronic/electric, aircraft, medical treatment, and aerospace industries due to their excellent properties.<sup>1–5</sup> Nevertheless, under the driving force for developing high-performance materials, many derivative polymers are synthesized to satisfy different demands. Poly-(oxy-1,4-phenylene-thio-1,4-phenylene) (PPSE), a new aromatic thermoplastic polymer, was developed and considered as a substitute for PAS or PAE. In recent years, extensive research has been devoted to the synthesis of high molecular weight PPSE. However, little is known about its thermal stability at elevated temperatures and fundamental data are not available. As we know, the thermal stability of a polymer determines the upper service temperature and/or the environmental conditions. It is reported that the thermal stability is related to kinetic parameters such as the initial degradation temperature and the degrada-

tion rate of a polymer.<sup>6</sup> These kinetic parameters can provide valuable information for both application and storage.<sup>7</sup> Therefore, the determination of kinetic parameters associated with the degradation process is always attractive. On the basis of our previous research concerned with synthesis of high molecular weight PPSE,<sup>8</sup> thermal degradation of PPSE and kinetic analysis were reported in this article.

Nevertheless, the two-step mass loss process of PPSE was observed in the thermogravimetric (TG) experiment. For kinetic study of such multistep reaction, inspection of the literature reveals that the apparent mass loss kinetic models develop into the three following types: (1) pseudo single-component overall model,<sup>9,10</sup> which regards the material as that consisting of a single pseudo component, and uses its solid-gas reaction kinetics during the overall temperature range to describe the material mass loss kinetics. However, the method cannot reflect the possible change with temperature increasing in mass loss kinetics. (2) Pseudo multi-component overall model,<sup>11,12</sup> which treats the material consisting of multiple pseudo components. Each pseudo component in the method represents a single real component or mixture of several real components and the material decomposition is modeled by superposition of the overall decompositions of these components. The method can reveal the kinetic variation to some extent, but optimization computation is used in the method to obtain the kinetic parameters, which

Correspondence to: Z. Yu (ziliyu@scu.edu.cn) or Y. Li (cnic7504@scu.edu.cn).

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makes kinetic study of thermodegradation complicated. Furthermore, there may be infinite sets of parameters able to meet the demand of the error between calculated and experimental data, and thus the obtained parameters are most likely short of kinetic significance. (3) First-order pseudo bi-component separate-step model, considering the material formed by two independent pseudocomponents, which decomposes respectively into two separate temperature regions. The temperature corresponding to the minimum in the derivative thermogravimetric (DTG) curve is regarded as the point of separation between two mass-loss steps.<sup>13</sup> Thus the two-step mass loss process is usually dealt with separately by using various kinetic models. The method is suitable for two main mass losses nearly separate in thermogravimetric study. However, when two DTG peaks are incompletely separated and have widely different peak areas (i.e., widely different  $E$  and  $A$  values), there is a certain interaction with each other that results in untrue value of dynamic parameter associated with the reactions involved.<sup>14</sup>

In the present work, PPSE was examined by non-isothermal means to determine the mass loss kinetics of the thermal decomposition with linear temperature programming in nitrogen atmosphere. The kinetic analysis was carried out by means of differential and integral method, namely Kissinger, Flynn–Wall–Ozawa (FWO), and Coats–Redfern. A kinetic description suitable for PPSE mass loss behavior in nitrogen is proposed and the kinetic parameters obtained from different kinetic methods are compared and discussed. The proposed kinetic model is validated by comparing the experimental parameters with calculated data. The thermal behavior of PPSE in air at a heating rate 10°C/min is also present and compared with that of PPSE in nitrogen.

## MATERIALS AND METHODS

### Materials

PPSE polymers were prepared according to our previous report<sup>8</sup> and five samples with different intrinsic viscosity were used in powdery form. Samples were dried completely under vacuum at 70°C for 24 h before determination.

### TG and DTG measurements

TG analysis was performed on a SDTQ600 thermal analyzer from ambient to 700°C with a heating rate of 10°C/min in air or nitrogen. In the dynamic model, heating rates of 2.5, 5, 10, 20, and 40°C/min were conducted under a nitrogen atmosphere. In all experiments, an air or a nitrogen stream was continuously passed into the furnace at a flow rate of

100 mL/min (at normal temperature and atmospheric pressure). Eight to 11 mg of PPSE was analyzed in each run.

