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Solvent-initiator compatibility and sensitivity of conversion of styrene homo-polymerization

Abstract: Efforts were made to synthesize polystyrene (PS) using free radical solution polymerization. Four common solvents with dissimilar polarities, acetone, chloroform, benzene and toluene, with two different initiators, were selected. The homo-polymerization was conducted in an ace round-bottom pressure flask of diameter 62 mm, with a thermo well, which housed the thermometer. The reaction temperature was maintained at 120°C using a heater with a temperature controller, coupled with a magnetically driven stirrer. One hundred experimental runs of 8 different groups were carried out. Polymerization was conducted in the mass concentration of 0.1 g for each initiator [benzoyl peroxide (BPO) and its blend]. The key parameter considered is the volume ratio of monomer to solvents under different types of solvents, initiators and reaction time. Initially, there was an increase in conversion with the solvent volume and time, until a certain point where there was a gradual decline in monomer conversion. Polymerization rate and monomer conversion were observed to be higher in polar solvents (acetone). Further presented in this study is the macromolecular architecture (molecular weight) and micro-structure of some of the solution polymerized monomer. A kinetic model was also presented to predict the conversion with time profile of the polymerization process. Molecular weight determined were between acceptable ranges while the model presented though with considerable error margin but seems to respond just fairly at extremely low monomer conversion. Similar response was observed from earlier model reported in literature when tested with our experimental data.

Keywords: free radical; molecular weight; polarity; polystyrene; solution polymerization.

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1 Introduction

The serious growing trends in demands of polymers have challenged the status of the present digital age as the plastic age. In terms of needs, polystyrene (PS) remains one of the giant fulcrums in the polymer industry. PS was first produced in 1930 by Dow and BASF in Florham Park, NJ, USA [1]. It is one of the most widely used thermoplastics in a variety of industrial applications such as packaging, consumer electronics, appliances and medical devices. After polyethylene, PS is among the most widely produced polymers globally [1]. In 1996, the world production capacity for styrene was near 19.2 million metric tonnes per year. Dow Chemical is the world's largest producer, with a total capacity of 1.8 million metric tonnes in the USA, Canada, and Europe [2]. Asia is the overall leader in the production and consumption of PS, with 53% of total world production and 47% of total consumption of PS in 2010. North America and Western Europe follow distantly at about 17–19% of the total production and consumption each. Asian consumption of all types of PS is forecast to increase at an average annual rate of slightly over 3% during 2010–2015. Demand for PS is driven by China, which is the largest electronics and the second largest packaging industry in the world [3]. In the last decades, polymers were not only used as industrial bulk materials, but also attracted great attention in high technology fields, e.g., nanotechnology, optics and biomaterials [4]. Each usage requires different specifications for the polymers. Jones et al. [5] revealed the global trends in polymer production in the last six decades until recently, while the portable equipment registration program (PERP) [6] specifically shows the PS end use consumption. Ring's [7] report on PS similarly shows the PS production on selected country basis. The inference from the above trend is that to an industrialist, the most important reaction of styrene is the reaction of styrene with itself.

The last three decades have already witnessed extensive investigation in the area of vinyl monomers homo-polymerization reaction engineering, most studies coming from both Euro-American and Asian researchers within the research circle of Chemistry, Material, Chemical and Polymer Engineering. Still, a formidable challenge remains by virtue of a bias trend noticed as a voluminous part of the previous studies focused primarily on reactor and catalyst design for the polymerization process, its catalytic kinetics including subsequent models development capable of describing the reaction behavior.

However, as an exemption from the above trend, the main production of PS is conducted by bulk and suspension free radical polymerization [8–10]. Malkin and Kulichikin [11] used a series of alkyl methacrylates and styrene, with a benzoyl peroxide initiator, to study rheokinetics of a polymer system. The research focused on the effects of the initial concentration of initiator, reaction temperature, and time on the viscosity of the polymer system. Tefera et al. [12] also investigated, both experimentally and theoretically, the free-radical suspension polymerization of styrene at different temperatures (i.e., 70°C, 75°C, and 80°C) and initiator concentrations [i.e., azobis-isobutyronitrile (AIBN): 0.15–0.45 wt% of styrene]. Devonport et al. [13] revisited the thermal initiation of styrene in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) at 125°C. They showed that low polydispersities and controlled molecular weights could be achieved under these conditions, although the degree of control was not as good as for unimolecular or bimolecular initiating systems. In recent years, McHale et al. [14] intensified research on styrene polymerization using supercritical CO_2 as a green solvent. Rasul et al. [15] successfully investigated the performance of base catalysts (MgO, BaO, and CaO) on the degradation of PS to styrene monomer, where special focus was placed on mixing the catalyst with PS particles in a reactor to increase the rate of degradation. Michael et al. [16], in 1997, studied the effect of free radical propagation rate coefficients of both methyl methacrylate and styrene using pulsed-laser polymerization. The data reported in their article strongly supports the existence of either a radical-solvent or radical-monomer complex, participating in the propagation reaction by modifying the reactivity of the reactants. The statement of Dhib and Al-Nidawy [17] on the correct use of initiator, serves as our impetus for this study. Our objectives in this study are to further investigate the use of varieties of initiators and solvents in improving the conversion of styrene to PS, achieving polymers of a desired molecular weight, and to create a link between the solvent properties and the polymer formation at any point in time under varied conditions.

