Soap-Free Emulsion Polymerization of *n*-Butyl Acrylate: Copolymerization with 1,1-(Dimethyl)-1-(3-Methacryloxyethyl)-1-(Sulfopropyl)Ammonium Betaine

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ABSTRACT: Emulsifier-free emulsion polymerization of *n*-butyl acrylate has been performed in the presence of a polymerizable sulfobetaine monomer, 1,1-(dimethyl)-1-(3-methacryloxyethyl)-1-(sulfopropyl)ammonium betaine (SPE). An investigation of the effect of various salts (NaCl, NaHCO$_3$, Na$_2$CO$_3$, and NaH$_2$PO$_4$) on the emulsifier-free emulsion polymerization of *n*-butyl acrylate revealed that the type and quantity of salt is important in determining the size and size distribution of the final latex particles. In the case of the copolymerizations, control of the monomer feeding protocol (batch vs. semicontinuous and unseeded vs. seeded reactions) and of the ionic strength of the reaction mixture via addition of electrolytes allowed the preparation of stable latexes at 10% solids content with controllable particle size distributions. The results indicate that the amphiphilic sulfobetaine is able to stabilize the latex in much the same way as a polymerizable surfactant or an ionic comonomer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 227–236, 1998

Keywords: surfactant-free emulsion polymerization; zwitterionic surfactant; polymerizable surfactant; sulfobetaine; *n*-butyl acrylate; copolymerization

INTRODUCTION

Emulsion polymerization has become an important method for the preparation of polymers over the past few decades. In particular, emphasis on environmental responsibility has increased the importance of this water-based technique. Conventional emulsion polymerization is performed in the presence of an emulsifier (also called surfactant or soap). The surfactants can have detrimental effects on the physical properties of the final polymer. Further, the polymer properties may change over time as the low molecular weight soap migrates to interfaces or to the polymer surface.

These concerns have led to an increased interest in emulsifier-free emulsion polymerization. In emulsifier-free emulsion polymerization, the stability of the latex is imparted by ionic initiator fragments that are located at the surface of the latex particles. For persulfate initiators, the latex is stabilized by the —SO$_4^-$ groups at the initiated end of the polymer chains. The difficulty in this approach is that the amount of polymer that can be stabilized is limited, and, therefore, the highest attainable solids content in emulsifier-free emulsion polymerization is much lower than in the soap-stabilized systems.

A number of approaches have been evaluated in dealing with the problem of low solids content.[1] Colloidal particles can be stabilized by electrostatic, hydrophobic, or steric forces, or combinations thereof. These factors determine the strategies followed to produce emulsifier-free latexes of high solids content. For example, copolymerization with monomeric acid salts can be performed to yield stable latexes by increasing the electrostatic stabilization of the latex particles. Copolymerization of a lipophilic monomer with a hydrophilic comonomer can effect hydrophobic stabilization of colloidal particles. Finally, copolymerization with nonionic polymerizable surfactants can lead to improved latex particle stabilization by steric or electrosteric mechanisms.

In recent years, polymerizable sulfobetaines have been used increasingly in the preparation of polymers. The research group of Galin has spent a considerable amount of time preparing and characterizing sulfobetaine homo- and copolymers. For example, a series of publications[2] from this group details the results of investigations into the preparation of copolymers of n-butyl acrylate and (sulfopropyl)ammonium betaines in solution, and their characterization. A significant result of this work is that the sulfobetaine copolymers are biphasic in the bulk, due to aggregation of the zwitterionic residues. It was further reported that these copolymers were able to solvate stoichiometric amounts of various salts, including $LiClO_4$, as indicated by the absence of crystallinity of the salts by X-ray analysis of the blends. The group of Laschewsky[3] has investigated the solution and emulsion polymerization of unsaturated zwitterionic surfactants in which the double bond was separated from the sulfobetaine moiety by a long alkyl chain (typically C_{10} or C_{11}). Although these authors failed to uncover any evidence for aggregation of the zwitterionic groups, they did state that the zwitterionic compounds behaved like surfactants. Finally, Huglin and Rego[4] have prepared copolymers of 2-hydroxyethyl methacrylate and a zwitterionic methacrylate crosslinked with a tetrafunctional monomer, to examine their hydrogel formation properties. They found that the zwitterionic group influenced the swelling behavior of the hydrogels, which displayed antipolyelectrolyte character (i.e., the presence of salts caused chain expansion and swelling, as opposed to deswelling observed for polyelectrolytes).