### Theoretical background

The rate of decomposition depends on the temperature and the mass change of sample and can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where  $\alpha$  is the degree of decomposition,  $t$  is the time,  $k(T)$  is the temperature-dependent rate constant,  $f(\alpha)$  is a function depending on the actual reaction mechanism,  $E$  is the apparent activation energy,  $A$  is the pre-exponential factor,  $T$  is the absolute temperature, and  $R$  is the gas constant.  $f(\alpha)$  is proportional to the concentration of nondegraded or unreacted material:

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

When the sample temperature is controlled by a constant heating rate  $\beta$  ( $\beta = dT/dt$ ), eq. (1) can be changed to

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

By mathematical transformation, eq. (3) gives the following integral form:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} P(u) \quad (4)$$

Equations (3) and (4) are the fundamental expressions for calculating kinetic parameters by TG data. A differential and two integral techniques, namely Kissinger, FWO, and Coats–Redfern, are taken into consideration in this study.

### Kissinger method

The dynamic parameter of thermal degradation under linear heating conditions can be determined with an equation derived by Kissinger<sup>15,16</sup>

$$\ln \frac{\beta}{T_{\max}^2} = \left\{ \ln \frac{A_k R}{E_k} \right\} - \frac{E_k}{RT_{\max}} \quad (5)$$

where  $\beta$  is the heating rate, and  $T_{\max}$  is the temperature corresponding to the maximum conversion rate on the TG curve.

The plot of  $\ln(\beta/T_{\max}^2)$  versus  $1000/T_{\max}$  should result in a straight line, and  $E_k$  and  $\lg A_k$  can be calculated from the slope and intercept of the line, respectively.

TABLE I  
Algebraic Expression of  $g(\alpha)$  for the Most Frequently Used Mechanisms  
of Solid-State Reaction

Symbol	$g(\alpha)$	Solid-State Processes
<i>Sigmoidal curves</i>		
A <sub>2</sub>	$[-\ln(1 - \alpha)]^{1/2}$	Nucleation and growth [Avrami eq. (1)]
A <sub>3</sub>	$[-\ln(1 - \alpha)]^{1/3}$	Nucleation and growth [Avrami eq. (2)]
A <sub>4</sub>	$[-\ln(1 - \alpha)]^{1/4}$	Nucleation and growth [Avrami eq. (3)]
<i>Deceleration curves</i>		
R <sub>1</sub>	$\alpha$	Phase boundary controlled reaction (contracting linear)
R <sub>2</sub>	$[1 - (1 - \alpha)^{1/2}]$	Phase boundary controlled reaction (contracting area)
R <sub>3</sub>	$[1 - (1 - \alpha)^{1/3}]$	Phase boundary controlled reaction (contracting volume)
D <sub>1</sub>	$\alpha^2$	One-dimensional diffusion
D <sub>2</sub>	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	Two-dimensional diffusion (Valensi equation)
D <sub>3</sub>	$[1 - (1 - \alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D <sub>4</sub>	$[1 - (2/3)\alpha] - (1 - \alpha)^{2/3}$	Three-dimensional diffusion (Ginstling–Brounshtein equation)
F <sub>1</sub>	$-\ln(1 - \alpha)$	Random nucleation with one nucleus on the individual particle
F <sub>2</sub>	$1/(1 - \alpha)$	Random nucleation with two nuclei on the individual particle
F <sub>3</sub>	$1/(1 - \alpha)^2$	Random nucleation with three nuclei on the individual particle

### FWO method

FWO method,<sup>17,18</sup> a integral method, is based on the following expression:

$$\lg \beta = \lg \frac{AE_0}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E_0}{RT} \quad (6)$$

where  $\beta$ ,  $A$ ,  $E_0$ , and  $T$  have the same meanings as above.

Moreover,  $A$  and  $R$  are constants and for a particular conversion,  $g(\alpha)$  is a constant too.  $E_0$  can be determined from the slope of  $\lg \beta$  versus  $1000/T$  plot at different heating rates without the knowledge of the reaction order.

### Coats–Redfern method

Coats–Redfern technique<sup>19</sup> is based on the following equation for studying thermal degradation kinetics:

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (7)$$

The equation is especially satisfied for a reaction that meets  $f(\alpha) = (1 - \alpha)^n$ , where  $n$  is the order of reaction,

$$n = 1 \quad \ln \left[ -\ln \frac{(1 - \alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT}$$

$$n \neq 1 \quad \ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \left[ \frac{AR}{\beta E} \right] - \frac{E}{RT}$$

According to the different degradation processes, the theoretical function  $g(\alpha)$  is listed in Table I<sup>20</sup> and

$E_c$  and  $\lg A_c$  can be determined from a plot of  $\ln[g(\alpha)/T^2]$  versus  $1000/T$ .

The obtained activation energy and pre-exponential factor are compared respectively with those from FWO and Kissinger methods by following equation:

$$|E_c - E_o|/E_o \leq 0.1, \quad |\lg A_c - \lg A_k|/\lg A_k \leq 0.2 \quad (8)$$

When both  $E_c$  and  $A_c$  obtained are satisfied with eq. (8) and their correlation is close to unity, the corresponding  $g(\alpha)$  is the probable mechanism.

