Polystyrene Latex Synthesized in Presence of Ultrasonic Initiation

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ABSTRACT: The low water solubility of styrene (St) monomer increase the need for a good initiator system to speed up the emulsion polymerization and remove unreacted monomers. Polymerization of styrene monomer in water was performed at 30, 50, and 70°C under ultrasonic irradiation using sodium dodecyl sulfate as surfactant and ammonium persulfate as initiator. Ultrasonic energy was used as a tool to speed up the polymerization. Combining ultrasonic and ammonium persulfate led to a higher conversion and higher rate of polymerization. Ultrasonic energy has an effect on the particle size distribution. The particle size distribution increases with an increase in the monomer conversion of styrene for ultrasonic polymerization, whereas the particle size distribution did not change with an increase in the monomer conversion compared with the conventional thermal polymerization results. Higher molecular weights were obtained under ultrasonic irradiation. FE-SEM and TEM pictures show different morphology with changing temperature polymerization. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2535–2542, 2011

Key words: styrene monomer; emulsion polymerization; ultrasonic irradiation; particle size distribution; morphology; removing unreacted monomers

INTRODUCTION

Emulsion polymers derived from styrene (St) monomers are commercially important class of emulsion polymers. Emulsion polymerization is the most important method to polymerize styrene monomers. The emulsion polymerization of styrene monomer has been studied intensively by many researchers.[1–3] High purity nanolatex with 95% conversion of styrene was achieved. $C_{12}N^+$ play a role as emulsifier, initiator, and a comonomer at the same time.[4] Monodisperse and stable polystyrene pure micro latex was prepared by gamma rays and ionic polymerizable surfactant (methacryloxyethyl dodecyldimethyl ammonium bromide, $C_{12}N^+$). This surfactant cause polystyrene microlatexes to develop surface-active groups and electrostatic stabilization.[5] Functionalized polystyrene latices were prepared by miniemulsion polymerization using a Y-type polymerizable surfactant bearing carboxylic acid groups as stabilizers. The prepared polystyrene had more narrow particle size distribution compared with by potassium persulfate.[6]

Ultrasonic energy was first used for vinyl monomers polymerization in early 1950s.[7] Most studies since that time have been concerned with homopolymerization of either a pure monomer melt or a monomer in a good solvent, particularly water.[8,9] For majority of cases ultrasonic energy study is used as a dispersant to prepare a homogeneous emulsion, which is initiated in presence of chemical initiator to produce free radicals either by heating or by UV radiation.[10] The ultrasonic energy has been approved to initiate and accelerate emulsion polymerizations. The ultrasonic energy effect is believed to be due to localized heating of the reaction medium due to the cavitations process. The cavitations process results in the adiabatic collapse of a bubble in solution, which results in temperatures of greater than 5000 K inside the bubble and at least 1250 K in the region immediately surrounding it.[11] Therefore, it is possible that any polymerization reactions occurring in the vicinity of a collapsing cavity will be greatly accelerated and will contribute to the overall rate increase.

Ultrasonic emulsion polymerization can produced higher conversion, higher molecular weight and faster polymerization as compared with ultrasonic bulk or solution polymerization. Also due to the high intense dispersion and emulsifying effect of ultrasonic waves, nanoscale latex particles can be produced. This technique provides an alternative route to produce polymertic nanoparticles beside miniemulsion and microemulsion.

St can be polymerized by different initiators. The water-soluble ionic initiators usually used for the emulsion polymerization of St are ammonium, sodium and potassium persulfate, and water-insoluble nonionic initiator, such as benzoyl peroxide, have also been used for nonemulsion polymerization.

The aim of this work is to present the effect of combination of ultrasonic and ammonium persulfate as an initiation system at different temperatures on St monomer conversion and rate of polymer production. Also to study the effect of ultrasonic energy on the particle size distribution, molecular weight and morphology properties of the prepared stable emulsion lattices of homopolymer styrene.

EXPERIMENTAL

Materials

Styrene (Aldrich, Milwaukee, WI) was purified by washing three times with 10% sodium bicarbonate (Aldrich) followed by three times with distilled water to remove the hydroquinone inhibitor, drying with anhydrous sodium sulfate (Aldrich) and the material was then refrigerated at 5°C until use. Sodium dodecyl sulfate (SDS) (Aldrich) was used as surfactant. Ammonium persulfate (Aldrich) was used as initiator. Methanol (Aldrich) was used to precipitate the polymer.

