

Role of Anionic and Nonionic Surfactants on the Control of Particle Size and Latex Colloidal Stability in the Seeded Emulsion Polymerization of Butyl Methacrylate

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ABSTRACT: The evolution of the main colloidal parameters in the seeded starved-feed semi-continuous emulsion polymerization of butyl methacrylate (BMA) was investigated, with the main purpose of assessing the effectiveness of the semi-empirical relationship $S = K \cdot S_S \cdot \Delta A/A_S$ as a tool to define the surfactant/monomer feed ratio ($\propto K$) best suited to achieve a target particle size. In particular, the effect of the type and amount of surfactant [i.e., anionic, sodium dodecyl sulfate (SDS), or nonionic, Brij 58P] added during the semi-continuous stage was considered. Coagulum formation was never observed under the adopted experimental conditions. To detect the occurrence of secondary nucleation or particle aggregation, or both, the particle size and number of particles, the surface tension and the particle surface cov-

erage ratio were correlated. The best results were obtained with SDS and $0.8 \leq K \leq 3$. In fact, under the selected experimental conditions, only with SDS did the number of particles remain nearly constant throughout the polymerization at the value defined by the seed latex; the particle size distribution was highly monodisperse, and the final particle diameter closely matched the calculated one (~ 120 nm). The above semi-empirical relationship based on the adjustable parameter K was validated by running test polymerizations aimed at lattices with well-defined particle size. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3083–3094, 2006

Key words: emulsion polymerization; particle nucleation; surfactants; adsorption

INTRODUCTION

Emulsion polymerization is a technologically and commercially important process and is the basis of a massive worldwide industry. The traditional output of this industry, mainly the production of synthetic latex, continues to expand as a result of the versatility of the reaction and the increasingly strict regulations limiting the use of solvent-based materials.^{1–3} More recently, renewed interest is arising, from both a scientific and an industrial perspective, prompted by new scientific and technological advances, such as the introduction of controlled radical polymerization⁴ and of clever processes targeted at nanoscale control of structure or shape, or both,⁵ as well as by the rapid growth of new application areas requiring a very accurate definition of functionality, morphology, and composition of the produced polymer particles.^{6,7}

However, even when conventional free radical polymerization is used, both the industrial operation and the final output can benefit greatly from a better

understanding of the key factors affecting the structure and morphology of the final polymer latex. In fact, even with the same monomer feed composition, such factors as the adoption of a batch, semi-batch, or continuous process, the addition of the rate of components, the use of a seed polymer, and the type and amount of surfactant can have a profound effect on the properties of the resulting latex polymer and of the material (e.g., latex film, membrane) produced. Among the features of the final latex, particle size,⁸ and shape⁹ and the means for achieving good control of them have been a constant subject of investigation, owing to the useful insights they can provide into the fundamental rheological^{10,11} and colloidal properties of the latex, as well as being key factors for many latex applications.

The most straightforward way to control particle size in a conventional semi-continuous emulsion polymerization involves the use of a seed latex prepared in situ or as a separate batch. This can permit control of the nucleation stage and, under appropriate conditions, the prevention of secondary nucleation during the feed addition. Besides using a seed latex, the composition of the feed and the rate of addition may also require adjustment to achieve good colloidal stability and to produce latex particles of well-defined and predetermined size and copolymer composition.

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Many papers in the technical and scientific literature deal with the various stages of the seeded emulsion polymerization process, either to better understand the influence of the key parameters on the overall kinetics or as a means to achieve specific features in the final latex. Chern and Hsu¹² showed the influence of the type of surfactant (e.g., anionic or nonionic) on the effectiveness of particle nucleation and growth. Other investigators have studied the role played by the seed concentration and size in relation to the type and concentration of the initiator on the final particle size and size distribution.^{13,14}

More recently, Sajjadi¹⁵ investigated the influence of the rate of feed addition and of the surfactant/monomer feed ratio on the colloidal properties of butyl acrylate (BA) lattices prepared by a seeded process. Both the volume-average density of particles and their colloidal behavior are affected by the instantaneous monomer concentration, with the limiting cases of monomer-flooded and monomer-starved conditions, and by the extent of surface coverage by the anionic surfactant sodium dodecyl sulfate (SDS). A quantitative correlation was found between the surface tension and the particle surface coverage ratio θ , where a surfactant-depleted surface leads to particle aggregation below a lower threshold value of $\theta = 0.25$ and a surfactant-rich surface can favor secondary nucleation at $\theta > 0.55$. Within this range there is a region in which the number of particles remains constant, producing a stable polymer latex with predictable properties and morphology. In the region in which secondary nucleation can occur, the number of newly nucleated secondary particles increases with the concentration of monomer in the aqueous phase, and hence with the feed rate. In contrast, in the range in which particle aggregation takes place, a higher monomer feeding rate further contributes to the loss of particles.

