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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 reaction is of great importance to 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 reaction, 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 reaction.

In this paper the styrene-acrylonitrile copolymerization reaction in bulk is evaluated for its thermal stability and runaway behavior. 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.

Keywords: copolymerization; styrene-acrylonitrile; thermal runaway; calorimetry

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 has been centered on predicting composition and conversion, but understanding chemical

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reactivity and runaway reactions are important because of the importance of processes that are both safe and economic.

In this research, copolymerization of styrene-acrylonitrile in bulk is evaluated for its thermal reactivity and runaway behavior using thermal analysis techniques. The Reactive System Screening Tool (RSST™) was used for preliminary analysis and the Automated Pressure Tracking Adiabatic Calorimeter (APTAC™) 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 study the effect of composition on the temperature and pressure behavior during a runaway scenario. At the same time, a theoretical evaluation was conducted to predict reaction pathways to explain the experimental results and also for comparison with literature values.

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 are also 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 monomers 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 Figure 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 reaction is the most rapid. The initiation, which produces an activated radical from a stable monomer, is by far the slowest step, whenever long chains are formed [2].

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

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

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

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 rises and possible instability. Runaway could cause a sharp reduction in polymer/copolymer molecular weight and an increased spread in molecular weight distribution [3].

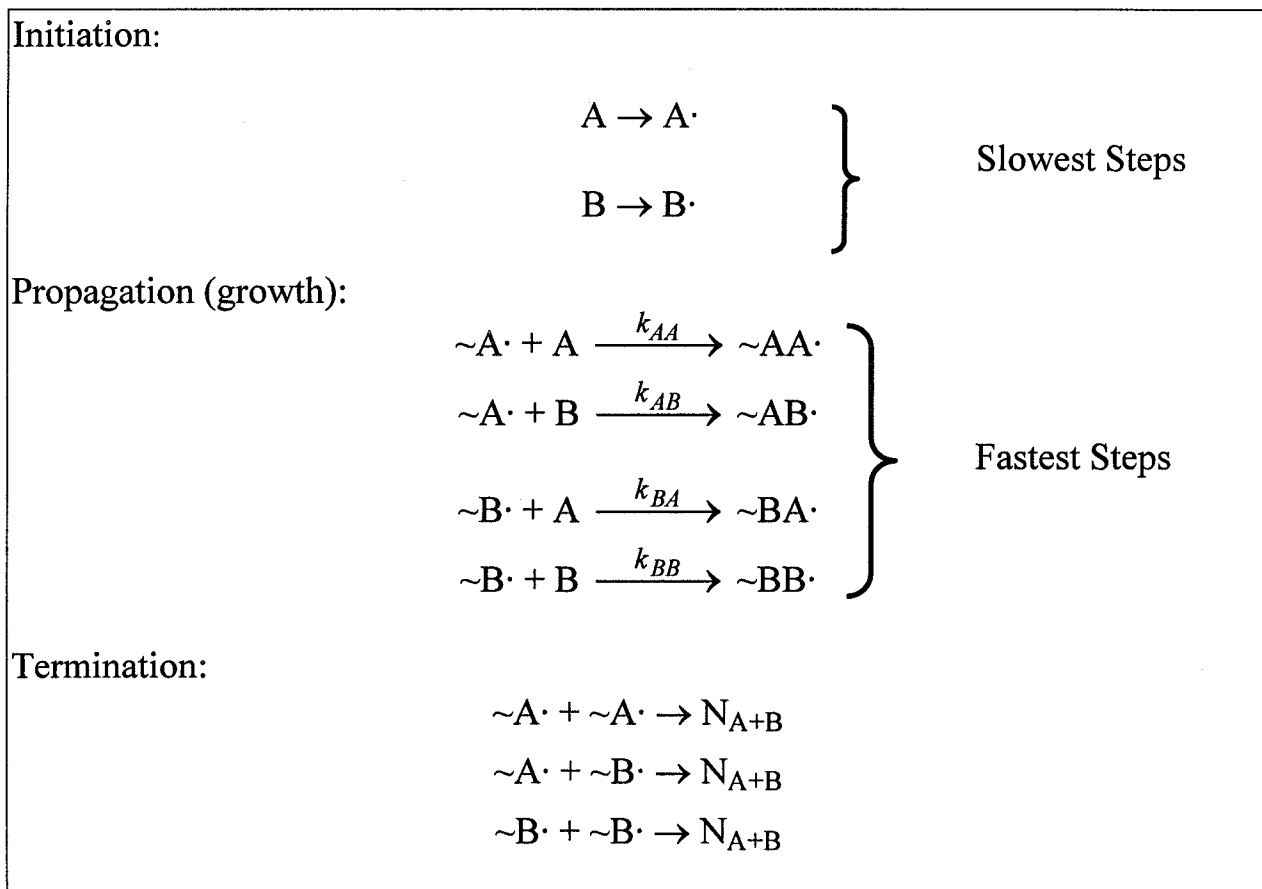


Figure 1. Typical free radical copolymerization reaction of two monomers, A and B

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 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 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.

