Minimizing risk. Maximizing potential.®

Polymerization Modeling for Emergency Relief Systems

An ioMosaic Corporation White Paper

G. A. Melhem, Ph.D., FAIChE

melhem@iomosaic.com

IOMOSAIC CORPORATION

Polymerization Modeling for Emergency Relief Systems

Pressure Relief and Effluent Handling Practices

authored by

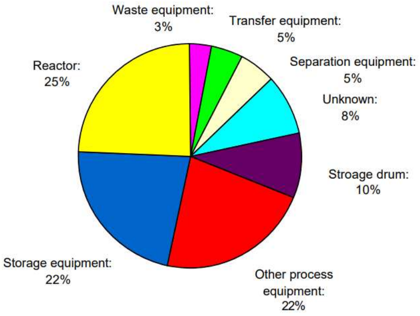
Georges A. MELHEM, Ph.D., FAIChE

July 3, 2020

Contents

1 Introduction

In a 2001 comprehensive investigation report on reactive chemicals, the United States Chemical Safety and Hazard Investigation Board (CSB) [1] reported that 22 % of reactive chemicals incidents occurred in storage equipment and 25 % occurred in reactors. 167 incidents were considered between 1980 and 2001. Although not specific to polymer systems, the storage equipment category includes monomer storage tanks and the reactors category includes polymerization reactors.



Free-radical polymerization reactions are the best studied reactions in all of chemistry [2]. In 1998, the chemical and petrochemical industries produced 87 billion lbs of polymers including thermoplastics, thermosets, synthetic fibers, and synthetic rubber. Acrylonitrile-Butadiene-Styrene (ABS) accounted for three billion lbs of thermoplastics [3]. Many chemical operators have developed and tuned polymerization models (anionic, free-radical, etc.) that can easily and readily be coupled with thermally-initiated polymerization kinetics for pressure relief systems design under runaway reaction conditions for storage and process vessels [4, 5, 6].

2 Types of Polymerization Reactions

Common polymerization reactions where emergency relief may be necessary include bulk, solution, suspension, and emulsion polymerizations. Bulk addition polymerization is the simplest of the four polymerization types. Bulk polymerization is a homogeneous system where the reaction occurs ”in bulk” and most often an initiator is used. If the polymer is soluble in the monomer, then the monomer concentration will decrease as more polymer is formed and as the mixture viscosity changes. If the polymer is not soluble in the monomer, initiation, propagation, and termination of polymerization might occur only in the monomer phase. Bulk polymerizations are inherently more difficult to control under runaway conditions because the increase in viscosity drastically reduces convection heat transfer/cooling.

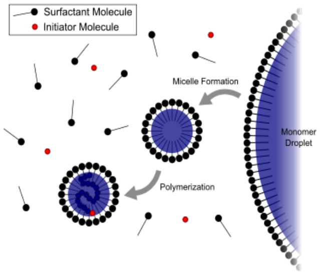
Solution polymerization reactions are bulk polymerization reactions but use a solvent or diluent for better heat control. The amount and rate of heat removed due to the presence of the solvent depend on whether the boiling point of the solvent is above or below the onset of the polymerization reaction, and whether the monomer, polymer, or both are soluble in the solvent.

If the monomer is not soluble (or slightly soluble) in the solvent and the monomer is mechanically dispersed, bulk polymerization can be carried out in small suspended droplets. The solvent phase becomes the heat sink. This type of polymerization is called suspension polymerization. Agitation and a suspension agent are required to keep the droplets separated and far apart. The suspension agent keeps the droplets from coalescing and becoming larger. The behavior inside the droplets can be assumed to be similar to bulk polymerization although faster reaction rates are possible because the droplets typically range from 100 nm to 5 mm. In general, the rate of suspension polymerization is similar to the rate of bulk polymerization with much better heat control.

The initiation, propagation, and termination reactions take place inside the droplets. Suspension polymerization is often called ”bulk polymerization within a droplet”. Agitation is critical in suspension polymerization. The most common method for controlling the droplet size is the change the stirring/agitation speed.

If a surfactant is added to a suspension polymerization and the small droplets are stabilized by the surfactant, the polymerization becomes an emulsion polymerization [7]. Emulsion polymerizations are usually carried out in water. The initiator can be soluble in either the aqueous or organic phase. While suspension polymerization is a mechanical process which requires a stabilizing suspension agent, emulsion polymerization is a chemical process which requires a surfactant to emulsify the monomer.

Initially, a small amount of agitation is necessary. Excess surfactant creates micelles with monomer and initiator diffusing into the micelles. The process results in a latex particle, which is a dispersion of polymer in water. In emulsion polymerization, monomers are first dispersed in the aqueous phase as droplets surrounded by surfactants. Initiator radicals are generated in the aqueous phase and migrate into the micelles that are swollen with monomer molecules. As the polymerization proceeds, more monomers migrate into the micelles to enable the polymerization to continue. Initiation takes place in the water phase while polymer propagation takes place in the separate polymer particle phase.



Since only one free radical [1] is present in the micelle prior to termination, very high molecular weights are possible. The viscosity of latexes are governed by the viscosity of the medium the particles are dispersed in (continuous medium). Chain transfer agents are added to control the molecular weight.

In Emulsion polymerization, the initiator is soluble in the aqueous phase. Initiation takes place in the aqueous phase and radicals formed are diffused to the polymer droplets where propagation and termination take place. There are normally very few active radicals in the polymer droplets. If the initiator is soluble in the organic / monomer phase, a suspension polymerization will take place.

In suspension polymerization, the initiator is soluble in the organic phase (reaction occurs in monomer droplets like having many batch reactors in the individual droplets). Suspension polymerization also requires an emulsifier to control the monomer droplet size, which is the polymer particle size (much larger scale compared to emulsion polymerization). In emulsion polymerization, monomer droplets are like those in suspension. But since the initiator is not soluble in the organic phase, the monomers diffuse out of these droplets and are initiated in the water phase. Initiated radicals diffuse to micelles or newly nucleated polymer droplets (much smaller and much more abundant than monomer droplets) where propagation and termination take place. Without an emulsifier a precipitation polymerization occurs which is similar to emulsion polymerization.

---

[1] Normally only one free radical is present in an actively polymerizing particle (some particles have none and very few particles have more than one)

3 Polymerization Heats of Reaction

Most polymerization reactions are exothermic and require heat removal to keep the reactions under control. Depending on the degree of polymerization and polymer mixture viscosity a variety of cooling methods are available including jacket cooling, reflux condensing, and internal cooling coils. Heats of polymerization for most reactions of interest are readily available or can easily be approximated from bond energies [8] as shown in Table 1.

Table 1: Bond contribution to heat of polymerization (ΔH_p)

Monomer Bond	Polymer Bond	ΔH_p kcal/gmol	ΔH_p BTU/lbmol
C=N	-C-N	-1.4	-2,518
C=S	-C-S-	-2	-3,598
C=O	-C-O	-5	-8,994
S=O	-S-O-	-7	-12,592
C=N	-C=N-	-7.2	-12,952
C=C	-C-C	-20	-35,977

Heats of polymerization estimates for a wide variety of monomers based on bond energies are shown in Table 2. Estimates based on bond energies represent a good starting point that should be confirmed by adiabatic and/or isothermal calorimetry.

