

# CHEMICAL KINETICS AND MECHANISM OF POLYSTYRENE THERMAL DECOMPOSITION

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## ABSTRACT

Chemical kinetics on thermal decomposition of polystyrene was studied by integrating the non-isothermal differential and integral methods. For decomposition of polystyrene in environment with only nitrogen, a mass loss stage was found at 282.9°C to 398.2°C. The maximum mass-loss rate was at 372.4°C. Kinetic analysis results indicated that it is a first-order chemical reaction.

Thermal decomposition of polystyrene was also investigated by the “pyrolysis gas chromatography mass spectrometry” Py/GC/MS technology. Decomposition of polystyrene would be enhanced when the temperature increased. Upon heating by external sources, polystyrene would be decomposed to larger radicals. The large radicals would then produce smaller products through a series of reactions such as decomposition, radical recombination and hydrogen transfer.

**KEYWORDS:** Polystyrene, Non-isothermal differential and integral methods, Chemical kinetics, Decomposition mechanism

## INTRODUCTION

In treating plastic refuses with polystyrene (PS), styrene monomer would be produced by thermal decomposition. The chemical kinetics and mechanisms of PS decomposition concerned should be better understood to give efficient treatment. Thermal decomposition process of PS is very complex, including the main chain breaking, carbon-hydrogen bond cleavage, free radical recombination and dismutation. Reaction mechanism and kinetic parameters of polystyrene decomposition had been reported in the literature. Polystyrene decomposition was proposed to be first-order chemical reaction. However, there are significant differences<sup>1</sup> in the activation energy  $E$ . In addition, reaction order was proposed to be between 0 to 1<sup>2,3</sup> or 1 to 1.1<sup>4</sup>. Such differences might be due to various experimental conditions and data processing method.

Non-isothermal model fitting methods have been widely used in studying the thermal decomposition kinetics. Recently, it was found that different results would be obtained even if the method was applied for studying the same material. That is because the pre-exponential factor  $A$  and mechanism function  $f(a)$  cannot be separated while processing the data. Therefore, the kinetic parameters were only deduced at the same time, not by steps. Kinetic compensation effect and synergetic change of  $E$  and  $\ln A$  in analyzing data on the reaction functions would give significant differences. This happens even if their integral or differential results have good linear distribution<sup>5</sup>. To obtain more reliable results when using the model fitting method to deal with the non-isothermal data, both the differential and integral methods are suggested for determining the kinetic mechanism. Kinetic parameters and the most probable mechanism functions can then be determined by comparing results from both methods<sup>6</sup>.

In this paper, the differential and integral methods are both adopted to analyze the kinetic data of polystyrene decomposition. The objective is to give more reliable estimation on the kinetic mechanism, activation energy  $E$  and pre-exponential factor  $A$  of these processes. In addition, the decomposition products of PS at different temperature were studied by PY/GC/MS technique for speculating the decomposition mechanism.

## EXPERIMENTAL STUDIES

Polystyrene sample of average molecular weight 250,000 was supplied by a commercial firm. Thermogravimetric (TG) experiments were performed in nitrogen environment with a flow rate of 20ml/min. The heating rate was 5°C/min, temperature ranged from 20°C to 600°C.

The products from decomposition of Polystyrene at 300°C, 400°C and 500°C in nitrogen were analyzed at a heating rate of 10°C/min.

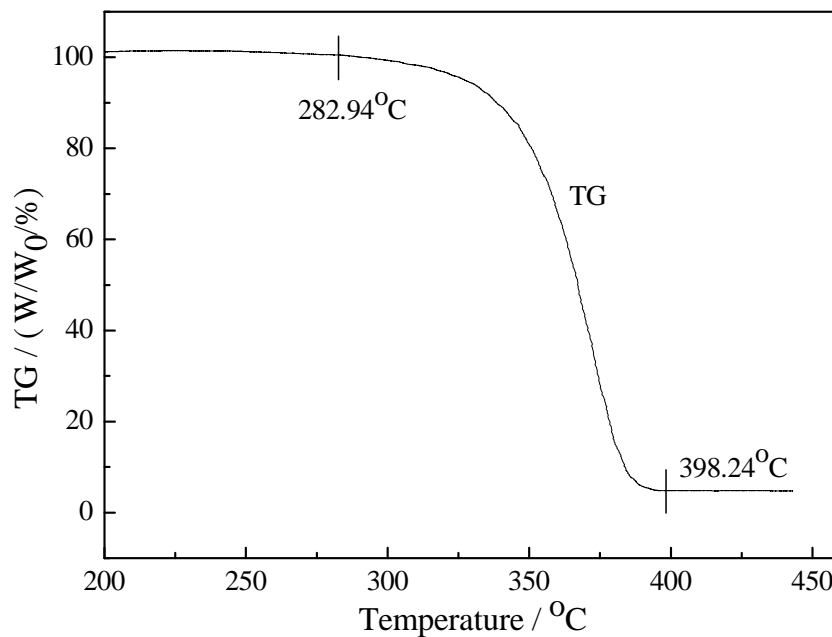
TG and differential thermogravimetric (DTG) curves of Polystyrene in nitrogen atmosphere are shown in Fig. 1 and Fig. 2. There is only one mass loss stage of decomposition at 282.94°C to 398.24°C with a 96% mass loss. The maximum mass loss rate was at about 372.44°C.

