

Kinetic Studies on the Non-isothermal Decomposition of Poly(methyl methacrylate)

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The model-fitting method and iso-conventional method are used for studying the kinetic mechanisms of poly(methyl methacrylate) decomposition under nitrogen and air. The decomposition of poly(methyl methacrylate) in nitrogen has two mass loss stages, corresponding to the end-chain scission model and the random chain-breaking model, respectively. The model-fitting results show that the decomposition rate of the first stage is controlled by diffusion process with average activation energy E of $158.5 \text{ kJ mol}^{-1}$. The rate-limiting step of the second mass loss stage is the random chain-breaking reaction itself, which is a 1.5 order chemical reaction with average activation energy E of $214.79 \text{ kJ mol}^{-1}$. In air, there are also two stages of mass loss for poly(methyl methacrylate) decomposition. The presence of oxygen restrains the decomposition of poly(methyl methacrylate) at the initial stage. The kinetic mechanism of the first mass loss stage is a first-order chemical reaction and the average activation energy E is $130.32 \text{ kJ mol}^{-1}$. It suggests that the reaction rate of this stage is influenced not only by the decomposition of the stable peroxy radical but also by the diffusion or random chain-breaking process. In the second mass loss stage, the reaction mechanism is also a first-order chemical reaction with the average activation energy of $78.25 \text{ kJ mol}^{-1}$. The transport-driven processes appear to dominate the rates of product formation. The relationship between the activation energy ' E_a ' and extent of conversion ' α ' of poly(methyl methacrylate) decomposition in air is obtained by the iso-conventional method. At initial stage, the activation energy ' E_a ' is high and then decreases gradually as the extent of conversion ' α ' increases. As $\alpha > 0.9$, E_a decreases rapidly. The result is well consistent with that of model fitting method.

Key Words: PMMA, Thermal decomposition, Model-fitting method, Iso-conventional method.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a transparent material, whose light transmission rate is *ca.* 92%. Besides, it has excellent corrosion resistance and insulativity. These advantages make it so popular and widely used in building and general consumer products¹. Unfortunately, its heat resistant quality is poor. Poly(methyl methacrylate) is a kind of thermoplastic and would be softened or melted upon heating; its oxygen index is *ca.* 17.3² and is a combustible material. These shortcomings restrict the application range of PMMA. Therefore, studying the thermal property of PMMA is important.

Many studies on thermal stability and kinetic parameters of PMMA decomposition have been reported in the literatures³⁻⁹. A majority of these studies have been conducted in the nitrogen atmosphere and widely different rate constants and activation energies were reported^{5,6}. The differences and disagreement may be induced by the different experimental conditions and data processing method.

Non-isothermal model fitting methods have been widely used in studying the thermal decomposition kinetic of materials. However, it was found that sometimes the different results

would be obtained even if the method was applied for studying the same material. The reason is that the pre-exponential factor A and mechanism function $f(\alpha)$ are inseparable during the data processing. Therefore, the kinetic parameters are achieved only at the same time, but not by steps. Due to the kinetic compensation effect and synergetic change of E and $\ln A$, when associate the data with mechanism functions, the corresponding E and A may have significant differences even if their integral or differential results have good linear distribution¹⁰. To avoid misleading and obtain reliable results when using the model fitting method to deal with the non-isothermal data, it is suggested to adopt both the differential and integral methods for determining the kinetic mechanism. The kinetic parameters and most probable mechanism functions can be determined by comparing the results from both methods¹¹.

Unlike the model fitting method, which yields a single overall value of activation energy of the process, the iso-conventional method may reveal complexity of the reaction mechanism in the form of a functional dependence of the activation energy on the extent of conversion¹². Because thermal degradation of polymers usually involves multiple steps, analysis of these data by the iso-conventional method is

well-suited to revealing the type of complexity that might be disguised in the model fitting kinetic analysis.

In this paper, thermal analysis techniques were employed to investigate thermal decomposition of PMMA in nitrogen and air, respectively. Both model fitting method and iso-conventional method were adopted to analyze the data. The purpose is to obtain reliable estimates for the kinetic mechanism, activation energy E_a and preexponential factor A of these processes.