In an attempt to produce novel polymeric materials, the copolymerization of n-butyl acrylate (n-BA) with 1,1-(dimethyl)-1-(3-methacryloxyethyl)-1-(sulfopropyl)ammonium betaine (SPE) is now described. It was anticipated that the zwitterionic "tail" on the sulfobetaine monomer would impart stability to the latex particles and eventually allow the preparation of high-solids latexes. Further, it is hoped that the zwitterionic moiety will impart novel physical properties to the copolymers. In this publication, we report our efforts to understand the emulsifier-free emulsion copolymerization of n-BA and SPE. Work on the physical properties of these materials is in progress and will be reported subsequently.

SPE
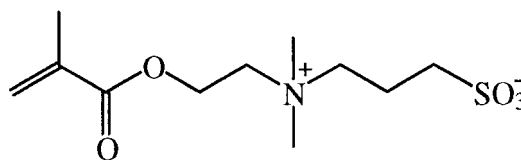
EXPERIMENTAL

Materials

Deionized water was used in all emulsion polymerization reactions. n-Butyl acrylate was obtained from Aldrich (99+%, inhibited with 10–55 ppm MEHQ), and 1,1-(dimethyl)-1-(3-methacryloxyethyl)-1-(3-sulfopropyl)ammonium betaine (SPE) from Raschig AG. Potassium persulfate ($K_2S_2O_8$, KPS), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), and sodium dihydrogen phosphate (NaH_2PO_4) were obtained from BDH; sodium carbonate (Na_2CO_3) was obtained from Baker. All reagents were used as received from the suppliers.

Emulsion Polymerization

A typical emulsion polymerization reaction was performed as follows: deionized water (300 g) was charged into a 1-L Pyrex reactor kettle fitted with a cover. The kettle was immersed in a water bath (73.5°C, reactor contents at 70°C), and fitted with a stirrer (four-blade, stirring rate 250 rpm), N_2 gas-bubbling tube (for degassing prior to reaction initiation, and for maintaining a N_2 blanket during the reaction), and a condenser. Nitrogen gas was bubbled through the water for 45 min, after which potassium persulfate (0.4 g) in deionized water (40 g) was added to the kettle. Monomers (35.9 g n-BA, and 4.1 g SPE in 20 g deionized water) were added to the kettle 10 min after the

initiator. Samples were removed from the reactor periodically to determine conversion.

Conversion

The conversion of monomer to polymer was monitored gravimetrically. Samples were weighed into aluminum dishes, placed in the fumehood for 4–6 h, and then placed in an oven (85°C) overnight. It should be noted that the conversions determined in this way are slightly overestimated due to residual unreacted SPE monomer, which was not removed.

Particle Size

Latex particle sizes and particle size distributions were determined on an ICI-Joyce Loebl Disk Centrifuge Photosedimentometer (DCP) supported by a Brookhaven Instruments DCP-1000 Data System. Water was used as the spin fluid, and a density gradient was produced using methanol. Latex samples were first diluted using a water/methanol (80/20 w/w) solution.

RESULTS AND DISCUSSION

Prior to performing any of the copolymerizations, a series of *n*-butyl acrylate homopolymerizations were conducted for comparison purposes. The variables studied included the reaction temperature, stirring speed, and initiator concentration. Three parameters that were monitored, in particular, included the amount of coagulum formed in the reactor at the end of the reaction, the particle size and particle size distribution of the resulting latex, and the rate of the reaction expressed by the change in conversion with time. Our goals were to minimize the formation of coagulum, to obtain "monodisperse" particles, and to achieve a rate of polymerization that would enable the addition of different ingredients at predetermined time intervals during the course of the reaction. If the reaction proceeded too quickly, it would be more difficult to add the comonomer at a desired *n*-BA conversion. In anticipation of the possible sensitivity of the zwitterionic comonomer to the pH or ionic strength of the reaction medium, a series of experiments was conducted to determine the effect of various electrolytes on *n*-BA homopolymerization.

