

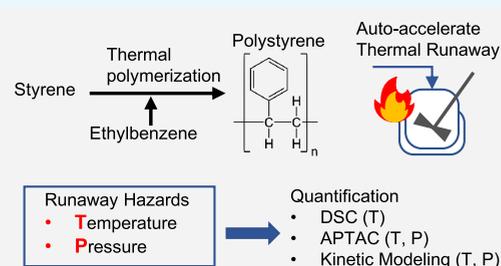
Probing into Styrene Polymerization Runaway Hazards: Effects of the Monomer Mass Fraction

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ABSTRACT: Polymerization reactions have caused a number of serious incidents in the past; they are prone to reaction runaways because of their exothermic and autoaccelerating nature. To minimize the risk, the reaction is commonly performed in a solvent as empirical industrial practice. In this work, the thermal runaway hazards of the ethylbenzene–styrene system with different monomer mass fractions were calorimetrically investigated up to temperatures where decomposition products are unlikely to be produced. Experiments showed that the polymerization runaway “onset” temperature inversely increased with the monomer mass fraction. Experiment and thermodynamic calculations showed that volatile diluent increased system vapor pressure even at a lower adiabatic temperature rise and verified that moderation of the risks could be achieved if the monomer mass fraction is below ca. 85%. A lumped kinetic model developed by Hui and Hamielec was used to predict the runaway profile of this reaction under different dilutions, and the agreement was excellent.



1. INTRODUCTION

Styrene is one of the most widely used monomers and has a variety of applications in the chemical industry to produce polystyrene, acrylonitrile–butadiene–styrene rubber, and many other polymers. However, the storage and polymerization processes are prone to runaways as monomers are thermally unstable. Barton and Nolan¹ reported that 48% of total runaway incidents that occurred over the period from 1962 to 1987 in the UK were polymerization reactions. A reactive chemical incidents report published by the Chemical Safety Board (CSB)² also denoted that almost 15% of incidents involving uncontrolled chemical reactions in 1980–2001 in the US are polymerization thermal runaways. An incident statistical study by Sales³ in 2006 showed that 17 out of 132 (13%) reactive chemical incidents recorded by the major accident reporting system in the European Commission were caused by the polymerization runaway reactions. More recently, Mihailidou⁴ analyzed 319 major industrial incidents with significant consequences based on the United Nations Environment Program (UNEP) criterion and found 34 out of 319 (11%) major incidents worldwide during the years 1917–2011 were related to the reactive monomer/polymer process. Saada⁵ analyzed 30 runaway incidents in a specific unit process during 1988–2013 and showed that over 33% of those were polymerization incidents. A significant number of these incidents were related to styrene production and handling as listed in Table 1.^{2,6–9} Despite this, lessons have not been learned, and the reoccurrence of styrene-related runaway incidents continues.

Table 1. Selected Thermal Runaway Incidents Related to the Styrene Process

date	location	consequences	
		injury	fatality
07/05/1994	Kaohsiung, Taiwan	0	1
01/26/1996	Chiayi, Taiwan	1	0
01/21/1998	Kaohsiung, Taiwan	4	0
12/24/1998	Kanagawa, Japan	0	0
06/27/1998	Channahon, IL, US	1	0
06/23/1999	Pasadena, TX, US	21	2
10/06/1999	Chiayi, Taiwan	1	0
03/27/2000	Pasadena, TX, US	71	1
04/02/2003	Addyston, OH, US	0	1
04/08/2004	Jiangsu, China	8	6
06/30/2005	Mesa, AZ, US	0	1

Several factors contribute to the highly hazardous styrene handling and polystyrene production process. First of all, the styrene polymerization reaction is relatively highly exothermic with a heat generation at around 71 kJ·mol⁻¹.¹⁰ At the same time, even without an initiator, two styrene molecules will undergo a Diels–Alder type of reaction and generate radicals to start self-polymerization upon heating.¹¹ This polymerization process auto-accelerates as the reaction progresses; the

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system viscosity dramatically increases, and the reaction becomes diffusion-controlled, which is known as the gel effect or Trommsdorff–Norrish effect. Figure 1 gives a schematic of how the gel effect might lead to the thermal runaway for polymerization.

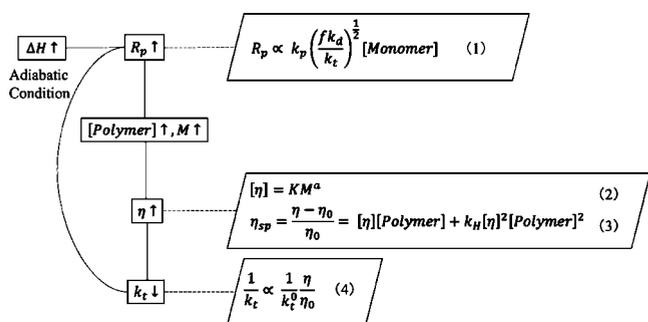


Figure 1. Gel effect in the polymerization system.

From a classic first-principle kinetic analysis, the polymerization rate R_p is proportional related to the propagation rate constant k_p , monomer concentration, and also to the square root of the initiator efficiency f , the initiator decomposition rate constant k_d , and the reciprocal of the termination rate constant k_t . As the monomers are consumed, the polymer concentration as well as polymer molecular weight M increases, and the latter can increase by orders of magnitudes compared with monomer molar weight. These long-chain polymers significantly elevate system viscosity via two different mechanisms. First of all, the intrinsic viscosity of polymer chains $[\eta]$ increases exponentially with molecular weight M because of the increase of the length of polymer chains, which can be described by the Mark–Houwink as eq 6. Parameters a and K depend on the specific polymer–solvent system. At the same time, bulk viscosity of the solution increases with polymer concentration, as formulated by Huggins in eq 7, where η_{sp} is the specific viscosity, η_0 is the solvent viscosity, and k_H is the Huggins coefficient. Thus, the mobility of polymer chains and diffusion is strongly hindered such that the termination rate dramatically drops compared with the initial termination rate constant k_t^0 according to eq 8,¹² resulting in a fastened polymerization reaction rate. This synergetic process could be further intensified under adiabatic conditions, as reaction heat generated during exotherm elevates the system temperature and reaction rate. To ease the gel effect and avoid sudden increase of viscosity and heat release, the industry employs a small portion of the organic solvent to reduce the system viscosity and enhance the mobility of polymer chains.¹⁰ A cascade of tower-type reactors is also employed to limit the reaction extent and viscosity increase.

