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Cost-Effective Control of Molecular Weight in Ultrasound-Assisted Emulsion Polymerization of Styrene

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Abstract

This paper focuses on the determination of economically most feasible conditions to obtain polystyrene with various target molecular weights through ultrasound-assisted emulsion polymerization. Briefly, batch polymerizations of styrene have been performed by ultrasound-assisted emulsion polymerization process using different reaction feed compositions. Polymerization rates were calculated using the monomer conversions at various reaction times. Also, molecular weights of the synthesized polymers, as well as the Mark-Houwink constants, were determined by intrinsic viscosity and gel permeation chromatography measurements. It was found that the polydispersity index of the polymers is ranging from 1.2 to 1.5, and the viscosity average molecular weights are in between 100000–1500000 g/mol depending on the reaction conditions. Finally, model equations were also developed for response variables, and the most economical ways of reaching various target molecular weights were interpreted by response surface methodology based multi objective optimization.

Keywords: Ultrasound, polystyrene, emulsion polymerization, molecular weight, cost performance

1. Introduction

Emulsion polymerization process is widely used in industry to polymerize various monomers in a continuous heterogeneous phase due to its economic advantages. Besides, water is used as a solvent in emulsion polymerization, making it environmentally friendly.[1,2] Upon introducing appropriate amounts of monomer, water, emulsifier, and initiator to a suitable reactor, a milky fluid called latex is obtained at the end of the reaction.[2,3] Among unsaturated organic compounds, the research activities related to styrene are increasing drastically since polystyrene (PS) has widespread applications in various fields such as automotive, electronics, food packaging, construction, and medical industries.[4] In fact, conventional emulsion polymerization of styrene has been systematically handled in many research articles with a particular focus on kinetic examinations.[3,5–16] For example, Smith-Ewart kinetic theory was developed for the polymerization of styrene and is still widely used in the field.[2,3,5,6] Likewise, rate of emulsion polymerization of styrene was investigated in numerous previous studies.[7–18] According to the examinations in means of mechanism and kinetics, emulsion polymerization follows the free radical addition polymerization by the reaction of free radicals with relatively hydrophobic monomers within submicron polymer particles.[2,18] Yet, it is important to note that polymerization mechanism is slightly different in US-assisted polymerization. Thanks to US-assistance, it is possible to conduct polymerization or achieve high polymerization yields at a lower surfactant amount than critical micelle concentration (CMC).

Apart from rate of polymerization, the molecular weight distribution of a polymer synthesized in an emulsion polymerization has also a significant influence on the processability, as well as the mechanical, and application properties of the final product.[18,19] For instance, various applications of emulsion polymerization products such as adhesives, paper coatings, paints, varnishes, carpet backings require the formation of a continuous film with high mechanical strength that directly depends on the molecular weight of the polymer.[20] Thus, controlling of the molecular weight in polymers synthesized by emulsion polymerization is critical to obtain a desired product. Intensive efforts have been made to control molecular weight of polystyrene thoroughly by emulsion polymerization method in the literature.[19,21–29] For example, Salazar et al. investigated the effect of commercial mercaptans on the molecular weight distribution of PS in a starved emulsion polymerization by developing a mathematical model.[19] Vicente et al. developed a calorimetric method for the on-line control of the molecular weight distribution for linear emulsion polymers by synthesizing polystyrene latexes.[24] Herrera-Ordonez et al. investigated the effect of initial monomer concentration on the molecular weight of polystyrene obtained by emulsion polymerization process above the critical micelle concentration.[25] A recent study conducted by Patrocinio et al. shows that high molecular weight polystyrene (above 1000 kDa) can be obtained at ~70% conversion and reaction times of longer than 12 hours by cationic emulsion polymerization catalyzed with imidazolium based ionic liquid.[28] All of these studies indicate that controlling of the molecular weight for linear emulsion polymers is a challenging topic and an effective control is a very important issue even in a highly studied monomer type such as styrene.

Although conventional emulsion polymerization is a useful method to polymerize many industrial monomers, ultrasound-assisted emulsion polymerization has some advantages over the conventional one, due to the improved reaction rate, suitability for obtaining polymers with a narrow molecular weight distribution, even in relatively mild reaction conditions.[29–31] In fact, ultrasonic waves could be applied to various chemical reactions, improving reaction rates. This is because, extreme temperatures and pressures could be reached through acoustic cavitation, and hence, the mass transport could be enhanced.[32,33] Besides, ultrasonication could also boost formation of various radicals depending on the liquid medium through transient implosive collapse of ultrasound associated bubbles.[34] During the conventional emulsion polymerization, monomer droplets coalesce due to the insufficient monomer dispersion, causing phase separation, and thus deceleration of the reaction rate.[35] Whereas, stable and uniform droplets can be obtained in ultrasound-assisted emulsion polymerization thanks to the acoustic cavitation activity at the interface of immiscible organic liquid phase.[29–37] For mentioned reasons, ultrasound-assisted polymerization of styrene has been investigated many times.[35,38–43] For example, Cheung and Gaddam carried out ultrasound-assisted emulsion polymerization of styrene and methyl methacrylate using AIBN, KPS and ferrous sulphate initiators.[38] Ooi and Biggs reported that the ultrasound-assisted emulsion polymerization of styrene could be performed with ~90% monomer conversion in the absence of initiator after 3 hours of irradiation time.[39] Zhang et al. performed the ultrasonically irradiated emulsion polymerization of styrene in the presence of carboxymethyl cellulose and alkyl poly(etheroxy) acrylate based polymeric surfactants.[41] Qiu et al. used Fe^{2+} in ultrasound-assisted emulsion polymerization of styrene to increase the reaction rate by increasing the sonochemical efficiency.[43] On the other hand, although there are many emulsion polymerization studies stating the positive effects of ultrasound, there are also some drawbacks such as energy consumption, contamination, probe erosion, and possibility of side reactions, particularly when ultrasound is irradiated for prolonged times.[44] Thus, accomplishing an emulsion polymerization where the desired products can be obtained with the use of short-term ultrasound is critical. In this context, Nagatomo et al. investigated the effect of ultrasonic pre-treatment on the emulsion polymerization of styrene to reach higher monomer conversions.[35] To sum up, many studies have been conducted to advance the ultrasound-assisted emulsion polymerization process. However, additional studies are still necessary, particularly on the molecular weight control at high monomer conversions to make this process more feasible.

In addition to this, such molecular weight control should be evaluated in accordance with economic considerations, because PS is widely used in industrial applications. However, to the best of our knowledge, there are no previous reports on the cost-molecular weight performance relationship of the emulsion polymerization of styrene. Accordingly, the main aim of this work is to determine the economically most feasible conditions to obtain PS with various target molecular weights through ultrasound-assisted emulsion polymerization. For this purpose, we performed ultrasound assisted emulsion polymerizations of styrene using different reaction feed compositions and correlate conversion efficiency, molecular weight and cost through a statistical approach.

2. Experimental Section

2. 1. Materials

Styrene (Reagent Plus ≥99%) was purchased from Sigma Aldrich and pre-distilled in a rotary evaporator to remove the inhibitor (hydroquinone). Sodium dodecyl sulfate (SDS), ammonium persulfate (APS), sodium bisulfite (SBS), toluene and methanol were also purchased from Sigma Aldrich at ACS reagent grade and used as-received. Double distilled water was used throughout the experiments to prepare necessary solutions, and all glassware's were cleaned with copious amounts of double distilled water after the reactions.