Apparatus

The Sonics and Materials 20 kHz Model VC-1500 ultrasonic generator (Newton, CT) with standard titanium horn for use with a capacity up to 15 L of liquid was connected to an air-cooled transducer. The oscillator power was ranged on scale of 0–100% and the acoustic energy corresponding to oscillator power was measured[12] calorimetrically by sonication of a known amount of water in a Dewar flask, recording the temperature change versus time, and calculating the total energy released. In this work, the power of acoustic energy intensity was set at 50 W (corresponding to 10 W/cm^2). The instrument used in this work has only one frequency i.e., 20 kHz. The average diameter of polymer particles was measured by Mastersizer 2000 model analyzer (Malvern Instruments Ltd., Malvern, UK) with Hydro 2000S accessory. The molar mass (M_n) and the polydispersity of the prepared polymers were performed by using WATERS 2000 (Milford, MA) heated GPC system operating at 50°C. Separation occurs on two PL Gel Mixed Bed B (7.5 × 300 mm^2) columns having (7.5 × 50 mm^2) guard column with toluene flowing at 1.0 mL/min. Detection is by differential refractive index detector stabilized at 50°C using toluene as reference. Calibration is performed using narrow MWD PS standards over the range 580–7,500,00 Daltons as Mp (peak maximum) and calibration curve fit is third order polynomial using a total of 22 individual PS standards. Images of PS particles were taken by FE-SEM (model NNL-200, Philips, 1 nm resolution) and TEM (model 2100 FEM, Jeol, 200 kv, 0.23 nm resolution).

Polymerization procedure

Different polymerization conditions were studied using ultrasonic and ammonium persulfate initiation. The emulsion polymerizations were performed in a 500-mL three neck round bottom flask for the conventional polymerization and in a 400 mL beaker for the ultrasonic polymerization. The ingredients for the polymerization are 60 g of styrene monomer, 0.5 g of surfactant, 0.3 g of initiator, and 90 g of water. Mechanical stirring was used for conventional polymerization at 500 rpm and there was no additional mechanical stirring for ultrasonic polymerizations. The tip of the horn was placed into the emulsion at 1.0 cm from the bottom of the beaker. Ar gas bubbling was introduced through the glass frit at 10 mL/min. into the mixture during the polymerization. The output of ultrasonic energy was fixed at 50% (corresponding to an acoustic intensity of 10 W cm^{-2}) for all experiments. The top of the beaker was covered with aluminum foil around the horn and ice bath was used to control temperature (final ultrasonic temperature was 10°C more than targeted temperature). The final percent of conversion was obtained by gravimetric analysis.

RESULTS AND DISCUSSION

Ultrasonic energy, combined with thermal initiator, was used to initiate emulsion polymerization of styrene homopolymer at different temperature 30, 50, and 70°C. The low water solubility of St monomer (0.032 g monomer/100 g H$_2$O) requires a good initiator system to speed up the polymerization and remove unreacted monomer. In general, the polymerization was faster and resulted in higher conversion as compared with conventional polymerization initiator as shown in Figure 1.

The percent conversion versus sonication time curves shown in Figure 1 were similar in shape to those shown by Stoffer[12] in study of ultrasonically initiated emulsion polymerization of Methylmethacrylate. The reverse s curves were observed due to gel effect. The gel effect is more noticed at higher temperature and this may be due to the suppression of the termination reaction as the viscosity in the polymerization locus increases with increasing conversion.
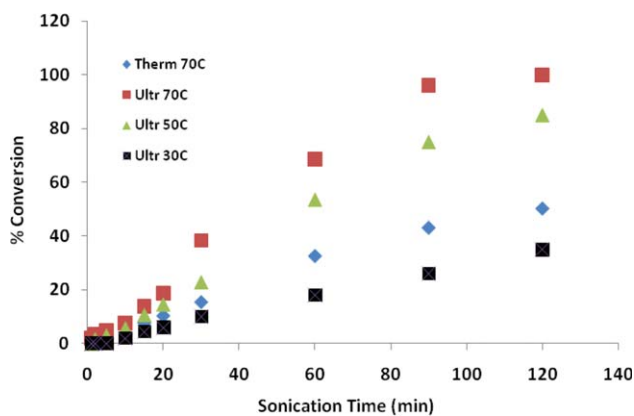
Figure 1 Percent conversion of ultrasonic verses conventional thermal polymerization. (Ultrasonic final temperature is 10°C higher than ambient initial temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The high rate of styrene polymerization may be due to the degassing effect of ultrasonic cavitations, which causes the efficient depletion of oxygen from the reaction medium and thus causes a lowering of the possibility for transfer reactions. This will lead to an induction period or dead time experienced before the polymerization begins, and a higher overall particle number and therefore polymerization rate.

Effects of ultrasonic energy include more rapid formation of emulsions and initiation, control over particle size and polymer molecular weight. Moreover, the dispersion could be formed and maintained during the polymerization by using ultrasonic energy. Also, production of free radicals in the aqueous phase could be used as a method of initiation. Also, since the polymer is in a dispersed phase, the viscosity does not increase to the same extent as in bulk polymerization so that the suppression of cavitations will not be as much of a problem.

