



## Calorimetric evaluation of polymerization thermokinetics of styrene, $\alpha$ -methylstyrene and *trans*- $\beta$ -methylstyrene

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### ABSTRACT

According to literature and our research, the styrene polymerization mechanism is identified by  $\alpha$ -methylstyrene (AMS). This study investigated the basic exothermic behavior of styrene and its major derivatives, AMS, and *trans*- $\beta$ -methylstyrene (TBMS), by two calorimeters, differential scanning calorimetry (DSC) and thermal activity monitor (TAM), to compare and evaluate their thermal kinetics on polymerization. DSC and TAM were employed for dynamic scanning and isothermal ageing tests to calculate thermokinetic parameters of styrene and styrene containing 10 ppm 4-tertiary-butylcatechol (TBC), AMS, and TBMS. Certain prominent differences were observed and discussed between AMS and TBMS obtained from DSC and TAM. All of the results could be provided to the relevant plants for lessening the degree of hazard. Results indicated that styrene, AMS, and TBMS have potential exothermic hazards, especially during the higher temperature.

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### 1. Introduction

Styrene is globally important raw chemical used in the petrochemical industry. However, it also has exothermic and explosive characteristics, such as low flash point (FP: 31 °C for closed cup), temperature of no return ( $T_{NR}$ : 54 °C for 55 gal drum) and self-accelerating decomposition temperature (SADT: 40 °C for 55 gal drum) at 25 °C ambient temperature, high reaction heat ( $\Delta H$ : 600 J g<sup>-1</sup>) and low apparent activation energy ( $E_a$ : 63 kJ mol<sup>-1</sup>) [1]. The above information indicates styrene possesses extremely probable thermal runaway characteristics. The main causes of accidents resulting from styrene and its derivatives, as listed in Table 1 from MHIDAS [2,3] and Table 2 [4], are external and internal unsafe actions in Asia, Europe, and USA, as follows:

1. Human failure: movement/procedure/assessment mistakes, invalid or obsolete safety and health management, unsafe behaviors, erroneous human factors, lack of protective tools.
2. Equipment damage: instrument/system breakdowns, breach/rust, overpressure, overheating, eccentric reactions, design undesirability.
3. Environmental conditions: power failures, cooling failures, abnormal climate, temperature too low or too high, humidity, radiation, poor ventilation, and inadequate layout.

4. Other factors: inappropriate design of boilers/heaters, reactors, tanks, pressure vessels, mixing machines, line and adjacent equipment, pumps and compressors, safety relief systems and so on [2,5].

Reaction mechanisms of 4-tertiary-butylcatechol (TBC) of various concentrations can effectively inhibit the exothermic onset temperature ( $T_0$ ) of styrene [4]. Inhibition behavior by TBC is described as follows. TBC scavenges radicals produced from decomposition of the styrene dimer to generate a conjugationally stabilized radical. Finally, TBC yields a di-radical and is deprived of its inhibition effect by reacting with excess radicals, as demonstrated in Fig. 1 [6].

On the other hand, arguments on the initial reaction and reaction order ( $n$ ) for styrene have remained controversial until now. In recent years, scientists and engineers have continuously studied certain initial reactions and reactions on styrene in order to obtain accurate thermokinetic parameters. Aromatic isomer is one order of the key-points for estimating accurate reaction mechanisms. In addition, derivatives may be observed as potential reaction mechanisms during polymerization for styrene. Various derivatives have been studied in experiments to search for possible reaction mechanisms on styrene. After experiments were finished, if a methyl group was sited at the 1st double bond on ethylene of styrene, an initial reaction on styrene polymerization could be successfully observed. Therefore,  $\alpha$ -methylstyrene (AMS) has been demonstrated as a possible polymerization mechanism for styrene, and