It is of great importance that such a highly hazardous reaction process should be carried out in compliance with the Occupational Safety and Health Administration (OSHA) 29 CFR 1910.119, process safety management (PSM) of highly hazardous chemicals standard.¹³ Among the 14 elements included in the PSM, process hazard analysis is essential in terms of identifying, evaluating, and controlling the hazard of the process. For reactive chemical systems in general, calorimeter studies provide valuable process safety data such as “onset” temperature of exothermic reactions, maximum temperature, maximum pressure, and noncondensable gas generation under intended or unintended (mal-operation)

conditions.¹⁴ These data would serve as the basis for designing the process itself, its protection layers, and methods to control reaction hazards, for example, cooling capacity design and relief valve sizing.

A considerable amount of the literature has been published on the assessment of the thermal hazards of the undesirable thermally initiated styrene polymerization using calorimeters. Whiting and Tou¹⁵ evaluated the thermal behavior of inhibited styrene in an accelerating rate calorimeter (ARC) to address the effects of the system thermal inertia. Gibson et al.¹⁶ tested the runaway reaction of inhibited styrene starting from 150 °C in an adiabatic Dewar and calculated the relief valve size. Frurip et al.¹⁷ discussed some general practices regarding hazard evaluation of polymerizable compounds and performed the ARC test on uninhibited styrene with peroxide at various concentrations. Chen et al. performed isothermal studies on inhibited⁶ and uninhibited¹⁸ styrene to investigate the runaway behavior and kinetic parameters of styrene at low temperatures using microcalorimeters. Leung et al.¹⁹ utilized the ARC to investigate the thermally initiated polymerization of inhibited styrene with 20% ethylbenzene added to the system.

A thorough literature review revealed that very few studies focused on the diluted styrene-solution system, which is more commonly employed in industrial practices, and the reaction hazards accruing from this system were not fully understood. From the inherent safer design (ISD) point of view,²⁰ the addition of solvent into the system is an effective “moderating” strategy because it lowers system viscosity and the reaction runaway severity as can be shown in Figure 1. At the same time, this moderating measure contradicts the “substituting” and “simplifying” principles of ISD by introducing an additional volatile and highly flammable species into the system. The system complexity also increases as one more component is involved, inevitably affecting the physical properties of the system and in particular the ones which are directly related with its safety (e.g., flash point, flammable limit, heat capacity, vapor pressure, thermal conductivity, and heat capacity). Furthermore, additional hazardous scenarios have to be introduced as the interaction between the solvent and styrene needs to be considered.

For a pure styrene calorimetry study, the most well-studied scenario was the worst-case runaway reaction, where the system cooling was lost and the reaction developed under adiabatic condition. For a binary solvent-styrene system, another possible scenario is that the solvent-to-monomer ratio deviates from the original design intent. By applying the hazard and operability study concept to this solvent-styrene system, the reaction recipe is chosen as the study node, and the deviations (guide words) are “high” and “low”, which adequately represent two types of mischarging scenarios. The quantification of the consequences of these scenarios provides useful information on how monomer fraction will affect runaway behavior and process hazards.

In this paper, the runaway hazards of the polymerization of uninhibited styrene in ethylbenzene were evaluated as a function of the monomer mass fraction in screening and adiabatic calorimeters to obtain quantitative reaction hazard information. A lumped kinetic modeling was employed to simulate the temperature and pressure profile, and the global rate of the thermal polymerization was evaluated to obtain critical reaction parameters for predicting runaway behavior.

2. MATERIALS AND METHODS

2.1. Materials. Ethylbenzene (Sigma-Aldrich, ReagentPlus, 99%) and alumina inhibitor remover (Sigma-Aldrich) were used without further purification. Styrene (Sigma-Aldrich, ReagentPlus, 99%) contained 15 ppm of 4-*tert*-butylcatechol (TBC) as an inhibitor; this inhibitor requires dissolved oxygen to become effective. To rule out the retardant effect of inhibitor, TBC was removed before testing. Alumina has been identified as an active adsorption material of TBC for industry practices.²¹ By passing the styrene slowly through a packed column with alumina inhibitor remover, the inhibitor-free monomer was obtained and used immediately. Purified styrene monomer was mixed with ethylbenzene to prepare a series of solutions with a monomer mass fraction that varied from 0.55 to 1.

2.2. Differential Scanning Calorimeter. Dynamic scanning tests with a small sample size were conducted in a Q20 differential scanning calorimeter (DSC, TA Instruments) to get preliminary results of styrene thermal behavior. Approximately 5 mg of test samples were heated from 30 to 300 °C at a fixed heating rate of 4 K·min⁻¹. To prevent sample boiling, high-pressure (15 MPa) stainless steel capsules were used for all tests. The measured heat flow was divided by the mass of the reactant to obtain the specific heat flow; then, the specific heat flow was integrated with respect to test time to get the specific heat of the sample. The specific heat of reaction of styrene monomer for styrene–ethylbenzene samples was calculated by dividing the heat of reaction of the entire sample by the mass fraction of styrene. The baselines for integration were obtained by rescanning the sample after each test.

2.3. Automatic Pressure Tracking Adiabatic Calorimeter. A DSC study only gives heat generation information for small sample quantities. The obtained data are not enough to adequately assess the thermal hazards of reaction at industrial scales under worst-case scenarios; only to flag severe thermal hazards. Furthermore, it is also not possible to obtain pressure-rise information during the runaway with DSC. In a thermal runaway incident, it is the pressure which rises, as the temperature increases, driving to potential rupture of the confined container or its explosion, loss of containment and potential domino effects such as fire. Adiabatic calorimeter tests have been proven to be extremely important for a more reliable evaluation of thermal hazards of reactive chemicals in bulk quantities under various conditions. The automatic pressure tracking adiabatic calorimeter (APTAC) enables the use of a relatively large sample size and maintains the reactant at near adiabatic conditions by keeping the temperature/pressure difference in and out of the test cell minimal.