Another important feature is the nature of the surfactant and, in the first instance, whether it is ionic or nonionic, or a mixture of both. The choice of surfactant type, in addition to its concentration, can play a major role in both the polymerization kinetics and the colloidal stability of the system. In a calorimetric study of the kinetics of the batch polymerization of styrene in a mixed surfactant system of SDS and the nonionic Triton X-405, El-Aasser and coworkers¹⁶ demonstrated that the anionic surfactant can synergistically interact with the nonionic one by promoting the formation of mixed micelles or mixed layers of adsorbed surfactants, thus lowering the partitioning of the nonionic surfactant within the oil phase and speeding up the polymerization kinetics. Both competition and synergistic interaction have been shown to occur in mixed surfactant systems, depending on the respective concentrations¹⁷; at lower concentrations, competitive adsorption can lead to the displacement of the anionic surfactant by

a newly introduced nonionic surfactant that, at higher concentrations, can then synergistically promote readsorption of the ionic surfactant possibly through complex formation within a multilayered surfactant shell at the particle surface.

The different stabilization mechanism of anionic and nonionic surfactants¹⁸ is also a key factor when seeded semi-continuous process conditions are adopted, affecting both nucleation and colloidal properties of the growing particles. Boutti et al.¹⁹ have shown that effective nucleation requires some ionic stabilization, either from the surfactant or from the macromolecule (ionic co-monomers or chain end from the initiator). In contrast, nonionic surfactant can provide the final latex with useful properties, such as improved colloidal stability and lower water sensitivity. It is therefore common practice to formulate a latex with mixed surfactants, the ionic preferably introduced during the nucleation stage for better control and reproducibility. Process design with these systems can be challenging, however, because of the additional complexity that arises from the interactions between surfactants and the ensuing partitioning between the particle surface and the aqueous phase.

The main focus of this work was thus the definition and the evaluation of a simple procedure for the synthesis of latex particles with well-defined and narrowly distributed size, based on a few simple measurements of the key colloidal parameters providing a detailed knowledge of the role played by the surfactants in a seeded emulsion polymerization process. Butyl methacrylate (BMA) was chosen as the monomer because of its low water solubility ($\sim 32 \text{ mmol L}^{-1}$ at 70°C^{20}) and high propagation rate constant ($1243 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 70°C^{21}). Two surfactants, the anionic SDS and the nonionic Brij 58P, were used, and their effectiveness during particle nucleation and growth was evaluated. In particular, they were used separately in a batch process to prepare the seed latex and in the following starved-feed semi-continuous seeded polymerization stage, where the chosen surfactant feed rate can contribute to maintaining the colloidal stability of the growing particles and either prevent or promote secondary nucleation.

EXPERIMENTAL

Materials and methods

Butyl methacrylate (Sigma-Aldrich, St. Louis, MO) was distilled in a vacuum before use. Potassium persulfate, SDS, BrijTM 58P (an oligoethoxylated cetyl alcohol with ~ 20 ethyleneoxide units, HLB = 15.7) and the buffering salts sodium hydrogen carbonate and ammonium carbonate (all from Fluka) were used as supplied. High-performance liquid chromatography (HPLC)-grade water was used for the polymerizations.