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### Nomenclature

$A$	final concentration of styrene (M)
$A_0$	initial concentration of styrene (M)
BP	boiling point ( $^{\circ}\text{C}$ )
$E_a$	apparent activation energy ( $\text{kJ mol}^{-1}$ )
$\Delta H$	heat of reaction ( $\text{J g}^{-1}$ )
$k$	constant of reaction rate ( $\text{s}^{-1} \text{M}^{1-n}$ )
MP	melting point ( $^{\circ}\text{C}$ )
$R$	rate of reaction ( $\text{M s}^{-1}$ )
SADT	self-accelerating decomposition temperature ( $^{\circ}\text{C}$ )
$t$	time (s)
$T_0$	exothermic onset temperature ( $^{\circ}\text{C}$ )
$T_{\text{NR}}$	temperature of no return ( $^{\circ}\text{C}$ )
$T_p$	exothermic peak temperature ( $^{\circ}\text{C}$ )

polymerization mechanisms on styrene, as listed in Table 3, have been clearly observed by AMS thermal curve [7]. Subsequently, if a methyl group was sited at the 2nd double bond on ethylene of styrene [8], reaction mechanisms were not the same as AMS and trans- $\beta$ -methylstyrene (TBMS), as delineated in Figs. 2 and 3. The molecular structure of TBMS was more readily damaged than AMS under low temperatures.

This study aimed to investigate the initial reaction and polymerization mechanisms, and to confirm the reaction order ( $n$ ) and thermokinetic parameters for styrene by AMS and TBMS. A comparison of reaction mechanisms on AMS and TBMS was also conducted. Finally, this study could be applied in the petrochemical industry to avoid accidents from occurring with similar runaway polymerization.

## 2. Materials and methods

### 2.1. Samples

Seven chemical samples, including pure styrene, styrene containing 10 ppm TBC (acquired from Grand Pacific Petrochemical Co., Taiwan), AMS and TBMS (purchased from Sigma–Aldrich), were used for a series of calorimetric experiments.

### 2.2. Differential scanning calorimetry (DSC)

DSC is one of the most popular instruments for determining kinetic equations of thermal polymerization or decomposition. In this study, dynamic screening experiments were conducted on a Mettler TA8000 system coupled with a DSC 821<sup>e</sup> measuring cell, which was a crucible that could withstand high-pressure up to 100 bar. The STAR<sup>e</sup> software functioned to acquire thermal curves and isothermal traces. To reach thermal equilibrium quickly, the scanning rate for the temperature-programmed ramp was set at  $4^{\circ}\text{C min}^{-1}$  [9].

### 2.3. Thermal activity monitor (TAM)

Reactions between 12 and  $90^{\circ}\text{C}$  were investigated with a microcalorimeter under the working temperature range. Temperature was maintained constant (within  $\pm 2 \times 10^{-4}^{\circ}\text{C}$  per day) in order to routinely measure a heat flow within fractions of a  $\mu\text{W}$ . TAM can detect heat flow down to  $\pm 50 \text{ nW}$ , produced or absorbed by a sample system. As planned, measurements on thermal polymerization were conducted isothermally in the temperature range from 50 to  $90^{\circ}\text{C}$  [10].