2. 2. Experimental Set-up

Bandelin® HD 2070 (frequency: 20 kHz, maximum power output: 70 W) ultrasonic homogenizer, equipped with a horn type probe (probe diameter: 13 mm) was used to deliver pulsed ultrasound. The pulse ratio was adjusted as 7 s on and 3 s off. The ultrasound power delivered to the reactor was calculated by calorimetric method. The details of calorimetric method and calorimetric results were given in the supporting information section. Polymerization experiments were carried out at 11.1, 14.6, 18.2 and 22.1 W calorimetric powers. Three necked round bottom glass reactor which equipped with a reflux condenser was put on a hot plate to ensure constant temperature within ± 1 °C. In a typical synthesis, a mixture of styrene, APS, SBS, SDS, and double distilled water were added to the reactor, and degassed by bubbling nitrogen gas at 25 °C. The reactor temperature was set to 60 °C and the experiments were conducted for a total of 3 hours. Ultrasound was applied at various ultrasonic calorimetric powers only for 1 hour in all experiments. After 1 hour of ultrasound exposure, experiments were continued for 2 hours in the absence of ultrasound. The experiment temperature was chosen as 60 °C since the decomposition of APS is faster at higher temperatures.[45,46] To calculate the monomer conversions, 1 ml of samples were taken from the reactor at 30 min time intervals throughout the experiments. The samples, were then dried in a vacuum oven at 80 °C until constant weight was attained, and the monomer conversions were determined gravimetrically.

2. 3. Polymerization Experiments and Characterizations

All of the polymerizations were conducted using the same reaction volume (200 ml) to ensure replicable acoustic power density dissipation. We first studied the effect of the APS/SBS molar ratio on the monomer conversion. The best APS/SBS molar ratio was determined as 1:1.2 in terms of obtaining higher monomer conversions. Therefore, the rest of the experiments were conducted by keeping APS/SBS ratio constant at 1:1.2 by mole and the effect of various initial monomer concentrations, initiator concentrations, emulsifier concentrations and ultrasound powers were studied accordingly. After 3 hours of polymerization reactions, the latex mixtures were dried at room temperature. Following this, the reaction products were washed with methanol for further purification. Finally, the polymers were vacuum filtered and dried at room temperature. Table 1 shows the polymerization conditions and the monomer conversions after 3 hours. It is important to note that CMC of SDS is 9.2 mM at 60 **°C**.[47] This means that in a total reaction volume of 200 ml, 0.531 g of SDS is required to achieve the CMC, and thus, the present work focuses US-assisted polymerization of styrene below CMC.

Intrinsic viscosities of the synthesized polymers were determined in toluene by an Ubbelohde-type viscometer at 25 °C using Huggins' viscosity equation given below[48]:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \qquad (1)$$

In a typical measurement, the efflux time of toluene was recorded as a reference. Then, a certain amount of PS was dissolved in 20 mL of toluene, and the efflux time was recorded again. Following this, the PS solution was diluted multiple times, and efflux times were recorded for various concentrations. Overall, specific viscosity (η_{sp}) and reduced viscosity (η_{sp}/c) values were calculated, which is followed by the determination of intrinsic viscosities by extrapolation of the reduced viscosity values to zero concentration procedure.

The weight average (M_w) and number average (M_n) molecular weight of the polymers were determined in ultra-pure THF using gel permeation chromatography (GPC) where the calibration was done using polystyrene standards, and the passage time of solvent was 1.0 ml/min. The glass transition temperature (T_g) values of the polymers were obtained by using DSC where the heating rate was 10 °C/min between 0 and 150 °C. Before the measurements, samples were preheated to 150 °C in order to eliminate thermal affects and then the measurements were started after they were cooled to 0 °C.

Table 1. Polymerization conditions and the final monomer conversions.

Polymer	Ultrasound calorimetric power (W) (A)	$[M]_0$ (mol/L)[a] (B)	APS (wt.%)[b] (C)	SDS (wt. %)[c] (D)	Conversion (%)
PS-1	14.6	0.50	0.50	0.5	85.7
PS-2	14.6	0.50	1.00	0.5	88.3
PS-3	14.6	0.50	1.25	0.5	89.4
PS-4	14.6	0.50	1.50	0.5	90.7
PS-5	14.6	0.50	2.00	0.5	93.9
PS-6	0	0.50	2.00	0.5	40.7
PS-7	11.1	0.50	2.00	0.5	94.1
PS-8	18.2	0.50	2.00	0.5	93.1
PS-9	22.1	0.50	2.00	0.5	91.7
PS-10	11.1	0.50	2.00	0.0	85.8
PS-11	11.1	0.50	2.00	1.0	93.6
PS-12	11.1	0.60	2.00	0.5	95.3
PS-13	11.1	0.75	2.00	0.5	97.8
PS-14	11.1	1.00	2.00	0.5	99.2

[a] Initial monomer concentration. Typically, (mole amount of styrene in the feed)/(total volume of the reaction solution) is 0.5 mol/L for PS-1.
[b] Based on the weight amount of monomer in the feed. Typically, (APS/Styrene)×100 is 0.5 for PS-1.
[c] Based on the weight amount of monomer in the feed. Typically, (SDS/Styrene)×100 is 0.5 for PS-1.

3. Results and Discussion

3. 1. Effect of Process Parameters on Monomer Conversion and Rate of Polymerization

PS has very broad application areas as explained previously, and thus it can be regarded as one of the industrialized polymers. Most manufacturers synthesize PS by emulsion polymerization since it allows high polymer yields at affordable prices. In this regard, monomer conversion could possibly be considered as the most significant parameter by the manufacturers as it dictates economic feasibility. In the present work, we prepared PS by ultrasound-assisted emulsion polymerization, which will decrease reaction time to reach high monomer conversions, and thus will directly reduce the cost. However, the power necessity of the ultrasound assistance will inevitably raise the costs in this case, and there should be a trade-off between ultrasound power and reduction in reaction time. In anyway, one should control monomer conversion to comment more on the effectiveness of ultrasound-assisted emulsion polymerization in terms of economic feasibility. In other words, the costs associated with the power necessity to reach high reaction yields in ultrasound-assisted polymerization should be compared with the costs associated with the extra reaction time to reach the same level of monomer conversion in the absence of ultrasound. This is why we first focused on to maximize monomer conversion in the present work.

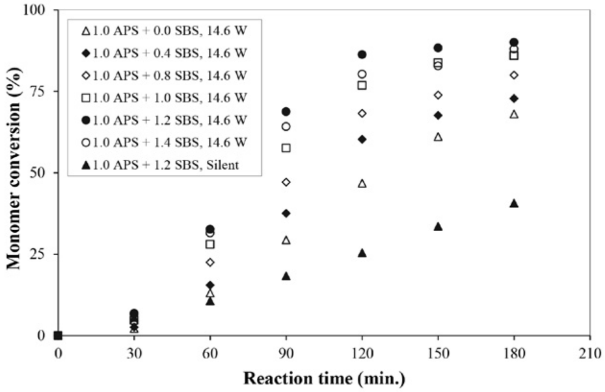

Fig. 1. The effect of molar APS/SBS ratios on the monomer conversion.

In preliminary experiments, we studied the effect of APS/SBS ratio on the outcome of emulsion polymerization. In fact, APS and SBS are expected to enter the polymerization reaction with a molar ratio of 1:1 in a typical synthesis. However, there might be some deviations in practice due to the hygroscopic nature of both APS and SBS. Accordingly, we first focused on to optimize the APS/SBS ratio, and Fig. 1 shows the effect of APS/SBS on the monomer conversion at various reaction times. The results show that the monomer conversion is higher when SBS is introduced together with APS, since persulfate ions are now expected to react with bisulfite ions to produce radicals for redox initiation, and thus, decreasing activation energy of bond scission.[2] In line with this, increasing the SBS concentration resulted in higher monomer conversions until reaching a molar APS/SBS ratio of 1:1.2. When APS/SBS ratio is increased to 1:1.4, monomer conversion decreased due to possible unexpected side reactions of excess radicals.