Combination of ultrasonic energy and a redox initiation of vinyl acetate emulsion polymerization at 25°C was studied. Higher conversion and higher rate of polymer production were observed.[13]

In previous work,[14,15] inert gas was an important factor to let ultrasonic polymerization to proceed. Inert gas may function as nuclei sites (weak spots) present in the liquid for bubble collapse to occur for larger sonochemical effects. Present of any dissolved oxygen in emulsion polymerization system may act as a powerful inhibitor for the polymerization reaction. This may lead to long induction periods and slow polymerization rate. It was reported[16] that initiation of styrene polymerization occurs primarily only when there is sufficient gas present to form a field of bubbles undergoing stable cavitation. In the absence of the gas, transient cavitation occurs, resulting in depolymerization and formation of colored compounds similar to a pyrolysis product. The com-

bination of ultrasonic energy and initiator can give low residual monomer[14] which is of prime concern for many latex producers.

The rate of polymerization can be determined from the slope of the first linear part of the curve of the conversion percentage versus the time (min) as shown in Figure 2, which occurs between 2 and 20% for St polymerization. Higher slope will imply higher rate of polymerization. It is clearly evident from Figure 2 that ultrasonic polymerization at 70°C and 50°C has higher slope, 0.863 min^{-1} and 0.745 min^{-1} respectively, than conventional thermal polymerization, 0.483 min^{-1}. This period may represent interval II in the curve of the emulsion polymerization rate versus time.[17] It has been proved[12] that ultrasonic energy can offer interesting energy savings in polymerization since it enhances the rate of polymerization substantially at ambient temperatures. Emulsion polymerization of Methyl Methacrylate[12] was carried out at −10°C as starting polymerization temperature and at ambient temperature as final polymerization temperature using only sodium lauryl sulfate as surfactant. Combining ultrasonic energy and initiator always leads to a faster rate of polymerization and higher conversion in comparison with just using initiator.

Effect of ultrasonic energy on the particle size distribution

There are three types of physically distinct emulsion polymerizations. These are conventional emulsion (macroemulsion) system, miniemulsion system and microemulsion system. The differences between them are in monomer droplet size and droplet size distribution prior to polymerization. The conventional emulsion has monomer droplet size of 0.3–10 μm and the polymerization occurs in monomer-swollen micelle or homogenous nucleation. The final particle size of polymers is between 100 and 600 nm.
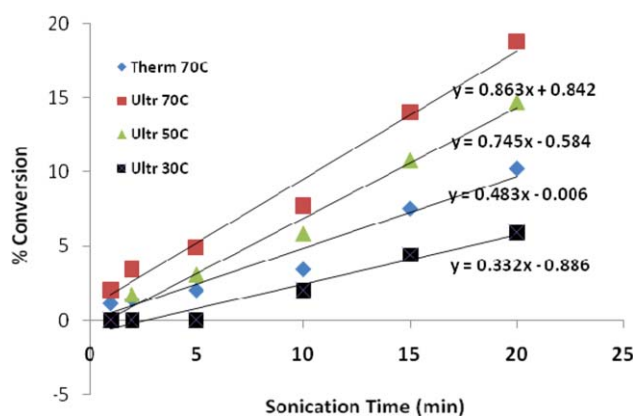

Figure 2 The slop of first part of percent conversion verses time curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The miniemulsion lay in between macro- and micro-emulsions in term of droplet size and emulsion stability. Miniemulsion has monomer droplet size (0.05–0.3 μm) and are often generated using a high-shear device, such as a sonicator. The final particle size of polymers is between 60 and 200 nm. Microemulsion is a transparent solutions and has monomer droplet size less than 100 nm. Microemulsion is a thermodynamically stable emulsion system as compared with other two emulsion systems. The final particle size of polymers is between 20 and 60 nm. In the case of miniemulsion and microemulsion systems, the polymerization occurs inside monomer droplet although it is believed that small fraction of these monomer droplets are initiated.

Biggs and Grieser[18] found that under ultrasonically initiated polymerization using 19 mm diameter 20 kHz horn sonifier, styrene monomer-swollen micelles were the main locus of polymerization at 25°C where only sodium dodecyl sulfate was used as a surfactant. Micelles of surfactant act as traps for oligomeric radicals formed in continuous phase. When one of these radicals penetrates a micelle, it causes rapid polymerization of monomer exist inside the micelle. Polymer chains get larger with further transfer of monomer from monomer droplets to micelles a cross the continuous phase. The polymer chain growth can be ended by two ways. Either a second radical enters the micelle leading to bimolecular termination, or all monomers must be depleted from the reaction system.

A batch process was used in this work to study the particle size and its distribution. This process involves an initial charge of deionized water, monomer, surfactant, and initiator into the reaction container. This is important because with batch processes, monoparticle size distribution or narrower molar mass distribution is expected.[19] But under the dispersion by the ultrasonic energy broader particle size distributions occur. It was reported[15] that bi or multidistribution particle size was obtained from ultrasonic batch emulsion polymerization of methyl methacrylate at 25 and 70°C as compared with monodistribution for thermal polymerization at 70°C using sodium dodecyl sulfate as surfactant and ammonium persulfate as initiator. Broad particle size distribution of styrene miniemulsion polymerization was reported[20] at 125°C using cetyl alcohol as cosurfactant and sodium laryl sulfate as surfactant. The main reason for this broadening is the particle coagulation.

