# Preparation of Polystyrene Latex with Ultrasonic Initiation

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ABSTRACT: The polymerization of a styrene in water (o/w) emulsion was performed at 30 °C (±5 °C) under ultrasonic irradiation in the absence of any added chemical initiator. The radicals formed as a consequence of the cavitation process were sufficient to cause polymerization. The latices formed in this way were stable bluish-white dispersions. The polymerization rate increased through a maximum at about 30% conversion before decreasing; no region with a steady rate was seen. The final latex diameters were around 50 nm and the polystyrene molecular weights were high ($>10^6$), suggesting at most a few polymer chains per particle. Calculations of the particle numbers as a function of monomer conversion suggested that there was a continuous nucleation of the particles. The small particle sizes, high polymerization rates, and continuous nucleation are postulated to be due to the continuous formation of very small oil droplets in the ultrasonic field which can efficiently scavenge the radicals formed during the cavitation process.

## Introduction

Polymer latices, prepared from the emulsion polymerization of vinyl monomer compounds, are widely used for many industrial applications. Included among these are uses in paints, adhesives, flocculants, and heavy-duty plastics as well as their original use in synthetic rubber compounds.[1]

Three types of physically distinct but related dispersions of styrene in water have been used previously to prepare polystyrene latex samples. These are the conventional emulsion system, a miniemulsion system, and a microemulsion system.[2] The main differences between these types of dispersion are in the monomer droplet size and droplet size distribution prior to polymerization. In conventional emulsion polymerization the monomer is located in three distinct regions: (a) monomer droplets of size 0.3–10 μm, (b) monomer-swollen micelles, and (c) dissolved in the aqueous phase. In the presence of a water-soluble initiator, radicals are generated in the aqueous phase and may either enter a micelle and polymerize its contents or polymerize monomer in the continuous phase, forming an oligomer which precipitates to a primary latex particle. The monomer droplets act only as feed reservoirs for the polymerizing particles. In the miniemulsion system, the main difference is that the monomer droplets are smaller and less polydisperse in size, their sizes ranging from 0.05 to 0.2 μm. In this case the polymerization is believed to occur within the droplets of monomer, although only a small fraction are actually initiated.[3] The remainder again act as supply pools of monomer for the polymerizing particles. A direct consequence of the fact that only a small fraction of the monomer droplets are initiated is that the final particle sizes always exceed the initial droplet sizes. Microemulsion polymerization of styrene is entirely different in that all the monomer in the system is dispersed within the microemulsion droplets, which have diameters of less than 20 nm and are homogeneously dispersed in the emulsion volume. In this case the polymerization occurs exclusively inside these small droplets and generally leads to a high polymerization rate and small particle sizes, typically less than 50 nm. However, once again the final particle size is greater than the initial droplet size since only a small fraction of the droplets, usually around 2%, are initiated.[4] In miniemulsion or microemulsion polymerization the limitation on the numbers of droplets initiated is believed to come from a barrier imposed by the surfactant interface which makes radical penetration difficult.[5] Despite this, the rates for polymerization by either of these two routes are higher than for conventional emulsion polymerization. It is commonly accepted that the main determinant for the polymerization rate in reactions of this type is the number of primary particles formed initially before all of the available monomer is absorbed into them; any subsequent polymerization can only then occur within the particles. Therefore, the greater the number of primary particles, the greater the rate.

The potential uses of ultrasound in physics and chemistry have been investigated for more than a century.[6] Despite this, it is only comparatively recently that its possible uses in synthetic chemistry have been examined in depth. Ultrasound was first used as an initiator for the polymerization of vinyl monomers in the early 1950s.[7] To date, the vast majority of studies have been concerned with the homopolymerization of either a pure monomer melt[8,9] or a monomer in a good solvent, particularly water.[7,10] Reports of emulsion polymerization reactions initiated by ultrasound are less common. In the majority of cases ultrasound is used purely as a dispersant to prepare a homogeneous emulsion, the reaction being initiated by an added chemical initiator such as potassium persulfate. In these cases, the initiator is activated to produce free radicals either by heating or with UV irradiation. Ultrasonic irradiation has been shown to accelerate these conventional emulsion polymerizations.[11] The acceleration is thought to be due to two properties of the irradiation. The first is the degassing effect of ultrasonic cavitation, which causes the efficient depletion of oxygen from the reaction medium and thus causes a lowering of the possibility for transfer reactions.[12] This directly leads to a shortening of the threshold or induction period experienced before polymerization begins and a higher overall particle number