Copolymerizations of *n*-BA and SPE were performed according to several different addition protocols. Using the work of Sakota and Okaya[5] as a starting point, a series of experiments was designed in which the feeding regime was varied to allow addition of the SPE solution at specified time intervals. The first series of experiments involved simple batch reactions in which both monomers were added to the reactor at the same time (batch unseeded reactions). In the second series, experiments were done in which the SPE solution was added batch-wise at a particular conversion in an *n*-BA batch homopolymerization (batch-seeded reactions). For example, the *n*-BA polymerization reaction would be allowed to proceed until a conversion of ∼ 10%, at which time all the SPE was added to the reactor as an aqueous solution.

In the last series of reactions the SPE solution was added in a continuous mode. This was performed by two different methods: either by commencing SPE feeding when the *n*-BA was added batch-wise to the reaction kettle (semicontinuous-unseeded reactions); or by commencing SPE feeding at some later point in the *n*-BA reaction, for example, at 10% conversion (semicontinuous-seeded reactions). The effect of electrolytes on particle size, particle size distribution, and total coagulum was determined for the semicontinuous-seeded copolymerization reactions.

BA Homopolymerizations

The first priority in this investigation was the determination of experimental conditions that would reproducibly yield clean and stable latexes with narrow particle size distributions in the absence of surfactants. Because our findings were in qualitative agreement with the results of Chern and Lin[6] for a detailed examination of the effect of temperature, agitation speed, and initiator concentration on surfactant-free emulsion polymerization of *n*-BA, it will suffice to state that the conditions found to meet our criteria were as follows: reaction temperature = 70°C, agitation speed = 250 rpm, and initiator concentration = 1 wt % based on monomer. These conditions produced latexes with a number-average particle diameter D_n = 300 nm, a particle size polydispersity D_w/D_n = 1.005, (<1 wt %) coagulum (based on total monomer added to the reactor), and a 45–60-min reaction time. It should be noted that a particle diameter polydispersity index D_w/D_n less than 1.01 is usually considered "monodisperse."

The results of our investigation into the effect of various electrolytes on the stability and poly-

Table I   Results on the Homopolymerization of *n*-BA with Added Electrolytes

Entry	Salt	Initial Ionic Strength	Final Conductance (mS)	Total Coagulum	Final Conversion (%)	Particle Size D_n (nm)	Particle Size Distribution (D_w/D_n)
1	NaCl	0.0171	2.63	1–3%	99	338	1.0071
2		0.0341	3.65	3–5%	96	625	1.0620
3		0.0423	4.41	>5%	95	737	1.1050
4	Na_2CO_3	0.0300	1.80	1–3%	100	307	1.0068
5		0.0433	2.35	3–5%	98	308	1.0065
6	$NaHCO_3$	0.0163	1.48	<1%	100	293	1.0071
7		0.0221	1.75	<1%	100	299	1.0083
8		0.0284	2.10	<1%	100	317	1.0088
9		0.0419	3.16	~1%	100	367	1.0073
10	NaH_2PO_4	0.0135	2.55	<1%	100	283	1.0060
11		0.0142	2.62	<1%	100	274	1.0066
12		0.0306	2.35	<1%	100	338	1.0088

dispersity of *n*-BA latexes are summarized in Table I. The results presented here and in the following tables are for single experiments. Only in selected cases was a reaction repeated to determine the reproducibility of the particle size and particle size distribution. It was found that the particle size was reproducible to within ±10%. Particle size polydispersity indices were reproducible to within ±0.1%.

Increasing the initial ionic strength by addition of sodium chloride resulted in a decrease in the stability of the latexes, as indicated by the increase in the amount of coagulum recovered from the reactor. A marked increase in the final latex particle size and broadening of the particle size distribution were also observed as the concentration of NaCl was increased. Furthermore, the latexes were unstable over time, and gross coagulation was observed after 30–60 days for entries 2 and 3 in Table I. When Na_2CO_3 was added to the reactor, the only observable effect was on the amount of recovered coagulum. The particle size and D_w/D_n remained unchanged compared to reactions without added salt (D_n = 300 nm). For both $NaHCO_3$ and NaH_2PO_4, it was found that increasing the ionic strength led to moderately larger particles with no increase in the breadth of the particle size distribution or in the amount of coagulum, in contrast to the reactions containing NaCl. The long-term stability of these latexes was good.

