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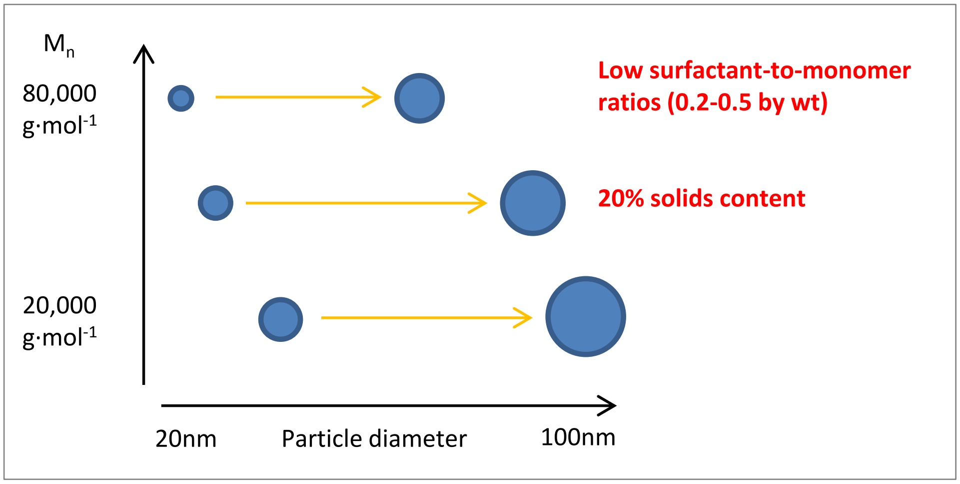
Independent control of molecular weight and particle size can be achieved in nitroxide-mediated n-butyl acrylate microemulsion polymerization



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ARTICLE TYPE

Nitroxide-Mediated Microemulsion Polymerization of *n*-Butyl Acrylate: Decoupling of Target Molecular Weight and Particle Size

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The independent control of particle size and molecular weight is a highly desirable yet challenging objective to achieve in SG1-mediated living radical emulsion polymerizations. For example, to preserve colloidal stability, reduction in particle size typically necessitates making higher molecular weight chains, severely constricting the usefulness of the process. The strong inverse correlation between target molecular weight and particle size has been successfully decoupled to a significant extent in nitroxide-mediated microemulsion polymerization of *n*-butyl acrylate using a two-stage differential monomer addition technique. These microemulsion polymerizations were carried out at 120°C using SG1-based alkoxyamine BlocBuilder® MA and the anionic surfactant Dowfax™ 8390 at low surfactant-to-monomer ratios (0.2:1 to 0.5:1 w/w) and a solids content of 20 wt.%. The nanolatexes were colloidally stable and the polymerizations showed living and controlled behaviour. The mean particle diameters obtained ranged from 20-100nm, although the focus was on particles in the 20-50 nm range, for target molecular weights from 20,000-80,000 g·mol^{-1}. These results show that changing the surfactant-to-monomer ratio, the BlocBuilder-to-buffer ratio, the initial monomer content in the seed stage, and surfactant feed rates can allow both molecular weight and particle size to be targeted independently in nitroxide-mediated microemulsion polymerization.

A Introduction

Living radical polymerization has emerged as an effective and powerful tool to produce tailored polymers with advanced characteristics. Nitroxide-mediated polymerization makes use of a stable free nitroxide radical to mediate the polymerization by acting as a regulator between the propagating polymer chains to establish a reversible termination process. The first nitroxide-mediated polymerizations were reported using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) in styrene polymerizations.[1] For the polymerization of acrylates, other nitroxides such as SG1 (1-diethylphosphono-2,2-dimethylpropyl) have been proven to be more effective in mediating the polymerization.[2] There is considerable interest in conducting living radical polymerizations in aqueous dispersions, especially when commercialization is desired.[3,4,5] Nitroxide-mediated polymerization has been successfully applied in microemulsion systems to yield controlled and living polymerizations.[1,2,6,7] Microemulsions are thermodynamically stable oil-in-water dispersions that can be used to obtain much smaller particle sizes due to the lower interfacial tensions achieved. Microemulsion polymerizations have been used to prepare the first stage seed particles in SG1-mediated emulsion polymerization.[7,22] As seed characteristics largely define final latex properties, being able to control the seed properties is important. Microemulsions are also potentially desirable for many applications such as adhesives, drug delivery, and microencapsulation as they provide a very large internal interfacial area for further functionalization.[8]

Compartmentalization effects comprising the segregation effect and the confined space effect have been shown to operate in microemulsion polymerizations as demonstrated by Tomoeda et al.[2] The segregation effect on termination enhances the rate of polymerization as the individual segregation of growing chains in different polymer particles reduces the probability of termination, slowing the accumulation of free nitroxide and giving higher polymerization rates. The confined space effect on the other hand results in a decrease in the rate of polymerization as a result of an increased rate of deactivation due to the close proximity of radicals within an individual small reaction volume (particle).[9] In living radical systems, the two effects combined generally result in a reduction in the overall rate of propagation as the confined space effect has a stronger influence than the segregation effect on the rate of polymerization.

In conventional (non-living) emulsion polymerizations, an increase in the initiator concentration results in a decrease in particle size due to an increase in the number of particles nucleated and the additional stabilization provided by the charged initiator end groups.[10] In NMP emulsion systems however, the opposite effect is observed where an increase in the initiator concentration results in an increase in particle size.[7] There are two reasons for this behaviour. The primary reason is superswelling, which is caused by a high concentration of short oligomers in the early stages of the polymerization, resulting in enhanced diffusion of monomer from monomer droplets to nucleated particles because of reduced monomer chemical potential in the particles.[11] The second reason has to do with the ionic strength contribution from the charged initiator end groups when using electrostatically stabilized systems. An increase in the ionic strength in the system can cause the electrical double layer of the particles to compress, lowering the repulsive forces between the particles. To address the superswelling problem, a two-stage polymerization approach[12,13] can be used which consists of creating a first stage living seed latex using initiator, nitroxide, water, surfactant, and a small amount of monomer. Semi-batch addition of the remaining monomer is then introduced. This approach eliminates the presence of monomer droplets during the time when most chains are oligomeric and the particles most prone to superswelling.

In most applications, it is desirable or essential to be able to produce particles with independent control of both molecular weight and particle size. One way this can be achieved is through the use of miniemulsion polymerization where the particle number and size are established at the beginning of the polymerization. However, this method is not easily implemented on an industrial scale as the droplet formation process can be a challenge at industrial scale. Microemulsions on the other hand can produce very small particles without the use of energy intensive processes. True microemulsions are thermodynamically stable oil-in-water dispersions and can be used to produce very small nanoparticles (<50 nm)[14] due to the large quantities of surfactants (and in some cases co-surfactants as well) typically used in microemulsions, which allow very low interfacial surface tensions to be achieved. The surfactant-to-monomer (S/M) ratios used in microemulsions are much higher than emulsions and are typically in the range of 1:1 to 3.3:1 by weight and are very dilute, with solids content in the range of ~1-10% by wt.[15] One disadvantage of using such a large quantity of surfactant in the microemulsion process is that it can hinder end-use performance of the final product. Other issues such as increased foaming, decreased adhesion, and reduced water resistance further limit the performance of traditional microemulsions and provide incentive to explore other ways to achieve stability with very small particle sizes.

