Kathmandu University
Journal of Science, Engineering and Technology

Owalabi *et al.* Vol. 11, No. II, December, 2015, pp 1-14.

ORIGINAL RESEARCH ARTICLE OPEN ACCESS

PROCESS SAFETY IN THE RADICAL POLYMERIZATION OF STYRENE: FROM BULK TO SOLUTION/EMULSION PROCESS

*Owolabi R. U., Usman M. A., Kehinde A. J.
University of Lagos, Chemical Engineering Department, Akoka, Yaba, Lagos State, Nigeria.

*Corresponding author's e-mail: rowolabi@unilag.edu.ng

Received 23 November, 2015; Revised 27 December, 2015

ABSTRACT

In this study, the influence of process parameters on the behaviour of free radical homo-polymerization of styrene in a well mixed batch reactor was examined.The reaction of styrene with itself in hydrocarbon solvents of dissimilar polarities (acetone and chloroform) and non-hydrocarbon solvent (distilled and de-ionized water) was studied experimentally over ranges of solvent volumes, temperature, reaction time and initiator type in a magnetically stirred thermo-well round bottom reactor.Similar reaction was carried out using equi-volume of the solvents blend to explore possibility of solvents synergy.This study uses the kinetic model of Coats-Redfern to evaluate kinetic parameters such as activation energy, order of reaction and rate constant. This aspect becomes especially important as it is necessary to know in advance the parameters that will assist the occurrence of runaway reaction.The right choice of operating conditions of the styrene polymerization of known kinetics according to this study is a defense mechanism against runaway reaction. Although not discussed in this study, mischarging of reactants, maintenance troubles, agitator breakdown, etc. may also cause runaway reactions. Solution molecular weights of polystyrene samples were measured using the Mark-Houwink Sakurada equation and other procedures earlier reported. The gel effect and heat accumulation within the reactor system was less pronounced giving a safety advantage to the solution/emulsion process compared to bulk. Further dilution of the monomer with the solvents effectively reduces the gel effects. Unlike in thermal polymerization process, the type of initiator and their mass concentration in the reacting mixtures reduces the reaction time thereby minimizing the use of energy making the process cost effective.

Keywords: Radical, Homo-polymerization, Polarities, Kinetic Model, Gel Effect.

INTRODUCTION

The widespread of the process industries comes with its challenges such as pollution, safety issues, energy utilization in spite of its limitation, use of hazardous chemicals etc. The polymerization of styrene in hydrocarbon solvents is of great interest in this study, not only perhaps the process would be safety conscious but also, the functionalized set of polystyrene that could be generated. Cherbanski et al.[1] made clear that polymerization is known to be the most frequent cause of thermal runaway incidents in industrial chemical processes. Vijayaraghavan et al. [2] also observed that explosions due to thermal runaway are one of the major safety issues faced by chemical industries. Tseng et al.[3] in his detailed study identified that runaway reactions can either be induced by hot spots or caused by insufficient heat removal.The safety measure therefore becomes an issue by virtue of thermal runaway reactions often associated with the bulk or thermal styrene polymerization technique [4] and its proneness to industrial accident as shown in Table 1.0. The bulk polymerization on a further negative side maintains a very high viscous reaction medium with polymer formation, accumulates heat of reaction which could facilitate runaway reaction. The problem of heat control of the reaction is compounded by the highly exothermic nature of the free radical process. The reaction vessel may be at risk from over-pressurization due to violent boiling or rapid gas generation. The situation was exactly what took place at around 1966 in New York where a polystyrene plant got a blazed claiming 11 lives and lots of properties as reported by Ronald [5] (See Fig 1.0 . Cheng [6] also attributed frequent explosions in polymerization due to the thermal decomposition of initiators with relevant mechanistic explanations.The R–O–O–R structure of the Benzoyl peroxide (BPO) is essentially thermally unstable, highly sensitive, and tends to form RO' radical easily, BPO possesess many hazardous characteristics, such as thermal sensitivity, enormous amount of heat evolution upon decomposition and explosion.There is also likelihood to have contaminants like inorganic acids, such as H_2SO_4, HNO_3, or H_3PO_4 which aid explosion Wu et al .[7]. In the recent report of Tina et al. [8], an alternative approach to produce polystyrene (PS) in a simple way is precipitation polymerization. The advantage of this method is the absence of the very expensive and difficult to remove stabilizers in comparison to heterogeneous polymerization technique such as emulsion and suspension polymerization. Sequel to all of these, approaches to reduce the stated risks is the pressing need of the moment. To our knowledge, the introduction of solvents into the reacting system will provide a precise control of the chemical reaction, resulting heat and viscosity. In this report , hydrocarbon solvents of different solvatochromic parameters such as acidity (α), basicity (β) and dipolarity/ polarizability (π^*) etc., using benzoyl peroxide and its blend with dicyclohexylphthalate (BPO blend) as initiator will be considered.Our approach in this study is the creation of alternative pathway for the polymerization with special emphasis on the use of solvents as heat transfer medium just as earlier described and the associated combination of process parameters for the process safety. On safe side in terms of PS quality,Atkinson et al. [9] Earlier debunked the possibility of co-polymerization of the solvents with monomers. Few other aspect of styrene polymerization by past researchers include the work of Tefera [10] who investigated, both experimentally and theoretically, the free-radical suspension polymerization of styrene at different temperatures (70 ^{0}C, 75 ^{0}C, and 80 ^{0}C) and initiator concentrations (AIBN: 0.15–0.45 wt.-% of styrene). Sergi et al. [11] reported oxidative polymerization of styrene using molecular oxygen as a regulator of the primary chain length and concluded that synthesis of highly branched polymers with a low amount of peroxide groups must be carried out at moderate initiator concentration and low rates of oxygen bubbling. Parouti et al. [12] reported a comprehensive experimental investigation on the batch and semibatch emulsion terpolymerisation of methyl methacrylate/butyl acrylate/acrylic acid (MMA/BuA/AA). The role of the non-ionic surfactant octylphenoxypolyethoxyethanol in emulsion polymerization of styrene, butyl acrylate as well as their copolymerization was investigated in the two papers of