The increase in latex particle size observed for the NaCl polymerizations was expected from the DLVO theory, which states that the ionic strength of the aqueous phase controls the thick-

ness of the ionic double layer.[7] The thickness of the double layer, in turn, determines the stability of the latex. As the thickness of the layer decreases with increasing ionic strength, the stability of the latex particles decreases, and the probability of coagulation increases. This decrease in particle stability results in fewer particles in the reactor at the end of Interval I, which can grow to a larger size. Hence, an increase in the ionic strength is expected to result in an increase in the particle size of the final latex, as observed with NaCl. However, it is noteworthy that this increase in particle size was not seen for the other salts.

The important difference between electrolytes like $NaHCO_3$ and NaH_2PO_4 on the one hand, and NaCl on the other, is that the former are buffering salts. Addition of $NaHCO_3$ to an *n*-BA homopolymerization leads to a latex with a final pH close to 7, while latexes without added electrolyte, with NaCl or NaH_2PO_4 have a final pH = 2.6–2.7. Goodwin et al.[8] investigated the effect of increased ionic strength arising from various electrolytes [NaCl, $MgSO_4$, and $La(NO_3)_3$] on the emulsion polymerization of styrene. It is not specified whether their latexes contained added surfactant, however. The authors found that at a specific ionic strength, $MgSO_4$ and $La(NO_3)_3$ yielded larger particles than NaCl. Further, they reported that the range of ionic strengths at which a particular salt could be used before gross coagulation occurred decreased in the series NaCl, $MgSO_4$, $La(NO_3)_3$. The suggestion was made that the 2+ and 3+ counterions were able

Table II   Results of Batch Unseeded *n*-BA/SPE Copolymerization Reactions

mol % SPE	Final Conductance (mS)	Total Coagulum	Final Conversion (%)	Particle Size D_n (nm)	Particle Size Distribution (D_w/D_n)
2	1.88	0	100	327	1.0064
5	1.64	<1%	100	253	1.0079
10	1.46	<1%	100	261	1.0650
20	1.34	1–3%	98	263	1.0580

to undergo specific interactions with the colloidal particles.

In an attempt to further our understanding of the effect of electrolytes in the *n*-BA polymerization reactions, the final latex conductance was measured to give an indication of the final ionic strength of the latex. In all cases, the reproducibility in the measurements for duplicate reactions was determined to be ±0.1 mS. The initial conductance, Λ, of reaction mixtures containing only water and initiator (no added electrolyte) just prior to addition of monomer was $\Lambda = 1.8$–1.9 mS. The final conductance of poly(*n*-butyl acrylate) latexes obtained *without* salts was $\Lambda = 2.6$–2.9 mS. The conductance of latexes obtained *with* added salts is given in Table I. It can be seen that addition of Na_2CO_3 or $NaHCO_3$ resulted in a significant decrease in the final conductance of the latex compared to the latex without salts (c.f., e.g., entries 6 and 7), at least at moderate salt amounts. For NaH_2PO_4, the conductance was only slightly reduced compared to the latex without salts. In the case of NaCl, the conductance given in entry 1 at a low ionic strength is the same as for the latex prepared without added electrolytes. For all the salts studied with the exception of NaH_2PO_4, as the ionic strength was increased, the final latex conductance also increased. This increase was most pronounced in the case of NaCl. It appears, based on these results, that addition of certain electrolytes can effectively reduce the ionic strength of the final latex. This may partly account for the reduced polydispersity observed in the case of Na_2CO_3, $NaHCO_3$, or NaH_2PO_4 relative to NaCl. At this time, it is unclear why a discrepancy between the effect of the different salt types is observed.

