American Journal of Analytical Chemistry, **2013, 4, 749-755**
Published Online December 2013 (http://www.scirp.org/journal/ajac)
http://dx.doi.org/10.4236/ajac.2013.412091

Thermal Stability and Decomposition Kinetics of Polysuccinimide

Li Zhang, Mingxing Huang, Cairong Zhou
[1]School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou, China
Email: zhanglizibo@163.com, zhoucairong@zzu.edu.cn

Received November 5, 2013; revised December 1, 2013; accepted December 9, 2013

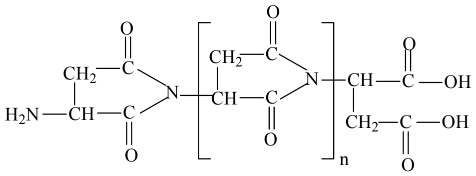
ABSTRACT

The thermal stability and decomposition kinetics of polysuccinimide (PSI) were investigated using analyzer DTG-60 under high purity nitrogen atmosphere at different heating rates (3, 6, 9, 12 K/min). The thermal decomposition mechanism of PSI was determined by Coats-Redfern method. The kinetic parameters such as activation energy (E), pre-exponential factor (A) and reaction order (n) were calculated by Flynn-Wall-Ozawa and Kissinger methods. The results show that the thermal decomposition of PSI under nitrogen atmosphere mainly occurs in the temperature range of 619.15 - 693.15 K, the reaction order (n) was $\frac{3}{4}$, the activation energy (E) and pre-exponential factor (A) were obtained to be 106.585 kJ/mol and $4.644 \times 10^9\ \text{min}^{-1}$, the integral and differential forms of the thermal decomposition mechanism of PSI were found to be $\left[-\ln\left(1-\alpha\right)\right]^{3/4}$ and $\frac{4}{3}\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right]^{1/4}$, respectively. The results play an important role in understanding the thermodynamic properties of polysuccinimide.

Keywords: Polysuccinimide; Thermal Gravimetric Analysis; Thermal Stability; Decomposition Kinetics

1. Introduction

Polyaspartic acid (PASP, CAS181828-06-8) has amino and carboxyl groups, which belongs to the biological macromolecule material and is a kind of polymer of amino acids. Since it has the characteristics of good biocompatibility and biodegradability, PASP has been widely used in industrial and medical fields as a new type of green chemicals [1]. Polysuccinimide (PSI, CAS6899-03-2) is the intermediate of PASP. The experimental formula and relative molecular mass of its monomer are $C_4H_3O_2N$ and 97.074 g/mol, respectively. The chemical structure of the monomer can be written as:



In view of this, PSI is a kind of linear polyimide with high activity and it is easy to open ring changing into poly asparagine with side chains. With the special property, many kinds of derivatives that were used as drug carriers have been prepared [2].

The thermal stability and decomposition kinetics of Polysuccinimide (PSI) were investigated by TG-DTA method. Kinetic parameters such as activation energy (E) and pre-exponential factor (A) were calculated by Flynn-Wall-Ozawa (F-W-O) and Kissinger methods. The kinetic mechanism function of thermal decomposition of PSI was established by Coats-Redfern method. Using TG-DTA method to study the stability of drugs has the advantages of less sample dose, short experimental period and reliable results. These data not only play an active role in understanding the thermodynamic properties of PSI but also provide a theoretical basis for practical application.

2. Experimental

2.1. Materials and Instruments

Polysuccinimide (the mass fraction was higher than 99.5%) was purchased from Henan Xinlianxin Fertilizer Limited

Co. α-Al_2O_3 (standard material, Shimadu Company in Japan) was used as standard material in the process of thermal analysis.

The TG-DTA analyzer (type DTG-60, Shimadzu Corporation, Japan) was used to determine the TG-DTA curves of the sample. SPN-500-type nitrogen generator (Hewleet-Packard, Beijing Institute of Technology, China) was used to provide a high purity nitrogen atmosphere for the experimental system of thermal analysis. Fourier Transform Infrared Spectrometer (type WQF, Beijing Beifen-Ruili Analytical Instrument (Group) Co, Ltd) was used to analyze PSI. Gel permeation chromatography (type Agilent1100, Agilent Corporation, America) was used to analyze PSI's purity and the number-average molecular weight (M_n) and polydispesity index (M_w/M_n).