Photon correlation spectroscopy (PCS), also referred to as quasi-elastic light scattering (QELS), was used to measure intensity-weighted z -average particle diameters by means of a Brookhaven 90 Plus Dynamic Laser Light Scattering (DLS) instrument collecting the scattered light at 90° . The z -average particle size was assumed as corresponding to the volume-average one in the calculations of the numbers of particles; this is an approximation, since the z -average can overestimate the volume-average by as much as 10%.²² Intensity-weighted average particle size (d_p), particle size distribution (PSD), and polydispersity (PD) were calculated from the decay constant obtained by a second-order fit of the cumulant analysis of the autocorrelation function, using non-negative least-squares (NNLS) data elaboration. The latter provides a more detailed description of the system, which is particularly useful in case of multimodal particle size distribution, including a dimensionless polydispersity $PD = \mu_2/(\Gamma)^2$, where μ_2 is the second moment of the cumulant expansion and (Γ) is the average decay constant, corresponding roughly to the first moment. One can regard as nearly monodisperse a sample with $PD < 0.020$, whereas $0.020 < PD < 0.080$ corresponds to a narrow distribution. The particle size measurements carried out on the latex samples collected at different times during the semi-continuous stage corresponded to different instantaneous conversions even under the adopted starved-feed conditions, as discussed later. This would imply that in the latex the particle are swollen by the unreacted monomer ($\leq 3.8 \text{ mol L}^{-1}$);²³ however, since the DLS measurements are performed on samples diluted $\leq 10^3$ times to avoid multiple scattering, even the small solubility of BMA in water ($\sim 7 \text{ mmol L}^{-1}$)²² should be sufficient to drain most of the monomer from the particles.

Monomer conversions were determined by gravimetry. Weighed samples withdrawn during the semi-continuous stage ($\sim 1.5 \text{ mL}$ each) were added with 1 mL of 3 wt % aqueous solution of hydroquinone to quench the polymerization, then oven-dried and weighed. Appreciable coagulum formation was never observed.

Surface tension measurements were carried out at room temperature by means of a KSV CAM-200 instrument, according to the pendant drop method. The reported surface tension values are the averages of five measurements recorded for each sample, with each measurement performed after checking the reading for deionized water.

Syntheses

Synthesis of seed lattices

Two sets of batch polymerizations were performed in the presence of variable concentrations of surfactant. The acronym is-S-X is used for seed lattices prepared with SDS as the ionic surfactant (is), nis-S-X

for the ones containing Brij 58P as the nonionic surfactant (nis); in both cases X indicates the surfactant concentration (wt% with respect to the total monomer content).

The polymerizations were carried out by introducing water, monomer, and surfactant in the reactor, followed by purging with nitrogen and heating at the polymerization temperature (80°C) under stirring (250 rpm). The solution of initiator and buffer (1.5 wt % each, based on the amount of monomer) was then added, and the polymerization was allowed to proceed for 1.5 h. SDS concentration was varied within the 1.0–5.0 wt % (1.0 – 9.0 mmol L^{-1}) range for the is-S-X runs and in the 2.0–8.0 wt% (0.5 – 5.5 mmol L^{-1}) range for the nis-S-X ones. All seed lattices were formulated based on a 5 wt % total solids content.

Synthesis of BMA latex by seeded semi-continuous process (SSCP)

In a round-bottomed cylindrical 250-mL glass reactor equipped with a mechanical stirrer, reflux condenser and two feed inlet ports were introduced 24.8–56.0 g of a pre-formed seed latex (based on the formulation is-S-4.1, 5 wt % total solids, 98–99% conversion, volume-average number of particles 2.7 – $3.6 \cdot 10^{17} \text{ L}^{-1}$). After purging 20 min with nitrogen and heating at 70°C , the appropriate amount of the monomer (BMA, based on a final 20% total solids for a quantitative conversion) and of an aqueous solution containing initiator (KPS, 0.26 phr), surfactant (SDS or Brij 58P at different concentrations) and buffer (NaHCO_3 or $(\text{NH}_4)_2\text{CO}_3$, 0.3 phr, $\text{pH} \approx 8.5$) were added as two separate streams during 3 h by means of metered syringe pumps. The mixture was then stirred at 250 rpm and 70°C for an additional 60 min.

The acronym is-BMA-K indicates the addition of ionic surfactant (is) during a seeded polymerization, where K is the value of an empirical parameter as discussed later; when the surfactant added during the semi-continuous stage was nonionic the acronym nis-BMA-K was used.