In this work, ca. 10 g of the sample was loaded into a glass test-cell of a thermal inertia factor (ρ -factor) of 1.25–1.26. To eliminate the dissolved oxygen, the sample was purged with nitrogen for 30 min in an ice bath before being tested. Styrene polymerization generates only condensable gases and has been identified as a vapor system by the Center for Chemical Process Safety (CCPS) regarding relief valve design.²² To suppress the boiling of the solution and minimize the tempering effects, the APTAC cell, together with the contained reactant, was pressurized with nitrogen to around 1000 kPa (147 psi) before heating. A heat–wait–search operating mode²³ was applied with temperature steps of 5 °C, a heating rate of 5 °C·min⁻¹, and a 30 min waiting period between temperature steps. APTAC entered adiabatic mode once the

self-heating rate exceeded 0.1 °C·min⁻¹. Temperature and pressure, as well as the rate of self-heating and pressure-rise, was measured and recorded throughout the experiment.

3. RESULTS AND DISCUSSION

3.1. DSC Test of Inhibited and Purified Styrene.

Inhibited and inhibitor-free styrene was first tested in DSC to check the effect of TBC on styrene thermally initiated self-polymerization reaction. The specific heat flow is shown in Figure 2, and the characteristic thermal hazards information

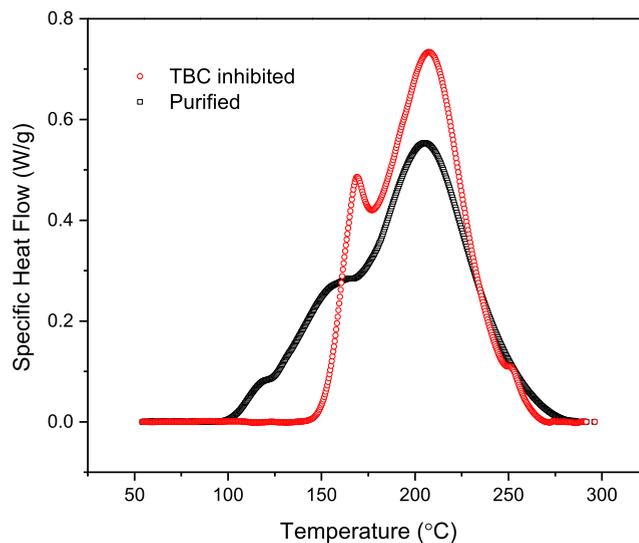


Figure 2. Dynamic DSC measurements of TBC inhibited styrene (○) and purified styrene (□).

Table 2. Dynamic DSC Experimental Data of TBC Inhibited Styrene and Purified Styrene

styrene	T_{on} (°C)	ΔH (J·g ⁻¹)	T_{peak} (°C)
TBC inhibited	149 (±4)	646 (±9)	205 (±3)
purified	101 (±1)	628 (±22)	205 (±0.1)

obtained from repeated trials are summarized in Table 2. As can be seen in Figure 2, three exothermic peaks were displayed in both cases. However, the time of their appearance and the heat flow generated are significantly different. For TBC inhibited styrene, the first exothermic peak was detected to be around 150 °C, followed by a higher peak at 205 °C and an almost invisible one at around 250 °C. This multippeak exothermic curve denoted a complex reaction pathway of thermal polymerization of styrene and had been observed in many other studies.^{15,18} Liao⁷ reported similar peak behavior for TBC inhibited styrene and performed kinetic modeling on each peak. It was identified that the first peak was typical of an autocatalytic behavior while the second peak was an n th order regarding styrene with a reaction order around 1.8–2. For inhibitor-free samples, the DSC curve showed a different thermal profile as three major exothermic peaks appeared at 120, 150, and 205 °C. As can be seen, the overall heat generation was approximately the same for both cases. However, in the case of the uninhibited monomer, the reaction became notable at a much lower temperature (101 °C) while its rate of heat generation was much slower than that

of the inhibited monomer. Also, the temperature range of the exothermic reaction was expanded. It is argued that thermally initiated radicals trigger the polymerization at a much lower temperature, which can be considered as a guiding value for deciding on styrene storage conditions in view of inhibitor depletion. When the TBC or other inhibitors are exhausted over time in a styrene tank, the self-reaction may significantly accelerate at around 101 °C. On the other hand, if unwanted polymerization occurs in an inhibited quantity of styrene, containment of the unwanted reaction may not be possible as the generation of heat will be more intense after 150 °C compared with uninhibited styrene. The maximum heat flow for either sample was detected at 205 °C, and this unaltered characteristic temperature indicated that 15 ppm of TBC effectively inhibited self-polymerization but only at the early stage. It is plausible that the first peak denotes the primary radical production, where the TBC acts as a radical scavenger and thus delays the polymerization until it is depleted at a higher temperature. The main peak is likely to represent the main polymerization process in the course of which the monomers add up to build the extended polymer chain. The heat of polymerization of styrene obtained from this study was between 629–646 J·g⁻¹, which is slightly lower than the value of 670 ± 11 J·g⁻¹ measured by Chen¹⁸ using 10 mg of styrene. This deviation may be owed to the more heat dissipation to the surrounding caused by the smaller sample size in this study.

3.2. DSC Study of the Mass Fraction Effect. To study the impact of the monomer mass fraction on self-polymerization, dynamic DSC tests of purified styrene–ethylbenzene solutions with different solvent additions were performed, and the results are summarized in Table 3. As can be seen from the

Table 3. Dynamic DSC Results of Styrene–Ethylbenzene Systems

styrene mass fraction (%)	T_{on} (°C)	ΔH of solution (J·g ⁻¹)	ΔH of styrene (J·g ⁻¹)	T_{peak} (°C)
100	101 (±1)	629 (±22)	629 (±22)	205 (±0.06)
85	100 (±1)	468 (±9)	551 (±9)	209 (±3)
70	100 (±0.1)	327 (±17)	468 (±17)	212 (±3)
55	103 (±2)	231 (±24)	434 (±24)	211 (±0.7)

table, the “onset” temperature (T_{on}) obtained from DSC test was observed at around 100 °C and did not shift upon ethylbenzene addition. Similarly, the maximum exothermic peak temperature (T_{peak}) appeared at approximately 205–210 °C and it was marginally if not at all, affected by the mass of styrene. The normalized heat, however, was substantially affected by the mass fraction of styrene in the solution.

