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High Intensity Ultrasound Initiated Polymerization of Butyl Methacrylate in Mini- and Microemulsions

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ABSTRACT: The polymerization of butyl methacrylate in oil-in-water emulsions stabilized by an anionic surfactant, sodium dodecylsulfate, was investigated using a chemical initiator free sonochemical polymerization technique. The effect of surfactant concentration on the rate of polymerization, the number of latex particles formed, particle diameters and the molecular weights of the polymers produced were examined. The rate of polymerization was significantly enhanced at surfactant concentration greater than 0.5 wt %. Stable latex dispersions containing nanoparticles (40−85 nm) with average polymer molecular masses of about 7×10^6 g mol^{-1} were obtained. The mechanism of latex particle formation is suggested to be through sonochemically produced radicals initiating polymerization of dispersed nanometer sized monomer droplets.

Introduction

It is well-known that immiscible liquids (e.g., a mixture of water and oil) can be brought together as a *macroscopically* homogeneous (but *microscopically* heterogeneous) phase by adding sufficient amounts of surfactant to the mixture to decrease the interfacial tension between the two immiscible liquids to near 0 mN/m. This very special class of "solution" is known as a microemulsion and is a thermodynamically stable and optically transparent mixture of oil, water and surfactant.

Microemulsions made using organic monomers are usually formed at larger surfactant to monomer ratios than those used in typical miniemulsion polymerization recipes.[1−8] The large number ($\sim 10^{15}$ mL^{-1}) of oil-in-water (o/w) microemulsion droplets formed in typical systems is responsible for the fast polymerization rates of monomers and the formation of nanosized latex particles smaller than 50 nm, containing high molecular weight polymers of approximately 10^6-10^7 g mol^{-1}.

Microemulsion polymerization has been investigated extensively since the first report by Stoffer and Bone in the 1980s in which they reported that increasing the chemical initiator concentration led to polymer latex products with smaller average molecular weights and high polydispersity indexes.[1] Many studies have been reported since then and among them, Guo et al.[2−4] have published extensively on the kinetics of microemulsion polymerization of styrene. They emphasized a few features of a microemulsion polymerization; namely, that the particle nucleation process is continuous throughout the course of polymerization and that particle nucleation occurs in micelles incorporating monomer.

It has been reported in a few studies that the use of a cosurfactant, such as pentanol, in microemulsion polymerization complicates the process for several reasons. In particular, the cosurfactant can act as a chain transfer agent as well as destabilize the latex particles by competitively displacing the surfactant from the surface of the polymer particles.[9−12] For these reasons, the three component system is inherently a less complex system (i.e., water, monomer and surfactant) and can be easily, and continuously, changed from macroemulsions to transparent microemulsions by simply increasing the amount of surfactant in the solution. For example, Ng and co-workers reported on the three component microemulsion polymerization of methyl methacrylate in which turbid emulsions were changed to transparent microemulsions with increasing amounts of added surfactant.[13] They reported that the polymer particles were approximately 30−60 nm in sizes and that polymer molecular weights in the range of $(5-7) \times 10^6$ g mol^{-1} were produced.

In recent years, a new method of making polymer latex particles has been developed using high intensity ultrasound.[14−20] High intensity ultrasound has been used in conventional emulsion polymerization as it allows the monomer to be efficiently dispersed as oil droplets into the aqueous phase. Ostroski and Stambaugh[21] were the first to ultilize ultrasound in conventional emulsion polymerization and they found that the rate of polymerization was accelerated in the presence of ultrasound. The action of ultrasound in liquid systems is 2-fold mechanical agitation and chemical. First, the large shear gradients surrounding the interfacial region of cavitation bubbles cause two immiscible liquids to be efficiently mixed. Second, the collapse of these cavitation bubbles is highly energetic and as a consequence, very high temperatures (∼5000 K)[22,23] and pressures (500 atm) are generated within the bubbles. These intense conditions are responsible for the homolysis of water molecules, present in the cavitation bubbles, into primary radicals ($^\bullet$OH and $^\bullet$H radicals). These primary radicals are known to initiate the polymerization process.[24]