## THERMAL ANALYSIS

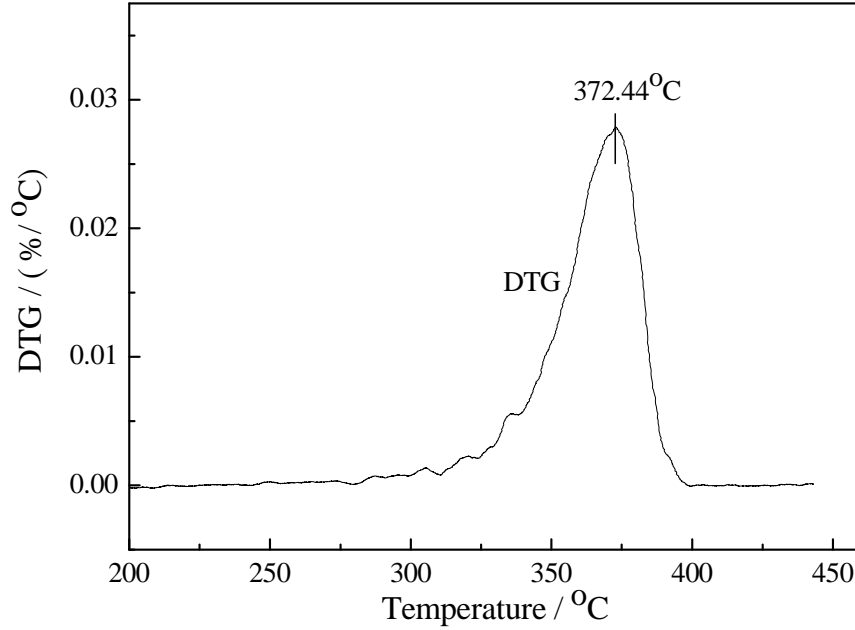
The mechanism functions and kinetic parameters were calculated by model fitting method. The universal kinetic equation for model fitting method is:

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

where  $f(a)$  is the function of reaction mechanism.



**FIGURE 1.** TG curves of polystyrene at the heating rate 5°C/min under N<sub>2</sub>



**FIGURE 2.** DTG curves of polystyrene at the heating rate 5°C/min under N<sub>2</sub>

By resolving the above equation, the kinetic mechanism, average apparent activation energy  $E$  and pre-exponential factor  $A$  can be obtained. The methods used for calculating these kinetic parameters are usually classified as differential or integral methods. Both methods were adopted for determining the most probable kinetic mechanisms<sup>7</sup> in this paper.

Integral  $g(a)$  and differential  $f(a)$  functions of kinetic mechanism commonly used are shown in Table 1<sup>5</sup>. Achar method (differential method)<sup>8</sup> and Coats-Redfern method (integral method)<sup>9</sup> adopted to calculate the kinetic parameter. The universal equations of the two methods are :

Achar method:

$$\ln \frac{da}{dTf(a)} = \ln \frac{A}{\beta} - \frac{E}{RT} \quad [2]$$

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),  $R$  is the gas constant (8.31J/K mol),  $T$  is temperature, and  $\beta$  is the heating rate.

The raw non-isothermal kinetic data  $a$ ,  $T$  and  $da/dT$  for the different steps of thermal decomposition deduced from the TG and DTG curves are used to calculate the  $f(a)$  and  $g(a)$  according to the 15 kinetic mechanism functions listed in Table 1. Curves on  $\ln[(da/dT)/f(a)]$  or  $\ln[g(a)/T^2]$  are then plotted against  $1/T$  by substituting the mechanism functions  $f(a)$  and  $g(a)$  into equation (2) and (3). By the linear least-squares method, the values for 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, and when  $E$  and  $A$  obtained from a certain pair of  $f(a)$  and  $g(a)$  are the closest, and the linear correlation coefficients  $r$  above 0.98, the corresponding model function may be the mechanism function of the reaction<sup>10</sup>. The values for the non-isothermal kinetic parameters  $E$ ,  $A$  and the linear correlation coefficients  $r$  of the probable kinetic functions are listed in Table 2.

