



Evaluation of styrene–acrylonitrile copolymerization thermal stability and runaway behavior

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Abstract

Evaluation of thermal stability and runaway behavior of any exothermic chemical system is of great importance for the design and operation of a chemical process. The evaluation process should be based on a thorough investigation of the reaction chemistry including reaction pathways, thermodynamic, and kinetic parameters. When addressing the reactivity hazards of any reacting system, the dominant pathway(s) should be identified. Identifying the main reaction pathway under specific conditions will lead to a better thermodynamic and kinetic characterization of the reacting system.

In this article, the thermal stability and runaway behavior of styrene–acrylonitrile copolymerization reaction system in bulk is evaluated. Traditional thermal analysis techniques (calorimetric analysis) are combined with computational quantum chemistry methods and empirical thermodynamic–energy correlations. Reaction pathways are identified from the theoretical approach and verified by experimental measurements. The results of this analysis are compared to literature data for this system.

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1. Introduction

In spite of the commercial interest in the styrene (S) and acrylonitrile (AN) copolymer (SAN), limited information is available on its thermal stability and runaway behavior under different monomer feeding ratios. Traditionally, modeling and simulation of copolymerization reactions have been centered on predicting composition and conversion, but understanding chemical reactivity and runaway reactions are necessary because of the importance of processes that are both safe and economic.

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Nomenclature

A	frequency parameter (s^{-1})
C_c	heat capacity of cell ($\text{cal g}^{-1} \text{K}^{-1}$)
C_{vs}	heat capacity of sample ($\text{cal g}^{-1} \text{K}^{-1}$)
E_a	activation energy (kcal mol^{-1})
E_a^0	intrinsic barrier of reaction (kcal/mol)
k	reaction rate constant (s^{-1})
m_c	mass of testing cell (g)
m_s	sample solution mass (g)
r	monomer reactivity ratio
R	gas constant ($1.987 \text{ cal mol}^{-1} \text{K}^{-1}$)
T_{\max}	maximum temperature due to decomposition reaction ($^{\circ}\text{C}$)
T_{onset}	onset temperature at which exothermic decomposition is first detected ($^{\circ}\text{C}$)
dT/dt	sample heating rate ($^{\circ}\text{C min}^{-1}$)

Greek letters

ΔH_r	heat of reaction (cal g^{-1})
ΔH_{vap}	enthalpy of vaporization (kcal mol^{-1})
ΔT_{ad}	adiabatic temperature rise ($^{\circ}\text{C}$)
ϕ	thermal inertia factor
γ_P	transfer coefficient

In this article, copolymerization of styrene–acrylonitrile in bulk is evaluated for its thermal reactivity and runaway behavior using thermal analysis techniques. The reactive system screening tool (RSSTTM) was used for preliminary analysis and the automated pressure tracking adiabatic calorimeter (APTACTM) was used for a more detailed characterization of the temperature and pressure profiles of the copolymerization reaction. Several styrene–acrylonitrile monomers feeding ratios were tested to analyze the effect of composition on the temperature and pressure behavior during a runaway scenario. At the same time, theoretical evaluation was conducted to predict reaction pathways to explain the experimental results and also to compare with literature values.

2. Copolymerization reactions

Copolymerization is a very useful process for synthesizing polymer with the required combination of properties and may be compared to alloying in metallurgy. Free-radical chain polymerization is the most common reaction mechanism, but other polymerization mechanisms also are possible, such as anionic and cationic polymerization. Free-radical chain polymerization can be obtained from mixtures of two or more monomers to form polymeric products that obtain two or more structures in the polymer chain, which is termed a copolymerization reaction to form a copolymer product.

Polystyrene is a good example to exhibit the features and importance of the copolymerization process. Polystyrene is a brittle plastic with a low impact strength and low solvent resistance, but copolymerization greatly enhances these properties and the applications of polystyrene. Also, styrene copolymers are useful not only as plastics but as elastomers. Thus, free-radical copolymerization of the styrene monomer with 20–35% by weight of the acrylonitrile monomer produces an enhanced impact and solvent resistant copolymer [1].

The process of two monomers to form a copolymer in random arrangement, is



The two monomer concentrations in the copolymer are determined by their relative initial concentrations and reactivities. The arrangement of monomer units in a copolymer can be random, alternative, block, or graft. For styrene–acrylonitrile copolymers, a random arrangement is the most common. The composition of the produced copolymer by simultaneous polymerization of two monomers is usually different from the composition of the monomer feed, which shows that different monomers have different tendencies to undergo copolymerization. These tendencies often have little or no resemblance to their behavior in homopolymerization. A typical free-radical copolymerization reaction of two monomers, A and B, will follow the scheme of three steps: initiation, propagation, and termination, as presented in Fig. 1.

It is well established today that initiation, growth, and termination are the principal, although not necessarily the only steps that determine the kinetics of free-radical chain polymerization/copolymerization reactions. The rates of these individual steps vary widely, but the propagation reactions are the most rapid. The initiation reaction, which produces an activated radical from a stable monomer, is by far the slowest step whenever long chains are formed [2].