Table 2: Typical heats of polymerization (ΔH_p) values

Monomer	ΔH_p kcal/gmol	ΔH_p BTU/lbmol	ΔH_p cal/g	ΔH_p BTU/lb
Methyl Styrene	-8.4	-15,110	-71	-128
Methyl Methacrylate	-13.5	-24,284	-135	-243
Styrene	-16.7	-30,041	-160	-288
Vinylidene Chloride	-18	-32,379	-186	-334
Methyl Acrylate	-18.8	-33,818	-218	-393
Isobutene	-12.3	-22,126	-219	-394
Vinyl Acetate	-21	-37,776	-244	-439
Isoprene	-17.8	-32,019	-261	-470
1,3-butadiene	-17.4	-31,300	-322	-579
Vinyl Chloride	-22.9	-41,193	-366	-659
Tetrafluoroethylene	-37.2	-66,917	-372	-669
Acrylonitrile	-20	-35,977	-377	-678
Propylene	-20.5	-36,876	-487	-876
Ethylene	-22.7	-40,834	-809	-1,456

4 Free Radical Bulk Polymerization Rates

The mechanism of free radical homopolymerization [2] involves three steps [3]: initiation, propagation, and termination [2, 3]:

$$\text{Initiation:} \quad I \xrightarrow{k_d} 2R^\bullet \quad \Rightarrow \quad -\frac{d[I]}{dt} = k_d[I] \tag{1}$$

$$\text{Propagation:} \quad M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet \quad \Rightarrow \quad -\frac{d[M]}{dt} = k_p[M^\bullet][M] \tag{2}$$

$$\text{Termination:} \quad M_n^\bullet + M_m^\bullet \xrightarrow{k_t} \text{dead polymer} \quad \Rightarrow \quad -\frac{d[M^\bullet]}{dt} = 2k_t[M^\bullet]^2 \tag{3}$$

$$\tag{4}$$

In the above equations [] is concentration in $\mathrm{kmol/m^3}$, t is time in seconds, k is reaction rate in SI units, M is monomer, R is radical, and I is initiator. At steady state ($t > 60$ s) the net rate of production of free radicals is zero such that the initiation and termination rates are equal.

Important relief systems design data that can be approximated using the steady state assumption include termination rates and the average degree of polymerization (molecular weight and viscosity):

$$\text{Termination:} \; M_n^\bullet + M_m^\bullet \xrightarrow{k_t} \text{dead polymer} \;\; \Rightarrow \;\; -\frac{d[M^\bullet]}{dt} = 2k_t[M^\bullet]^2 = 2k_d f[I] \tag{5}$$

$$\text{Average Degree of Polymerization:} \; \overline{\text{DP}} = \frac{[M]}{\sqrt{I}} k^{"} \;\; \text{where} \;\; k^{"} = \frac{k_p}{\sqrt{2k_d k_t f}} \tag{6}$$

The average degree of polymerization [4] is the ratio of molecular weight of the polymer over the molecular weight of monomer. f is the initiator efficiency, typically 1/2.

A free-radical initiated polymerization rate expression of a monomer is well known and is commonly used in the following form:

$$-\frac{1}{V_l}\frac{dN}{dt} = \frac{k_p}{\sqrt{k_t \theta}} \left(\sqrt{2 f k_d [I]} \right) [N] \tag{7}$$

Where N is the number of moles of monomer in kmol, V_l is the liquid volume in $\mathrm{m^3}$, and θ is a gel effect constant ranging from 0 to 1. θ is usually fit from calorimetry or test data as a function of temperature and polymer mass fraction (viscosity and conversion). As gel effects

---

[2] Copolymerizations are more complex

[3] There are some other minor heat producing reactions (chain transfers), but these are the major heat producing reactions.

[4] Equation 6 is applicable when termination is by disproportionation. For termination by combination, $\overline{\text{DP}}$ = 2 x this value. Chain transfer kinetics also influence $\overline{\text{DP}}$.

become significant, k_t reduces dramatically due to diffusion limits of radicals coming into contact and k_c increases significantly (much faster polymerization rate).

We can easily rearrange this form to take advantage of adiabatic calorimetry data:

$$-\frac{1}{V_l}\frac{dN}{dt} = k_c[N]\sqrt{[I]} \text{ where } k_c = k_p\left[\frac{2fk_d}{\theta k_t}\right]^{1/2} = A_c \exp\left[-\frac{E_c}{T}\right] \tag{8}$$

The rate constant is a composite constant that can be regressed from adiabatic calorimetry data, isothermal calorimetry data, or a combination of adiabatic and isothermal calorimetry data. The composite pre-exponential constant and activation energy can be estimated from initiation, propagation, and termination constants.

$$k_c = A_c \exp\left[-\frac{E_c}{T}\right] \text{ where } A_c = A_p\sqrt{2\frac{f}{\theta}\frac{A_d}{A_t}} \text{ and } E_c = E_p + \frac{1}{2}(E_d - E_t) \tag{9}$$

The initiator decomposition rate expression and concentration are best represented computationally in parts per million weight (ppmw) since the total quantity of initiator used is often very small compared the total quantity of monomer.

$$k_d = A_d \exp\left[-\frac{E_d}{T}\right] \text{ and } \frac{dI_{\text{ppmw}}}{dt} = -k_d I_{\text{ppmw}} \tag{10}$$

The rate parameters for propagation, termination, and initiator decomposition are often determined from isothermal calorimetry measurements. However, we can use adiabatic calorimetry to establish the value of k_c from ARC/APTAC/VSP measurements using a specific initiator with a well known decomposition rate such as lauroyl peroxide. This provides an implicit measurement of k_p and k_t:

$$k_c = k_p\left[\frac{2fk_d}{\theta k_t}\right]^{1/2} \tag{11}$$

One can also establish k_p and k_t individually, partly from the literature and partly from experiments. In order for this to work we assume that k_p and k_t are monomer specific and do not depend on the specific initiator used. If the system of interest uses a solvent, select the initiator, propagation, and termination constants that were established using the same solvent.