RESULTS

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 feeding ratios

S:AN weight ratio	80:20	70:30	60:40	50:50	40:60	30:70	20:80
S:AN mole ratio	2.0:1.0	1.2:1.0	0.8:1.0	0.5:1.0	0.3:1.0	0.2:1.0	0.1:1.0

All experiments were conducted in nitrogen after vacuuming air from the test cells. Temperature and pressure profiles were obtained from both RSST™ and APTAC™ tests. The heat of reaction for the copolymerization reaction was calculated using Equation (2):

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

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

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 the 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 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 RSST™ testing can be calculated from Equation (3a), and for the APTAC™ testing from Equation (3b):

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

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

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 Equation (3) into (4) results in Equation (5):

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

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

RSSTTM Analysis

Experimental screening analysis using the RSSTTM was performed for the seven monomers feeding ratios. Styrene-acrylonitrile monomers were mixed at room temperature and then injected to the RSSTTM glass cell that was vacuumed of air and then 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 to 3.3 °C/min were applied for samples masses of 7.6 to 8.2 g placed in the cell with a thermal inertia (ϕ -factor) of about 1.05. Stirring was present during the experiments.

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

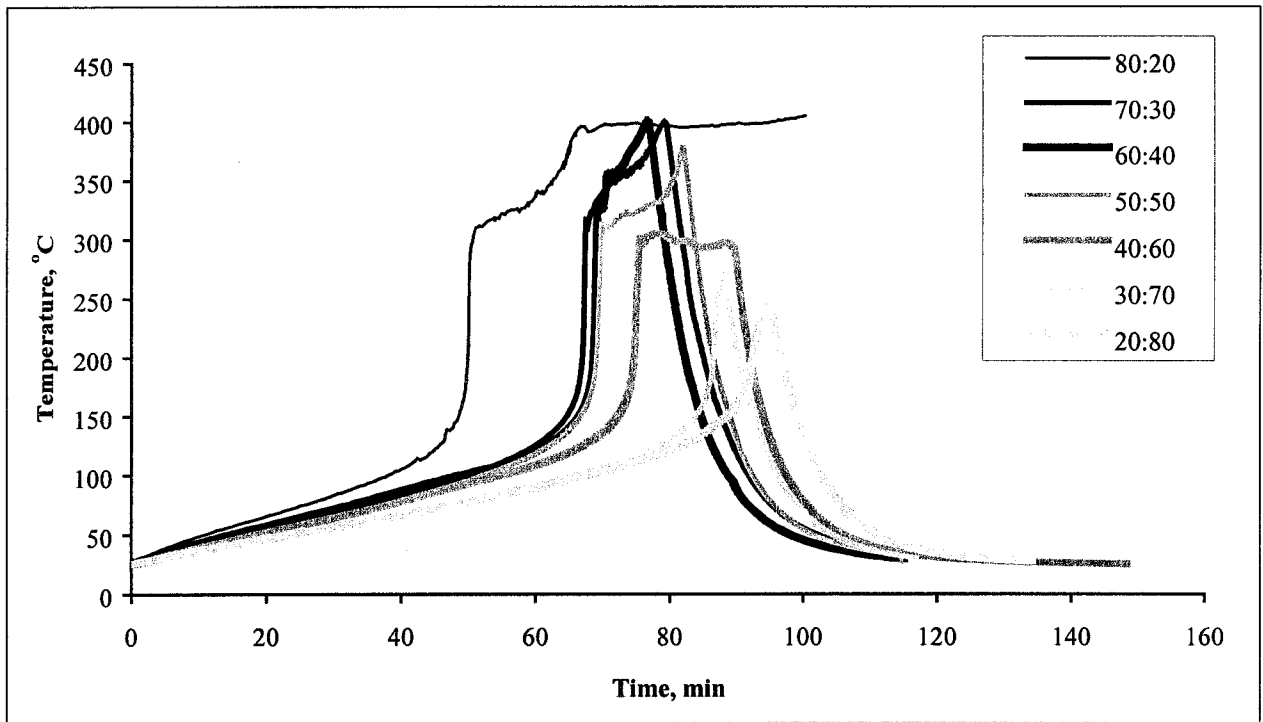


Figure 2. Temperature profiles of the styrene-acrylonitrile copolymerization runaway, RSST™