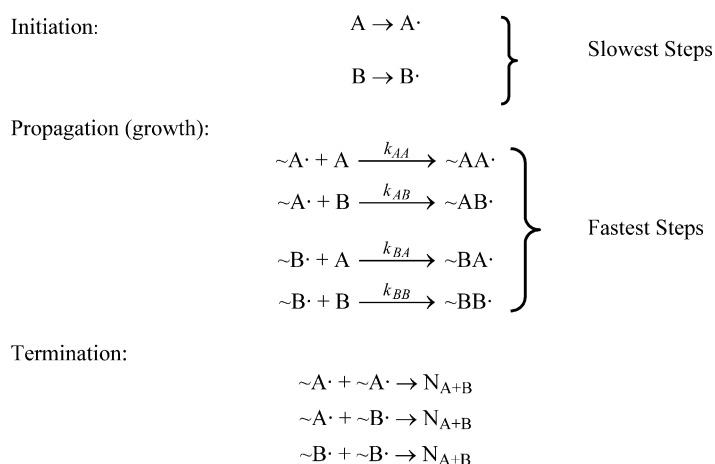


Fig. 1. Typical free-radical copolymerization reaction of two monomers, A and B.

From the four growth reactions in Fig. 1, the parameters r_A and r_B can each be defined as a monomer reactivity ratio and are represented as

$$r_A = \frac{k_{AA}}{k_{AB}} \quad \text{and} \quad r_B = \frac{k_{BB}}{k_{BA}} \quad (1)$$

The monomer reactivity ratio is the ratio of rate constants for a reactive propagating species addition to its own type of monomer to the rate constant for its addition to the other monomer. The monomer reactivity ratio can be considered to be the relative tendency for homopolymerization and cross-propagation copolymerization [1].

3. Thermal hazard evaluation

The thermal runaway in polymerization reactors is characterized by a rapid increase in reaction rate and an accelerating temperature rise. The consequence of thermal runaway may not be only the large temperature rise and possible instability. Runaway could cause also a sharp reduction in polymer/copolymer molecular weight and an increased spread in molecular weight distribution [3].

The evaluation of thermal hazards due to chemical reactivity should be based on a thorough understanding of reaction chemistry, which includes reaction thermodynamic, kinetic, and stoichiometric parameters. Calorimetric analysis is a very fundamental procedure for reactivity thermal hazards evaluation, but this procedure is expensive for the study of copolymerization reactions. Also, calorimetric analysis will provide an overall thermal hazard evaluation, with poor reaction stoichiometric information. Introducing theoretical analysis steps to the experimental evaluation process will help to reduce the cost of experimental analysis and it will help to improve the understanding of the reaction mechanisms. In a previous work [4], a systematic approach for evaluating chemical reactivity was presented. The same basic concepts of that systematic approach are applied in this evaluation study.

Theoretical analysis may be based on thermodynamic and kinetic parameters available in the literature or they can be calculated using computational quantum chemistry methods and empirical, thermodynamic–energy correlations.

4. Results

4.1. Experiment

Styrene >99% and acrylonitrile >99% monomers from Aldrich were used for experimental analysis at several feeding ratios, as presented in Table 1.

Table 1
Styrene–acrylonitrile monomers feed ratios

S:AN weight ratio	80:20	70:30	60:40	50:50	40:60	30:70	20:80
S:AN mole ratio	1.0:0.49	1.0:0.84	1.0:1.31	1.0:1.96	1.0:2.94	1.0:4.58	1.0:7.85

All experiments were conducted in nitrogen following evacuation of air from the test cells. Temperature and pressure profiles were obtained from both RSSTTM and APTACTM tests. The measured heat of reaction for the copolymerization reaction was calculated using Eq. (2):

$$\Delta H_r = \phi C_{vs}(T_{\max} - T_{\text{onset}}) \quad (2)$$

where ϕ is the thermal inertia factor: $\phi\text{-factor} = (m_s C_{vs}) + (m_c C_c) / (m_s C_{vs})$.

The heat capacity of the monomer mixture, C_{vs} , was estimated at an average temperature between T_{onset} and T_{\max} considering the proportion of styrene and acrylonitrile in each sample and based on correlations available in the literature [5]. Implicitly, we assumed that the change in average heat capacity during the decomposition reaction is negligible. In fact, heat capacity estimation is one of the main sources of uncertainty in the determination of the measured heat of reaction because of continuous temperature and composition changes during the experiment.

Assuming that this reaction can be represented by a first order kinetic equation, the reaction rate constant, k , of the RSSTTM and APTACTM testing can be calculated from Eqs. (3a) and (3b), respectively:

$$k = \frac{(dT/dt) - (\text{RSST}^{\text{TM}} \text{ temperature ramping rate})}{T_{\max} - T} \quad (3a)$$

$$k = \frac{dT/dt}{T_{\max} - T} \quad (3b)$$

Relating the reaction rate to the temperature through the Arrhenius expression, we have:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

Substituting the experimental value of k from Eq. (3) into (4) results in Eq. (5):

$$\log(k) = \log(A) - \frac{E_a}{2.303R} \frac{1}{T} \quad (5)$$

which is used to estimate the Arrhenius parameters of activation energy, E_a , and frequency factor, A .