Accordingly, the optimum APS/SBS ratio in terms of best monomer conversion was found to be 1:1.2, and the rest of the tests were conducted at this concentration. However, it is important to note that the redox systems are known to be effective only at sub-ambient temperatures in general.[2] Interestingly, our results suggest that such temperature requirement might not be necessary in ultrasound-assisted emulsion polymerization. This was ascribed to the generation of acoustic waves, which might provide more activation energy through acoustic cavitation and allowing use of redox systems at relatively higher temperatures. To check this idea, another set of experiments were conducted at optimum APS/SBS ratio (1:1.2) in the absence of ultrasound (Fig. 1). In this case, a monomer conversion of only ~41% was achieved after 3h, adding credibility to the afore-mentioned claim. The difference between both processes, lies in the polymer particle nucleation mechanism. Based on Smith-Ewart kinetic theory, nucleation occurs in micelles, and surfactant concentration should be above the CMC of the surfactant in conventional emulsion polymerization. The monomer droplets act as reservoir and monomer is transported to the growing polymer particles. In miniemulsion polymerization, the reaction starts with substantially smaller droplets (in the range 50–500 nm) that are stabilized with the surfactant available and hence monomer swollen micelles are not present. Therefore, nucleation occurs in monomer droplets.[49,50] In the experiments reported in this work, the concentration of SDS is below the CMC (9.2 mM for SDS at 60°C)[47] in all the cases, which means that no micelles are present. Thus, in the polymerizations carried out without ultrasound, polymer particles can only be formed by the so-called homogeneous nucleation and in this case, the number of particles should be small and the size relatively large (couple of hundreds of nanometers). As a result, polymerization rate is slow in our conditions. When ultrasound is applied the polymerization system, size of the droplets changes to the nanometer scale, and therefore polymerization rate increases.

Fig. 2 shows the effects of initiator concentration, ultrasound calorimetric power, SDS amount and initial monomer concentration on the monomer conversion. As seen in Fig. 2a, monomer conversion increased with the increase of APS concentration for the ultrasound-assisted polymerization having ultrasound calorimetric power of 14.6 W. As the amount of initiator increases, there will be more radicals per monomer in the system, and thus time-dependent polymerization rates increase.[2] At the end of the reaction, over 85% monomer conversions were obtained at all initiator concentrations studied in this work when the ultrasonic calorimetric power was 14.6 W. On the other hand, the effect of ultrasound power on the monomer conversion was shown in Fig. 2b. As expected,

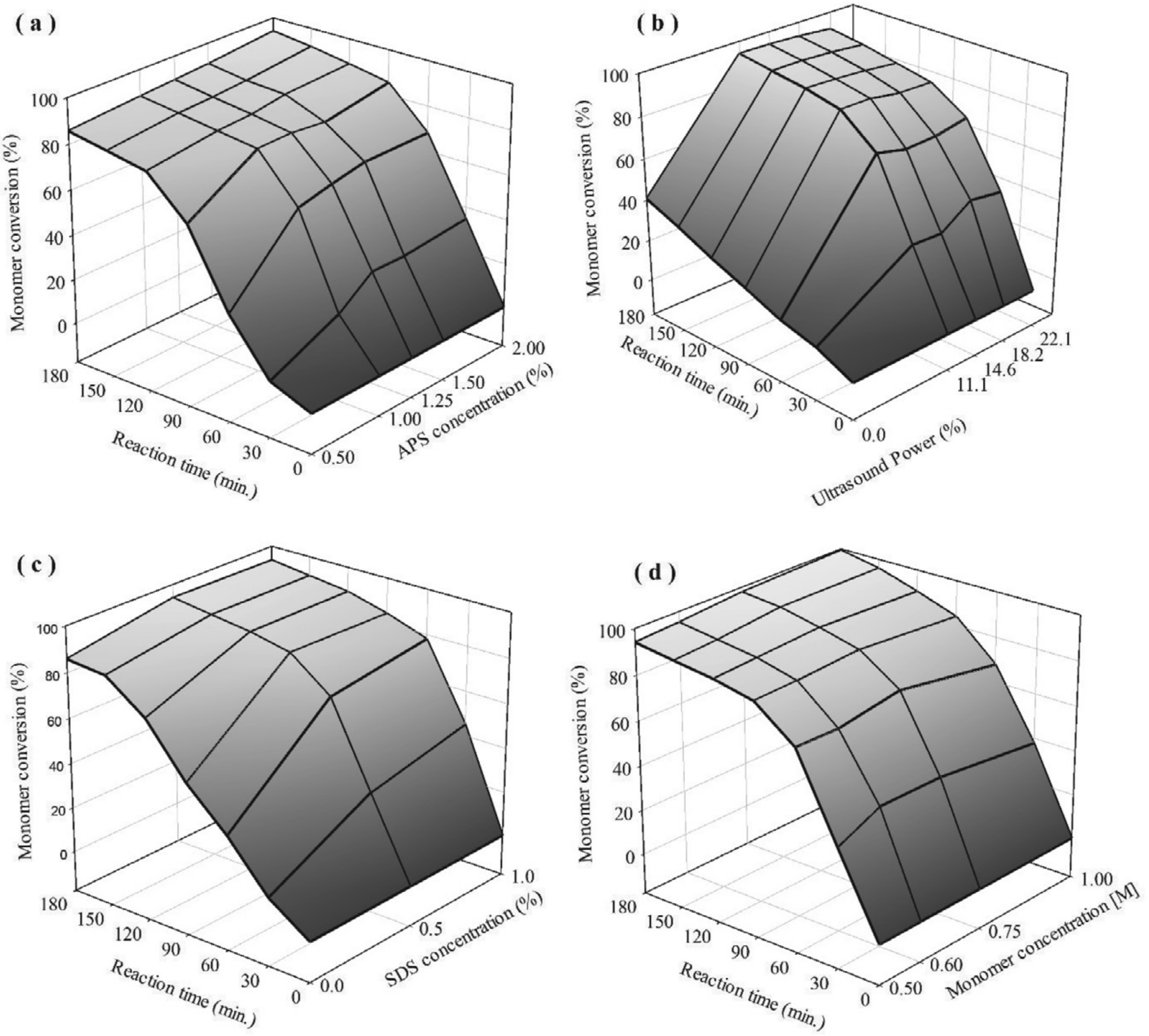

Fig. 2. (a) Effects of initiator concentration, (b) ultrasound calorimetric power, (c) SDS amount and (d) initial monomer concentration on the monomer conversion.

presence of ultrasound in the reaction medium increases the monomer conversion, accordingly. Acoustic cavitation associated with the ultrasound contributes to the dispersion of monomer droplets. Besides, with the application of ultrasound to the polymerization reaction, the initiator produces more radicals due to its further degradation.[45] The primary radicals that originated by the decomposition of the initiator, might directly enter a monomer droplet through acoustic cavitation, and generate monomeric radicals at the bubble/solution interface, and hence contribute to the polymerization.[31] The results show that while we reached a monomer conversion of higher than 80% after 90 mins for the ultrasound-assisted polymerization even at 11.1 W ultrasonic calorimetric power, the monomer conversion was only ~41% in the absence of ultrasound even after 3 hours. In fact, sonication should be conducted with a power above the acoustic threshold to create cavitation bubbles.[36] Yet, we found that the effect of ultrasound power on the monomer conversion is negligible between ultrasound calorimetric powers of 11.1 W and 22.1 W. This means that 11.1 W ultrasonic calorimetric power is sufficient to improve reaction rate considerably, and it seems that it won't be feasible to further increase ultrasound power beyond this point. This might be due to the choice of the appropriate reaction volume and geometry that fits with the appropriate probe diameter in our system, which might provide better dispersion even at low ultrasound powers.[36]

In order to make clarify the effect of ultrasound, rate of polymerization (R_p) for our system was also studied. As known, suitable numerical differentiation formulas can be used to evaluate the rate of a reaction in a batch reactor when the data points in the independent variable are equally spaced.[51] Thus, the rate of polymerization as a function of reaction time was calculated from conversion values using below equations (Equation 2 is given for intermediate data points and Equation 3 is given for last data points)[51,52]:

$$-\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t}\left(C_{A(i+1)} - C_{A(i-1)}\right) \qquad (2)$$

$$-\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{C_{A(i-2)} - 4C_{A(i-1)} + 3C_{Ai}}{2\Delta t} \qquad (3)$$

where C_A is the monomer concentration in mol/L, i is equally spaced intermediate data points (from $i = 1$ to $i = 6$, i.e., C_{A0} means the data at 0 min, C_{A1} means data at 30 min, etc.), and Δt ($t_1 - t_0 = t_2 - t_1 = 30$ min) is time interval, respectively.