The specific heat flow profiles of the samples are shown in Figure 3a. The total heat of reaction was calculated as described in the experimental section and summarized in Table 3 as ΔH of the solution. The heat of reaction of the samples was the total heat released by the samples. This value is useful for the calculation of the cooling system for the polymerization. The monotonically decreasing heat release indicated that addition of the solvent significantly reduced the overall thermal hazards. The heat flow was then divided by the styrene mass fraction to produce Figure 3b, and the overall reaction heat of styrene is reported as ΔH of styrene in Table 3. Three

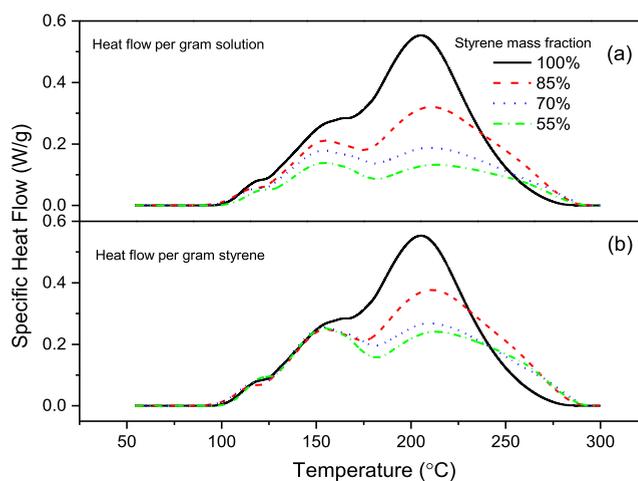


Figure 3. DSC results of thermal polymerization of styrene in ethylbenzene with various mass fractions: 100% styrene (—), 85% styrene (— —), 70% styrene (- - -), 55% styrene (- · - ·). (a) Specific heat flow per gram of solution (b) specific heat flow per gram of styrene.

major exothermic peaks for all polymerization reactions irrespectively of styrene concentrations were obtained. As can be seen in Figure 3b, in all cases, the first two peaks had approximately the same position and area. In other words, the same amount of heat was produced by styrene, regardless of ethylbenzene addition up to around 150 °C. This observation led to the hypothesis that the thermally initiated polymerization process of styrene was not affected by the addition of solvent at the initial stage (before around 150 °C). The last exothermic peak shifted from 205 to 210 °C as styrene mass fraction in the solution was reduced from 100 to 55%. In addition to that, the respective peak became wider as the solvent increased; the severity of the reaction step was decreased as the specific heat released in each case was declining (smaller peak area) with a lower monomer mass fraction. This is a clear indication that the final peak corresponds to chain-addition/termination course, a process which has been known to be strongly affected by the gel effect.

The DSC results denoted the decline of the overall reaction heat resulted from the reduced severity of the main exothermic step, as shown in Figure 3b. When the mass fraction of styrene in the test sample was lowered, the collisions between active reactant species were significantly reduced, resulting in a slower chain addition process. At the same time, in the more diluted solution, the mobility of the polymer chains was increased which facilitated the termination process, thus resulting in reduced chain length and therefore reduced reaction severity. Therefore, the DSC results confirmed that when the reaction takes place in a dilute solution, it becomes significantly less thermally hazardous because of the reduced heat generated. However, as this is partially owed to the shorter polymer chains production, product quality standards also need to be considered so that the objective of performing the polymerization is not compromised.

3.3. APTAC Study of the Mass Fraction Effect. The runaway behavior of similar bulk samples was also characterized under adiabatic conditions employing one of the best instruments serving such studies. A larger sample size was used in which case the heat and mass transfer effects became more significant, which adequately mimicked the real reaction

Table 4. Thermokinetic Data of the Styrene–Ethylbenzene System from APTAC Tests

styrene mass fraction (%)	T_{on} (°C)	ΔT_{ad} (°C)	TMR (min)	ΔP (kPa)	dP/dt_m (kPa·min ⁻¹)	dT/dt_m (°C·min ⁻¹)
100	106 (±2)	290 (±8)	121 (±6)	1299 (±16)	241 (±25)	58 (±6)
85	109 (±0.5)	238 (±3)	134 (±7)	1403 (±24)	78 (±2)	10 (±0.1)
70	117 (±0.1)	177 (±5)	145 (±1)	1254 (±56)	21 (±2)	2 (±0.1)
55	126 (±4)	104 (±4)	181 (±10)	822 (±33)	3 (±0.3)	0.6 (±0.02)

vessels. The results of the respective measurements are summarized in Table 4. The corresponding temperature and pressure trajectories are shown in Figure 4 and Figure 5. The

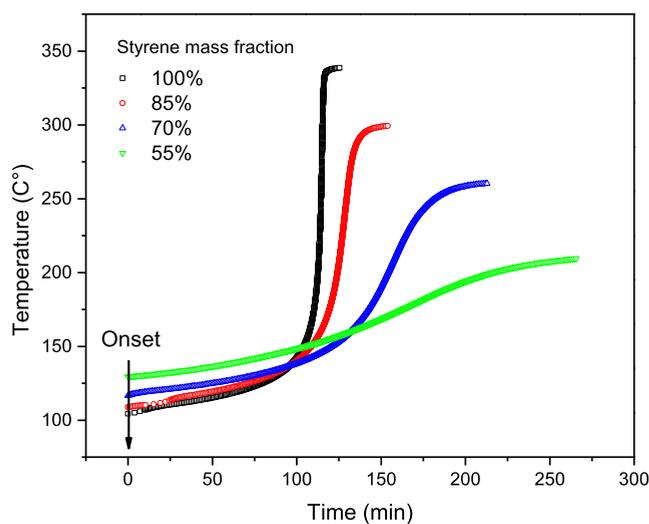


Figure 4. Adiabatic temperature rises during the adiabatic runaway reaction of styrene–ethylbenzene systems at various styrene mass fractions: 100% styrene, 85% styrene, 70% styrene, 55% styrene.