**Table 1**  
Selected accidents related to styrene and its derivatives in USA, Europe, and Asia since 2001 [3]

Date	Location	Fatalities (F)/injuries (I)	Hazard	Chemical
4 April 2001	Zhejiang, China	0 F/0 I	Leakage	Styrene
17 April 2001 <sup>a</sup>	Shanghai, China	0 F/0 I	Leakage	Styrene
31 August 2001 <sup>a</sup>	Brownsville, TX, USA	0 F/0 I	Fire	Styrene
29 October 2001	Marietta, OH, USA	0 F/0 I	Leakage	Styrene
12 October 2002 <sup>a</sup>	Amite, LA, USA	0 F/0 I	Fire	Styrene
13 February 2003	Hangzhou, China	0 F/0 I	Leakage	Styrene
13 February 2003 <sup>a</sup>	Carling, Ontario, Canada	0 F/0 I	Fire	Styrene
12 March 2003	Yeochon, South Korea	1 F/0 I	Explosion	Styrene
8 April 2004	Jiangsu, China	6 F/8 I	Leakage	Styrene
07 June 2004 <sup>a</sup>	Canada, USA	0 F/0 I	Leakage	Styrene
18 September 2004 <sup>a</sup>	Herrjansdam, Netherlands	0 F/0 I	Fire	Styrene
13 October 2004 <sup>a</sup>	Atlanta, GA, USA	0 F/0 I	Fire	Styrene
16 November 2004	Guangdong, China	0 F/1 I	Leakage	Styrene
30 June 2005 <sup>a</sup>	Shrewsbury, MA, USA	0 F/0 I	Fire	Styrene
05 August 2005 <sup>a</sup>	Troy, OH, USA	0 F/0 F	Fire	Styrene
09 August 2005 <sup>a</sup>	Louisville, KY, USA	0 F/0 I	Fire	Styrene
17 August 2005	Guangdong, China	0 F/0 I	Leakage	Styrene
28 August 2005 <sup>a</sup>	Cincinnati, OH, USA	0 F/0 I	Fire	Styrene
28 February 2006	Chilin, China	0 F/0 I	Leakage	AMS

<sup>a</sup> Data from MHIDAS [4].

**Table 2**  
Selected accidents related to styrene and its derivatives in Taiwan since 1998 [5]

Date	Location	Fatalities (F)/injuries (I)	Hazard	Chemical
21 January 1998	Kaoshiung, Taiwan	0 F/4 I	1. Leakage 2. Fire 3. Explosion	Styrene
27 April 1998	Kaoshiung, Taiwan	0 F/0 I	1. Leakage	Styrene
06 October 1999	Chiayi, Taiwan	0 F/1 I	1. Explosion	Styrene
15 August 2001	Yunlin, Taiwan	0 F/1 I	1. Tank lorry accident	Styrene
17 May 2005	Kaoshiung, Taiwan	0 F/1 I	1. Leakage	Styrene

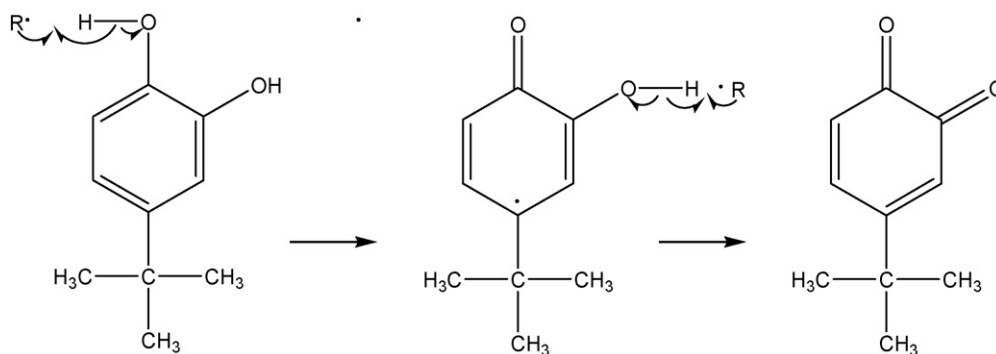


Fig. 1. The flowchart for inhibition behavior by TBC [6].

**Table 3**  
The structure formula and characteristics of styrene, AMS and TBMS [7]

Chemical	Structure formula	BP range (°C)	MP range (°C)	Flash point (closed cup) (°C(°F))	Explosion limits (vol.%)	Auto ignition temperature (°C)	CAS #
SM		145	-33	31 (87.8)	1.1–7.0	490	100-42-5
AMS		164–168	-24	46 (114.8)	0.9–6.1	574	98-83-9
TBMS		178–180	NA	52 (125.6)	0.9–NA	NA	873-66-5

Remarks: NA indicates “Not Applicable”.