4.2. RSSTTM analysis

Experimental screening analysis using the RSSTTM was performed for each of the seven monomer feeding ratios. Styrene–acrylonitrile monomers were mixed at room temperature, injected into an evacuated RSSTTM glass cell, and pressurized with nitrogen. RSSTTM testing was performed with a nitrogen backup pressure of about 300 psig to reduce liquid boiloff before copolymerization. Temperature ramping rates of 0.7–3.3 °C/min were applied for samples masses of 7.6–8.2 g in the cell with a thermal inertia (ϕ -factor) of about 1.05. Stirring at a constant speed was present during the experiments.

Temperature and pressure profiles during the copolymerization reaction are shown in Figs. 2 and 3, respectively. Table 2 summarizes the onset temperatures, measured heats of reaction, and Arrhenius parameters determined from the RSSTTM data.

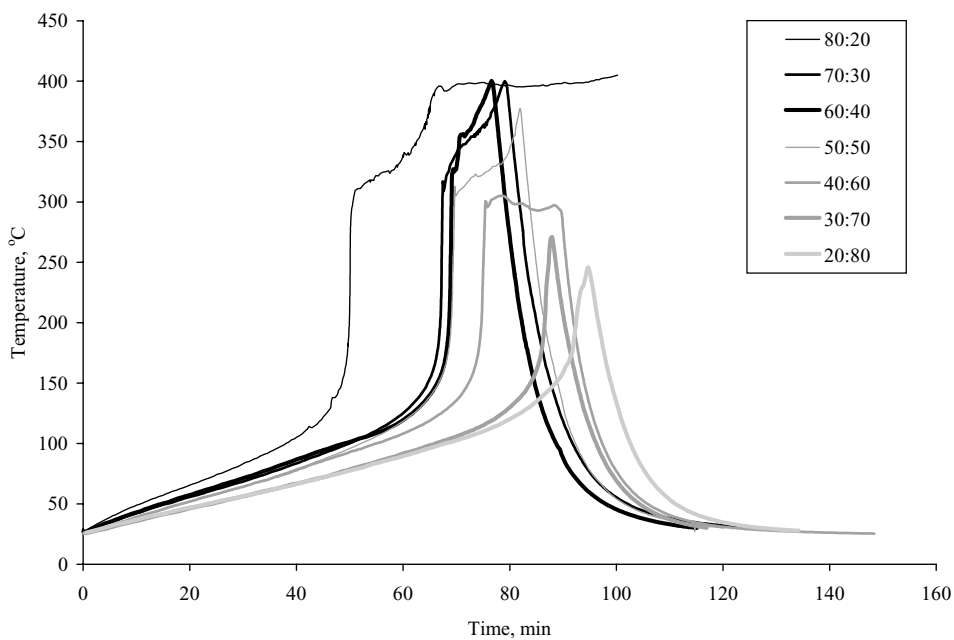


Fig. 2. Temperature profiles of the styrene–acrylonitrile copolymerization runaway, RSST™.

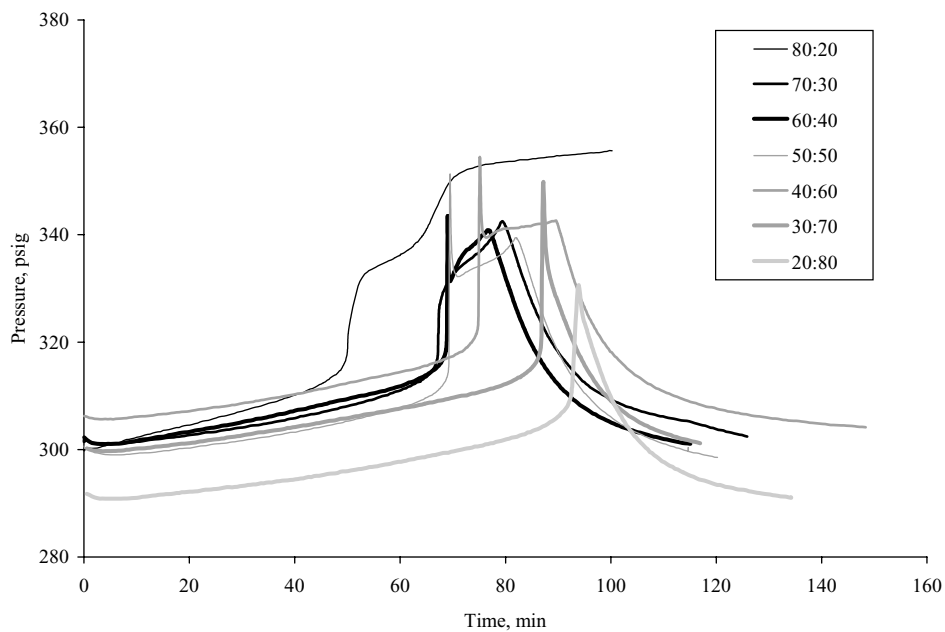


Fig. 3. Pressure profiles of styrene–acrylonitrile copolymerization runaway by the RSST™.