APTAC™ Analysis

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

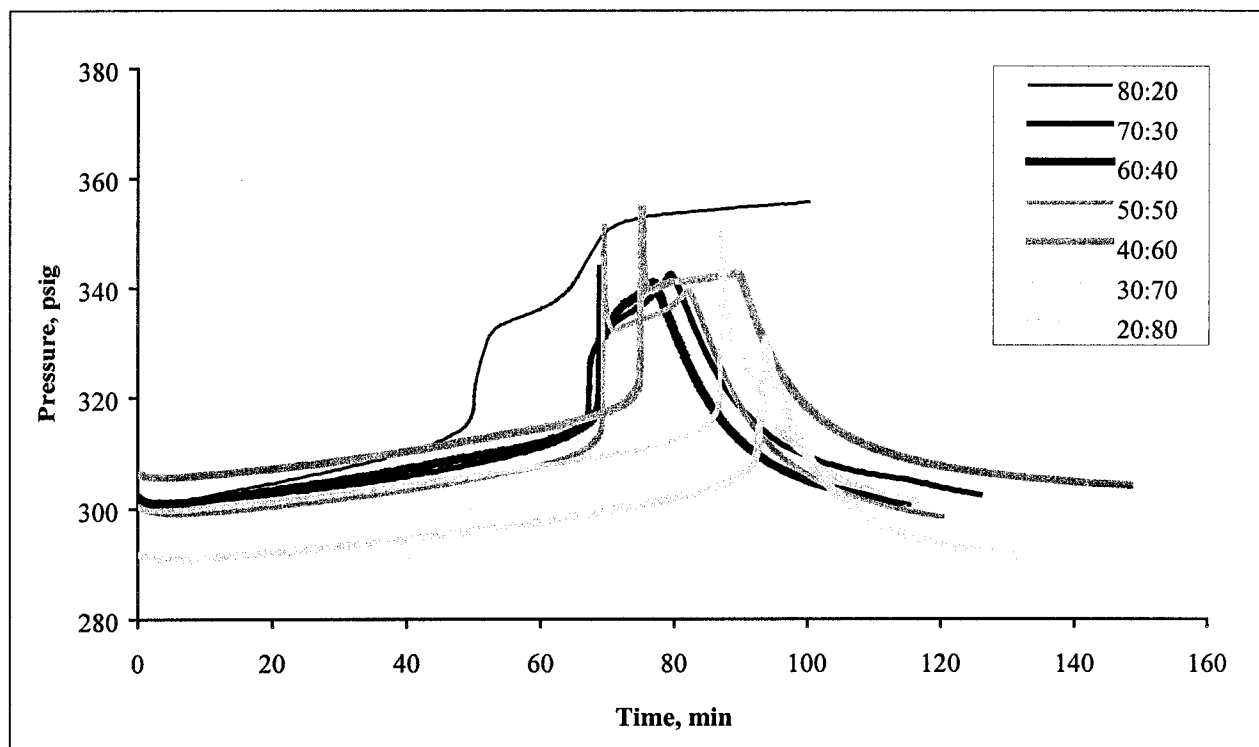


Figure 3. Pressure profiles of styrene-acrylonitrile copolymerization runaway by the RSST™

Table 2. Onset temperature, heat of reaction, and Arrhenius parameters the styrene-acrylonitrile copolymerization runaway measured by the RSST™

S:AN weight ratio	$T_{\text{onset}}, ^\circ\text{C}$	$\Delta H_r, \text{cal/g}$	$E_A, \text{kcal/gmol}$	$\log(A), \text{s}^{-1}$
80:20	108 ± 3	-150 ± 16	20.7 ± 1.0	7.7 ± 0.7
70:30	103 ± 1	-184 ± 8	20.4 ± 0.7	7.3 ± 0.3
60:40	107 ± 5	-150 ± 8	21.3 ± 1.3	7.9 ± 0.6
50:50	104 ± 4	-158 ± 4	21.0 ± 1.4	7.8 ± 0.6
40:60	114 ± 7	-139 ± 5	23.8 ± 3.7	9.3 ± 2.0
30:70	102 ± 4	-117 ± 6	21.9 ± 0.6	8.3 ± 0.3
20:80	102 ± 4	-104 ± 7	19.4 ± 0.6	7.1 ± 0.0

Temperature and pressure profiles during the copolymerization reaction are shown in Figures 4 and 5, respectively. Table 3 summarizes the onset temperatures, heats of reaction, and Arrhenius parameters determined from the APTAC™ data. The onset temperature of the APTAC™ tests was determined at a self-heating rate of $0.1 ^\circ\text{C}/\text{min}$.