Batch Emulsifier-Free Emulsion Copolymerization of *n*-BA and SPE

Batch Unseeded Copolymerization

Copolymerization of *n*-BA and SPE was first performed *via* emulsion polymerization in which both monomers were added to the reactor simultaneously. It was observed (Table II) that the inclusion of SPE resulted in a decrease in the particle size upon addition of 5 mol% SPE. Further addition of SPE had no effect on the final latex particle size. It was also observed that D_w/D_n increased steadily with increasing SPE content. In fact, monodisperse latexes could only be obtained at SPE contents of 5 mol% or less. At greater SPE contents (10 mol %), the particle size distributions became very broad. Surprisingly, the final latex conductance was observed to decrease steadily with increasing SPE content.

Several researchers have shown that the final latex particle size in an emulsion polymerization reaction can be reduced by copolymerization with ionic comonomers. Kim et al.[9] and Shouldice et al.[10] have investigated the emulsifier-free emulsion copolymerization of styrene and sodium styrene sulfonate (NaSS). Both groups demonstrated that addition of NaSS resulted in a smaller final latex particle size. Furthermore, Kim et al. found that at low concentrations of NaSS (1 wt % based on styrene), a monodisperse product was obtained, while at higher NaSS concentrations, the particle size distribution became more polydisperse, and at NaSS contents greater than 3 wt %, multimodal distributions were obtained. They proposed that at higher NaSS concentrations, significant polymerization of the sodium styrene sulfonate occurred in the aqueous phase. The water-soluble polymer was suggested to subsequently act as a locus of polymerization.

The size of latex particles can also be decreased by copolymerization with a polymerizable surfactant. Semibatch emulsion copolymerization (i.e., using continuous feeding of all the monomer over 3 h) of *n*-BA with 2–5% polymerizable surfactant (sodium dodecyl allyl sulfosuccinate) in the presence of sodium dodecyl sulfate (SDS) led to a latex particle size decrease from 300 nm to ∼ 90 nm. This effect was attributed to an increase in surface charge density imparted by the sodium dode-

Table III   Results of Seeded Emulsion Copolymerization of *n*-BA and SPE

Entry	mol % SPE	% Conversion[a]	Final Conductance (mS)	Particle Size D_n (nm)	Particle Size Distribution (D_w/D_n)
1	2.0	3.5	1.94	267	1.0089
2		11	1.82	273	1.0095
3		84	1.78	292	1.0065
4	5.0	7.1	1.51	293	1.0078
5		21	1.65	292	1.0068
6		88	1.59	283	1.0077
7	10	6.1	1.49	260	1.0073
8		51	1.43	259	1.0077
9	20	13	1.37	291[b]	1.0150

[a] Conversion of the *n*-BA reaction at which all SPE was added.
[b] DCP results indicate the presence of a small ($\sim$ 5 wt %) peak at $\sim$ 350 nm.

cyl allyl sulfosuccinate.[11] Urquiola et al.[12,13] compared the emulsion polymerization of vinyl acetate (VA) in the presence of polymerizable sodium dodecyl allyl sulfosuccinate and of the nonpolymerizable hydrogenated form of this surfactant. The authors found that, in both cases, the final latex particle size decreased with increasing surfactant concentration. It was also determined that the aqueous phase and the particle/water interface acted as loci for the copolymerization of the polymerizable surfactant with VA.

The effect of sulfobetaine surfactants on emulsion polymerizations has been investigated by a number of groups. Kato et al.[14,15] performed emulsion polymerization of styrene in the presence of *N,N*-dimethyl-*n*-laurylbetaine (a sulfobetaine surfactant), and found that the latex particle size decreased as the surfactant concentration increased, as normally seen with conventional ionic surfactants.[16] Essadam et al.[17] were able to prepare polystyrene latexes with a narrow size distribution in the presence of sulfobetaine surfactants (NC12 $\equiv$ CH$_3$(CH$_2$)$_{11}$N$^+$(CH$_3$)$_2$)$_3$SO$_3^-$ and OXC18 $\equiv$ CH$_3$(CH$_2$)$_{17}$N$^+$(CH$_3$)$_2$(CH$_3$)$_2$CH$_2$)$_2$N-(COCH$_3$)(CH$_2$)$_3$SO$_3$). Surfactant NC12 behaved similarly to SDS in terms of reducing the final latex particle size, although for the surfactant NC12 the size distribution was narrower than for SDS when either surfactant was used at or above the critical micelle concentration (cmc). Reactions performed with OXC18 yielded larger particles, with a polydispersity similar to NC12.