Ozdeger et al. [13a-c] using the calorimetry as the main tool for the kinetics analysis. Dissociation initiators $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ or redox systems $K_2S_2O_8/Na_2S_2O_4$ are most often used in emulsion polymerization system Lovell et al. [14]. Chern [15] reported that batch emulsion polymerization is commonly used in the laboratory to study reaction mechanism, develop new latex products and obtain kinetic data for process development and reactor scale-up.Our second approach is the use of distilled and de-ionised water (DDW) as the dispersion medium which is eco- friendly (compared to the hydrocarbon solvents) and also allows excellent heat dissipation during the course of the polymerization. Etienne et al.[16] performed free radical polymerization of ethylene in water from a water soluble initiator 2,2-azobis (2-amidinopropane) dihydrochloride) where stable polyethylene latex were obtained though the authors claimed that the polymerization process was not a standard one. The surge of interest in the non-hydrocarbon solvent (DDW) as reaction medium has been accelerated by the growing desire for cleaner chemical processes due to the public sensitivity to environmental issues. The task is to synthesize polymer products of high quality in a consistently safe manner.

Almeida et al. [17] in their study stated clearly the role of reduction of reaction time played by multi-functional intiators. Kim et al. [18] in addition concluded that with properly chosen multifunctional initiators, one can achieve both high monomer conversion and significantly high molecular weight polymers simultaneously. Although not considered in this study, Mohammad et al. [19] submitted that for smooth and safe polymer production line, advance and upgrade of control system is important for energy reduction and cost minimization. Reduction of reaction time for less energy consumption is among others earlier mentioned remain our focus in this study.Reduction of reaction time can be achieved by the use of active initiators which will be added only at the beginning of the polymerization. This approach avoids the use of a continuous dosage system and its associated respective control. We finally aim to homo-polymerize styrene under moderate operating conditions in the selected hydrocarbon and water as solvent economically, optimally, safely and environmentally benign manner in a bid to generate safety data for teaching and industrial purpose to reduce the degree of hazard.

Table 1.0: Selected accidents related to Styrene/BPO initiator and its derivatives (US Chemical Safety and Hazard Investigation Board) Liao et al [20].

Date	Location	Fatalities	Injuries	Hazard
07/05/1994	Kaoshiung , Taiwan	1	0	Explosion
21/01/1998	Kaoshiung , Taiwan	0	4	
23/06/1999	Pasadena , Texas, USA	2	4	Explosion
25/07/1999	Hong Kong , China	0	0	Explosion
06/10/1999	Chiayi , Taiwan	0	1	Explosion
27/03/2000	Pasadena , Texas, USA	1	71	Explosion
12/03/2003	Yeochon , South Korea	1	0	Explosion
May,1990[1]	Japan (BPO)	17	9	Explosion
June,1993[1]	China (BPO)	33	27	Explosion
May,2001[1]	Taiwan (BPO)	121	1	Explosion
January,2003[1]	USA (BPO)	1	0	Explosion

Thermal runaway reaction of Reactor burst by thermal BPO in reactor area [6]

Figure 1: Polystyrene plant building: Accident occurred on October 13, 1966 in New York.

The process steps that led to the industrial accident as indicated in Fig1.0 include

- Loading the reactor with styrene
- Adding polymerization Catalyst (Initiator)
- Heating to 95 ^{0}C
- Holding time of 2 to 8 hours

Typical bulk polymerization approach

Ronald J. Willey [5]

According to industrial technology research institute hand book of prevention of runaway reactions, the situation above could be as a result of inadequate understanding of chemical reactivities, inadequate engineering designs, control systems, operating procedures and practices for styrene polymerization. Furthermore, a knowledge of the thermo-kinetics of exothermic reaction system such as polymerization not only help in mitigating disastrous events such as catastrophic fires and explosions but also provides the means for designing in-built safety system and assessing thermal sensitivity of reaction mixtures and products.