Table 2

Onset temperature, heat of reaction, and Arrhenius parameters for the styrene–acrylonitrile copolymerization runaway measured by the RSST™

S:AN weight ratio	T_{onset} (°C)	ΔH_r (cal/g)	E_A (kcal/gmol)	$\log(A)$ (s ⁻¹)
80:20	108 ± 3	-155 ± 11	21.3 ± 1.7	7.8 ± 0.7
70:30	103 ± 1	-179 ± 7	20.6 ± 0.6	7.5 ± 0.3
60:40	107 ± 5	-148 ± 9	20.9 ± 0.1	7.8 ± 0.0
50:50	103 ± 5	-154 ± 4	21.1 ± 1.1	7.9 ± 0.5
40:60	114 ± 7	-136 ± 5	23.7 ± 4.1	9.4 ± 2.2
30:70	102 ± 4	-114 ± 6	21.2 ± 0.8	8.0 ± 0.5
20:80	103 ± 4	-101 ± 8	19.8 ± 1.5	7.4 ± 0.6

4.3. APTAC™ analysis

Adiabatic experimental analysis using the APTAC™ was performed for each of the same seven monomers feeding ratios. Styrene–acrylonitrile monomers were each mixed at room temperature, frozen with liquid nitrogen at -102 °C in an evacuated APTAC™ glass cell, and then pressurized with nitrogen. APTAC™ testing was performed under nitrogen environment for all the reported experiments. A heat-wait-search operating mode was applied with a heating rate of 2 °C/min for samples masses of 5–10 g in the cell for a thermal inertia (ϕ -factor) of 1.6–3.5.

Temperature and pressure profiles for the copolymerization reaction in the APTAC™ are shown in Figs. 4 and 5, respectively. Table 3 summarizes the onset temperatures, measured heats of reaction, and Arrhenius parameters determined from the APTAC™ data. The onset temperature for each APTAC™ test was determined at a self-heating rate of 0.1 °C/min.

The RSST™ screening analysis results show that the onset temperature, T_{onset} , was ~106 °C while for the APTAC™ analysis the onset temperature was ~91 °C. From both RSST™ and APTAC™ results we can conclude that monomer feed ratio does not significantly affect the reaction T_{onset} temperature. However, the difference in T_{onset} values for RSST™ and APTAC™ is due to heat losses from the open cell of the RSST™, which result in higher measured T_{onset} values, compared to the closed cell and nearly adiabatic conditions of the APTAC™.

Table 3

Onset temperature, heat of reaction, and Arrhenius parameters for the styrene–acrylonitrile copolymerization runaway measured by the APTAC™

S:AN weight ratio	T_{onset} (°C)	ΔH_r (cal/g)	E_A (kcal/gmol)	$\log(A)$ (s ⁻¹)
80:20	91 ± 3	-260 ± 2	20.5 ± 0.5	8.9 ± 0.2
70:30	91 ± 3	-261 ± 2	21.2 ± 0.6	9.6 ± 0.4
60:40	90 ± 0	-245 ± 10	21.9 ± 0.2	9.9 ± 0.2
50:50	89 ± 2	-269 ± 5	21.2 ± 0.3	9.5 ± 0.2
40:60	91 ± 6	-249 ± 10	28.6 ± 0.3	13.6 ± 0.5
30:70	98 ± 6	-228 ± 5	25.5 ± 3.9	12.0 ± 2.0
20:80	93 ± 4	-227 ± 5	23.8 ± 0.9	9.32 ± 0.5

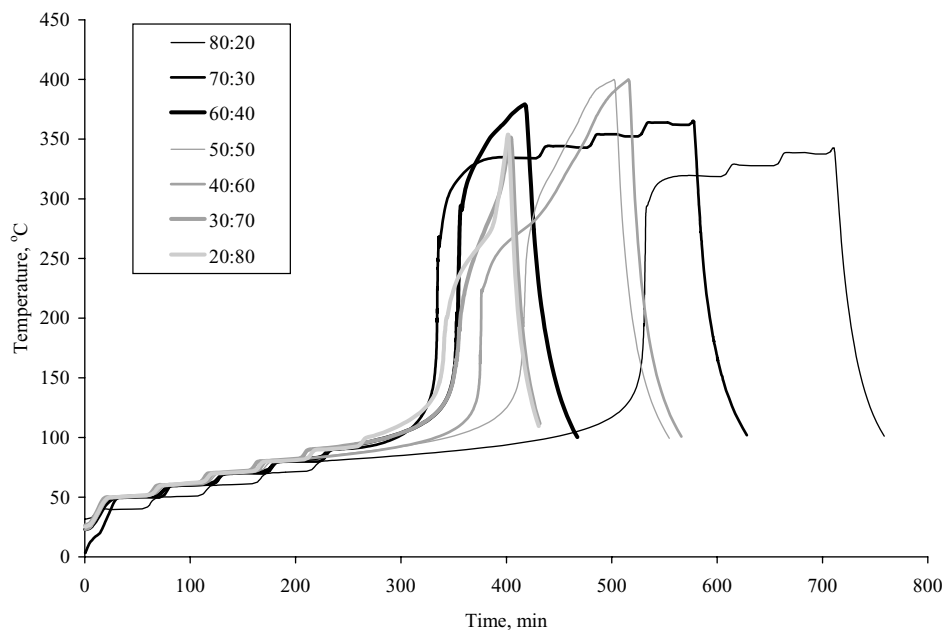


Fig. 4. Temperature profiles of styrene-acrylonitrile copolymerization runaway by the APTAC™.

