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THERMOKINETICS EVALUATION AND SIMULATIONS FOR THE POLYMERIZATION OF STYRENE IN THE PRESENCE OF VARIOUS INHIBITOR CONCENTRATIONS

C. C. Liao[1]*, S. H. Wu*[1]*, T. S. Su*[2]*, M. L. Shyu*[3] *and C. M. Shu*[1*]

[1]Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering,
National Yunlin University of Science and Technology, 123, University Rd., Sec. 3, Touliu, Yunlin, Taiwan 64002, ROC
[2]Department of Safety, Health, and Environmental Engineering, Central Taiwan University of Science and Technology,
11, Buh-Tzyy Alley, Buh-Tzyy Village, Beei-Twen District, Taichung, Taiwan 406, ROC
[3]University of Miami, Coral Gables, FL 33124, USA

Styrene is an important commodity chemical that is globally applied in various polymerization processes. The aim of this study was to obtain integrated thermokinetics and safety parameters for polymerization of styrene. We mainly used differential scanning calorimetry (DSC), thermal activity monitor (TAM), and simulative methods to investigate thermal polymerization of styrene and styrene containing various levels of 4-*tertiary*-butylcatechol (TBC). The results obtained included the rate constant (k), reaction order (n), apparent activation energy (E_a), frequency factor (A), and so on, from various DSC curves and simulative methods. From DSC curves, the exothermic onset temperature (T_0) was about 105 and 132°C for styrene and styrene containing 10 ppm TBC. On the other hand, the test results from TAM indicated that styrene polymerization displays an autocatalytic phenomenon from 50–85°C. By means of this study, the intrinsic safety of a system for styrene during transportation and storage could be established.

Keywords: *DSC, styrene, TAM, TBC, thermal polymerization*

Introduction

Since its discovery in the eighteenth century, the commercial value of styrene has dramatically increased [1]. In the USA, Europe, and Asia, styrene is widely applied to produce homopoly(styrene), styrene-butadiene rubber (SBR), elastomer, acrylonitrile-butadiene-styrene (ABS) terpolymer, unsaturated polyesters (UP), emulsion polymers (EP), styrene-acrylonitrile (SAN) copolymer, and so on [2]. However, because of a lack of understanding of chemical reactivities, inadequate engineering designs, control systems, operating procedures, and practices for styrene [3], there have been sporadic releases, runaway reactions, fire, and thermal explosion accidents from 1994 to 2005, as shown in Tables 1 and 2 [4, 5]. As can be seen from Table 2, on July 27, 1997 in Kaoshiung, a total of six silos that contained fine powders (SAN and ABS powders) exploded sequentially. This was an emergence of the bulked brush discharging which resulted in a severe dust explosion in the silos area of an ABS plant. All the top plates and bag-filters of the silos flew away in various directions [6].

This study mainly investigated the polymerization behavior of both styrene and styrene containing various levels of 4-*tertiary*-butylcatechol (TBC) (10, 20, 40 and 50 ppm), and combined with practical processes in the petrochemical industries [7].

In theory, thermal polymerization of styrene is based on the following steps. First, ethylenic double bonds disappear and then bulked heat is released. Finally, there is an increase of density from monomer to polymer [1]. In essence, styrene is extremely unstable during transportation and storage if the system is handled under higher temperatures [8]. Normally, inhibitor, TBC, is used for styrene, butadiene, vinyl chloride, chloroprene, and other polymerizable monomers. Polymerization inhibition behavior by TBC is ascribed 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 loses its inhibition effect by reaction with excess radicals [9].

Primarily, this study was to investigate the kinetic behavior of polymerization for styrene in both the absence and presence of inhibitor under temperatures ranging from 50 to 85°C by differential scanning calorimetry (DSC) and simulative methods using ChemInform Saint Petersburg (CISP) software [10]. Experimental results from DSC showed that the polymerization exothermic onset temperature (T_0) was about 105 and 132°C for styrene and styrene containing 10 ppm TBC. Previous studies have

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[*] Author for correspondence: shucm@yuntech.edu.tw

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Table 1 Selected accidents related to styrene and its derivatives in USA, Europe and Asia since 1998 [4]