EXPERIMENTAL

Poly(methyl methacrylate) slab (supplied by manufactures of cone calorimeter for calibrating the equipment, referred to those provided by Polymer Laboratories, Thermal Sciences Division in this paper) was cut and ground into powder for measurement. Thermogravimetric experiments were performed using a Pyris-1 TGA in air or nitrogen with a flow rate of 30 mL min⁻¹. Temperature range was from 293 to 873 K.

RESULTS AND DISCUSSION

Fig. 1 shows the TG and DTG curves of poly(methyl methacrylate) (PMMA) in nitrogen and air. It can be seen that there are two mass loss stages of PMMA decomposition in nitrogen. The temperature range of first stage is 491~588 K with a 26 % mass loss. The second stage is from 588 to 673 K with a 73 % mass loss. The DTA curves of PMMA in nitrogen and air are shown in Fig. 2. In nitrogen, there exist two endothermic peaks which corresponding to the two mass loss stages observed in TG curves, indicating the two mass loss processes are both endothermic reactions. In air atmosphere, the initial decomposition temperature of PMMA is *ca.* 528 K, 40 K higher than that for the process under nitrogen. In addition, two overlapped peaks are observed in the DTG curves of PMMA in air, which suggest there also exist two mass loss stages when PMMA decomposition in air. The temperature range of first stage is 528~623 K with a 70 % mass loss. The second stage is from 623 to 673 K with a 30 % mass loss. The corresponding DTA curves only show a broad endothermic peak, which is weaker than the result in nitrogen. Comparing the TG and DTG results of PMMA in nitrogen and air, as shown in Fig. 1, the turning point temperature of the two mass loss stages in air is *ca.* 623 K and the corresponding extend of conversion ($1-W/W_0$) is 70 %, which is higher than that for the process under nitrogen (~26 %). In order to obtain further insight into the kinetic mechanisms for PMMA decomposition in air and nitrogen, model fitting method and iso-conventional method are both used to analyze the TG and DTG data.

Model fitting method: The universal kinetic equation for model fitting method is shown below:

$$\frac{da}{dT} = \frac{A}{\beta} e^{-E/RT} f(a) \quad (1)$$

where T is temperature, a is the extent of conversion, β is the heating rate and $f(a)$ is the function of reaction mechanism. By resolving the above equation, the kinetic mechanism, average apparent activation energy E and preexponential factor A can be obtained. The methods used for calculating these

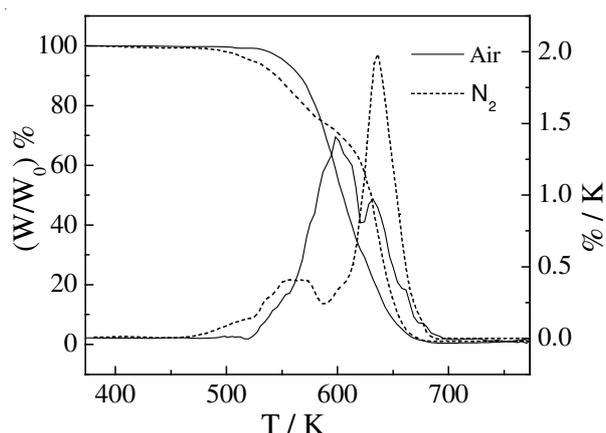


Fig. 1. TG and DTG curves of PMMA at the heating rate 10 K min⁻¹ under air and nitrogen

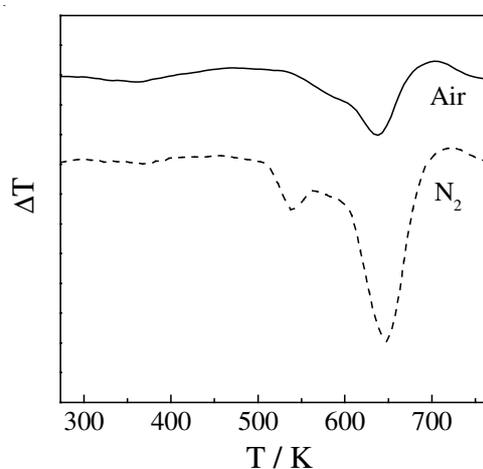


Fig. 2. DTA curves of PMMA at the heating rate 10 K min⁻¹ under air and nitrogen

kinetic parameters are usually classified as differential and integral methods. The most probable kinetic mechanisms can be determined by comparing the results from the both methods¹¹.