2.2. Experiment Methods

The PSI sample was dried in the vacuum oven at 378.15 K before analysis. The thermogravimetric measurements were carried out at different heating rates (3, 6, 9, 12 K/min) from room temperature to 873.15 K under high purity nitrogen atmosphere (20 ml/min). Mass of each powdered sample was about 4 - 5 mg.

2.3. Characterization of PSI

2.3.1. FTIR Analysis of PSI

FTIR spectra of PSI were recorded in the wave number range of 4000 - 500 cm^{-1}. The result is shown in **Figure 1**. From **Figure 1**, we can know that the carboxyl group of branched chain in the opened ring appears at 1400 cm^{-1}, the carbon-carbon bond appears at 1165 cm^{-1}, the coupled carbonyl group appears at 1720 cm^{-1} and the carbonyl group in the ring obviously appears at 1797 cm^{-1}.

2.3.2. Gel Permeation Chromatography Analysis of PSI

The analysis diagram of PSI by gel permeation chromatography is shown in **Figure 2**. The analysis results show that the number-average molecular weight (M_n) of PSI is 2.7941×10^4 g/mol, the polydispersity index of relative molecular mass (M_w/M_n) of PSI is 21.644 and Polymerization degree of PSI is obtained to be 287.5.

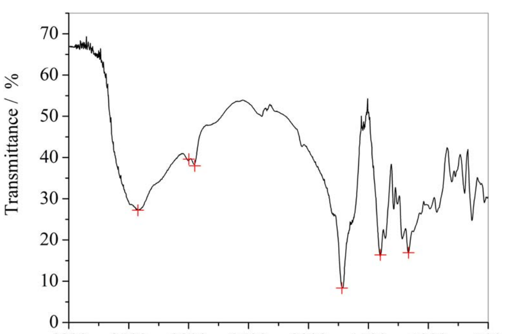


Figure 1. FTIR spectra of PSI.

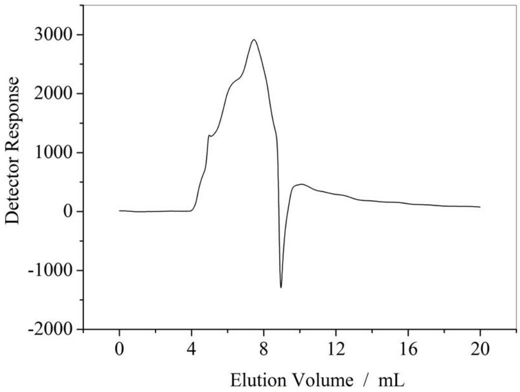


Figure 2. The analysis diagram of PSI by gel permeation chromatography.

2.4. Theoretical Analysis

There are two major categories to study the thermal decomposition kinetics of polymer, which are differential method and integral method. The differential method contains Kissinger [3-5], Caroll-Freeman [6] and Friedman [7] methods while Coats-Redfern [8-12], Doyle [13] and Flynn-Wall-Ozawa (F-W-O) [14-16] methods belong to the integral method. Coats-Redfern, Flynn-Wall-Ozawa (F-W-O) and Doyle methods are usually used for investigating thermal decomposition kinetics of polymers.

In general, the thermal decomposition of a solid polymer under inert atmosphere can be summarized as: $B_{\text{solid}} \rightarrow C_{\text{solid}} + D_{\text{gas}}$. Polymer is finally decomposed into solid residue (C) and gaseous matter (D).

The kinetic analysis of solid-state sample is usually given by Equation (1) [17]

$$r = \frac{d\alpha}{dt} = K(T) f(\alpha) \qquad (1)$$

where $\frac{d\alpha}{dt}$ is the rates of conversion; α is the conversion degree that can be defined as $\alpha = \frac{m_o - m_t}{m_o - m_f}$ in which m_0 and m_f are the initial and final masses of the sample, respectively; m_t is the mass of the sample at time t (or temperature T) of the decomposition process, mg. In Equation (1), $k(T)$ is the temperature dependent rates constant and is normally assumed to obey the Arrhenius equation:

$$k(T) = A e^{-\frac{E}{RT}} \qquad (2)$$

where A is the pre-exponential factor (min^{-1}), E is the activation energy (kJ/mol) of the kinetic process, R is the gas constant (8.314 J/(mol·K)) and T is the absolute temperature (K).