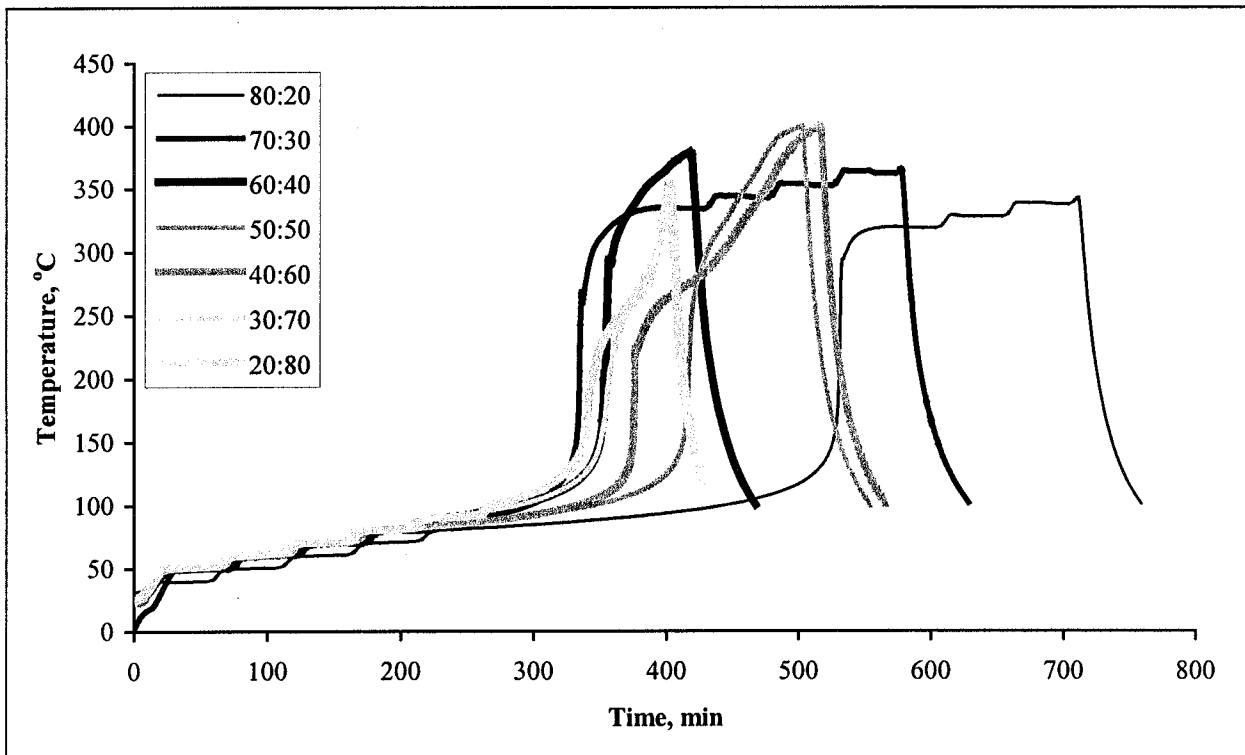


Figure 4. Temperature profiles of styrene-acrylonitrile copolymerization runaway, APTAC™

The RSST™ screening analysis results show that the onset temperature, T_{onset} , was $\sim 106^{\circ}\text{C}$ while for the APTAC™ analysis the onset temperature was $\sim 91^{\circ}\text{C}$. From both RSST and APTAC™ results we can conclude that monomer feed ratio will not significantly affect the reaction T_{onset} temperature. However the difference in T_{onset} values for RSST™ and APTAC™ is due to high heat losses in the RSST™ compared to the nearly adiabatic conditions of the APTAC™. The heat losses in the RSST™ as an open cell system will shift the measured T_{onset} to higher values.

The effective heat losses in the RSST™ is obvious also when comparing the measured heats of reaction as shown in Figure 6. An average difference of about 107 cal/g (43% of the APTAC™ measured ΔH_r) is observed between the APTAC™ and the RSST™ 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. Figure 6 indicates that the copolymerization reaction rate will be reduced when the styrene monomer concentration is less than 50% by weight, which is equivalent to a styrene : acrylonitrile mole ratio of 0.5:1.0.