2 Materials and methods

2.1 Stage (i): reagents and apparatus

The reagents and apparatus used during the experimental stage are listed. All of the glass wares prior to polymerization were inspected, to ascertain that there was no trace of dirt or remnants of materials. A glass reactor was preferred to stainless steel in this study, to view and monitor the reaction as it progresses and to further prevent radical reaction interference with the alloy wall (Fe, Cr, Ni, C) of the stainless steel reacting vessel. A 100 ml Ace round-bottom pressure flask with a thermo-well Steinhein, Germany was used as the reactor; this can withstand a maximum pressure of 60 psig at 120°C. All of the reagents used were of analytical grade, purchased from Sigma Aldrich, Steinhein, Germany, and used as received, except for styrene monomer which was destabilized.

The apparatus included: a heater with a magnetic stirrer, an Ace round-bottom pressure flask with a thermo-well, Petri dish, beakers, a separating funnel, a glass rod, an Ubbelohde viscometer, a measuring cylinder, a stop watch, a water bath, and a thermometer.

The reagents were: styrene (99%) inhibited by 10–15 ppm 4-tertbutylcatechol, benzoyl peroxide (75%), benzoyl peroxide blend with dicyclohexyl phthalate (contains 0.5% water), methanol (CH_3OH) (99.8%), sodium sulfate (Na_2SO_4) (99%), sodium hydroxide (NaOH) (98%), acetone (99.9%), chloroform ($CHCl_3$) (99%), benzene (99%) and toluene (99.8%).

2.2 Stage (ii): destabilization of the styrene monomer

All the reagents were used as purchased, without further purification, except for the styrene monomer which was destabilized. The removal was done as stated below following the report of Arai and Saito [18]. The styrene monomer (100 ml) which contains a phenol (often 4-tert-butylcatechol) as a polymerization inhibitor was added to 100 ml of 10% NaOH solution. The mixture was strongly agitated and was allowed to settle by gravity in a separating funnel. The bottom layer, consisting of the inhibitor, was carefully drained off. The styrene was dried over anhydrous Na_2SO_4. As the sodium sulfate binds with any water that is present, it clumped after some minutes.

2.3 Stage (iii): polymerization of styrene

The reaction initiators include benzoyl peroxide and benzoyl peroxide blend with dicyclohexyl phthalate, and acetone, chloroform, benzene and toluene were the solvents used. Specific amounts of each initiator and styrene monomer (constant throughout) were dissolved in the desired and varying volume of solvent at different reaction times. The solution was manually charged into the reactor. The reaction temperature was maintained at 120°C (±2°C) under agitation provided by a magnetic driven bar stirrer at a speed of about 500 rpm. The pressure equal to the vapor pressure of the reaction mixture was maintained. After a 10 min interval reaction time, the reactor was opened up and cooled to collect the resulting polymer solution.

2.4 Stage (iv): polymer precipitation and solvents removal/recovery

The clear polymer solution was added to about 2–3 ml of methanol in a beaker, with continuous stirring to precipitate the polymer. The top clear solvent was decanted, while the bottom polymer samples were air-dried to remove excess solvent and dried for 2 weeks at room conditions until a constant weight was reached.

2.5 Stage (v): post polymerization analysis

Monomer conversion into polymer (x%) and the rate of polymerization (R_p) were estimated. The synthesized PS were further subjected to solubility and density tests in various solvents, and molecular weights were also determined.