Moreover, taking into account the heating rates $\beta = \mathrm{d}T/\mathrm{d}t$ under non-isothermal condition, $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ can be described by Equation (3):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) = \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{3}$$

Equation (4) can be obtained by combing Equations (1)-(3), which describes the thermal decomposition kinetics. Based on TGA data, the kinetic parameters can be calculated from Equation (4). [18]:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{A}{\beta}\mathrm{e}^{-\frac{E}{RT}} f(\alpha) \tag{4}$$

2.4.1. Kissinger Method

The formula of Kissinger method is given by Equation (5) [3-5]:

$$\ln\frac{\beta_i}{T_{pi}^2} = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{R}\frac{1}{T_{pi}} \tag{5}$$

where i = 1, 2, 3, 4 (or even more); T_{pi} is the peak temperatures of different DTA curve at different heating rates. By plotting $\ln\left(\beta_i / T_{pi}^2\right)$ versus $1/T_{pi}$, the activation energy E_k and pre-exponential factor A_k can be calculated based on its slope ($-E_k/R$) and intercept $\ln(A_kR/E_k)$, respectively.

2.4.2. Flynn-Wall-Ozawa (F-W-O) Method

F-W-O method can be used directly to calculate the activation energy E. The integral formula of F-W-O method [14-16] is showed in Equation (6):

$$\lg\beta = \lg\left(\frac{AE}{Rg(\alpha)}\right) - 2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{6}$$

In Equation (6), since the value of $\lg\left(AE/\left(Rg(\alpha)\right)\right)$ is approximately constant when the values of α are the same at the different heating rates β_i, so it is easy to obtain values of E by plotting $\lg\beta$ against $1/T$ at the certain conversion degree α.

2.4.3. Coats-Redfern Method

Coats-Redfern method can be described as Equation (7). [8-10,12]:

$$\ln\frac{g(\alpha)}{T_i^2} = \ln\frac{A_c R}{\beta_i E} - \frac{E_c}{RT_i} \tag{7}$$

where $g(\alpha)$ comes from one of 34 forms of integral formula in the literature which are shown in **Table 1** [11]. From Equation (7), the values of both E_c and A_c can be obtained for any selected $g(\alpha)$ and fixed β_i (i = 1, 2, 3, 4, even more). The calculating steps in detail are: 1) choose the same α_j for each heating rates β_i and calculate the corresponding $g(\alpha_{ij})$; 2) give the corresponding temperature T_{ij} according to α_{ij}; 3) describe the sketch of $\ln\frac{g(\alpha)}{T_i^2}$ versus $1/T_i$ for each fixed β_i, and calculate the values of both E_c and $\ln(A_c)$ according to the slope and intercept of the line, respectively; 4) determine the mechanism function of the thermal decomposition process. Generally, the selected mechanism functions should meet all the conditions, which are: 1) $0 < E_c < 400$ kJ/mol; 2) $\left|\left(E_0 - E_c\right)/E_0\right| \le 0.3$ where E_0 come from F-W-O method 3) $\left|\left(\ln A_c - \ln A_k\right)/\ln A_c\right| \le 0.3$ in which $\ln(A_k)$ are obtained from Kissinger method. If $g(\alpha)$ meet the requirements mentioned above, $g(\alpha)$ can be regarded as the probable mechanism function for the thermal decomposition process.

2.5. Determination of High Temperature Heat-Resistance of PSI

The activation energy data obtained by above-mentioned methods can be used to evaluate the high temperature heat-resistance of PSI. The relationship between activa-

Table 1. 34 types of thermal decomposition mechanism functions.

N_O	$g(\alpha)$	N_O	$g(\alpha)$
1 - 6	$\alpha^n \quad n = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, 1, 2, \frac{3}{2}$	27	$(1-\alpha)^{-1} - 1$
7	$\alpha + (1-\alpha)\ln(1-\alpha)$	28	$(1-\alpha)^{-1/2}$
8	$\left(1 - \frac{2}{3}\alpha\right) - (1-\alpha)^{3/2}$	29	$(1-\alpha)^{-2}$
9 - 19	$\left[-\ln(1-\alpha)\right]^n \quad n = \frac{1}{2}, \frac{1}{4}, \frac{1}{3}, \frac{2}{5}, \frac{2}{3}, \frac{3}{4}, 1, \frac{3}{2}, 2, 3, 4$	30 - 31	$\left[1-(1-\alpha)^{1/2}\right]^n \quad n = \frac{1}{2}, 2$
20 - 25	$1-(1-\alpha)^n \quad n = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, 2, 3, 4$	32 - 33	$\left[1-(1-\alpha)^{1/3}\right]^n \quad n = \frac{1}{2}, 2$
26	$(1-\alpha)^{-1}$	34	$\left[(1+\alpha)^{1/3} - 1\right]^2$