**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	$1/(2a)$	$a^2$
6	Valensi	Two-dimensional	$[-\ln(1-a)]^{-1}$	$a+(1-a)\ln(1-a)$
7	Ginstling-Broushtein	Three-dimensional	$3/2[(1-a)^{-1/3}-1]$	$(1-2a/3)-(1-a)^{2/3}$
8	Avrami-Erofeev	n=2	$2(1-a)[-\ln(1-a)]^{1/2}$	$[-\ln(1-a)]^{1/2}$
9	Avrami-Erofeev	n=3	$3(1-a)[-\ln(1-a)]^{2/3}$	$[-\ln(1-a)]^{1/3}$
10	Avrami-Erofeev	n=4	$4(1-a)[-\ln(1-a)]^{3/4}$	$[-\ln(1-a)]^{1/4}$
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	$(1-a)^2$	$(1-a)^{-1}-1$

**TABLE 2.** The thermal analysis results of polystyrene under N<sub>2</sub> atmosphere

No.	Achar			Coats-Refern		
	$E/ \text{J}\cdot\text{mol}^{-1}$	$\ln A / \text{min}^{-1}$	$R$	$E/ \text{J}\cdot\text{mol}^{-1}$	$\ln A / \text{min}^{-1}$	$R$
1	-13131	-5.20452	0.2035	33359.61	3.742805	-0.99546
2	1415.92	-2.25062	-0.02208	47906.53	6.770921	-0.99617
3	30509.76	3.48727	-0.41949	77000.37	12.57792	-0.99673
4	117791.3	20.17772	-0.85399	164281.9	29.33299	-0.99718
5	292354.4	52.86547	-0.96163	338845	62.05155	-0.99738
6	326662.4	59.08891	-0.98053	357812.9	65.24263	-0.99884
7	341102.8	60.49145	-0.98624	365645.6	65.33906	-0.99918
8	95364.12	16.54165	-0.94703	94154.39	16.23734	-0.99757
9	60552.27	9.65098	-0.8831	59342.54	9.290526	-0.99735
10	43146.34	6.1207	-0.80189	41936.61	5.700759	-0.99709
11	158795.5	27.74091	-0.95756	179814.9	31.86412	-0.99924
12	172463.5	30.08756	-0.97242	185694.2	32.67588	-0.9992
<b>13</b>	<b>199799.7</b>	<b>36.69039</b>	<b>-0.98604</b>	<b>198589.9</b>	<b>36.43924</b>	<b>-0.99776</b>
14	240803.9	44.94672	-0.98556	220819	41.01902	-0.99177
15	281808	53.20306	-0.9757	246290.3	46.25059	-0.98156

It can be seen that all the 15 integral  $g(a)$  functions and 4 differential  $f(a)$  functions have the linear correlation coefficients above 0.98. Therefore, the calculated values of  $E$  and  $A$  obtained from  $f(a)$  and  $g(a)$  of functions 13 are closest. The results suggest that the corresponding kinetic mechanism of PS decomposition in nitrogen is first-order chemical reaction and the equation is:

$$\frac{da}{dt} = Ae^{-E/RT}(1-a)$$

Plotting  $\ln[(da/dT)/f(a)]$  and  $\ln[g(a)/T^2]$  versus  $1/T^{11}$  would give the average activation energy  $E$  of 199.2kJ/mol and  $\ln A$  36.56. This indicated that the reaction rate-limiting step of this stage is random chain-breaking reaction.