Microemulsion polymerizations have been carried out using much lower than typical surfactant-to-monomer ratios in the past in non-living polymerization systems in an attempt to reduce the large quantities of surfactant.[16,17] These are not true microemulsions as they are not thermodynamically stable. The work by the groups of Pan and Rempel[13,18] in the low surfactant ranges by free radical polymerization have shown successful polymerization of polystyrene and PMMA and latexes with particle sizes in the 20 nm range using S/M ratios as low as 0.05:1 by wt. This is possible by the use of a two-stage differential monomer addition technique[12,13] as described before. Previous work in the Cunningham group in living systems with methyl methacrylate and styrene have shown that very small particles (20-30 nm) can be obtained using much lower S/M ratios (0.13:1-0.28:1 wt/wt) at much higher solids content (~40% solids by wt.).[7] Lower surfactant levels can be used for non-living systems as superswelling does not occur due to the similar rate of propagation between all particles. Previous work in the Cunningham groups has investigated this behaviour in emulsion systems in relation to effects of ionic strength, pH, buffer, and surfactant concentration on the 1st stage particle size.[20,21] Research on NMP in microemulsions of *n*-butyl acrylate using SG1 or TEMPO by Okubo and Zetterlund have shown successful polymerizations of stable latexes with particle sizes in the range of 20-60 nm but using higher S/M ratios (~2.5:1 wt/wt) and lower solids content (6-10 wt.%).[2,19] Tomoeda et al.[2] demonstrated controlled and living characteristics in a microemulsion of *n*-butyl acrylate with M_w/M_n of 1.6-2.0 using excess SG1 at a surfactant to monomer ratio of 2.5:1 (wt/wt) and 6 wt.% solids content, yielding D_n values of 20-184 nm depending on the ratio of excess nitroxide to initiator.

In nitroxide-mediated emulsion polymerization, a coupling effect between the particle size and molecular weight makes the independent control of each property difficult. Making low target molecular weight polymer requires a high concentration of chains, which exacerbates the superswelling problem. Furthermore, when using BlocBuilder® MA, more base (NaOH) must be added to the aqueous phase to solubilize the BlocBuilder® MA; this increases the ionic strength and further decreases colloidal stability. The combined effect is an increase in particle size. The essence of the problem is that the alkoxyamine concentration (which determines molecular weight) significantly impacts particle size even when using added anionic surfactant, and therefore the molecular weight and particle size cannot be independently controlled. This severely compromises the potential value of nitroxide-mediated microemulsions. However we have found that by careful manipulation of the reactant feed rates and concentrations, this problem can be overcome. It should be noted that the decoupling of the molecular weight and particle size has been previously demonstrated by Monteiro and co-workers[41-44] using RAFT in a nanoreactors system. In this paper, an approach to decouple the target molecular weight and particle size in nitroxide-mediated microemulsion polymerizations is presented. Stable *n*-butyl acrylate latexes were prepared by NMP in microemulsion using BlocBuilder® MA at low surfactant-to-monomer ratios (0.2:1 to 0.5:1 wt/wt) and moderate solids content (20 wt.%) without the use of excess SG1, with final particle diameters mostly ranging from 20-60 nm (increasing to 100nm) at target molecular weights of 20,000-80,000 g·mol^{-1}. These polymerizations were controlled and living with M_w/M_n maintained at ~1.4 and increasing to 1.8-2.0 at higher conversions. This work seeks to present a range of polymerization conditions and strategies that will allow both final particle size and molecular weight to be targeted separately in *n*-butyl acrylate microemulsions using BlocBuilder.

To our knowledge, this is the first report of the successful decoupling of particle size and target molecular weight to a significant extent in microemulsion using NMP at moderate solids content and low surfactant concentrations, allowing the independent control of both properties.

B Experimental

B.1 Materials

The compounds *n*-butyl acrylate (BA, Aldrich, 99%), 2-((tert-butyl(1-(diethixyphosphoryl)-2,2-dimethylpropyl)amino)oxy-2-

methylpropanoic acid (BlocBuilder® MA or BB, supplied by Arkema, 99%), Dowfax™ 8390 (Dow Chemicals, 25 wt% solution in water), sodium carbonate (Na_2CO_3, Aldrich, >99%) were used as received. Distilled, deionized water purified by a Millipore Synergy ion exchange unit was used for all experiments.

B.2 Microemulsion Polymerization of *n*-Butyl Acrylate

A two-stage polymerization method was adapted from that described by Charleux and coworkers.[22] BlocBuilder® MA (0.432 g, 1.134 mmol), Na_2CO_3 (0.300 g, 2.830 mmol), and DIW (8 g) were mixed overnight to form the ionized alkoxyamine initiator in solution. The 1st stage latex was prepared with *n*-butyl acrylate (3.6 g, 28.08 mmol), Dowfax™ 8390 solution (28.3 g, 15.40 mmol), DIW (225 g), and the ionized BlocBuilder solution in a 1L RC1 reaction calorimeter from Mettler Toledo (LM06). *N*-*b*utyl acrylate, Dowfax™ 8390, and DIW were combined in the reactor and sealed. Following a 30 minute purge of the reactor with nitrogen and a 10 minute purge of the ionized BB solution, the reactor was heated to 90°C at which point the ionized BB solution was added. The reactor was then heated to 120°C. *N*-butyl acrylate was purged with nitrogen for 20 minutes before being pumped into the reactor over one hour at a rate of 0.70 $mL \cdot min^{-1}$. The reactor contents were mixed by an anchor impeller at a rotation speed of 200 RPM. The polymerizations proceeded for 6 hours with samples withdrawn periodically.

B.3 Characterization

Monomer conversions were determined gravimetrically. Samples were withdrawn periodically and cooled in an ice water bath to stop polymerization. Subsequently, the samples were dried under air overnight at room temperature, then for 4 hours at 85°C in a ventilated oven. Molecular weight and polydispersity of the polymer samples were measured using gel permeation chromatography (GPC). Distilled THF was used as the eluent at a flow rate of 1 $mL \cdot min^{-1}$. A Waters GPC equipped with a Waters 2960 separation module containing four Styragel® columns (HR 0.5, HR 1, HR 3, HR 4) coupled with a Waters 410 differential refractive index detector calibrated with polystyrene standards ranging from 347 to 441,000 $g \cdot mol^{-1}$ was used. Mark-Houwink parameters used for the polystyrene standards are $K = 1.14 \times 10^{-4}$ $dL \cdot g^{-1}$, $a = 0.716$ [23] and for *n*-butyl acrylate are $K = 1.22 \times 10^{-4}$ $dL \cdot g^{-1}$, $a = 0.70$ [24], respectively. Particle size and zeta potential measurements were performed on a Malvern Zetasizer Nano ZS using a glass cuvette (83301-03) for particle size analysis and a universal dip cell (ZEN1002) for zeta potential. Particle size analysis using dynamic light scattering was done at 25°C and an angle of 173°, with dilution of samples with DIW prior to measurement. Reported intensity-average values are the average of 12 runs each. The refractive index for water used for the measurements is 1.330. The pH of the polymer latexes were measured with a Fisher Scientific AR25 pH meter calibrated with aqueous standards (pH 4, 7, and 10). Surface tension measurements were obtained using a TensioCAD tensiometer at room temperature by the Wilhelmy Plate method. Surfactant coverage analysis was done using the soap titration method by Maron et al.[25] with 3 min of stirring after each addition of surfactant.

C Results and Discussion

SG1-mediated microemulsion polymerizations of *n*-butyl acrylate were carried out using a two-step approach, with the first stage latex prepared using approximately 8% of the total monomer. Low surfactant-to-monomer ratios were used ranging from 0.2:1 to 0.5:1 (wt/wt). BlocBuilder® MA to Na_2CO_3 (buffer) ratios ranged from 0.4 to 1.0 (mol/mol). The effects of varying feed conditions, surfactant, monomer, and nitroxide concentrations, and target molecular weights on the final particle size were investigated to better understand the fundamental aspects of the latex stability and thereby allow development of a strategy to reduce the coupling effects between molecular weight and particle size. Stable microemulsions of 20 wt % solids were achieved with monomodal particle size distributions and mean particle sizes ranging from 20 to 100 nm.

C.1 Effects of Varying Overall Surfactant Concentration and Ionic Strength

The surfactant-to-monomer ratio (S/M) was varied to examine the effect on the final particle size when targeting different molecular weights. Theoretically, with the same amount of monomer, the particle size should decrease as the surfactant concentration is increased because of the ability to stabilize a higher number of smaller particles (i.e. higher overall particle surface area). To target different polymer molecular weights at the same solids content, the initiator concentration is usually varied. When targeting lower molecular weights, an increase in the number of initiator groups is necessary to obtain a higher number of polymer chains. In our NMP system, this means an increase in BlocBuilder® MA and base required for its ionization. However, this change in initiator concentration can lead to changes in the ionic strength of the system as this introduces more charged species into the system which raises the overall ionic strength. This increase in ionic strength can lead to an increase in particle size due to a decrease in the thickness of the electrical double layer of the particles.[20,26] Providing the system with more stabilizing groups may help to reduce this effect. However, the opposite trend was observed in our microemulsions where we obtained larger particle sizes with an increase in surfactant concentration.