Date	Location	Fatalities	Injuries	Hazard	Chemical(s)
06/27/1998	Channahol, Illinois, USA	0	1	1. leakage	1. ethylbenzene 2. styrene
06/23/1999	Pasadena, Texas, USA	2	4	1. fire 2. explosion	1. styrene 2. butadiene
07/25/1999	Hong Kong, China	0	0	1. explosion	1. styrene 2. trichloroethylene
09/13/1999	Newton, Massachusetts, USA	0	22	1. leakage	1. styrene
02/05/2000	Hong Kong, China	0	0	1. leakage	1. styrene
03/14/2000	Fredericton, New Brunswick, Canada	0	0	1. leakage	1. alcohol 2. styrene
03/27/2000	Pasadena, Texas, USA	1	71	1. leakage 2. fire 3. explosion	1. butadiene 2. cyclohexane 3. styrene
10/31/2000	Channel Islands, France	0	0	1. leakage	1. isopropyl alcohol 2. methyl ethyl ketone 3. styrene
04/04/2001	Zhejiang, China	0	0	1. leakage	1. styrene
04/17/2001	Shanghai, China	0	0	1. leakage	1. styrene
10/29/2001	Marietta, Ohio, USA	0	0	1. leakage	1. styrene
02/13/2003	Hangzhou, China	0	0	1. leakage	1. styrene
03/12/2003	Yeochon, South Korea	1	0	1. explosion	1. styrene
04/08/2004	Jiangsu, China	6	8	1. leakage	1. styrene
06/07/2004	Canada, USA	0	0	1. leakage	1. styrene

Table 2 Selected accidents related to styrene and its derivatives in Taiwan since 1994 [4]

Date	Location	Fatalities	Injuries	Hazard	Chemical(s)
05/07/1994	Kaoshiung, Taiwan	1	0	1. explosion 2. fire	1. styrene
05/16/1994	Miaoli, Taiwan	0	0	1. leakage	1. acrylonitrile
07/08/1995	Kaoshiung, Taiwan	0	0	1. fire	1. polystyrene
01/26/1996	Chiayi, Taiwan	1	0	1. explosion	1. ABS terpolymer
07/27/1997	Kaoshiung, Taiwan	0	0	1. explosion	1. ABS terpolymer
01/21/1998	Kaoshiung, Taiwan	0	4	1. leakage 2. fire 3. explosion	1. styrene
04/27/1998	Kaoshiung, Taiwan	0	0	1. leakage	1. styrene
10/06/1999	Chiayi, Taiwan	0	1	1. explosion	1. styrene
08/15/2001	Yunlin, Taiwan	0	1	1. tank lorry accident	1. styrene
05/17/2005	Kaoshiung, Taiwan	0	1	1. leakage	1. styrene

indicated that styrene polymerization displays an autocatalytic phenomenon at lower temperatures, 50 to 85°C, as determined by a thermal activity monitor (TAM) [11]. In this study, an evaluation of the thermokinetics and safety parameters for styrene polymerization was conducted by using both experimental and simulative methods [12].

Experimental

Samples

Styrene (99.7 mass%) and styrene containing inhibitor (10, 20, 40 and 50 ppm TBC) were acquired from Sigma-Aldrich and then stored at 4°C in a refrigerator.

DSC

To establish the kinetic parameters for the polymerization, dynamic DSC screening experiments were performed using a Mettler TA8000 system coupled with a model 821^e cell that can withstand relatively high-pressure (100 bar); STAR^e software was installed for acquiring curves and isothermal traces. From thermal equilibrium, the scanning rate for the temperature-programmed ramp was chosen to be 4°C min^{-1} [13–15].

TAM

Basically, reactions can be investigated between 12 and 90°C in the working temperature range of the TAM microcalorimeter. Constant temperature is maintained within $\pm 2\cdot 10^{-4}$°C per day, which allows heat flow in fractions of a μW to be measured routinely. TAM is capable of detecting quite small heat flow, ±50 nW produced or absorbed by a sample system. As planned, measurements on the thermal polymerization were conducted isothermally in the desired temperature range from 50 to 85°C [16].