It was reported[21] that increasing the power intensity of ultrasonic polymerization of styrene using sodium dodecyl sulfate as surfactant has only effect on conversion rate but has almost no effect on particle size. In this work the effect of ultrasonic energy on particle size distribution was studied at an acoustic
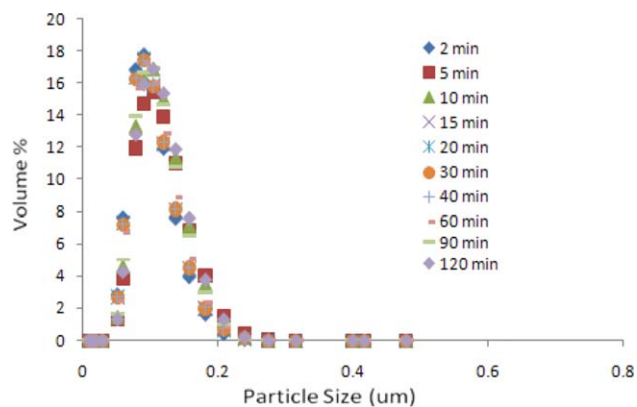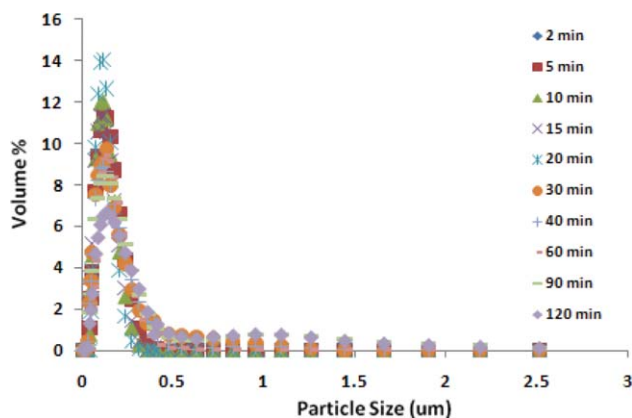

Figure 3 Particle size distribution of thermal polymerization at 70°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intensity of 10 W cm^{-2} and the frequency of 20 kHz as the instrument only work at one frequency.

Most of problems with paint dispersions, such as low gloss, low film buildup, and low pigment loading, come from the paint stability, particle size, and film-formation process of polymer dispersions. A broad particle size distribution is often advantageous because the packing factor is strongly affected by the particle size distribution.

In this work, the particle size distribution increases with an increase in the monomer conversion of styrene for ultrasonic polymerization at 70°C, whereas a monomodel particle size distribution of conventional polymerization with an almost constant average particle size of $d_{0.5} = 98$ nm, as shown in Figure 3. This suggests that the polymerization takes place almost only in the micelle, with a constant diffusion from the monomer droplet to the monomer-swollen micelle. Induction period experienced before polymerization begins, 2 min, occur for ultrasonic polymerization at 70°C and 50°C, where this dead time is extended to 5 min for ultrasonic polymerization at 30°C. This is probably due to the efficient depletion of oxygen from the reaction medium by ultrasonic dispersion energy and thus causes a lowering of the possibility for transfer reactions. The ultrasonic polymerization of St at 70°C shows a broader size distribution and average particle size gets larger with increase in monomer conversion. It increases from 122 nm at 5 min to 260 nm at 120 min. Also it increase from 115 nm at 5 min to 195 nm at 120 min for ultrasonic polymerization at 50°C and from 109 nm at 10 min to 166 nm at 120 min for ultrasonic polymerization at 30°C as shown in Figure 4-6.