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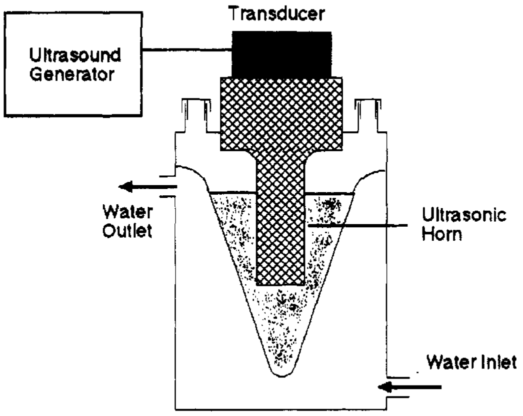

**Figure 1.** Schematic representation of the reaction cell used for the ultrasonically initiated emulsion polymerizations.

and therefore polymerization rate. The second effect is believed to be due to localized heating of the reaction medium due to the cavitation process. In general, these emulsion polymerization reactions are carried out at between 50 and 70 °C to promote a rapid polymerization rate. Ostroski and Stambaugh[11] showed that by application of ultrasound to a polymerization at 40 °C there was a substantial increase in the polymerization rate. During ultrasonic irradiation, the sonifier itself will experience a temperature increase. It was shown however that this was insufficient to account for the increased rate. The cavitation 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.[6] It is possible therefore that any polymerization reaction occurring in the vicinity of a collapsing cavity will be greatly accelerated and will contribute to the overall rate increase observed. Despite these previous investigations, to our knowledge, there are no in-depth reports in the literature on the initiation of emulsion polymerization with ultrasound; the only reference we have found was of a brief conference abstract.[13]

We have recently employed ultrasonic initiation to prepare a wide range of colloidal materials commonly initiated by free-radical species.[14-15] In the present study we report the preparation of polystyrene latex particles by the ultrasonic initiation of styrene emulsion polymerization.

## Experimental Section

**Reagents.** Styrene (Aldrich) was washed with 10% NaOH three times to remove the inhibitor before being distilled under reduced pressure. The sealed purified sample was stored at 4 °C until required. Sodium dodecyl sulfate (SDS) (Aldrich) was used as supplied. All water used here was of Millipore Milli-Q grade (surface tension = 72 mN m$^{-1}$ at 25 °C).

**Polymerization.** All the ultrasonically initiated polymerization reactions reported here were performed using a conventional 19 mm diameter 20 kHz horn sonifier (Branson 450) attached to a custom-built reaction vessel shown in Figure 1. Typically, the power rating of the horn was at 10–20 W/cm$^2$. In general, for all the polymerizations reported here the concentration of monomer was 10% (w/w) in water. The effects of different concentrations of surfactant (SDS) on the resultant latices produced as well as on the reaction kinetics were investigated. The following description for a polymerization at the above monomer concentration and with an SDS concentration of 1% (w/w) is typical of all the polymerizations performed here.

An emulsion of 10 g of styrene and 85 g of water was thoroughly deoxygenated by bubbling with nitrogen in the reaction vessel (Figure 1) thermostated at 25 °C. Five grams of a stock SDS solution (concentration 20% w/w) was then added via a syringe prepurged with nitrogen. At this point, the nitrogen gas stream was removed from the emulsion and was instead allowed to pass over the surface of the emulsion. A 30 s burst of ultrasound was sufficient to form a well-dispersed, stable emulsion. The polymerization reaction was then initiated by subjecting this emulsion to continuous cycles of 15 min of sonication and 10 min of rest. No external agitation of the polymerization medium was employed. At polymerization times of between 15 min and 3 h of applied sonic power, small aliquots were withdrawn from the reaction solution. After weighing, each of these samples was dialyzed against water for 7 days, the dialysate being changed frequently.