This unusual behaviour has been previously observed by Tauer et al.[27] in a conventional free radical microemulsion polymerization of *n*-butyl acrylate. The authors described this correlation using particle nucleation theory, suggesting that the low monomer concentration caused by such a high amount of surfactant in the system causes short oligomers to grow out of the micelles with a lower average chain length and because more of them are needed to form a nucleus, the higher number of chains per critical nucleus results in larger nuclei. The increase in particle size with surfactant concentration was also observed by Loh et al.[28] in a methyl methacrylate emulsion system using CTAB (cetyl trimethylammonium bromide) at surfactant-to-monomer ratios exceeding 1.72, but not in an isobutyl methacrylate system, likely because of the more hydrophilic nature of MMA. Gan et al.[29] also observed the same trend in MMA microemulsion latexes but thought it was due to the interaction between CTAB micelles and polymer particles as measured by dynamic light scattering. The possibility that the

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Table 1 Final particle sizes and zeta potentials obtained for *n*-butyl acrylate microemulsion experiments by varying the surfactant to monomer ratio and target molecular weights.

Expt.	$M_{n,\ theo}$ ($g{\cdot}mol^{-1}$)	$M_{n,\ expt}$ ($g{\cdot}mol^{-1}$)	PDI	Particle Diameter[a] (nm)	ζ-potential (mV)	N_p/L_{aq}	Conversion
S21	19,000	20,600	1.64	70.02	-37.9	$9.27\text{x}10^{17}$	0.90
S22	20,200	18,400	1.71	104.2	-15	$2.64\text{x}10^{17}$	1.00
S41	37,000	44,000	1.67	41.54	-69.3	$4.63\text{x}10^{18}$	0.92
S42	41,000	45,800	1.83	49.43	--	$2.85\text{x}10^{18}$	0.97
S43	38,800	31,500	2.25	64.89	-44.5	$1.19\text{x}10^{18}$	0.99
S81	65,000	53,300	1.94	37.11	-53.7	$6.63\text{x}10^{18}$	0.82
S82	76,300	50,200	2.28	51.87	-36.8	$2.34\text{x}10^{18}$	0.95

[a] Particle size listed is the intensity average particle size (d_z) from the Malvern Nanosizer.

All experiments listed here have 20 wt.% solids content and a BlocBuilder/Na_2CO_3 molar ratio of 0.4.

high surfactant concentration leads to a reduced number of micelles as they form higher order structures resulting in larger particles has also been suggested by no evidence was provided in a styrene microemulsion system using SDS as surfactant and 1-pentanol as cosurfactant.[30] These studies show that different types of monomer and surfactant used can lead to different effects of increased surfactant concentration on the stabilization mechanisms and kinetics.

SG1-mediated microemulsion polymerizations were carried out at low surfactant-to-monomer ratios, from 0.2:1 to 0.5:1 (wt/wt). The overall surfactant concentration was varied while keeping all other variables the same, except for the amount of BlocBuilder, which was varied to target different molecular weights (Table 1). The amount of monomer at the seed stage was kept constant. For a target M_n of 40,000 $g{\cdot}mol^{-1}$, the mean particle size increased from 42 to 65 nm as the S/M ratio increased from 0.2:1 to 0.5:1 (S41-S43), opposite to what was expected. Lowering the surfactant-to-monomer ratio to 0.1:1 (wt/wt) resulted in a bimodal particle size distribution with particle diameters of 42 nm and 350 nm. This was likely due to an insufficient amount of surfactant to stabilize all the growing particles, causing some particles to aggregate. It is suspected that at the low surfactant concentration range studied, the ionic strength of the system plays a more important role in colloidal stability, resulting in an increase in particle size. If there is sufficient surfactant present, the excess surfactant molecules that are not adsorbed onto the surface of the particles will remain free in the aqueous phase, or form micelles above the CMC. With a higher number of excess surfactant molecules, the ionic strength contribution would be greater, thus exerting a larger influence on the electrical double layer. Comparatively, a lower amount of excess surfactant would impart lower ionic strength effects and would result in a thicker double layer.

Surface tension experiments, using a soap titration method developed by Maron et al.[25] revealed a slightly lower surfactant coverage for the run at a higher S/M ratio at 76 % for S/M = 0.5:1 (S43) and 83 % for S/M = 0.2:1 (S41). Calculations based on this show that a larger total particle surface area is covered in S41 with smaller particles than in S43 with larger particles. This suggests a higher amount of excess surfactant in the aqueous phase for S43 which will contribute to a higher ionic strength. The same trend of increased particle size with an increase in surfactant was observed for target molecular weights of 20,000 and 80,000 $g{\cdot}mol^{-1}$ as shown in Figure 1.

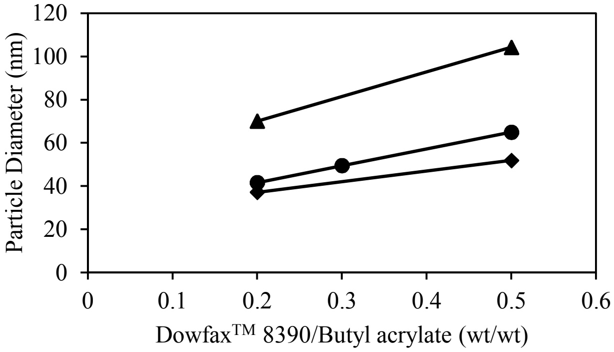

Fig. 1 Particle sizes obtained from varying the surfactant-to-monomer ratio at target M_n of 20,000 $g{\cdot}mol^{-1}$ (▲), 40,000 $g{\cdot}mol^{-1}$ (●), 80,000 $g{\cdot}mol^{-1}$ (◆).

The final number of particles is consistent with the particle size observations. Although a higher surfactant concentration is able to support more particles, it appears that this is not the case as fewer particles are obtained. One possibility could be due to the ionic strength contribution from the excess surfactant being sufficiently high enough to cause the electrical double layer to contract and allow the particles to aggregate more easily, resulting in a fewer number of larger particles. Another possibility could be due to insufficient monomer in the seed stage to nucleate a larger number of particles. The higher micelle concentration allows for more sites for particle nucleation, but the lower amount of monomer available in the aqueous phase may

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Table 2 Formulations for the salt substitution microemulsion polymerizations of *n*-butyl acrylate.

Expt.	Salt	BA:Dowfax^{TM} 8390:BB ratio	[Dowfax^{TM} 8390] (M)	[Salt] (M)	$M_{n,\ theo}$ (g·mol^{-1})	$M_{n,\ expt}$ (g·mol^{-1})	PDI	Particle Diameter^a (nm)	Conversion
SB1	--	309:13:1	0.06	--	38,800	31,500	2.25	40.4	0.99
SB2	--	309:31:1	0.14	--	40,100	30,500	2.27	64.9	0.99
SB3	NaCl	309:13:1	0.06	0.08	37,500	30,400	2.14	78.1	0.94
SB4	CH_3SO_3Na	309:13:1	0.06	0.08	33,900	38,000	1.55	76.8	0.89

^{a} Particle size listed is the intensity average particle size (d_z) from the Malvern Nanosizer.

The alkoxyamine initiator BlocBuilder® MA (BB) was added to the aqueous phase in its carboxylated form , neutralized with Na_2CO_3 at a molar ratio of BB/Na_2CO_3 of 0.4:1.

All experiments listed are based on a target molecular weight of 40,000 g·mol^{-1} at 20 wt.% solids.