EXPERIMENTAL METHODS

Monomer preparation: Styrene for commercial purpose from the manufacturer in its usual form contains stabilizers which strongly affect the kinetics of the polymerization Boundy, [21].The styrene monomer contains a phenol (often 4-tert-butylcatechol) as a polymerization inhibitor which was removed by method described by Arai and Saito [22] and Wu et al. [23].The styrene was de-inhibited first by extraction with 10 % NaOH solution. The mixture was strongly agitated and allowed to settle by gravity in a separating funnel. The bottom layer consisting of the inhibitor was carefully drained off. Repeated water washing took place and the styrene was dried with anhydrous Na_2SO_4.

Polymerization: The polymerization was conducted in a 62 mm diameter round bottom pressure thermo-well reaction flask. Specific amount of benzoyl peroxide and styrene monomer (constant throughout) were dissolved in varying volume of solvent (acetone, chloroform) at different reaction times. For other solvent such as water, 2,2-Azobis (2-ethylpropionamidine) dihydrochloride (AIBA) and potassium persulfate (PPSF) water were used as water soluble initiators. The solutions were manually charged into the 62 mm diameter round bottom pressure thermo-well reaction flask The reaction temperature was reached shortly and maintained at 120 ^{0}C (± 2) under agitation provided by a magnetic driven bar stirrer at a speed of about 500 rpm.For reactions at lower temperature (90 ^{0}C and 60 ^{0}C), polymerizations were performed in sealed 100 ml glass beakers (71mm length, 51mm diameter) in a water bath equipped with a shaker and a digital temperature controller. The pressure equal to the vapour pressure of the reaction mixture was maintained. After 10 minutes interval reaction time, the reactor was opened up, cooled to collect the resulting polymer solution.

Analysis: Monomer conversion and polymerization rate were gravimetrically determined. The clear polymer solution was added to about 2-3 ml of methanol in a beaker with continuous stirring to precipitate the polymer. The polymer samples were air-dried to remove excess solvent and dried for 2 weeks at room conditions until a constant weight was reached. The synthesized polymers were further subjected to solubility and density test in various solvents and molecular weight were also determined. Details of the analysis and molecular weight determination can be found in one of our earlier papers (Kehinde et al.) [24].

Estimation of kinetic parameters using the Coats-Redfern method: The Coats –Redfern plot is shown in Fig 6.0 and Tables 1.0 - 4.0.These tables further show that the activation energy (E) and reaction order (α) for the polymerization of styrene in acetone-chloroform blend at 10 minutes reaction time are 0.66 and14.37 kJ/mol respectively, at 30 minutes reaction time are 0.66 and 10.95 kJ/mol respectively and at 50 mimutes reaction time are 0.66 ,and 8.77 kJ/mol respectively with estimated R^2 values of 0.619- 0.988.

$$\ln\left[\frac{1-(1-x)^{1-\alpha}}{T^2(1-\alpha)}\right] = \ln\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \quad [25] \qquad (1.00)$$

This is a linearized equation of the form $y = mx + c$. The plot $\ln[\frac{1-(1-x)^{1-\alpha}}{T^2(1-\alpha)}]$ against $\frac{1}{T}$ should result in a straight line of slope $\frac{-E}{R}$ for correct value of α.

When $\alpha = 0$, eq. (1.00) becomes

$$\ln\left[\frac{x}{T^2}\right] = \ln\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \qquad (2.00)$$

When $\alpha = 0.25$, 0.5, 0.66, 0.75 , eq. (1.00) remains as it is.

When $\alpha = 1$ eq. (1.00) becomes

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \qquad (3.00)$$

$$Slope(s) = -\frac{E}{R} \qquad (4.00)$$

If we assume that $1-\frac{2RT}{E} \approx 1$, the frequency factor and the subsequent rate constant can be determined.

RESULTS AND DISCUSSION

The polymerization conditions and results have also been summarized in Fig 2.0-6.0

Styrene polymerization in hydrocarbon solvents:

Figure 2.0 and 3.0 exhibit almost similar profiles for the different reaction times irrespective of the type of initiator. Initially, the conversion increased as the volume of the solvent increases but later decreased at higher volume of solvent. This change of behavior was noted at about after 5 to 10 ml of solvent. The reduced conversion observed was believed to be due to the reduced efficiency of the styrene polymerization at certain points. We have attributed the reduced efficiency to dilution of the initiator as a result of increase in solvent volume, chain transfer to solvent and reduced monomer concentration with time. About 90 % conversion in acetone was obtained at 5vml acetone solvent volume, 120 ^{0}C and 30 minutes reaction time. An approximate conversion of 90 % at similar reaction conditions was obtained at an extended time of 40 minutes.