RESULTS AND DISCUSSION

To understand the influence of type and concentration of surfactant on the polymerization of BMA, accurate knowledge of the surfactant distribution is required. In a batch process, which is usually adopted for the preparation of a seed latex, the surfactant can partition between aqueous phase, either as unimer or as a combination of unimers and micelles, and the organic phase, that is monomer droplets and monomer-swollen particles. In a seeded semi-continuous process run under monomer-starved conditions the situation can be comparatively simpler, since monomer droplets are virtually absent and the variation in

the total interfacial area can be much smaller. However, there is always a partitioning of the still unreacted monomer between the swollen particles and the aqueous phase. Therefore, the critical micelle concentration (CMC) of the surfactant in conditions closer to the real systems had to be determined as a preliminary step.

Tensiometric determination of critical micelle concentrations in BMA-saturated solution

The CMC of ionic and, particularly, nonionic surfactants can be influenced by a number of factors, including surfactant purity, ionic strength, temperature, and, above all, presence of even low concentrations of sparingly water-soluble monomers that can be surface active and that can modify the partitioning of the surfactant between water and micelle or, if present, the organic phase. Surface tension measurements were carried out on aqueous solutions saturated with BMA and containing KPS and NaHCO_3 at the same concentrations adopted for the seeded polymerization experiments (1.96 and 7.40 mmol L^{-1} , respectively), while the concentration of the surfactant was varied. In the case of SDS, its concentration range was 0 – 20 mmol L^{-1} , and for Brij 58P it was 0 – 1 mmol L^{-1} .

From the plots of the surface tension against the molar concentration of surfactant (Fig. 1), the following values were found: $\text{CMC}(\text{Brij 58P}) = 0.14 \pm 0.02 \text{ mmol L}^{-1}$; $\text{CMC}(\text{SDS}) = 2.9 \pm 0.8 \text{ mmol L}^{-1}$. Comparison with the experimental values reported for Brij 58P ($0.0039 \text{ mmol L}^{-1}$) and SDS (8.3 mmol L^{-1}) in pure water at 25°C ²⁴ clearly shows that the presence of a low concentration of a hydrophobic monomer can strongly affect the micellization process, particularly when a less hydrophilic nonionic surfactant is involved.

Effect of the type and concentration of surfactant on the particle size of the seed (is-S-X, nis-S-X)

To study the effect of the surfactant concentration and distribution between the aqueous phase and the particle surface during a seeded semi-continuous polymerization (SSCP), it is preferable to start from a well-defined seed latex consisting of small monodisperse particles at the lowest possible amount of surfactant, which should then be adsorbed effectively on the surface of the particles. Under these circumstances, secondary particle nucleation and the evolution of particle size during the following SSCP stage are easier to control, allowing a more straightforward correlation with the process conditions and polymerization kinetics.

Ionic surfactants, and in particular SDS,¹¹ are known to be more efficient than nonionic surfactants