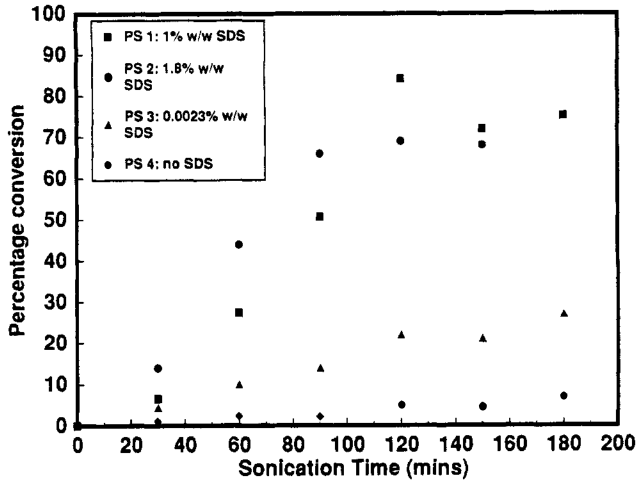

**Figure 2.** Conversion versus sonication time curves for styrene polymerizations with ultrasound at different surfactant levels.

Electron microscope grids for each sample were then prepared to allow particle size determination of the latices. Each sample was then dried by solvent evaporation under a stream of nitrogen gas, and the dry weight of polymer was obtained. From these data the conversion–time curve for the polymerization was determined.

**Molecular Weight Determination.** The molecular weight and molecular weight distribution of each polymer sample was determined in THF solution via gel permeation chromatography (GPC) using an Ultrastyragel separation column attached to two separate detectors, a differential refractometer (Waters 401), and a multiangle light scatterer (DAWN-F, Wyatt Technology Corp.).

**Particle Sizing.** Average particle sizes and particle size distributions for each latex sample were determined from transmission electron microscope images by sizing at least 200 particles in each image.

## Results

All of the polymerization systems reported here were milky white opaque emulsions at the outset of the reaction. At the completion of the polymerization and dialysis, a stable bluish-white dispersion was formed, indicative of small particle sizes.

The experimental conversion–time curves for the emulsion polymerization of styrene initiated by ultrasound at three surfactant concentrations are shown in Figure 2. Data for the conversion of styrene in the absence of any surfactant are also given in Figure 2. It is clear that there is a rapid increase in the polymerization rate at or above the cmc for this surfactant. Below the cmc, only very low monomer conversions of less than 20% were found after up to 3 h of total sonication time.

**Table 1. Molecular Weight Data as a Function of Monomer Conversion for Samples of Polystyrene Prepared with Ultrasonic Initiation at Three Surfactant Concentrations**

| sonication | PS 1 | | | PS 2 | | | PS 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| time (min) | $M_n$ (×10$^{-6}$) | $M_w$ (×10$^{-6}$) | $M_w/M_n$ | $M_n$ (×10$^{-6}$) | $M_w$ (×10$^{-6}$) | $M_w/M_n$ | $M_n$ (×10$^{-6}$) | $M_w$ (×10$^{-6}$) | $M_w/M_n$ |
| 30 | 2.05 | 2.75 | 1.34 | 2.31 | 4.3 | 1.86 | | | |
| 60 | 2.61 | 3.52 | 1.35 | 2.38 | 4.77 | 2 | 0.61 | 1.04 | 1.69 |
| 90 | 1.89 | 3.58 | 1.89 | | | | 0.59 | 1.19 | 2.00 |
| 120 | | | | 2.31 | 5.01 | 2.17 | 0.77 | 1.45 | 1.88 |
| 150 | 1.55 | 2.89 | 1.86 | | | | 0.73 | 1.54 | 2.09 |
| 180 | | | | 2.54 | 5.17 | 2.04 | 0.48 | 1.40 | 2.60 |

**Table 2. Average Particle Size Data as a Function of Monomer Conversion for Samples of Polystyrene Latex Prepared with Ultrasonic Initiation at Three Surfactant Concentrations**

| | PS 1 | | | PS 2 | | | PS 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| sonication time (min) | $D_n$ (nm) | $D_w$ (nm) | $D_w/D_n$ | $D_n$ (nm) | $D_w$ (nm) | $D_w/D_n$ | $D_n$ (nm) | $D_w$ (nm) | $D_w/D_n$ |
| 30 | 20.9 | 33.9 | 1.6 | | | | 19.7 | 26.6 | 1.4 |
| 60 | 21 | 38 | 1.8 | | | | 25.7 | 31.6 | 1.2 |
| 90 | 27.9 | 36.2 | 1.3 | | | | 31.9 | 44.9 | 1.4 |
| 120 | 33.2 | 47.3 | 1.4 | | | | 34.6 | 49.2 | 1.4 |
| 150 | 25.9 | 40.5 | 1.6 | | | | 32.6 | 44.9 | 1.4 |
| 180 | | | | 42.5 | 61.4 | 1.4 | | | |