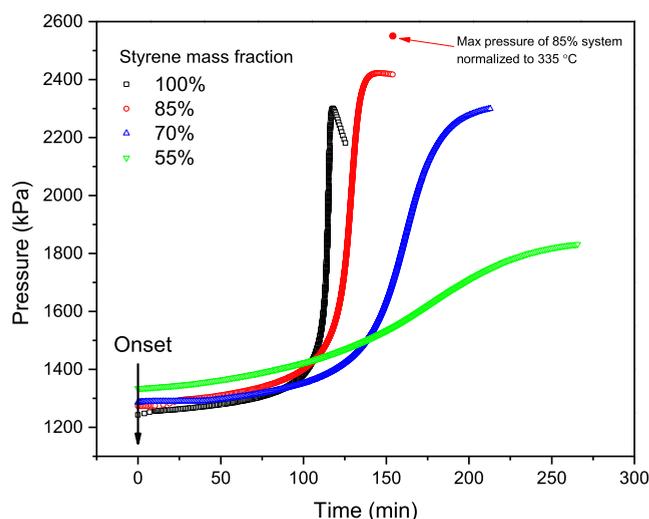


Figure 5. Adiabatic pressure rises during the adiabatic runaway reaction of styrene–ethylbenzene systems at various styrene mass fractions: 100% styrene, 85% styrene, 70% styrene, and 55% styrene.

first column of Table 4 represents the “onset” temperature (T_{on}) of the adiabatic reaction, which is taken as the temperature when the self-heating rate of the reaction exceeds $0.1\text{ °C}\cdot\text{min}^{-1}$, and the APTAC enters the adiabatic mode from the heat–wait–search mode. The apparent adiabatic temperature rise was calculated as the difference between the maximum temperature at the end of the exothermic process

and the “onset” temperature T_{on} . This number was multiplied by the φ factor to obtain the true adiabatic temperature rise (ΔT_{ad}) as shown in the second column. The time-to-maximum rate (TMR) is the time needed for the runaway reaction to reach its maximum self-heating rate. The maximum pressure increase (ΔP) was calculated by subtracting the initial value of the adiabatic pressure from the peak pressure. The last two columns of Table 4 display the maximum pressure-rise rate (dP/dt_m) and maximum self-heating rate (dT/dt_m) during the adiabatic reaction. The data during the heat–wait–search period were omitted in Figures 4 and 5, and the time in these two figures was normalized by setting the “onset” time at 0 min.

For pure styrene system, the detected adiabatic “onset” temperature was 106 °C , denoting that the polymerization reaction started to have a self-heating rate higher than $0.1\text{ °C}\cdot\text{min}^{-1}$. Soon after the “onset”, a steep increase in temperature was observed starting at 100 min of the reaction, resulting in a temperature increment of 200 °C within 15 min. Such rapid, explosive-like reaction behavior indicates the severity of uncontrolled thermal polymerization of pure styrene. Correspondingly, the pressure inside the test cell increased by 1300 kPa (189 psi), indicating how severe threat to process vessels and relief valves a runaway can pose. These data also explain why it is a common practice in the industry to avoid using 100% pure styrene for polymer production. The maximum temperature obtained was about 20 °C below the decomposition “onset” temperature of polystyrene in nitrogen as obtained by Peterson,²⁴ indicating that no decomposition was initiated by the runaway reaction.

From the temperature data, it is clear that as the monomer mass fraction decreased, heat generated by the reaction dissipated to the solvent, and a significant delay and mitigation of thermal polymerization was observed. The adiabatic “onset” temperature increased to 126 °C for 55% styrene. This is a clear indication that the solvent will “delay” a potential runaway such that the same self-heating rate was achieved at a much higher temperature for diluted samples. However, at the same time, from a scientific point of view, this research demonstrates the misleading role that the “onset” temperature can play if it is considered as a “physical property” of the reactant. What actually these measurements indicate is that the enhanced transfer of heat of reaction because of the dilution of the monomer substantially delays the reaction runaway.

Additionally, the adiabatic temperature rise dropped from 290 to 104 °C , which was almost 1/3 of the value for pure styrene when the mass fraction was reduced to 55%. Unsurprisingly, the time for the reaction to reach its summit increased as the styrene mass fraction dropped. For all samples, the main exothermic activity was observed after 100 min. For pure styrene, it took only 121 min for the adiabatic reaction to reach its maximum speed. As the mass content dropped, a longer time was required for the polymerization to develop fully, and the TMR prolonged. The 55% styrene–ethylbenzene system took almost 3 h to reach its maximum heat release rate.