Calculations and applications of safety parameters

The corresponding mathematical model is represented by Eqs (1) to (3) as follows:

$$r_1 = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_0(T)(1-\alpha)^{n_1}(z+\alpha^{n_2}) \qquad (1)$$

$$r_2 = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_0(T)(1-\alpha)^{n_1} \qquad (2)$$

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \sum_{i=1}^{2} Q_i^{\infty} r_i \qquad (3)$$

where α_1 and α_2 are the conversion degree of A and B$_1$, respectively; r_i and Q_i^{∞} denote the reaction rate and heat effect of the *i* stage (*i*=1 and 2); d*Q*/d*t* is the overall rate of heat generation. In addition, $k_i(T)$ was from the Arrhenius law as Eq. (4):

$$k_i(T)=A_{0i}\exp(-E_{ai}/RT) \qquad (4)$$

where A_{0i}, E_{ai} and R are the frequency factor, activation energy of the *i* stage, and gas constant (8.314 J mol^{-1} K^{-1}), respectively.

For the estimation of safety parameters or hazard classifications, the temperature of no return (T_{NR}), self-accelerating decomposition temperature (SADT), and time to maximum reaction rate (TMR) are three important parameters. These parameters have been acquired to evaluate the related reaction hazards [17, 18].

Definition of safety parameters

Temperature of no return (T_{NR})

Temperature of no return, T_{NR}, can be calculated via the relationship between heat generation rate and heat removal rate [19]. It may, in turn, be applied to design a cooling system and to inform fire fighters of how much time remains to implement a rescue action [19]. When the maximum self-heating rate compared with the time constant is the same in the system, then the temperature will rise to T_{NR}. The following equations were used to compute the T_{NR}.

$$(T_{NR}+273.15)^2 = \frac{mE_a\Delta Hk}{RU(1.8)a} \qquad (5)$$

$$(T_{NR}+273.15)^2 = \frac{mE_a\Delta HA\mathrm{e}^{-E_a/R(T_{NR}+273.15)}}{RU(1.8)a} \qquad (6)$$

Self–accelerating decomposition temperature (SADT)

Self-accelerating decomposition temperature, SADT, is used to estimate whether temperature needs to be controlled during transportation and storage stages [18]. According to NFPA 43B, a self-reactive substance must be subjected to temperature control during transportation if its SADT is less than or equal to 55°C [20]. Using a previously described method to transform Eq. (3) and then substituting the T_{NR} into Eq. (7), the SADT can be obtained.

$$\mathrm{SADT} = T_{NR} - \frac{R(T_{NR}+273.15)^2}{E_a} \qquad (7)$$

Time to maximum rate (TMR)

Normally, TMR is adopted to investigate the degree of safety, perniciousness, and so on. TMR provides an indication of how imminent the reaction is a specific time for a reaction to occur approaches. Calculating the TMR for a runaway reaction can provide firefighters information about how much time remains to salvage, or instruct workers on how to curtail the degree of hazard. Equation (8) was used to compute the TMR:

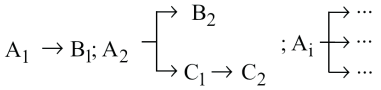
$$\mathrm{TMR} = \frac{RT^2}{AE_a\Delta T_{ad}}\mathrm{e}^{-E_a/RT} \qquad (8)$$

$$\Delta T_{ad} = \frac{Q}{C_p} \qquad (9)$$

Simulative methods

Kinetics models

Formal models can represent complex multi-stage reactions that may consist of several independent, parallel and consecutive stages [19].



Formal models

In general, there are three kinds of reaction mechanisms which could be expressed as follows:

- Simple single-stage reaction

$$A\rightarrow B$$

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} f(\alpha) \tag{10}$$

where α is the conversion of the reactant A

$$f(\alpha) = \begin{cases} (1-\alpha)^n & - n^{th} \text{ order reaction} \\ (1-\alpha)^{n_1}(\alpha^{n_2} + z) & - \text{autocatalytic reaction} \end{cases}$$

- Reaction including two consecutive stages

$$A\rightarrow B\rightarrow C$$

$$\begin{aligned} \frac{d\alpha}{dt} &= Ae^{-E_{a1}/RT}(1-\alpha)^{n_1}; \\ \frac{d\gamma}{dt} &= A_2 e^{-E_{a2}/RT}(\alpha-\gamma)^{n_2} \end{aligned} \tag{11}$$

where α and γ are conversions of the reactant A and product C, respectively.