The composite polymerization rate constant established with a specific initiator can be used in conjunction with the decomposition rate of any other initiator to provide a free-radical polymerization model for the other initiator. A composite rate is often sufficient for emergency relief systems design if accurate viscosity and molecular weight data can also be determined or supplied independently:

$$-\frac{1}{V_l}\frac{dN}{dt} = k_{c0}\left[\frac{f}{f_0}\frac{\theta_0}{\theta}\frac{k_d}{k_{d0}}\right]^{1/2}[N]\sqrt{[I]} \tag{12}$$

The subscript $_0$ indicates a baseline composite data value. If we assume the same initiator and gel effect constants, the expression above can be simplified to:

$$-\frac{1}{V_l}\frac{dN}{dt} = k_{c0}\left[\frac{k_d}{k_{d0}}\right]^{1/2}[N]\sqrt{[I]} \tag{13}$$

As a result, the new initiator specific rate constant parameters can be calculated from the baseline constants and the initiator specific decomposition constants:

$$-\frac{1}{V_l}\frac{dN}{dt} = A_{c0}\left[\frac{A_d}{A_{d0}}\right]^{1/2}\exp\left[\frac{-E_{c0}+\frac{(E_{d0}-E_d)}{2}}{T}\right][N]\sqrt{I_{\text{ppmw}}} \tag{14}$$

Initiator specific decomposition rates are available from a variety of literature sources as shown in Table 3. To establish the rate constants for a first order initiator decomposition using published half life data use the following equations:

$$E_d = \frac{\ln\left[\frac{t_2}{t_1}\right]}{\frac{1}{T_2}-\frac{1}{T_1}} \tag{15}$$

$$A_d = \frac{\frac{1}{t_1}\ln 2}{\exp\left(-\frac{E_d}{T_1}\right)} \tag{16}$$

Where t is time in seconds and T is temperature in Kelvin.

Table 3: Initiator specific decomposition rates are available from a variety of literature sources

Initiator	Formula	Mw	CAS #	Reference	Solvent	A_d, /s	E_d, /K
2,2-Azo-bis-isobutyronitrile (AIBN)	$C_8H_{12}N_4$	164.21	78-67-1	Polymer Handbook	Benzene	1.438×10^{15}	15,449
2,2-Azo-bis-isobutyronitrile (AIBN)	$C_8H_{12}N_4$	164.21	78-67-1	Principles of Polymerization	Benzene	1.881×10^{14}	14,842
2,2-Azo-bis-isobutyronitrile (VAZO-64)	$C_8H_{12}N_4$	164.21	78-67-1	Published 1/2 Life Data		1.635×10^{14}	14,695
2,2-Azo-bis-isobutyronitrile (VAZO-64)	$C_8H_{12}N_4$	164.21	78-67-1	Dupont VAZO website 2007	Toluene	1.308×10^{16}	16,445
1,1-Azobis-cyanocyclohexane (VAZO-88)		244.33	2094-98-6	Dupont VAZO website 2020		1.418×10^{16}	17,638
VAZO-67		192.3		Dupont VAZO website 2007	1,3,5-trimethylbenzene	9.476×10^{16}	17,251
VAZO-52				Dupont VAZO website 2007	Toluene	6.290×10^{15}	15,582
VAZO-68WSP				Dupont VAZO website 2007		2.196×10^{12}	13,631
VAZO-56WSP				Dupont VAZO website 2007	Water	3.248×10^{14}	14,796
Benzoyl peroxide	$C_{14}H_{10}O_4$	242.00		Polymer Handbook	Benzene	5.281×10^{12}	13,990
Benzoyl peroxide	$C_{14}H_{10}O_4$	242.00		Principles of Polymerization	Benzene	7.390×10^{12}	14,950
Benzoyl peroxide	$C_{14}H_{10}O_4$	242.00		ATOFINA Catalogue		3.184×10^{14}	15,318
Benzoyl peroxide	$C_{14}H_{10}O_4$	242.00		Journal of Applied Polymer Science Vol. 18, PP.1603-1609, 1974		6.470×10^{13}	14,946
Butadiene Polyperoxide				Butadiene Safety Manual		2.40×10^{7}	9,864
Cumyl peroxide				Polymer Handbook	Benzene	1.318×10^{18}	20,481
Cumyl peroxide				Principles of Polymerization	Benzene	1.290×10^{18}	20,482
Di-t-Butyl Peroxide (DTBP)	$C_8H_{18}O_2$	146.23		ioMosaic ARC data	Toluene	1.050×10^{16}	18,954
tert-Butyl peroxide (TBP)	$C_8H_{18}O_2$	146.23		Polymer Handbook	Benzene	8.568×10^{13}	17,110
tert-Butyl peroxide (TBP)	$C_8H_{18}O_2$	146.23		Principles of Polymerization	Benzene	3.236×10^{14}	17,668
Diisopropyl Peroxydicarbonate	$C_8H_{14}O_6$	206.18		Lucidol Bulletin for Free Radical Initiators for PVC. Tech Bulletin 30.90, August 1970		4.96×10^{14}	14,442
Di(sec-butyl) Peroxydicarbonate	$C_{10}H_{18}O_6$	234.00		Lucidol Bulletin for Free Radical Initiators for PVC. Tech Bulletin 30.90, August 1970		4.110×10^{13}	13,637
Lauroyl Peroxide	$C_{24}H_{46}O_4$	398.63		Polymer Handbook	Benzene	2.142×10^{15}	15,298
Lauroyl Peroxide	$C_{24}H_{46}O_4$	398.63		ATOFINA Catalogue		1.300×10^{16}	16,272
Lauroyl Proxide	$C_{24}H_{46}O_4$	398.63		Lucidol Bulletin for Free Radical Initiators for PVC. Tech Bulletin 30.90, August 1970		3.760×10^{15}	15,751
Potassium Persulfate	$K_2O_8S_2$	270.33		Dupont Vazo Technical Bulletin		4.072×10^{18}	18,171
Sodium Persulfate	$Na_2O_8S_2$	238.09				1.430×10^{10}	11,373
tert-Butyl hydroperoxide	$C_4H_{10}O_2$	90.12		Polymer Handbook	Benzene	3.223×10^{15}	20,531
tert-Butyl hydroperoxide	$C_4H_{10}O_2$	90.12		Principles of Polymerization	Benzene	2.868×10^{15}	20,531
tert-Butyl hydroperoxide	$C_4H_{10}O_2$	90.12		ATOFINA Catalogue		1.523×10^{12}	17,321
tert-Butyl perbonzoate				Polymer Handbook	Benzene	2.314×10^{15}	17,462
tert-Butyl perbonzoate				ATOFINA Catalogue		1.754×10^{14}	16,465
tert-Butyl peroxyacetate (trigonox F-C50)	$C_6H_{12}O_3$	132.18		ioMosaic ARC data	Isopar-H	2.900×10^{16}	18,273
t-Butyl peroxypivalate	$C_9H_{18}O_3$	174.2		Lucidol Bulletin for Free Radical Initiators for PVC. Tech Bulletin 30.90, August 1970		3.540×10^{14}	14,644

Propagation and termination rate constants are also available from a variety of literature sources [2, 9] as shown in Table 4. References [2, 9] provide guidance and typical values for activation energies, pre-exponential factors, rate constants, and rate constant ratios.