Bradley and Grieser have recently proposed a reaction mechanism for the sonochemical emulsion polymerization (shown in Scheme 1).[16] As the detailed description of the mechanism has been published elsewhere,[16] the main reactions are highlighted as follows. The $^\bullet$H and $^\bullet$OH radicals produced by the homolysis of water (reaction 1) react with the monomer molecules found at the interface of the cavitation bubble (reaction 2) forming monomeric radicals in the bulk solution. These monomeric radicals may undergo three reaction pathways to initiate polymerization; they can add to a monomer molecule and undergo a bulk polymerization, enter a droplet or enter a micelle (reactions 4−6). The dominant pathway will of course depend on the

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Scheme 1. Mechanism for Ultrasound Initiated Emulsion Polymerization[a]

Initiation:			
H_2O	$\xrightarrow{)))}$	$\bullet H + \bullet OH$	1
$\bullet OH/ \bullet H + M_s$	$\rightarrow$	$HOM_s\bullet/ HM_s\bullet$	2
Propagation:			
$M_s\bullet$	$\rightarrow$	$M_b\bullet$	3
$M_b\bullet + M_b$	$\rightarrow$	$M_{ib}\bullet$	4
$M_b\bullet/ M_{ib}\bullet + D$	$\rightarrow$	$D\bullet$	5
$M_b\bullet/ M_{ib}\bullet$ + micelle	$\rightarrow$	$M_{micib}\bullet/M_{micb}\bullet$	6
$D\bullet$	$\rightarrow$	$D_p\bullet$	7
Termination:			
$M_b\bullet/ M_{ib}\bullet + D_p\bullet$	$\rightarrow$	Polymer particle	8
$M_{micib}\bullet + M_b\bullet/ M_{ib}\bullet$	$\rightarrow$	Oligomer	9
$D_p\bullet$ + SDS	$\rightarrow$	Polymer particle + SDS•	10

[a]))) refers to ultrasonic waves, M for monomer, *s* for the surface of the cavitation bubble, *b* for bulk solution monomer, D for monomer droplet, *i* for two or more monomer molecules per radical, and *mic* for micelle.

relative concentrations of M_b, D, and M_{mic}. Reaction 7 refers to a monomer droplet undergoing polymerization. There are several ways in which termination may occur, as represented by reactions 8–10. Termination typically occurs by recombination (reactions 8 and 9) or by chain transfer (reaction 10).

Biggs and co-workers[18,19] reported the successful emulsion polymerization of polystyrene using ultrasound irradiation. They found experimentally that the polymerization reactions under sonochemical conditions exhibit similar behavior to those of conventional emulsion polymerization. They have also noted that the kinetic results appeared to follow that of a microemulsion polymerization and the polymerization resulted in small polystyrene latex particles at low surfactant concentrations.

We have previously reported on the effect of surfactant concentration and selection of emulsion type (mini or micro) on the polymerization of BMA using high frequency (213 kHz) ultrasound.[17] The aim of this study was to examine the kinetics and mechanism of ultrasonically initiated polymerization of oil soluble monomers in a three component system ranging from miniemulsions to microemulsions using high intensity ultrasound at a low frequency of 20 kHz, typical of horn type reactors.

Experimental Details

Chemicals. *n*-Butyl methacrylate (BMA, $H_2C{=}C(CH_3)$-$COO(CH_2)_3CH_3$) (99% purity) was obtained from Aldrich. The monomer was filtered twice through basic aluminum oxide to remove the inhibitor, hydroquinone. The purified monomer was sealed and stored below 4 °C until required. The emulsifier used was high purity (99% grade) sodium dodecylsulfate (SDS) supplied by BDH, Australia. Milli-Q filtered water (18 MΩ cm) was used as the polymerization medium. High purity argon, provided by BOC gases, was used for sparging solutions.