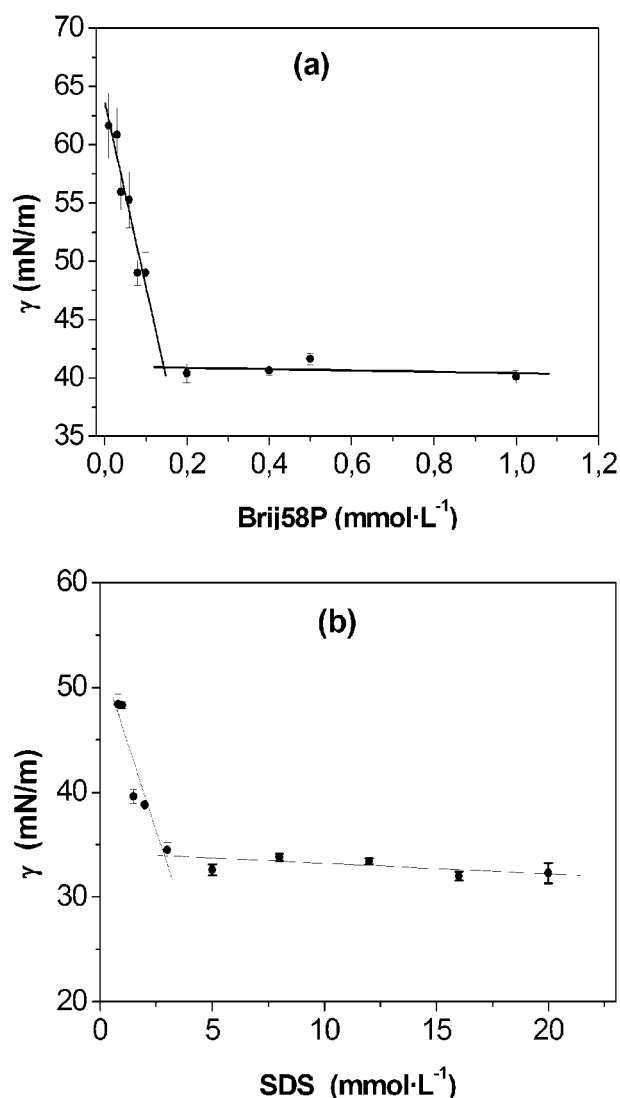


Figure 1 Surface tension of BMA saturated aqueous solutions of (a) Brij 58P and (b) SDS.

during particle nucleation, and better colloidal stabilizer in the initial stage of particle growth in batch emulsion polymerizations. In fact, it has been reported that the nucleation step and the initial stage can also depend on the interactions between monomers and surfactants.^{25,26} These interactions are more remarkable in the case of nonionic surfactants that can be soluble in the monomer droplets or in the particles. The ensuing partitioning can lower the surfactant concentration in water at the early stage of polymerization, and prevent micellization even at concentrations above the CMC. As the monomer is consumed, the surfactant concentration increases and, if the CMC is reached, secondary nucleation can take place.

In our study, we were interested in the minimization of the particle size of a BMA homopolymer latex to be used as seed latex in the following SSCP experiments, while keeping the initial surfactant concentra-

tion as low as possible. Therefore, the effect of the concentration of either the anionic SDS or the nonionic Brij 58P was studied for the batch polymerization of BMA.

The concentration of the surfactant was varied in the 1.82–36.5 and 0.88–5.36 mmol L⁻¹ range for SDS and Brij 58P, respectively. As shown in Figure 2, the anionic SDS was much more effective in decreasing the final particle size. Furthermore, increasing the concentration of the nonionic Brij 58P, beyond 7 mmol L⁻¹ did not produce significant variations in the final particle size, which remained in the range of 130–150 nm. It is worth pointing out that the entire range of concentrations explored for Brij 58P lies well above its CMC of 0.14 mmol L⁻¹, whereas in the case of SDS the transition between the unimer and the micellar regime occurs at concentrations above its CMC of 2.95 mmol L⁻¹. This is reflected in the sharp drop of the final particle size as the result

of onset of micellar nucleation, replacing homogeneous nucleation as the dominant mechanism.

Based on the above results, the BMA latex is-S-4.1, obtained with 4.1 wt % SDS, was used as the seed latex for the following SSCP experiments. Latex is-S-4.1 was considered the best compromise between required small particle size and low concentration of free unimer surfactant in solution.

Seeded emulsion polymerization of BMA (is-BMA-X, nis-BMA-X)

The use of seed latex, if the initial particle number N_{p0} is sufficiently high (typically $N_{p0} \geq 1 \cdot 10^{16} \text{ L}^{-1}$), allows efficient capture of free radical species from the aqueous phase and of all the primary particles formed by homogeneous nucleation.²⁷ In a typical seeded procedure, the rate of the feed addition was adjusted to ~ 3 h for both streams, well below the threshold for the monomer-starved condition in this system. Under these conditions, to control the particle growth, the surfactant should be added at a rate sufficient to stabilize the latex particles and to maintain the colloidal stability, but not so high as to promote secondary nucleation due to micelle formation.

In all the experiments, the surfactant already available at the start of the feed addition (as the seed was used without purification), as well as the surface charge provided by the ionic chain ends from the initiator, were always sufficient to prevent coagulum formation, and also when no additional surfactant was added in the semi-continuous stage ($K = 0$). The appropriate total amount of surfactant S to be fed with the monomer in the semi-continuous stage, and thus the surfactant/monomer feed ratio, was estimated using the empirical equation:

$$S = K \cdot S_s \cdot \frac{\Delta A}{A_s}, \quad (1)$$

where S_s is the moles of surfactant in the seed latex, K is a dimensionless adjustable parameter, and $\frac{\Delta A}{A_s}$ is the ratio between the relative variation of surface area (ΔA) due to the growth of the particles in the semi-continuous stage and the surface area of the seed (A_s):

$$\frac{\Delta A}{A_s} = \left[\left(\frac{d_{\text{calc}}}{d_s} \right)^2 - 1 \right] \quad (2)$$

where d_s and d_{calc} are the particle diameter of the pre-formed seed, as determined by PCS, and the final particle diameter, respectively; the latter is calculated under the assumption that the total particle number remains constant throughout the polymerization.