2.6 Monomer conversion and rate of polymerization estimation

Both the x% and R_p were gravimetrically determined (dried weight method):

$$\%\ \text{Conversion}=\frac{\text{Mass of Polymer}}{\text{Mass of Monomer}}\times 100. \tag{1}$$

This is in form of the mass concentration; it could also be in the form of molar concentration:

$$\%\ \text{Conversion}=\frac{[\text{Polymer}]}{[\text{Monomer}]}\times 100, \tag{2}$$

or in terms of volume

$$\%\ \text{Conversion}=\frac{\text{Volume of Polymer}}{\text{Volume of Monomer}}\times 100. \tag{3}$$

We, however, gravimetrically calculated the R_p as:

$$R_p=\frac{[\text{Polymer}]}{\text{Reaction time}}\left\{\frac{\text{mol}}{\text{l.s}}\right\}, \tag{4}$$

where

$$[\text{Monomer}]_0=\left[\left(\frac{\%\times\text{density of monomer}}{\text{Molecular weight of monomer}}\right)\times 10\right] \tag{5}$$

[19].

2.7 Polymer molecular weight determination

The molecular weight of the polymer sample was determined using the solution viscosity method found in the book by Bello [21]. Viscosities of concentrations of polymer solutions were measured with toluene as the solvent at 30°C using an Ubbelohde glass viscometer. In the viscosity method, the time taken for the polymer solution to flow through the capillary was compared with the time for a pure solvent. With the flow time for the solvent being t_0 and that of the polymer solution t, the relative viscosity is:

$$\eta_r=\frac{t}{t_0}. \tag{6}$$

The specific viscosity is:

$$\eta_{sp}=\eta_r\text{-}1 \text{ or } \frac{t\text{-}t_0}{t_0}. \tag{7}$$

The Solomon Gatesman Equation was used to determine the intrinsic viscosity [20]:

$$\eta=\frac{\sqrt{2(\eta_{sp}\text{-}\ln\eta_r)}}{C}, \tag{8}$$

where C is the concentration of the sample. It is important to note that the intrinsic viscosity is not the viscosity as such, but the volume per unit mass that the polymer occupies in a solution.

The Mark-Houwink-Sakurada equation for viscosity of polyethylene and PS found in the review of Herman [22], in 1985, was used to calculate the intrinsic viscosity molecular weight [21, 22]:

$$\eta=KM^a\ \frac{\text{ml}}{\text{g}}\ \text{at a particular temperature.} \tag{9}$$

K and a are constants which are dependent on the solvent, the type of the polymer and the temperature.

2.8 Kinetic model development for monomer conversion

The elementary steps, i.e., initiation, propagation and termination, are shown below [23].

Initiation:

$$I \xrightarrow{k_I} nR^{\bullet}$$
$$r_{R^{\bullet}} = 2fk_I C_I. \tag{10}$$

Chain initiation:

$$R^{\bullet} + M \xrightarrow{k_{CI}} P^{\bullet}$$
$$r_{R^{\bullet}} = -k_{CI} C_M C_{R^{\bullet}} \tag{11}$$

Propagation:

$$P_1^{\bullet} + M \xrightarrow{k_P} P_{1+i}^{\bullet} \tag{12}$$

Termination by combination:

$$P_i^{\bullet} + P_j^{\bullet} \xrightarrow{k_{tc}} D_{i+j} \tag{13}$$

Termination by disproportionation:

$$P_i^{\bullet} + P_j^{\bullet} \xrightarrow{k_{td}} D_i + D_j. \tag{14}$$

For the monomer conversion model, the following assumptions were made: (i) steady state approximation for radical concentration and (ii) rate of initiation is equal to the rate of termination.

Mass balance on the generated radicals gives:

$$r_{R^{\bullet}} = 2fk_I C_I - k_{CI} C_M C_{R^{\bullet}} \approx 0 \tag{15}$$

$$C_{R^{\bullet}} = \frac{2fk_I C_I}{k_{CI} C_M}. \tag{16}$$

Finally, our model is as shown below:

$$\mathrm{In}(1-x) = \frac{2R_P}{K_I C_M}\left[e^{-\frac{k_I t}{2}} - 1\right]. \tag{17}$$

3 Results and discussion

Tables 1 and 2 describe the estimation of the solution viscosity molecular weight of the PS. The estimation was carried out using the Mark Houwink Sakurada equation of the form $\eta = 3.7 \times 10^{-4} \times M^{0.62}$ [21, 22] at 30°C, where η is the intrinsic viscosity and M is the solution viscosity molecular weight. The Solomon Gatesman equation described in Eq. (8) was employed against the cumbersome graphical method for the determination of the intrinsic viscosity. Bastiaan [20] and many researchers have satisfactorily used the equation. All of the samples exhibited molecular weights within an acceptable range except for sample ISC12, synthesized using chloroform as the solvent, which recorded a value above the acceptable range. Other samples synthesized using the same solvent recorded relatively high molecular weights in comparison. However, as seen in Figures 1 and 2, no actual and serious trend could be established between the type of initiator, the solvent used and reaction time to the molecular weight of the PS samples. The observed trend is irregular or fluctuating. This result is in contrary to the observation of Devonport et al. [13] who previously showed that the number of average molecular weights increased in an almost linear fashion with conversion. They revisited the thermal initiation of styrene in the presence of TEMPO at 125°C after conflicting results were reported almost simultaneously

Table 1 Recommended value of Mark-Houwink constants for polystyrene [24].