This broadening occurs even in the absence of cosurfactant like in miniemulsion case. This increase gives additional confirmation of high rate of particle formation. This may also suggest that additional places for polymerization to occur such as monomer droplet which causes this particle size broadening.
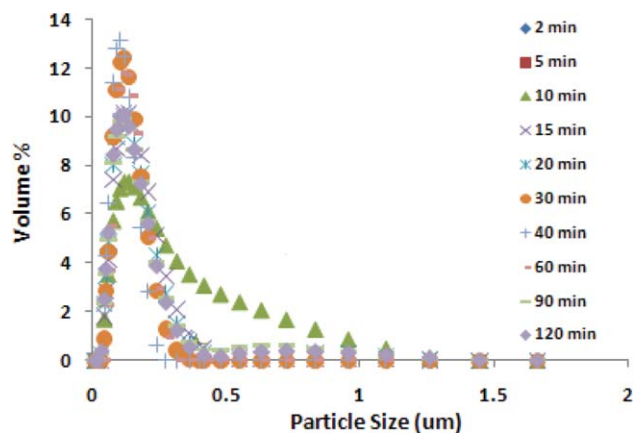
Figure 4 Particle size distribution of ultrasonic polymerization at 70°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Under the ultrasonic dispersion the size of monomer droplets get smaller and compete in number and surface areas with the micelle, which then gives additional place for the emulsion polymerization to occur. The overall reaction process involved in the preparation of polystyrene latex as suggested by Bradley and Grieser[22] is depicted in Figure 7. They suggested that the latex particles are formed during ultrasonic initiation through the generation of monomeric radical species in an emulsion. The foremost primary radical species present on the collapse of the microbubble in an aqueous solution are most likely ·OH and ·H radicals. These primary radicals may react with the monomer molecules adsorbed at the cavitation bubble/solution interface and generate monomeric radicals, which may then diffuse into a monomer droplet and initiate the polymerization reaction. Another path way is the generated monomeric radicals may enter the micelle and form the polymer particles. They conducted the polymerization at 30°C using only a cationic surfactant, dode-
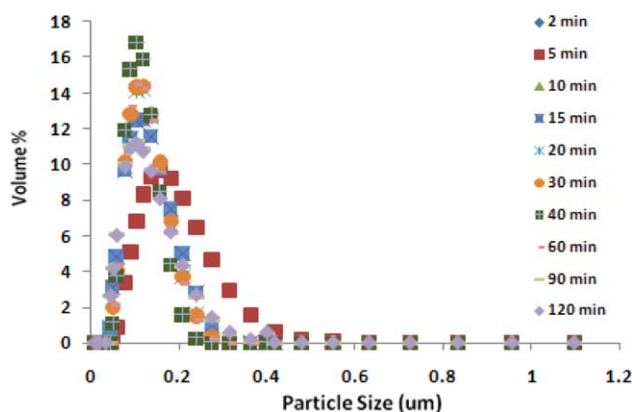
Figure 5 Particle size distribution of ultrasonic polymerization at 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Particle size distribution of ultrasonic polymerization at 30°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cyltrimethylammonium chloride, and metylmethacrylate and butylacrylate as monomers.[22]

This may give an explanation for polystyrene particle size broadening. These results suggest that this system is similar to conventional miniemulsion polymerization process.

It was suggested that small latex diameter in the final samples meant little coagulation during the polymerization process, which would lead to a larger final particle size. The lack of coagulation may be explained by the formation of a surface charge on the primary particles, which confers on them electrostatic stabilization. The driving force for particle size coagulation is their instability in comparison with larger particles. Once the particles reach a large size with high colloidal stability, there is no longer a driving force for coagulation, and further growth occurs only by the polymerization.[18]

Source of free radical in ultrasonic versus conventional polymerization and its effect on molecular weight distribution

The use of ultrasonic energy in initiating an emulsion polymerization will produce a high concentration of free radicals as a result of high local temperature and pressure produced when the bubble collapses. The source of free radicals not only comes from the initiator, but also may come from the aqueous phase, the monomers[22] and the surfactant.[12] It has been reported[12] that free radicals may come from Sodium lauryl sulfate surfactant by using radical trapping experiment. This experiment involved ultrasonically irradiating a radical scavenger, bromoform, with water and sodium lauryl sulfate at an acoustic intensity of 13.0 Wcm^{-2} under an argon gas flow rate of 0.74 mL/s over 30 min of sonication followed by GC/MS analysis which indentified the existence of 1-bromododecane. This confirms the source of radicals as
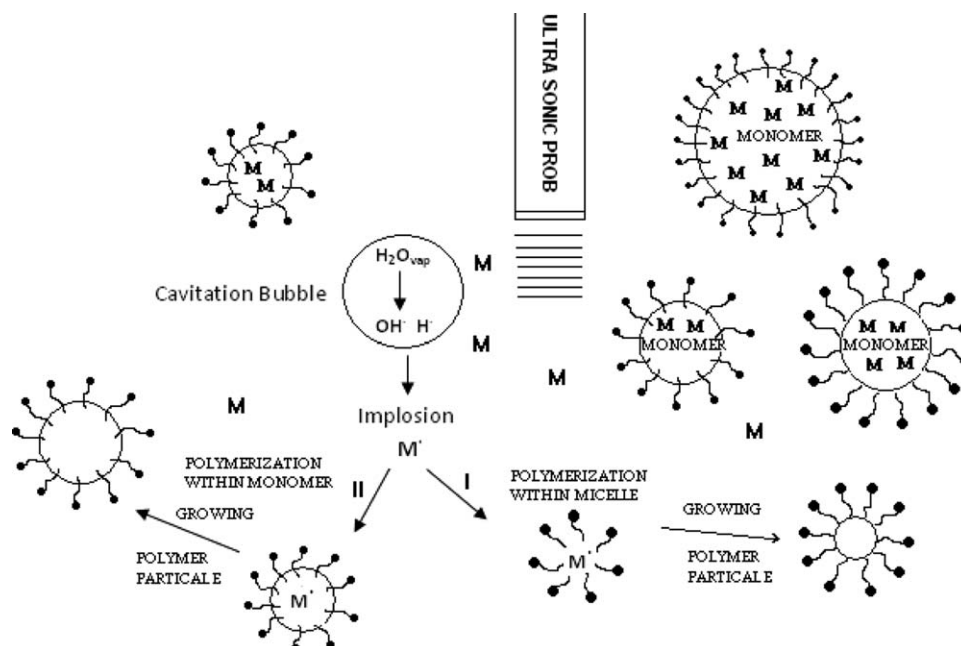
Figure 7 Schematic diagram of proposed ultrasonic polymerization of styrene monomer. (The scheme does not represent the true sizes of the system (horn, monomer, micelle, polymer particles, etc.) shown in the diagram).