### 3. Results and discussion

#### 3.1. Dynamic scanning tests

First, dynamic scanning tests were performed with styrene to thoroughly observe the exothermic behavior by DSC. Fig. 3 indicates

that an enormous exothermic peak for styrene can be observed during polymerization. A standard thermal curve of styrene by DSC could obtain basic thermodynamic data, such as exothermic onset temperature ( $T_0$ : 103.31 °C), exothermic peak temperature ( $T_p$ : 205.81 °C), and reaction heat ( $\Delta H$ : 601.73 Jg<sup>-1</sup>), which well agreed with the literature [1]. Thermokinetic parameters can also

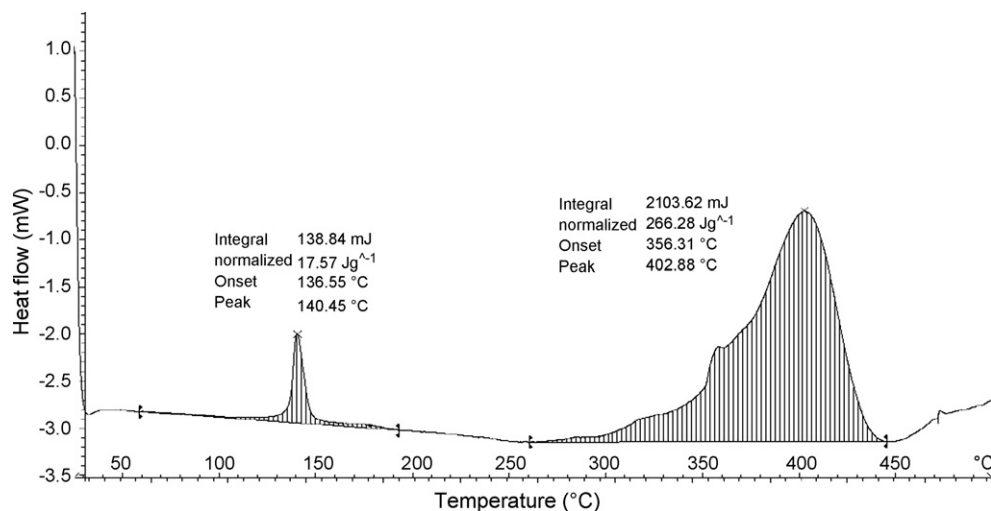


Fig. 2. Dimerization and thermal polymerization curve of AMS by DSC test.

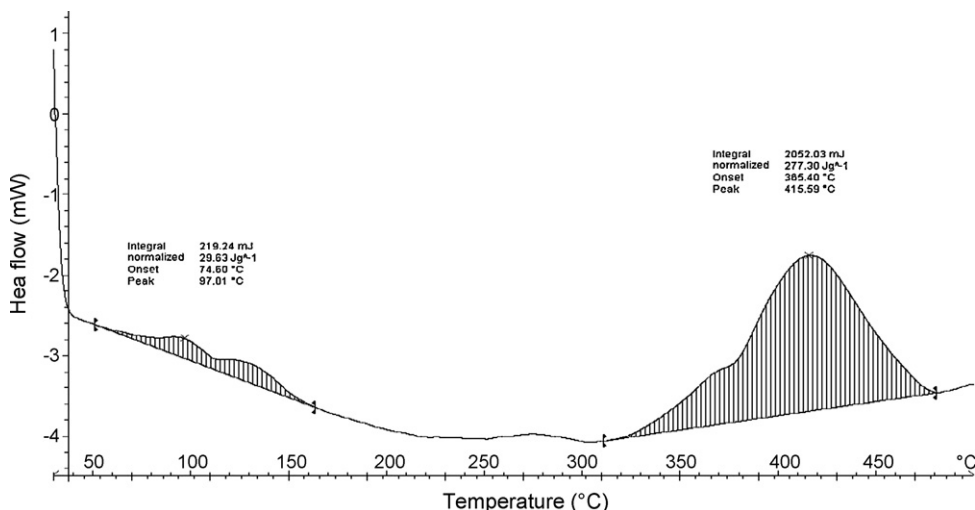


Fig. 3. Thermal polymerization curve of TBMS by DSC test.

be effectively estimated and polymerization mechanisms identified from dynamic scanning data. In accordance with previous literature, styrene has four reaction processes: initiation, propagation, chain transfer reaction, and termination under temperature ranges of 40–400 °C [11], as depicted in Fig. 3.