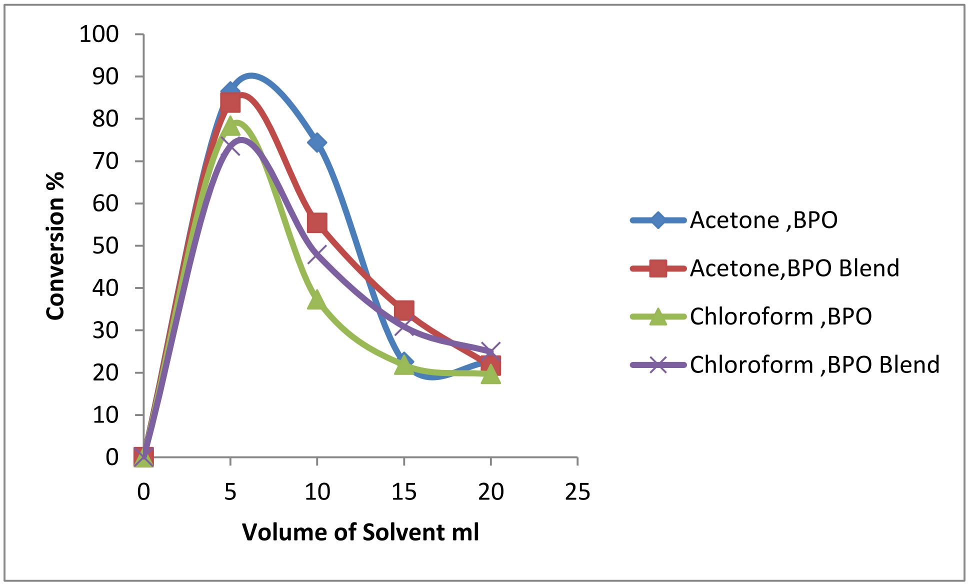

Figure 2 : Conversion versus volume of solvent at 30 minutes reaction time and 120 ^{0}C

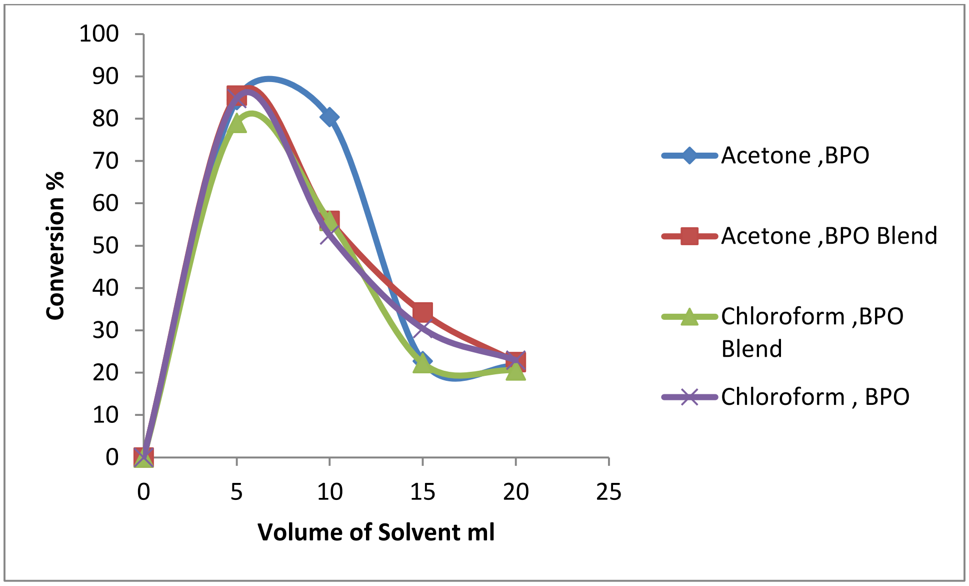

Figure 3: Conversion versus volume of solvent at 40 minutes reaction time and 120 ⁰C