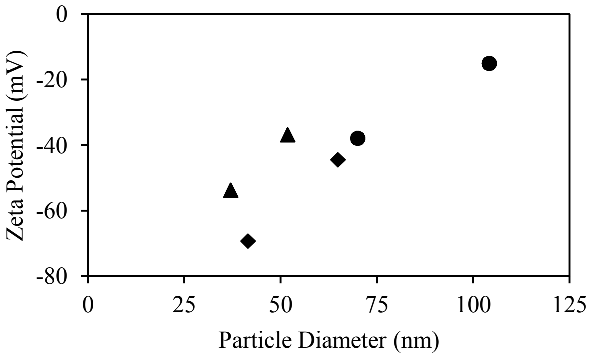

Fig. 2 Plot of zeta-potential vs. particle diameter obtained from the microemulsion polymerization of *n*-butyl acrylate using a surfactant-to-monomer ratio of 0.2:1 and 0.5:1 at a target M_n of 20,000 g·mol^{-1} (▲), 40,000 g·mol^{-1} (●), 80,000 g·mol^{-1} (◆).

prevent oligomeric radicals from reaching the critical chain length for entry into particles in the seed stage. Thus, the number of particles established in the seed stage is lower.

The increase in particle size was accompanied by an increase in the zeta-potential as can be observed in Figure 2. The zeta-potential, being affected by the ionic strength of the system, changes with the surface charges on the polymer particles and the properties of the surrounding medium. An increase in the ionic strength of the medium will lower the zeta-potential as the accumulation of counterions close to the surface of the polymer particles causes the surface charges to be screened. The higher the zeta-potential, the stronger the electrostatic repulsion between the particles and the more stable the latex. A drop in the zeta-potential from -69.4 mV to -44.5 mV was observed with an increase in the surfactant concentration (Table 1), indicating a weaker stabilization, which was likely caused by an increase in ionic strength from the additional Dowfax^{TM} 8390. The structure of Dowfax^{TM} 8390 is shown in Figure 3a.

Dowfax^{TM} 8390 is an anionic disulfonated surfactant, having a higher local charge density compared to monosulfonated surfactants. It is possible that the effect of the ionic strength contribution from the surfactant is higher than the effect of the stabilization it provides under these conditions causing the particle size to increase. Minute amounts of impurities in the Dowfax^{TM} 8390 solution can negatively affect colloidal stability. Other than the active ingredients (disodium hexadecyldiphenyloxide disulfonate and disodium dihexadecyldiphenyloxide disulfonate), 0.2% NaCl and 0.5% Na_2SO_4 are also present. To investigate the ionic strength contribution from Dowfax^{TM} 8390, a substitution experiment was carried out. The ionic strength effect from increasing the S/M from 0.2:1 to 0.5:1 (wt/wt) was investigated by substituting the difference in surfactant concentration with a molar equivalent of a salt.

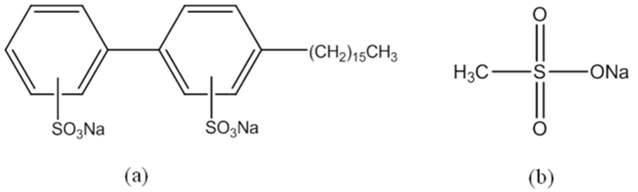

Fig. 3 Structure of (a) the anionic surfactant Dowfax^{TM} 8390 and (b) sodium methanesulfonate.

Sodium methanesulfonate (CH_3SO_3Na), depicted in Figure 3b, and sodium chloride (NaCl) were chosen to mimic the ionic strength effects of Dowfax^{TM} 8390. Sodium methanesulfonate was selected as it has the same sulfonate end as Dowfax^{TM} 8390 but without the long alkyl chain that provides stabilization. This allows the non-stabilizing effects of the surfactant to become apparent. Without substitution with a salt, the difference in particle diameter between the run at S/M = 0.2:1 (SB1) and that at S/M = 0.5:1 (SB2) was approximately 25 nm (Table 2). With the substitution of CH_3SO_3Na (SB4), the particle diameter was about 10 nm larger than that of SB2. This difference is likely attributable to the stabilization provided by the additional Dowfax^{TM} 8390 in SB2 compared to SB4. The same experiment was carried out using NaCl (SB3) and the effect on particle size is almost identical to that using CH_3SO_3Na as seen in Figure 4. From these experiments, it is believed that the increase in ionic strength from the charged species and contaminants from the additional Dowfax^{TM} 8390 results in the aggregation of the particles and leads to larger particle sizes as van der Waals forces take over. The addition of salts is known to aid coagulation in polymer colloids and the similarity between the effect of CH_3SO_3Na and NaCl show that Dowfax^{TM} 8390 is likely to increase the overall ionic strength in the system enough to cause some particles to aggregate.

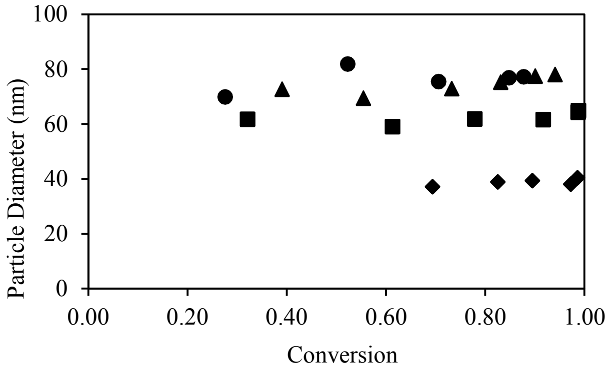

Fig. 4 Particle size evolution for the salt-substituted microemulsion polymerizations. The molar difference in additional surfactant was substituted with a molar equivalence of salt to mimic the higher surfactant concentration runs. S/M = 0.2:1 (SB1,◆), S/M = 0.5:1 (SB2,■), S/M = 0.2:1 with NaCl (SB3, ▲), S/M = 0.2:1 with CH_3SO_3Na (SB4, ●).

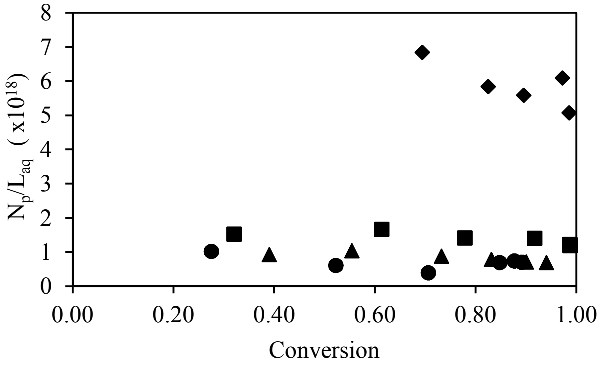

Fig. 5 Number of particles vs. conversion profiles for the salt-substituted microemulsion polymerizations SB1-SB4. The molar difference in additional surfactant was substituted with a molar equivalence of salt to mimic the higher surfactant concentration runs. S/M = 0.2:1 (SB1,◆), S/M = 0.5:1 (SB2,■), S/M = 0.2:1 with NaCl (SB3, ▲), S/M = 0.2:1 with CH_3SO_3Na (SB4, ●).

The number of particles formed in the system is also consistent with the particle sizes obtained as observed in Figure 5. Experiment SB1 yielded the smallest particle size and had the most number of particles, while the runs with the larger particle sizes (SB2-4) had a lower number of particles in the system. This is in good agreement with the observation that the number of particles decreases as the surfactant concentration increases leading to larger particles. Both the rate of free radical generation and the ionic strength have a large effect on the particle number.[31]

The salt substitution experiments show that the overall ionic strength contribution plays a major role in determining the minimum particle size achievable in microemulsions using very low concentrations of surfactant. Beyond a certain S/M ratio, further increase in available surfactant seizes to result in a higher number of particles. This is mostly due to the fact that the monomer in the system already experiences maximum stabilization and the further addition of surfactant no longer aids in the generation of new particles. As the interfacial tension cannot decrease beyond the minimum possible, the excess free surfactant molecules will result in an accumulation of free ions in the system, hence increasing the ionic strength.

C.2 Effect of Monomer Concentration at the Seed Stage

In the S series of experiments, the monomer content in the first stage was kept constant while varying the concentration of BlocBuilder, so that the monomer units available to add to each alkoxyamine group varied between the different target molecular weight experiments. As the particle nucleation process is extremely sensitive in the seed stage, the interactions between the surfactant, nitroxide, initiator, and monomer can vary significantly with changes in their proportions. The extent to which the final particle size can be varied within a target molecular weight range by changing the initial monomer content, while keeping the overall monomer content the same, was explored in an attempt to further decouple the two effects.