Because it possesses extremely high thermal hazard during manufacturing, transportation, storage, disposal, and so on, styrene containing various inhibitor concentrations has gradually replaced uninhibited styrene to lessen the system risk from any thermal hazard. Wei and Shu reported, by TAM, that thermal curves were 134, 139, 146, and 154 °C on styrene containing 10 and 20 ppm TBC, respectively. Styrene containing 10 and 20 ppm TBC could enhance both the SADT (44.8 and 56.5 °C) and  $T_{NR}$  (61.6 and 75.4 °C) on a 55 gal drum during transportation and storage from SADT (40.1 °C) and  $T_{NR}$  (54.3 °C), respectively [4].

From Fig. 2, two exothermic peaks, dimerization and thermal polymerization, could be successfully separated from AMS under a temperature range of 25–500 °C. The  $T_0$  (136.5 and 356.31 °C),  $T_p$  (140.45 and 402.88 °C), and  $\Delta H$  (17.57 and 266.28 Jg<sup>-1</sup>) have an extremely large difference between the 1st and 2nd peaks in the thermal curve. The pathways of dimerization and thermal polymerization formation on AMS shown are as follows:

1. Initiation: first, two monomers undergo a Diels–Alder reaction to form a dimer under heated environment. Because the structure on a dimer is very unstable under dynamic conditions, a dimer undergoes a Retro–Diels–Alder reaction to decompose two monomers again.
2. Propagation: followed by Diels–Alder and Retro–Diels–Alder reactions (Fig. 4) [12], all monomers carry out the next step with external thermal source.
3. Chain transfer reaction: all monomers undergo a free-radical reaction to generate unsaturated dimers, saturated dimers, and trimers during thermal polymerization. Since the structure of saturated dimers is very unstable, it gradually decomposes to monomers and combines unsaturated dimers.

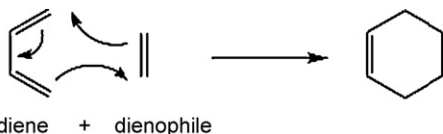


Fig. 4. Diels–Alder and Retro–Diels–Alder reactions [12].

4. Termination: finally, all monomers and unsaturated dimers synthesize to yield a high molecular polymer.

Furthermore, the differences in thermodynamic data ( $T_0$ ,  $T_p$ , and  $\Delta H$ ) and polymerization mechanisms for AMS and TBMS were compared by DSC. From Fig. 6, two exothermic peaks could be successfully separated from TBMS under the temperature range from 25 to 500 °C. In addition, the thermodynamic data ( $T_0$ ,  $T_p$ , and  $\Delta H$ ) and polymerization mechanisms were very close. Fig. 5 reveals the differences in the thermal curves of styrene (without TBC), styrene (with 10 ppm TBC), AMS, and TBMS under dynamic scanning conditions. The initial reaction on styrene has been demonstrated by dimerization and thermal polymerization on AMS and TBMS. Through this study and previous literature [13,14], calorimetric analysis can corroborate that styrene will undergo Diels–Alder and Retro–Diels–Alder reactions to carry out further reaction.