Solvent	Temp. (°C)	K (ml/g)$\times 10^{-4}$	a	Molecular weight range$\times 10^5$
Toluene	–	1.28	0.70	5.5–20.5
Toluene	–	0.55	0.80	1.1–3.4
Toluene	–	0.01	1.12	1.1–1.7
Toluene	30°C	3.7	0.62	2.0–18
Butanone	40°C	7.0	0.53	2.0–18

K and a are Mark-Houwink constants. K and a are constants which are dependent on the solvent, the type of the polymer and the temperature.

Table 2 Molecular weight determination t_o=69 s, [P] (g/ml)=0.13, initiator: BPO blend.

Samples	t (s)	$\eta_{sp} = \frac{t-t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\sqrt{[2(\eta_{sp} - \ln\eta_r)]}}{c}$	$M = \sqrt[a]{\frac{\eta}{K}} \times 10^5$
1SA11	87	0.261	1.261	1.851	9.25988
1SA12	89	0.290	1.290	2.041	10.83979
1SA13	88	0.275	1.275	1.948	10.05999
1SA14	87	0.261	1.261	1.851	9.25988
1SA15	88	0.275	1.275	1.948	10.05999
2SA12	77	0.116	1.116	0.856	2.66814
2SA13	82	0.188	1.188	1.364	5.66169
2SA14	83	0.203	1.203	1.463	6.33218
2SA15	79	0.145	1.145	1.062	3.77582
2SA16	77	0.116	1.116	0.856	2.66814
3SA13	76	0.101	1.101	0.752	2.16616
3SA14	88	0.275	1.275	1.948	10.05999
1SC12	103	0.493	1.493	3.300	23.54255
1SC13	93	0.348	1.348	2.413	14.19704
1SC14	89	0.290	1.290	2.041	10.83979
1SC15	91	0.319	1.319	2.229	12.48749
2SC13	92	0.333	1.333	2.331	13.42340
2SC15	90	0.304	1.304	2.146	11.74900
2SC16	91	0.319	1.319	2.229	12.48749

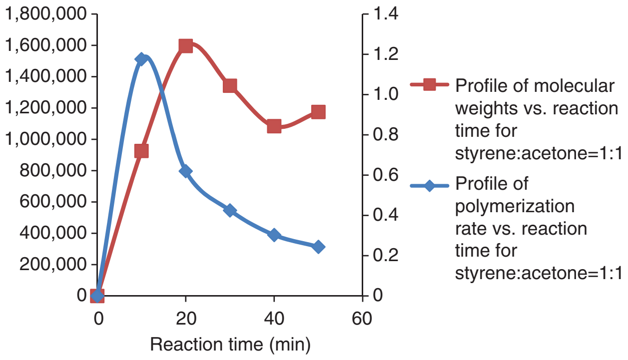

Figure 1 Molecular weight/polymerization rate (R_p) reaction time using benzoyl peroxide (BPO) .

Table 3 Solubility and density test of synthesized polystyrene (PS).

Solvents	Density (g/cm³) [33, 34]	Position of PS	Solubility
Acetone	0.791	Bottom	Solvated to form napalm
H_2O	1.000	Top	Insoluble
Toluene	0.869	Bottom	Soluble
Ethanol	0.789	Bottom	Insoluble
Benzene	0.879	Bottom	Soluble
Chloroform	1.496	Top	Soluble

by [25–27]. Singh et al. [28] also observed at ambient temperature enzyme mediated styrene polymerization that molecular weight of styrene increases with reaction time. Hui and Hamielec [29], studied the variations of number-average molecular weight with conversions at four temperatures (100, 140, 170, and 200°C) and concluded that the molecular weights reduced throughout with the increase in conversion. Shi et al. [30] also conducted similar study at four different temperatures (140°C, 160°C, 180°C, and 200°C) and found that the number-average molecular weights did not vary significantly with conversions. The above are just a few of the numerous inconsistencies in molecular weight data with time or conversion. However, despite the above statements, the validity of the presented data remains as the report by Sueo et al. [31], published online in 2003, that the molecular weight of polymer formed at lower temperatures increases proportionally with the reaction time. In the polymerization at 100°C and 140°C, the molecular weight is independent of reaction time. Reports from researchers globally seem to be conflicting, which is due to the complex nature and sensitivity of the polymerization reaction, even to slight variations in thermodynamic conditions. Unlike simple molecules, polymers are not formed until an appreciable n-1 number of self-reactions has taken place.