The RSST™ analysis temperature profiles (shown in Figure 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 APTAC™ analysis temperature profiles (shown in Figure 4). However for the APTAC™ 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. RSST™ did not measure these temperature changes because of nature of the test. During the test, the RSST™ applies a constant temperature ramping, which obscures the secondary temperature activity, while for the

APTAC™, the adiabatic operating mode continues to detect temperature changes even after the first maximum temperature is attained. Studying the APTAC™ pressure profiles (shown in Figure 5) will enhance an understanding of this phenomenon.

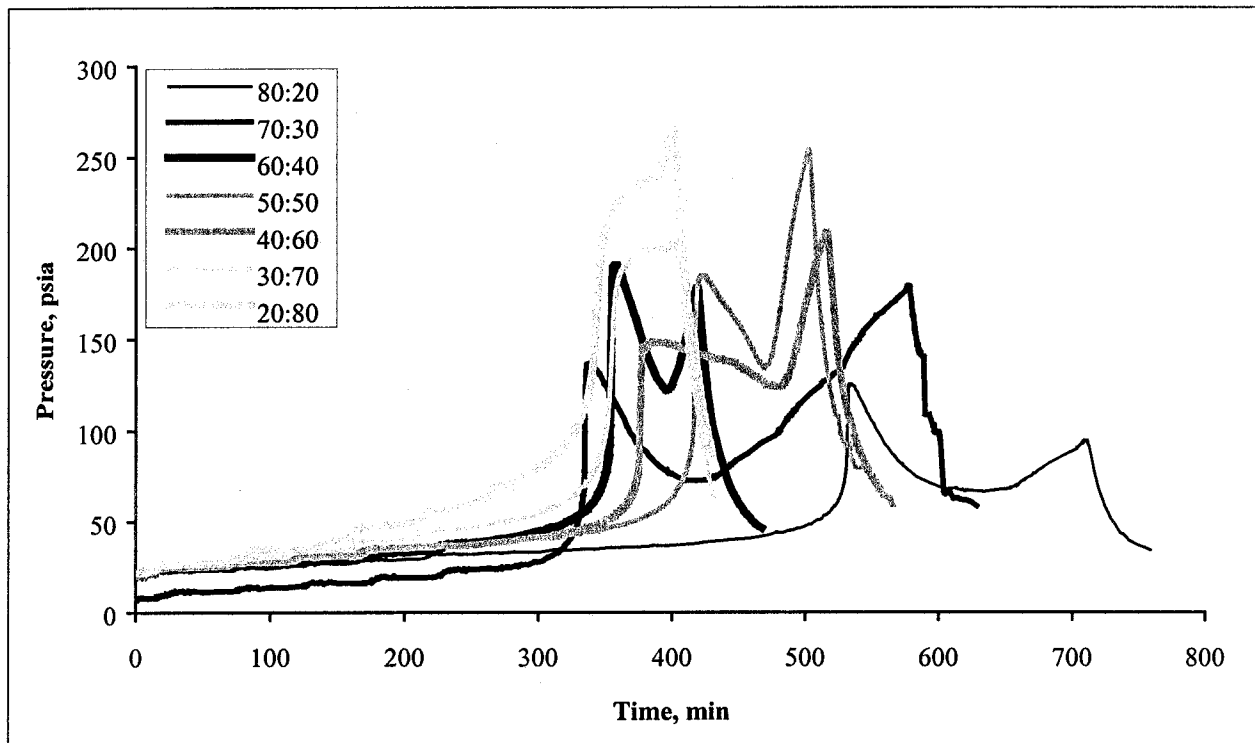


Figure 5. Pressure profiles of styrene-acrylonitrile copolymerization runaway by the APTAC™

For each copolymerization feeding ratio there were two maximum pressure peaks. Comparing 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 copolymerized 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 group together more closely as shown in Figure 5, until they form a wide peak as in styrene-acrylonitrile feed ratios of 30:70 and 20:80.