In this study, Achar method (differential method)¹³ and Coats-Redfern method (integral method)¹⁴ that are widely used in thermal analysis are adopted to calculate the kinetic parameter of PMMA decomposition. The universal equations of the two methods are shown below:

$$\text{Achar method: } \ln \frac{da}{dTf(a)} = \ln \frac{A}{\beta} - \frac{E}{RT} \quad (2)$$

$$\text{Coats-Redfern method: } \ln \left[\frac{g(a)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (3)$$

where A is pre-exponential factor, E is the activation energy (kJ mol⁻¹), R is the gas constant (8.31 J K⁻¹ mol⁻¹), T is temperature and β is the heating rate. The commonly used integral $g(a)$ and differential $f(a)$ functions of kinetic mechanism are shown in Table-1¹⁰.

The series of data a , T and da/dT of different mass loss stages of PMMA thermal decomposition, obtained from the TG and DTG curves, are used to calculate the $f(a)$ and $g(a)$ according to the kinetic mechanism functions¹⁵ listed in Table-1. Then, plot the $\ln[(da/dT)/f(a)]$ or $\ln[g(a)/T^2]$ versus $1/T$ by

TABLE-1
CLASSIFICATION OF KINETIC MECHANISMS OF SOLID DEGRADATION

No.	Function	Reaction model	f(a)	g(a)
1	Mampel power law	–	$4a^{3/4}$	$a^{1/4}$
2	Mampel power law	–	$3a^{2/3}$	$a^{1/3}$
3	Mampel power law	–	$2a^{1/2}$	$a^{1/2}$
4	Mampel power law	–	1	a
5	Parabola law	One-dimensional diffusion	$1/(2a)$	a^2
6	Valensi	Two-dimensional diffusion	$[-\ln(1-a)]^{-1}$	$a+(1-a)\ln(1-a)^2$
7	Ginstling-Broshtein	Three-dimensional diffusion	$3/2[(1-a)^{-1/3}-1]$	$(1-2a/3)-(1-a)^{2/3}$
8	Avrami-Erofeev	n = 2	$2(1-a)[- \ln(1-a)]^{1/2}$	$[-\ln(1-a)]^{1/2}$
9	Avrami-Erofeev	n = 3	$3(1-a)[- \ln(1-a)]^{2/3}$	$[-\ln(1-a)]^{2/3}$
10	Avrami-Erofeev	n = 4	$4(1-a)[- \ln(1-a)]^{3/4}$	$[-\ln(1-a)]^{3/4}$
11	Phase boundary reaction	Contraction cylinder	$2(1-a)^{1/2}$	$1-(1-a)^{1/2}$
12	Phase boundary reaction	Contracting sphere	$3-(1-a)^{2/3}$	$1-(1-a)^{1/3}$
13	Chemical reaction	n = 1	1-a	$-\ln(1-a)$
14	Chemical reaction	n = 1.5	$(1-a)^{3/2}$	$2[(1-a)^{-1/2}-1]$
15	Chemical reaction	n = 2	$(1-a)^2$	$(1-a)^{-1}-1$

substituting the mechanism functions $f(a)$ and $g(a)$ into eqns. 2 and 3. By the linear least-squares method, the values of the non-isothermal kinetic parameters E , A and linear correlation coefficient r of the different kinetic model functions are calculated. If all conditions are in good agreement, viz., when the calculated values of E and A , obtained from a certain pair of $f(a)$ and $g(a)$, respectively, are closest and the linear correlation coefficients r above 0.98, the corresponding model function is regarded as the mechanism function of the reaction¹⁵. The calculated values of parameters E , A and linear correlation coefficients r that meet the above conditions are summarized in Table-2. The corresponding curves of $\ln[(da/dT)/f(a)] \sim 1/T$ and $\ln[g(a)/T^2] \sim 1/T$ of different mass loss stages of PMMA decomposition in nitrogen and air are shown in Figs. 3 and 4, respectively. The kinetic parameters of PMMA decomposition in nitrogen and air obtained by summarizing the above results of thermal analysis are listed in Table-3, in which the activation energy E and preexponential factor A are the average values of the results obtained from integral and differential methods. As reported in the literatures^{16,17}, the two mass loss stages observed in the TG curves of PMMA decomposition under nitrogen correspond to the two decomposition models of PMMA, end-chain scission and random chain-breaking, respectively. The activation energy (E) of the first mass loss stage is $158.50 \text{ kJ mol}^{-1}$, which is much higher than energy of the end-chain initiation¹⁸ (ca. 75 kJ mol^{-1}) and the corresponding kinetic mechanism is three-dimensional diffusion equation. The result suggests that the reaction rate-limiting step of