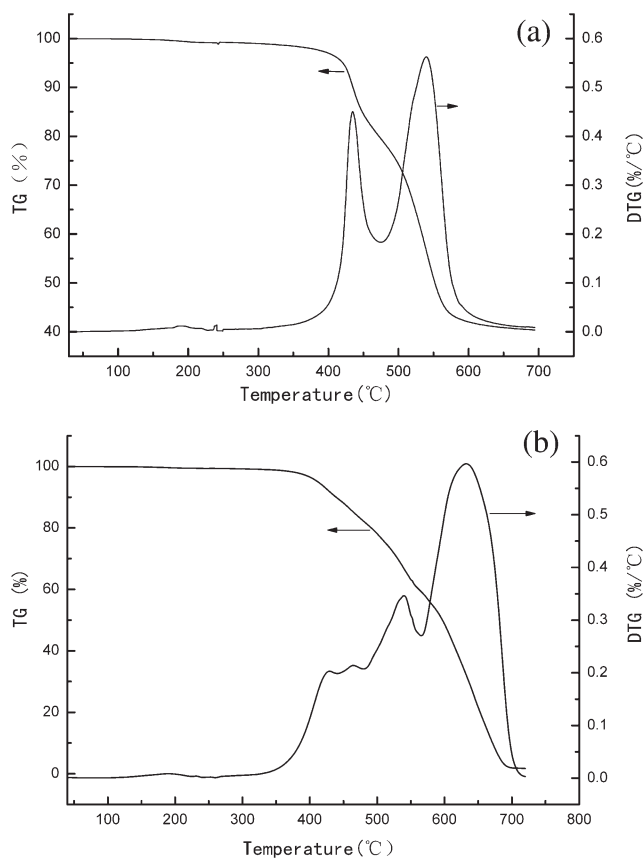
## RESULTS AND DISCUSSION

### Characteristics of PPSE decomposition

The TG and DTG curves of PPSE-4 sample at 10°C/min display multiple degradation steps (Fig. 1). In nitrogen, the degradation of sample shows two consecutive steps with about 40% residue at 700°C. In air, on the other hand, the TG curve of PPSE-4 mainly shows a three-step weight loss and the weight loss is nearly 100% at 700°C. Figure 1 also indicates that PPSE has different decomposition temperatures in nitrogen and air. The initial temperature (5% weight loss) and the  $T_{\max}$  values for the first- and second-step degradation in air shift 23, 5, and 6°C to low temperature, respectively, in comparison with those in nitrogen. The descent of thermal stability in air is caused by the oxidative degradation. Other PPSE samples presented very similar thermal behavior at overall scanning process.

### Thermal decomposition behavior of PPSE with different intrinsic viscosity

Figure 2 shows typical DTG curves of PPSE at varying scanning rates. The weight loss of about 10 and



**Figure 1** (a) TG/DTG curve under  $N_2$  flow of PPSE-4 at  $10^\circ C/min$ . (b) TG/DTG curve under air flow of PPSE-4 at  $10^\circ C/min$ .

50% is observed for the first and second decomposition steps, respectively. This observation implies that PPSE is extremely sensitive to temperature above  $450^\circ C$ . For PPSE with different intrinsic viscosities, the detailed data from TGA and DTG curves [i.e., the temperature corresponding to initial 5% weight loss ( $T_{5\%}$ ), the temperatures of maximum weight loss rate ( $T_{m1}$  for the first decomposition step and  $T_{m2}$  for the second decomposition step), the corresponding weight loss ( $\alpha_1$ ) for the first step decomposition and the residue at  $700^\circ C$ ], are given in Table II. The results indicate that  $T_{5\%}$ ,  $T_{m1}$  of polymers shifts to higher temperature with the increase of intrinsic viscosity. Thus the thermal stability of PPSE can be enhanced by increasing molecular weight. The conclusion will be further addressed in the following activation energy-related discussion. However,  $T_{m2}$ , the second degradation step of polymers, displays similar value and trends to a constant with increasing heating rate. At  $40^\circ C/min$ ,  $T_{m2}$  of all PPSE samples is the same ( $578.70^\circ C$ ). The phenomena may be attributed to recombination of PPSE fragments with temperature increasing.