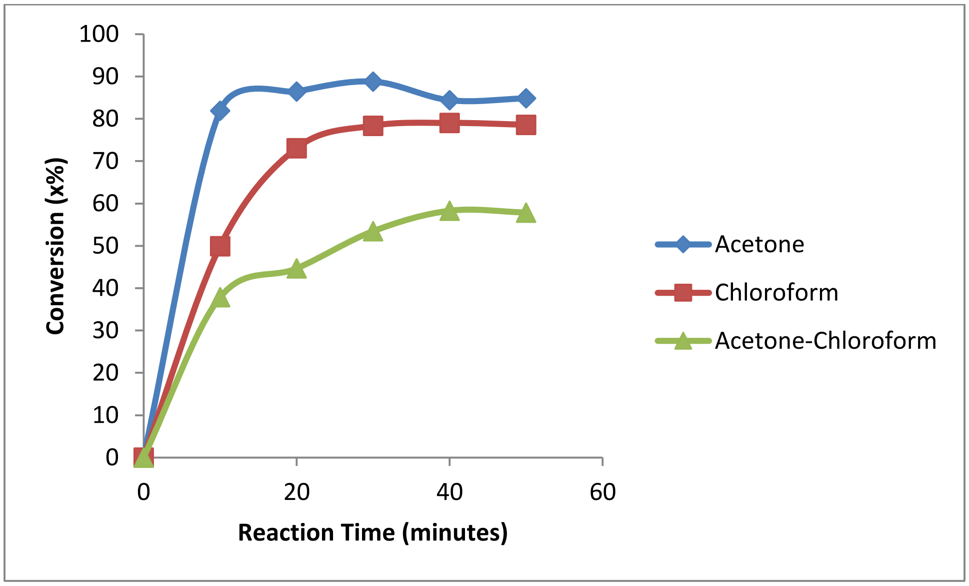

Figure 4: Styrene conversion versus reaction time for different hydrocarbon solvent media at 120 ^{0}C using benzoyl peroxide

At 45 minutes reaction time, 50% conversion was observed using acetone/chloroform co-solvents as depicted in Fig 4.0 while 80-90% conversion was achieved with acetone and chloroform used separately. There is therefore no synergy between the solvents. However, the molecular weight of the PS obtained in the co-solvent medium still fall within acceptable range.

Kathmandu University
Journal of Science, Engineering and Technology
Owalabi *et al.* Vol. 11, No. II, December, 2015, pp 1-14.

Styrene polymerization in distilled and de-ionized water

Fig 5.0 shows styrene polymerization carried out in distilled and de-ionized water at different reaction temperatures under different types of initiators. Styrene monomer conversion was observed to be a function of temperature. 2,2-Azobis(2- ethylpropionamidine)dihydrochloride (AIBA) and Ppotassium persulfate (PPSF) water soluble initiators used performed competitively well. No significant variation was obtained in the styrene conversion, although the polymerization technique and mechanism differ. Maximum styrene conversion of about 45 % was obtained irrespective of the water soluble initiator used at maximum temperature of 120 ^{0}C.

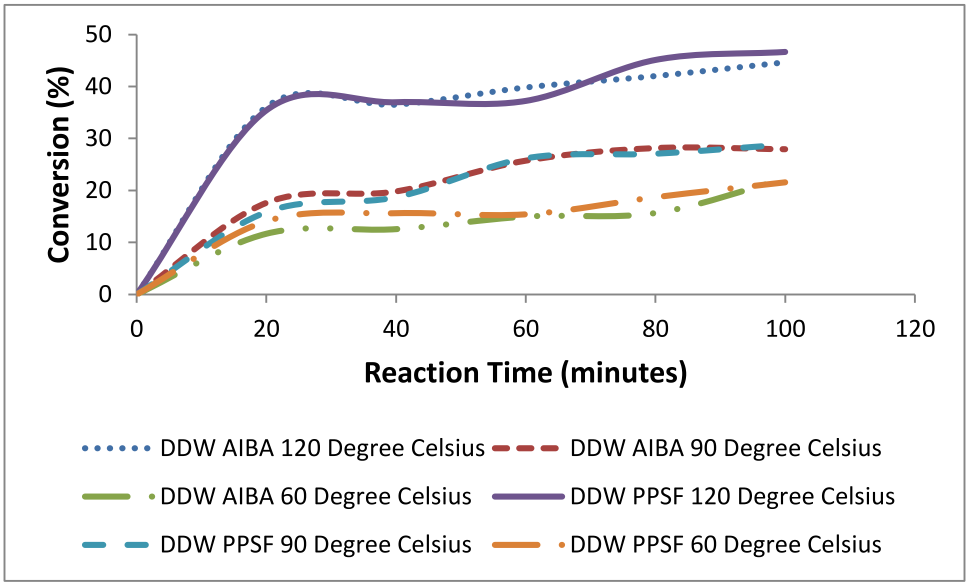

Figure 5: Styrene EmulsionPolymerization Conversion versus Reaction Time using different Initiators

Table 1: Tables of values for the The plotofln$[\frac{1-(1-x)^{1-\alpha}}{T^2(1-\alpha)}]$ against $\frac{1}{T}$ in acetone - chloroform mixture using BPO for 10 minutes reaction time

1/T	**A at Reaction Time = 10 minutes**											
	α =0		**α = 0.25**		**α =0.5**		**α =0.66**		**α = 0.75**		**α = 1**	
2.54 exp-3	-13.00	R^2	-12.95	R^2	-12.9	R^2	-12.87	R^2	-12.85	R^2 =	-12.80	R^2 =
2.75 exp-3	-13.39	=0.988	-13.36	=0.987	-13.33	=0.988	-13.31	=0.988	-13.30	0.987	-13.28	0.984
3.00 exp-3	-13.71	S=-1535	-13.69	S=-1599	-13.68	S=-1686	-13.67	S=-1729	-13.66	S=-1750	-13.65	S=-1836