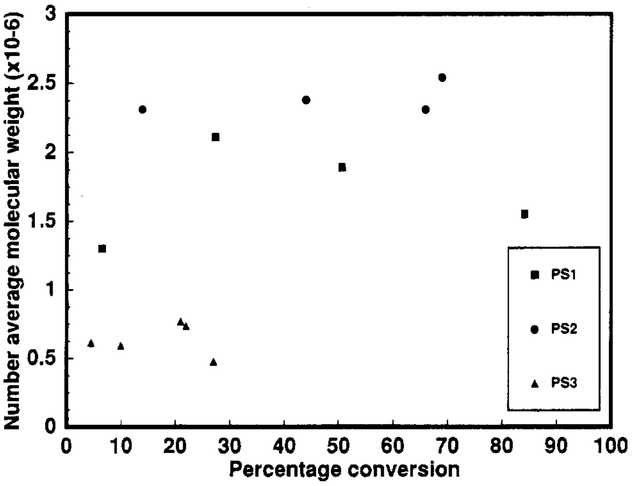

**Figure 3.** Number-average molecular weight versus conversion data for styrene polymerizations with ultrasound at different surfactant levels. PS 1, PS 2, and PS 3 refer to polymerizations at different surfactant levels; for details, see Figure 2.

In Figure 3 the values of the number-average molecular weight ($M_n$) as a function of monomer conversion are given for each polymerization except that with no surfactant. Data for number- and weight-average molecular weights, $M_n$ and $M_w$, respectively, as well as the molecular weight distribution ($M_w/M_n$) for each polymer sample examined are given in Table 1. The GPC data showing the changing molecular weight distribution with increasing monomer conversion are presented for sample PS 1 in Figure 4. These data are typical for each of the polymerizations reported here. No clear trends in the molecular weight data as a function of monomer conversion were apparent. In all cases, however, a broadening of the molecular weight distribution with polymerization time was seen.

Data for the latex particle sizes and the size distributions of each sample are given in Table 2. A representative electron micrograph picture of one of the latex samples is shown in Figure 5. In general, for the samples investigated here, increased sonication time was seen to lead to an increase in the average particle diameter for each sample. The particle size distribution was seen to remain approximately constant over the entire sonication period. A graphical representation of the evolution of the particle size with increased sonication time (monomer conversion) is given in Figure 6. It is clear that there is a general shift toward larger particle sizes with increased monomer conversion.

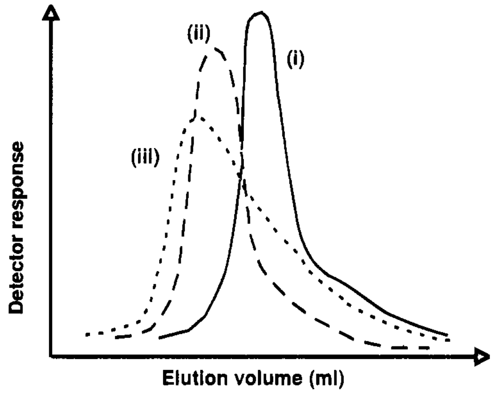

**Figure 4.** Representative GPC elution traces for sample PS 1 (SDS = 1% w/w) at three different degrees of monomer conversion: (i) 26% conversion; (ii) 51% conversion; (iii) 70% conversion.

## Discussion

It is evident from the data presented in Figure 2 that there is a dramatic increase in the rate of styrene polymerization when the concentration of surfactant is above its cmc. This result suggests that the monomer-swollen micelles are the main locus of polymerization, which is consistent with results for the more traditional chemically initiated emulsion polymerization reactions.[1,2] Surfactant micelles are thought to act as traps for the oligomeric radicals formed in the continuous phase.[1] When one of these radicals penetrates a micelle, it causes rapid polymerization of the monomer contents of that micelle core. Further transfer of monomer from droplets to these micelles, across the continuous phase, leads to growth of the polymer chain. The polymer growth can be ended in one of two ways. Either a second radical enters the micelle, leading to bimolecular termination, or the radical is transferred to some other species in the micelle which can then rapidly desorb from this micelle. Without these micelles to trap the radicals from the continuous phase therefore the rate is greatly reduced.