TABLE-2
THERMAL ANALYSIS RESULTS OF PMMA
UNDER NITROGEN AND AIR

Weight loss stage	Function no.	Calculation method	E (kJ mol ⁻¹)	ln A (min ⁻¹)	r
Nitrogen	I	7	156.02	27.10	-0.9945
		7	160.98	28.27	-0.9997
	II	14	211.25	39.82	-0.9977
		14	218.33	41.09	-0.9998
Air	I	13	129.32	24.62	-0.9943
		13	131.32	24.99	-0.9997
	II	13	77.80	13.97	-0.9860
		13	78.69	13.97	-0.9994

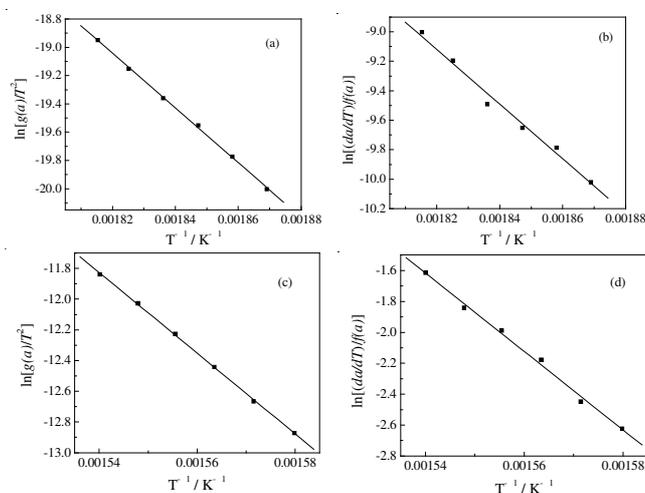


Fig. 3. (a) $\ln[g(a)/T^2] \sim 1/T$ curves of the first mass loss stage of PMMA decomposition under nitrogen; (b) $\ln[(da/dT)/f(a)] \sim 1/T$ curves of the first mass loss stage of PMMA decomposition under nitrogen; (c) $\ln[g(a)/T^2] \sim 1/T$ curves of the second mass loss stage of PMMA decomposition under nitrogen; (d) $\ln[(da/dT)/f(a)] \sim 1/T$ curves of the second mass loss stage of PMMA decomposition under nitrogen

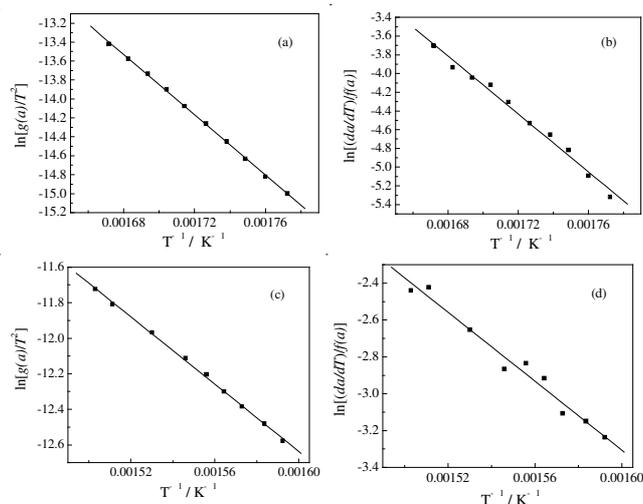


Fig. 4. (a) $\ln[g(a)/T^2] \sim 1/T$ curves of the first mass loss stage of PMMA decomposition under air; (b) $\ln[(da/dT)/f(a)] \sim 1/T$ curves of the first mass loss stage of PMMA decomposition under air; (c) $\ln[g(a)/T^2] \sim 1/T$ curves of the second mass loss stage of PMMA decomposition under air; (d) $\ln[(da/dT)/f(a)] \sim 1/T$ curves of the second mass loss stage of PMMA decomposition under air