Table 2: Tables of values for the The plot of $\ln[\frac{1-(1-x)^{1-\alpha}}{T^2(1-\alpha)}]$ against $\frac{1}{T}$ in acetone-chloroform mixture using BPO for 30 minutes reaction time

1/T	**A at Reaction Time = 30 minutes**											
	α =0		**α = 0.25**		**α =0.5**		**α =0.66**		**α = 0.75**		**α = 1**	
2.54 exp-3	-12.57	R^2	-12.49	R^2	-12.40	R^2	-12.34	R^2	-12.31	R^2 =	-12.22	R^2 =
2.75 exp-3	-13.14	=0.564	-13.10	=0.590	-13.07	=0.601	-13.04	=0.619	-13.03	0.609	-13.00	0.617
3.00 exp-3	-13.05	S=-999.3	-13.02	S=-1105	-12.99	S=-1232	-12.97	S=-1317	-12.95	S=-1337	-12.92	S=-1463

Table 3: Tables of values for the The plot of $\ln[\frac{1-(1-x)^{1-\alpha}}{T^2(1-\alpha)}]$against $\frac{1}{T}$in acetone-chloroform mixture using BPO for 50 minutes reaction time

1/T	**A at Reaction Time = 50 minutes**											
	α =0		**α = 0.25**		**α =0.5**		**α =0.66**		**α = 0.75**		**α = 1**	
2.54 exp-3	-12.50	R^2	-12.40	R^2	-12.30	R^2	-12.23	R^2	-12.20	R^2 =	-12.09	R^2 =
2.75 exp-3	-12.85	=0.682	-12.80	=0.705	-12.75	=0.722	-12.71	=0.737	-12.70	0.720	-12.65	0.719
3.00 exp-3	-12.84	S=-714.6	-12.80	S=-842.2	-12.76	S=-969.8	-12.73	S=-1055	-12.71	S=-1075	-12.66	S=-1201

Prediction of kinetic parameters using the Coats-Redfern method: Table 4.0 shows that we obtained E value between 8.77 kJ/mol and 14.37 kJ/mol with R^2between 0.619- 0.988 at the different reaction times.These values predicts that the reaction is highly sensitive especially to the process parameters.A very slight change in process conditions affect in no small measure the reaction output.The low value of E is an indication of the minimum energy required for effective collision between the styrene molecules (6.023×10^{23}**)**to take place. A constant 0.66 as order of reaction was obtained throughout.The less than a unit value is an indication of the complexity and non-linearity of the reaction.

Table 4: Kinetic parameters of styrene polymerization (acetone & chloroform/BPO)

S/N	**Time (mins)**	**Temp (K)**	**Slope**	**α / Ea (KJ/mol)**	
				α	**Ea (kJ/mol)**
1.	10	393	-1729	0.66	14.37
2.	30		-1317	0.66	10.95
3.	50		-1055	0.66	08.77
4.	10	363	-1729	0.66	14.37
5.	30		-1317	0.66	10.95
6.	50		-1055	0.66	08.77
7.	10	333	-1729	0.66	14.37
8.	30		-1317	0.66	10.95
9.	50		-1055	0.66	08.77

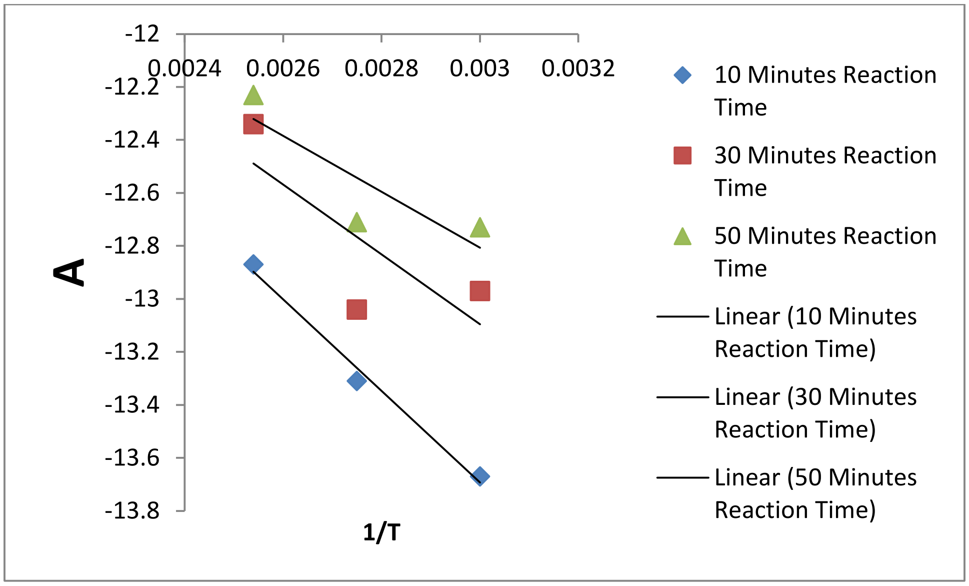

Figure 6: Plot of A against $\frac{1}{T}$ for benzoyl peroxide (acetone /chloroform) where A $=\ln[\frac{1-(1-x)^{1-\alpha}}{T^2(1-\alpha)}]$