Table 4: Propagation and termination rate constants, (m^3, s, kmol, K)

Monomer	A_p	E_p	k_p at 60 C	A_t	E_t	k_t at 60 C	$\frac{k_p}{k_t}$
Vinyl Chloride	3.300×10^6	1,924	10,231	1.474×10^{12}	2,117	2.564×10^9	3.990×10^{-6}
Vinyl Acetate	1.532×10^6	2,165	2,307	7.899×10^{10}	2,634	2.910×10^7	7.926×10^{-5}
Acrylonitrile	6.813×10^5	1,948	1,965	2.719×10^{11}	2,717	7.800×10^7	2.519×10^{-5}
Methyl acrylate	1.000×10^8	3,572	2,205	2.884×10^{10}	2,670	9.534×10^6	2.313×10^{-4}
Methyl methacrylate	8.700×10^6	3,175	631	1.876×10^9	1,431	2.555×10^7	2.471×10^{-5}
Styrene	4.500×10^6	3,127	377	1.079×10^9	962	6.008×10^7	6.281×10^{-6}
Ethylene	1.862×10^5	2,213	243	8.636×10^8	156	5.401×10^8	4.494×10^{-7}
1,3-Butadiene	1.200×10^7	2,923	1,859				
1,3-Butadiene	8.050×10^7	4,292	205	1.130×10^{10}	711	1.337×10^9	1.530×10^{-7}

4.1 Vinyl Chloride Bulk Free Radical Polymerization Rate

To derive a composite rate for a free radical initiated polymerization using A_p, E_p, A_t, E_t, A_d, and E_d constants provided in this paper use the following equations:

$$A_c = A_p \sqrt{\frac{2fA_d}{\theta A_t}} \tag{17}$$

$$E_c = E_p + \frac{1}{2}\left(E_d - E_t\right) \tag{18}$$

If we use the above equations to establish composite rates for vinyl chloride free radical polymerization using VAZO-64 we calculate the following:

$$A_c = A_p \sqrt{\frac{2fA_d}{\theta A_t}} = 3.3 \times 10^6 \sqrt{\frac{1.635 \times 10^{14}}{1.474 \times 10^{12}}} = 3.475 \times 10^7 \tag{19}$$

$$E_c = E_p + \frac{1}{2}\left(E_d - E_t\right) = 1,924 + \frac{1}{2}\left(14,695 - 2,117\right) = 8,213 \tag{20}$$

Note that the initiator concentration for the above composite rate model is in $\mathrm{kmol/m^3}$.

The composite constants used above can also be measured using adiabatic calorimetry. The rates established using adiabatic calorimetry yield composite constants for the specific initiator used in the test. These composite constants can easily be converted for use with a different initiator assuming that A_p, E_p, A_t, and E_t, are monomer properties that do not change. If we were to convert A_c and E_c for vinyl chloride for use with t-butyl hydroperoxide we would use the following equations:

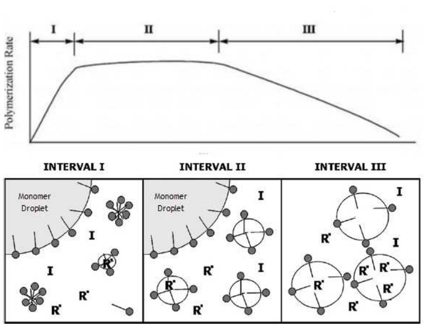
$$A_{c1} = A_{c0}\left[\frac{A_d}{A_{d0}}\right]^{1/2} = 3.475 \times 10^7 \left[\frac{3.223 \times 10^{15}}{1.635 \times 10^{14}}\right]^{1/2} = 1.543 \times 10^8 \tag{21}$$

$$E_{c1} = E_{c0} - \frac{1}{2}\left(E_{d0} - E_d\right) = 8,213 - \frac{1}{2}\left(14,695 - 20,531\right) = 11,131 \tag{22}$$

Where A_{c1} and E_{c1} are the composite rate constants using the t-butyl hydroperoxide initiator.

5 Emulsion Polymerization Rates

Emulsion polymerization proceeds in three intervals, commonly referred to as intervals I, II, and III in the polymer literature. Interval I is called the nucleation phase where initial seeds are formed. This interval is an important step which determines the number of particles in the emulsion and as a result the final particle size. After the particles are formed, three phases exist in the reactor: (1) a water phase containing initiator and trace amounts of monomer, (2) a large monomer droplet phase from monomer fed to the reactor, and (3) small polymer particles (Interval II).



In this interval monomer diffuses from the monomer droplets to the water phase in trace amounts where the monomer then will either quickly diffuse to one of the polymer particles or be initiated together with the decomposing initiator in the water phase. From the water phase, these short growing radicals quickly diffuse to one of the polymer particles which are swollen with monomer.

We are mostly concerned with Intervals II and III for runaway reactions assessment where polymerization takes place in the polymer particles according to the following rate expression:

$$R_{p_e} = k_p[N_e][P^\bullet] \tag{23}$$

$$P^\bullet = n\frac{N_{micelles}}{N_A} \tag{24}$$

where k_p is the rate of propagation, $[N_e]$ is the concentration of monomer in the particles, $[P^\bullet]$ is the concentration of radical chains in the polymer particles where, n is the average number of radicals per particle, $N_{micelles}$ is the number of particles in the emulsion, and $N_A$is Avagadros number. R_{p_e} can be expressed as:

$$R_{p_e} = k_p[N_e]n\frac{N_{micelles}}{N_A} \tag{25}$$

$N_{micelles}$ is determined by the nucleation kinetics of the first interval of emulsion polymerization and the average number of radicals per particle, n, is dependent on initiation kinetics as well as the diffusion rate of monomer from the water phase to the polymer particles.

An exact expression for n is difficult to obtain, but in general it is proportional to the standard peroxide initiator decomposition rate of $\sqrt{fkd\,[I_{water}]}$ like normal free radical polymerization. If we assume that n is equal to $k_e * \sqrt{fk_d\,[I_{water}]}$ where k_e is a diffusion rate contribution, then:

$$R_{p_e} = k_p k_e \frac{N_{micelles}}{N_A}[N_e]\sqrt{fk_d\,[I_{water}]} \tag{26}$$

Note that in the emulsion case, it is the concentration in the water phase that is important while the monomer composition in the polymer phase is important. For a bulk free radical bulk polymerization, R_{p_b} is given by:

$$R_{p_b} = \frac{k_p}{\sqrt{k_t\theta}}\left(\sqrt{2fk_d[I_b]}\right)[N_b] \tag{27}$$

where k_t is the termination rate, $[N_b]$ is the monomer concentration in the single reactive phase and $[I_b]$ is the initiator composition in the same phase.

Comparing the rate expression for an emulsion polymerization versus a standard free radical bulk polymerization process, we expect the same k_p and k_d dependencies on monomer and initiator concentrations. However, the other contributions to the effective rate constant are different. In emulsion polymerization, this effective rate depends heavily on the number of particles and diffusion of monomer while for a standard bulk polymerization free radical process, the effective rate is mostly dependent on the initiator decomposition and termination rate. The effective polymerization rate for an emulsion process is different than a standard bulk polymerization free radical process:

$$\frac{R_{p_e}}{R_{p_b}} = \frac{k_p k_e \frac{N_{micelles}}{N_A}[N_e]\sqrt{fk_d\,[I_{water}]}}{\frac{k_p}{\sqrt{k_t\theta}}\left(\sqrt{2fk_d[I_b]}\right)[N_b]} = k_e\sqrt{k_t\theta}\left(\frac{N_{micelles}}{N_A}\right)\left(\frac{[N_e]}{[N_b]}\right)\sqrt{\frac{[I_{water}]}{2[I_b]}} \tag{28}$$

For large particle emulsions (due to low amount of initial surfactant and therefore low $N_{micelles}$), the process can be quite slow. For small particle emulsions, the polymerization process can be faster than the bulk polymerization process although heat generation is easier to control. Calorimetry testing of emulsion polymerization systems should consider the impact of surfactant on particle size and corresponding polymerization rates under runaway conditions. The application of bulk polymerization rate models may not be conservative in some cases for establishing relief requirements for small particle emulsion polymerizations runaway reactions where the rates can be up to 100 times faster.