coming from the surfactant molecule and that sonication degrades the surfactant into $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and OSO_3Na radicals, all of which could initiate the polymerization. In this work, higher conversion and rate for ultrasonic polymerization were observed as compared with conventional polymerization as shown in Figure 1. Ultrasonic polymerization was conducted in the absence of the initiator at 70°C. The percentage of conversion was 10% for styrene polymerization after 60 min of ultrasonic irradiation. This provides evidence that the free radicals not only come from initiator but also may come from the aqueous phase, the monomers and the surfactant.

Price[23] reported that any polymerization process in solution is subject to sonication, the degradation will always occur concurrently with chain growth. Also Price has experimentally shown that ultrasonic irradiation is more effective in more suitable solvents. The more extended the polymer the smaller was the final number average molecular weight. In this work, the number average molecular weight of ultrasonic polymerization increased in the beginning

then degradation may occur concurrently with chain growth. M_n was 90,124 with a molecular weight distribution of 3.3 at 5 min, and fell to 86,799 with a molecular weight distribution of 3.2 at 120 min of ultrasonic polymerization at 70°C, M_n was 68,563 with a molecular weight distribution of 3.5 at 5 min, and fell to 62,854 with a molecular weight distribution of 3.7 at 120 min of ultrasonic polymerization at 50°C and M_n was 117,526 with a molecular weight distribution of 3.1 at 5 min, and fell to 93,073 with a molecular weight distribution of 3.8 at 120 min of ultrasonic polymerization at 30°C. Whereas M_n was 56,533 with a molecular weight distribution of 3.9 at 5 min, and increased to 70,475 with a molecular weight distribution of 3.1 at 120 min of conventional thermal polymerization at 70°C as shown in Table I and Figure 8. This may be due to the high concentration of free radicals produced by ultrasonic energy as the polymerization time proceeded. The degradation process occurs in parallel with the ultrasonic polymerization once long chains are formed. It was reported[12] that the average molecular weight of

TABLE I
Average Molecular Weights of Polystyrene

Time min	Thermal 70°C			Ultrasonic 70°C			Ultrasonic 50°C			Ultrasonic 30°C		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
5	56,533	220,479	3.9	90,124	297409	3.3	68,563	239,970	3.5	117,526	364,331	3.1
10	60,988	213,458	3.5	92,770	303358	3.27	91,255	282,890	3.1	152,814	504,286	3.3
60	66,734	213,549	3.2	86,518	277915	3.21	81,097	275,730	3.4	104,034	374,522	3.6
120	70,475	218,473	3.1	86,799	282097	3.25	62,854	232,560	3.7	93,073	353,677	3.8
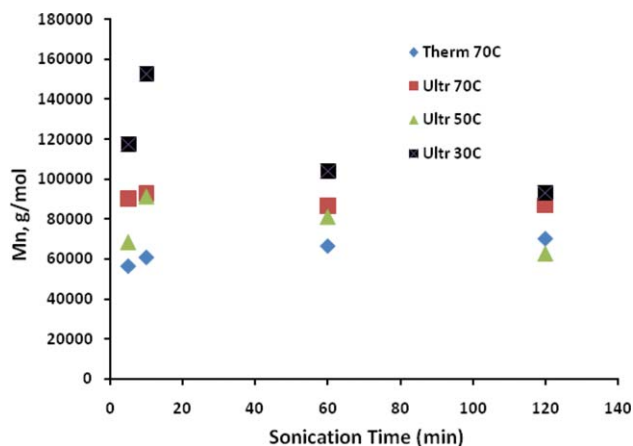
Figure 8 Average number molecular weight of ultrasonic polymerizations and conventional thermal polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
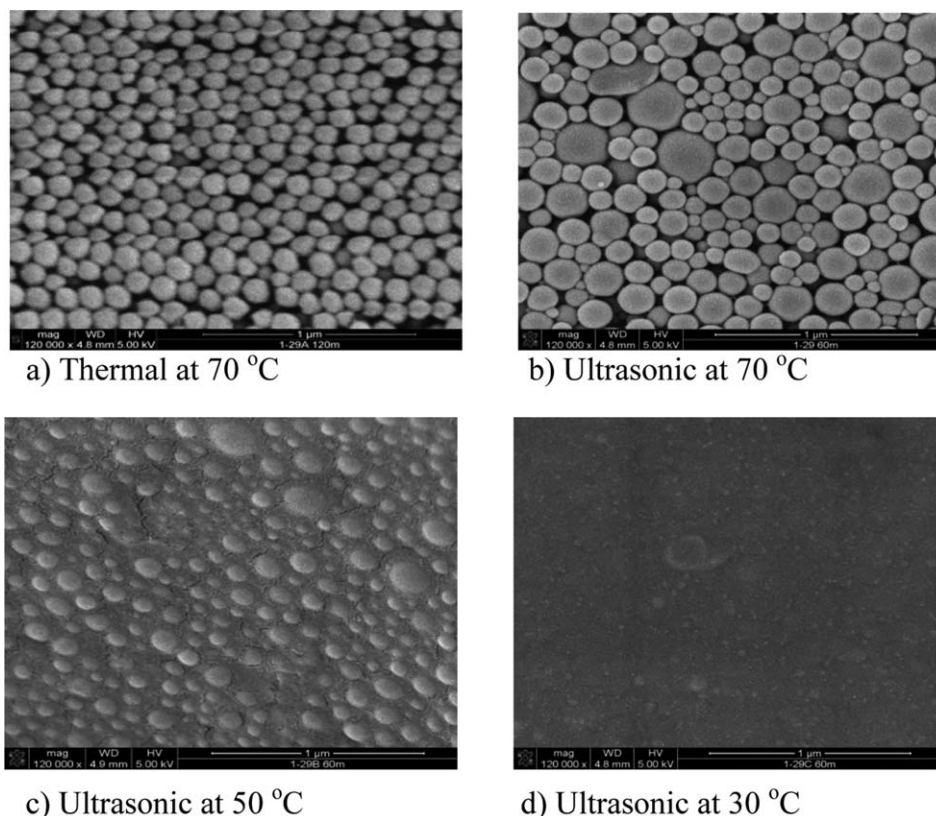
methyl methacrylate increased at the 0.21 power of acoustic intensity with the acoustic intensity increasing from 6.8 to 13.0 W cm^{-2}.