Molecular weight of synthesized PS

The production of polymers with end use properties is of significant importance to the polymer industry as it directly affects the physical, mechanical, optical and rheological properties of the final product [26]. Seferlis and Kiparissides [27) in their report reiterate that polymer properties are directly or indirectly linked with the molecular structural properties of polymer chains. All the PS synthesized from both solvents exhibited molecular weight within acceptable range of 10,000 – 1,000,000 thereby guarantees the process ability of the synthesized PS under the relative safe process into final polymeric materials. As stated before, the details of the molecular weight determination can be found in one of our earlier papers [24]. As also expected, the samples were readily soluble in non-polar solvents.

Solvent removal/energy consumption for polymer separation: The ease of solvent removal from the synthesized PS is another important factor that contributes to the safety measures of solvent environment in the solution polymerization of styrene. The energy to separate the solvent from the synthesized PS by distillation/evaporation should be considered for design purposes. Convincingly, the energy requirement for acetone and chloroform (boiling point of 56.1 ^{0}C and 61 s^{0}C respectively) and (heat of vaporization of 29.10 kJ/mol and 29.40 kJ/mol respectively) is quite low. These superior thermodynamics properties of acetone solvent especially coupled with its high styrene conversion further confirm its potentials as the ideal solvent for styrene polymerization. Similar conclusion for acetone was drawn by Schleicher et al [28] while remarking on the solvent effect on the Diels-Alder reaction in ionic liquids using multi-parameter linear solvation energy relationships. Furthermore, acetone is relatively inexpensive, for scale up purpose which can be obtained by bio-renewable method (acetone-butanol-ethanol, ABE) fermentation.

CONCLUSION AND RECOMMENDATION

The chemical industries spend a lot of money for process control techniques to ensure safety and to prevent environmental threats. Hence, alternative production routes or technologies to achieve safety benefits cannot be over-emphasized. In certain reactions, inhibitors are introduced to deliberately slow the reaction, and keeping the rate below the point at which it runs away. Emergency devices that open automatically if the reaction pressure exceeds a safe value to prevent the reaction vessel from exploding with violent force act as the safety measures in some other reactions. In this study however, introduction of solvent to the reacting mixture during styrene polymerization in the company of stirring device helped to break up areas where reaction speed is too great and dissipate heat gradually through the mixture.We have approached the avoidance of the commonly encountered runaway reaction using solvents as heat transfer medium and the associated choice of proper combination of process parameters such as reaction temperature, pressure,volume fraction of styrene/solvent,initiator type,concentration of initiator,type and nature of solvents. Styrene polymerization was also carried out in DDW as a clean and eco-friendly reaction medium. All the reaction media used for the polymerization resulted in high styrene monomer conversion and PS of acceptable molecular weight with no threat of thermal runaway or reactor over-pressurization. It can therefore be concluded that a proper design of reactor plant, reaction environment and the right choice of operating conditions have potentials of reducing accidents.

REFERENCES

[1] Cherbanski R, Milewska A & Molga E, Safety aspect in batchreactors for styrene suspension polymerization, Industrial and Engineering Chemistry Research, (2007)46, 5898**.**

[2] Vijayaraghavan R, Surianarayanan, & MacFarlane D R, Ionic liquids as moderators in exothermic polymerization reactions, Angew. Chem, (2004) 116, 5477.

[3] Tseng J O & Lin, Y F, Evaluation of a tert-Butyl Peroxybenzoate Runaway Reaction by Five inetic Models, Industrial and Engineering Chemistry Research, (2011) 50, 4783.

[4] Joshua U O, Polymerization Processes (Lecture notes), Material science and Engineering department, Iowa State University, U.S.A (2001).

[5] Ronald J W, A, batch polystyrene reactor runaway: a case history .A product of the CCPS-AICHE, New York New York (2000).

[6] Cheng Y C, Thermokinetic parameters analysis for tert-butyl peroxybenzoate, Master's Thesis, YunTech, Yunlin, Douliou, Taiwan (2008).

[7] Wu S H, Chi J H, Huang, C C Lin, N K, Peng, J J & Shu, C M, Thermal hazard analyses and incompatible reaction evaluation of hydrogen peroxide by DSC, Journal of Thermal Analysis and Calorimetry, (2010)102, 563.