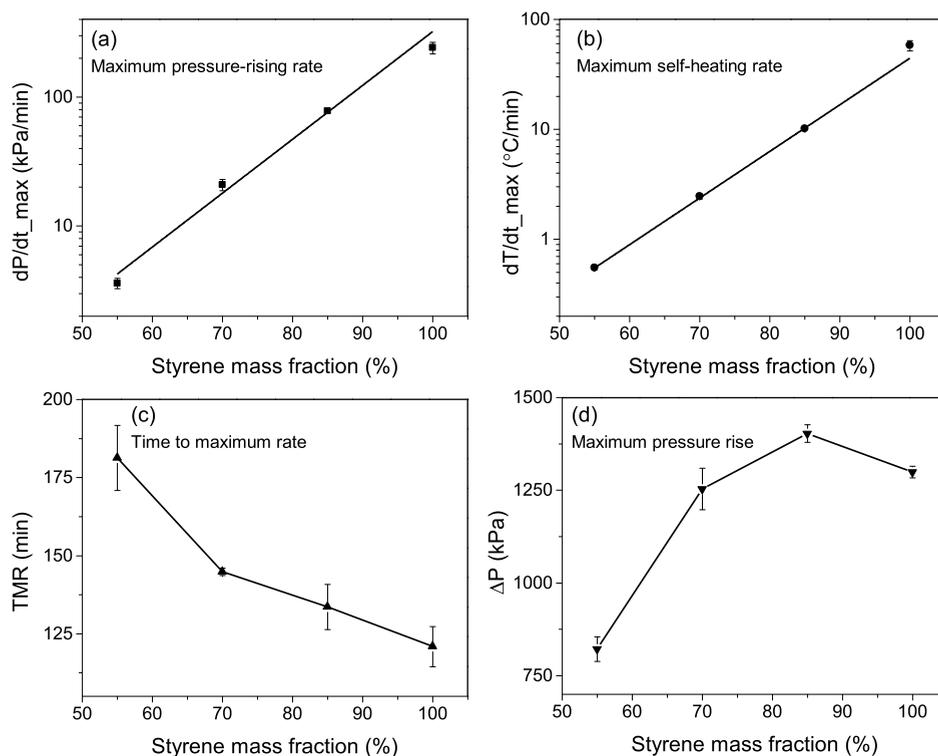


Figure 6. Summary of styrene mass fraction effects on the adiabatic runaway behavior of the ethylbenzene–styrene system. (a) Maximum pressure-rising rate, (b) maximum self-heating rate, (c) TMR, and (d) maximum pressure increase.

It is clear that the pure styrene system brings difficulties to hazard mitigation or emergency responding, and adding solvents is a practical solution to mitigate the sudden temperature increase. In the case of a loss-of-cooling scenario, systems with longer TMR have a lower risk of catastrophic consequences as more time is available to respond and implement mitigation measures.

However, the effect of styrene concentration on pressure change was not as straightforward as temperature. All experiments had approximately the same initial pad pressure of 1000 kPa (147 psi) but their “onset” temperatures were different, leading to a slight variation on the “onset” pressure. The peak pressure and pressure difference did not change monotonically with the mass content. When styrene was diluted from 100 to 85%, a higher pressure building up was observed. The pressure changes then declined upon further ethylbenzene addition. As there was no noncondensable gas production during this reaction, the pressure increases primarily consisted of two parts: (1) the vapor pressure of volatile components, which is also a function of temperature and (2) the expansion of pad gas at higher temperature practically obeying the gas law. For the polymer mixture system, the former one was also affected by the polymers produced. According to Flory’s free volume theory,²⁵ the vapor pressure of polymer itself is usually omitted, but the polymer chains had significant effects on the activity of solvent and monomer, leading to a change of vapor pressure of these volatile species. In this study, a pure styrene system had the highest temperature increase, leading to a higher expansion of nitrogen pad. At the same time, as no solvent was present, monomers reacted to form a nonvolatile polymer, which contributed very little to the total pressure. The pressure trajectory denoted that the system pressure reached its maximum before the end of the adiabatic reaction, and

gradually decreased afterward. Similar pressure behavior was also observed by Gibson¹⁶ in Dewar bottle and Tou¹⁵ in the ARC, where the maximum pressure during the runaway reaction of styrene was significantly higher than the final pressure. The experimental data reinforced the speculation that monomer vapor pressure contribution first increases and then decreases during the reaction.

For the 85% styrene–ethylbenzene system, the lower temperature increment resulted in a less-expanded nitrogen pad. However, the ethylbenzene was not consumed during the reaction and then contributed to building up vapor pressure. The summation of these two factors led to an overall higher pressure (2400 kPa) than the pure system (2200 kPa). It is worth mentioning that this higher pressure was observed at a lower temperature (298 °C) compared with that of the pure styrene (335 °C). If this maximum pressure was normalized to 335 °C, then the potential pressure rise could increase further to around 2562 kPa, which was also denoted in the figure. As more solvent was added, the reaction extent and temperature increase were lowered, even though more solvent vaporized at a lower temperature, and the expansion of pad gas was not significant, resulting in a lowered total pressure increase. From a safety perspective, the real hazard of a runaway reaction is the uncontrolled pressure, as the direct cause of the loss of containment is the overpressure. Toxic or flammable reactants may be released when the pressure build up exceeds the ultimate strength of the process vessel, followed by fire or explosion. Although diluting the monomer by 15% helps lower heat release, the elevated pressure change may pose another concern of possible loss of containment.

These key hazard indicators obtained from adiabatic tests were plotted in Figure 6. The maximum pressure-rising rate (dP/dt_m) and the maximum self-heating rate (dT/dt_m) during

the runaway both raised exponentially with respect to styrene mass fraction.

3.4. Hui and Hamielec Kinetic Verification of Adiabatic Data. To predict the thermal runaway behavior of the styrene–ethylbenzene system and also obtain the optimum solvent dosage ratio to minimize both thermal and pressure hazards, kinetic simulation needs to be carried out. The Design Institute for Emergency Relief Systems (DIERS)²⁶ has recommended the use of the Hui and Hamielec²⁷ model to predict the thermal runaway temperature profile of the thermally initiated styrene polymerization in ethylbenzene in a bulk quantity (32 L). This model was developed in the 1970s for the thermally initiated polymerization of styrene taking into consideration of the gel effect and viscosity change at higher conversions. The initiation was assumed to be a third-order reaction with respect to the monomer concentration. Other reaction rate constants were empirically correlated with the polymer mass fraction and temperature.

The overall polymerization rate of Hui and Hamielec kinetic model can be cast as follows

$$\frac{dx}{dt} = A[M]^{3/2}x \quad (5)$$

$$A = A_0 \exp(A_1x_p + A_2x_p^2 + A_3x_p^3) \quad (6)$$

$$A_0 = 1.964 \times 10^5 \exp\left(\frac{-10\,040}{T}\right) \quad (7)$$

$$A_1 = 2.57 - 5.05 \times 10^{-3}T \quad (8)$$

$$A_2 = 9.56 - 1.76 \times 10^{-2}T \quad (9)$$

$$A_3 = -3.03 + 7.85 \times 10^{-3}T \quad (10)$$

where x is the mass fraction of styrene in the system; x_p is the mass fraction of polymer; $[M]$ is the monomer molar concentration in $\text{mol}\cdot\text{L}^{-1}$; and temperature-related parameters A_0, A_1, A_2, A_3 are independent of conversion. For the styrene/ethylbenzene/polystyrene system in this study, thermodynamic properties such as density, heat capacity, and pure component vapor pressure were calculated with empirical correlations.¹⁹ The adiabatic temperature profile was simulated for different runs employing 55–100% monomer in solution for which adiabatic measurements were performed. The heat loss correction was performed using the thermal inertia factor obtained in the experimental section. The comparison of the self-heating rate between experimental results and the simulated ones employing eqs 5–10 are shown in Figure 7.