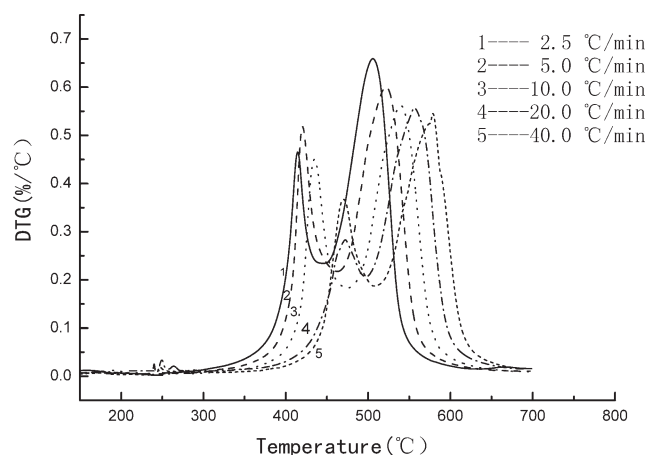
### Effect of heating rate

In dynamic thermogravimetry, the heating rate is a crucial factor affecting the shape of thermogram and characteristic temperature of decomposition.<sup>21</sup> The TG curves of PPSE-4 in nitrogen at the heating rates of 2.5, 5, 10, 20, and  $40^\circ C/min$  are illustrated in Figure 3. The results shows that the decomposition curves shift to higher temperature direction with the increase of heating rate. In other words, the whole characteristic temperature ( $T_{5\%}$ ,  $T_{m1}$ , and  $T_{m2}$ ) shifts to higher value with the increase of heating rate, as indicated in Table II and Figure 3. These phenomena are attributed to the temperature retardancy. The other specimens also behave in a similar trend, although the intrinsic viscosities are different.

However, for all samples the weight loss corresponding to each step or the final residue at  $700^\circ C$  is roughly independent of the heating rate, as indicated by the data in Table II.

### Kinetic model of the mass loss process

As discussed previously, the decomposition occurring in PPSE is a two-step process and the whole process shows two overlapping peaks in the DTG curves. This means that the fundamental reaction mechanism is dependent on temperature. According to the supposition, PPSE is decomposed via two parallel reactions into gas and nondegradable solid. Because both reactions, termed 1 and 2, occur with very different rate at the same time, the individual profiles of simulated conversion appear shifted. The reactions 1 and 2 affect the conversion fraction  $\alpha_1$  and  $\alpha_2$  of the raw PPSE resin, respectively. The remaining fraction  $\alpha_3$ , namely  $\alpha_3 = 1 - \alpha_1 - \alpha_2$ , characterizes the nondegradable residue. The whole expression of the thermal degradation reaction is given as follows:



**Figure 2** DTG curves of PPSE-4 in nitrogen at various heating rate.

TABLE II  
Intrinsic Viscosity and Dynamic TG Data of PPSE at Varying Heating Rates

Heating rate	Polymer	$\eta$ (dL/g)	$T_{5\%}$ (°C)	$T_{m1}$ (°C)	% <sub>1</sub>	$T_{m2}$ (°C)	Residue (wt %)
2.5°C/min	PPSE-1	0.15	336.76	357.73	8.95	495.40	31.60
	PPSE-2	0.23	372.30	398.14	10.16	498.74	33.23
	PPSE-3	0.38	387.20	406.27	9.57	505.59	36.39
	PPSE-4	0.47	390.72	410.50	10.01	506.17	36.77
	PPSE-5	0.55	402.35	416.65	8.16	508.79	37.51
5°C/min	PPSE-1	0.15	354.50	366.40	7.41	520.60	33.42
	PPSE-2	0.23	389.20	411.93	9.18	520.81	35.67
	PPSE-3	0.38	399.83	417.34	9.07	521.59	39.11
	PPSE-4	0.47	404.84	420.47	10.21	521.64	36.26
	PPSE-5	0.55	415.93	428.49	8.38	522.53	38.90
10°C/min	PPSE-1	0.15	368.62	382.53	7.65	534.12	40.22
	PPSE-2	0.23	406.30	430.87	10.06	535.01	38.90
	PPSE-3	0.38	415.79	433.58	8.88	540.36	41.77
	PPSE-4	0.47	420.70	434.81	9.84	540.36	40.41
	PPSE-5	0.55	427.60	444.07	9.18	540.80	39.07
20°C/min	PPSE-1	0.15	380.90	399.69	7.65	558.07	42.67
	PPSE-2	0.23	422.60	444.27	9.92	558.15	45.39
	PPSE-3	0.38	425.73	447.35	8.47	558.20	39.09
	PPSE-4	0.47	432.05	450.20	7.18	558.78	40.78
	PPSE-5	0.55	442.54	454.35	7.40	559.09	43.09
40°C/min	PPSE-1	0.15	403.48	421.15	7.87	578.70	44.32
	PPSE-2	0.23	448.62	467.74	7.74	578.70	45.39
	PPSE-3	0.38	447.74	467.90	8.97	578.70	43.72
	PPSE-4	0.47	451.19	470.51	10.47	578.70	41.61
	PPSE-5	0.55	463.92	476.35	7.24	578.70	43.18

$$\frac{d\alpha}{dT} = A_1 f(\alpha_1) \exp\left(-\frac{E_1}{RT}\right) + A_2 f(\alpha_2) \exp\left(-\frac{E_2}{RT}\right) \quad (9)$$

where  $A_1$  and  $A_2$  are the frequency factors, and  $E_1$  and  $E_2$  are the activation energies associated with each reaction.