Apparatus. All sonochemical polymerization experiments were performed using a Branson 450, 20 kHz ultrasound generator, equipped with a horn type transducer of 19 mm in diameter. A custom-made 100 mL glass reaction cell was used with a water jacket through which thermostatted water was circulated to maintain a constant temperature at 30 °C.

Polymerization Procedure. The polymerization reactions were all performed at 30 °C with a total sample volume of 80 mL, and surfactant concentrations varying from 0.1 to 10.5 wt %. The reaction mixture was extensively sparged with argon for 45 min to remove any dissolved oxygen. Throughout sonolysis, a constant flow of argon was kept above the liquid surface in order to maintain an argon saturated environment within the reaction cell. The calorimetrically determined power delivered into the reaction mixture was set at 8 W/cm^2. A syringe was used to withdraw approximately 1.5 mL of the latex samples at different polymerization time intervals. The latex samples were then oven-dried overnight at 80 °C. The monomer conversion was determined gravimetrically.

Particle Sizing. The latex samples were diluted by a factor of ~100 in Milli-Q water and particle size measurements were performed using a dynamic light scattering instrument (Malvern Autosizer 4700 utilizing a 4800 Malvern spectrometer). The measurements were performed at a scattering angle of 90° at 25 °C.

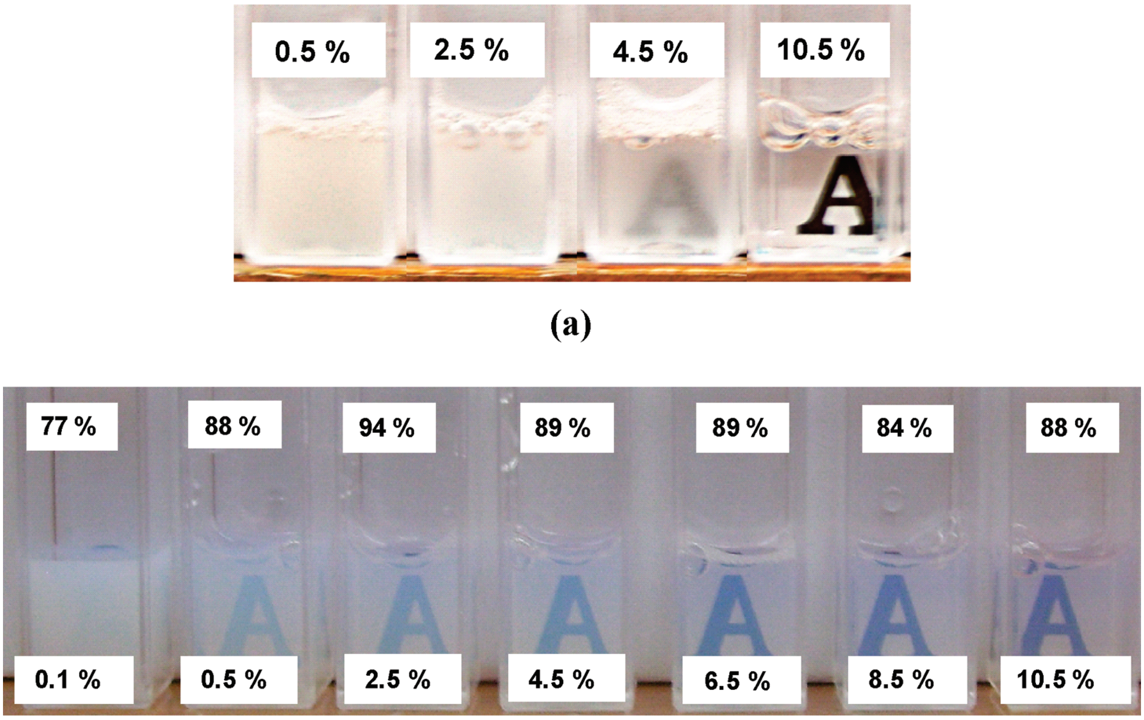
Molecular Weight Determination. The molecular weights of the polymer latex samples were measured using size exclusion chromatography (SEC), which only requires a single calibration of a narrow molecular weight pMMA standard. The SEC is equipped with refractive index (Optilab EOS, Wyatt) and multi-angle light scattering (DAWN DSP, Wyatt) detectors. THF was used as an eluent with 3 Penomenex phenogel columns (500, 10^4 and 10^6 Å) operating at 1 mL/ minute and the column temperature was set at 30 °C.