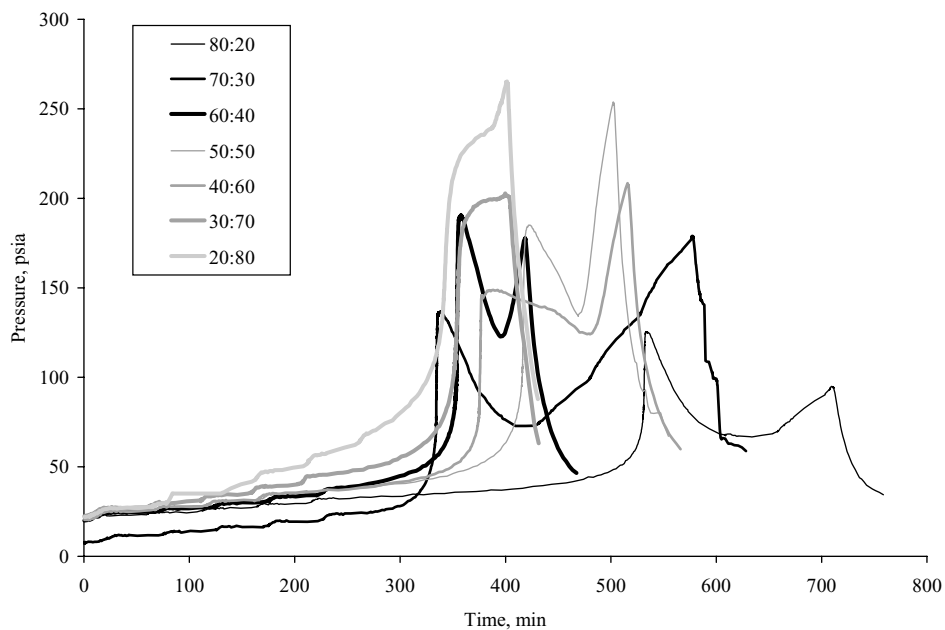


Fig. 5. Pressure profiles of styrene-acrylonitrile copolymerization runaway by the APTAC™.

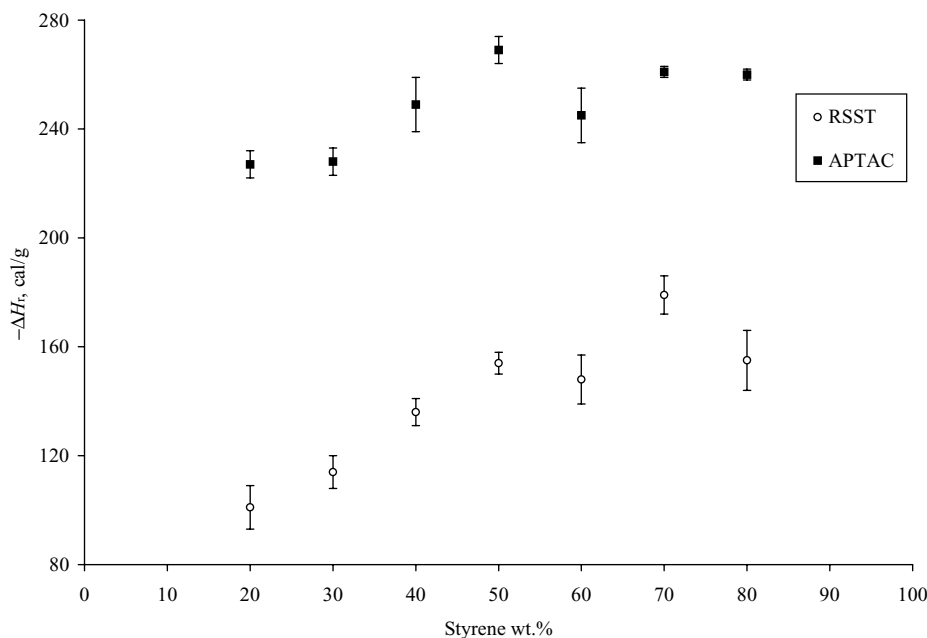


Fig. 6. Measured heats of reaction of styrene–acrylonitrile copolymerization runaway reaction.

The effects of heat losses in the RSSTTM are obvious also when comparing the measured overall heats of reaction as shown in Fig. 6. An average difference of about 107 cal/g (43% of the APTACTM measured ΔH_r) is observed between the APTACTM and the RSSTTM measured heat of reaction values. Also, from these results we can see that there is a slight reduction in the heat of reaction as the acrylonitrile concentration is increased.

The RSSTTM analysis temperature profiles in Fig. 2 show that the maximum temperature reached by the exothermic runaway reaction is decreased as the styrene concentration is reduced, and the same phenomena is noticed from the APTACTM analysis temperature profiles in Fig. 4. However, in the APTACTM profiles, another temperature activity is observed after reaching the maximum temperature. A temperature increase is observed even after reaching the copolymerization runaway maximum temperature, and it is more noticeable as the acrylonitrile concentration increases. RSSTTM did not measure these temperature changes because of the nature of the test. During the test, the RSSTTM applies a constant temperature ramping, which obscures the secondary temperature activity, while for the APTACTM, the adiabatic operating mode continues to detect temperature changes even after the first maximum temperature is attained. A study of the APTACTM pressure profiles in Fig. 5 will enhance an understanding of this phenomenon.