### 3.2. Isothermal ageing tests

Through this study, accurate thermokinetic parameters were obtained by isothermal ageing tests on TAM. First, this study applied different isothermal times (0.00–2.01 days) to carry out oven tests, and measured  $\Delta H$  by dynamic scanning tests on DSC. The  $\Delta H$  is linearly proportional to the concentration changes. From previous

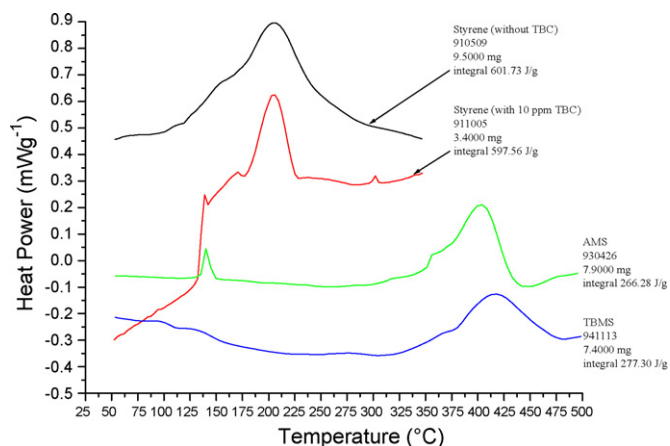


Fig. 5. Comparisons of dimerization and thermal polymerization curves of styrene, AMS, and TBMS by DSC tests.

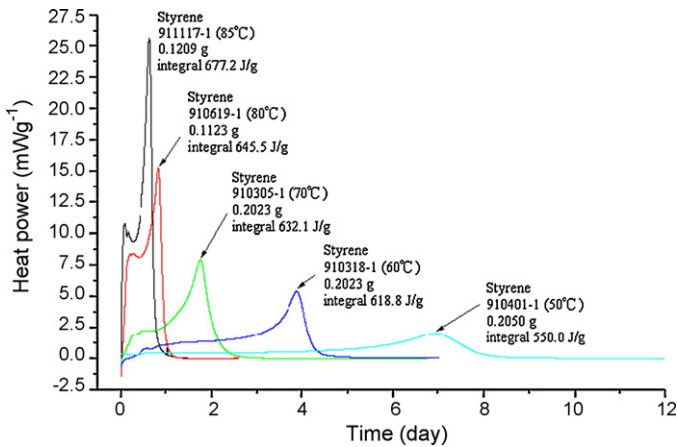


Fig. 6. Heat power vs. time for polymerization of 99 mass% styrene under by TAM various isothermal conditions.

studies [15–17], the reaction order was recognized as 2.5 for styrene during polymerization:

$$R = \frac{d[A]}{dt} = -k[A]^{2.5} \quad (1)$$

$$-\frac{2}{3}([A]^{-3/2} - [A_0]^{-3/2}) = -kt \quad (2)$$

According to the above equations, the rate constant ( $k$ :  $7.16 \times 10^{-7} \text{ s}^{-1}$ ) was determined by plotting  $-(2/3)\{[A]^{-3/2} - [A_0]^{-3/2}\} = -kt$  against time. Different isothermal temperatures can also be employed to obtain the apparent activation energy ( $E_a$ : about  $84 \text{ kJ mol}^{-1}$ ) by TAM, as disclosed in Fig. 6. From the above parameters, the frequency factor ( $A$ :  $4.76 \times 10^6 \text{ s}^{-1}$ ) can be obtained by the Arrhenius equation.

Isothermal calorimeters can be used to investigate whether a reaction is autocatalytic or  $n$ th-order kinetics. The thermal curves of AMS that reacted in the TAM at five different temperatures (70, 75, 80, 85 and  $90^\circ\text{C}$ ) were recorded and demonstrated in Fig. 7. The experimental results indicated that AMS belongs to autocatalytic reaction under low temperature ( $70\text{--}90^\circ\text{C}$ ); TBMS is ascribed as an  $n$ th-order reaction under low temperature (50 and  $90^\circ\text{C}$ ), as delineated in Fig. 8. By TAM, various isothermal ageing tests at  $85^\circ\text{C}$  can be observed and compared for styrene, AMS, and TBMS, as depicted in Fig. 9.