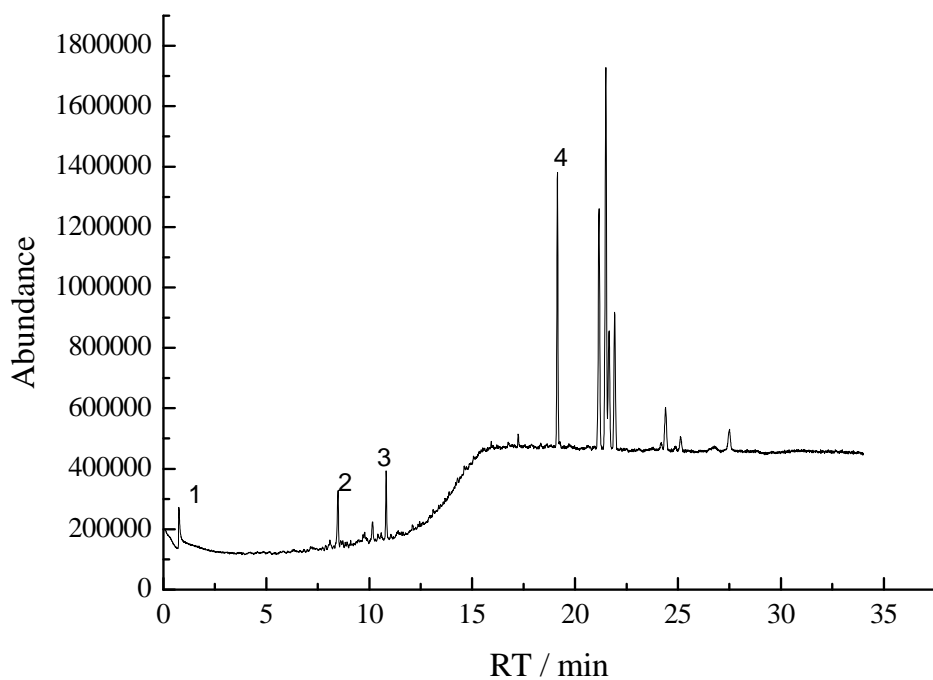
In general, the thermal decomposition of polymer follow the chemical reaction equation. However as shown in Table 2, the  $E$  and  $\ln A$  values derived from chemical mechanism functions 13, 14 and 15 have significant differences since their integral or differential results have good linear distribution. This means that if only one method for kinetic analysis is adopted, it is hard to avoid deviation due to the kinetic compensation effect and synergetic change of  $E$  and  $\ln A$ . In addition, under certain conditions, the mass loss rate of polymer decomposition may be controlled not only by the chemical reaction itself, but also by the diffusion or transportation process of products<sup>12</sup>, which makes it more difficult for identifying the kinetic mechanism. To obtain more reliable results, it is suggested to adopt both the differential and integral methods for determining the kinetic mechanism.

## PY/GC/MS ANALYSIS

The total ion chromatogram (TIC) of polystyrene decomposition under 300°C is shown in Fig. 3. The main decomposition products of PS were styrene dimer and trimer, and their low absolute abundance indicated only very small amount of polystyrene decompose. The four species which have comparatively strong peaks during the retention time of 21 to 22 min might be due to the decomposition products of some additives existed in polymer. The results showed that under 300°C, the additives would decompose firstly and the polymer itself is relatively stable.

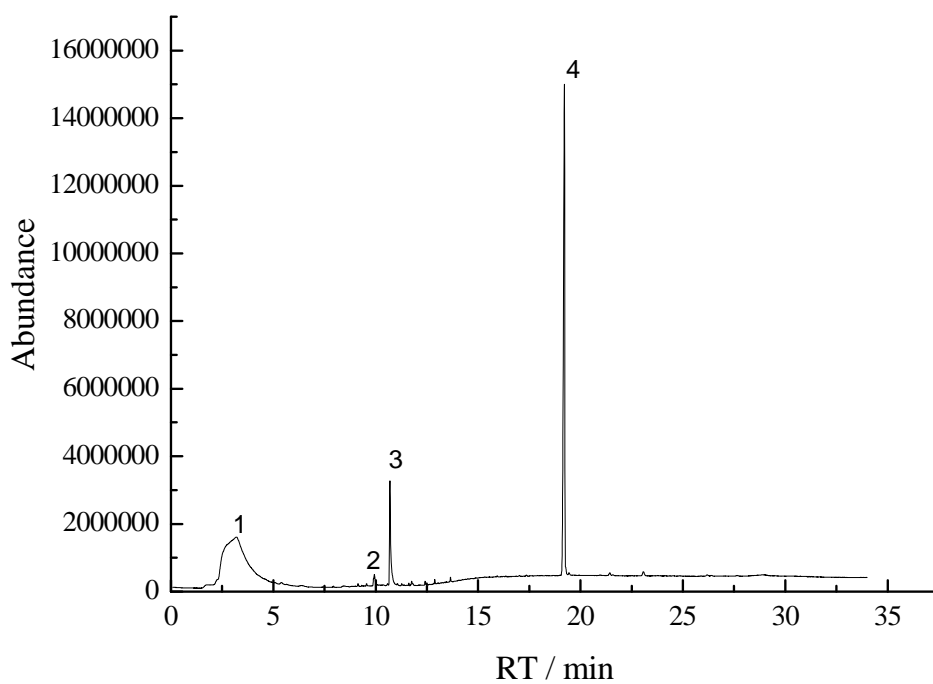
After decomposition at 300°C, the polymer continued to decompose under 400°C and the TIC is shown in Fig. 4. The main products were styrene trimer, dimer and monomer. Their absolute abundance was much stronger than that under 300°C and followed the order of trimer > dimer > monomer, which implied that under 400°C, the polystyrene would decompose and the main decomposition reaction is the random chain-breaking.