Depending on the target molecular weight, the number of *n*-butyl acrylate units available to add on to each chain varied. A set of experiments were carried with the monomer content in the seed stage varying from 4 to 16 wt. %, while the overall monomer content remained constant. It is important to note that while the overall surfactant to monomer ratio is kept the same, varying the initial monomer concentration changes this ratio in the seed stage. Increasing the monomer content from 4% to 16% in the 1st stage decreases the S/M ratio from 5.4:1 to 1.4:1 (wt/wt) in the 1st stage for overall S/M = 0.2:1 and from 12.4:1 to 3.1:1 (wt/wt) for overall S/M = 0.5:1.

For all target molecular weights, increasing the initial monomer seed content led to a decrease in the final particle size. In addition, larger particle sizes were obtained at higher surfactant concentrations, consistent with the trend observed in the S series of experiments, as shown in Figure 6a-c. Increasing the monomer content led to an increase in the number of particles generated in the system, resulting in a decrease in the particle size. This trend was also consistent at both S/M ratios of 0.2:1 and 0.5:1. Another interesting observation is that the difference in the particle sizes obtained between S/M ratios of 0.2:1 and 0.5:1 appear to decrease as the amount of initial monomer is increased. It could be possible that with enough initial monomer to begin with, this trend may be reversed. As the number of chains is fixed by the amount of BlocBuilder added to the system, the increased monomer available in the 1st stage could mean that chains can nucleate particles faster as the oligomeric radicals can reach the critical length for entry sooner. The higher rate of monomer addition can also ensure that the growing chains are sufficiently water insoluble so they remain inside the monomer swollen micelles for nucleation. If there is not enough monomer, the oligomeric radicals may still be sufficiently water soluble to exit micelles and remain in the aqueous phase, leading to a lower number of seed particles before further monomer addition. The more seed particles generated, the smaller each particle will be, provided there is sufficient surfactant to stabilize all the growing polymer particles. It is evident that the segregation effect[32-34] is in play here as the higher number of particles achieved at a higher 1st stage monomer concentration led to an increase in the rate of polymerization as observed in the conversion-time profiles in Figure 7.

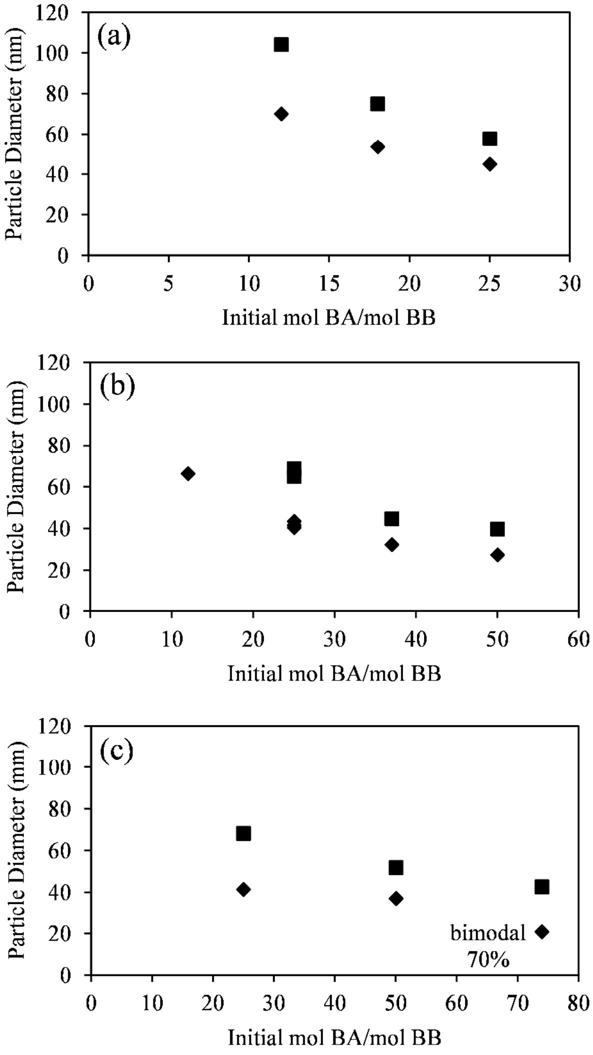

Fig. 6 Final particle sizes for microemulsion experiments at target M_n of (a) 20,000 g·mol^{-1}, (b) 40,000 g·mol^{-1}, (c) 80,000 g·mol^{-1}, at S/M = 0.2:1 (◆) and S/M = 0.5:1 (■) for a BB/Na_2CO_3 molar ratio of 0.4:1.

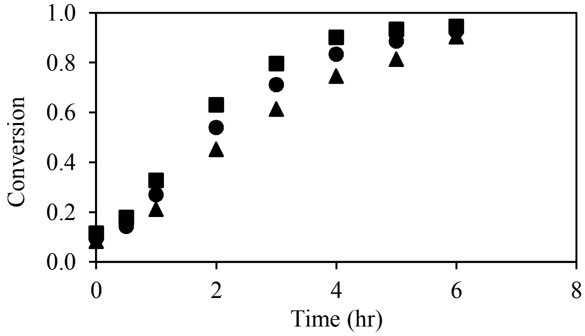

Fig. 7 Conversion-time profiles for *n*-butyl acrylate microemulsion experiments carried out at target M_n = 20,000 g·mol^{-1}at initial monomer contents of 8% (▲), 12% (●), and 16% (■) at S/M = 0.2:1.

The larger number of smaller-sized particles results in increased segregation of the radicals leading to reduced chances of termination. The increased monomer concentration in the seed stage also helps to maximize the number of chains generated in the system by reducing the likelihood of biradical termination early on in the polymerization. The more monomer available means that the oligomeric radicals are more likely to react with a monomer unit than with another oligomeric radical in the aqueous phase before entry into a micelle. However, too much monomer present in the seed stage could lead to superswelling of the particles resulting in decreased colloidal stability and larger particle sizes.[11]

By varying the monomer content in the seed stage from 4% to 16% at an overall surfactant to monomer ratio of 0.2:1, particle sizes from 45-70 nm, 28-66 nm, and 21-44 nm can be obtained at target molecular weights of 20,000 g·mol^{-1}, 40,000 g·mol^{-1}, and 80,000 g·mol^{-1} respectively. This further broadens the range of particle sizes obtainable at different target molecular weights and is another technique that can be used to decouple the two effects.

C.3 Effect of Semi-Batch Addition of Surfactant

A series of four experiments were carried out to examine the effects of varying the feed of Dowfax^{TM} 8390 to the reactor on the final particle size. The amount of surfactant fed into the reactor over time was set at 0%, 25%, 50%, and 75% of the total surfactant in the formulation (Table 3). The surfactant concentrations at the seed stage for all experiments are above the CMC. The results obtained were expected, with the smallest particle sizes obtained with all of the surfactant present in the reactor at the beginning (F1, 0% feed) and the largest particle sizes obtained with the least amount of surfactant to begin with (F4, 75% feed). Figure 8 shows a significant particle size difference of approximately 40 nm between runs F1 and F4. There is however, not a significant difference between the particle sizes obtained from surfactant feeds of 25% and 50% of the total surfactant concentration. The initial concentration of surfactant in the system is crucial in establishing the number of particles as it dictates the number of micelles generated, so a lower amount of surfactant will lead to a lower number of micelles and vice versa. The number of particles established in each of the four runs is shown in Figure 9 with respect to the initial Dowfax^{TM} 8390 concentration in the system and is in agreement with the particle sizes obtained, where the smallest particle sizes were achieved at the highest number of particles.