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 [32]. Aside from the molecular weight, the synthesized PS were further subjected to both solubility and density tests, as shown in Table 3. As expected, the samples were readily soluble in non-polar solvents and the density fell between the expected ranges, which is in line with reports in the literature. Solvation of the PS sample was observed with acetone. Further investigation reveals that a product called Napalm was formed when PS dissolves in acetone. This was, however, accidentally discovered in our studies.

From our previous control experiment, the styrene monomer and initiator are all needed for polymerization. However, Gao and Penlidis [35] surprisingly cited experimental data from Hui and Hamielec [29], which showed that monomer conversion for styrene thermal and self-initiation reached 40% conversion after 5 h at 120°C, and later 94% after 30 h. One advantage identified from their work is the absence of an initiator, which reduces the production cost; we, however, considered it to be a waste of time or just an academic exercise, with no industrial value. Benzoyl peroxide (BPO) and its blend both gave a

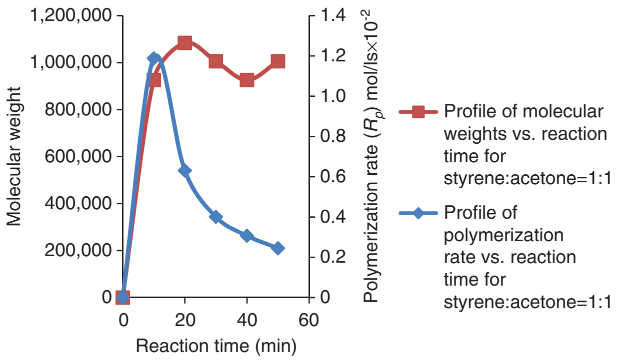

Figure 2 Molecular weight/polymerization rate (R_p) reaction time using BPO blend.

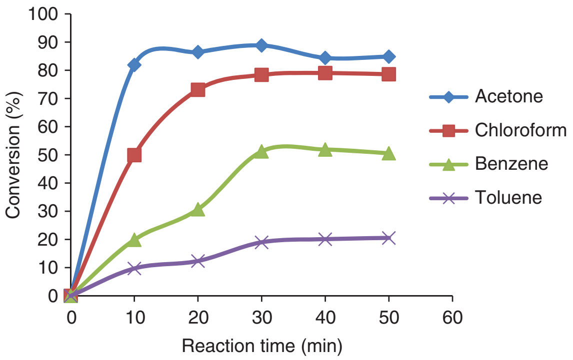

Figure 3 Conversion vs. reaction time profile at $\frac{\text{styrene}}{\text{solvent}}=1$, BPO as initiator.

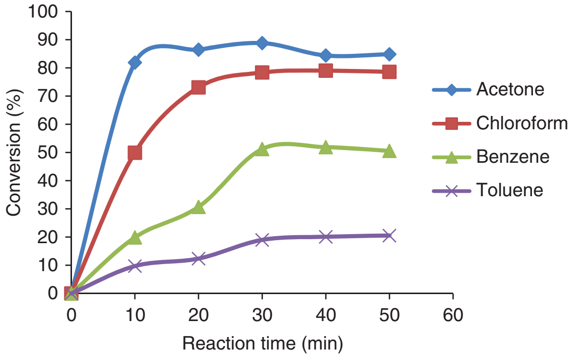

Figure 4 Conversion vs. reaction time profile at $\frac{\text{styrene}}{\text{solvent}}$=1, BPO blend as initiator.