### The decomposition activation energy

According to eq. (5), the activation energy of degradation for the first and second steps was calculated and the results are shown in Figure 4 and Table III.

The activation energy was also determined by using the method of Flynn-Wall-Ozawa represented by eq. (6). Based on the hypothesis that the thermodegradation of PPSE follows two parallel reactions, the conversion values of 0.05, 0.07, 0.09, 0.11, and 0.13 are applied in computation for the first decomposition step. Similarly, the conversion values of 0.25, 0.28, 0.30, 0.32, 0.34, and 0.36 are adopted for the second degradation step. FWO plot of PPSE-4 on various conversions is shown in Figure 5 as an example. These isoconversional plots display that the straight lines are nearly parallel, indicating the applicability of this method to PPSE degradation in the chosen conversion range. Furthermore, the fact also suggests that a single reaction mechanism is operative.<sup>20,22</sup> The activation energies corresponding to the different conversions for PPSE with different intrinsic viscosities are shown in Figure 6. The

results display that the activation energy of PPSE increases greatly with increasing intrinsic viscosity. This means that the decomposition reaction is more difficult to proceed when molecular weight of PPSE increases. By average values at different conversions, the activation energy of PPSE-1, -2, -3, -4, and -5 were obtained and listed in Table III. In comparison with the activation energies from Kissinger's, the FWO method gives a similar value for the first step decomposition; however, the lower value is for the second step decomposition.

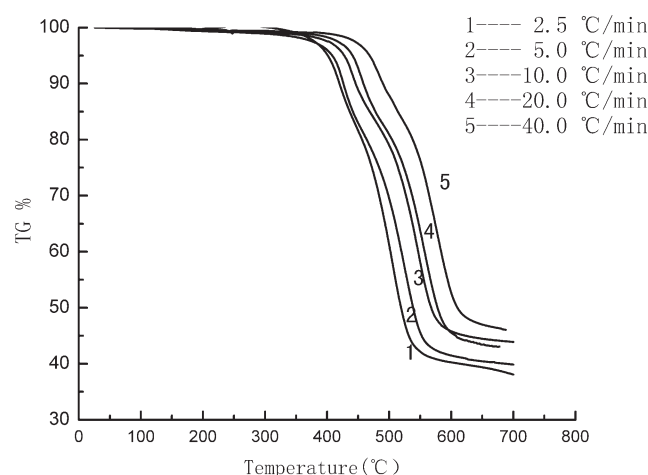
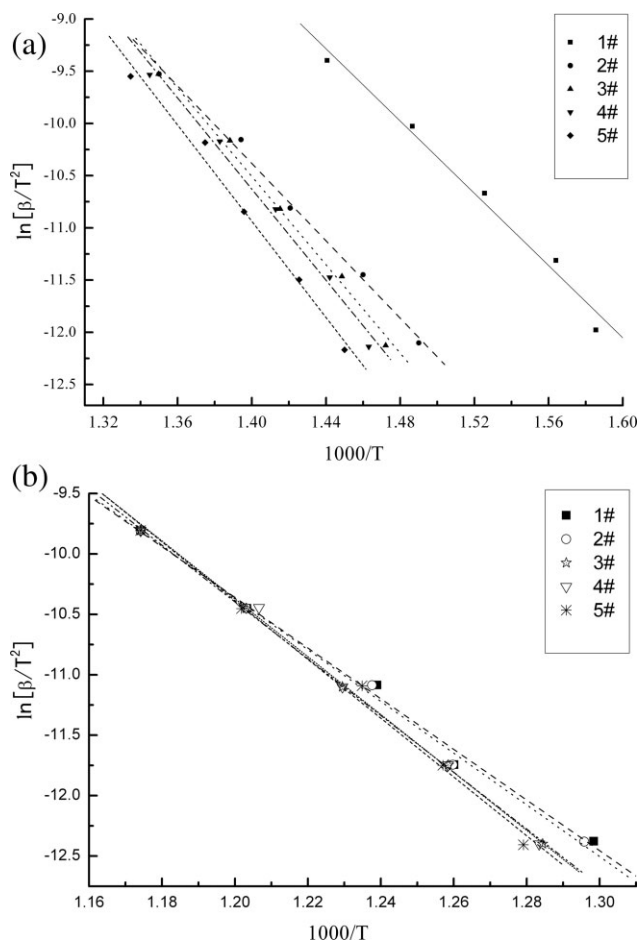


Figure 3 TG curves of PPSE-4 obtained at several heating rates.