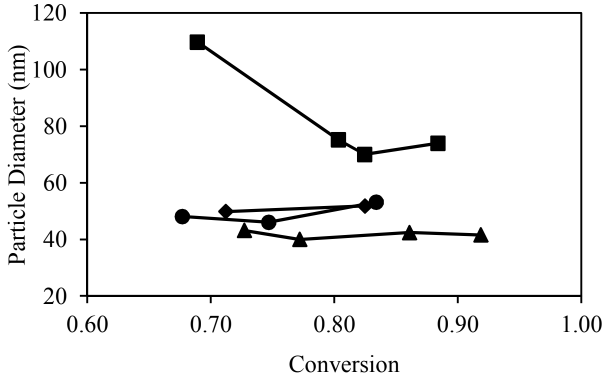

Fig.8 Particle size evolution for *n*-butyl acrylate microemulsion experiments with semi-batch addition of Dowfax^{TM} 8390 at 0% (F1, ▲), 25% (F2, ◆), 50% (F3, ■), and 75% (F4, ●) of the total Dowfax^{TM} 8390 content.

Table 3 Summary of the final particle size and zeta potential measurements of *n*-butyl acrylate microemulsion experiments with semi-batch addition of Dowfax™ 8390.

Expt.	Surfactant Feed (%)	$M_{n,\,theo}$ ($g{\cdot}mol^{-1}$)	$M_{n,\,expt}$ ($g{\cdot}mol^{-1}$)	PDI	Particle Diameter[a] (nm)	ζ-potential (mV)	Conversion
F1	0	37,000	44,000	1.67	40.4	-69.3	0.92
F2	25	35,100	39,000	1.66	51.8	-59.3	0.83
F3	50	35,200	41,000	1.83	53.2	-47.1	0.83
F4	75	34,300	37,000	1.86	74.0	-46.7	0.88

[a] Particle size listed is the intensity average particle size (d_z) from the Malvern Nanosizer.

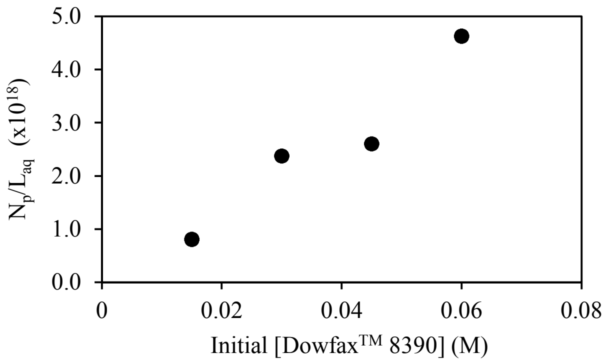

Fig. 9 Number of particles attained by varying the initial surfactant concentration in the SG1-mediated microemulsion polymerization of *n*-butyl acrylate.

From Figure 9, it is clear that the subsequent feed of surfactant does not help to reduce the particle size back down to that of F1 even though the overall surfactant concentration in the system is the same. The difference is the surfactant concentration in the 1st stage latex. Most of the activity during particle nucleation occurs at the initial stage of the polymerization and it is the reactions at this step that are crucial in establishing the particle number. Once the micelles and particles have been established, further addition of surfactant mainly helps with stabilization of existing particles and if present above the CMC, will form micelles but will not likely generate new particles.

It is important to note that in this series of experiments, the decrease in surfactant concentration in the first stage with the overall surfactant concentration in the system staying constant leads to larger particle sizes. In comparison to the S series of experiments where the decrease in overall surfactant concentration leads to smaller particles, the key difference between the two observed trends is the surfactant concentration in the 1st stage. With regards to experiments S1 to S3, the particle nucleation stage experiences the full amount of stabilization and ionic strength effects as all of the surfactant is present in the initial stage. Even though the number of micelles is expected to be greater in runs S42 and S43 in comparison to S41, the increase in ionic strength at this stage can cause the nucleated particles to aggregate early on resulting in larger than expected particles leading to a lower particle number as well. In experiments F1 to F4, the particle nucleation stage is affected by only a partial amount of stabilization and ionic strength effects. The overall surfactant concentration remains the same so the degree of compression of the electrical double layer between the runs due to ionic strength effects is expected to be relatively the same. Once the particles have been established, additional surfactant fed to the system mainly provides stabilization to the growing particles and is not likely to contribute to new particle formation as all the chains have likely already gained entry into particles or micelles. As a result, the particle size cannot decrease from what was initially established at the seed stage. Varying the feed of surfactant over time provides another way to control the particle size within the same formulation and still obtain stable latexes. The addition of surfactant using a semi-batch approach can be used to increase particle sizes at a given target molecular weight.

C.4 Effect of BlocBuilder to Na_2CO_3 Ratio

Several experiments were carried out at different molar ratios of BlocBuilder® MA to Na_2CO_3 for a series of target molecular weights and surfactant concentrations. The addition of the base serves two purposes, to ionize the BlocBuilder and to provide buffering capacity for the system to prevent the pH from dropping too low. Thomson et al.[20] observed an increase in particle size with a decrease in pH when varying the buffer concentration in high solids nitroxide-mediated emulsion polymerization using Di-BlocBuilder. The ratio of BlocBuilder to Na_2CO_3 in the system is crucial for a successful microemulsion polymerization that is stable, controlled, and living. Previous studies in our laboratory[20] have compared the use of different types of base to ionize BlocBuilder® MA and found that Na_2CO_3 is the most suitable for obtaining very small particles. Compared to the use of NaOH, the final particle size was approximately 130 nm smaller when using Na_2CO_3 because of the difference in ionic strength contribution.

There does not appear to be a significant impact when changing the BB/Na_2CO_3 ratio from 0.4:1 to 0.8:1 but an increase in particle size was observed when increasing from 0.8:1 to 1.0:1 as seen in Figure 10. The same trend is observed at different S/M ratios as well for both target M_n of 40,000 and 80,000 $g{\cdot}mol^{-1}$. One reason for the increase in particle size at higher BB/Na_2CO_3 ratios is the possible incomplete ionization of BlocBuilder. If

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Table 4 Summary of the final particle size, molecular weight, and zeta-potential measurements by varying the BlocBuilder to Na_2CO_3 molar ratios of SG1-mediated microemulsion polymerizations of *n*-butyl acrylate at a solids content of 20 wt.%.

Expt.	S/M (wt/wt)	BB/Na_2CO_3 (mol/mol)	$M_{n,\,theo}$ ($g{\cdot}mol^{-1}$)	$M_{n,\,expt}$ ($g{\cdot}mol^{-1}$)	PDI	Particle diameter[a] (nm)	ζ-potential (mV)	Conversion
B41	0.2	0.4	37,000	44,000	1.67	41.5	-69.3	0.92
B42	0.2	0.8	37,400	40,700	1.89	41.1	-69.6	0.97
B43	0.2	1.0	36,800	41,000	1.83	48.1	-71.3	0.89
B44	0.5	0.4	43,300	49,400	1.86	68.7	-44.5	1.00
B45	0.5	0.8	40,900	44,000	1.88	74.1	--	1.00
B46	0.5	1.0	41,200	42,900	1.87	93.7	--	1.00
B81	0.2	0.4	65,100	53,400	1.94	37.1	-53.7	0.82
B82	0.2	0.8	68,000	47,200	2.29	39.0	-69.6	0.91
B83	0.2	1.0	68,700	48,500	2.18	29.1[b]	-73.3	0.86
B84	0.5	0.4	76,300	50,200	2.28	51.9	-36.8	0.95
B85	0.5	0.8	78,100	51,200	2.47	51.1	-41.3	0.98
B86	0.5	1.0	77,400	44,900	2.77	54.3	-56.4	0.97

[a] Particle size listed is the intensity average particle size (d_z) from the Malvern Nanosizer.

[b] Bimodal particle size distribution (63%- 29.1nm, 33%- 275.7nm)

B41-B46 have target M_n=40,000 $g{\cdot}mol^{-1}$.

B81-B86 have target M_n=80,000 $g{\cdot}mol^{-1}$.