Results and Discussion

The photograph of mini- and microemulsions before sonication and the final latex particles in solutions containing different amounts of SDS are presented in Figure 1. The variation in the transparency of the latex solutions indicates that the latex particles get smaller as the SDS concentration increases. The bluish appearance of the latex samples is caused by the Tyndall effect of light scattering of particles smaller than 100 nm.[25,26] The polymer latices obtained by the sonochemical initiated free radical polymerization were stable, irrespective of the concentration of surfactant used. During sonication, the clear microemulsions and turbid miniemulsions quickly change to translucent bluish solutions indicating the onset of polymerization induced by ultrasound. The monomer conversion as a function of sonication time for the mini/microemulsion polymerization of BMA under ultrasound irradiation for varying amounts of SDS is shown in Figure 2. The polymerization rate was relatively fast at high surfactant concentrations and almost full conversion was attained within 15 min, with no significant differences in the polymerization rate at surfactant concentrations greater than 0.5 wt %. The main purpose of the surfactant was to stabilize the monomer droplets/ formed particles and therefore should not have any effect on the nucleation process.[27] However, this observation was different from that of Biggs et al.,[18,19] where they observed an increase in the rate of monomer conversion as the SDS concentration was increased and they suggested that monomer swollen micelles may be the primary locus of polymerization.

Experiments performed at low surfactant concentration (0.1 wt %) had similar conversion profiles as those at higher surfactant levels but the rates of polymerization were considerably slower than those at higher surfactant concentrations. Also the full conversion of monomer to polymer was not achieved even after 30 min of sonication. This is an indication that at a low surfactant concentration of 0.1 wt %, the amount of surfactant present was not sufficient to produce enough monomer droplets to kinetically compete with other pathways open to the initiating radicals; i.e., the monomer droplets are driven to coagulation as supported by the data on the number of polymer particles produced (discussed later) and therefore the polymerization rate decreases.

The polymerization of BMA at all SDS concentrations exhibits first order kinetics as shown in Figure 3 (note that not all treated data are shown in this plot), an indication that the monomers are steadily being consumed in the system, hence representing a



(a)

(b)

Figure 1. (a) Photograph of mini- and microemulsions before sonication. The row of numbers refers to the wt % of SDS present in the system. (b) Photograph of the final latices stabilized by different amounts of SDS. The top row of numbers refers to the conversion % of the latices at which the photograph was taken and the bottom row of numbers refers to the wt % of SDS present in the system.

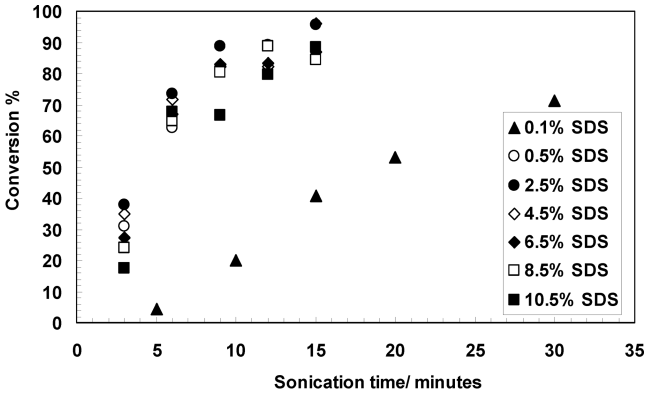


Figure 2. Effect of SDS concentration on BMA polymerization using ultrasound at a frequency of 20 kHz and power delivered of 8 W/cm^2.