The rate of monomer conversion as a function of the fractional conversion is shown in Figure 7. This curve

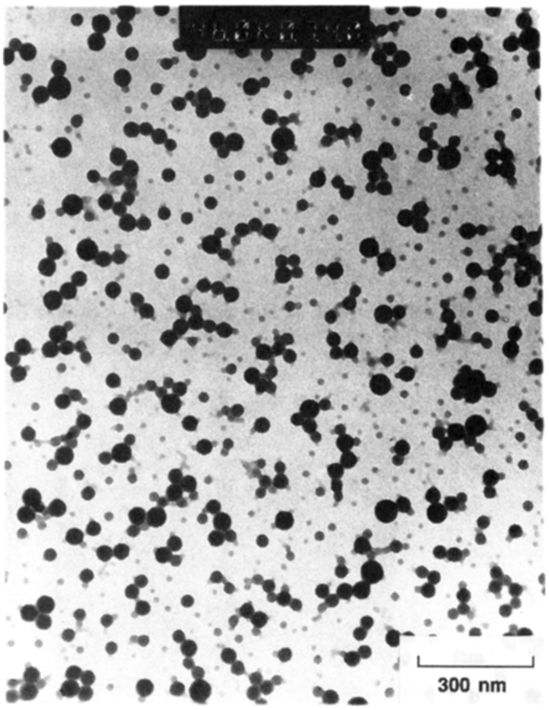

**Figure 5.** TEM micrograph for polystyrene latex: sample PS 1; conversion = 44%; SDS = 1% w/w.

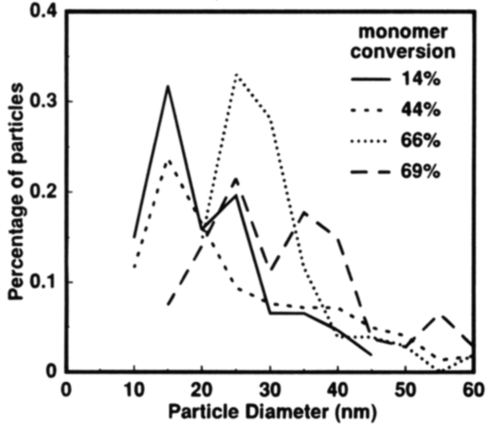

**Figure 6.** Particle size distributions for polystyrene latex sample PS 1 at different degrees of monomer conversion: SDS = 1% w/w.

was determined from the best fit to the PS 1 conversion data shown in Figure 2. Essentially the polymerization curves showed only two intervals; there was no extended region of constant rate as is often seen for conventional emulsion polymerization. This type of rate versus conversion behavior has been seen previously for microemulsion polymerization of styrene.[4] Interval I of this rate curve, which extends from 0 to 30% conversion, is characterized by a continuously increasing rate of conversion. After this, in interval II, the rate declines continuously. It is conventional to interpret this first interval as the particle nucleation stage during which time all of the particles are formed.[1,2] At the conclusion of this interval all of the monomer is adsorbed by these particles and so no new particle formation occurs but instead these particles grow as the monomer in them is polymerized. However, for microemulsion polymerization this is not the case; particles are instead nucleated throughout the reaction.[4] This continuous nucleation is explained by the very high amounts of surfactant employed, which means that throughout the reaction there will be monomer-swollen micelles available to act as nucleation sites. The decreasing rate is solely due to the decreasing overall monomer concentration with increased conversion.