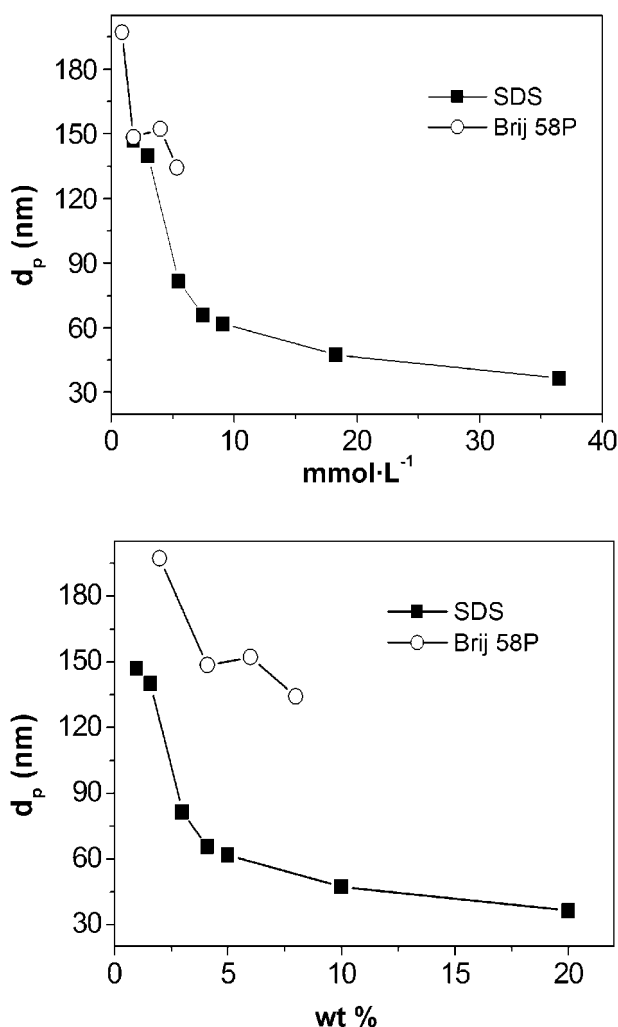


Figure 2 Particle diameter of is-S-X and nis-S-X latexes as a function of surfactant in the batch: (a) molar concentration, and (b) weight percent (wt %).

TABLE I
Polymerization Recipe for the Seeded Semi-Continuous Process
With Added Nonionic Surfactant

	$d_p(\text{seed})$ (nm)	Final latex				d_p (nm)	PD
		BMA (g)	Brij 58P ^a (phr)	Brij 58P (mmol L ⁻¹)	Conversion (%)		
BMA-0	66	17.5	0	0	93.3	129	0.019
nis-BMA-0.2	69	17.5	0.3	0.53	93.9	131	0.034
nis-BMA-0.5	63	17.5	0.8	1.43	90.9	126	0.029
nis-BMA-1.2	69	17.5	1.8	3.21	91.7	131	0.018
nis-BMA-3	63	17.5	4.6	8.21	91.3	132	0.032
nis-BMA-6	67	17.5	9.2	16.4	88.8	135	0.005

^a An additional total 0.5 phr of SDS with respect to the final latex comes from the seed latex.

According to eq. (1), the request for additional surfactant is proportional to the increase in surface area; this is based on the assumption that the adsorption-desorption equilibrium for the surfactant remains unperturbed during the particle growth and the surface density of the surfactant molecules adsorbed onto the particles be constant. To check the range of applicability of eq. (1), a series of experiments were performed in which K was varied between 0 and 6, using two different surfactants: the anionic SDS and the nonionic Brij 58P. The recipes for the various polymerization runs are reported in Tables I and II. The final particle diameter was set at 120 nm for all experiments, as calculated from the amount of monomer added in the semi-continuous stage and the estimated density of the final polymer, assuming quantitative monomer conversion and a constant number of particles, N_p .