**Figure 4** (a) Plots of  $\ln(\beta/T^2)$  against  $1000/T$  for first decomposition of PPSE with various intrinsic viscosity. (b) Plots of  $\ln(\beta/T^2)$  against  $1000/T$  for second decomposition of PPSE with various intrinsic viscosity.

### Determination of kinetic model and pre-exponential factor

From eq. (7) proposed by Coats–Redfern, the activation energy for every  $g(\alpha)$  function listed in Table I can be obtained at constant heating rates by plots of  $\ln[g(\alpha)/T^2]$  versus  $1000/T$ . For this study, the same

conversion values are used as those used in the FWO method. The thermal degradation mechanism of PPSE-4 is illustrated at a constant heating rate of  $10^\circ\text{C}/\text{min}$ . Table IV shows the activation energies,  $\lg A_c$ , and correlation for conversions in the range of 0.05 to 0.13 and 0.25 to 0.36.

From Table IV, the activation energy and pre-exponential factor in PPSE degradation for the first and second step are all coincided with eq. (8), corresponding to  $R_n$  or F1 mechanism. Although the correlations of mechanisms  $R_n$  are better, mechanism F1 is the probable thermodegradation kinetic mechanism of PPSE because the correlation coefficient of F1 for the first and second steps is closer to unity.

### Mathematical verification of kinetic model

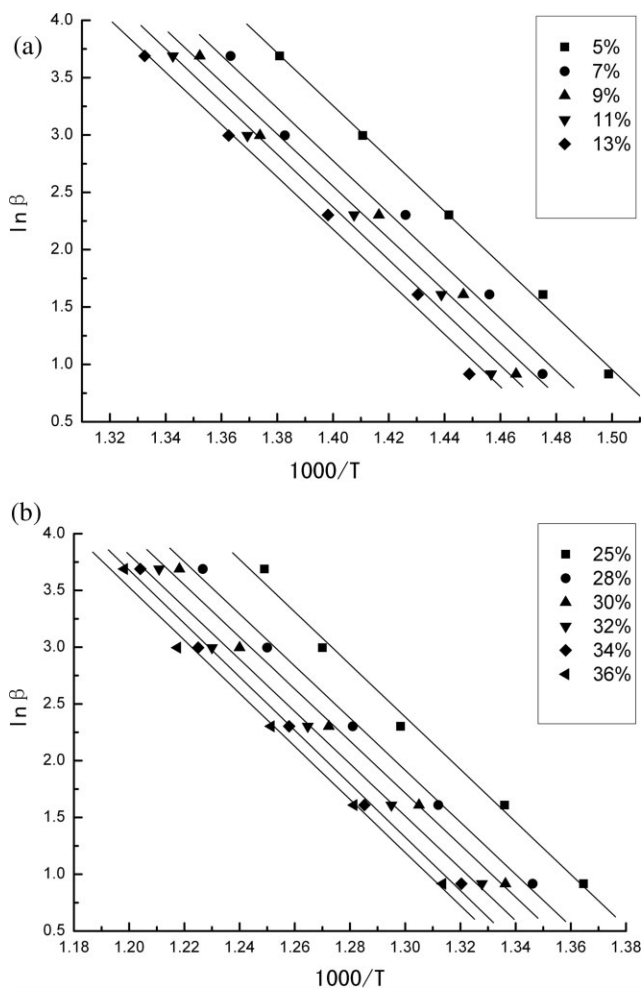
To verify the proposed model and test the validity of the kinetic parameters experimentally, both TG and DTG curves from experimental and theoretical calculation should be compared. With this idea in mind, the obtained apparent kinetic parameters were first substituted into eq. (4) to obtain the calculated TG curves in overall thermodegradation temperature range. The calculated TG curve was then substituted into eq. (3) and led to the calculated DTG curve. The precision of the fit to the experimental TGA curve was evaluated from an objective function (OF), defined as follows by the mean relative error on the unreacted fraction  $x$ ,  $N$  being the number of data in any experiment.

$$OF = \frac{1}{N} \sum_N \frac{|\chi - \chi_{\text{calc}}|}{\chi_{\text{exp}}}$$

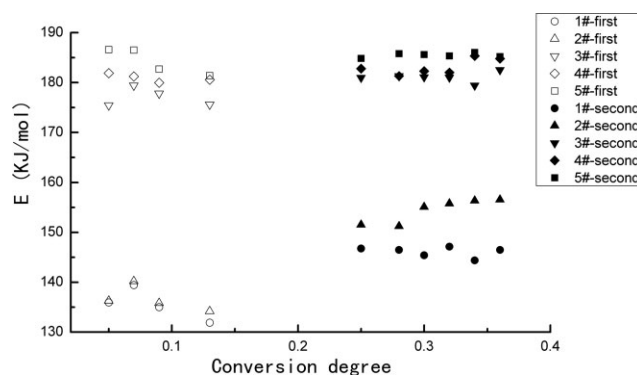
As can be observed in Figure 7, there is good agreement between the experimental and calculated TG and DTG curves. The value for TG and DTG is found to be 2.05 and 0.53%, respectively. Furthermore, Figure 7(c) shows the individual contributions of the two decomposition steps to the total

