

A study on the kinetics of thermal decomposition of polyaniline

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Abstract

The kinetic analysis of the thermogravimetric curves for the thermal decomposition processes of polyaniline in undoped and doped state (udpan and dpan) was performed. Various forms of non-isothermal methods of analysis for determining the kinetic parameters were used. The results show that the apparent activation energies for both udpan and dpan in static air are 126.5 and 78.5 kJ mol⁻¹, and those in N₂ are 45.2 and 36.6 kJ mol⁻¹, respectively. The mean reaction orders obtained from integral method for udpan and dpan in static air are 2.1 and 2.0, and those in N₂ are 1.9 and 2.1, respectively. Therefore the reaction function $f(x) = (1 - x)^2$ for the thermal decomposition of both udpan and dpan is reasonable. The thermal decomposition processes for udpan and dpan in N₂ may be a random degradation of polymer chain, whereas in air it should be an oxidation degradation involving the participation of oxygen. Thus the maximum of reaction rate in nitrogen is only 20–26% of those in air and the apparent activation energies for them are only 1/2–1/3 of those in air. But the temperatures corresponding to the maximum reaction rate are higher by about 230–320 K than those in air. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polyaniline; Thermal decomposition; Kinetics

1. Introduction

Polyaniline, as one of the most promising conducting polymers, has attracted much attention for many years due to its excellent environmental stability, good conductivity at room temperature and other potential applications in electronic and microelectronic industries. A lot of literatures have reported its preparation methods and doping mechanism and conductivity property [1]. Few concerns have been made on its thermal stability [2], especially on its kinetics of thermal decomposition in different atmospheres. In the present work, a kinetic study of thermal decomposition process of undoped and doped polyaniline was made both in air and in nitrogen. The activation

energies and reaction order are presented accordingly and their most probable decomposition mechanisms are proposed.

2. Experimental

Polyaniline was chemically synthesized according to the literature method [3], and then changed to intrinsical polyaniline (labeled as udpan), whose viscosity average molecular weight was measured in concentrated sulfuric acid as 11 300 by Ubbelohde viscometer. The doped polyaniline (labeled as dpan) was obtained by treatment of udpan with 1 mol dm⁻³ hydrochloric acid. All the samples used were dried under vacuum at 353.2 K for 24 h before measurement.

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Non-isothermal thermogravimetric experiments were performed using a self-made spiral quartz spring thermogravimetric balance under both in static air and in commercial N₂ at a flow rate of 45 dm³ min⁻¹. All the samples studied were in powder form.

3. Theoretical analysis

A commonly used form for thermal decomposition of a solid can be expressed as Eq. (1):

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

where n is the reaction order and α is the reaction extent of sample at a certain time, which is defined by $\alpha = (w_0 - w)/(w_0 - w_r)$, in which w_0 , w_r and w are the weights of the sample before reaction, after reaction and at $t = t_r$, respectively. At a certain heating rate $\beta = dT/dt$, we have

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

Eq. (2) can be treated with three methods as follows:

1. *Differential method for sample at a single heating rate:*

$$\ln\left[\frac{d\alpha/dt}{(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \quad (3)$$

Plotting $\ln[(d\alpha/dt)/(1-\alpha)^n]$ vs $1/T$ at different n , we can obtain the activation energy E and preexponential factor A from the slope and the intercept of the regression line, respectively.

2. *Integral method for sample at a single heating rate:*

From Eq. (2), we have

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \quad (4)$$

Assume $x = -E/RT$, $p(x) = \exp(x)x^{-2}(1 - 2!/x + 3!/x^2 - 4!/x^3 + \dots)$.

When $E/RT \geq 20$, integrate Eq. (4) and take the first approximation of $p(x)$, thus

$$\int_0^{\alpha_m} \frac{d\alpha}{(1-\alpha)^n} = \left(\frac{ART_m^2}{\beta E}\right) \exp\left(\frac{-E}{RT_m}\right) \quad (5)$$

where α_m and T_m are the corresponding reaction extent and temperature at the maximum reaction rate, respectively.