- Two parallel reactions

$$A\rightarrow B+\ldots \text{ – initiation stage}$$

$$A+B\rightarrow 2B+\ldots \text{ – autocatalytic reaction}$$

The above equations represent a very useful model for full autocatalysis:

$$\frac{d\alpha}{dt} = K_1(\alpha) + K_2(\alpha) \tag{12}$$

$$K_1(\alpha) = k_1(T)(1-\alpha)^{n_1} \tag{13}$$

$$K_2(\alpha) = k_2(T)\alpha^{n_2}(1-\alpha)^{n_3} \tag{14}$$

Results and discussion

The 1st and 2nd exothermic peaks for reaction of pure styrene and inhibited styrene solutions (10, 20, 40 and 50 ppm TBC) by DSC and simulative methods are displayed in Tables 3–6.

The isothermal ageing tests, dynamic scanning tests, and computer simulations for styrene, both inhibited and uninhibited (10, 20, 40 and 50 ppm TBC) by TAM, DSC and simulative methods, respectively, are illustrated in Figs 1–6.

Thermal analysis

Figure 1 reveals the exothermic phenomena for styrene reaction under various isothermal conditions from ageing tests by TAM. Various exothermic phenomena can be observed at low temperatures, 50–85°C. Experimental results showed the reaction time (15.0, 7.0, 3.0 and 1.6 days), time to peak (7.8, 3.8, 1.7 and 0.8 days), and Δ*H* of peak (550.0, 618.8, 632.1 and 645.5 J g^{-1}) at lower temperatures, 50, 60, 70 and 80°C, respectively. From the curves, the temperature was found to be linearly proportional to the heat power, but inversely proportional to the reaction time. From this study, the thermal hazard of styrene during transportation and storage stages could be evaluated.

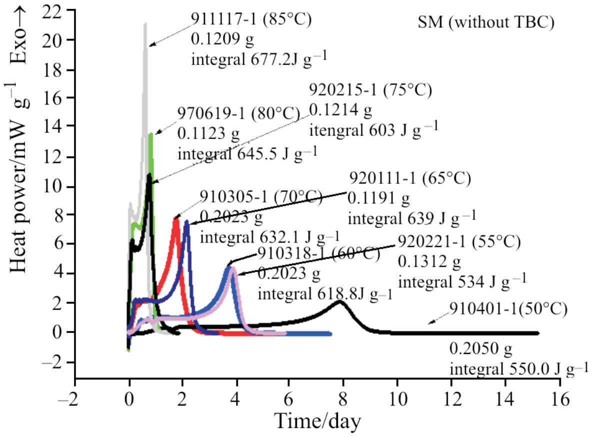


Fig. 1 Isothermal ageing tests for styrene at various temperatures, 50 to 85°C, by TAM

Previous studies have shown that styrene has a self-accelerating polymerization reaction at lower temperature about 50–85°C; another follows an n^{th} order reaction at higher temperature (above 120°C) [21]. T_0 alleviate the degree of reaction hazard, the TBC concentration was varied regularly to assess the impact of inhibitor on styrene polymerization. In addition, DSC was used to investigate, under scanning conditions, the reaction of both uninhibited and inhibited styrene. Figure 2 demonstrates the exothermic phenomena for uninhibited and inhibited styrene (10, 20, 40 and 50 ppm) under a temperature range of 50–350°C. From dynamic scanning by DSC, the exothermic onset temperatures were 104, 134, 139, 146 and 154°C of styrene and inhibited ones (10, 20, 40 and 50 ppm), respectively. In the temperature range of 50–350°C, styrene with 10 ppm TBC had a delay phenomenon in which