6 Styrene Polymerization

6.1 Free Radical Polymerization of Styrene

If we use the above tables to establish a composite reaction rate for bulk styrene polymerization assuming a di-t-butyl peroxide (DTBP) initiator efficiency of 0.5 and a gel effect constant of one, we calculate the following:

$$A_c = A_p\sqrt{\frac{2fA_d}{\theta A_t}} = 4.5\times 10^6\sqrt{\frac{1.05\times 10^{16}}{1.079\times 10^9}} = 1.4\times 10^{10} \tag{29}$$

and

$$E_c = E_p + \frac{1}{2}\left(E_d - E_t\right) = 3,127 + \frac{1}{2}\left(18,954 - 962\right) = 12,123 \tag{30}$$

Note that the initiator concentration for the above composite rate model is in $\mathrm{kmol/m^3}$ and not ppmw. The pre-exponential constant would have to be divided by approximately 1000 in order to use ppmw of peroxide in the rate model.

6.2 Thermal Polymerization of Styrene

The following kinetic rate expression for the thermally initiated bulk polymerization of styrene was obtained from Hui-Hamielec [10]:

$$-\frac{1}{V_l}\frac{dN}{dt} = A_0\exp\left(A_1S + A_2S^2 + A_3S^3\right)[N]^{2.5} \tag{31}$$

$$A_0 = 1.964\times 10^5\exp\left(-\frac{10,400}{T}\right) \tag{32}$$

$$A_1 = 2.57 - 5.05\times 10^{-3}T \tag{33}$$

$$A_2 = 9.56 - 1.76\times 10^{-2}T \tag{34}$$

$$A_3 = -3.03 + 7.85\times 10^{-3}T \tag{35}$$

Where the rate of styrene polymerization is in $\frac{\mathrm{kmol}}{\mathrm{m^3.s}}$, A is a rate constant in $\left(\frac{\mathrm{m^3}}{\mathrm{kmol.s^{2/3}}}\right)^{3/2}$, S is the mass fraction of polystyrene, and T is temperature in K. The styrene polymerization model has been compared to ARC and VSP calorimetry data. Data agreement is found to be excellent. The polymerization of styrene yields a heat of reaction of -670,174 $\mathrm{J/kg}$ of Styrene (Mw = 104.15) or -288 $\mathrm{BTU/lb}$.

6.3 Thermal Decomposition of Polystyrene

When heated to elevated temperatures, polystyrene will depolymerize and decompose to form styrene monomer, dimer, trimer, toluene and small quantities on non-condensable gas [11, 12, 13, 14, 15]. The decomposition is endothermic with an estimated heat of reaction of 294 BTU/lb. This model uses a one step decomposition rate expression and constants reported by reference [5]:

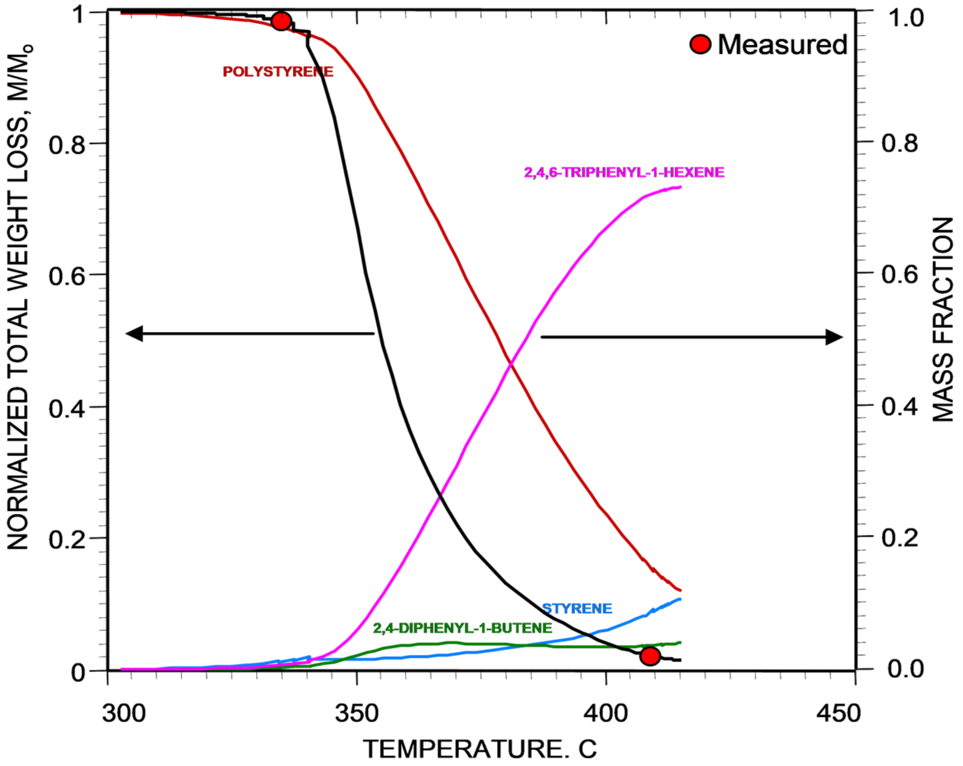
$$-\frac{1}{V_l}\frac{dN_{polymer}}{dt} = 4.0 \times 10^{14} \exp\left[-\frac{26,208}{T}\right][N_{polymer}] \tag{36}$$

The decomposition stoichiometry used in this model to fit the reported data only produces styrene monomer, dimer, and trimer according to the following expression:

$$1041.5 \text{ lbs of polymer } \rightarrow 6\ C_8H_8 + 0.667\ C_{16}H_{16} + 0.888\ C_{24}H_{24} \tag{37}$$

This expression is found to reproduce low heating rate TGA data reasonably well. A sample TGA simulation using the above rate expression and stoichiometry yields the mass loss curve as a function of temperature at 1 bar shown in Figure 1. It is important to note that reported TGA polymer decomposition rate data depends on heating rate. Values at the lower heating rates (5 C/min or less) are more realistic and preferred for pressure relief systems design applications. The predictions of this simple one step model are heavily influenced by the stoichiometry.

Figure 1: TGA Curve Simulation Using SuperChems for Polystyrene Decomposition



Typical polystyrene decomposition products are given by Fisher [16] as shown in Table 5.