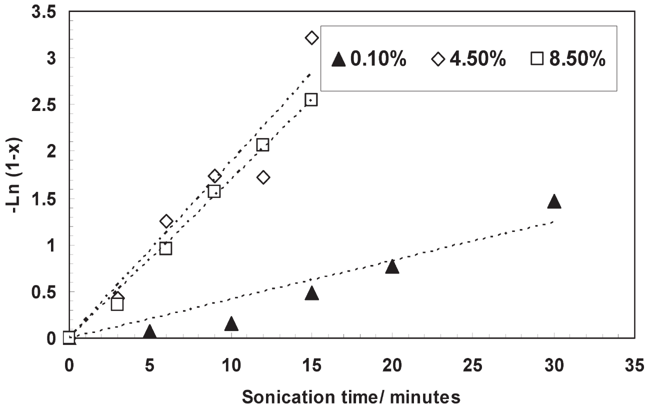


Figure 3. First order kinetic treatment (x as the fractional conversion of the monomer) as a function of sonication time for 0.1, 4.5, and 8.5 wt % SDS.

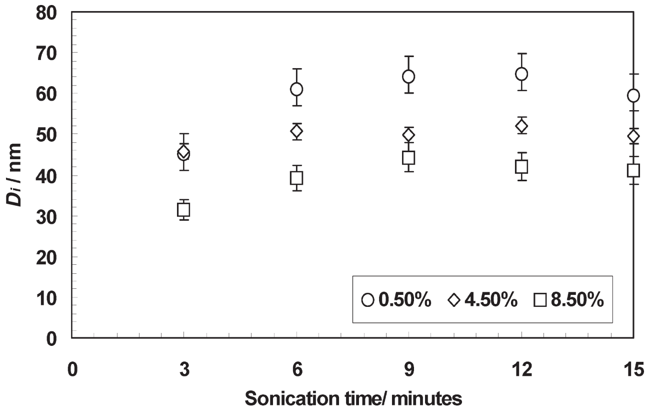


Figure 4. Effect of SDS concentration on the evolution of polymer particles as a function of sonication time for poly (BMA) microemulsion polymerization.

controlled reaction. Referring back to Figure 2, the increase in the polymerization reaction rate when larger amounts of SDS (4.5% and 8.5 wt %) were used was as expected. At higher surfactant concentration, the droplet size is smaller, implying that there are a larger number of nucleation sites; the number density of particles is higher and as a consequence results in a faster polymerization rate.[17]

It is known that the surfactant concentration of a microemulsion affects the ensuing particle sizes of the latex particles. The effect of surfactant concentration on the variation in the particle diameter of the latex particles with the progress of polymerization are summarized in Figure 4. Particle sizes decreased significantly from about 60 to 35 nm as the SDS concentration was increased from 0.5 to 8.5 wt %. The polydispersities ($D_v/D_n \approx 1.1$, where D_v and D_n refers to the volume averaged and number averaged diameters, respectively) of the particles, however, did not change

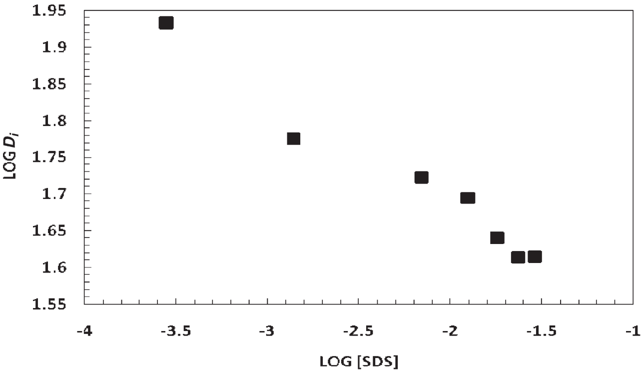


Figure 5. Linear relationship between the final diameter of latex particles and concentration of SDS.