The experimental variations of the instantaneous number density of particles, N_p , and the deviations of the particle size with respect to the calculated one during the feed addition were to be related to the reaching of a lower and an upper threshold of surface coverage ratio θ , respectively, that is of the density of surfactant molecules adsorbed onto the particle surface (see later). In fact, in a simplified

phenomenological description, a decrease of N_p indicates the outset of the particle aggregation and/or coagulation and should result from a reduction of θ below the lower threshold granting colloidal stability. In contrast, an increase of N_p due to the occurrence of secondary nucleation might result from an increase beyond the upper threshold.

The feed rate and composition were kept constant at 0.3 wt % initiator (6 mmol L⁻¹ in the feed) and 0.35 wt % buffer (22.7 mmol L⁻¹ in the feed) with respect to the monomer. During the feed stage, 7 aliquots of 1.5 mL were withdrawn and analyzed by PCS to follow the particle growth, and by gravimetry to obtain the instantaneous conversion, IC, versus the relative time, $\tau = t/t_{\text{feed}}$, where t_{feed} is the total duration of the monomer addition in the semi-continuous stage. Thus a relative time $t = 1.0$ indicates the end of the feeding stage, followed by a further polymerization time to complete the decomposition of the initiator and increase overall monomer conversion.

As illustrated in Figures 3 and 4, the initially modest IC slowly levels off at 75–85%. An IC that is lower than expected at the early stage of polymerization may be attributable to the fact that the absolute amount of unconverted monomer (at the same time swelling the growing seed particles and stored in the rapidly but

TABLE II
Polymerization Recipe for the Seeded Semi-Continuous
Process With Added Ionic Surfactant

	$d_p(\text{seed})$ (nm)	Final latex				d_p (nm)	PD
		BMA (g)	SDS ^a (phr)	SDS (mmol L ⁻¹)	Conversion (%)		
BMA-0	66	17.5	0	0	93.3	129	0.019
is-BMA-0.2	69	17.5	0.3	2.08	92.8	129	0.027
is-BMA-0.8	67	17.5	1.2	8.33	91.9	130	0.018
is-BMA-1.2	67	17.5	1.8	12.5	91.3	129	0.029
is-BMA-3	67	17.5	4.6	31.9	92.1	132	0.062
is-BMA-6	67	17.5	9.2	63.9	92.5	119	0.163 ^b

^a An additional total 0.5 phr of SDS with respect to the final latex comes from the seed latex.

^b Multimodal particle size distribution.

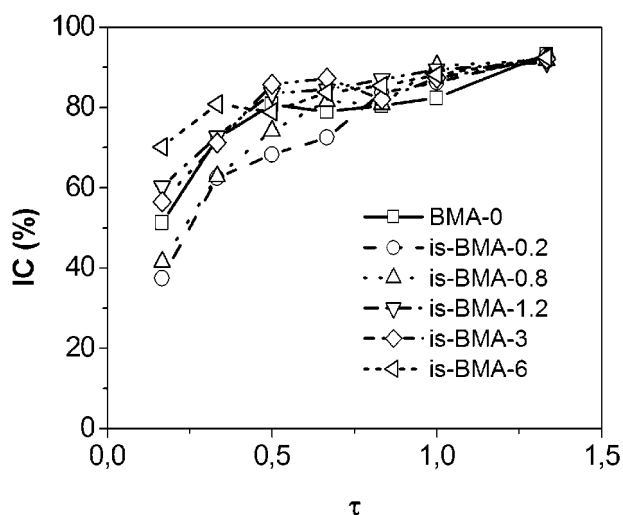


Figure 3 Instantaneous conversion during the polymerization runs is-BMA-K.

not instantaneously depleted monomer droplets from the feed) is likely to remain nearly constant throughout the starved-feed polymerization. This should result in a fraction of unconverted monomer that is not negligible at the earlier stage of the feed addition, when the overall monomer fed to the reactor is still relatively small. The dependence of IC from the surfactant concentration in the is-BMA runs, indicating a faster polymerization rate promoted by a higher concentration of SDS, can actually be ascribed to an increase of the number of propagating free radicals as the SDS concentration exceeds the CMC, thus promoting the onset of a micellar nucleation mechanism.