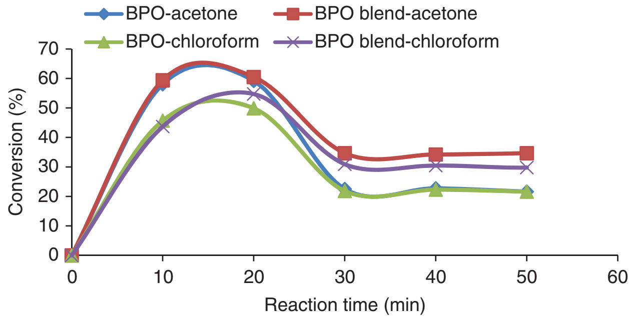

Figure 6 Conversion vs. reaction time profile at $\frac{\text{styrene}}{\text{solvent}}$=0.33.

convincing account of their roles as initiators when used in our studies, where we experienced polymer build up as early as at 10 min. Four solvents, on the basis of different polarity, were investigated in the reaction to explore monomer, solvent, initiator and polymer compatibility. Figures 3 and 4 showed the same trend. The curves showed that conversion varied markedly with the kind of solvent used. Two stages were clearly experienced; namely, the acceleration and stationary stage, which were more pronounced in acetone and chloroform and also occurred at an approximately equal time of 10 min and 20–50 min, respectively, for all if the solvents used irrespective of the initiator. Figure 5 exhibited similar behavior but with low conversion. The low conversion was due to reduced radical formation for more diluted reaction mixtures. Figures 5 and 6 introduced the decelerating stage into the profile, in addition to the earlier trends. The decrease in concentration of the monomer with time was believed to be responsible for the decelerating stage. Figure 7 unexpectedly tends to resume to the earlier stationary stage. This was also attributed to probably the gravimetric and most direct method used in our studies. The conversion of monomer to polymer was determined by direct stopping of the polymerization, isolating and weighing the resulting polymer. The handling of the polymer during precipitation, filtration and drying may lead to losses.

In all, the highest conversions were observed in acetone, a polar solvent, irrespective of the type of initiator used and solvents volume. Toluene recorded the least conversion in all cases. A relationship between the solvent properties, conversion and polymerization rate, as shown in Figure 8, was established. The higher the polarity index of the solvents, the higher both the conversion and the polymerization rate. Polymerization rates were calculated from the molar conversion of styrene with respect to polymerization time.

Figures 9 and 10 exhibited almost similar profiles for the different reaction times. Initially, the conversion increased as the volume of the solvent increased, but later decreased at a higher volume of solvent. This change of behavior was noted after approximately 5–10 ml of solvent. The reduced conversion 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.
- Chain transfer to solvent.
- Reduced monomer concentration

Eq. (18) presented our model for the prediction of monomer conversion. The predictive capability of the kinetic model

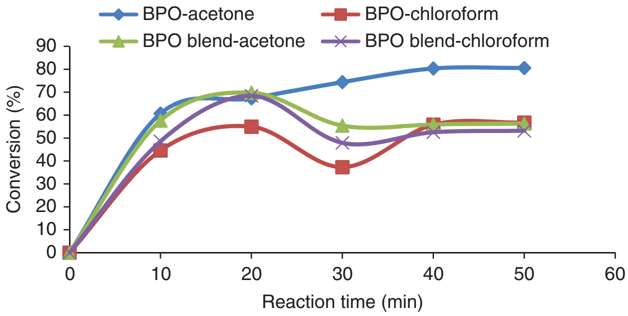

Figure 5 Conversion vs. reaction time profile at $\frac{\text{styrene}}{\text{solvent}}$=0.5.

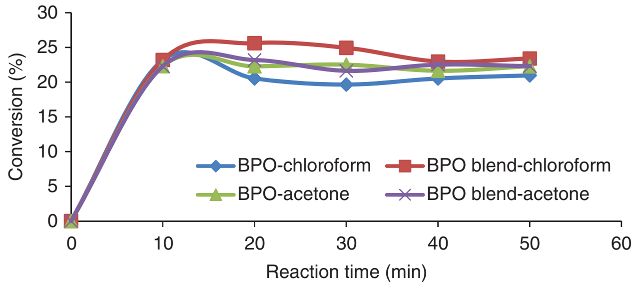

Figure 7 Conversion vs. reaction time profile at $\frac{\text{styrene}}{\text{solvent}}$=0.25.

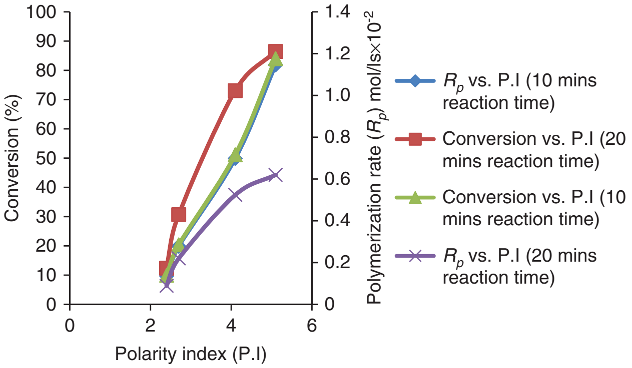

Figure 8 Polymerization rate (R_p)/conversion profile vs. polarity index (PI) using BPO.