TIC of PS decomposition under 500°C is shown in Fig. 5. From the figure, the products are much more than those under 400°C. Besides styrene trimer, dimer and monomer, many small molecular products including toluene, allyl benzene, diphenyl methane, diphenyl ethane, 1,2-diphenyl propane, 1,3-diphenyl propane, 1,4-diphenyl butadiene and 1,4-diphenyl butylenes were identified.



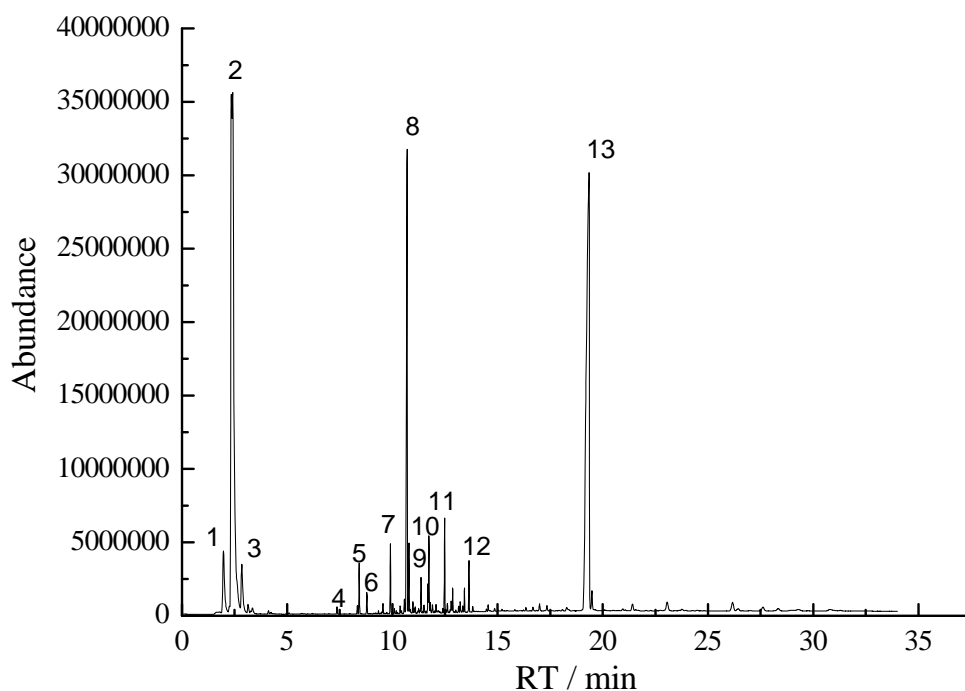
1: air 2: phthalate 3: styrene dimer 4: styrene trimer

**FIGURE 3.** TIC of PS decomposition under 300°C



1: styrene monomer 2: 2-phenylpropane 3: dimer 4: trimer

**FIGURE 4.** TIC of PS decomposition under 400°C

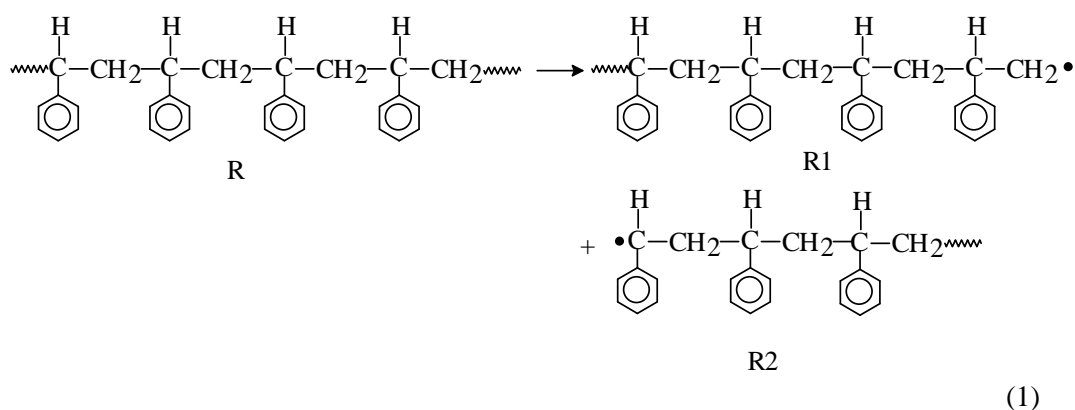


1. toluene    2. styrene monomer    3. allyl benzene    4. diphenyl methane    5. diphenyl ethane  
 6. 1,2-diphenyl propane    7. 1,3-diphenyl propane    8. styrene dimer    9. 1,4-diphenyl butadiene  
 10. 1,4-diphenyl butylene    11. 2,5-diphenyl-1,5-hexadiene    12. 1,5-diphenyl-1,5-hexadiene  
 13. styrene trimer