The information discussed above, including the results of the present study, strongly suggest that SPE behaves remarkably like polymerizable surfactants and ionic comonomers. This contradicts at least one claim in the literature[16] that zwitterionic surfactants are rarely used in the coatings industry because they are unable to provide a net charge on the polymer particles.

The decrease in conductance with increasing SPE content is somewhat surprising. A possible explanation for this could be that the sulfonate and/or ammonium moiety are able to complex various ions in solution, and thus to decrease their mobility. However, comparison of Raman spectra obtained for a 1.5-*M* SPE solution with that for a solution containing 1.5 *M* SPE and 1.5 *M* NaCl failed to reveal any evidence of such interactions. The bands associated with the quaternary ammonium and the sulfonate group did not shift in the presence of NaCl, as would be expected in the case of strong ionic interactions. Conductometric titrations of various solutions of NaCl (0.002–1.5 *M*) with either a solution of SPE monomer or with solid SPE homopolymer also failed to reveal any such evidence. In this case, a decrease in conductance resulting from a lower mobility of the ions in solution would have been evidence in favor of the presence of ionic interactions. Therefore, no satisfactory explanation can be provided for the effect of SPE on latex conductance at this time.

Batch-Seeded Copolymerization

The results of the seeded batch copolymerization reactions are shown in Table III. All reactions were clean (1% coagulum formation), and proceeded to complete conversion. There does not appear to be any correlation between particle size and addition time, nor does the final particle size

seem to correlate with the SPE content. However, it is clear from a comparison of results from Tables II and III that the polydispersity of the samples containing over 5 mol % SPE was greatly improved with the seeded batch copolymerization procedure. In fact, the latex samples containing 10 mol % SPE (examples 7 and 8) can be considered monodisperse. Even the sample containing 20 mol % (entry 9) had $D_w/D_n = 1.015$. However, DCP analysis indicated the presence of a small amount of a second size population at ~ 350 nm, accounting for about 5% of the total sample weight. Clearly, delayed addition of SPE had a major influence on the progress of the reaction. The trend of decreasing conductance with increasing SPE content is similar to that found in the unseeded reactions. However, only a slight variation in final latex conductance was observed as a function of SPE addition time for a given SPE content.

The procedure developed for these seeded reactions was based on the work of Sakota and Okaya on the preparation and characterization of carboxylated isoprene/styrene copolymer latexes,[5] and the work of Kim et al. on highly sulfonated polystyrene model colloids.[9,18] These authors both found that, in simple batch reactions of carboxylated isoprene with styrene, or sodium styrene sulfonate with styrene, only a small fraction of the water-soluble surface-active comonomer was incorporated in the latex particles. Most of the comonomer homopolymerized to form a polyelectrolyte. To overcome this problem, the authors performed two-stage reactions, in which the surface-active comonomer was added later in the reaction. The modified addition protocol was found to increase the fraction of bound comonomer to almost 100% in the case of styrene and sodium styrene sulfonate. Furthermore, the latex particles prepared by this two-stage technique were monodisperse.

Because the surface-active comonomer was added late in the reaction (90% conversion) to incorporate most of the comonomer on the surface of the particles, the resulting chain composition heterogeneity of the mixture would be expected to be very high. The goal in the present work was to produce polymer chains with minimal composition heterogeneity. To achieve this, the surface-active comonomer (SPE) was added much earlier in the reaction. The reactivity ratios for similar zwitterionic methacrylate monomers[2] and preliminary reactivity ratio analysis results for the n-BA/SPE[19] system indicate that SPE preferen-

tially reacts with itself rather than with n-BA. For batch reactions, this reactivity leads to a drift in the relative concentration of the two monomers, the more reactive monomer being preferentially consumed earlier in the reaction. The resulting chain composition heterogeneity would thus be expected to be quite high. This was qualitatively confirmed by dialyzing a latex produced by the batch method using a 12,000–14,000 molecular weight cutoff regenerated cellulose membrane (SPECTRA/POR) for 24 h. Analysis of the water-soluble fraction by ^{1}H-NMR revealed the presence of a small proportion of chains with a high SPE content (5 wt % based on total SPE added, 1 wt % based on total monomer).