As can be seen from the figure, the empirical rate equations provided by Hui and Hamielec are in good agreement with the adiabatic experimental data in terms of self-heating rate change regarding the reciprocal of temperature. Figure 8 shows a comparison of a series of simulation results with experimentally detected maximum temperature and maximum self-heating rates. The model showed a linear trend of maximum adiabatic temperature increase and an exponentially increasing peak self-heating rate with the monomer mass fraction. The model predicted a slightly lowered maximum self-heating rate for all cases. Adjustment of the value of parameters A_0 – A_3 using experimental data may result in more accurate predictions of the self-heating rates and pressures.

The total pressure of the system was also simulated by considering both pad gas pressure and vapor pressure, as

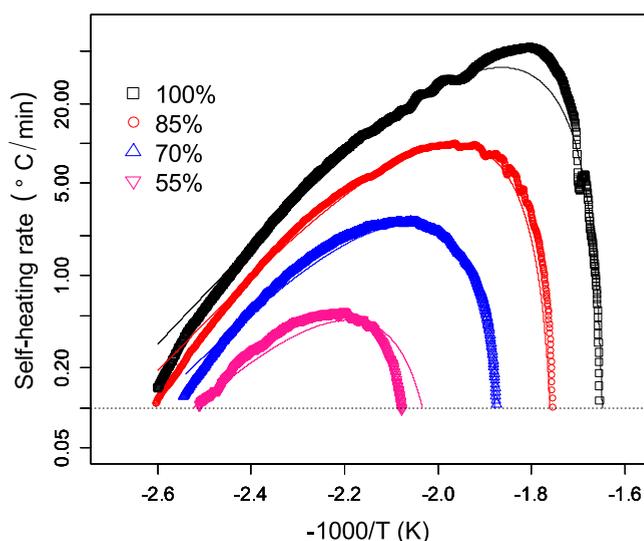


Figure 7. Self-heating rate during adiabatic runaway reaction for different styrene–ethylbenzene mass fractions: 100% (\square), 85% (\circ), 70% (\triangle), 55% (∇), and Hui and Hamielec kinetic prediction (solid lines).

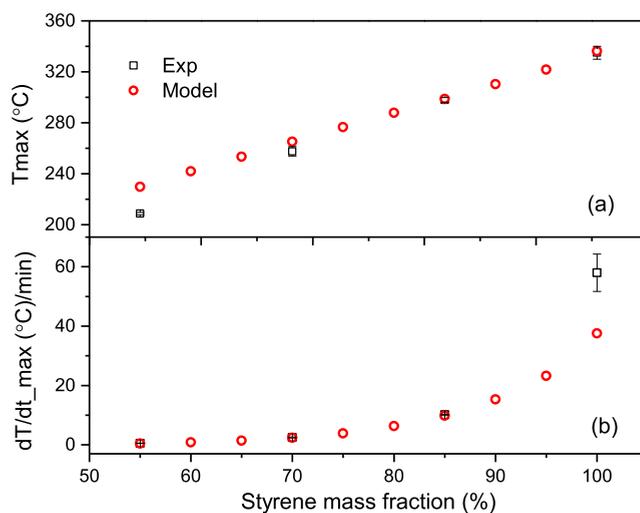


Figure 8. Hui and Hamielec model results (\circ) and APTAC experiment results (\square). (a) Maximum adiabatic temperature and (b) maximum temperature rising rate.

discussed before. The vapor pressure of volatile components (monomer and ethylbenzene) was calculated based on the partial vapor pressure of each component over a monomer/polymer/solvent system via the following Flory–Huggins equation²⁸ (eq 11) to correct the respective activities. P_i^0 is the pure compound vapor pressure; ϕ_i is the volume fraction of the compound; ϕ_p is the volume fraction of polymer chains; and χ is the polymer–solvent interaction parameter, which was measured by Flory to be around 0.45 for polystyrene in ethylbenzene.²⁹

$$\frac{P_i}{P_i^0} = \Delta\mu_i = \phi_i \exp(\phi_p + \chi\phi_p^2) \quad (11)$$

The pad-pressure change of nitrogen was assumed to follow the ideal gas law, while the gas-phase temperature increased during exotherm, and the headspace volume expanded because of the contraction of the liquid phase caused by polymer-

ization. In such a way, each pressure contributor was simulated separately, as shown in Figure 9.

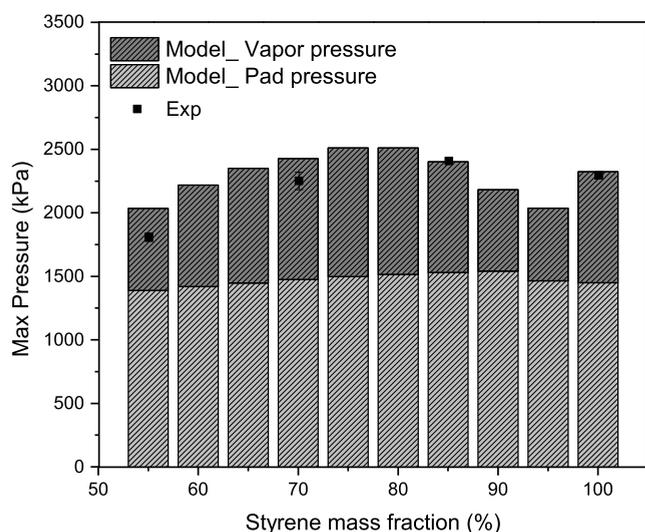


Figure 9. Hui and Hamielec kinetic modeling and experiment results of the maximum pressure change for ethylbenzene–styrene systems.

The simulation results showed that the maximum pressure during the adiabatic thermal runaway was not a monotonic function of the monomer mass fraction, which was confirmed by the experiments. It was expected that as the reaction temperature increased during the adiabatic runaway polymerization, the pad gas expansion would result in a respective rise of pressure. However, as the monomer with lower density gradually reacted to build up polymer chains with higher density, a contraction of the liquid phase and an expansion of the gas phase was introduced. This volume change counterbalanced the temperature change effect and moderated the pad-pressure increase. The vapor pressure of monomer and ethylbenzene increased with temperature, while at the same time the monomer was consumed and thus its contribution to the total vapor pressure during the reaction decreased.