[8] Tina E, Carlos G S, Juergen, V, Richard, Hand & Ulrich S S, Recent developments in the utilization of green solvents in polymer chemistry, Chemical Society Review**.**, (2009)39**,** 3317.

[9] Atkinson W H, Bamford, C H & Eastmond G C, Non-ideal polymerization: A new analysis analysis and its application to vinyl chloride .Transactions of the Faraday society, (1970) 66,1446.

[10] Tefera N, Weickert G, Bloodworth R & Schweer J, Free Radical Suspension Polymerization Kinetics of Styrene up to High Conversion ,Macromolecular Chemistry and Physics, (1994)195, 3067.

[11] Sergei A K, Mikhail A S, Evgeniya O P & Vyacheslav P G, Molecular oxygen as a regulator of primary chain length of branced polymers formed in 3D radical polymerization. Oxidative polymerization of styrene. Polymer, (2013)54, 31.

[12] Parouti S, Kammona O, Kiparissides C & Bousquet J, A Comprehensive Experimental Investigation of the Methyl Methacrylate / Butyl Acrylate/Acrylic Acid Emulsion Terpolymerization. Polymer Reaction Engineering, (2003) 11, 829.

[13a] Özdeger E, Sudol E D, El-Aasser M S & Klein A, Journal of Polymer Science, Part A: Polymer Chemistry. (1997) 35, 3813.

[13b] Özdeger E, Sudol E D, El-Aasser M S & Klein A, Role of the non-ionic surfactant Triton X-405 in emulsion polymerization. II. Homopolymerization of n-butyl acrylate, Journal of polymer science.,Part A, (1997) 35, 3827.

[13c] Özdeger E, Sudol E D, El-Aasser, M S & Klein A, Role of the nonionic surfactant Triton X-405 in emulsion polymerization. III. Copolymerization of styrene and n-butyl acrylate Journal Polymer Science, Part A Polymer Chemistry, (1997) 35, 3837.

[14] Lovell P A & El-Aasser M S, Emulsion Polymerization and Emulsion Polymers. Wiley, Chichester (1997).

[15] Chern C S, Emulsion polymerization mechanisms and kinetics, progress in polymer science, (2006) 31, 443.

[16] Etienne G, Pierre-Y G, Jean-Pierre B, Christophe B, Roger S & Vincent M, New insights in free radical polymerization of ethylene in the medium pressure range: from solution process to emulsion , Communication orale - MACRO 2010 - 43rd IUPAC World Polymer Congress, Glasgow – UK (2009).

[17] Almeida A S, Wada K & Secchi A R, Simulation of styrene polymerization reactors: kinetic and thermodynamic modeling, Brazilian Journal of Chemical Engineering, (2008) 25, 2, 337.

[18] Kim K J & Choi K Y, Steady state behavior of a continuous stirred tank reactor for styrene polymerization with bi-functional free radical initiators , Chemical Engineering Science, (1997) 43(4),965.

[19] Mohammad A H, Mohd A Z & Farouq S M, Hybrid modeling and kinetic estimation for polystyrene batch reactor using Artificial Neutral Network (ANN) approach, Asia-Pacific Journal of Chemical Engineering ,(2011) 6(2)274.

[20] Liao J Y, Chen W T, Chen W C, Liu S H & Shua C M, Proceedings of the 6th International Conference on Process Systems Engineering (PSE ASIA) 25 - 27 June 2013, Kuala Lumpur, Malaysia.

[21] Boundy R H & Boyer R F, Styrene its polymers, copolymer and derivatives, Reinhold, New York (1952).
[22] Arai K & Saito, S, Simulation model for the rate of bulk polymerization over the complete course of reaction, Journal of Chemical Engineering, (1976) 9, 302.
[23] Wu G Z A, Denton, L A & Laurence R L, Batch polymerization of styrene-optimal temperature histories, Polymer Engineering & Science, (1982) 22, 1, 1.
[24] Kehinde A J, Usman M A & Owolabi R U, Solvent –initiator compatibility and sensitivity of conversion of styrene homo-polymerization, Journal of Polymer Engineering, (2013) 33, 9,775.
[25] Coats A W, Redfern, J P, Kinetic Parameters from Thermogravimetric Data. Journal of Polymer Science Part B: Polymer Letters, 3(11): 917–920, Article first published online: 10 MAR 2003, DOI: 10.1002/pol.1965.110031106 (1965).
[26] Verros G D, Calculation of Molecular Weight Distribution in Non-Linear Free Radical Co-Polymerization, Polymer, (2003)44, 7021.
[27] Seferlis P & C Kiparissides, Optimizing control of molecular weight properties for batch free-radical polymerization reactors. IFAC, (2001)251.
[28] Schleicher J C & Scurto A M, Kinetics and solvent effects in the synthesis of ionic liquids: imidazolium , Green Chemistry. (2009)11, 694.

.