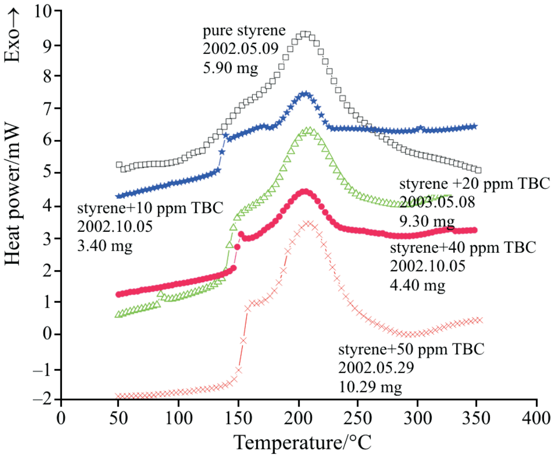


Fig. 2 Dynamic scanning tests for both uninhibited and inhibited styrene (10, 20, 40 and 50 ppm TBC) polymerization by DSC with scanning rate of 4°C $\min^{-1}$

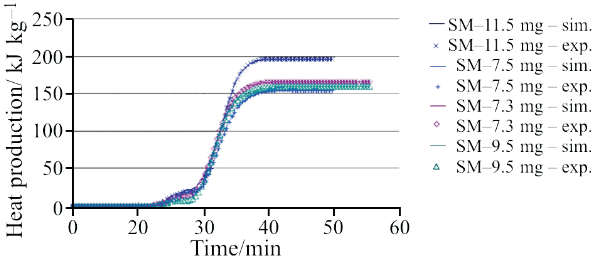


Fig. 3 Heat production *vs*. time from simulative and experimental data by TAM on thermal polymerization of styrene

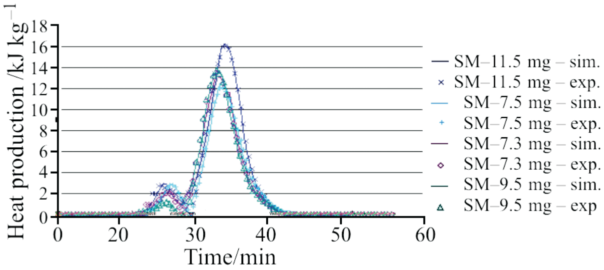


Fig. 4 Heat production *vs*. time from simulative and experimental data by TAM on the thermal polymerization of styrene

the exothermic onset temperature is higher than 30°C of styrene, as well as other inhibitor concentrations (20, 40 and 50 ppm). Furthermore, through the fitting based upon autocatalytic and n^{th} order reaction of styrene from Fig. 2, we calculated the related thermokinetic and safety parameters by simulative methods, as given in Tables 3 and 4.

In Figs 3–6 and Tables 3–6, the solid line represents the simulative data and the dotted one is the DSC test data. Figures 4–6 delineate exothermic phenomena in initial reaction, and there was a large amount of heat production before the end of the initial reaction. Figure 4 shows that the polymerization behavior (2$^{\mathrm{nd}}$ peak) appeared later than (about 25 min) the heat generation (1$^{\mathrm{st}}$ peak). In Fig. 6, there was a valley between the two peaks, and the heat production of inhibited styrene at the 1$^{\mathrm{st}}$ peak is higher than in Fig. 4. Because of inhibitor effect, the activation energy (E_{a}) demonstrated significant influences at the first reaction, whereas the 2$^{\mathrm{nd}}$ peak did not have a prominent change. As a result, T_0 increased after dosing inhibitor that could enhance process safety, because of delay of runaway reaction, during storage and transportation stages.

Kinetics evaluation

From Fig. 2, we can see that the dynamic scanning curve consisted of two exothermic peaks. The polymerization behavior of styrene described by a model of complete reaction could be clearly expressed as follows:

$$A \xrightarrow{\alpha_1} B_1 \ (1^{\mathrm{st}}\ \text{peak}) \qquad (15)$$

Table 3 Thermokinetics and safety parameters derived from an autocatalytic polymerization of styrene from dynamic scanning tests by DSC (the 1$^{\mathrm{st}}$ exothermic peak)

Styrene	Parameters						
	m/mg	E_{a}/kJ mol^{-1}	T_0/°C	n_1	n_2	T_{NR}/°C	SADT/°C
pure styrene 30-350-4	7.5	161.0	103.6	1.4	0.3	49.0	38.2
	11.5	156.8	106.7	1.4	0.3	45.0	38.4
pure styrene 35-400-4	7.3	156.7	104.6	1.4	0.3	51.0	38.1
	9.5	157.3	103.9	1.5	0.3	66.0	37.4