tion energy and lifetime of polymer can be expressed by Equation (8) [19]:

$$\ln t_f = \frac{E}{RT_f} + \ln\frac{E}{\beta R}\cdot P\left(\frac{E}{RT_\alpha}\right) \qquad (8)$$

where t_f is the lifetime of PSI at the temperature of T_f, T_α is the temperature at the conversion degree α. Combined Equations (4) and (8), T_f can be shown as:

$$T_f = \frac{ER^{-1}}{\ln\left(\frac{At_f}{\left|\ln\left(1-\alpha\right)\right|}\right)} \qquad (9)$$

3. Results and Discussion

3.1. Thermal Decomposition of PSI

TG and DTA curves of PSI sample are shown in **Figures 3** and **4**. The thermal analysis data are summarized in **Table 2**. In **Figure 3**, the thermal decomposition temperature at different heating rates increases with the increasing of β. That indicates the decomposition temperature is affected by the heating rate β. Besides, each TG curve of PSI under nitrogen atmosphere has an obvious mass loss process where percentage of mass loss increases gradually with the increasing of heating rates and TG curve moves toward to the right.

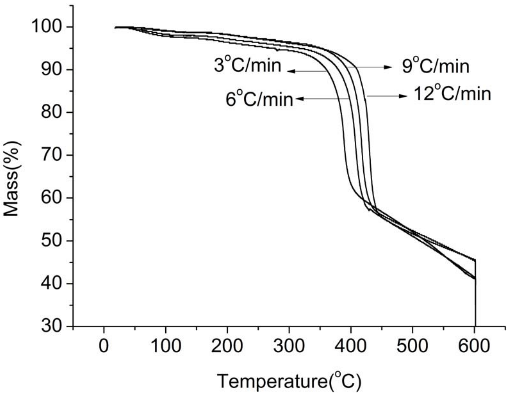


Figure 3. The TG curves of PSI in nitrogen atmosphere.

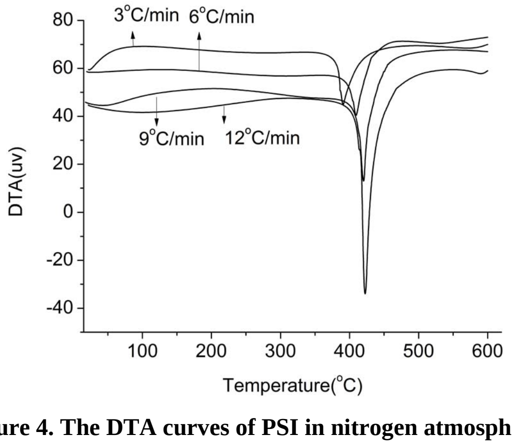


Figure 4. The DTA curves of PSI in nitrogen atmosphere.

Table 2. Basic data of kinetics of PSI from TG.

β/(K·min^{-1})	T_p/K	$(1/T_p)$/K^{-1}	FWO $\ln\beta$	Kissinger $\ln\left(\beta/T_p^2\right)$
3	663.94	0.001516	1.099	−11.898
6	682.76	0.001473	1.792	−11.261
9	693.17	0.001451	2.197	−10.885
12	696.97	0.001444	2.485	−10.609

From **Figures 3** and **4**, the thermal decomposition of PSI under nitrogen atmosphere mainly occurs in the temperature range of 619.15 to 693.15 K. Mass loss is accompanied by heat absorption, so thermal decomposition process and solid rearrangement reaction may simultaneously happen in this process.

3.2. Non-Isothermal Kinetic of PSI

Plots of $\ln\frac{\beta}{T_p^2}$ against $1/T_p$ of PSI by Kissinger method is shown in **Figure 5**. The values of activation energy E_k and exponential factor $\ln(A_k)$ calculated by Kissinger method are 143.874 kJ/mol and 23.897 min^{-1}, respectively. The linear correlation coefficient (R^2) is 0.9852.

The activation energies calculated at different conversion degree using Flynn-Wall-Ozawa method are shown in **Table 3** and the relationship between E_0 and conversion degree α are showed in **Figure 6**.