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

Table 3. Onset temperature, heat of reaction, and Arrhenius parameters the styrene-acrylonitrile copolymerization runaway measured by the APTAC™

S:AN weight ratio	$T_{\text{onset}}, ^\circ\text{C}$	$\Delta H_r, \text{cal/g}$	$E_A, \text{kcal/gmol}$	$\log(A), \text{s}^{-1}$
80:20	91 ± 3	-263 ± 2	22.4 ± 0.5	8.5 ± 0.3
70:30	91 ± 3	-261 ± 0	22.4 ± 1.1	8.7 ± 0.7
60:40	90 ± 0	-243 ± 7	23.2 ± 0.8	9.0 ± 0.4
50:50	88 ± 2	-269 ± 4	22.4 ± 0.4	8.6 ± 0.2
40:60	91 ± 6	-240 ± 11	26.8 ± 1.5	11.1 ± 0.6
30:70	98 ± 6	-228 ± 5	25.0 ± 3.2	10.0 ± 1.8
20:80	90 ± 4	-237 ± 5	23.8 ± 0.9	9.32 ± 0.5

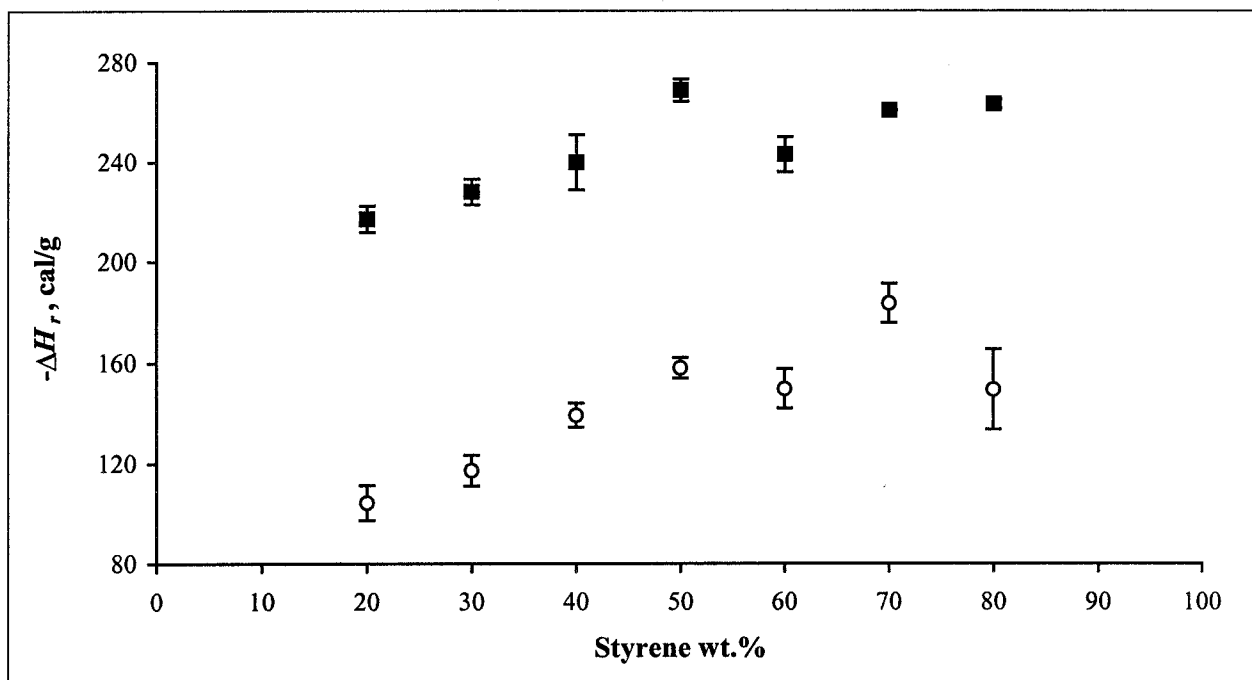


Figure 6. Heats of reaction of styrene-acrylonitrile copolymerization runaway reaction

Theoretical Evaluation

As discussed earlier, the propagation steps in the copolymerization reactions are by far the fastest reaction steps and are responsible for the large release of energy. To predict the relative tendency for homopolymerization and cross-propagation copolymerization, enthalpy of reactions were calculated using the semi-empirical computational method, AM1 [7]. These calculations are 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. Figure 7 presents the two reactive ends that were used for each molecule. The results 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, but for more accurate thermochemical predictions, a more advanced computational models should be used.