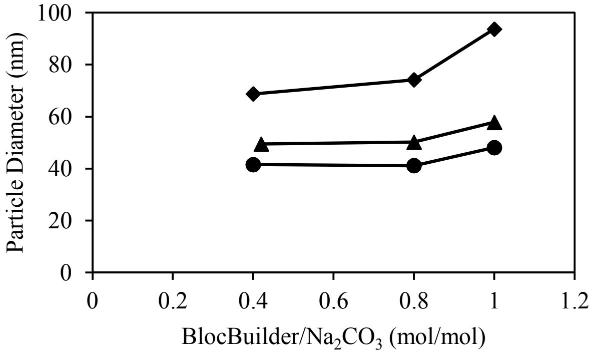

Fig. 10 Particle sizes obtained by varying the BlocBuilder to Na_2CO_3 molar ratio at a target M_n of 40,00 $g{\cdot}mol^{-1}$ and at S/M = 0.2:1 (●), S/M = 0.3:1 (▲), and S/M = 0.5:1 (◆).

there is insufficient sodium carbonate to convert the alkoxyamine to its water-soluble form, some of the alkoxyamine initiators will not be able to initiate chains in the aqueous phase leading to a decrease in the number of chains in the system. This can lead to the nucleation of fewer particles and hence each particle will be larger in size. The initiator can also be buried inside empty micelles, eliminating them from the particle nucleation process, resulting in lower than expected molecular weights. The pH of the microemulsions dropped from ~8.8-9.1 to ~5.3-5.6 throughout the course of the polymerization and did not vary too much between the different BB/Na_2CO_3 ratios used. This indicates sufficient buffering of the system as the pH of all experiments was maintained above 5.0 at full conversion. Increasing the amount of sodium carbonate over the range studied did not affect the particle size significantly but at even lower BB/Na_2CO_3 ratios, the particle size is expected to increase as the excess Na_2CO_3 contributes more to the ionic strength of the system. Similar to the effect of increased Dowfax^{TM} 8390, additional Na_2CO_3 can contribute to poorer stabilization causing the polymer particles to aggregate and form larger particles.

C.5 Molecular Weight Distributions

The molecular weight distributions showed controlled and living behaviour with M_w/M_n maintained around 1.4 up to approximately 70% conversion, where it then increased to approximately 1.8 at higher conversions, likely caused by increased termination as the supply of monomer reaches depletion approaching full conversion. This is comparable to other SG1-mediated microemulsions of *n*-butyl acrylate by other groups.[2,12] Tailing observed in the GPC traces at the low molecular weight end indicate termination of short chains early on in the polymerization. In some of the experiments, there is a slight overlap of the GPC traces at the low molecular weight end at higher conversions which indicate newly formed chains in the later stages of the polymerization (Figure 11). In all the experiments carried out, the experimental M_n matched closely with that of the theoretical M_n except for the target M_n of 80,000 $g{\cdot}mol^{-1}$ as shown for the M series in Table 5.

For the runs carried out at a target M_n of 80,000$g{\cdot}mol^{-1}$, the experimental M_n was always less than the theoretical M_n, reaching approximately 70-80% of the theoretical M_n at full conversion. The molecular weight distributions are also very broad for these, with $M_w/M_n > 2.0$. It is usually normal to observe a higher than expected molecular weight, especially with biradical termination by combination. However, a lower than

Table 5 Summary of the molecular weights obtained for the M series of SG1-mediated microemulsion polymerizations of *n*-butyl acrylate at solids content of 20 wt.%.

Expt.	$M_{n,\ theo}$ (g·mol^{-1})	$M_{n,\ expt}$ (g·mol^{-1})	PDI	Conversion
M21^{b}	19,000	20,600	1.64	0.90
M22^{b}	18,900	26,800	1.38	0.93
M23^{b}	19,200	19,100	1.64	0.95
M24^{c}	20,200	18,400	1.71	1.00
M25^{c}	19,900	16,600	1.95	1.00
M26^{c}	20,200	--	--	1.00
M41$_{b}$	33,200	28,300	1.69	0.78
M42^{b}	37,000	44,000	1.67	0.92
M43^{b}	36,300	29,300	1.66	0.92
M44^{b}	37,800	31,300	--	0.98
M45^{c}	38,800	31,500	2.25	0.99
M46^{c}	39,800	--	--	0.98
M47^{c}	40,600	50,500	1.58	1.00
M81^{b}	70,900	44,600	2.51	0.86
M82^{b}	65,000	53,300	1.94	0.82
M83^{b}	72,400	--	--	0.92
M84^{c}	78,300	40,000	2.65	0.98
M85^{c}	76,000	50,200	2.28	0.95
M86^{c}	76,000	45,000	3.26	0.97

[a] Particle size listed is the intensity average particle size (d_z) from the Malvern Nanosizer.

[b] S/M (wt/wt) = 0.2:1

[c] S/M (wt/wt) = 0.5:1

theoretical M_n indicates that there are more chains in the system than theoretically possible, assuming the maximum number of chains is solely determined by the concentration of BlocBuilder in the system, or most of the chains are shorter than what they should be. This behaviour is often observed in styrene polymerizations where thermal initiation will result in the generation of radicals at high temperatures[35] and chain transfer to monomer can also occur.[36] Backbiting in *n*-butyl acrylate polymerizations have been shown to lead to this as well.[37] Therefore, the observed result could possibly be due to thermal initiation or chain transfer to monomer or polymer. Thermal initiation results in the generation of new radicals which can propagate and form new polymer chains, thus resulting in shorter chains as there are less monomer units available for each chain to add. Thermal initiation in *n*-butyl acrylate systems is possible but should not be too significant at temperatures below 140 °C,[38] so new chain formation originating from that should be minimal. Dowfax^{TM} 8390 is thermally stable at temperatures up to 180 °C so thermal degradation should also not be a problem. The cause of new radical generation could be from impurities from the *n*-butyl acrylate monomer as it was not purified by passing though an inhibitor removal column prior to use. Chain transfer to monomer results in one dead chain of length *n* and a monomeric radical that can continue to propagate. This mechanism could be operational in our system and can be the reason for the generation of lower molecular weight species later on in the polymerization as observed in the overlapping GPC traces. The possibility of β-scission can also be a cause of dead chains in the system leading to higher polydispersities.

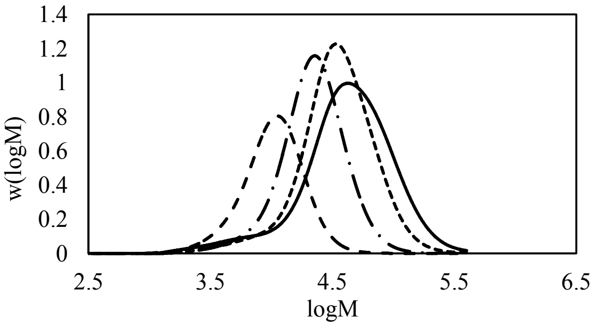

Fig. 11 Molecular weight distribution scaled proportional to conversion showing the generation of new lower molecular weight species in the later stages of polymerization for expt. SB1 ($M_{n,expt}$ = 30,500 g·mol^{-1}. $M_{n,theo}$ = 40,100 g·mol^{-1}). Conversions are at 45% (––), 69% (---), 82% (--), and 99% (–).

The thermal initiation of *n*-butyl acrylate was further investigated in an experiment carried out with just monomer, surfactant, and water. The microemulsion was left to react at 120 °C for 5 hours. After just one hour, polymerization was clearly evident as the reaction mixture turned a slight milky white with a conversion of 12%, and reaching 37% in 5 hours. By comparison to the controlled polymerizations using BlocBuilder, the percent of thermally initiated chains was approximately 1-3 % of the total generated chains. Whether the polymerization was a result of radicals generated from *n*-butyl acrylate or Dowfax^{TM} 8390, these events can explain why lower molecular weight species are created in the middle of the polymerization and why there are more chains formed than theoretically anticipated resulting in a lower than theoretical M_n, as well as broader molecular weight distributions.