The results show that the correlation coefficients (R^2) of FWO method is better, the values of activation energy is between 81.509 and 122.205 kJ/mol and increase with the increasing of conversion degree. From **Table 3** and **Figure 6**, the average value of activation energy E_o is 104.202 kJ/mol and the pre-exponential factor $\lg A_o$ is 9.967.

The kinetic parameters calculated by Coats-Redfern method are listed in **Table 4**. The values of activation energy and exponential factor calculated by Coats-Redfern method compare respectively with the average value of activation energy calculated using FWO method and the value of pre-exponential factor obtained by Kissinger method, the results are listed in **Table 5**.

The thermal decomposition process of PSI in the temperature stage of 619.15 to 693.15 K is consistent with the sequence number 14 in **Table 1**, this is because E_c and $\ln(A_c)$ meet better with the conditions of both $\left|\left(E_0 - E_c\right)/E_0\right| \le 0.3$ and $\left|\left(\ln A_c - \ln A_k\right)/\ln A_c\right| \le 0.3$ than others; besides, the relative coefficients (R^2) are much better. The integral and differential forms of the mechanism function are $g\left(\alpha\right) = \left[-\ln\left(1-\alpha\right)\right]^{3/4}$ and $f\left(\alpha\right) = \frac{4}{3}\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right]^{1/4}$, respectively. The values of E_c and $\ln(A_c)$ are obtained to be 108.967 kJ/mol and 16.802 min^{-1}. So the activation energy and pre-exponential factor of thermal decomposition process of PSI can be regarded as 106.585 kJ/mol and 4.644×10^9 min^{-1} (*i.e.* average values obtained by the Coats-Redfern and FWO methods). The thermal decomposition kinetic equation of PSI can be described as:

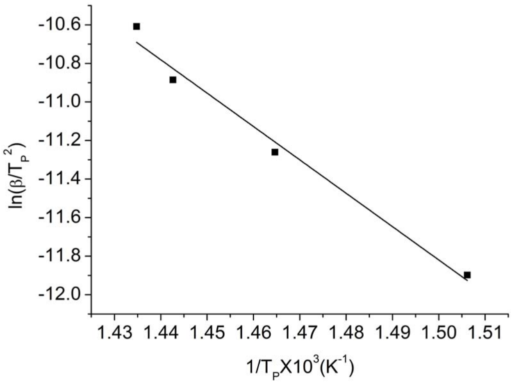


Figure 5. Plots of $\ln\frac{\beta}{T_p^2}$ and $1/T_p$ of PSI of Kissinger method.

Table 3. The activation energy E_o and exponential factor $\lg A_o$ of PSI.

α	E_o(kJ/mol)	$\lg A_o$(min^{-1})	R^2
0.15	81.509	8.134	0.9853
0.20	95.987	9.285	0.9895
0.25	106.373	10.131	0.9885
0.30	114.936	10.839	0.9902
0.35	122.205	11.447	0.9912
Mean*	104.202	9.967	0.9889

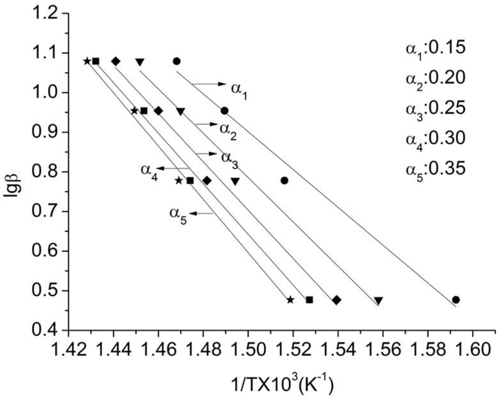


Figure 6. FWO curves of PSI at different conversion.

Table 4. Results of 34 types of kinetic equations of PSI calculated with Coats-Redfern method.

