Thermal hazard analysis of styrene monomer at Low temperature conditions during storage and transportation

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Abstract

Styrene Monomer (SM) has been widely used for producing polystyrene (PS), acrylonitrile-butadiene-styrene (ABS) and styrene-acryonitrile (SAN) in the petrochemical industry. From 1994 to 2001, several serious accidents occurred in Taiwan due to styrene monomer's inherent instability, deviation of operation and others. In this research, thermal polymerization under low temperature is characterized by an isothermal microcalorimeter, thermal activity monitor (TAM). Thermograms show that an autocatalytic reaction occurs in the temperature range from 50℃ to 80℃. In addition, the exothermic kinetics is also investigated. Such weakly exothermic phenomena could not be detected by traditional calorimeters such as differential scanning calorimeters (DSC) and vent sizing package (VSP) because of the tiny signal level. Heat of thermal polymerization was determined to be 670±11 KJmol^{-1}; activation energy was also evaluated to be 63±3 KJmol^{-1} by Arrhenius plot.

Keywords: Styrene Monomer (SM), Thermal Activity Monitor (TAM), Autocatalytic Reaction, Thermal Polymerization, Activation Energy.

Introduction

Styrene monomer (SM) has been widely used in the petrochemical industry for producing acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), styrene-acrylonitrile (SAN) and styrene-butadiene rubber (SBR) in the polymerization process. In recent years, several serious fire and explosion incidents, as shown in Table 1, happened due to thermal instability or deviation in process control.

Since the 1980s, DIERS technology has been developed for vent sizing evaluation to prevent uncontrolled runaway reactions in case of emergency relief. Calorimeters and related technology have also been widely applied in determining the reactivity of SM around the process conditions. For example, 20-80 wt% of an ethylbenzene-styrene solution was used to simulate thermal runaway reaction of polymerization, and based upon experimental data, such as self-heat rate, pressure-rising rate, to evaluate vent sizing (Fauske, E. H., 1985). The experimental data was shown to be in excellent agreement with the previously published kinetic model, which was proposed by Hui and Hamielec in 1972 (Leung, J. C., 1986).

An accident on July 05, 1994 deserves to be mentioned (Table 1). The cause was suspected to be friction igniting a fire in the process area for producing expandable

polystyrene, with the fire extending to the tank yard. Fire fighters put out the fire three times from the beginning to the end, and the investigation report of this accident claimed that the main cause could be attributed to the exothermic property of SM in the burning tank under about 50℃.

The aim of this study was to investigate the thermal and kinetic behaviors of SM in the temperature range from 50℃ to 80℃. Isothermal thermograms acquired from the thermal activity monitor (TAM) showed that the SM in this temperature range will proceed as a slow exothermic reaction and then accelerate in the later reaction stage, similar to an autocatalytic reaction. In 1952 Boundy pointed out that the SM behaves much like an autocatalytic reaction. A temperature increase accelerates the rate of polymerization, which in turn liberates heat and further raises the temperature of the reactant (Boundy, R. H. and R. F. Boyer, 1952).

Table 1. Selected Thermal Explosion Accidents Related to Styrene Monomer in Taiwan since 1994.

Date	Location	Injuries/ Fatalities	Hazard	Cause	Chemical
05/07/1994	Kaoshiung, Taiwan	1/0	Explosion, fire (runaway reaction)	Friction to cause explosion in storage tank	SM, PS
07/08/1995	Kaoshiung, Taiwan	0/0	Fire	Release	PS
01/26/1996	Chia-Yi, Taiwan	1/0	Explosion (flammability gas explosion)	Electrical welding	ABS
07/27/1997	Kaoshiung, Taiwan	0/0	Dust explosion	Static electricity	ABS
01/21/1998	Kaoshiung, Taiwan	0/4	Release, fire, thermal explosion	Truck collision	SM
10/06/1999	Chia-Yi, Taiwan	0/1	Explosion (confined gas explosion)	Sparking to cause explosion	SM
08/15/2001	Yunlin, Taiwan	0/1	No release	Car accident	SM

Previous studies have shown that the onset temperature is 104℃ for uninhibited styrene by the DSC test (Duh, Y. S., 1998); a temperature of 115℃ for inhibited with 15 ppm t-butyl catechol (TBC) was also investigated by using VSP in a 20-80 wt% of ethylbenzene-styrene solution (Leung, J. C., 1986). In this study, for the chosen temperature range, 50℃ to 80℃, TAM can successfully detect a weak exothermic reaction, a signal in comparison to DSC or VSP, which is merely within the noise level. The experimental data, such as heat of reaction, onset temperature and autocatalytic behaviors were compared to the literature.