Effect of ultrasonic energy on the morphology of styrene polymer

Examination of the morphology of polystyrene beads, synthesized by conventional thermal process, through SEM and TEM, [Figs. 9(a), 10(a)], revealed that the conventional method resulted in almost uniform size, spherical beads It is also confirmed by particle size measurement as mono particle size distribution (Fig. 3). On the other hand, application of ultrasonic radiation resulted in spherical beads with various sizes [Figs. 9(b–d), 10(b–d)], as evidenced by particle size measurement as broad particle size distribution (Figs. 4–6). Moreover, increasing the temperature when applying ultrasonic radiation resulted in larger beads, which can be attributed to higher rate of polymerization. The polymerization did not take place at 30°C without applied ultrasonic energy. However, at the same temperature and applying ultrasonic energy, the polymerization took place at low rate (slope = 0.332 min^{-1}) as shown in Figure 2. When increasing the temperature the slope gets steeper which implies higher reaction rate as shown in Figure 2. This illustrated in SEM pictures [Fig. 9(b–d)] and illustrated in TEM pictures [Fig. 10(b–d)].

This clearly provide another evidence of ultrasonic effect on particle size and polymerization rate. The ultrasonic disrupt the size of monomer droplets. The monomer droplets get smaller under ultrasonic irradiation and compete in number and surface areas with the micelle, which then gives a new places for the emulsion polymerization to occur beside the

a) Thermal at 70 °C

b) Ultrasonic at 70 °C

c) Ultrasonic at 50 °C

d) Ultrasonic at 30 °C

Figure 9 FE-SEM of St Emulsion polymer.