	β = 3 K/min			β = 6 K/min			β = 9 K/min			β = 12 K/min		
No	E_c/(kJ·mol^{-1})	$\ln A_c$	R^2	E_c/(kJ·mol^{-1})	$\ln A_c$	R^2	E_c/(kJ·mol^{-1})	$\ln A_c$	R^2	E_c/(kJ·mol^{-1})	$\ln A_c$	R^2
1	12.759	−2.491	0.926	25.349	0.969	0.948	26.880	1.676	0.951	31.494	2.782	0.969
2	20.575	−0.678	0.948	37.511	3.417	0.957	39.043	4.106	0.959	45.789	5.520	0.976
3	36.204	2.558	0.961	61.836	8.030	0.964	63.367	8.703	0.965	74.378	10.733	0.982
4	83.094	11.400	0.970	134.812	21.146	0.970	136.341	21.806	0.970	160.144	25.684	0.986
5	176.872	28.178	0.973	280.755	46.555	0.972	282.285	47.209	0.972	331.679	54.781	0.987
6	129.981	19.859	0.972	207.783	33.917	0.971	209.313	34.573	0.971	245.912	40.298	0.987
7	185.510	29.230	0.971	294.174	48.401	0.970	295.704	49.054	0.970	347.600	56.992	0.986
8	71.090	8.701	0.977	116.155	17.352	0.977	117.685	18.013	0.977	138.012	21.381	0.990
9	43.011	4.068	0.954	72.413	10.150	0.957	73.945	10.820	0.958	86.931	13.140	0.976
10	16.162	−1.586	0.922	30.638	2.140	0.941	32.169	2.837	0.944	37.771	4.089	0.964
11	25.112	0.413	0.941	44.563	4.898	0.950	46.094	5.581	0.952	54.157	7.189	0.971
12	32.272	1.911	0.948	55.703	7.028	0.954	57.234	7.704	0.955	67.267	9.597	0.974
13	60.910	7.532	0.959	100.267	15.243	0.960	101.797	15.907	0.960	119.705	18.940	0.979
14	69.859	9.227	0.960	114.193	17.756	0.961	115.723	18.418	0.961	136.092	21.807	0.979
15	96.708	14.227	0.963	155.962	25.218	0.962	157.492	25.876	0.963	185.253	30.333	0.981
16	150.400	24.018	0.965	239.518	39.948	0.964	241.048	40.603	0.964	283.574	47.195	0.982
17	204.100	33.672	0.966	323.065	54.547	0.965	324.595	55.201	0.965	381.895	63.929	0.983
18	311.492	52.793	0.967	490.168	83.565	0.966	491.698	84.218	0.966	578.538	97.216	0.983
19	418.884	71.787	0.968	657.272	112.460	0.966	658.801	113.111	0.966	775.181	130.378	0.983
20	93.175	12.110	0.965	150.483	22.778	0.964	152.013	23.437	0.965	178.743	27.744	0.982
21	92.019	12.158	0.965	148.679	22.720	0.965	150.209	23.379	0.965	176.606	27.637	0.983
22	89.733	12.089	0.966	145.129	22.442	0.966	146.659	23.101	0.966	172.383	27.261	0.983
23	70.820	9.515	0.977	115.731	18.140	0.977	117.261	18.802	0.977	137.522	22.161	0.990
24	59.848	7.583	0.983	98.679	15.209	0.983	100.209	15.873	0.983	117.319	18.771	0.994
25	50.119	5.764	0.989	83.547	12.505	0.989	85.077	13.172	0.990	99.419	15.665	0.997
26	17.893	−0.548	0.787	33.271	3.307	0.833	34.802	4.001	0.843	41.333	5.412	0.876
27	111.674	17.306	0.956	179.217	29.666	0.955	180.746	30.323	0.956	212.872	35.419	0.976
28	3.604	−4.956	0.378	11.067	−1.911	0.689	12.597	−1.133	0.735	14.972	−0.329	0.761
29	46.471	6.017	0.861	77.680	12.390	0.871	79.211	13.059	0.875	94.056	15.685	0.908
30	39.523	2.951	0.957	66.993	8.721	0.961	68.525	9.392	0.961	80.498	11.564	0.979
31	190.149	29.474	0.970	301.391	49.070	0.968	302.921	49.724	0.969	356.163	57.858	0.985
32	40.667	3.002	0.956	68.771	8.874	0.959	70.302	9.545	0.960	82.608	11.765	0.978
33	194.722	29.587	0.969	308.499	49.601	0.967	310.029	50.256	0.967	364.602	58.585	0.984
34	164.725	23.498	0.975	261.874	40.758	0.974	263.404	41.414	0.974	309.331	48.480	0.989

Table 5. Calculation of 6 types of kinetics equations for PSI with Coats-Redfern method.