Results and Discussions
Thermal analysis

There are two methods, dynamic or isothermal, which could offer a rapid and simple approach for the study of reaction kinetics. By using the dynamic method, we determined the heat of polymerization reaction integrated by thermograms to be about

670 $\pm$ 11 Jg^{-1}, as listed in Table 2. Compared to other data from previous studies, heat of polymerization reaction is between 597 to 716 J/g. (Leung, J. M., 1986)(Bond, J., 1985)(Duh, Y. S., 1998)(Grewer, T., 1994) (Odian, G. G., 1991) (Brighton, C. A., 1979)(Ferguson, 1994). The experimental data have good agreement with the results in literature. According to the isothermal method, it can provide thermal equilibrium within the reactant, which can generate more precise kinetics, simple interpretation and simple thermograms observed, because the isothermal method can eliminate thermal lag effects and minimize interference during electric heating (Williams, 1999).

Table 2. Experimental Data of Exothermic Polymerization Reaction of Pure SM Conducted by DSC

Mass (mg)	Ramp (℃ min^{-1})	Onset Temp. (℃)	Polymerization enthalpy (Jg^{-1})	Peak temperature (℃)
7.6	4.0	104.7	655.8	205.8
8.4	4.0	104.8	686.2	205.2
6.8	4.0	105.3	668.5	206.4
11.7	4.0	104.6	670.9	205.9
9.5	4.0	103.6	670.3	205.8

The thermogram shows that 99.7 wt% SM is thermostated in the temperature from 50℃ to 80℃ executed by TAM in Figure 1. In this temperature range, TAM can successfully detect extraordinarily weak exothermic behavior. The slow thermal polymerization reaction took 2 days to 15 days for specific experimental conditions. Peak power of these exothermic curves was from 2.0 to 14 mWg^{-1}, which is almost the noise level of conventional calorimeters, such as DSC or adiabatic calorimeter (VSP). Previous studies have shown that the onset temperature is 104℃ for uninhibited SM by the DSC test (Duh, Y. S., 1998), and a temperature of 115℃ for the monomer inhibited with 15 ppm TBC was studied using 20-80 wt% of an ethylbenzene-styrene solution (Leung, J. C., 1986). This study shows that the onset temperature is much lower than previous literature for at least 50℃. The critical findings verify that the styrene monomer will proceed extra weak exothermically (Furguson, 1994) even if very close to ambient temperatures.
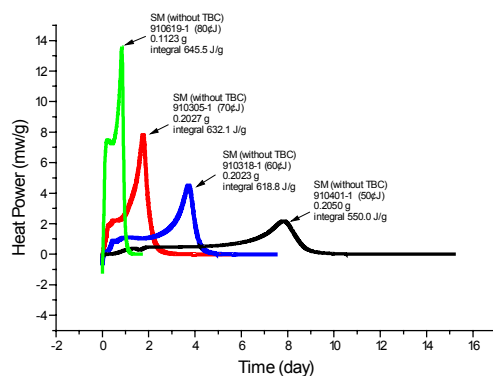

Figure 1. The heat power versus time for thermal polymerization of 99.7 wt% SM under various temperatures.

Weak exothermic reaction with autocatalytic behavior

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Heat accumulation is considered to be potentially hazardous because unexpected accidents may occur. In addition, weak exothermic reactions are not often noticed by engineers in the temperature range below 50℃ because conventional calorimeters such as DSC and VSP cannot detect such weak heat power.

The isothermal method can readily determine whether or not a reaction is autocatalytic (Sima, 1999). Table 3 shows that a weak exothermic reaction was characterized by the isothermal microcalorimeter (TAM); however, the lower temperature corresponding to the longer operating time needing to be spent and more residual enthalpy will be detected by using temperature-programmed scanning with DSC.

Table 3. Experimental Data of Exothermic Polymerization Reaction of Pure SM Conducted by TAM.