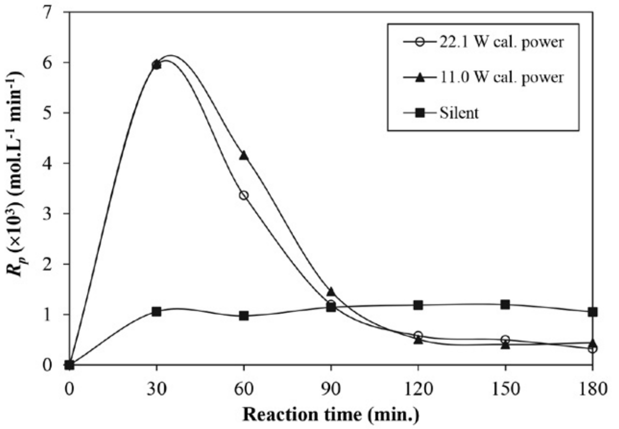

Fig. 3. Rate of polymerization versus reaction time at different ultrasound calorimetric powers (APS: wt. % 2, SDS: wt. % 0.5).

Fig. 3 shows the R_p (mol L^{-1} min^{-1}) as a function of reaction time at different ultrasonic power conditions. As can be seen in this figure, R_p attains maximum level in the first 30 minutes of the reaction and then reduces with reaction time, indicating that ultrasound assisted mini-emulsion polymerization proceeds in two intervals,[23,30,49,50] whereas conventional emulsion polymerization proceeds in three intervals.[2,14,18,49] Observation of faster reaction rate in the early stage of ultrasound-assisted mini-emulsion polymerization can be attributed to the fact that the cavitation jets facilitate transporting of free radicals to monomer droplets in this process.[29] Briefly, the presence of ultrasonic cavitation in reaction medium improves the polymerization rate considerably.

The effect of surfactant concentration on the monomer conversion was also investigated between 0% and 1%, while keeping other parameters constant (APS concentration: 2 wt. % of styrene feed, ultrasound calorimetric power: 11.1 W, and initial monomer concentration: 0.5 M). Fig. 2c shows that monomer conversions were increased with the increase of the SDS concentration. With the aid of ultrasound, it can easily perform mini-emulsion polymerizations without the use of surfactant or below the critical micellar concentration. Also, ultrasound prevents agglomerations that may occur during the polymerization reaction. In conventional emulsion polymerization, particles tend to collide and agglomerate due to Brownian and bulk fluid motion.[15] Considering that SDS is an ionic surfactant, it could stabilize particles and solve the agglomeration problem through electrostatic repulsion that could counteract van der Waals interactions.[53,54] Therefore, there might be a certain amount of SDS to effectively counteract the van der Waals interactions, and above this point the importance of SDS might tend to vanish in terms of monomer conversion as there is already enough SDS to overcome agglomeration.

The effect of initial monomer concentration on the monomer conversion is also studied between 0.5 M and 1.0 M, while keeping other parameters constant (Ultrasound calorimetric power: 11.1 W, APS concentration: 2 wt. % of styrene feed, and SDS concentration: 0.5 wt. %). It can be seen from Fig. 2d and Fig. 4 that the increase in the initial monomer concentration also increases the monomer conversion and reaction rate to some extent. In fact, the effect of monomer/water ratio on the rate of polymerization should have no influence according to the Smith-Ewart kinetic model for conventional emulsion polymerization.[2,3,49] However, in practice, rate of polymerization is affected from the solubility of the monomer in water and polymer phases.[2] Thus, the increase in the reaction rate with the increase of monomer concentration can be explained by the enhancement of solubility of the monomer in the water phase and reduction in the size of monomer droplets under the influence of ultrasonic cavitation.

In the present study, we focused on a narrow monomer concentration region and didn't increase the initial monomer concentration above 1.0 M to further increase

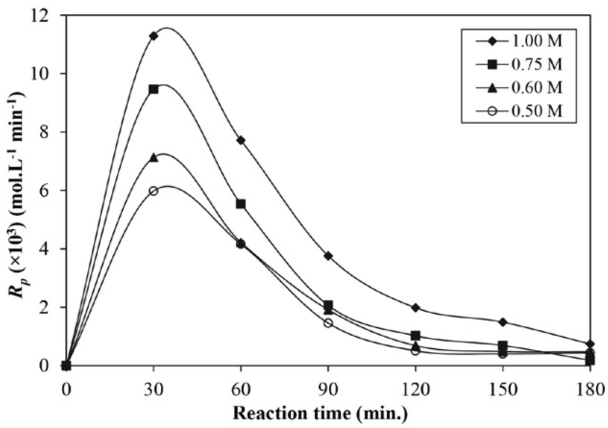

Fig. 4. Rate of polymerization versus reaction time at different initial monomer concentrations (Ultrasound calorimetric power: 11.1 W, APS: wt. % 2, SDS: wt. % 0.5).

the monomer conversion. Because, when we tried to increase the initial monomer concentration, monomer particles tended to adhese on the ultrasound probe, eventually halting the process. Thus, 1 M initial monomer concentration seems to be the highest allowable concentration at this SDS amount to apply ultrasound in our system effectively.

3. 2. Evaluation of Molecular Weight, Intrinsic Viscosity, and Cost of Synthesized Polymers

Regarding molecular weight, we first focused on intrinsic viscosity $[\eta]$ values of the synthesized polymers. In general, intrinsic viscosity value of a polymer is a measure of the capacity of a polymer molecule to improve the viscosity of a polymer solution, and it reflects the chain length of a polymer in a specific solvent.[48,55–57] Thus, it can be said that intrinsic viscosity of polymers is highly correlated with their molecular weight. On the other hand, it is already known that molecular weight of a polymer can be calculated from intrinsic viscosity values by Mark-Houwink equation, as given below:

$$[\eta] = KM_v^{\alpha} \qquad (4)$$

where $[\eta]$ is intrinsic viscosity values of polymer, M_v is viscosity average molecular weight, and K and α are Mark-Houwink constants for polymer-solvent combinations. However, this necessitates knowledge of the Mark-Houwink parameters. Although these constants are available in the literature, most of the previously reported values are only valid in definite molecular weight regions.[57] In order to find more suitable Mark-Houwink constants for our system, we determined the M_w of some representative samples through GPC (Table 2). Then, the K and α values that could be used for our polymers were calculated as 0.0116 ml/g and 0.687, respectively, by using a logarithmic plot of $[\eta]$ versus M_w as given in Fig. 5. Finally, the viscosity average molecular weight (M_v) values were calculated using the determined Mark-Houwink constants. Glass transition temperature (T_g) of synthesized polymers are also given in Table 2. The T_g of polystyrene increases with molecular weight until it reaches about 107 °C at molecular weight values of above 100000, which results are in good accordance with previous reports.[58–60] Also, particle size analysis was conducted by using Malvern laser diffraction particle size analyser to further comment on the microstructure of the resultant polymers and the results are given in Table 2. In general, particle sizes on the latex samples are naturally much smaller.[35] However, we conducted particle size analysis on dried polymers since the aim of this work is to perform cost-target molecular weight optimization for commercial applications, and the particle size results on Table 2 are actually comparable with commercial PS.[61] Table 3 shows the $[\eta]$ and M_v values of all polymers synthesized in this work.