At the maximum reaction rate, $d^2\alpha/dT^2 = 0$, that is $d(d\alpha/dT)/dT = d[(A/\beta) \exp(-E/RT)(1-\alpha)^n]/dT$, we get

$$E = \frac{nRT_m^2[(A/\beta) \exp(-E/RT_m)(1-\alpha_m)^n]}{(1-\alpha_m)} = \frac{nRT_m^2(d\alpha/dt)_m}{(1-\alpha_m)} \quad (6)$$

$$\frac{1}{n(1-\alpha_m)^{n-1}} = \left(\frac{ART_m^2}{\beta E}\right) \exp\left(\frac{-E}{RT_m}\right) \quad (7)$$

Comparing Eq. (5) with Eq. (7), we have

$$\int_0^{\alpha_m} \frac{d\alpha}{(1-\alpha)^n} = \frac{1}{n(1-\alpha_m)^{n-1}} \quad (8)$$

Integrating Eq. (8), we obtain

$$1 - \alpha_m = \frac{1}{e} \quad (\text{when } n = 1),$$

$$1 - \alpha_m = n^{1/(1-n)} \quad (\text{when } n \neq 1) \quad (9)$$

To a given sample, therefore, the reaction order and activation energy can be derived from Eqs. (9) and (6) when we get α_m , T_m and $(d\alpha/dt)_m$ from the thermogravimetric curve (TG) and differential thermogravimetric curve (DTG).

3. *Integral method for sample at multi-heating rates:*

Ozawa [4] proposed that

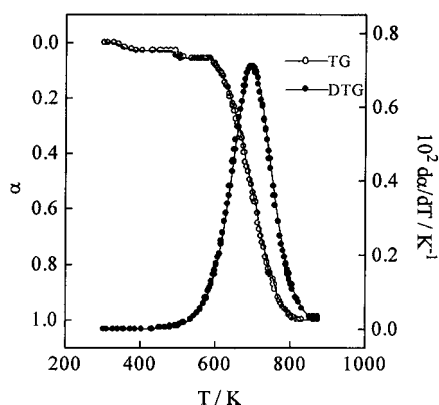
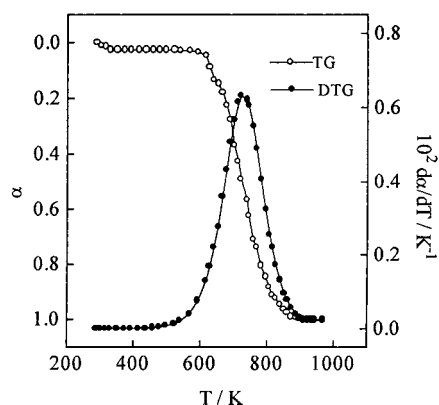
$$\ln[(1-\alpha_i)^n] = \ln\left(\frac{AE}{R}\right) - \ln \beta_i - 5.33 - \frac{1.05E}{RT_i} \quad (10)$$

To a certain α_i , we have a series of T_i values from different TG curves at different heating rates β_i , thus Eq. (10) changes to

$$\ln \beta_i = \text{constant} - \frac{1.05E}{RT_i} \quad (11)$$

where $E = (\text{slope}) \times R/1.05$.

This simplified form can be widely used in the study of kinetics of thermal degradation of polymers if the reaction function $f(\alpha) = (1-\alpha)^n$ has nothing to do with the thermal history of the sample.

Fig. 1. TG and DTG curves for udpan at 3.8 K min⁻¹.Fig. 3. TG and DTG curves for udpan at 7.7 K min⁻¹.

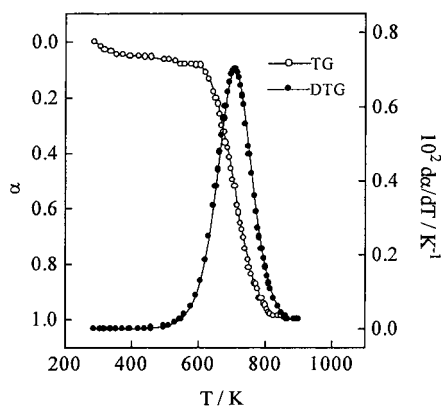
4. Results and discussion

4.1. TG and DTG curves for udpan in static air

In static air, the TG and DTG curves for udpan were obtained at 3.8, 5.7, 7.7 and 11.8 K min⁻¹, respectively (Figs. 1–4).

4.1.1. The integral method for a single heating rate

Table 1 gives the results of udpan using integral method at a single heating rate. From Table 1, we calculate the mean activation energy E to be 123.7 kJ mol⁻¹ and the mean reaction order $n = 2.1$. We find that the results at the different heating rates are almost the same, indicating that the simplified integral method is reasonable for the given sample under conditions studied.