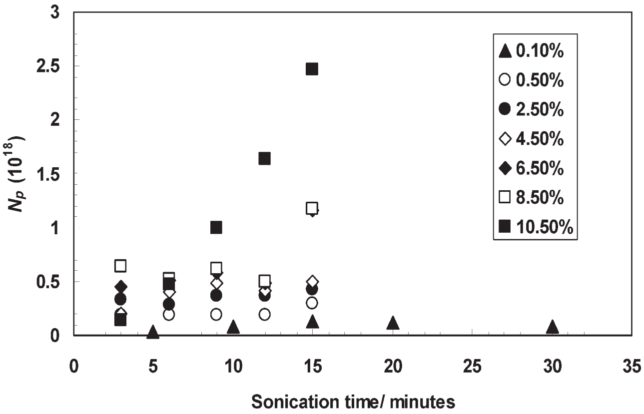


Figure 6. Number of particles (N_p) in the reaction as a function of sonication time (N_p calculated from D_v).

significantly. The decrease in particle size with increasing surfactant concentration can be expected, as SDS acts to stabilize the monomer droplets.

The particle diameter (D_i) increased slightly during the initial polymerization reaction and remained constant throughout the course of the reaction. In Figure 5, the final particle diameter of the latex particles is plotted as log D_i against log [SDS]. It shows a linear relationship between the concentration of SDS and the final diameter of the particles. As seen, an increase in the surfactant concentration leads to the formation of smaller latex particles since SDS adsorbs at the monomer/ water interface and stabilizes the droplets against coalescence. This observation is consistent with the results reported by Ng and co-workers using a conventional polymerization process.[13]

The number of latex particles (N_p) was calculated using the conversion (at which particle sizing was performed) and the volume fraction data of the polymer latex. Figure 6 illustrates the effect of SDS concentration on the evolution of N_p, which increases at high concentrations of SDS (6.5−10.5 wt %), and decreases at low SDS concentration (0.1 wt %), whereas Figure 7 represents a linear relationship between log N_p against log [SDS]. The increase in the number of particles during the entire polymerization process at high surfactant concentration indicates that there is a continuous nucleation of particles in the system.

At low surfactant concentration (0.1 wt %), the number of particles decreases over the course of the polymerization reaction. This indicates that there is a very low amount of SDS present to stabilize the nucleated particles and so the small particles are driven to coagulation over time. This observation in the decrease in number of particles over the course of the reaction is supported by the particle size of poly (BMA) as a function of sonication time shown in Figure 4. The adsorbed amount of SDS on the monomer droplet surface was calculated from the molecular adsorption area[28] (shown in Table 1).These calculations indicate that below 2.5 wt % SDS, there are effectively no free SDS molecules left in the solution demonstrating that the droplet nucleation process (reaction 5 in Scheme 1) is the main reaction pathway for particle formation. Alternatively, when the amount of SDS in the system is above 2.5 wt %, it is reasonable to conclude from the data presented in Table 1 that second micellar nucleation process (reaction 6) is likely given that the concentration of micelles is much higher than the concentration of monomer droplets.[29]

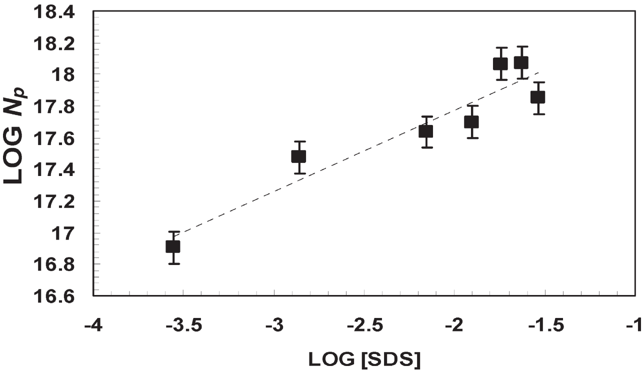


Figure 7. Effect of SDS concentration on the number of polymer latex particles per mL (N_p).