Sequence number of mechanism function $g(\alpha)$	β K/mol	E_c kJ/mol	$\ln A_c$ min^{-1}	R^2	$\left\lvert\frac{E_o - E_c}{E_o}\right\rvert$	$\left\lvert\frac{\ln A_c - \ln A_k}{\ln A_k}\right\rvert$
4	3	83.094	11.400	0.970	0.203	0.523
4	6	134.812	21.146	0.970	0.294	0.115
4	9	136.341	21.806	0.970	0.308	0.088
4	12	160.144	25.684	0.986	0.537	0.075
8	3	71.090	8.701	0.977	0.318	0.636
8	6	116.155	17.352	0.977	0.115	0.274
8	9	117.685	18.013	0.977	0.129	0.246
8	12	138.012	21.381	0.990	0.324	0.105
13	3	60.91	7.532	0.959	0.415	0.685
13	6	100.267	15.243	0.960	0.038	0.362
13	9	101.797	15.907	0.960	0.023	0.334
13	12	119.705	18.940	0.979	0.149	0.207
14	3	69.859	9.227	0.960	0.330	0.614
14	6	114.193	17.756	0.961	0.096	0.257
14	9	115.723	18.418	0.961	0.111	0.229
14	12	136.092	21.807	0.979	0.306	0.087
23	3	70.82	9.515	0.977	0.320	0.602
23	6	115.731	18.140	0.977	0.111	0.241
23	9	117.261	18.802	0.977	0.125	0.213
23	12	137.522	22.161	0.990	0.320	0.073
24	3	59.848	7.583	0.983	0.426	0.683
24	6	98.679	15.209	0.983	0.053	0.364
24	9	100.209	15.873	0.983	0.038	0.336
24	12	117.319	18.771	0.994	0.126	0.215

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 4.644\times10^{9}\,\mathrm{e}^{-106.585\times10^{3}/RT}\left(1-\alpha\right)^{3/4} \qquad (10)$$

3.3. High Temperature Heat-Resistance of PSI

Selecting $t_f = 60$ s and $\alpha = 15\%$ as the evaluation indexes of the high temperature heat-resistance of the polymer. According to Equation (12), value of T_f of PSI in nitrogen atmosphere is 259.27°C. The result shows that the high temperature heat-resistance of PSI is not very well.

4. Conclusion

The thermal behavior of polysuccinimide under non-isothermal condition was investigated using TG-DTA method at different heating rates in nitrogen atmosphere. The results show that the thermal decomposition of PSI under nitrogen atmosphere mainly occurs in the temperature range of 619.15 - 693.15 K, the reaction order (n) was 3/4, the activation energy (E) and pre-exponential factor (A) were obtained to be 106.585 kJ/mol and 4.644 × 10^9 min^{-1}, the integral and differential forms of the thermal decomposition mechanism of PSI were found to be $\left[-\ln\left(1-\alpha\right)\right]^{3/4}$ and $\frac{4}{3}\left(1-\alpha\right)\left[-\ln\left(1-\alpha\right)\right]^{1/4}$, respectively.

REFERENCES

[1] A. W. Yang, G. P. Cao and M. H. Zhang, "Synthesis of Polysuccinimide and Determination of the Intrinsic Viscosity," *Polymer Materials Science & Engineering*, Vol. 26, 2010, pp. 4-7.

[2] J. H. Jeong, H. S. Kang, S. R. Yang and J. D. Kim, "Polymer Micelle-Like Aggregates of Novel Amphiphilic Biodegradable Poly(Asparagine) Grafted with Poly(Caprolactone)," *Polymer*, Vol. 44, No. 3, 2003, pp. 583-591. http://dx.doi.org/10.1016/S0032-3861(02)00816-9

[3] A. Rotaru, M. Anca, G. Popa, P. Rotaru and E. Segal, "Non-Isothermal Kinetics of 2-Allyl-4-((4-(4-Methylbenzyloxy)Phenyl) Diazenyl) Phenol in Air Flow," *Journal of Thermal Analysis and Calorimetry*, Vol. 97, No. 2, 2009, pp. 485-491. http://dx.doi.org/10.1007/s10973-009-0214-1

[4] H. E. Kissinger, "Variation of Peak Temperature with Heating Rate in Different Rate in Differential Thermal Analysis," *Journal of Research of the National Bureau of Standards*, Vol. 57, No. 4, 1956, pp. 217-221. http://dx.doi.org/10.6028/jres.057.026

[5] H. E. Kissinger, "Reaction Kinetic in Differential Thermal Analysis," *Analytical Chemistry*, Vol. 29, No. 11, 1957, pp. 1702-1706. http://dx.doi.org/10.1021/ac60131a045

[6] E. S. Freeman and B. Carroll, "The Application of Thermoanalytical Technique to Reaction Kinetics," *Journal of Physical Chemistry*, Vol. 3, 1958, pp. 394-397.