Fig. 2. TG and DTG curves for udpan at 5.7 K min⁻¹.

4.1.2. The differential method for a single heating rate

At a certain heating rate, plotting the straight-line of $\ln[(d\alpha/dt)/(1-\alpha)^n]$ vs $1/T$ at different n based on Eq. (3), we can obtain

$$E = (\text{slope}) \times R \text{ and } A = \exp(\text{intercept}).$$

Table 2 gives the results of udpan using differential method at a single heating rate.

The mean activation energy is $E = 116.4$ kJ mol⁻¹ which is in good agreement with the results obtained by the integral method, indicating that the reaction function $f(\alpha) = (1-\alpha)^2$ is reasonable and F₂ mechanism is the most probable one for the thermal decomposition of udpan in static air.

4.1.3. Ozawa method for udpan at multi-heating rates

Taking $\alpha = 0.3, 0.4, 0.5, 0.6$ and 0.7 and plotting $\ln \beta_i$ vs $1/T_i$, we get a group of paralleled lines (Fig. 5).

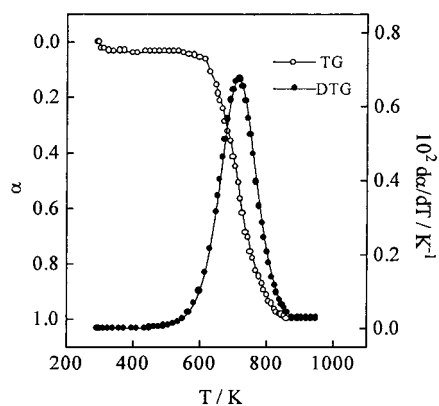
Fig. 4. TG and DTG curves for udpan at 11.8 K min⁻¹.

Table 1
The results of udpan using integral method at a single heating rate

β (K min ⁻¹)	3.8	5.7	7.7	11.8
T_m (K)	696.7	709.2	714.7	722.7
α_m	0.5164	0.5209	0.5100	0.4929
$10^2(d\alpha/dT)_m$	0.7170	0.7000	0.6767	0.6320
n	2.18	2.23	2.11	1.93
E (kJ mol ⁻¹)	130.4	136.2	123.7	104.4

The activation energy can be obtained from the slope of the regression line: $E = 17609.24 \times R/1.05 = 139.4$ kJ mol⁻¹.

Therefore the mean activation energy for udpan in static air is 126.5 kJ mol⁻¹ by the three methods.

4.2. TG and DTG curves for dpan in static air

In static air, the TG and DTG curves for dpan were obtained at 3.4, 5.4, 7.5 and 10.4 K min⁻¹ (Figs. 6–9).

4.2.1. The integral method for a single heating rate

Table 3 gives the results of dpan using integral method at a single heating rate. From Table 3, we get the mean activation energy $E = 75.2$ kJ mol⁻¹ and mean reaction order $n = 2.0$. We also find that the

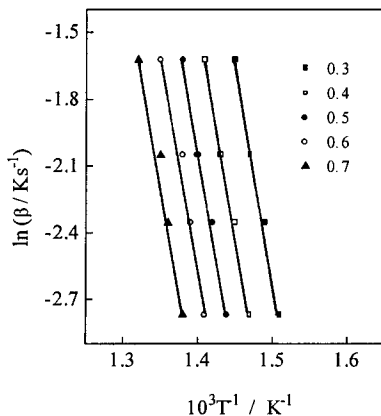


Fig. 5. Plot of $\ln \beta$ vs $1/T$ for udpan.

Table 2
The results of udpan using differential method at a single heating rate ($n = 2$)

β (K min ⁻¹)	3.8	5.7	7.7	11.8
E (kJ mol ⁻¹)	119.6	121.7	112.3	112.1
A (min ⁻¹)	1.27×10^8	1.83×10^8	4.10×10^7	3.91×10^7

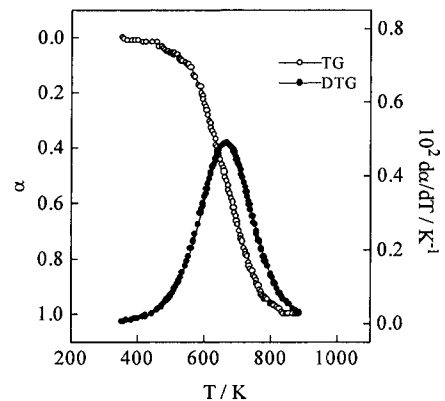


Fig. 6. TG and DTG curves for dpan at 3.4 K min⁻¹.