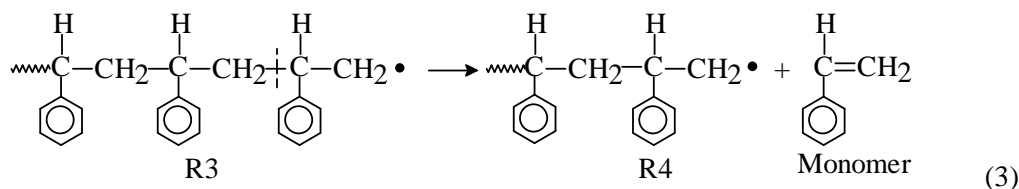
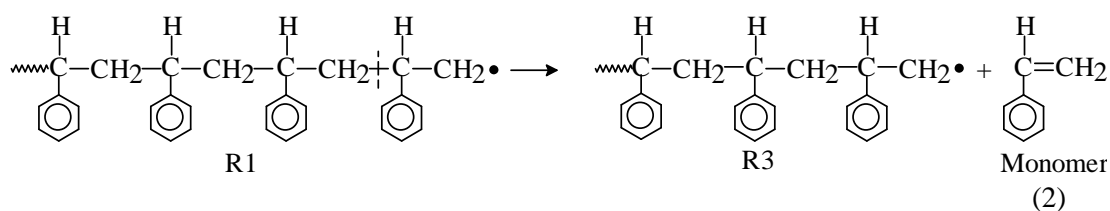
**FIGURE 5.** TIC of PS decomposition under 500°C

Based on the experimental results, combining with the basic theory of organic chemistry, the main course of polystyrene thermal decomposing in nitrogen was speculated.

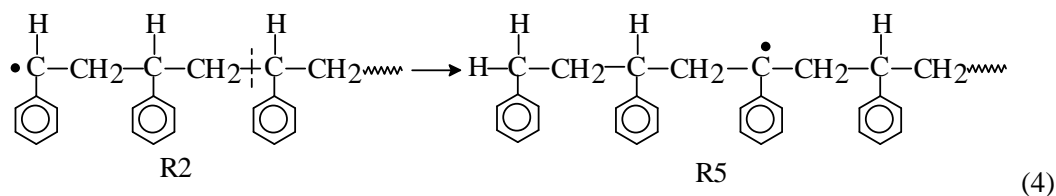
Firstly, polystyrene would decompose to produce the free radicals  $R_1$  and  $R_2$  by the random chain-breaking (reaction 1).



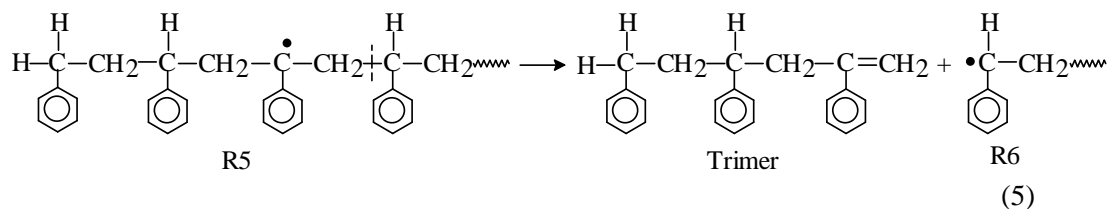
The large free radicals continue to decompose to form styrene monomer and some radicals  $R_3$  and  $R_4$  which have a shorter carbon chain (reactions 2 and 3).



The free radical R2 would occur the 1,5-hydrogen transfer reaction. The hydrogen radical produced by the breaking of main chain C-H bond can combine with 1-carbon radical to form the R5 (reaction 4).

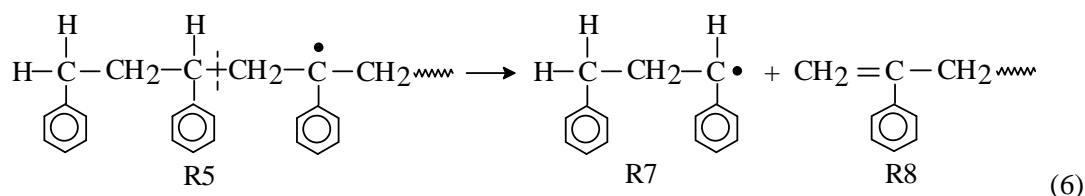


R5 decompose to generate the styrene trimer and radical R6 (reaction 5).