Table 4 Thermokinetics and safety parameters derived from an n^{th} order polymerization of styrene from dynamic scanning tests by DSC (the 2$^{\mathrm{nd}}$ exothermic peak)

Styrene	Parameters				
	m/mg	n_1	k_0	E_{a}/kJ mol^{-1}	$T_{\max}$/°C
pure styrene 30-350-4	7.5	1.9	33.6	157.0	208.2
	11.5	1.8	33.6	157.0	212.3
pure styrene 35-400-4	7.3	2.0	33.3	154.6	208.6
	9.5	2.0	32.6	152.0	207.5

Table 5 Thermokinetics and safety parameters derived from an autocatalytic polymerization of inhibited styrene (10, 20, 40 and 50 ppm TBC) from dynamic scanning tests by DSC (the 1st exothermic peak)

Styrene	Parameters						
	m/mg	E_a/kJ mol^{-1}	T_0/°C	n_1	n_2	T_{NR}/°C	SADT/°C
styrene+TBC10 ppm	9.2	157.4	132.3	1.8	0.5	67.0	37.4
styrene+TBC20 ppm	9.3	161.8	138.9	1.9	0.5	71.0	37.2
styrene+TBC40 ppm	4.4	162.5	145.5	1.7	0.6	82.0	36.7
styrene+TBC50 ppm	10.3	163.3	149.6	1.8	0.6	86.0	36.5

Table 6 Thermokinetics and safety parameters derived from an n^{th} order polymerization of inhibited styrene (10, 20, 40 and 50 ppm TBC) from dynamic scanning tests by DSC (the 2nd exothermic peak)

Styrene	Parameters				
	m/mg	n_1	k_0	E_a/kJ mol^{-1}	T_{max}/°C
styrene+TBC10 ppm	9.2	1.5	32.3	151.0	203.3
styrene+TBC20 ppm	9.3	1.6	32.8	153.3	203.9
styrene+TBC40 ppm	4.4	1.4	34.2	157.7	203.1
styrene+TBC50 ppm	10.3	1.5	34.4	160.8	204.5

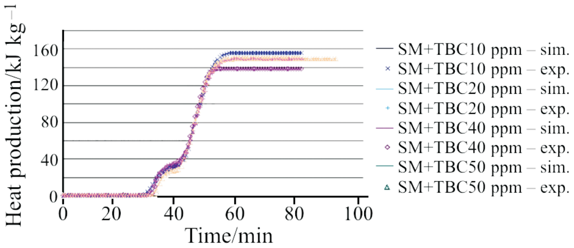


Fig. 5 Heat production *vs*. time from simulative and experimental data by TAM on thermal polymerization of inhibited styrene (10, 20, 40 and 50 ppm TBC)

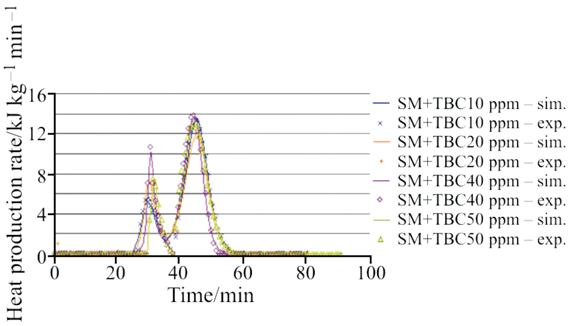


Fig. 6 Heat production *vs*. time from simulative and experimental data by TAM on thermal polymerization of inhibited styrene (10, 20, 40 and 50 ppm TBC)

$$\mathrm{B}_1 \xrightarrow{\alpha_2} \mathrm{B}\ (2^{nd}\ \text{peak}) \qquad (16)$$

where the 1st peak was a single reaction belonging to an autocatalytic phenomenon; correspondingly, the 2nd one was an n^{th} order reaction. In the 1st peak, A was an initiator agent which induced the propagation B_1, and then formed the 2nd peak B (the biggest peak); finally, the polymerization was carried out to termination.