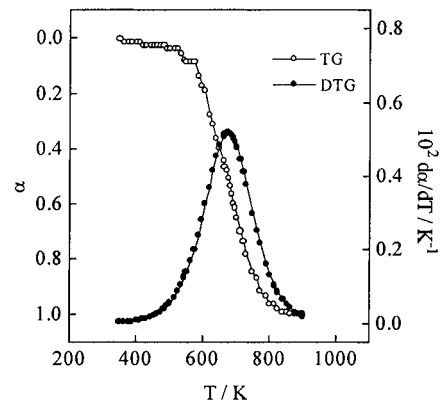


Fig. 7. TG and DTG curves for dpan at 5.4 K min⁻¹.

results at the different heating rates are almost the same, indicating that the simplified integral method is reliable for the given sample under conditions studied.

4.2.2. The differential method for a single heating rate

At a certain heating rate, plotting the straight-line of $\ln[(d\alpha/dt)/(1-\alpha)^n]$ vs $1/T$ at different n based on Eq. (3), we can obtain

$$E = (\text{slope}) \times R \text{ and } A = \exp(\text{intercept}).$$

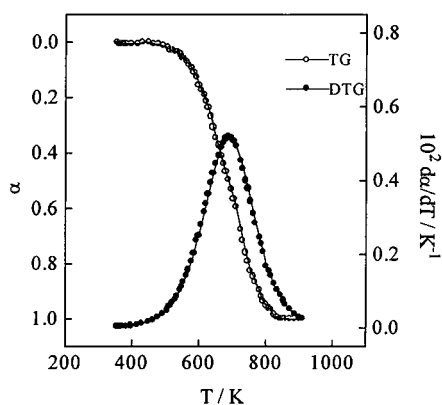
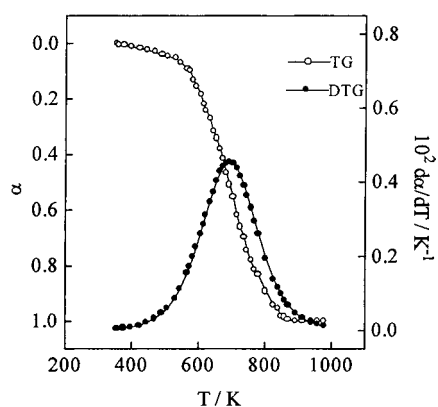
Fig. 8. TG and DTG curves for dpan at 7.5 K min⁻¹.Fig. 9. TG and DTG curves for dpan at 10.4 K min⁻¹.

Table 4 gives the results of dpan using differential method at a single heating rate. The mean activation energy is $E = 76.7 \text{ kJ mol}^{-1}$ which is in good agreement with the results by integral method, indicating that the reaction function $f(\alpha) = (1 - \alpha)^2$ is reasonable and F_2 mechanism is the most probable one for the thermal decomposition of dpan in static air.

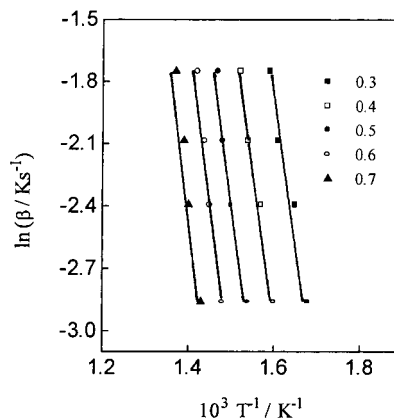
4.2.3. Ozawa method for dpan at multi-heating rates

Taking $\alpha = 0.3, 0.4, 0.5, 0.6$ and 0.7 and plotting $\ln \beta_i$ vs $1/T_i$, we get a group of paralleled lines

Table 3

The results of dpan using integral method at a single heating rate

β (K min ⁻¹)	3.4	5.4	7.5	10.4
T_m (K)	664.7	672.2	687.7	693.2
α_m	0.5063	0.4815	0.4959	0.5113
$10^2(d\alpha/dT)_m$	0.4862	0.5175	0.5169	0.4534
n	2.07	1.82	1.96	2.12
E (kJ mol ⁻¹)	74.9	68.2	79.0	78.6

Fig. 10. Plot of $\ln \beta$ vs $1/T$ for dpan.