**TABLE III**  
Kinetic Parameters for Two-Step Mass Loss of PPSE by the Kissinger and FWO Equation Under  $\text{N}_2$

Polymer	Kissinger Method						FWO Method	
	First Step Mass Loss			Second Step Mass Loss			$E_{o1}$ (kJ/mol)	$E_{o2}$ (kJ/mol)
	$E_{k1}$ (kJ/mol)	$\lg A_{k1}$ ( $\text{min}^{-1}$ )	$R_1$	$E_{k2}$ (kJ/mol)	$\lg A_{k2}$ ( $\text{min}^{-1}$ )	$R_2$		
1	143.79	10.84	0.9918	174.24	10.74	0.9968	134.56	146.10
2	154.04	11.86	0.9969	177.93	10.98	0.9978	136.49	154.40
3	175.86	12.62	0.9965	195.24	12.10	0.9998	176.35	181.26
4	181.28	12.82	0.9943	199.03	12.35	0.9986	180.82	183.01
5	191.48	13.62	0.9940	202.23	12.55	0.9961	183.35	185.32



**Figure 5** (a) Heating rate versus the reciprocal absolute temperature for the first step decomposition of PPSE-4. (b) Heating rate versus the reciprocal absolute temperature for the second step decomposition of PPSE-4.



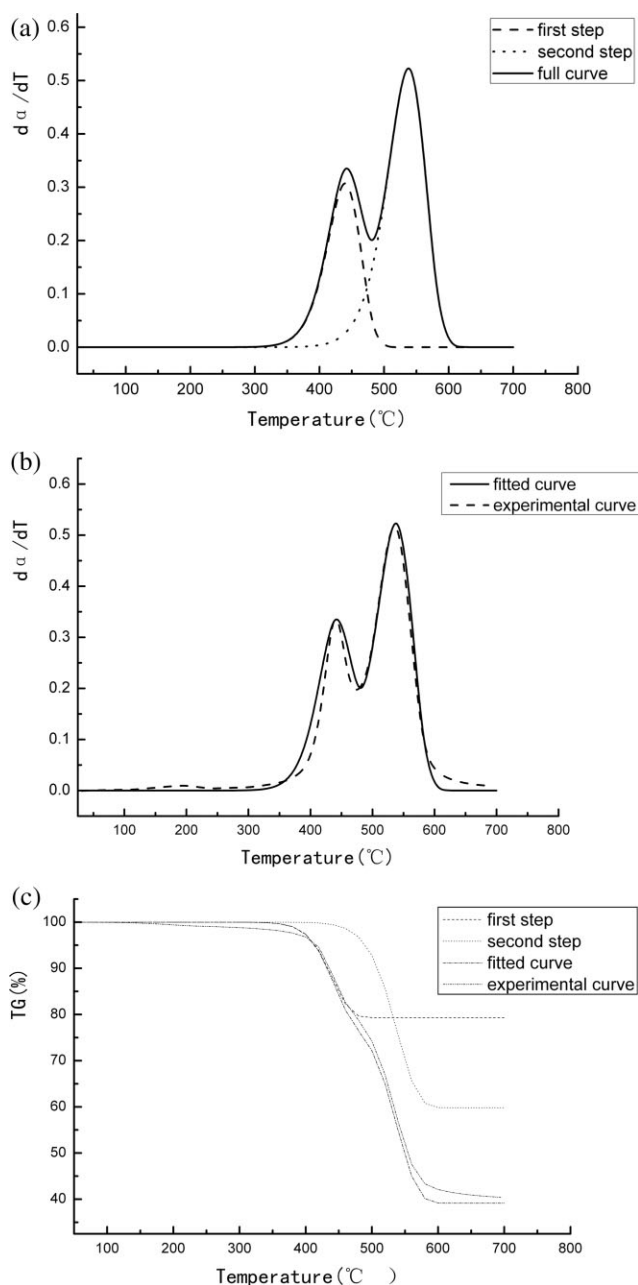
**Figure 6** Activation energies of PPSE with various intrinsic viscosities corresponding to the first and second step mass loss of PPSE.

conversion. Conversion degree ( $\alpha_1$  and  $\alpha_2$ ) of the first and second decomposition step of PPSE-4 increases with temperature, and the value of  $\alpha_2$  becomes significant when the first decomposition step is close to end. For example, as shown in Figure 7(c),  $\alpha_2 = 2.5\%$  when  $\alpha_1 = 90\%$  at  $460^\circ\text{C}$ . These results indicate that the two mass loss steps do not overlap very much. As a good approximation, the decomposition of PPSE in an inert atmosphere can be also modeled as the reaction of each step following independent process. Comparison between experimental and fitted curve for PPSE-4 at 20 and  $40^\circ\text{C}/\text{min}$  is also discussed and shows better agreement (OF < 2.6%). The results show that the kinetic model consisting of two parallel reactions is suitable to describe the mass loss behaviors of PPSE and the mechanism F1 is the most appropriate.