Table 5: Typical polystyrene decomposition products

Decomposition Product	Weight %
Non-condensable Gas (carbon monoxide)	0.1
Toluene	5.6
Styrene Monomer	41.8 - 62.5
Styrene Dimer 2,4-diphenyl-1-butene 1,3-diphenyl propane Diphenyl butane	19.3 - 20.0
Styrene Trimer 2,4,6-triphenyl-1hexene Triphenyl-1,3,5-hexane Triphenyl- 1,3,5-pentane	2.9 - 20
Non-volatile Char (residue)	9.6
Total	100.0

6.4 Model Verification Using VSP Test Data

The free radical styrene polymerization model derived above based on literature data using DTBP as an initiator was verified using the vent sizing package (VSP). 60.08 g of styrene were loaded into a stainless steel VSP test cell along with 0.0188 g of DTBP (312 ppmw). The test cell contents were heated at 0.5 C/min and an exotherm was detected at 80 C.

The test data measured above was modeled using SuperChems Expert. Excellent agreement was obtained as shown in Figure 2. Note that the free radical initiated polymerization causes the thermally initiated styrene polymerization to initiate as well. The final free radical polymerization model constants are as follows:

$$-\frac{1}{V_l}\frac{dN}{dt} = 7.0 \times 10^6 \exp\left[-\frac{12,123}{T}\right][N]^{2.5}[I]^{0.5} \tag{38}$$

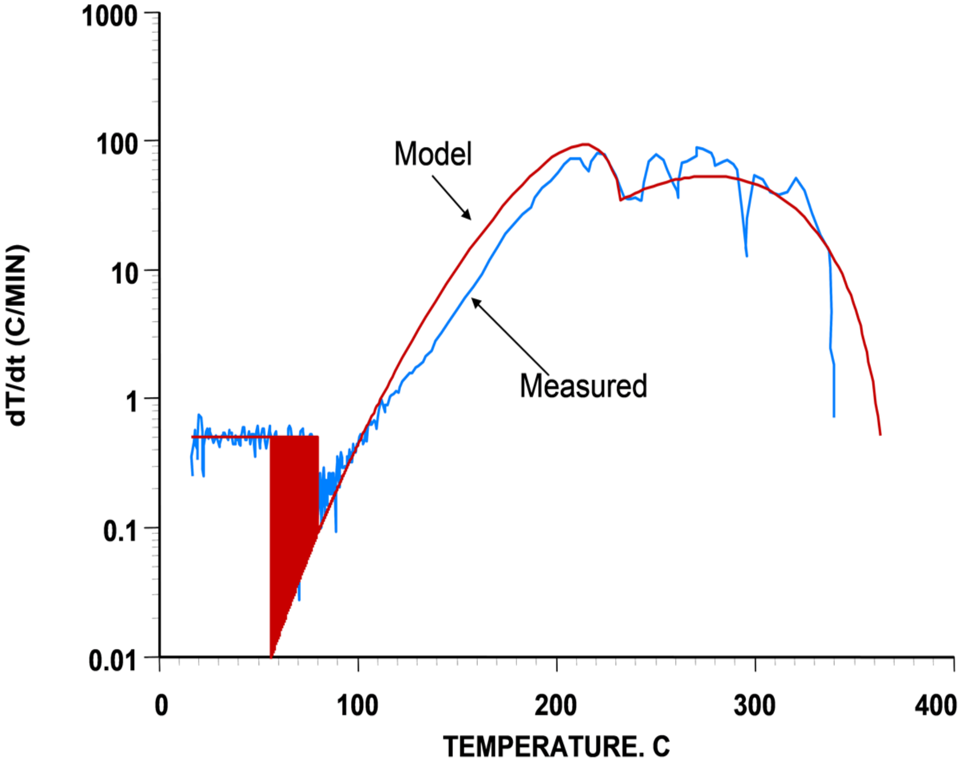
$$-\frac{dI}{dt} = 1.05 \times 10^{16} \exp\left[-\frac{18,954}{T}\right][I] \tag{39}$$

Where [I] is the DTBP concentration in ppmw (≥ 1) and [N] is the monomer concentration in $\mathrm{kmol/m^3}$. Note that this expression can be used with other initiators using the expression derived in the section above. The free radical polymerization rate can also be expressed where the initiator concentration is in $\mathrm{kmol/m^3}$ instead of ppmw. The best fit rate expression based on our test data is:

$$-\frac{1}{V_l}\frac{dN}{dt} = 2.75 \times 10^9 \exp\left[-\frac{12,123}{T}\right][N]^{2.5}[I]^{0.5} \tag{40}$$

$$\tag{41}$$

Figure 2: dT/dt Model predictions using combined free radical and thermally initiated polymerization models vs. VSP test data



Note that the pre-exponential factor established from our data set is approximately a factor of 5 smaller than the value computed from literature data, 2.75×10^9 vs. 1.4×10^{10}.

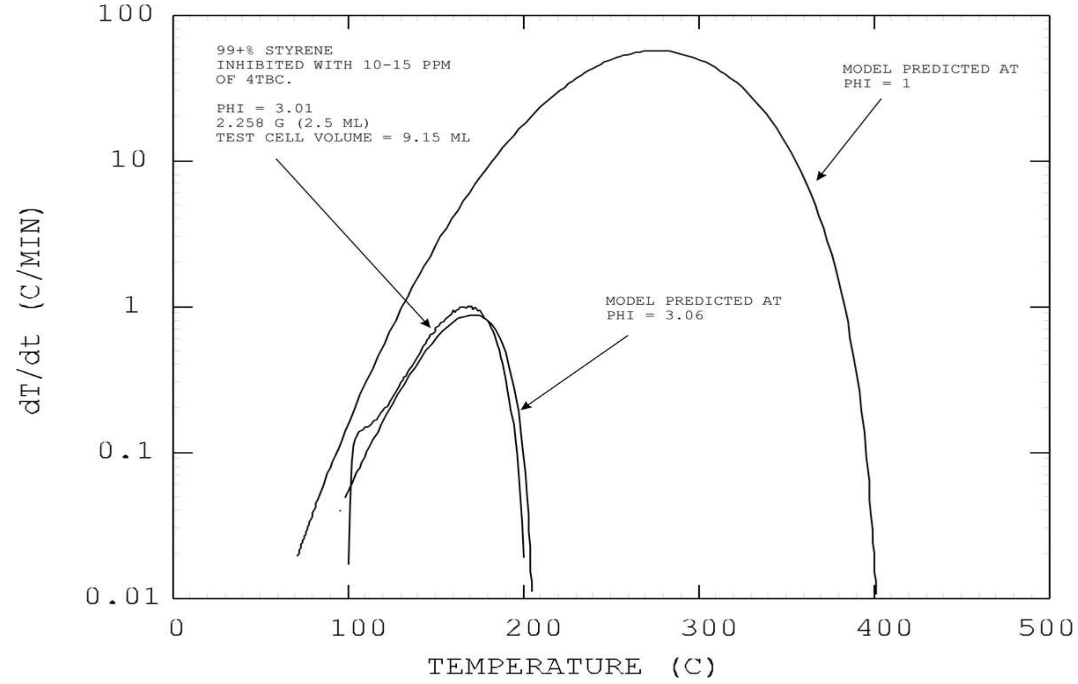
The rate expression where the initiator is expressed in $\mathrm{kmol/m^3}$ is more versatile. For example, using this form of the rate expression one can simulate metered additions of an initiator into a reactor to assess the impact on runaway conditions. In addition, when large amounts of initiator are used, the actual decomposition products of the initiator can be accounted for in pressure relief modeling.