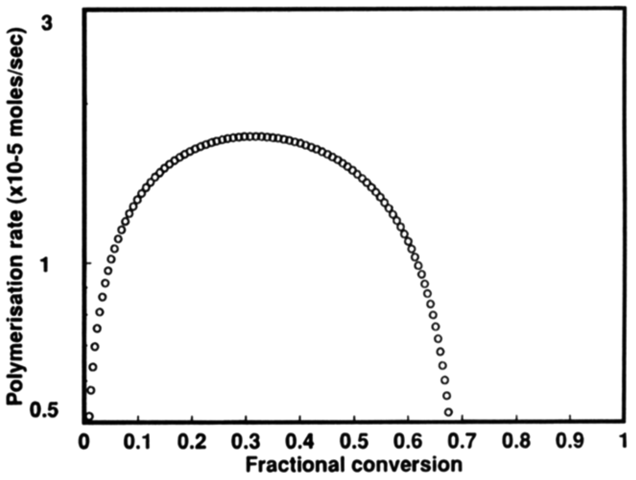

**Figure 7.** Polymerization rate versus conversion for sample PS 1: SDS = 1% w/w.

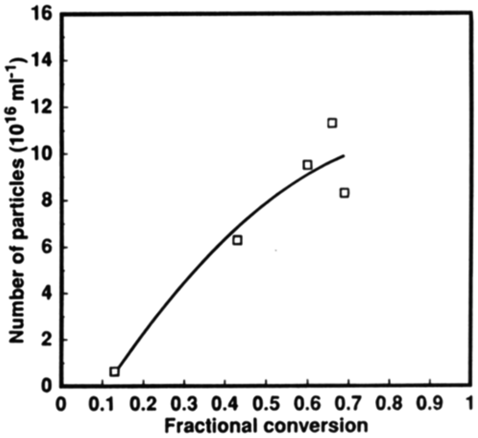

**Figure 8.** Number of polymer particles versus fractional conversion for sample PS 1: SDS = 1% w/w.

In the reactions reported here the concentration of surfactant is not as high as for microemulsion polymerization although we attain similar polymerization rates and the same conversion–rate relationship.[4] Thus, although we are using a concentration of surfactant that is comparable to a conventional emulsion polymerization, the rate data are related more closely to those seen for a microemulsion system. From a knowledge of the conversion data and the weight-average particle sizes (Table 2), we are able to calculate particle numbers at any fractional conversion. A plot of the particle number as a function of the fractional conversion for sample PS 1 is given in Figure 8. It is clear from these data that the numbers of particles are continuously increasing with monomer conversion. This continuous nucleation is also directly analogous to the microemulsion polymerization results. The total number of particles formed here is very high, suggesting that the flux of radicals is continuously very high and that the capture efficiency by either swollen micelles, small monomer droplets, or nascent particles is very high.

Temperature effects on the high polymerization rates seen here can be neglected since for the reactions reported here the polymerization was thermostated at between 25 and 30 °C, which is lower than the 50–70 °C usually employed for styrene o/w polymerization. Despite this, the reaction rates observed were comparable with those for the quickest types of reaction conditions usually employed (i.e., microemulsion). By performing cycles of 15 min of sonication followed by 10 min of rest, the global reaction solution temperature was maintained at below 30 °C, and this small rise in temperature from the initial 25 °C is insufficient to account for the observed rates.[11] The possible acceleration of the rate due to local heating of the solution caused by cavitation would seem to be a more important factor here although from these data its effects cannot be shown unambiguously.

The high rates of particle formation must be linked to a high flux of radicals and an efficient scavenging of these radicals by the reactive monomer-rich regions of the reaction system. Ultrasonic cavitation in aqueous solution forms radical species by the cleavage of chemical bonds in any vapor molecules within the cavity as it collapses. The high temperatures and pressures inside this collapsing cavity are sufficient for bond cleavage, the radicals thus formed being expelled into the surrounding medium. It is unclear from these results whether there is any direct formation of styrene radicals within the cavity or whether it is the primary radicals formed from the cleavage of water (i.e., $H^\bullet$, $OH^\bullet$) which act as the initiating species. The presence of dissolved styrene in the aqueous continuous phase means that its presence inside any cavity cannot be discounted although its effective concentration will be low. It seems more probable therefore that it is the radicals generated by the cleavage of water that contribute primarily to the initiation of polymerization.

Previous studies have determined that the particle sizes attainable by ultrasonic dispersion of styrene in water were in the range 50–200 nm.[16] It is clear therefore that the sizes of the latex particles formed here are smaller than these droplet sizes. This result is particularly interesting since for all the other methods of preparing polymer latices the initial droplet sizes are always less than the final particle sizes. This is further confirmation that the rate of particle formation is very high. The particle size distribution ($D_w/D_n$) is effectively invariant throughout the polymerization reactions (Table 2), a result which is expected if the initial particle formation rate is high and all of the available monomer is rapidly adsorbed into these primary particles. In the cases of miniemulsion and microemulsion polymerization, the fine dispersion of droplets should also lead to an extremely rapid primary particle formation rate.[3,4] As noted above, however, the barrier imposed by the surfactant interface is sufficient to hinder radical entry into particles and hence lower this initial particle formation rate.[5] In the case reported here, the droplet sizes are also small but they do not have this interfacial surfactant barrier and so the capture efficiency of the radicals will be greater, leading to more particles and smaller diameters.