**TABLE IV**  
The Activation Energies and lgA for Different Mechanism

Mechanism	$E_{c1}$ (kJ/mol)	1 <sup>a</sup>	$\lg A_{c1}$ ( $\text{min}^{-1}$ )	2 <sup>b</sup>	R1	$E_{c2}$ (kJ/mol)	3 <sup>c</sup>	$\lg A_{c2}$ ( $\text{min}^{-1}$ )	4 <sup>d</sup>	R2
A <sub>2</sub>	93.62	0.48	5.885	0.54	0.9978	93.40	0.49	4.973	0.60	0.9983
A <sub>3</sub>	58.52	0.68	3.215	0.75	0.9975	128.90	0.30	8.308	0.33	0.9984
A <sub>4</sub>	40.97	0.77	1.828	0.85	0.9972	40.16	0.78	1.315	0.89	0.9976
R <sub>1</sub>	175.24	0.03	11.54	0.10	0.9964	188.49	0.030	11.08	0.10	0.9978
R <sub>2</sub>	179.42	0.007	11.50	0.10	0.9965	194.13	0.061	11.18	0.095	0.9982
R <sub>3</sub>	183.82	0.017	12.76	0.005	0.9952	196.03	0.071	11.14	0.098	0.9983
D <sub>1</sub>	362.20	1.00	24.63	0.92	0.9985	390.07	1.13	18.19	0.47	0.9980
D <sub>2</sub>	367.72	1.03	24.76	0.93	0.9986	397.50	1.17	18.40	0.49	0.9982
D <sub>3</sub>	373.36	1.06	24.54	0.91	0.9986	405.14	1.21	18.27	0.48	0.9984
D <sub>4</sub>	369.60	1.04	24.25	0.89	0.9986	400.05	1.19	17.92	0.45	0.9983
F <sub>1</sub>	182.01	0.006	12.19	0.05	0.9972	199.16	0.088	11.93	0.03	0.9985
F <sub>2</sub>	5.39	0.97	9.068	0.29	0.9240	10.17	0.94	9.155	0.26	0.9459
F <sub>3</sub>	-	-	-	-	No	-	-	-	-	No

<sup>a</sup>  $|E_{c1} - E_{o1}|/E_{o1}$ .  
<sup>b</sup>  $|\lg A_{c1} - \lg A_{k1}|/\lg A_{k1}$ .  
<sup>c</sup>  $|E_{c2} - E_{o2}|/E_{o2}$ .  
<sup>d</sup>  $|\lg A_{c2} - \lg A_{k2}|/\lg A_{k2}$ .



**Figure 7** Experimental and fitted TG/DTG curves for PPSE-4 at 10°C/min.

## CONCLUSIONS

The dynamic thermal decomposition of PPSE was investigated under various conditions. The TG analysis displays that weight loss of PPSE is a two-step process in nitrogen and a three-step process in air. At 700°C, the weight residue of PPSE is found to be approximately 40% in nitrogen and 0% in air. Initial 5% weight loss ( $T_{5\%}$ ) and the peak decomposition temperature ( $T_{\max,1}$ ) increase with the increase in molecular weight and heating rate. Based on the results of the decomposition activation energy, we conclude that the thermal stability of PPSE is excel-

lent and can be improved further by increasing molecular weight. By comparing activation energy and pre-exponential factor from Coats–Redfern method with those from FWO and Kissinger method, the thermal degradation mechanism of PPSE is postulated in nitrogen. A simple kinetic model consisting of two parallel reactions is suitable to describe the mass loss behavior of PPSE. With the kinetic model, the model function of first order gives the best fits to the experimental data compared with other model function. Furthermore, the validity of the model function of first order (F1) is also verified by comparison with fitting curves and experimental curves. These results suggest the possibility that the F1 (first order) reflects the real mechanism. Therefore, the mass loss process of PPSE is considered to be modeled by the kinetic model, as described by the following expression:

$$\frac{d\alpha}{dT} = (1 - \alpha) \left[ A_1 \exp\left(-\frac{E_1}{RT}\right) + A_2 \exp\left(-\frac{E_2}{RT}\right) \right]$$

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