Branching in the SG1-mediated microemulsions of *n*-butyl acrylate was also investigated as the presence of branched samples will result in deviations from the true molecular weight because their molecular density is higher than in linear chains. ^{13}C NMR was performed to identify the presence of branching in the polymer. Figure 12 shows the NMR spectrum obtained with peak assignments shown in Table 6, showing evidence of branching by chain transfer to polymer. The assignment of peaks was verified against previous chain transfer studies by NMR of *n*-butyl acrylate.[39,40] As the signal intensities do not necessarily reflect the abundance of carbon in the sample using a fast pulse interval due to different relaxation times and nuclear Overhauser effects (NOE), the extent of branching was quantified using NOE suppression by ^{13}C NMR with inverse gated decoupling using a slower pulse interval. The mole percent branching was calculated by comparison of the integrations of the branched CH and CH_2 carbon resonances to that of the total backbone carbons. Comparison of the quaternary carbon integral can also be made to the total backbone carbon integral but was found to be less accurate in a study by Ahmad et al..[39] They also found that the relative intensities of the CH and CH_2 carbon signals from a fast pulse spectrum reflect quite accurately the actual abundance of the corresponding carbons. This means that as long as the branching calculations incorporate the branched CH and CH_2 carbon signals and not the quaternary carbon signal, an inverse gated experiment using a slower pulse interval is not necessary. The percent branching of sample M82 was calculated to be approximately 2.8 mol %. Although the extent of branching is

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Table 6 ^{13}C NMR peak assignments of poly(*n*-butyl acrylate) in $CDCl_3$ corresponding to the spectrum in Figure 12.

Peak	Chemical shift/ppm	Assignment	Integration
A	28.4-30.0	end group - $CH_2CH_2COO(CH_2)_3CH_3$	0.21
B	30.6	2-CH_2 in n-butyl side group	1.59
C	31.8	end group - $CH_2CH_2COO(CH_2)_3CH_3$	0.07
D	33.9-37.1	main chain CH_2	0.84
E	41-42.0	main chain CH	1.00
F	48.4	branch quaternary carbon	0.03
G	37.1-38.6	CH_2 adjacent to branch	0.04
H	38.6-40.0	CH adjacent to branch	0.11

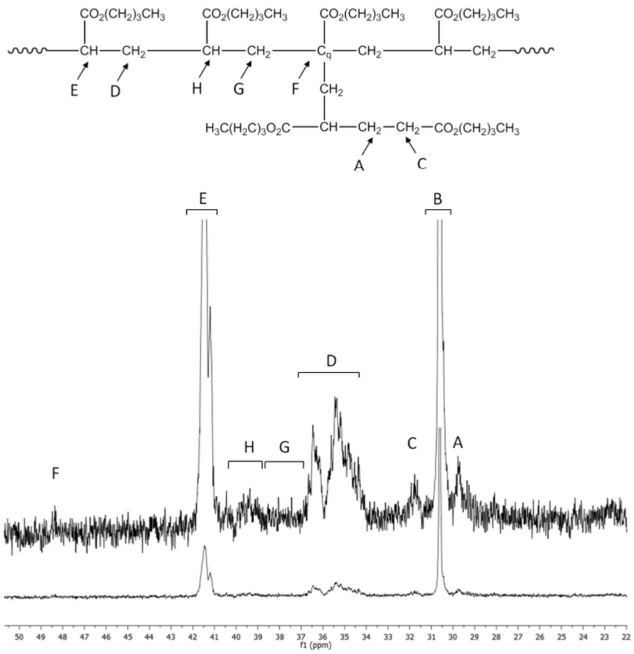

Fig. 12 ^{13}C NMR spectrum of poly(*n*-butyl acrylate) M82 recorded using CDCl3 as solvent. The assignments of the labelled peaks are given in Table 5.

small, it can cause slight discrepancies between the actual and theoretical molecular weights determined by GPC because of different spatial orientations of the polymer chains in solution.

C.6 Decoupling Target Molecular Weight and Particle Size

Combining all the different methods discussed to alter the particle size at different target molecular weights, the extent to which the particle size can be decoupled from the target molecular weight with respect to the different strategies presented is shown in Figure 13.

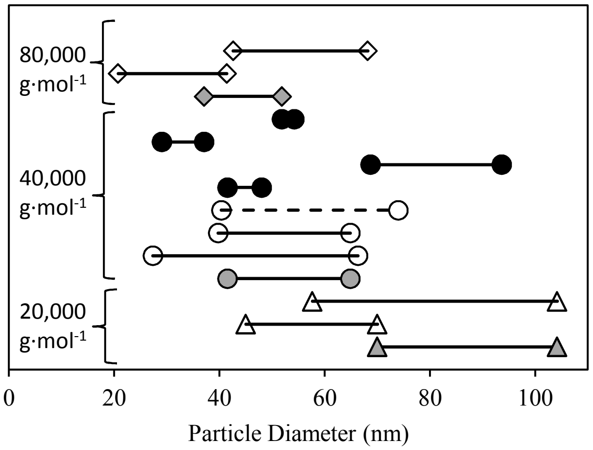

Fig. 13 Range of particle sizes achieved by SG1-mediated microemulsion polymerization of *n*-butyl acrylate at target M_n of 20,000 g·mol^{-1} (▲), 40,000 g·mol^{-1} (●), and 80,000 g·mol^{-1} (◆) by varying the surfactant-to-monomer ratio (wt/wt) (S series, gray), by varying the monomer content in the seed stage (M series, empty solid line), by semi-batch addition of surfactant (F series, empty dotted line), and by varying the BlocBuilder to Na_2CO_3 molar ratio (B series, black).

Careful manipulation of the surfactant-to monomer ratio (wt/wt), the BlocBuilder to Na_2CO_3 ratio (mol/mol), the monomer content in the seed stage, and by using a semi-batch addition of the surfactant resulted in successful decoupling of the particle size from the target molecular weight to a significant extent. At the target molecular weights of 20,000, 40,000, and 80,000 g·mol^{-1}, the particle size was successfully varied from ~20 to 70 nm, ~25 to 95 nm, and 45 to 105 nm, respectively. Increasing the surfactant to monomer ratio from 0.2:1 to 0.5:1 (wt/wt) led to an increase in the particle size due to the increase in ionic strength from the additional surfactant. Increasing the initial monomer content in the seed stage from 4 to 16 wt. % resulted in a decrease in the final particle size as a result of an increased availability of monomer allowing for a higher number of particles to be nucleated in the seed stage. By semi-batch addition of the surfactant, larger particle sizes can be obtained by increasing the portion of surfactant fed into the system over time.

Over the range studied, the molar ratio of BlocBuilder to Na_2CO_3 did not lead to a drastic change in the final particle size, although a minimum ratio must be kept to maintain the buffering capacity of the system. A large excess of Na_2CO_3 is expected to cause an increase in the particle size as a result of increased ionic strength effects. The polymerizations showed controlled and living behaviour with M_w/M_n maintained at approximately 1.4 up to about 70% conversion, and increasing to ~1.8 at higher conversions. The experimental M_n matched the theoretical value for target molecular weights of 20,000 and 40,000 $g{\cdot}mol^{-1}$, but were lower for target molecular weights of 80,000 $g{\cdot}mol^{-1}$.

D Conclusion

Stable poly(*n*-butyl acrylate) latexes were obtained by nitroxide-mediated microemulsion polymerization at a solids content of 20 wt. % using the alkoxyamine initiator, BlocBuilder® MA, and the anionic surfactant, Dowfax^{TM} 8390. The particle size was successfully decoupled from the target molecular weight to a significant extent by careful manipulation of the surfactant-to monomer ratio (wt/wt), the BlocBuilder to Na_2CO_3 ratio (mol/mol), the monomer content in the seed stage, and by using a semi-batch addition of the surfactant.

To our knowledge, the decoupling of the target molecular weight and particle size of *n*-butyl acrylate microemulsions using NMP has not previously been done to this extent. The strategies presented here can be used to produce polymer latexes with near independently specified molecular weight and particle size via nitroxide-mediated microemulsion polymerization. Although there are still some difficulties in extending the particle size range down to 20 nm for the low target molecular weights (< 20,000 $g{\cdot}mol^{-1}$), the range achieved in this work covers the typical desired size range (~40 to 80 nm). In addition, this work shows that stable microemulsions of *n*-butyl acrylate can be obtained using much lower surfactant-to-monomer ratios usually used in microemulsion systems and at higher solids content than typically reported for NMP microemulsions, while still maintaining controlled and living behaviour.

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Notes and references

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