The small latex diameters in the final samples also suggest that there has been little particle coagulation during the polymerization reaction, which would lead to a larger final particle size. This lack of coagulation may be explained by the formation of sufficient surface charge on the primary particles to confer on them electrostatic stabilization. Current understanding is that adsorbed anionic surfactant leads to electrostatic charge on the particle surface. In conventional reaction systems, a great deal of particle growth occurs initially from coagulation of the primary particles due to insufficient surface charge.[1,2] This is only prevented when the amount of adsorbed surfactant per unit area of each particle is sufficiently high to give electrostatic stabilization; this will of course rise as the particles coagulate, lowering the total surface area. A more interesting result was for the latex prepared in the absence of any surfactant. Although the conversion for this sample was low, the eventual latex sample was stable after dialysis. The formation of surfactant-free latex samples by conventional means is believed to be successful due to the presence of charged initiator fragments at the surface which confer electrostatic stabilization on the system. In this case this is clearly not a plausible explanation as there is no added initiator. The charge stabilization must come therefore from some other form of surface modification, the origin of which is as yet not entirely clear.

**Table 3. Average Number of Chains per Latex Particle ($N_c$) as a Function of Conversion for Sample PS 1**

| sonication time (min) | $D_w$ (nm) | $M_w$ ($\times 10^{-6}$) | $N_c$ |
|---|---|---|---|
| 30 | 33.9 | 2.75 | 4.5 |
| 60 | 38.0 | 3.52 | 4.9 |
| 90 | 36.2 | 3.58 | 4.2 |
| 120 | 47.3 | | |
| 150 | 40.5 | 2.89 | 7.2 |

From the data for the molecular weights of the polymers and with a knowledge of the particle sizes, we can determine the average number of chains per particle. Results for calculations of this type based upon the weight-average diameter and the weight-average molecular weights as a function of conversion for sample PS 1 are given in Table 3. The number of chains appears to remain fairly constant throughout the reaction at about 4 chains/particle, with a slight rise at the conclusion of the reaction. This low number of chains, small particle size, and high molecular weights suggest that the polystyrene in these particles is present in a highly compact globular form. Qian et al.[17] have reported similar globular polystyrene particles of about 20 nm diameter containing 1–2 chains/particle prepared via a microemulsion technique but using high initiator concentrations. The high polydispersities in the molecular weights for the samples examined here are consistent with a high radical flux and a high capture efficiency, which would lead to an increased amount of bimolecular termination relative to radical transfer to monomer. Under normal reaction conditions the molecular weight and polydispersity are controlled primarily by chain transfer to monomer and bimolecular termination is insignificant.[1,2] The slight lowering of the molecular weights and the increased polydispersity of the samples (Table 1) with increasing monomer conversion are most easily explained from the decreasing monomer concentration within the monomer droplets and the nascent particles.

In summary, the results presented here appear to show that polymerization of styrene emulsions with ultrasound has many similarities with microemulsion polymerization but at a considerably reduced surfactant level. An explanation for this may rest with both the cavitational effects and the mechanical effects of ultrasonic irradiation. Throughout the polymerization reaction the emulsion is subjected to the turbulent shearing conditions caused by the ultrasound and so we may expect that there will be a constant formation of very small monomer droplets and swollen micelles with a high surface area which will scavenge the radicals. As these are polymerized they are replaced by new droplets which can also act as radical scavengers. At the same time, the intense ultrasound leads to a constant high flux of free radicals capable of initiating the polymerization. Thus, the reaction at any instant contains a high number of very small monomer droplets not unlike a microemulsion or miniemulsion system.

## Conclusions

The ultrasonic initiation of emulsion polymerization appears to offer an alternative route for the synthesis of relatively small latex particles. A particular advantage of this route is the need for only low levels of surfactant to stabilize the emulsion prior to polymerization. These preliminary results have indicated that there are both similarities and differences with more classical emulsion polymerization techniques, the kinetics appearing to more closely resemble those seen for microemulsion polymerization.

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