Although these seeded batch reactions appear to yield copolymers with a high chain composition heterogeneity, the resulting particle size distributions are quite narrow. This approach, therefore, shows promise for the preparation of monodisperse homogeneous latex particles via appropriate adjustment of the reaction parameters.

Semicontinuous Emulsifier-Free Emulsion Copolymerization of n-BA and SPE

It was anticipated that batch-wise addition of SPE to an n-BA homopolymerization would result in polymer chains with a relatively high composition heterogeneity, because for methacrylate/acrylate copolymerizations the methacrylate generally has a higher reactivity ratio than the acrylate. To obtain copolymer chains with a higher composition homogeneity, unseeded and seeded copolymerizations were performed in which the SPE solution was fed continuously over the course of the n-BA batch polymerization reaction. This would stabilize the SPE concentration over the course of the reaction, and minimize the homopolymerization of SPE and copolymer composition drift.

Semicontinuous-Unseeded Copolymerization

The results of the semicontinuous-unseeded copolymerization of n-BA and SPE (Table IV) are similar to the results of the batch-unseeded copolymerization reactions, except that in the semicontinuous reactions the particle size increased initially for the 5 mol % SPE sample, and then decreased. Reactions were clean, and proceeded to complete conversion. Once again, monodisperse latexes could only be obtained at SPE loadings of less than 5 mol %. Latexes containing more than 5 mol % SPE were polydisperse (D_w/D_n

Table IV Results of Semicontinuous Unseeded Emulsion Copolymerization of *n*-BA and SPE

mol % SPE	Final Conductance (mS)	Particle Size D_n (nm)	Particle Size Distribution (D_w/D_n)
2	1.40	344	1.0078
5	1.60	376	1.0077
10	1.34	335	1.0250
20	1.29	268	1.0450

> 1.01). The final latex conductance decreased with increasing SPE content, except for the 5 mol % sample. The conductance was slightly lower for the semicontinuous reactions than for the batch reactions.

Semicontinuous-Seeded Copolymerization

A short delay between the addition of *n*-BA to the reactor and the beginning of SPE solution feeding resulted in smaller particles compared to the unseeded reactions, and in much improved particle size distributions, especially at higher SPE loadings (Table V). The reactions were clean, and proceeded to complete conversion. Also, as the SPE loading was increased, the particle size decreased, in contrast to the unseeded reactions, in which no correlation between SPE loading and particle size was observed. In the present case, D_w/D_n increased with increasing SPE content, but the resulting latex particles remained essentially monodisperse. The final latex conductance also displayed a smaller increase at 5 mol % SPE content, followed by a steady decrease at higher SPE loadings.

It is not clear why the latex particle size should decrease with increasing SPE loadings in the seeded copolymerization reactions. For the batch-unseeded systems, such a trend could

be explained in terms of formation of a larger number of primary particles in the initial stages of the reaction, because of a higher surface charge density on the particles. In the present case, different explanations can be suggested for this effect. First, it is possible that a second generation of smaller particles was produced later in the reaction. This would effectively reduce the amount of monomer available to contribute to the growth of the main particles. However, these smaller particles, if present, could not be detected by DCP particle size analysis (DCP detection limit 100 nm). Second, it is possible that excessive amounts of SPE homopolymer or SPE-rich water-soluble copolymer was formed. Again, this would reduce the amount of monomer that could contribute to particle growth. Dialysis experiments, of the type used on a semicontinuous-seeded latex, did not indicate the formation of a significant amount of soluble SPE-rich polymer (1 wt % based on total SPE added). Another possibility is that Interval I was not complete when the SPE was added to the reactor.[20] Presumably, if the SPE were added in Interval II, the number of particles in the reactor would be set, and a decrease in the final latex particle size would not be observed. However, if the reaction was still in Interval I when the SPE was added, and if SPE provided additional stabilization, the coagulation of particles may have been inhibited, leading to a higher final number of particles. This would result in a smaller average particle size. Based on this argument, one would expect to see a similar decrease in particle size for the batch-seeded copolymerization reactions, which is not the case experimentally. In the batch-seeded copolymerization reactions, however, the larger D_w/D_n values obtained may mask this effect.