For each copolymerization feeding ratio there were two maximum pressure peaks. A comparison of the temperature and pressure profiles indicates that the first pressure peak is for the copolymerization reaction. It was found that styrene–acrylonitrile in bulk will copolymerize in the vapor phase [6]. So initially the monomers will evaporate causing a pressure increase then copolymerize to the liquid phase causing the pressure to decrease,

and this activity will form the first pressure peak. However, due to the high temperature increase caused by the thermal runaway, acrylonitrile monomers will begin to decompose exothermally. The decomposition products will cause the temperature and pressure to increase again forming the second maximum peaks. As the acrylonitrile monomer increases in the feed, the second decomposition temperature and pressure peaks reach higher values. Also as the acrylonitrile concentrations increase, the main copolymerization reaction peaks and acrylonitrile decomposition peaks are grouped together more closely as shown in Fig. 5, until they form a single wide peak as in the styrene–acrylonitrile feed ratios of 30:70 and 20:80.

These significant differences between the RSSTTM and APTACTM results will be reflected critically on the design of pressure relief systems. For example, use of the RSSTTM alone for designing pressure relief systems will not provide a sufficient understanding of the homopolymerization/copolymerization behavior of the SAN system, and it will underestimate the complex pressure behavior under reaction runaway scenarios. For the copolymerization part of the reaction, the Arrhenius parameters show less significant differences between the two calorimeters, which indicates that the overall reaction kinetics are about the same, but this overall reaction modeling was developed based on the temperature–time data only. It is well known that for an open-cell testing such as with the RSSTTM, the measured pressure behavior is associated with material losses to the surrounding environment making the results of less value for relief system design when compared to closed-cell testing.

To enhance an understanding of the styrene–acrylonitrile reaction mechanism, a theoretical evaluation is conducted in the following section.

4.4. Theoretical evaluation

As discussed earlier, the propagation steps in the copolymerization reactions are by far the fastest reaction steps and are responsible for most of the released energy. To predict the relative tendency for homopolymerization and cross-propagation copolymerization, enthalpy of reactions were calculated using the computational method, AM1 [7]. This is a semi-empirical method, which employs an approximate form of the Schrödinger equation with appropriate parameters derived from experimental data for the type of chemical system under investigation. These calculations were performed for the styrene and acrylonitrile homopolymerization and for the styrene–acrylonitrile and acrylonitrile–styrene cross-propagation copolymerization. Since styrene and acrylonitrile are non-symmetric molecules, there are two reactive ends for each molecule and hence the orientation of the reactive sites was considered in the computations. Fig. 7 presents the two reactive ends that were used for each molecule. The styrene monomer is defined as A–B and the acrylonitrile monomer is defined as C–D. Based on these A–B and C–D monomer definitions, the different monomer orientation possibilities during the reaction were considered. The enthalpies of reaction calculated using AM1 for these different monomer orientation possibilities are presented in Table 4.

In this theoretical evaluation, the semi-empirical AM1 method was used for its simplicity and low calculation cost. These calculations are used for relative comparisons and are not intended for exact prediction of reaction enthalpies. For more accurate thermochemical predictions, more advanced computational models should be used.

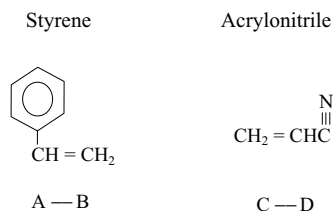


Fig. 7. Styrene and acrylonitrile reactive ends as identified in the AM1 calculations.

Evans and Polanyi [8,9] examined the relationship between the thermodynamics of a reaction and the activation barrier represented by the activation energy E_a . They showed empirically that as a reaction type becomes more exothermic, its activation barrier generally decreases. Evans and Polanyi also noted that in many cases the activation barrier, E_a , for a given reaction is related to the heat of reaction, ΔH_r , by an equation that is called the Polanyi equation:

$$E_a = E_a^0 + \gamma_P \Delta H_r \quad (6)$$

Table 4

Heats of reaction for styrene and acrylonitrile homopolymerization and styrene–acrylonitrile cross-polymerization using the semi-empirical level of theory AM1 and density functional level of theory B3LYP/6-31G(d)