Safety parameters

To ensure chemical safety during storage and transportation, two important parameters, T_{NR} and SADT, play crucial roles. In previous theories, Townsend [17] and Fisher [18] have evaluated the related reaction hazards and acquired these parameters. In theory, T_{NR} can be calculated via the relationship between heat generating rate and heat removing rate, and then be used to design a cooling system and to inform firefighters on how much time is remaining for conducting a rescue. In contrast to T_{NR}, SADT is used to determine whether temperature needs to be controlled during transportation or not. SADT is defined as the lowest ambient air temperature at which a self-reactive substance of specified stability (contaminant level, inhibitor concentration, and so on) undergoes an exothermic reaction in a specified commercial package in a period of seven days or less [18]. According to NFPA 30, a self-reactive substance should be subjected to temperature control during transportation if its SADT is equal to or less than 55°C [8].

$$(T_{NR}+273.15)^2 = \frac{mE_a\Delta HA\exp\left[-\dfrac{E_a}{R(T_{NR}+273.15)}\right]}{RU1.8a} \qquad (17)$$

$$\mathrm{SADT} = T_{NR} - \frac{R(T_{NR}+273.15)^2}{E_a} \qquad (18)$$

Subsequently, we integrated all parameters and carried out T_{NR} and SADT calculation.

$$(T_{\mathrm{NR}}+273.15)^2=\frac{150.880\cdot 43.290\cdot 634.95\cdot 4.420\cdot 10^4 \mathrm{e}^{-\frac{43.290}{8.314(T_{\mathrm{NR}}+273.15)}}}{8.314\cdot 11.34\cdot 1.8\cdot 1.51} \tag{19}$$

By means of safety parameters of T_{NR} and SADT, the system with styrene could avoid the occurrence of the related runaway accidents and effectively promote process safety in petrochemical industries. For instance, the above case has reached T_{NR}=49°C and SADT=38.2°C.

Conclusions

From dynamic scanning tests by DSC, it has been shown that styrene and inhibited styrene (10 ppm TBC) displays T_0 at 104 and 134°C, respectively. It was found that T_0 and T_{NR} were linearly proportional to the increase in TBC concentration. From dynamic scanning and isothermal ageing tests by DSC and TAM, it was demonstrated that polymerization of both uninhibited and inhibited styrene, in the temperature range above 120°C, followed an n^{th} order reaction model. It followed an autocatalytic model from 50 to 85°C. As far as process safety design is concerned, thermal curves from a weakly exothermic reaction can be used to assess thermal runaway of reactive chemicals and estimate safety parameters, such as T_{NR}, SADT and TMR. By increasing TBC concentration, any system containing styrene can enhance its safety, or at least prolong its T_0, during storage and transportation. Finally, the acquired parameters can be provided to proactively prevent the system from unexpected accidents at low temperature environments during various upsets.

Nomenclature

A	frequency factor [$\mathrm{s}^{-1}\ \mathrm{M}^{1-n}$]
A_2	frequency factor [$\mathrm{s}^{-1}\ \mathrm{M}^{1-n}$]
a	vessel wetted surface area [m^2]
C_p	specific heat capacity [$\mathrm{J\ g^{-1}\ K^{-1}}$]
E_a	apparent activation energy [$\mathrm{kJ\ mol^{-1}}$]
k	rate constant [$\mathrm{s}^{-1}\ \mathrm{M}^{1-n}$]
K_i	rate of at stage i
m	mass of reactant [g]
n	reaction order, dimensionless
Q	calorific capacity [$\mathrm{J\ g^{-1}}$]
R	gas constant [$8.314\ \mathrm{J\ mol^{-1}K^{-1}}$]
SADT	self-accelerating decomposition temperature [°C]
T	temperature [°C]
T_0	exothermic onset temperature [°C]
$T_{\max}$	maximum temperature during overall reaction [°C]
TMR	time to maximum rate [min], [h], [day]
T_{NR}	temperature of no return [°C]
t	time [min, day]
U	heat transfer coefficient [$\mathrm{kJ\ min^{-1}\ m^{-2}\ K^{-1}}$]
ΔH	heat of reaction [$\mathrm{J\ g^{-1}}$]
ΔT_{ad}	adiabatic temperature rise [°C]
α	degree of conversion, dimensionless
γ	degree of conversion, dimensionless
z	auto catalytic constant

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