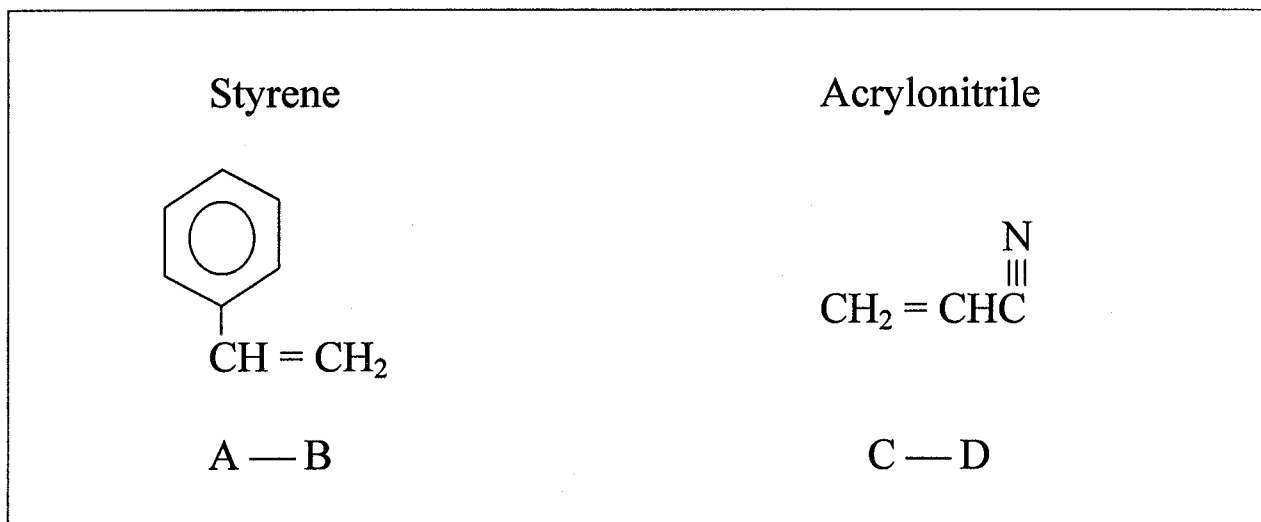


Figure 7. Styrene and acrylonitrile reactive ends identified for AM1 calculations

Evans and Polanyi [8] [9] examined the relationship between the thermodynamics of a reaction and the activation barrier (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:

$$E_a = E_a^o + \gamma_p \Delta H_r \quad (5)$$

where, E_a^o is the intrinsic barrier of the reaction and γ_p is the transfer coefficient, and they 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 more difficult or less probable than other reactions based on the activation energies. Also, activation barriers to reaction will allow predicting whether one reaction pathway is favored over another reaction pathway [10]. This principle will be used for predicting the most favored propagation reaction pathway. The highest exothermic reactions will be considered the most probable reactions to take place since it will require the smallest amount of activation energy.

From the results presented in Table 4 it is clear that Reactions 8, 12, 13, and 15 are most exothermic reactions among the cross-propagation reactions, and when compared to the

homopolymerization reaction, the cross-propagation reactions will be 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 mechanisms. This finding is in agreement with conclusions in the literature. Hill et al. [11] [12] reported the reactivity ratios of styrene (S) - acrylonitrile (A) copolymerization as $r_{SS} = 0.22$, $r_{AA} = 0.03$, $r_{AS} = 0.63$, and $r_{SA} = 0.09$ using the penultimate model as the most appropriate model. In this study, researchers described the reactivity ratios as

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

Table 4. Heats of reaction for styrene and acrylonitrile homopolymerization and styrene-acrylonitrile copolymerization using the semi-empirical method AM1