6.5 Model Validation Using ARC Test Data

This model was also verified against numerous ARC data sets and the agreement is found to be excellent. Some of the ARC data sets used included isothermal aging experiments. These tests in particular proved to be very useful in establishing and validating the TBC inhibitor depletion model. Typically, styrene is inhibited with 15 ppm of TBC. This data can be made available as SuperChems Expert project file upon request.

In one of the ARC tests, 2.258 g (2.5 ml) of 99+ % styrene inhibited with 10-15 ppm of 4TBC was charged into a Hastelloy C test cell with a volume of 9.15 ml and a weight of 19.170 g. The detected onset temperature was 100 C and the measured adiabatic temperature rise was 101 C.

Figure 3: Styrene polymerization temperature rise rate from model predictions and experimental ARC data



Model performance was evaluated using SuperChems Expert and comparisons with experimental data are illustrated in Figures 3, 4, 5, and 6.

7 Conclusions

This paper develops a method for establishing composite polymerization rate models for use in pressure relief systems design and evaluation. The composite rate models can be developed from published literature data, adiabatic calorimetry data, or a combination of both. The composite rate models developed in this paper can be easily converted to work with different free radical initiators. The composite rate model and methodology are validated for styrene polymerization using literature, VSP, and ARC calorimetry data with excellent agreement.

Figure 4: Styrene polymerization pressure rise rate from model predictions and experimental ARC data

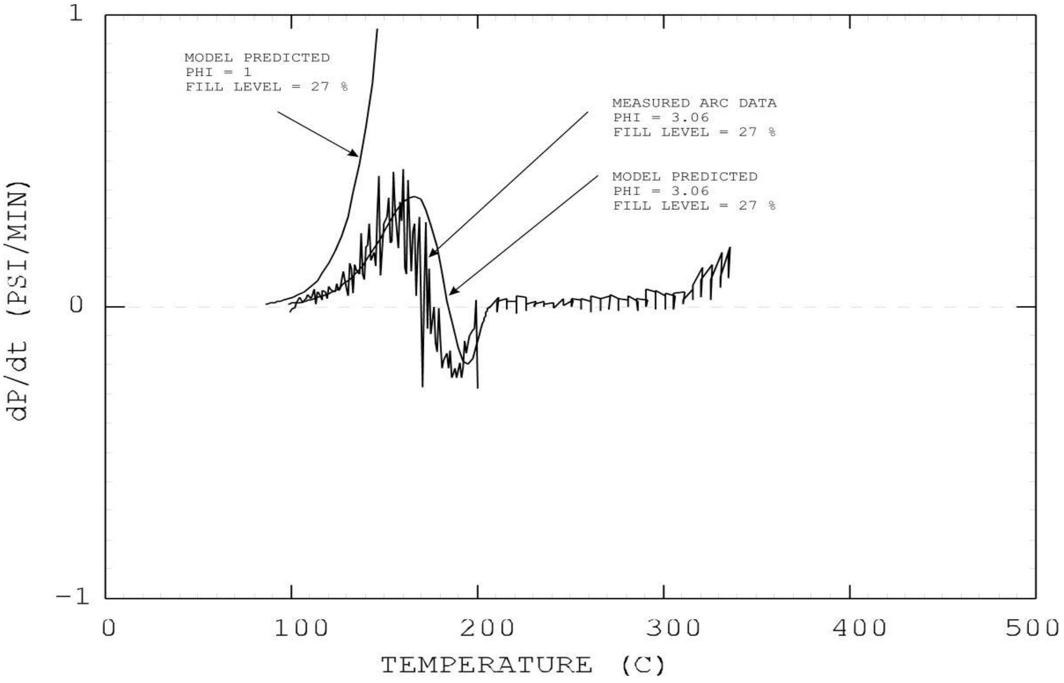


Figure 5: Styrene polymerization pressure rise rate from model predictions at a thermal inertia of 1

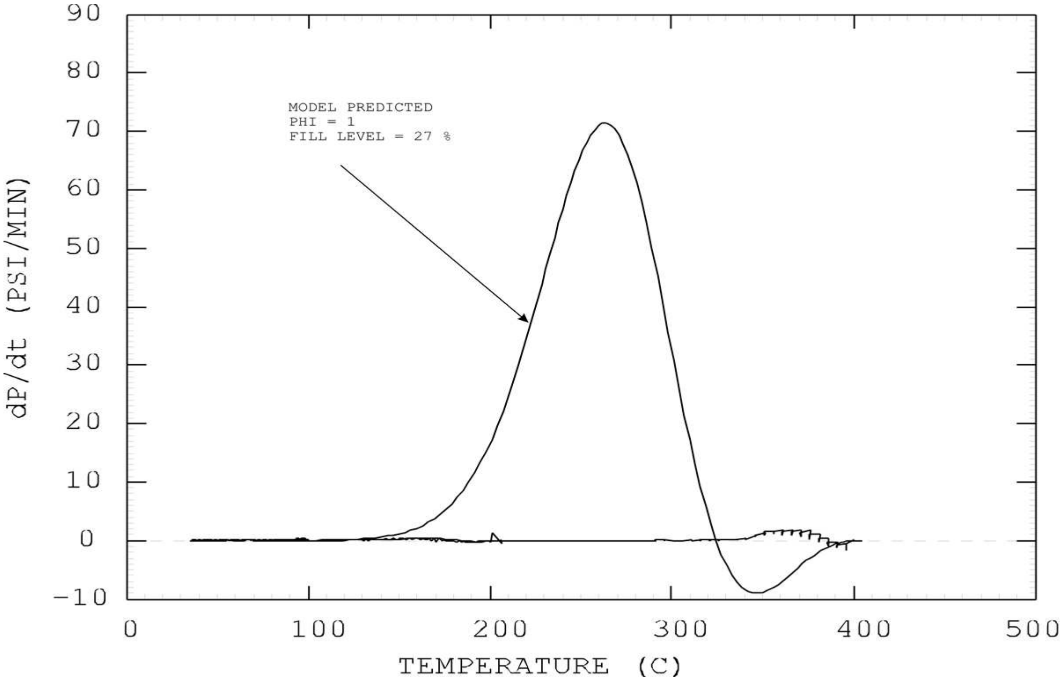
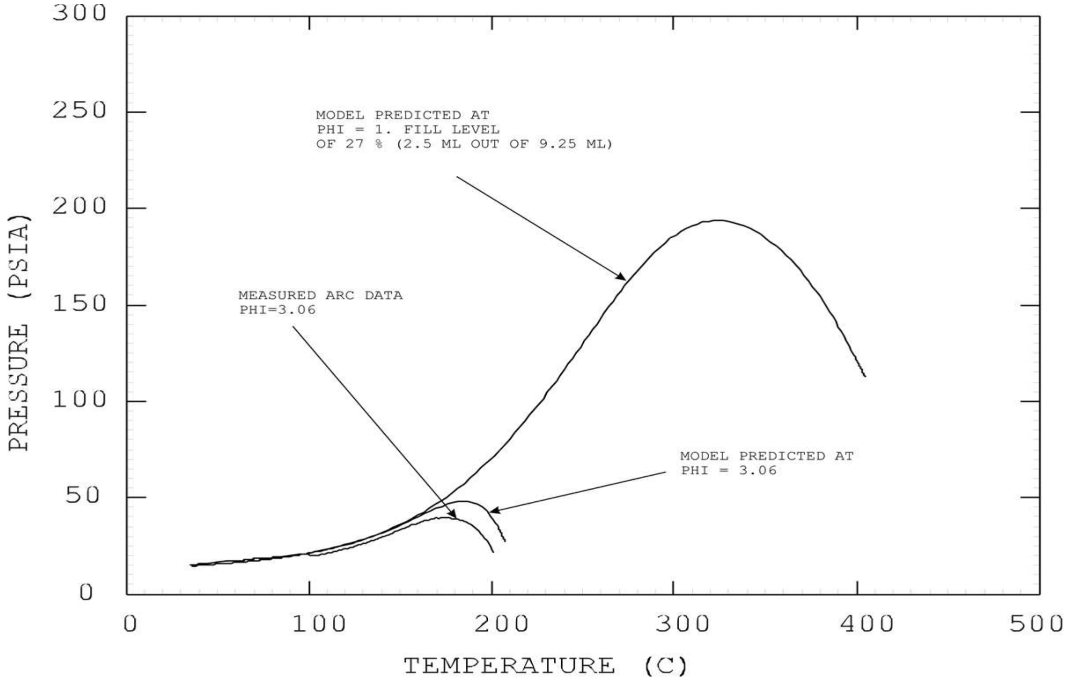