Reaction no.	Propagation reaction	Heat of reaction (kcal/mol)	
		AM1	B3LYP/6-31G(d)
1	$\bullet\text{AB-AB}\bullet + \text{AB}^a \rightarrow \bullet\text{AB-AB-AB}\bullet$	-40.2	
2	$\bullet\text{AB-AB-AB}\bullet + \text{AB} \rightarrow \bullet\text{AB-AB-AB-AB}\bullet$	-37.3	
3	$\bullet\text{CD-CD}\bullet + \text{CD}^b \rightarrow \bullet\text{CD-CD-CD}\bullet$	-48.4	
4	$\bullet\text{CD-CD-CD}\bullet + \text{CD} \rightarrow \bullet\text{CD-CD-CD-CD}\bullet$	-44.6	
5	$\bullet\text{AB-CD}\bullet + \text{AB} \rightarrow \bullet\text{AB-CD-AB}\bullet$	-31.3	
6	$\bullet\text{AB-CD}\bullet + \text{BA} \rightarrow \bullet\text{AB-CD-BA}\bullet$	-47.8	
7	$\bullet\text{AB-DC}\bullet + \text{AB} \rightarrow \bullet\text{AB-DC-AB}\bullet$	-41.0	
8	$\bullet\text{AB-DC}\bullet + \text{BA} \rightarrow \bullet\text{AB-DC-BA}\bullet$	-58.1	-30.8
9	$\bullet\text{BA-CD}\bullet + \text{AB} \rightarrow \bullet\text{BA-CD-AB}\bullet$	-24.2	
10	$\bullet\text{BA-CD}\bullet + \text{BA} \rightarrow \bullet\text{BA-CD-BA}\bullet$	-49.6	
11	$\bullet\text{BA-DC}\bullet + \text{AB} \rightarrow \bullet\text{BA-DC-AB}\bullet$	-41.6	
12	$\bullet\text{BA-DC}\bullet + \text{BA} \rightarrow \bullet\text{BA-DC-BA}\bullet$	-57.6	-38.7
13	$\bullet\text{CD-AB}\bullet + \text{CD} \rightarrow \bullet\text{CD-AB-CD}\bullet$	-57.2	-32.5
14	$\bullet\text{CD-AB}\bullet + \text{DC} \rightarrow \bullet\text{CD-AB-DC}\bullet$	-48.0	
15	$\bullet\text{DC-AB}\bullet + \text{CD} \rightarrow \bullet\text{DC-AB-CD}\bullet$	-58.2	-35.7
16	$\bullet\text{DC-AB}\bullet + \text{DC} \rightarrow \bullet\text{DC-AB-DC}\bullet$	-47.9	
17	$\bullet\text{CD-BA}\bullet + \text{CD} \rightarrow \bullet\text{CD-BA-CD}\bullet$	-41.1	
18	$\bullet\text{CD-BA}\bullet + \text{DC} \rightarrow \bullet\text{CD-BA-DC}\bullet$	-30.2	
19	$\bullet\text{DC-BA}\bullet + \text{CD} \rightarrow \bullet\text{DC-BA-CD}\bullet$	-41.6	
20	$\bullet\text{DC-BA}\bullet + \text{DC} \rightarrow \bullet\text{DC-BA-DC}\bullet$	-30.5	

^a AB: CH(C₆H₅)CH₂.

^b CD: CH₂CH(CN).

where E_a^0 is the intrinsic barrier of reaction and γ_P is the transfer coefficient, and E_a^0 and γ_P are constants for the same reaction mechanism. The intrinsic activation barrier is the energy to distort the reactant orbitals to the transition-state geometry. The Polanyi equation could be used to quantify the behavior of some elementary reactions to be less probable than other reactions based on the activation energies. Also, activation barriers to reaction will allow predictions that one reaction pathway is favored over another reaction pathway [10]. This principle will be used here to predict the most favored propagation reaction pathways. Since all the of the propagation steps, as presented in Table 4, share the same reaction mechanism, it is expected based on Polanyi equation that these steps have approximately the same intrinsic barrier of reaction and the same transfer coefficient. Therefore, the highest exothermic reactions will have the lowest activation energies and hence will be considered the most probable reactions.

From the results presented in Table 4, it is clear that reactions 8, 12, 13, and 15 are the most exothermic reactions among the cross-propagation reactions, and when compared to the homopolymerization reaction, the cross-propagation reactions are dominant. This indicates that in the presence of the two monomers in the mixtures, the two monomers will most probably go through a cross-propagation mechanism. This finding is in agreement with conclusions in the literature. Hill et al. [11,12] reported that the styrene–acrylonitrile copolymerization follows the Penultimate model, in which the rate constants of the monomer addition onto the macro-radical depend on the nature of the monomer and the last two monomer units of the macro-radical. The reactivity ratios of styrene (S)–acrylonitrile (A) copolymerization are defined as

$$r_{SS} = \frac{k_{SSS}}{k_{SSA}}, \quad r_{AA} = \frac{k_{AAA}}{k_{AAS}}, \quad r_{AS} = \frac{k_{ASS}}{k_{ASA}}, \quad r_{SA} = \frac{k_{SAA}}{k_{SAS}}$$

In their study, researchers reported the experimental reactivity ratios of the copolymerization reactions as $r_{SS} = 0.22$, $r_{AA} = 0.03$, $r_{AS} = 0.63$, and $r_{SA} = 0.09$.

Other researchers [2,5,13] indicated that r_S has values ~ 0.41 and r_A has values ~ 0.04 . Both r_S and r_A were defined in Eq. (1). These findings suggest that most of the monomers will go through a copolymerization mechanism. Acrylonitrile will have a very weak tendency to go through a homopolymerization path, but styrene exhibits a better tendency to do so.