Reaction No.	Propagation Reaction	Enthalpy of Reaction, kcal/mol
1	$\cdot\text{AB-AB}\cdot + \text{AB} \rightarrow \cdot\text{AB-AB-AB}\cdot$	-40.2
2	$\cdot\text{AB-AB-AB}\cdot + \text{AB} \rightarrow \cdot\text{AB-AB-AB-AB}\cdot$	-37.3
3	$\cdot\text{CD-CD}\cdot + \text{CD} \rightarrow \cdot\text{CD-CD-CD}\cdot$	-48.4
4	$\cdot\text{CD-CD-CD}\cdot + \text{CD} \rightarrow \cdot\text{CD-CD-CD-CD}\cdot$	-44.6
5	$\cdot\text{AB-CD}\cdot + \text{AB} \rightarrow \cdot\text{AB-CD-AB}\cdot$	-31.3
6	$\cdot\text{AB-CD}\cdot + \text{BA} \rightarrow \cdot\text{AB-CD-BA}\cdot$	-47.8
7	$\cdot\text{AB-DC}\cdot + \text{AB} \rightarrow \cdot\text{AB-DC-AB}\cdot$	-41.0
8	$\cdot\text{AB-DC}\cdot + \text{BA} \rightarrow \cdot\text{AB-DC-BA}\cdot$	-58.1
9	$\cdot\text{BA-CD}\cdot + \text{AB} \rightarrow \cdot\text{BA-CD-AB}\cdot$	-24.2
10	$\cdot\text{BA-CD}\cdot + \text{BA} \rightarrow \cdot\text{BA-CD-BA}\cdot$	-49.6
11	$\cdot\text{BA-DC}\cdot + \text{AB} \rightarrow \cdot\text{BA-DC-AB}\cdot$	-41.6
12	$\cdot\text{BA-DC}\cdot + \text{BA} \rightarrow \cdot\text{BA-DC-BA}\cdot$	-57.6
13	$\cdot\text{CD-AB}\cdot + \text{CD} \rightarrow \cdot\text{CD-AB-CD}\cdot$	-57.2
14	$\cdot\text{CD-AB}\cdot + \text{DC} \rightarrow \cdot\text{CD-AB-DC}\cdot$	-48.0
15	$\cdot\text{DC-AB}\cdot + \text{CD} \rightarrow \cdot\text{DC-AB-CD}\cdot$	-58.2
16	$\cdot\text{DC-AB}\cdot + \text{DC} \rightarrow \cdot\text{DC-AB-DC}\cdot$	-47.9
17	$\cdot\text{CD-BA}\cdot + \text{CD} \rightarrow \cdot\text{CD-BA-CD}\cdot$	-41.1
18	$\cdot\text{CD-BA}\cdot + \text{DC} \rightarrow \cdot\text{CD-BA-DC}\cdot$	-30.2
19	$\cdot\text{DC-BA}\cdot + \text{CD} \rightarrow \cdot\text{DC-BA-CD}\cdot$	-41.6
20	$\cdot\text{DC-BA}\cdot + \text{DC} \rightarrow \cdot\text{DC-BA-DC}\cdot$	-30.5

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

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 must slow down 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 temperature and pressure increase.

Also we can see from the results of Table 4 that enthalpy 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 the monomers in the styrene-acrylonitrile copolymer chain.

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 about this reaction mechanism.

ACKNOWLEDGMENT

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APPENDIX

A	frequency parameter, s^{-1}
C_c	heat capacity of cell, $cal\ g^{-1}\ K^{-1}$
C_{vs}	heat capacity of sample, $cal\ g^{-1}\ K^{-1}$
E_A	activation energy, $kcal\ mol^{-1}$
E_a°	intrinsic barrier of the 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, $1.987\ cal\ mol^{-1}\ K^{-1}$
T_{max}	maximum temperature due to decomposition reaction, $^\circ C$
T_{onset}	onset temperature at which exothermic decomposition is first detected, $^\circ C$
dT/dt	the sample heating rate, $^\circ C\ min^{-1}$
ϕ	thermal inertia factor
ΔH_r	heat of reaction, $cal\ g^{-1}$
ΔT_{ad}	adiabatic temperature rise, $^\circ C$
γ_P	transfer coefficient

REFERENCES

- [1] M. Chanda, *Advanced Polymer Chemistry*, Marcel Dekker, New York, 2000.
- [2] R. Boundy, R. Boyer, and S. Stoesser, *Styrene Its polymers, Copolymers, and Derivatives*, Reinhold Publishing, New York, 1952.
- [3] D. Sebastian and J. Biesenberger, in: V. Weekman, Jr. and D. Luss (Ed.), *Chemical Reaction Engineering, The Fifth International Symposium on Chemical Reaction Engineering*, Houston, Texas, 1978, American Chemical Society, Washington, 1978, pp. 173-186.
- [4] A. Aldeeb, W. Rogers, and 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 and W. Thiel, *J. Am. Chem. Soc.*, 99 (1977) 4899.
- [8] M. Evans and M. Polanyi, *Trans. Faraday Soc.*, 32 (1936) 1333.
- [9] M. Evans and M. Polanyi, *Trans. Faraday Soc.*, 34 (1938) 11.
- [10] R. Masel and W. Lee, *J. Catal.*, 165 (1997) 80.
- [11] D. Hill, J. O'Donnell, and P. O'Sullivan, *Macromolecules*, 15 (1982) 960.
- [12] D. Hill, A. Lang, P. Munro, and J. O'Donnell, *Eur. Polym. J.*, 28 (1992) 391.
- [13] F. Lewis, F. Mayo, and W. Hulse, *J. Am. Chem. Soc.*, 67 (1945) 1701.