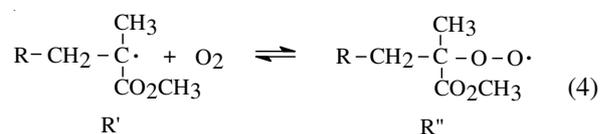
TABLE-3
 KINETIC PARAMETERS OF PMMA DECOMPOSITION UNDER NITROGEN AND AIR

	Weight loss stage	Weight loss rate (%)	Range of temp. (K)	Reaction model	E (kJ mol ⁻¹)	ln A (min ⁻¹)
Nitrogen	I	26	491~588	Three-dimensional diffusion	158.50	27.69
	II	73	> 588	Chemical reaction: n = 1.5	214.79	40.46
Air	I	70	528~623	Chemical reaction: n = 1	130.32	24.81
	II	30	> 623	Chemical reaction: n = 1	78.25	13.97

this stage may be associated with the diffusion processes of the methyl methacrylate monomer within and from the bulk matrix. The value of activation energy of the second mass loss stage is 214.79 kJ mol⁻¹, which consist with that of random chain-breaking initiation (*ca.* 210 kJ mol⁻¹)¹⁹ and the kinetic mechanism is 1.5 order chemical reaction, which indicates that the rate-limiting step of this stage is the random chain-breaking reaction itself.

Under air, the average apparent activation energy of the first mass loss stage of PMMA decomposition is *ca.* 130 kJ mol⁻¹ (Table-3), which is different from the values of end-chain scission or random chain-breaking reactions. Furthermore, the switch of the two mass loss stages in nitrogen occurs at *ca.* 26 % mass loss, while this switch in air is achieved until 70 % mass loss. This demonstrates that the rate-controlling step of the first mass loss stage of PMMA in air could not be governed by the two models of PMMA decomposition.

From the TG curves in Fig. 1, the initial decomposition temperature of PMMA in air atmosphere is higher than that of the process under nitrogen, which indicates that the presence of oxygen restrains the decomposition of PMMA at the initial stage. Peterson *et al.*⁵ proposed the stabilizing mechanism of oxygen on the thermal decomposition of PMMA, as shown in the following reactions:



They suggested that oxygen will react with R' produced from the decomposition of PMMA to form peroxy radical R''. The peroxy radical R'' is thermally more stable than R' and the formation of R'' is a reversible exothermic reaction. At lower temperature, there will be more radical R', further unzipping of the polymer chain will be inhibited. But once the temperature is raised, the above chemical reaction equilibrium will shift. An increase in temperature will favour the formation of radical R' and lots of active radical R' will be produced by the decomposition of PMMA and so the rate of unzipping of PMMA will increase. This indicates that in the presence of oxygen, reaction (4) can affect the rate of PMMA decomposition. The average activation energy of the reverse reaction²⁰ of reaction (4) is *ca.* 100 kJ mol⁻¹, which is lower than that of the first mass loss stage (temperature below 623 K) of PMMA decomposition (130.32 kJ mol⁻¹). This suggests that the decomposition rate of PMMA is influenced not only by the decomposition of the peroxy radical R'' but also by other reactions such as diffusion or random chain-breaking process. Above 623 K (the second mass loss stage of PMMA), the average activation energy of PMMA decomposition decrease to 78.25 kJ mol⁻¹ and the reaction mechanism is a first-order

chemical reaction, which indicates that transport-driven processes (*e.g.* desorption, vaporization, heat transfer) appear to dominate the rates of product formation²¹.