The APTACTM results were used to compare the measured heats of reaction to the AM1 predictions of propagation reactions. In order to perform this comparison, the APTACTM heats of reaction were corrected for the enthalpies of vaporization, ΔH_{vap} , of styrene–acrylonitrile mixtures according to Eq. (7):

$$\text{corrected } \Delta H_f = \text{APTAC}^{\text{TM}} \text{ measured } \Delta H_f - \Delta H_{\text{vap}} \quad (7)$$

Values of enthalpies of vaporization were estimated at reaction onset temperature, T_{onset} , considering the proportion of styrene to acrylonitrile in the mixture and based on the correlations available in the literature [5]. A pseudo-molecular weight based on the mean molecular weight of the initial mixture styrene–acrylonitrile ratio was used for this comparison, and Table 5 presents the corrected heats of reaction. According to the results obtained from Table 4, the calculated heats of reaction for the most exothermic reactions among the cross-propagation reactions were about -57.8 kcal/mol. This value is much higher than the APTACTM values measured and then corrected. As mentioned earlier, the AM1 level of

Table 5
Enthalpy of vaporization corrections for the APTACTM heats of reaction of styrene–acrylonitrile copolymerization

S:AN weight ratio	Pseudo-molecular weight (g/mol)	Enthalpy of vaporization (kcal/mol)	APTAC TM measured heat of reaction (cal/g)	APTAC TM measured heat of reaction (kcal/mol)	Corrected heat of reaction (kcal/mol)
80:20	87.1	9.00	–260	–22.7	–31.7
70:30	80.9	8.67	–261	–21.1	–29.8
60:40	75.8	8.40	–245	–18.6	–27.0
50:50	70.1	8.17	–269	–18.9	–27.0
40:60	64.9	7.92	–249	–16.2	–24.1
30:70	61.6	7.64	–228	–14.0	–21.7
20:80	57.7	7.53	–227	–13.1	–20.6

theory was not used for absolute property estimation but as a relative prediction approach to determine the most critical or dominant reactions. According to these values, AM1 systematically overestimated the heats of reaction. In addition, the density functional level of theory B3LYP/6-31G(d) was used to calculate the heats of reactions 8, 12, 13, and 15 as presented in Table 4. This higher and more expensive level of theory provides more reliable values of heats of reaction on an absolute basis (–30.8 to –38.7 kcal/mol), and the calculated values are more consistent with the APTACTM measured values as shown in Table 5.

From a comparison of these calculations to the results of the experimental analysis, a conclusion is that as the concentration of acrylonitrile increases, the copolymerization rate must decrease since most of styrene monomers are consumed either by the cross-propagation copolymerization reaction or by the homopolymerization reaction. Since the tendency of acrylonitrile for homopolymerization is low in the presence of styrene monomer, most of the un-copolymerized acrylonitrile monomers will start to decompose at the rapidly increased temperatures due to the copolymerization runaway, and this activity will cause another increase in temperature and pressure.

Also we can see from the results of Table 4 that heat of reaction is a function of the chain end active site regardless of what is attached to that site from the other side. For example, comparing reactions 13 and 15 shows that heat of reaction will be the same (57–58 kcal/mol) as long as the reactive site on the copolymer chain and the monomer are the same with no effect from what is attached to the other end of the copolymer chain or in what order. This conclusion also is consistent with the random arrangement of monomers in the styrene–acrylonitrile copolymer chain.

5. Conclusion

The effect of the monomer feed ratio of styrene–acrylonitrile copolymerization runaway scenario was evaluated using thermal (calorimetric) analysis. As the styrene monomer concentration increases, the copolymerization heat of reaction increases. A secondary exothermic reaction was detected as the acrylonitrile concentration increases. Theoretical analysis showed that a cross-propagation reaction is the main mechanism of styrene and acrylonitrile monomers. However, the very low tendency of homopolymerization by acrylonitrile will

cause the remaining acrylonitrile monomers to decompose at high temperatures due to the copolymerization runaway reaction.

The combination of the experimental analysis with screening theoretical calculations improved the understanding of the runaway reaction scenario of styrene–acrylonitrile copolymerization and yielded a good agreement with other research findings concerning this reaction mechanism.

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References

- [1] M. Chanda, *Advanced Polymer Chemistry*, Marcel Dekker, New York, 2000.
- [2] R. Boundy, R. Boyer, S. Stoesser, *Styrene its Polymers, Copolymers, and Derivatives*, Reinhold Publishing, New York, 1952.
- [3] D. Sebastian, J. Biesenberger, in: V. Weekman Jr., D. Luss (Eds.), *Proceedings of the Fifth International Symposium on Chemical Reaction Engineering*, Houston, Texas, American Chemical Society, Washington, DC, 1978, pp. 173–186.
- [4] A. Aldeeb, W. Rogers, M. Mannan, *Trans. Inst. Chem. Eng. Part B* 80 (2002) 141.
- [5] C. Yaws, *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health Related Properties for Organic and Inorganic Chemicals*, McGraw-Hill, New York, 1999.
- [6] American Cyanamid Company, *The Chemistry of Acrylonitrile*, American Cyanamid Company, New York, 1959.
- [7] M. Dewar, W. Thiel, *J. Am. Chem. Soc.* 99 (1977) 4899.
- [8] M. Evans, M. Polanyi, *Trans. Faraday Soc.* 32 (1936) 1333.
- [9] M. Evans, M. Polanyi, *Trans. Faraday Soc.* 34 (1938) 11.
- [10] R. Masel, W. Lee, *J. Catal.* 165 (1997) 80.
- [11] D. Hill, J. O'Donnell, P. O'Sullivan, *Macromolecules* 15 (1982) 960.
- [12] D. Hill, A. Lang, P. Munro, J. O'Donnell, *Eur. Polym. J.* 28 (1992) 391.
- [13] F. Lewis, F. Mayo, W. Hulse, *J. Am. Chem. Soc.* 67 (1945) 1701.