Table 2. Representative GPC, thermal analysis and particle size analysis results of synthesized polymers.

Polymer	M_w (g/mol)	M_n (g/mol)	PDI	T_g (°C)	D_{50} (μm)
PS-1	1353000	1027000	1.32	106.6	292
PS-5	392000	291200	1.35	107.1	92
PS-6	101600	78900	1.29	100.4	225
PS-12	532800	392400	1.36	106.8	88
PS-14	605000	407900	1.48	107.4	170

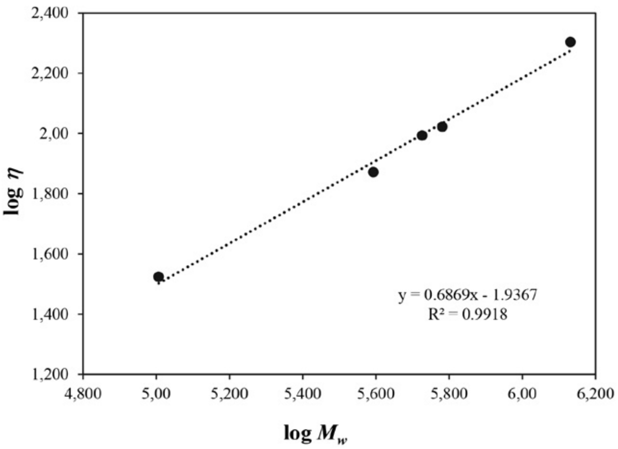

Fig. 5. Change of log M_w of the polymers with the change of log η.

Overall, the results show that the molecular weight is decreasing with APS, SDS and ultrasound power, while increasing with initial monomer concentration. When more and more APS and SDS are introduced to the system, more radicals can be formed to initiate the polymerization, but with the expense of chain length (Table 3). For example, the M_v of the PS decreased sharply from 1483600 to 348200 g/mol with the increase of APS concentration as seen in Fig. 6a. This is because, more monomers might be reacting with these radicals in this case rather than attaching to the active monomer chains, and thus resulting in shorter polymer chains in the final structure, yielding a lower molecular weight. Similar situation could also be persistent for the ultrasound power as seen in Fig. 6b. It might be easier for the radicals to decompose due to acoustic cavitation under higher applied ultrasound power, and thus causing shorter polymer chains in the final structure, similar as explained for the effect of APS and SDS. Moreover, the polydispersity index (PDI) values of the synthesized polymers were ranged between 1.28 and 1.48 (Table 2) and were actually relatively lower, particularly considering free radical polymerization.[2,55] This is expected, because the acoustic cavitation might break down the longer polymer chains, further decreasing the molecular weight and causing all polymer chains to a similar length.[29,31,39,41] However, Kojima et al. reported that sonication for 3 h at 92 kHz in polymerization of styrene gives very high polydispersity (5.0) indicating that sonication time is very important to

Table 3. Molecular weight of synthesized polymers, and cost-molecular weight relationship.

Polymer	**Actual Results**			**Model Predictions**		
	[η] (ml/g)	**M_v (g/mol)**	**Cost (\$/ton PS)**	**[η] (ml/g)**	**M_v (g/mol)**	**Cost (\$/ton PS)**
PS-1	201.2	1483600	44518.9	199.4	1420100	44457.2
PS-2	154.5	1010000	44271.1	158.4	1068100	44321.7
PS-3	134.3	824200	44224.7	137.9	892100	44254.0
PS-4	125.2	743700	44146.5	117.4	716100	44186.3
PS-5	74.3	348200	43622.5	76.4	364100	44050.8
PS-6	33.4	108800	100295.4	NA*	NA*	NA*
PS-7	91.2	468800	43496.7	91.5	465300	43913.9
PS-8	63.4	276500	44028.9	60.9	259900	44191.5
PS-9	43.1	157600	44739.9	44.1	147100	44343.0
PS-10	95.8	504000	34530.0	97.6	510900	33283.1
PS-11	83.5	412800	55791.6	85.3	419700	54544.7
PS-12	98.5	524500	42941.6	94.8	492500	43303.3
PS-13	104.0	567700	41844.4	99.8	533340	42387.4
PS-14	105.3	577800	41204.7	108.1	601400	40860.9

* Outside the validity region of the developed models.

prevent undesired effects of ultrasound.[40] These results show that ultrasound assisted emulsion polymerization of styrene in our conditions is suitable for obtaining narrow molecular weight distributions. On the other hand, we ascribed the slightly positive effect of initial monomer concentration on the molecular weight to the possible increase of the biradical coupling ratio to the disproportionation in the termination step, which might be occurring due to the very low APS concentration (2 wt. % of initial monomer concentration) in our system.[2]

3. 3. Statistical Analysis

We used a statistical approach to interpret the economic feasibility of the ultrasound-assisted emulsion polymerization of styrene through Design Expert (trial version). Statistical optimization tools are widely used nowadays in various fields to converge scientific studies to industrial applications.[62–65] Considering that polystyrene is an industrialized polymer, economic considerations are important for manufacturers as mentioned before. Therefore, a multi objective optimization procedure, which is particularly focusing on to determine the minimum cost to reach a PS with any desirable molecular weight would be beneficial. For this purpose, we assigned ultrasound power, initial monomer concentration, APS concentration, and SDS concentration as independent variables (factors), while defining molecular weight, intrinsic viscosity, and cost as the response variables in Design Expert (trial version). Then, a cost equation (Equation 5) was established to determine the expenses in PS synthesis at the experimental conditions of this work. It is important to note that although cost of SBS was added to the cost equation, the amount of SBS was not introduced as a factor, since we used a definite APS:SBS ratio of 1.2, and thus, SBS is not an independent variable.

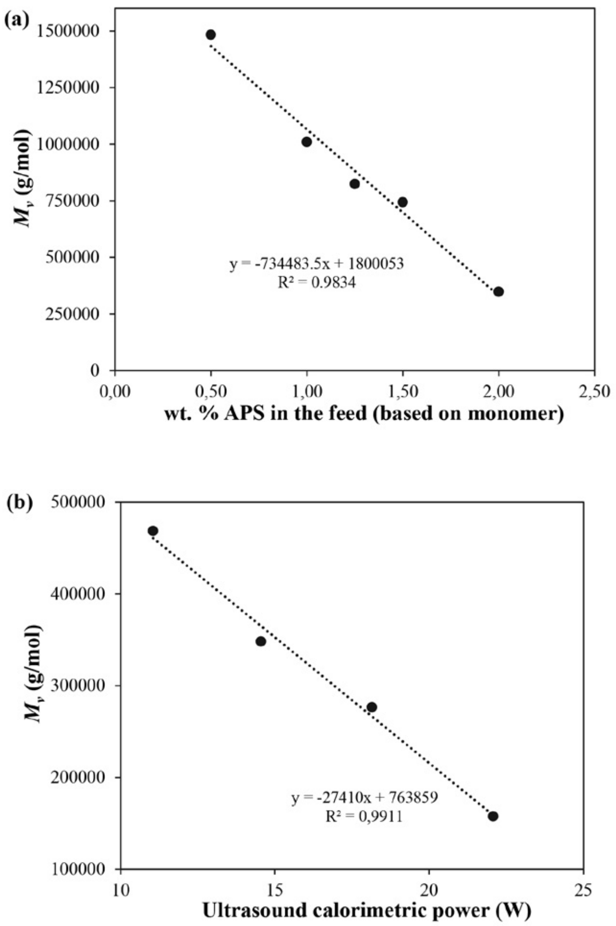

Fig. 6. (a) Change of viscosity average molecular weight with the change of weight fraction of APS in the feed (Ultrasound calorimetric power: 14.6 W, SDS: wt. % 0.5, $[M]_0$ = 0.5 M), (b) Change of viscosity average molecular weight with the change of ultrasound power (APS: wt. % 2, SDS: wt. % 0.5, $[M]_0$=0.5 M).