Table 1. Concentration of Micelles in Varying SDS Concentration[a]

SDS (wt %)	N_p (10^{17})	[SDS$_{free}$] (mM)	[micelle] (mM)	[monomer droplets] (mM)
10.5	5	283	5	0.010
8.5	6	201	4	0.014
4.5	2	109	2	0.004
2.5	3	~0	~0	0.007
0.5	1	~0	~0	0.004

[a] The amount of free SDS in solution was calculated from the molecular adsorption area of 60 Å/ molecule[28] and the concentration of micelle in the solution was calculated from the aggregation number of SDS micelles of 55[29].

Table 2. Effect of SDS Concentrations on the Molecular Weights of Poly(BMA) Latex Particles at Final Conversion

SDS (wt %)	$M_w \times 10^6$ (g/mol)	N_c (chains/particle)
10.5	6.95	3
6.5	7.17	3
4.5	7.27	4
0.5	7.34	7

It should be emphasized here that the profile of the particle number during the course of polymerization reaction depends not only on the number of particles generated, but also on their stability against flocculation.[30] It has also been discussed by Nomura and co-workers that the rate of desorption and readsorption of free radicals in emulsion polymerization will affect the number of particles generated in the system.[31,32] As the rate of desorption of monomeric radicals from smaller particles is considered to be faster than from larger particles, these radicals can therefore re-enter the monomer swollen micelles during the polymerization reaction and take part in the nucleation process. On the basis of these reasons, the increase in the number of particles during the course of the reaction should be the highest for the system containing the smallest particle sizes, which is what is observed in this study.

The weight average molecular weights (M_w) and number of polymer chains per latex particle (N_c) of poly (BMA) at final conversions are shown in Table 2. The molecular weight was observed to decrease with increasing amount of SDS. We have previously reported on this trend in molecular weights with variation in surfactant concentration[17] and has also been observed by other researchers.[33,34] One possible reason proposed for the decrease in molecular weight is the occurrence of chain transfer (reaction 10 in Scheme 1) to the surfactant as the ratio of surfactant to monomer increases (for example, for 10.5 wt % of SDS, the ratio of SDS to monomer is 4:1).[17,33] At high surfactant concentrations, the ensuing droplet size is smaller and it might be the case that the increasing proximity of the growing polymeric radical in the droplet to the surfactant adsorbed layer leads to an increase in chain transfer to the surfactant.

From the experimental molecular weight data and particle size (D_v), the number of polymer chains per latex particle (N_c) can be approximated. N_c increases from roughly 3 polymer chains per latex particle at high SDS concentration to about 7 polymer chains per latex particle at 0.5 wt % SDS with the growth of polymer particles.

On the basis of the results discussed above, a plausible mechanism for sonochemical microemulsion polymerization is the continuous particle nucleation mechanism which is supported by three main observations:[35] (1) a particle size which is usually larger than the initial monomer droplets, (2) a small number of polymer chains per latex particle, and (3) an increase in the number of particles over the course of the polymerization reaction. A comparison of the current results with previous studies conducted using high frequency ultrasound[17] shows that there are no apparent differences in the rates of polymerization nor the particle size and molecular weight trends, as the applied frequency was varied. Therefore, this type of polymerization appears to be largely independent of the applied frequency.

Conclusions

In this study, 20 kHz ultrasound was used as an alternative method to chemically synthesize near monodispersed, stable, and translucent latices. The effect of surfactant concentration on the properties of poly (BMA) latices was examined. The sonochemical microemulsion polymerization appears to offer an effective and controlled route in making polymer particles as evidenced in the linear first order kinetic plots and formation of polymers with narrow molecular weight and particle size distributions. The results from this study have led to the conclusion that the sonochemical microemulsion polymerization follows a continuous particle nucleation mechanism where polymerization initiation appears to take place within the monomer droplets. This is also the case for miniemulsion polymerization; however, in this case, the monomer droplets are ultrasonically dispersed.

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