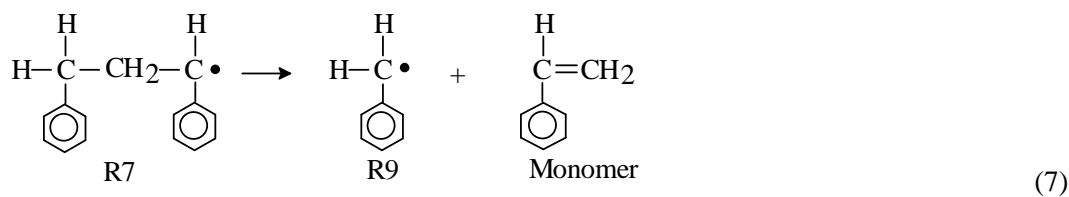
Meanwhile, R5 may produce the styrene dimer through the scission, combination and dehydrogenation process. The possible reactions are shown as reactions 6 to 9.

Firstly, R5 decomposes to form the radical R7 and polymer R8 which contain the terminal double bond (reaction 6).

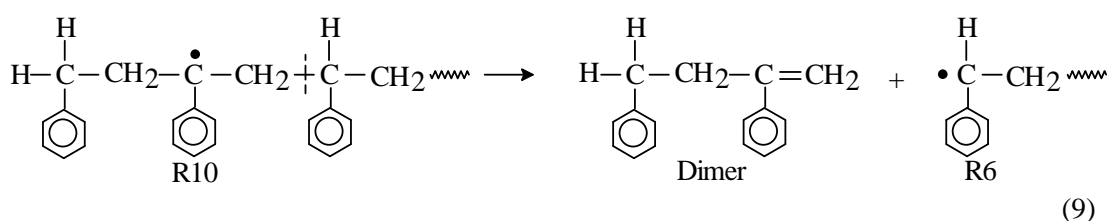
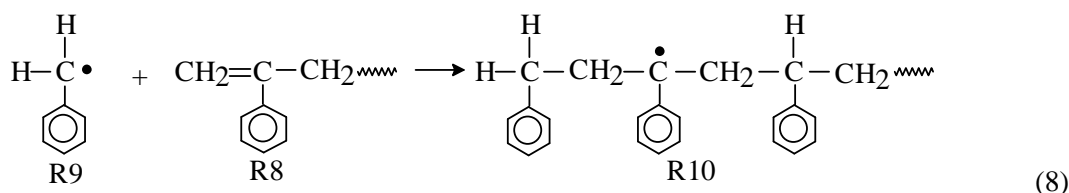


Benzyl R9 and styrene monomer may be obtained by the scission of R7 and subsequent 1,3-hydrogen transfer reaction (reaction 7).



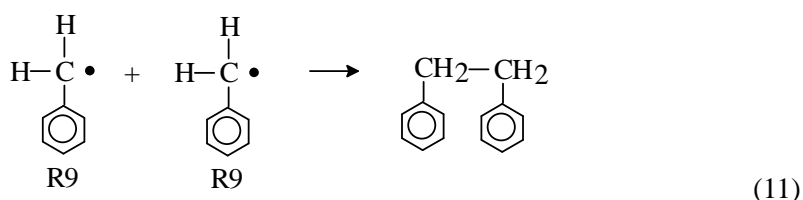
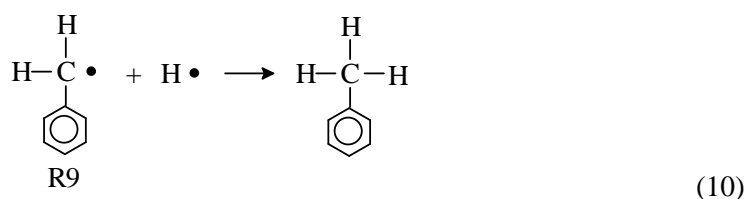


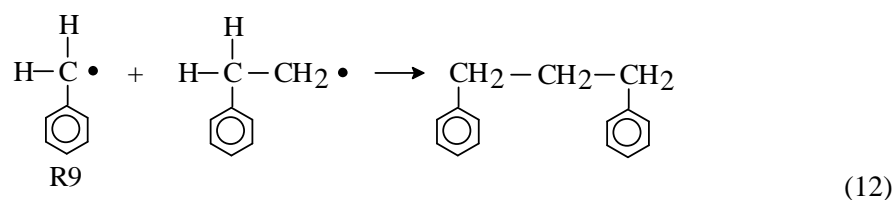
The addition reaction between benzyl R9 and polymer R8 form the radical R10 (reaction 8), which can generate the styrene dimer by the scission and dehydrogen reaction (reaction 9).