Table V Results of Semicontinuous Seeded Emulsion Copolymerization of *n*-BA and SPE

Entry	mol % SPE	% Conversion[a]	Final Conductance (mS)	Particle Size D_n (nm)	Particle Size Distribution (D_w/D_n)
1	2	15	1.52	321	1.0053
2	5	16	1.58	291	1.0061
3	10	11	1.48	261	1.0069
4	20	15	1.35	217	1.0120

[a] Conversion of the *n*-BA reaction at which feeding of the SPE solution was initiated.

Table VI   Results of Semicontinuous Seeded Emulsion Copolymerization with Added Electrolytes

Entry	mol % SPE	% Conversion[a]	Salt	Initial Ionic Strength	Final Conductance (mS)	Particle Size D_n (nm)	Particle Size Distribution (D_w/D_n)
1	2	6.3	$NaHCO_3$	0.0259	1.99	261	1.0100
2	5	11	Na_2CO_3	0.0446	2.26	288	1.0083
3		8	$NaHCO_3$	0.0259	1.85	275	1.0091
4		11	NaH_2PO_4	0.0210	1.72	273	1.0062
5	10	6	NaCl	0.0312	3.24	272	1.0100
6		5.2	$NaHCO_3$	0.0259	1.74	276	1.0079
7	20	12	NaCl	0.0315	3.10	263	1.0150
8		13	Na_2CO_3	0.0441	2.01	230	1.0100
9		12	$NaHCO_3$	0.0256	1.61	242	1.0062
10		17	NaH_2PO_4	0.0204	1.41	288	1.0066

[a] Conversion of the *n*-BA reaction at which feeding of the SPE solution was initiated.

Effect of Electrolytes on Seeded Copolymerizations

The effect of SPE content and type of added electrolyte on the semibatch-seeded copolymerizations was investigated. It should be noted that the salts in these reactions were added with the SPE solution over time, rather than at the beginning of the reaction, as was done with the *n*-BA homopolymerizations, because batch addition of the salts led to reactions that were difficult to reproduce. The results of the experiments are summarized in Table VI. Interestingly, the final latex particle size in these reactions remained constant at 270 nm, and essentially independent of the type of electrolyte added, except at 20 mol % SPE loading. In this case, the final particle size was more dependent on the type of salt added to the emulsion, the more acidic latexes (with NaCl or NaH_2PO_4) having larger particle sizes than the neutral latexes (with $NaHCO_3$ or Na_2CO_3). It can also be seen from Table VI that the addition of NaCl or Na_2CO_3 resulted in latexes with a higher D_w/D_n (c.f. entries 5, 7, and 8), although only entry 7 (containing NaCl) would be considered polydisperse. Finally, comparing entry 4 of Table V with entries 7–10 of Table VI, it can be seen that the addition of buffering salts such as $NaHCO_3$ and NaH_2PO_4 allowed the preparation of latexes with a narrower particle size distribution at high SPE loadings.

CONCLUSIONS

It has been shown that the addition of different electrolytes to *n*-butyl acrylate surfactant-free emulsion homopolymerization reactions can lead to differing results, depending on the type of salt added. The addition of NaCl led to an increase in the final latex particle size (in qualitative agreement with the DLVO theory for colloidal particle stabilization) and particle size distribution. Buffering salts such as $NaHCO_3$, in contrast, only altered the particle size slightly at comparable ionic strength, the particle size distribution remaining monodisperse.

It has been demonstrated that different addition protocols can be used for the preparation of stable soap-free latexes of *n*-BA and a zwitterionic methacrylate, SPE. Monodisperse latexes could be produced at high (20 mol %) SPE loadings by employing a seeded emulsifier-free emulsion copolymerization technique with addition of buffering salts such as $NaHCO_3$ and NaH_2PO_4. The zwitterionic sulfobetaine SPE acted as a surface-active comonomer capable of improving the stability of emulsifier-free *n*-BA latexes. Further work is in progress on high solids reactions and on different acrylate/sulfobetaine comonomer systems, as well as on the analysis of the physical properties of the copolymers prepared.

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20. Care must be taken in applying the principles of emulsion polymerization developed for hydrophobic monomers like styrene to systems in which the monomers are much more water soluble, as is the case in the present work. See also ref. 1.