(Fig. 10). The activation energy can be obtained from the slope of the regression line: $E = 10501.26 \times R / 1.05 = 83.2 \text{ kJ mol}^{-1}$, which is higher by about 10% than that from the former two methods.

Therefore the mean activation energy for dpan in static air is 78.5 kJ mol^{-1} by the three methods.

4.3. TG and DTG curves for udpan and dpan in N₂

TG and DTG curves for udpan and dpan (Figs. 11 and 12) were obtained in N₂ with a flow rate of $45 \text{ dm}^3 \text{ min}^{-1}$. The heating rates for both the samples were 9.7 K min^{-1} .

Table 5 gives the results of udpan and dpan using integral method at a single heating rate.

Table 4

The results of dpan using differential method at a single heating rate ($n = 2$)

β (K min ⁻¹)	3.4	5.4	7.5	10.4
E (kJ mol ⁻¹)	75.9	76.0	83.7	71.0
A (min ⁻¹)	7.57×10^4	9.34×10^4	4.49×10^5	5.30×10^4

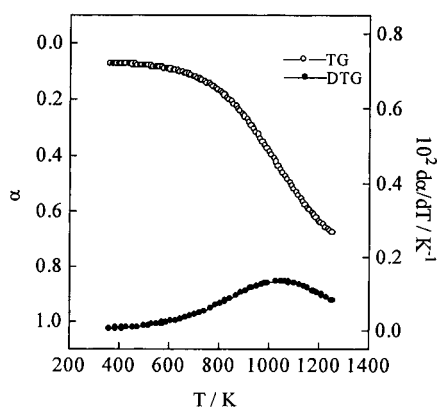
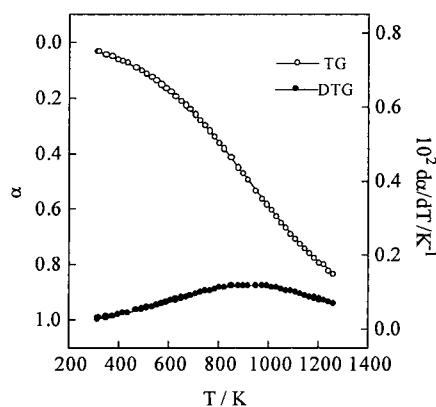
Fig. 11. TG and DTG curves for udpan in N₂.Fig. 12. TG and DTG curves for dpan in N₂.

Table 5

The results of udpan and dpan using integral method at a single heating rate

Sample	T_m (K)	α_m	n	$10^2(d\alpha/dT)_m$	E (kJ mol ⁻¹)
Udpan	1050.2	0.488	1.9	0.1342	45.2
Dpan	919.6	0.514	2.1	0.1182	36.6

Comparing Table 5 with Tables 1 and 3, we find that the activation energy of thermal decomposition of udpan in N₂ is lower by 64% than in static air, and the maximum of reaction rate is only 26% of that in air, but the temperature corresponding to the maximum reaction rate is higher by about 330 K than in air. In the case of dpan, the activation energy of thermal decomposition in N₂ is lower by 54% than in static air, and the maximum of reaction rate is only 26% of that in air, but the temperature corresponding to the maximum reaction rate is higher by about 230 K than in air.

5. Conclusions

The apparent activation energies for udpan and dpan in static air are 126.5 and 78.5 kJ mol⁻¹, and those in N₂ are 45.2 and 36.6 kJ mol⁻¹, respectively. The mean reaction orders for udpan and dpan in static

air are 2.1 and 2.0, and those in N₂ are 1.9 and 2.1, respectively. Therefore the reaction function $f(\alpha) = (1 - \alpha)^2$ for the thermal decomposition of both udpan and dpan is reasonable. In N₂, the thermal decomposition processes for udpan and dpan may be a random degradation of polymer chain, whereas in air it should be an oxidation degradation involving the participation of oxygen in air. Thus the maximum of reaction rate in N₂ is only 20–26% of those in air and the apparent activation energies for them are only 1/2–1/3 of those in air. But the temperatures corresponding to the maximum reaction rate are higher by about 230–320 K than in air.

Acknowledgements

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