$$Cost\ (per\ ton\ of\ PS) = \\ = \frac{(C_{elec}+C_{styrene}+C_{APS}+C_{SDS}+C_{SBS})\ x\ 1000000}{W_{PS}} \quad (5)$$

where C_{elec} represents the expenses associated with the electricity consumption of the ultrasonic homogenizer. The power consumption in our system was measured and recorded by Unit UT 71E True RMS digital multimeter in Watts. Then, C_{elec} was calculated by converting the measured W to kWh for 1 hour of ultrasound assistance during the polymerization and multiplying with the tariffs in Turkey as retrieved from the Turkish Electricity Distribution Corporation. Other expenses include the prices of styrene ($C_{styrene}$), APS (C_{APS}), SDS (C_{SDS}), and SBS (C_{SBS}), which were calculated for their respective amounts in our polymerization reactions using their base prices retrieved from Sigma Aldrich. Simply, we used the price tags of 2.5 L reagent plus grade styrene, 2.5 kg ACS reagent grade APS, 2.5 kg ACS reagent grade SBS, and 100 g ACS reagent grade SDS from the official website of Sigma Aldrich/Merck (accessed on 1 January 2022) as the base prices, to determine the values of $C_{styrene}$, $C_{APS,}$ C_{SDS}, and C_{SBS}, which were calculated for the actual amounts introduced to our system. In order to introduce the effect of conversion to the cost calculations, the equation is divided by $W_{polystyrene}$, which is the total weight of the synthesized polystyrene after each experiment. Also, the equation is multiplied by 1000000 to reflect the cost per ton of synthesized PS. Following the necessary cost calculations, experimental intrinsic viscosity and molecular weight results were inputted to Design Expert (trial version), together with the as-calculated cost results to formulate mathematical models for the afore-mentioned response variables. The model estimations are listed in Table 3 and the validity regions of these models are given in Table 4. Simply, the developed models are only valid between these lower and higher levels of the factors in Table 4. The corresponding models that developed in this work are given below:

$$Intrinsic\ viscosity = +133.72 - 32.33A + 8.36B - 61.50C - 6.15D\ (codec\ equation) \quad (6)$$

$$Intrinsic\ viscosity = +292.01 - 4.24A + 32.88B - 82.02C - 12.30D \quad (7)$$

$$Mol.weight\ = +8.76e^5 - 2.17e^5A + 6.80e^4B - 5.28e^5C - 4.56e^4D\ (codec\ equation) \quad (8)$$

$$Mol.weight\ = +2.10e^6 - 28.54e^3A + 2.67e^5B - 7.03e^5C - 9.12e^4D \quad (9)$$

$$Cost\ = +4.28e^4 + 293.24A - 1.53e^3B - 2.03e^2C + 10.63e^4D\ (codec\ equation) \quad (10)$$

$$Cost\ = +3.64e^4 + 39.09A - 6.11e^3B - 2.71e^2C + 2.13e^4D \quad (11)$$

Table 4. The validity regions of the developed models.

Factors	**Levels**	
	–1	**+1**
Ultrasound calorimetric power (A) (W)	10.0	25.0
Monomer concentration (B) ([M])	0.5	1
APS concentration (C) (%)	0.5	2
SDS concentration (D) (%)	0	1

Considering the coefficients of the factors in the developed models and their respective higher and lower levels, we could conclude that while APS concentration is the most significant term for both intrinsic viscosity and molecular weight, SDS concentration is the most significant term for cost, which result is in good accordance with the experimental observations. Besides, comparison of the experimental results with the theoretical predictions in Table 3 indeed suggest that the developed models have high accuracy in estimating the actual results. In addition to this, analysis of variance (ANOVA) was also conducted as given in Table 5 to further verify the validity of the developed models.

The effectiveness of statistical models could be identified by the F values, p values, R^2 values and adequate precision, since F values correspond to the ratio of mean square of factors to error mean square, and should be as high as possible to signify greater dispersion, p-values represent the possibility of null hypothesis and should be less than 0.05, R^2 shows the variations between the predicted and actual data, and should be close to 1 in acceptable fittings, while adequate precision corresponds the signal to noise ratio, and should be higher than 4 in valid models.[66] Therefore, ANOVA results in Table 5 further confirms that all of the developed models are statistically significant as they all possess high F-values, low p-values, high adequate precision, and R^2, $R^2_{\ adj.}$ and $R^2_{pred.}$ values of close to 1. Besides, the $R^2_{\ adj.}$ and $R^2_{pred.}$ values are within 0.2 of each other.

Finally, we used multi objective optimization to prepare PS at various targeted molecular weights and also to

Table 5. Statistical indicators of the intrinsic viscosity, molecular weight and cost models.

Model	F-value	p-value	R^2	$R^2_{adj.}$	$R^2_{pred.}$	Adequate precision
η	378.68	< 0.0001	0.9928	0.9902	0.9791	74.14
M_v	252.75	< 0.0001	0.9892	0.9853	0.9652	58.68
Cost	138.57	< 0.0001	0.9805	0.9735	0.8726	57.97

Table 6. Multi objective optimization results.

Target M_v (g/mol)	Most feasible conditions to reach target M_v				Cost predictions at optimum conditions		Desirability
	A	B	C	D	Cost ($/ton PS)	Std Error	
250000±34800	20.12	0.52	2.00	0.06	34799.9	588.3	0.995
500000±22480	13.17	0.61	1.95	0.14	35759.3	379.9	0.971
750000±22500	12.69	0.60	1.62	0.15	35928.1	380.3	0.967
1000000±23600	12.11	0.61	1.28	0.19	36937.4	398.9	0.942
1250000±27510	12.09	0.59	0.92	0.22	37770.8	465.0	0.921

A: Ultrasound calorimetric power (W), B: Initial monomer concentration (mol/L), C: wt. % of APS, D: wt. % of SDS. Cost to prepare PS (Mv=108800) without ultrasound assistance is 100295.4 USD per ton of PS.

minimize the cost simultaneously. In fact, various ways might be used to reach a desired molecular weight in the final polymer such as by changing the initial monomer concentration, ultrasound power, initiator concentration, etc. considering the afore-mentioned effects of these individual factors. However, only one of these condition sets will become the most economical solution and the multi objective optimization was conducted to find this optimum point. The economically most feasible solutions with highest desirability values to reach polystyrene with target viscosity average molecular weights of 250000, 500000, 750000, 1000000 and 1250000 are given in Table 6 for illustration. The standard errors are lower than 35000 for molecular weight and 600 USD per ton of PS for cost in all of these optimization studies, increasing the reliability. In addition to these, the cost of preparing a ton of PS in the absence of ultrasound (based on sample PS-6) is also given as a dip note of Table 6 for better comparison. The results clearly show that ultrasound-assisted emulsion polymerization is economically more feasible comparing to conventional emulsion polymerization of styrene. Besides, the most feasible conditions are differing depending on the target molecular weight, and manufacturers should keep this into account in designing their processes to reach higher profits.