When the mass fraction of monomer increased from 55 to 100%, the nonreactive volatile components fractions dropped, and the total pressure increase with conversion showed a significant change. Two different pressure change patterns were observed as shown in Figure 10.

For samples with monomer mass fraction below 95%, the calculated maximum pressure was observed at the end of the reaction ($P_{\max} = P_{\text{final}}$). In these cases, although the monomer was completely consumed at the final stage, the solvent vapor pressure reached its maximum and had a significant contribution to the total pressure. The simulations for a styrene mass fraction of 95 and 100% showed that the total pressure first increased with conversion and then dropped at the end of the reaction ($P_{\max} > P_{\text{final}}$). In other words, the peak thermal hazard and peak pressure hazard appeared at different stages of the adiabatic runaway reaction. For the pure styrene sample, simulation denoted peak pressure value was at around 77% monomer conversion, at which point 23% of the monomer still had a significant contribution to the total pressure. After more monomers were consumed, the simulated vapor pressure of monomer dropped to 0 psi at the end point (100% conversion). The total pressure was then equal to the pad gas pressure. The experimental results were in good

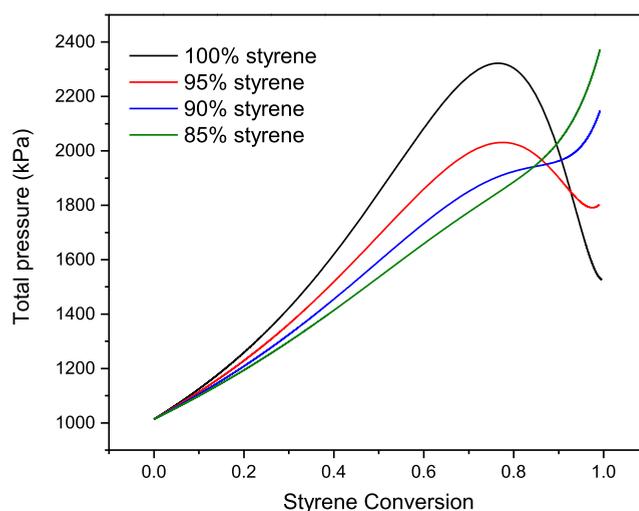


Figure 10. Hui and Hamielec kinetic modeling of pressure change as a function of styrene conversion for selected ethylbenzene–styrene systems.

agreement with the prediction within the mutual error. The results showed that the addition of solvent or the lowering of mass fraction was an effective measure to prolong TMR and moderate the rate of heat release. However, volatile solvents lead to a higher pressure rise even at lower temperatures, which introduces a different kind of hazard which has to be taken into consideration when designing the vapor relief systems.

The experimental and lumped kinetic modeling results reported herein should be considered in the light of some limitations. First of all, other species which are present in the polymer production such as initiators, chain-transfer agents, or possible contaminants may also have an impact on the thermal runaway behavior. Other scenarios and further studies are necessary to be conducted to evaluate the synergistic effects which arise from their presence. At the same time, the lumped kinetic simulation with Hui and Hamielec model matched well with the adiabatic self-heating rate for the concentrated samples at higher temperature range while overestimated the rate of polymerization at the initial stage. This deviation may be caused by the simplified empirical correlation which was insufficient to provide detailed expressions of rate constants for individual step in the free-radical polymerization reaction. A series of more detailed kinetic studies have been carried out by a working party of the International Union of Pure and Applied Chemistry (IUPAC) since 1988^{30,31} to obtain the accurate values of the critical rate constants for a variety of free-radical polymerization systems. More specifically, for the styrene system, the pulsed laser polymerization–size exclusion chromatography (PLP–SEC) method was first used to obtain the benchmark value of the propagation rate coefficient of styrene.³² The change of initiator efficiency of 2,2'-azoisobutyronitril in styrene was evaluated under different temperature and pressure conditions.³³ Most importantly, the experimental method to accurately assess the termination rate coefficient has been carefully reviewed for various free-radical polymerization systems,^{34,35} followed by a recent experimental evaluation of the styrene termination rate coefficient that covers the entire conversion range.³⁶ These benchmark values and IUPAC recommended PLP–SEC experimental method have facilitated the development of numerous new kinetic models as summarized by Achilles.¹² The future utilization of

these detailed nonempirical kinetic modeling would enable a deeper understanding of styrene polymerization thermal runaway behavior at bulk quantities.

4. CONCLUSION

The effect of styrene mass fractions on the thermally initiated polymerization runaway hazards of the styrene–ethylbenzene system was studied using screening and adiabatic calorimeters. DSC results confirmed a multiphase reaction exotherm between 100 and 300 °C. The addition of diluent effectively reduced overall heat release by affecting the late stage of the reaction at higher temperatures (>150 °C). Adiabatic tests identified a delayed and milder self-polymerization upon dilution, with higher detected “onset” temperature and linearly decreased adiabatic temperature rise. Both screening and adiabatic test results confirmed that the overall heat release and reaction severity was reduced by the addition of the solvent. At the same time, the pressure build-up rate and temperature rate exponentially decreased with lower monomer mass fraction, proving that dilution with solvent is an effective measure to moderate reaction thermal hazards and as such it may form a sound inherently safer design option, especially when the monomer mass fraction drops below 0.8. However, when the monomer was diluted in ethylbenzene to 85% w/w, the presence of volatile species resulted in a higher pressure-rise during reaction runaway compared with the pure styrene system even at lower temperatures. The lumped kinetic model developed by Hui and Hamielec presented an excellent agreement with the experimental data for both thermal and pressure hazards during the adiabatic thermal runaway. The study revealed the complex role of solvent (ethylbenzene) regarding the polymerization runaway hazards. Addition of solvents into the polymerization system to mitigate the thermal risk may introduce pressure risks because of the volatile nature of the solvent. Optimum process design should be based on a thorough assessment of all types of hazards present in the system.

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Notes

The authors declare no competing financial interest.

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