Iso-conventional method: Although model-fitting method is widely used for studying the thermal kinetics, its disadvantages are also obvious. Some kinetic equations are only suitable for elementary reactions, while in general, the overall reaction is not elementary reaction and the kinetic mechanism may change with temperature. So describing the kinetic mechanism of the whole reaction using a fixed function f(a) is unreasonable. In addition, the use of model-fitting methods only yields a single value of average apparent activation energy for the whole process. However, an overall reaction usually involves multiple elementary steps that are most likely to have different activation energies. The relative contribution of these steps to the overall reaction rate changes with both temperature and extent of reaction. This means that the effective activation energies determined from thermal analysis data should be a function of these two variables^{22,23}. In order to realize the reaction complexity of PMMA decomposition in air, iso-conventional method¹² is used to analyze a series of TG curves with different heating rates and the relationship between the activation energy E and extent of conversion a or temperature T is obtained.

The iso-conventional approach to kinetic analysis rests upon the iso-conventional principle, according to which the reaction rate at a constant extent of conversion is only a function of temperature¹².

$$\left(\frac{d \ln(da/dt)}{dT^{-1}} \right)_a = -E_a / R \quad (5)$$

The kinetics of heterogeneous decompositions is traditionally described by the basic kinetic equation:

$$\frac{da}{dt} = A e^{-E/RT} f(a) \quad (6)$$

where f(a) is the differential function of reaction mechanism. For non-isothermal conditions, when the temperature varies with time at a constant heating rate, $\beta = \frac{dT}{dt}$, eqn. 6 is represented as follows:

$$\frac{da}{f(a)} = \frac{A}{\beta} e^{-E/RT} dT \quad (7)$$

The integral form of eqn. 7 is:

$$\int_0^a \frac{da}{f(a)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (8)$$

Let us introduce two functions g(a) and I(E,T):

$$g(a) = \int_0^a \frac{da}{f(a)} \quad (9)$$

$$I(E,T) = \int_0^T e^{-E/RT} dT \quad (10)$$

From eqns. 9 and 10, eqn. 8 becomes the following form:

$$g(a) = \frac{A}{\beta} I(E, T) \quad (11)$$

According to a general assumption²⁴⁻²⁶ that the reaction model is independent of the heating rate, eqn. 11 can be written for a given conversion and a set of experiments carried out at different heating rates β_i ($i = 1, \dots, n$) as:

$$\frac{A_a}{\beta_1} I(E_a, T_{a,1}) = \frac{A_a}{\beta_2} I(E_a, T_{a,2}) = \dots = \frac{A_a}{\beta_n} I(E_a, T_{a,n}) \quad (12)$$

Then it follows:

$$\sum_i^n \sum_{j \neq i}^n \frac{I(E_a, T_{a,i}) \beta_j}{I(E_a, T_{a,j}) \beta_i} = n(n-1) \quad (13)$$

where the subscripts i and j represent original numbers of two experiments performed under different heating programs. The subscript a denotes the values related to a given extent of conversion.

For a set of TG experiments carried out at different heating rates β_i ($i = 1, \dots, n$), the activation energy E can be calculated by substituting the temperature T_i ($i = 1, \dots, n$) at a given conversion a into eqn. 13. However, since the T_a values are measured with experiments error, eqn. 13 can only be satisfied as an approximate equality. Consequently, the activation energy is determined at any particular value of a by the following equation:

$$\left| n(n-1) - \sum_i^n \sum_{j \neq i}^n \frac{I(E_a, T_{a,i}) \beta_j}{I(E_a, T_{a,j}) \beta_i} \right| = \min \quad (14)$$

Substituting experimental values of T_a and β into the eqn. 14 and varying E_a to reach the minimum gives the value of the activation energy at a given conversion. The minimization procedure is repeated for each value to find the dependence of the activation energy on the extent of conversion.

The TG curves of PMMA decomposition in air at different heating rate ($\beta = 5 \text{ K min}^{-1}$, 10 K min^{-1} and 15 K min^{-1}) are shown in Fig. 5. It can be seen that the TG curves of PMMA shift to high temperature with the heating rate increasing. This is attributed that there exist a temperature difference between the oven and sample, as well as a temperature gradient within the sample. The difference will be enhanced with increasing the heating rate.