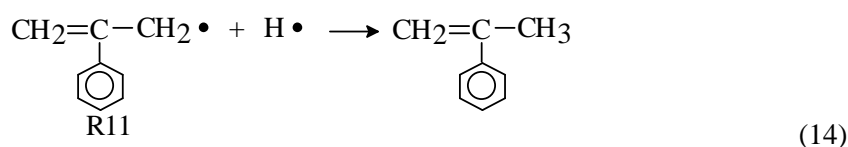
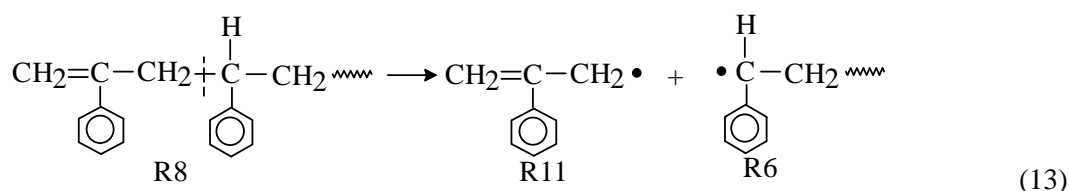
Besides the main products, there also exist some small molecular species with low content, such as toluene, allyl benzene, diphenyl methane, diphenyl ethane, and 1,2-diphenyl propane during the decomposition process. These products may be generated by the reaction among benzyl, hydrogen radical and other small free radicals.

The reaction between benzyl R9 and hydrogen radical may produce toluene as shown in reaction 10. The combination of two benzyl R9 radicals would generate the diphenyl ethane (reaction 11). Diphenyl propane may be obtained by the reaction between benzyl and the radical formed by chain scission (reaction 12).





Reactions 13 and 14 show the possible process for allyl benzene generation. The radical R11 formed by the scission of polymer R8 can react with hydrogen radical to produce the allyl benzene.



## DISCUSSION

Model fitting methods have been widely used for calculating these kinetic parameters from TG data. From the above TG kinetic analysis results of polystyrene, it further demonstrated that if only one method for kinetic analysis is adopted, it is hard to avoid deviation due to the kinetic compensation effect and synergetic change of  $E$  and  $\ln A$ . For decomposition of polystyrene in environment with only nitrogen, the kinetic analysis results based on the non-isothermal differential and integral methods indicated that the corresponding kinetic mechanism is a first-order chemical reaction. Combining with the Py/GC/MS analysis result, it suggests that the corresponding chemical reaction is the random chain-breaking and the main products are styrene trimer, dimer and monomer. The reaction is the rate-controlling step of mass loss stage of PS thermal decomposition. The kinetic parameters of the reaction can be determined accurately by adopting both the differential and integral methods. The study provides an effective approach to obtain more reliable kinetic mechanism from TG analysis.

It was reported by Cullis and Hirschle<sup>13</sup> that polymer decomposition usually included two broad stages. Firstly, polymer was heated by a heat source and decomposed to form monomer or large molecule products. Then, the generated monomer or large molecule products decomposed to produce small molecule gaseous products. Results from Py/GC/MS indicated that during the initial stage of polystyrene decomposition, the main products were styrene trimer, dimer and monomer and their absolute abundance followed the order of trimer > dimer > monomer. When the decomposition temperature was increased, the relative abundance of trimer decreased significantly while that of styrene monomer increased. This suggested that if heated by external sources, the polystyrene would firstly decompose to styrene multimer such as trimer. Then, the multimer would decompose to styrene monomer and further to small molecule products. The analysis revealed the main process of polystyrene decomposition in nitrogen. Further studies on identifying the intermediate chemical reaction mechanism and simulation by the synchrotron radiation technique are in progress.

## CONCLUSION

Non-isothermal differential and integral methods were used in calculating the chemical kinetics parameters of thermal decomposition of polystyrene. A mass loss stage was found at 282.9°C to 398.2°C for decomposition of polystyrene in nitrogen. The maximum mass-loss rate was at 372.4°C. Kinetic analysis results indicated that it is a first-order chemical reaction given by:

$$\frac{da}{dt} = Ae^{-E/RT} (1-a)$$

The average activation energy  $E$  was 199.2kJ/mol and  $\ln A$  was 36.56.

Pyrolysis gas chromatography mass spectrometry Py/GC/MS technology was used for investigating the thermal decomposition mechanism of polystyrene. Decomposition of polystyrene would be enhanced with the temperature increasing. Upon heating by external sources, polystyrene would decompose to generate larger radicals. The large radicals would then produce smaller products through a series of reactions such as decomposition, radical recombination and hydrogen transfer.

## ACKNOWLEDGEMENT

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