4. Conclusions

The present work involves preparation of polystyrene via ultrasound assisted emulsion polymerization of styrene. We first studied the effects of ultrasound power, initial monomer concentration, initiator concentration and surfactant concentration on the monomer conversion, intrinsic viscosity and viscosity average molecular weight. The viscosity average molecular weights were determined through intrinsic viscosity measurements and calculation of Mark-Houwink constants using GPC results. Briefly, we found that increasing the amount of initial monomer and initiator concentrations increase the polymerization rate and monomer conversion. However, SDS amount is found to be having only a slight effect on the monomer conversion. In addition to this, the results also suggest that while application of ultrasound increases the polymerization rate and monomer conversion at first, upon increasing the ultrasound calorimetric power above 11.1 W, its effect starts to vanish, and instead, higher ultrasound powers tended to provide lower conversions due possibly to the breakdown of longer polymer chains under extreme acoustic cavitation. Regarding molecular weight, we report a strong negative correlation between molecular weights of polymers and the amount of initiator and ultrasound power. On the other hand, initial monomer concentration and SDS amount have only a slight influence on the viscosity average molecular weight. Finally, we opted a statistical approach to comment on the economic feasibility of the ultrasound assistance. For this purpose, we developed theoretical models for intrinsic viscosity, molecular weight and overall expenses during the synthesis of polystyrene. Then, the most economical solutions were found to reach a polystyrene with various target molecular weights through multi objective optimization. The results show that ultrasound-assisted emulsion polymerization is much more economical comparing to conventional emulsion polymerization, and the economically most feasible reaction conditions could vary based on the targeted molecular weight. We believe that our methodology can be used to control the molecular weight of polymers obtained from styrene-like monomers in the future.

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5. References

1. W. D. Harkins, *J Am Chem Soc*, **1947**, *69*, 1428–1444. **DOI:**10.1021/ja01198a053
2. H. Y. Erbil, Vinyl acetate emulsion polymerization and copolymerization with acrylic monomers, CRC Press, Boca Raton, **2000. DOI:**10.1201/9781420038804
3. W. V. Smith, R. H. Ewart, *J Chem Phys*, **1948**, *16*, 592–599. **DOI:**10.1063/1.1746951
4. T. Arfin, F. Mohammad, N. A. Yusof, in: C. Lynwood (Ed.): Polystyrene: synthesis, characteristics and applications, Applications of polystyrene and its role as a base in industrial chemistry, Nova Publishers, New York, **2014**, pp. 269–280.
5. W. V. Smith, *J Am Chem Soc*, **1948**, *70*, 3695–3702. **DOI:**10.1021/ja01191a045
6. W. V. Smith, *J Am Chem Soc*, **1949**, *71*, 4077–4082. **DOI:**10.1021/ja01180a058
7. M. Harada, M. Nomura, H. Kojima, W. Eguchi, S. Nagata, *J Appl Polym Sci*, **1972,** *16*, 811–833. **DOI:**10.1002/app.1972.070160402
8. M. Nomura, M. Harada, W. Eguchi, S. Nagata, *J Appl Polym Sci*, **1972,** *16*, 835–847. **DOI:**10.1002/app.1972.070160403
9. L. V. de la Rosa, E. D. Sudol, M. S. El-Aasser, A. Klein, *J Polym Sci Part A Polym Chem*, **1996**, *34*, 461–473. **DOI:**10.1002/(SICI)1099-0518(199602)34:3<461::AID-POLA15>3.0.CO;2-N
10. X. Wang, E. D. Sudol, M. S. El-Aasser, *J Polym Sci Part A Polym Chem*, **2001**, *39*,3093–3105. **DOI:**10.1002/pola.1290
11. X. Wang, E. D. Sudol, M. S. El-Aasser, *Langmuir*, **2001**, *17*, 6865–6870. **DOI:**10.1021/la010641n
12. S. Y. Lin, C. S. Chern, T. J. Hsu, C. T. Hsu, I. Capek, *Polymer*, **2001**, *42*, 1481–1491. **DOI:**10.1016/S0032-3861(00)00526-7
13. M. F. Kemmere, J. Meuldijk, A. A. H. Drinkenburg, A. L. German, *J Appl Polym Sci*, **2001**, *79*, 944–957. **DOI:**10.1002/1097-4628(20010131)79:5<944::AID-APP180>3.0.CO;2-5
14. C. S. Chern, *Prog Polym Sci*, **2006**, *31*, 443–486. **DOI:**10.1016/j.progpolymsci.2006.02.001
15. S. Feiz, A. H. Navarchian, *Chem Eng Sci*, **2012**, *69*, 431–439. **DOI:**10.1016/j.ces.2011.10.063
16. T. Sirirat, T. Vatanatham, N. Hansupalak, G. L. Rempel, W. Arayapranee, *J Polym Res*, **2015**, *22*,16. **DOI:**10.1007/s10965-014-0643-9
17. E. S. Schultz, N. Sheibat-Othman, A. Mitsos, A. Mhamdi, *Ind Eng Chem Res*, **2020**, *59*, 16368–16379. **DOI:**10.1021/acs.iecr.0c02771
18. C. S. Chern, Principles and applications of emulsion polymerization, John Wiley & Sons, New Jersey, **2008**. **DOI:**10.1002/9780470377949
19. A. Salazar, L. M. Gugliotta, J. R. Vega, G. R. Meira, *Ind Eng Chem Res*, **1998**, *37*, 3582–3591. **DOI:**10.1021/ie980009y
20. A. Echevarria, J. R. Leiza, J. C. De La Cal, J. M. Asua, *AIChE J*, **1998**, *44*,1667–1679. **DOI:**10.1002/aic.690440718
21. Z. F. M Said, *Die Makromol Chemie*, **1991**, *192*, 405–414. **DOI:**10.1002/macp.1991.021920220
22. C. M. Miller, P. A. Clay, R. G. Gilbert, M. S. El-Aasser, *J Polym Sci Part A Polym Chem*,1997, *35*, 989–1006. **DOI:**10.1002/(SICI)1099-0518(19970430)35:6<989::AID-POLA2>3.0.CO;2-C
23. L. M. Gugliotta, A: Salazar, J. R. Vega, G. R. Meira, *Polymer*, **2001**, *42*, 2719–2726. **DOI:**10.1016/S0032-3861(00)00730-8
24. M. Vicente, S. Benamor, L. M. Gugliotta, J. R. Leiza, J. M. Asua, *Ind Eng Chem Res*, **2001**, *40*, 218–227. **DOI:**10.1021/ie000387e
25. J. Herrera-Ordonez, O. Rivera, H. Maldonado-Textle, J. C. Ramirez, *J Polym Sci Part A Polym Chem*, **2005**, *43*, 1963–1972. **DOI:**10.1002/pola.20661
26. Y. Kim, K. Kim, B. H. Lee, S. Choe, *Macromol Res*, **2012**, *20*, 977–984. **DOI:**10.1007/s13233-012-0144-9
27. K. Yan, X. Gao, Y Luo, *Macromol Rapid Commun*, **2015**, *36*, 1277–1282. **DOI:**10.1002/marc.201500052
28. V. M. B. Patrocinio, T. Agner, G. V. S Dutra, F. Machado, B. A. D. Neto, P. H. H. Araújo, C. Sayer, *Macromol React Eng*, **2019**, *13*:1800061. **DOI:**10.1002/mren.201800061
29. B. A. Bhanvase, D. V. Pinjari, S. H. Sonawane, P. R. Gogate, A. B. Pandit, *Ultrason Sonochem*, **2012**, *19*, 97–103. **DOI:**10.1016/j.ultsonch.2011.05.016
30. B. A. Bhanvase, S. H. Sonawane, D. V. Pinjari, P. R. Gogate, A. B. Pandit, *Chem Eng Process Process Intensif,* **2014**, *85*, 168–177. **DOI:**10.1016/j.cep.2014.08.014
31. B. M. Teo, S. W. Prescott, M. Ashokkumar, F. Grieser, *Ultrason Sonochem*, **2008**, *15*, 89–94. **DOI:**10.1016/j.ultsonch.2007.01.009
32. L. A. Crum, T. J. Mason, J. L. Reisse, K. S. Suslick, Sonochemistry and sonoluminescence Springer Science & Business Media, Washington, **1998.**
33. Y. Liao, Q Wang, H. Xia, X. Xu, S. M. Baxter, R. V. Slone, S. Wu, G Swift, D. G. Westmoreland, *J Polym Sci Part A Polym Chem*, **2001**, *39*, 3356–3364. **DOI:**10.1002/pola.1318
34. V. L. Gole, P. R. Gogate, *Chem Eng Process Process Intensif*, **2012**, *53*, 1–9. **DOI:**10.1016/j.cep.2011.12.008
35. D. Nagatomo, T. Horie, C. Hongo, N. Ohmura, *Ultrason Sonochem*, **2016**, *31*, 337–341. **DOI:**10.1016/j.ultsonch.2016.01.010
36. I. Korkut, M. Bayramoglu, *Ultrason Sonochem*, **2014**, *21*, 1592–1599. **DOI:**10.1016/j.ultsonch.2013.12.028
37. T. G. Leighton, *Prog Biophys Mol Biol*, **2007**, *93*, 3–83. **DOI:**10.1016/j.pbiomolbio.2006.07.026
38. H. M. Cheung, K. Gaddam, *J Appl Polym Sci*, **2000**, *76*, 101–104.