Figure 6: Styrene polymerization pressure/temperature from model predictions and experimental ARC data



8 How can we help?

In addition to our deep experience in chemical reaction systems and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of compliance and legal requirements. When you work with ioMosaic you have a trusted partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and compliance that you can evergreen. We invite you to connect the dots with ioMosaic.

Figure 7: Connect the dots with ioMosaic

We are with you every step of the way for the long haul as you journey to PSM excellence and shareholder value

Learn PSM Competencies
Enhance Skills with Process Safety Learning®

Practice PSM
Maximize Safety with Process Safety Office®

Manage PSM
Leverage Data with Process Safety Enterprise

Talk About PSM
Improve Safety Culture with Process Safety tv®

Expand PSM
Collaborate and Scale Up Just In Time with PSPOM™

References

[1] CSIB. Hazard investigation - improving reactive hazard management. Technical Report 2001-01-H, U.S. Chemical Safety and Hazard Investigation Board, October 2002.

[2] R. B. Seymour and C. E. Carraher Jr. *Polymer Chemistry, An Introduction*. Mercel Dekker, New York, 9th edition, 1981.

[3] `http://www.stanford.edu/class/cheme160/lectures/lecture1.pdf`.

[4] Identification and validation of a VSL polymerization reactor model. `http://www.uni-bayreuth.de/departments/math/~kschittkowski/proj_bay.htm`, 1998-2002.

[5] M. C. Iovu et al. Styrene-butadiene rubber synthesized by anionic polymerization. `http://www.sun.ac.za/unesco/Conferences/Conference2000/Abstracts2000/Iovu/IOVU.pdf`, 2000.

[6] A. Sirohi and K. Ravindranath. Modeling of ionic polymerization process: Styrene and butadiene. In *Spring Meeting, Houston*. AIChE, 1999.

[7] Stuart Thickett and Robert G. Gilbert. Emulsion polymerization: State of the art in kinetics and mechanisms. *Polymer 48*, 24:6965–6991, October 2007.

[8] `http://www.stanford.edu/class/cheme160/lectures`.

[9] G. Odian. *Principles of Polymerization*. Wiley, 3rd edition, 1991.

[10] A. W. Hui and A.E. Hamielec. Thermal polymerization of styrene at high conversions and temperatures: An experimental study. *Journal of Applied Polymer Science*, 16:749–769, 1972.

[11] T. M. Kruse et al. Mechanistic modeling of polymer degradation: A comprehensive study of polystyrene. *Macromolecules*, 35:7830–7844, 2002.

[12] Fire-safe polymers and polymer composites. Technical Report DOTBAAIAR-04111, DOT, September 2004.

[13] S. L. Madorsky and S. Straus. Pyrolytic fractionation of polystyrene in a high vacuum and mass spectrometer analysis of some of the fractions. Technical Report Research Paper - 1886, NBS, May 1948.

[14] A. Marcilla and M. Beltran. Kinetic study of the thermal decomposition of polystyrene and polyethylene-vinyl acetate graft polymers by thermogravimetric analysis. *Polymer Degradation and Stability*, 50:117–124, 1995.

[15] H. G. Fisher. DIERS users group presentation. In *DIERS Users Group Meeting*. AIChE, MAY 2002.

[16] H. G. Fisher. A comprehensive reaction model to simulate the overpressure and size emergency relief devices for process vessels and storage tanks. In *DIERS Users Group Meeting*. AIChE, 2006.

About the Author

Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

Contact Information

Georges. A. Melhem, Ph.D., FAIChE
E-mail. melhem@iomosaic.com

ioMosaic Corporation
93 Stiles Road
Salem, New Hampshire 03079
Tel. 603.893.7009, x 1001
Fax. 603.251.8384
web. www.iomosaic.com

ioMosaic®

Minimizing risk. Maximizing potential.®

US Offices

New Hampshire (Salem) – *Headquarters*
Texas (Houston)
Minnesota (Minneapolis)
California (Berkeley)

International Offices

Kingdom of Bahrain (Al Seef)
United Kingdom (Bath)

Software Solutions

[Process Safety Enterprise®](#)

Centralize the process safety management lifecycle to accelerate business goals

[Process Safety Office®](#)

Identify, evaluate, and control process hazards with tools used by process safety consultants

[Process Safety Learning®](#)

Build your process safety competencies incrementally with online training

[Process Safety tv®](#)

View, share, and discuss PSM worldwide on a secure platform

Contact Us

www.ioMosaic.com
sales@ioMosaic.com
1.844.ioMosaic

About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training and software development.

As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

Consulting Services

- Asset Integrity
- Auditing and Due Diligence
- Combustible Dust Hazard Analysis and Testing
- Facility Siting
- Fault Tree/SIL/SIS Analysis
- Fire and Explosion Dynamics
- Incident Investigation, Litigation Support and Expert Testimony
- Liquefied Natural Gas Safety
- Pipeline Safety
- Process Engineering Design and Support
- Process Hazards Analysis (PHA)
- Process Safety Management (PSM)
- Reactive Chemicals Evaluation and Testing
- Relief and Flare Systems Design and Evaluations
- Risk Management Program Development
- Quantitative Risk Assessments (QRA)
- Software Solutions
- Structural Dynamics
- Training

Laboratory Testing Services (ISO accredited)

- Chemical Reactivity
- Combustible Dust
- Battery Safety
- Specialized Testing