a) Thermal at 70 °C

b) Ultrasonic at 70 °C

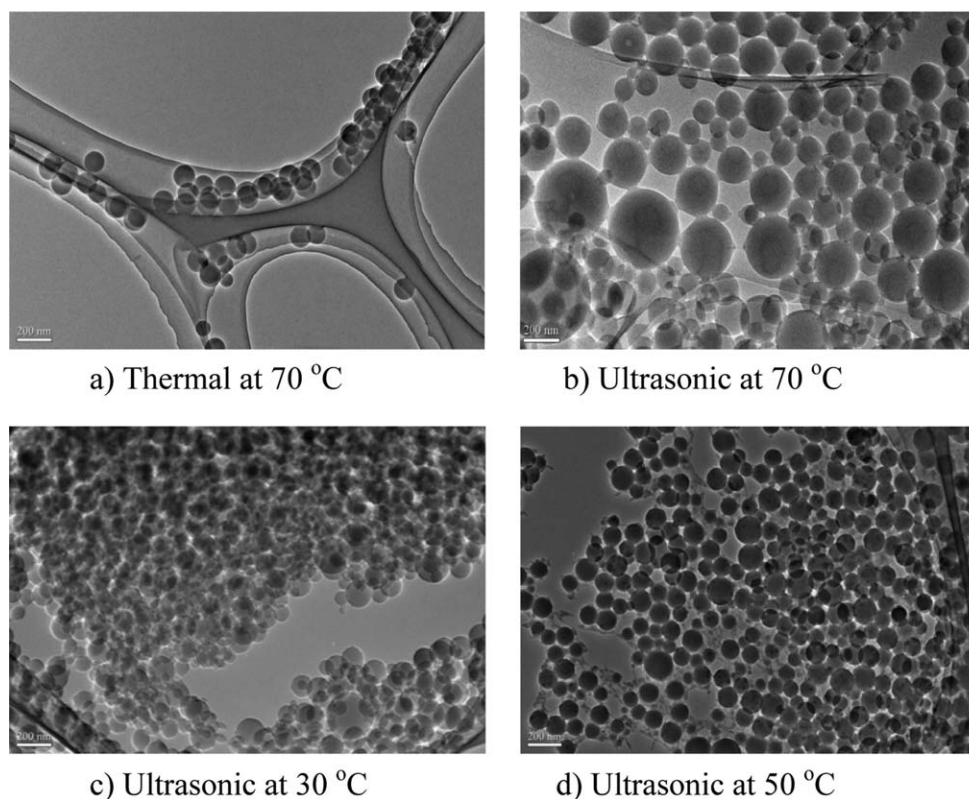c) Ultrasonic at 30 °C

d) Ultrasonic at 50 °C

Figure 10   TEM of St Emulsion polymer.

micelles. This may explain the differences in particle sizes as compared with conventional thermal polymerization process.

CONCLUSIONS

Combining ultrasonic and thermal initiator provides a good initiation system to produce a high polymer conversion and a high rate of polymerization in comparison with just using a thermal initiator. Ultrasonic energy has an effect on the particle size distribution. The particle size distribution increases with an increase in the monomer conversion of styrene for ultrasonic polymerization, whereas the particle size distribution did not change with an increase in the monomer conversion as compared with the conventional thermal polymerization results. Higher molecular weights were obtained under ultrasonic irradiation. FE-SEM and TEM pictures show different morphology of Styrene polymer with changing temperature of polymerization. It give evidence that polymerization not only occurs inside the micelles but also in other places such as monomers for ultrasonic polymerization. Collectively, the obtained results are similar with conventional miniemulsion polymerization process.

References

1. El-AAsser, M. S.;Sudol, E. D. In Emulsion Polymerization and Emulsion Polymers, 1st ed.; El-AAsser, M. S.; Lovell, P. A. Eds.; Wiley: New York, 1997, Chapter 2.
2. Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. Macromolecules 1991, 24, 1629.
3. Tang, L. G.; Weng, Z. X.; Pen, Z. R. Eur Polym J 1996, 32, 1139.
4. Zheng, Y.; Cao, Y.; Pan, G. Ultrasonics Sonochem 2008, 15, 314.
5. Wang, X.; Zhang, Z.; Chen, J.; Wang, S. Mater Lett 2007, 61, 2662.
6. Chen, J.; Zhang, Z.; Zhang, Q. Radiation Phys Chem 2009, 78, 906.
7. Lindstrom, O.; Lamm, O. J Phys Colloid Chem 1951, 55, 1139.
8. Barr, N. J.; Bengough, W. I.; Beveridge, G.; Park, B. Eur Polym J 1978, 14, 245.
9. Henglein, A. Makromol Chem 1954, 14, 15.
10. Ostroski, A. S.; Stambaugh, R. B. J Appl Phys 1950, 21, 478.
11. Suslick,K. S. Ultrasound: Its Chemical, Physical and Biological Effects, VCH Publishers: Weinheim, Germany, 1988, Chapter 1.
12. Joe Chou, H. C.; Stoffer, J. O. J Appl Polym Sci 1999, 72, 797.
13. Bahattab, M. A. J Appl Polym Sci 2005, 98, 812.
14. Bahattab, M.; Stoffer, J. Polym Prepr 2000, 41, 40.
15. Bahattab, M.; Stoffer, J.; Forciniti, D. Polym Prepr 2002, 43, 1031.
16. Kruus, P.; Lawrie, J.; O'Neill, M. 1988, 26, 352.
17. Odian, G. Principles of Polymerization, 3rd ed.; Wiley: New York, 1991, Chapter 4.
18. Biggs, S.; Grieser, F. Macromolecules 1995, 28, 4877.
19. El-Aasser, M. S.; Makgawinata, T.; Vanderhoff, J. W.; Pichot, C. J Polym Sci Polym Chem Ed 1983, 21, 2363.
20. Sudol, P. G.; Dimonie, V. L.; El-Aasser, M. S. Macromolecules 2001, 34, 481.
21. Ooi, S.; Biggs, S. Ultrasonics Sonochem 2000, 7, 125.
22. Bradley, M.; Grieser F. J Colloid Interface Sci 2002, 251, 78.
23. Price, G. J. Ultrasonic Sonochem 1996, 3, S229.