DOI:10.1002/(SICI)1097-4628(20000404)76:1<101::AID-APP13>3.0.CO;2-F

39. S. K. Ooi, S. Biggs, *Ultrason Sonochem*, **2000**, *7*, 125–133. **DOI:**10.1016/S1350-4177(99)00040-1
40. Y. Kojima, S. Koda, H. Nomura, *Ultrason Sonochem*, **2001**, *8*, 75–79. **DOI:**10.1016/S1350-4177(00)00064-X
41. J. Zhang, Y. Cao, Y. He, *J Appl Polym Sci*, **2004**, *94*, 763–768. **DOI:**10.1002/app.20948
42. D. Kobayashi, H. Matsumoto, C. Kuroda, *Chem Eng J*, **2008**, *135*, 43–48. **DOI:**10.1016/j.cej.2007.05.015
43. G. Qiu, M. Nie, Q. Wang, *Ultrason Sonochem*, **2008**, *15*, 269–273. **DOI:**10.1016/j.ultsonch.2007.12.003
44. T. J. Mason, D. Peters D, Practical sonochemistry: Power ultrasound uses and applications. Woodhead Publishing, Cambridge, 2002.
45. G. J. Price, A. A. Clifton, *Polymer*, **1996**, *37*, 3971–3973. **DOI:**10.1016/0032-3861(96)00197-8
46. I. M. Borisov, R. S. Luksha, S. T. Rashidova, *Russ Chem Bull,* **2015,** *64,*2512–2513. **DOI:**10.1007/s11172-015-1185-y
47. J. P. Marcolongo, M. Miranda, *J Chem Educ*, **2011**, *88*, 629–633. **DOI:**10.1021/ed900019u
48. M. L. Huggins, *J Am Chem Soc*, **1942**, *64*, 2716–2718. **DOI:**10.1021/ja01263a056
49. P. A. Lovell, F. J. Schork, *Biomacromolecules*, **2020**, *21*, 4396–4441. **DOI:**10.1021/acs.biomac.0c00769
50. J. M. Asua, *Prog Polym Sci*, **2002**, *27*,1283–1346. **DOI:**10.1016/S0079-6700(02)00010-2
51. H. F. Scott, Elements of chemical reaction engineering. Prentice Hall International Series in the Physical and Chemical Engineering Sciences, New Jersey, **2016.**
52. B. Carnahan, H. A. Luther, J. O. Wilkes, Applied Numerical Methods. John Wiley & Sons, New York, **1969.**
53. C. D. Immanuel, F. J. Doyle III, C. F. Cordeiro, S. S. Sundaram, *AIChE J*, **2003**, *49*, 1392–1404. **DOI:**10.1002/aic.690490606
54. N. Vogel, S. Goerres, K. Landfester, C. K. Weiss, *Macromol Chem Phys*, **2011**, *212*, 1719–1734. **DOI:**10.1002/macp.201100187
55. S. Ozbay, H. Y. Erbil, *Colloids Surfaces A Physicochem Eng Asp*, **2014**, *452*, 9–17. **DOI:**10.1016/j.colsurfa.2014.03.054
56. S. Ozbay, H. Y. Erbil, *Colloids Surfaces A Physicochem Eng Asp*, **2015**, *481*, 537–546. **DOI:**10.1016/j.colsurfa.2015.05.049
57. J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. R. Bloch, Polymer Handbook. John Wiley and Sons, New York, **1999.**
58. R. Claudy, J. M. Létoffé, Y. Camberlain, J. P Pascault, *Polym Bull*, **1983***, 9*, 208–215. **DOI:**10.1007/BF00283709
59. L. Singh, P. J. Ludovice, C. L. Henderson, *Thin Solid Films*, **2003**, *449,* 231–241. **DOI:**10.1016/S0040-6090(03)01353-1
60. L. P. Blanchard, J. Hesse, S. L. Malhatro, *Can J Chem,* **1974***, 52,* 3170–3175. **DOI:***10.1139/v74-465*
61. Y. Li, M. Li, Z. Li, L. Yang, X. Liu, *Chemosphere,* **2019**, *231,* 308–314. **DOI:**10.1016/j.chemosphere.2019.05.116
62. B. Akgul, F. Erden, S. Ozbay, *Powder Technology*, **2021**, *391*, 11–19. **DOI:**10.1016/j.powtec.2021.06.007
63. G. E. P. Box, K. B. Wilson, *J R Stat Soc Series B Stat Methodol*, **1951**, *13*, 1–45.
64. M. H. Esfe, H. Hajmohammad, R. Moradi, A. A. A Arani, *Appl Therm Eng*, **2017**, *112*, 1648–1657. **DOI:**10.1016/j.applthermaleng.2016.10.129
65. M. H. Esfe, S. Esfandeh, M. Rejvani, *J Therm Anal Calorim*, **2018**, *131*, 1437–1447. **DOI:**10.1007/s10973-017-6680-y
66. M. Kul, F. Erden, K. O. Oskay, O. Karasungur, M. Simsir, L. C. Kumruoglu, I. Karakaya, *J Sustain Metall,* **2021**, *7*, 1224–1240. **DOI:**10.1007/s40831-021-00406-7

Povzetek

Raziskava se osredotoča na določitev ekonomsko najbolj optimalnih pogojev za pridobitev polistirena z različnimi ciljnimi molekulskimi masami z ultrazvočno podprto emulzijsko polimerizacijo. Šaržne polimerizacije stirena z ultrazvočno podprtim postopkom emulzijske polimerizacije so bile izvedene pri različnih sestavah reakcijskih komponent. Hitrost polimerizacije je bila izračunana na osnovi pretvorbe monomera pri različnih reakcijskih časih. Molekulske mase sintetiziranih polimerov in Mark-Houwinkove konstante so bile določene z meritvami intrinzične viskoznosti in gelske izključitvene kromatografije. Ugotovljeno je bilo, da je indeks polidisperznosti polimerov v razponu od 1,2 do 1,5, povprečne molekulske mase viskoznosti pa so med 100. 000–1.500.000 g/mol, odvisno od reakcijskih pogojev. Na koncu so bile razvite tudi modelne enačbe za določitev glavnih spremenljivk, najbolj ekonomični načini za doseganje različnih ciljnih molekulskih mas pa so bili razloženi z metodologijo odzivne površine, ki temelji na optimizaciji več ciljev.