[7] H. L. Friedman, "Kinetics and Gaseous Products of Thermal Decomposition of Polymers," *Journal of Macromolecular Science: Part A—Chemistry*, Vol. 1, No. 1, 1967, pp. 57-59. http://dx.doi.org/10.1080/10601326708053917

[8] A. W. Coats and J. P. Redfern, "Kinetic Parameters from Thermogravimetric Data," *Nature*, Vol. 201, 1964, pp. 68-69. http://dx.doi.org/10.1038/201068a0

[9] C. R. Zhou, Q. H. Li and H. F. Wang, "Thermal Analysis for the Thermal Decomposition of Methylsulfonate Tin," *Journal of Chemical Engineering of Chinese Universities*, Vol. 20, 2006, pp. 669-672.

[10] C. R. Zhou, X. H. Shi, H. F. Wang and D. G. Jiang, "Thermal Decomposition and the Non-Isothermal Decomposition Kinetics of DL-2-Naproxen," *Journal of Chemical Engineering of Chinese Universities*, Vol. 25, 2011, pp. 442-446.

[11] L. G. Lu, Q. Zhang, X. N. Xu, X. L. Dong and D. W. Wang, "Thermal Degradation Kinetics of Novel Intumescent Flame Retardant Polypropylene," *China Plastics*, Vol. 23, 2009, pp. 53-60.

[12] C. Y. Ou, C. H. Zhang, S. D. Li, L. Yang and J. J. Dong, "Thermal Degradation Kinetics of Chitosan-Cobalt Complex as Studied by Thermogravimetric Analysis," *Carbohydrate Polymers*, Vol. 82, No. 4, 2010, pp. 1284-1289. http://dx.doi.org/10.1016/j.carbpol.2010.07.010

[13] C. D. Doyle, "Kinetic Analysis of Thermogravimetric Data," *Journal of Applied Polymer Science*, Vol. 5, No. 15, 1961, pp. 285-292. http://dx.doi.org/10.1002/app.1961.070051506

[14] T. Ozawa, "Kinetic Analysis of Derivative Curves in Thermal Analysis," *Journal of Thermal Analysis*, Vol. 2, No. 3, 1970, pp. 301-310. http://dx.doi.org/10.1007/BF01911411

[15] F. X. Chen, C. R. Zhou and G. P. Li, "Study on Thermal Decomposition and the Non-Isothermal Decomposition Kinetics of Glyphosate," *Journal of Thermal Analysis and Calorimetry*, Vol. 109, No. 3, 2012, pp. 1457-1462.

[16] Q. F. Wang, L. Wang, X. W. Zhang and Z. T. Mi, "Thermal Stability and Kinetic of Decomposition of Nitrated HTPB," *Journal of Hazardous Materials*, Vol. 172, No. 2-3, 2009, pp. 1659-1664. http://dx.doi.org/10.1016/j.jhazmat.2009.08.040

[17] C. D. Gamlin, N. K. Dutta, N. R. Choudhury, D. Kehoe and J. Matisons, "Evaluation of Kinetic Parameters of Thermal and Oxidative Decomposition of Base Oils by Conventional, Isothermal and Modulated TGA, and Pressure DSC," *Thermochimica Acta*, Vol. 392-393, 2002, pp. 357-369. http://dx.doi.org/10.1016/S0040-6031(02)00121-1

[18] X. Y. Li, Y. Q. Wu, D. H. Gu and F. X. Gan, "Thermal Decomposition Kinetics of Nickel(II) and Cobalt(II) Azo Barbituric Acid Complexes," *Thermochimica Acta*, Vol. 493, No. 1-2, 2009, pp. 85-89. http://dx.doi.org/10.1016/j.tca.2009.04.010

[19] Z. W. Zhou and Q. X. Wu, "Studies on Thermal Properties of Poly(Phenylene Sulfide Amide)," *Journal of Applied Polymer Science*, Vol. 66, No. 7, 1997, pp. 1227-1230. http://dx.doi.org/10.1002/(SICI)1097-4628(19971114)66:7<1227::AID-APP2>3.0.CO;2-I