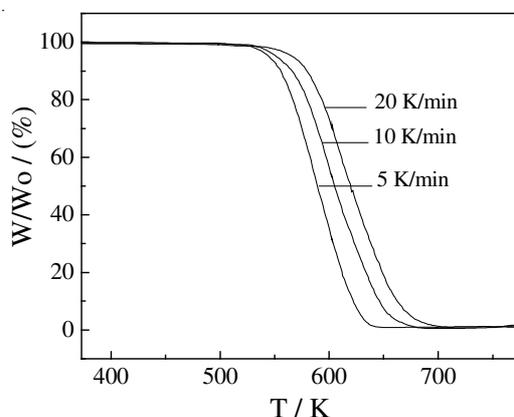


Fig. 5. TG curves at various heating rates for thermal decomposition of PMMA in air

Fig. 6 shows the dependence of activation energy ' E_a ' on the extent of conversion ' a ' for PMMA decomposition under air. The activation energy is high at initial stages, which may be attributed that the more stable group of peroxy radical R'' inhibit the further decomposition of PMMA (explained as eqn. 4). With the extent of conversion ' a ' increasing, the value of ' E_a ' decreases rapidly, which is believed to associate with the active free radicals R' produced by the decomposition of radical R'' at high temperature promoting the PMMA decomposition. When the extent of conversion ' a ' is above 0.2, the activation energy ' E_a ' decreases slowly and the average value is *ca.* 130 kJ mol^{-1} , which coincide with the result obtained from model-fitting method (the first mass loss stage of PMMA under air, shown as Table-3). This suggests that the decomposition of peroxy radical R'' has an important effect on the reaction rate of PMMA decomposition in air. As ' a ' > 0.9 , the activation energy ' E_a ' decreases rapidly, also consistent with the results from model-fitting method (the second mass loss stage of PMMA in air, shown as Table-3). This may indicate that in this stage, the PMMA begin to burn and the reaction rate is controlled by the transport-driven processes.

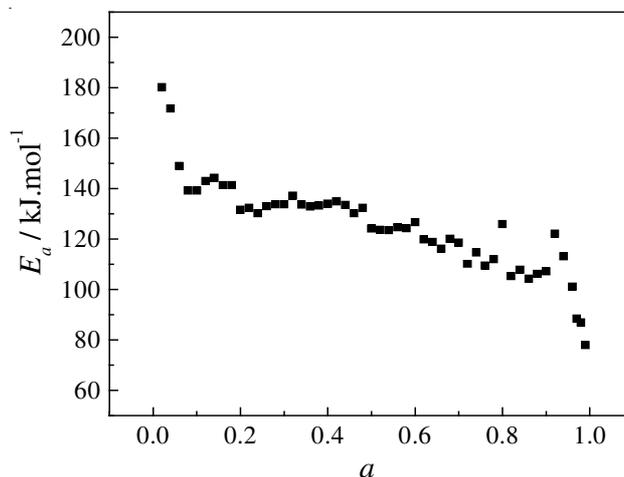


Fig. 6. Dependencies of the activation E_a on extent a for PMMA decomposition in air

Conclusion

Poly(methyl methacrylate) decomposition under nitrogen has two mass loss stages. The corresponding decomposition models are end-chain scission and random chain-breaking, respectively. Model-fitting results show the reaction rate of end-chain scission is controlled by diffusion process and the average activation energy E is $158.5 \text{ kJ mol}^{-1}$. The rate-limiting step of the second stage is the random chain-breaking reaction itself, which is 1.5 order chemical reaction with an average activation energy E of $214.79 \text{ kJ mol}^{-1}$. For PMMA decomposition in air, there are also two stages of mass loss. The presence of oxygen restrains the decomposition of PMMA at the initial stage. In the first stage, the reaction rate is influenced not only by the decomposition of the stable peroxy radical but also by the diffusion or random chain-breaking process. The associated kinetic mechanism is a first-order chemical reaction and the average activation energy E is $130.32 \text{ kJ mol}^{-1}$. In the second mass loss stage, PMMA begin to burn and the mechanism is also a first-order chemical reaction with the average activation

energy of 78.25 kJ mol⁻¹. The transport-driven processes appear to dominate the rates of product formation of this stage. The dependence of activation energy E_a on the extent of conversion a of PMMA decomposition in air is obtained by iso-conversional method. At initial stage, the activation energy E_a is high due to the inhibition effect of oxygen. With the increase of extent of conversion a, E_a decreases gradually. As 'a' > 0.9, 'E_a' decreases rapidly. These results coincide with that of the model-fitting method.

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