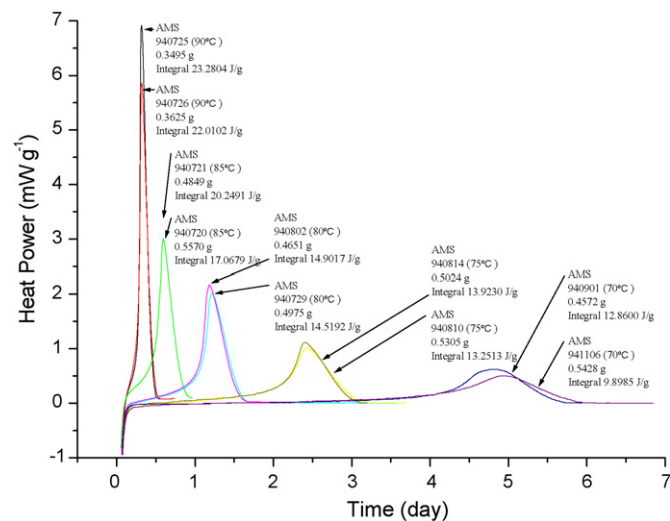


Fig. 7. Heat power vs. time for polymerization of 99 mass% AMS by TAM under various isothermal conditions.

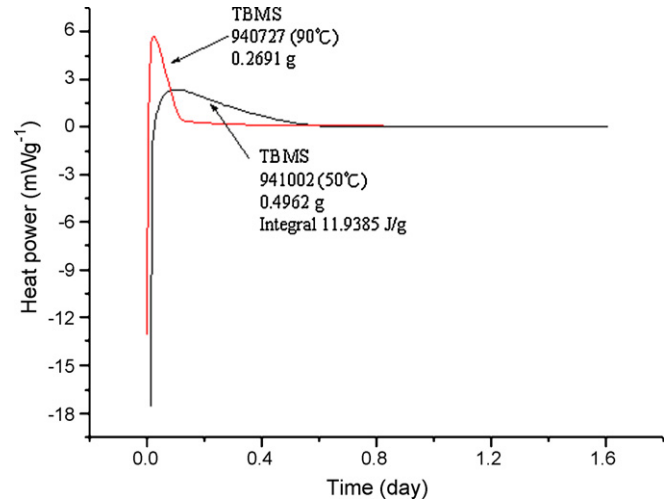


Fig. 8. Heat power vs. time for polymerization of 99 mass% TBMS by TAM under two 50 and  $90^\circ\text{C}$  conditions.

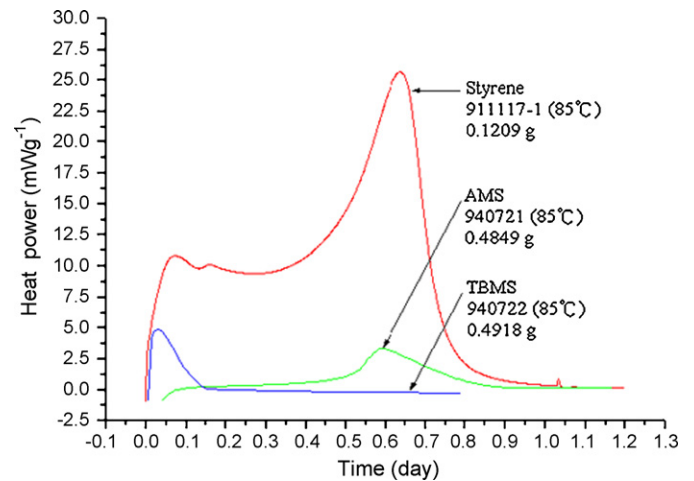


Fig. 9. Comparisons of heat power vs. time for polymerization of 99 mass% styrene, AMS, and TBMS by TAM under the same isothermal conditions ( $85^\circ\text{C}$ ).

#### 4. Conclusions

Through this study, we readily and meticulously obtained polymerization mechanisms and thermokinetic parameters for styrene. We carefully investigated the exothermic behavior of styrene and its major derivatives (AMS and TBMS) by calorimetric experiments. Similarly, this study can be applied to various reactive monomers or peroxides to identify the mechanism alteration and evaluate the degree of hazard during transportation and storage, if perturbed situations occur.

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