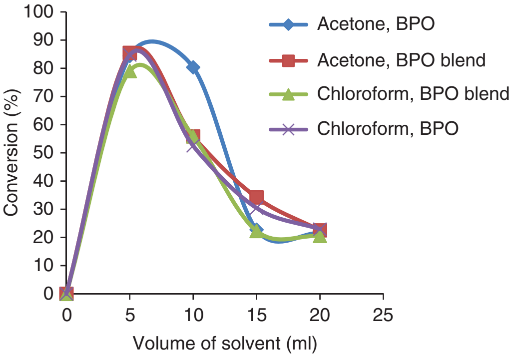

Figure 10 Conversion vs. volume of solvent at 40 min reaction time.

was demonstrated by a direct comparison of model predictions with experimental measurements on monomer conversion.

Figures 3–5 exhibited almost similar profiles for different reaction times for all of the four solvents used. In each case, the highest conversions were observed in acetone, a polar solvent, irrespective of the type of initiator used and solvents volume. Toluene recorded the least conversion in all cases. As shown in Figure 8, the higher the polarity index of the solvents, the higher both the conversion and the polymerization rate. Figures 9–11 similarly exhibited almost similar profiles for the different reaction times. Initially, the conversion increased as the volume of the solvent increased, but later decreased at a higher volume of solvent. This change of behavior was noted after approximately 5–10 ml of solvent.

Eq. (17) presented our model for the prediction of monomer conversion. Tables 2 and 4 compare the experimental values with the model or predicted value. Figures 11 and 12 compare the profiles of the data. The model responded fairly at extremely low conversion with a minimum error of 12.36%. Our unsatisfactory response from the model prompted us to test the reliability of our data with a similar model by Jiguang et al. [36], as shown in Eq. (18). Their model, as shown in Figure 13, responded to our data similarly at low conversion, where we had an intercept of 1.074 as against 1.000, and an initial monomer concentration of 13.31 mol/l, as against 8.612 mol/l:

$$\frac{1}{1\text{-}X}=1+k_p\left[\frac{k_{i1}}{k_{t1}}\right]^{\frac{1}{2}}[M_0]\theta=1+k_{1a}[M_0]\theta=1+K_1\theta \qquad (18)$$

where:

$$k_{1a}=9.46\times10^6\exp\left(\frac{-9500}{T}\right). \qquad (19)$$

4 Conclusion

The polymerization technique adopted in this study is solution polymerization. Most free-radical polymerizations are highly exothermic; the introduction of solvent,

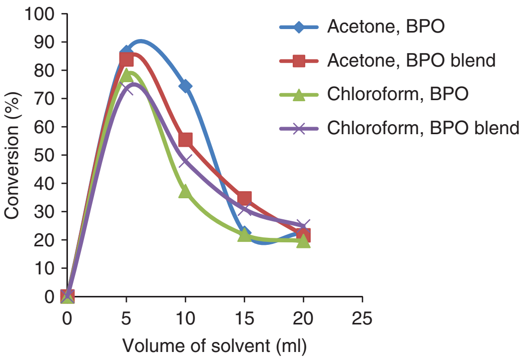

Figure 9 Conversion vs. volume of solvent at 30 min reaction time.

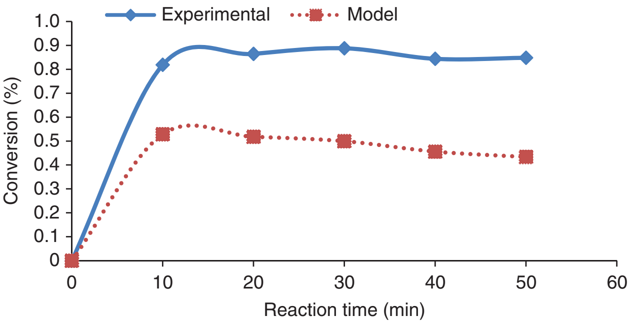

Figure 11 Experimental data vs. model data for high conversion (styrene:acetone=1:1) using BPO.

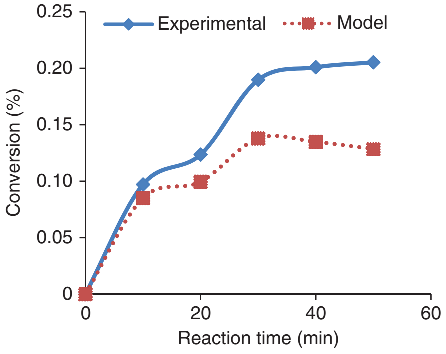

Figure 12 Experimental data vs. model data for low conversion (styrene:toluene=1:1) using BPO.