Sample	Mass (g)	Cell	Reaction Time (day)	Time to Peak (day)	ΔH of Peak (Jg^{-1})
50℃	0.2050	Glass	15.0	7.8	550.0
60℃	0.2023	Glass	7.0	3.8	618.8
70℃	0.2027	Glass	3.0	1.7	632.1
80℃	0.1123	Glass	1.6	0.8	645.5

Exothermic kinetics

In order to confirm the kinetics of thermal polymerization for SM, the activation energy must first be determined. In this research, activation energy is determined by Arrhenius plot (heat power versus various 1/T with reproducible experiments). Based on isothermal microcalorimeter measurement results from Figure 1, the plot of ln Q versus 1/T with different temperatures is a straight line, the slope providing the calculated activation energy for SM Polymerization as shown in Figure 2. The activation energy was determined to be 63±3 KJmol^{-1}, which is more accurate and precise than the values in literature.
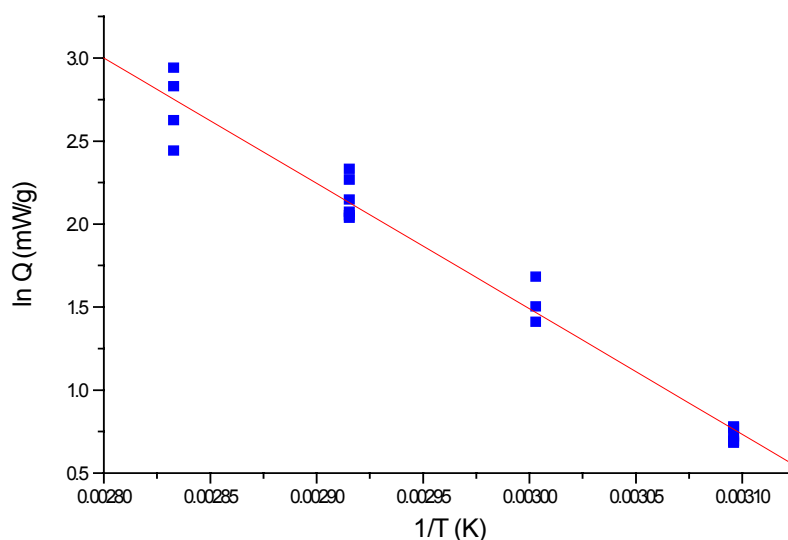

Figure 2. Determination of activation energy of SM from isothermal data conducted

by TAM.

Table 4 summarizes the related kinetic parameters from this work; along with the other studies, the activation energy was between 44.3 KJmol^{-1} to 75.3 KJmol^{-1}. The different results may ascribed to two main reasons: (1) the type of polymerization in addition to the solvent effect and which kind of initiator was added, and (2) different temperature range of polymerization.

Table 4. Thermokinetic Parameters Derived from Thermal Polymerization of SM.

Item Literature	Sample	Apparatus	Heat of Polymerization (Jg^{-1})	Ea (KJmol^{-1})
Leung, 1986	EB/SM (20wt%/80wt%)	VSP	687	40.5
Duh, 1998	SM	DSC	647	NA
Grewer, 1994	SM	NA	701*	NA
Ferguson, 1994	SM	NA	597	NA
Brighton, 1979	SM	NA	716 (90℃)	NA
Burnett, 1947	SM	NA	NA	45.5
Bamford and Dewar, 1946	SM	NA	NA	44.3
Compton, 1992	SM	NA	NA	75.3**
Odian, 1993	SM	NA	701	45.1
Mayo, 1953	Pure SM in bromobenzene	NA	NA	121.2 (Initiation step)
Bond, 1985	SM	NA	699	NA
This work	Pure SM	TAM+DSC	670	62.8

NA: Not Applicable

*$\triangle$H = 73 KJ•mol^{-1} = 701 J•g^{-1}

**Using n-BuLi for initiation

Conclusions

This study determines the application of the isothermal microcalorimeter for investigating the weakly exothermic and slow thermal polymerization of SM. No detectable signals were observed in VSP or DSC apparatus in these temperature ranges. Ultra-sensitive Isothermal microcalorimetry is a promising approach to assess other petrochemical chemicals associated with tiny heat of reaction, based on its high sensitivity. The data of thermokinetics such as $\triangle$H (heat of reaction), $\triangle$T$_{ad}$ (adiabatic temperature rise), Ea and TMR (time to maximum rate) will be also determined.

Data from weak exothermic reaction thermograms can be used to assess thermal runaway of reactive chemicals and to determine useful parameters such as T$_{onset}$ (exothermic onset temperature) and T$_{SADT}$ (self-accelerating decomposition temperature) for process safety design.

Further study should be focused on determination of kinetics of autocatalytic phenomena and identification of intermediates, especially in mechanism needed to be confirmed during slow thermal polymerization. It is worth discussing a high temperature model in the temperature range from 100℃ to 230℃ and trying to establish the low temperature model, both of which should be compared.

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