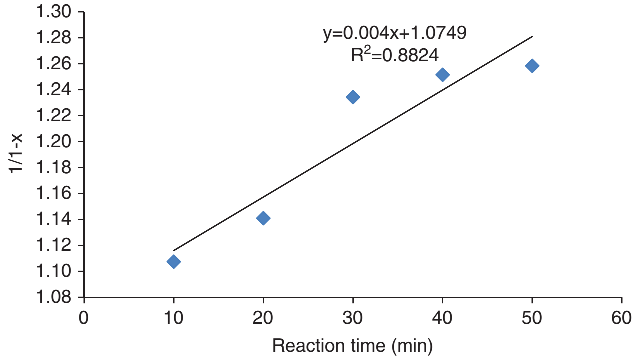

Figure 13 Graph of 1/1-x vs. reaction time at low conversion for BPO.

however, allowed better temperature control through improved heat transfer, and also provided reduction in viscosity, making stirring much easier. If excess heat is not adequately dissipated, the product temperature will rise, with a subsequent rise in the rate of polymerization. At higher temperatures, runaway polymerization is possible. When that occurs, temperature can quickly exceed the boiling point of styrene monomer. Vapors may erupt violently from the glass reactor vent, or excessive pressure can be generated, which may rupture the reactor. Such a situation was not, however, experienced throughout, which infers that we operated below or around the maximum pressure of 60 psig at 120°C, which the glass reactor can withstand.

Table 4 Molecular weight determination t_0=69 s, [P] (g/ml)=0.13, initiator: BPO.

Samples	t (s)	$\eta_{sp}=\frac{t-t_0}{t_0}$	$\eta_r=\frac{t}{t_0}$	$\eta=\frac{\sqrt{[2(\eta_{sp}-\ln\eta_r)]}}{c}$	$M=\sqrt[a]{\frac{\eta}{K}}\times10^5$
1SA11	87	0.261	1.261	1.851	9.25988
1SA12	95	0.377	1.377	2.595	15.96324
1SA13	92	0.333	1.333	2.331	13.42340
1SA14	89	0.290	1.290	2.041	10.83979
1SA15	90	0.304	1.304	2.146	11.74900
2SA12	88	0.275	1.275	1.948	10.05999
2SA13	89	0.290	1.290	2.041	10.83979
2SA14	87	0.261	1.261	1.851	9.25988
2SA15	82	0.188	1.188	1.364	5.66169
2SA16	78	0.130	1.130	0.960	3.20863
3SA13	80	0.159	1.159	1.164	4.38402
3SA15	79	0.145	1.145	1.062	3.77582
1SC12	86	0.246	1.246	1.756	8.50959
1SC13	89	0.290	1.290	2.041	10.83979
1SC14	92	0.333	1.333	2.331	13.42340
1SC15	95	0.377	1.377	2.595	15.96324
2SC13	97	0.406	1.406	2.779	17.84361
2SC15	82	0.188	1.188	1.364	5.66169
2SC16	85	0.232	1.232	1.659	7.75466
1SB13	80	0.159	1.159	1.164	4.38402
1SB14	77	0.116	1.116	0.856	2.66814
1SB15	75	0.087	1.087	0.647	1.69794

In this polymerization, the rate of the reaction is limited, since the reaction temperature is limited by the decomposition temperature of the styrene monomer. The potential health implication on the continuous use of organic solvents and their environmental impact, which may increase the cost through additional separation processes to recycle the solvent, is a major drawback. Another potential issue is contamination of the polymer if removal of the solvent is difficult.

It is, however, clear from our results that the solvents are not actually spectators in the free radical reaction, or just to provide an inert medium for heat dissipation, but influence the propagation step of the reaction. The different conversions obtained from the solvents used are an indication that their interaction in the reaction medium is felt. However, their choice should be strictly selective, especially in terms of their relatively inert roles, easy dissolution of the initiator used, with a completely different boiling point compared to the solvents used during polymer precipitation.

As stated earlier, industrially, PS is synthesized using the bulk polymerization approach; similar high yields are obtained with purer products. To counter these advantages using the solution polymerization, there is no buildup of heat and as a result, the process safety which cannot be quantified in terms of cost, is guaranteed. Acetone gave high conversion and chloroform gave high molecular weights of polymers. The blend of both acetone and chloroform in various proportions is recommended to have a high conversion of monomer to polymer and polymers of high molecular weight.

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