The monomer conversion at the end of polymerization, that is after 1 h of further reaction following the end of the feeding time, was ~ 90% for all samples, independent of the type and amount of added surfactant.

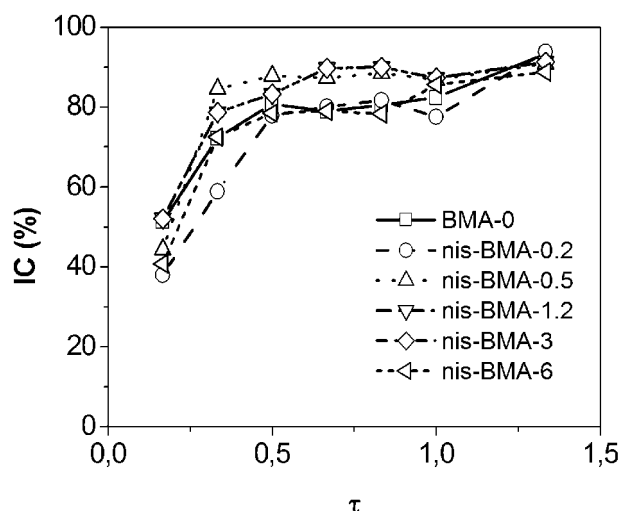


Figure 4 Instantaneous conversion during the polymerization runs nis-BMA-K.

Colloidal stability of the growing latex particles

The instantaneous number of particles, N_p , during the semi-continuous stage of the polymerizations was calculated from the measured particle size according to the following expression:

$$N_p = \frac{6(m_s + m_i \cdot x_t)}{\pi \rho d_p^3} \quad (3)$$

where m_s and m_i are the amounts (g) of seed polymer and of BMA monomer fed to the reactor at time t , respectively; x_t is the instantaneous fractional monomer conversion, ρ is the polymer density (estimated as 1.05 g/cm³),²⁸ and d_p is the intensity-average particle diameter as determined by PCS.

The graphs displayed in Figures 5(a) and 6(a) plot the dimensionless numbers of particles as the function of relative time, where the instantaneous total number of particles N_p is divided by the total num-

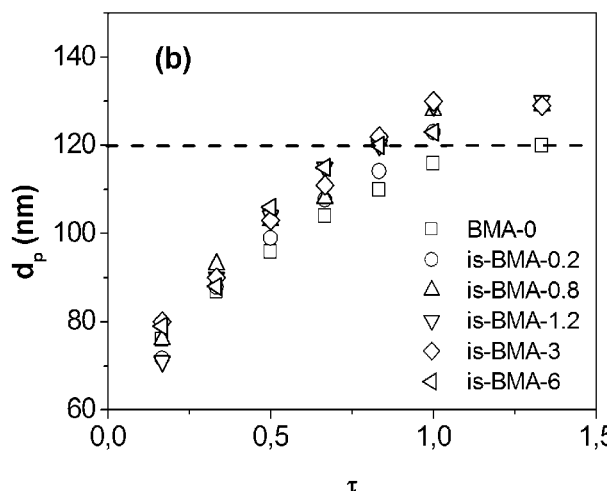
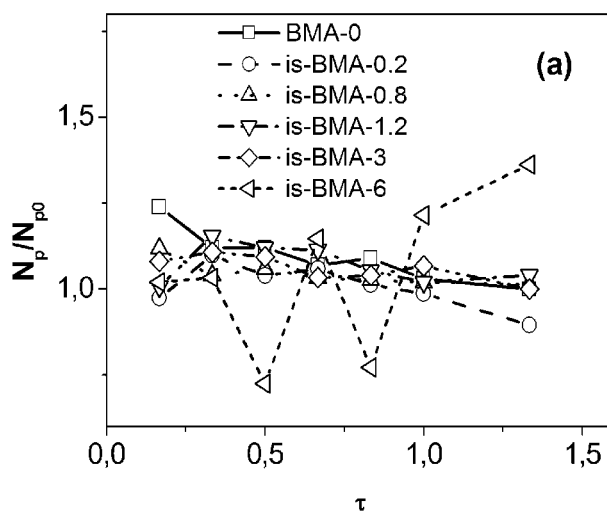


Figure 5 Evolution of (a) number of particles, and (b) particle diameter during the semi-continuous stage of is-BMA-K polymerizations.

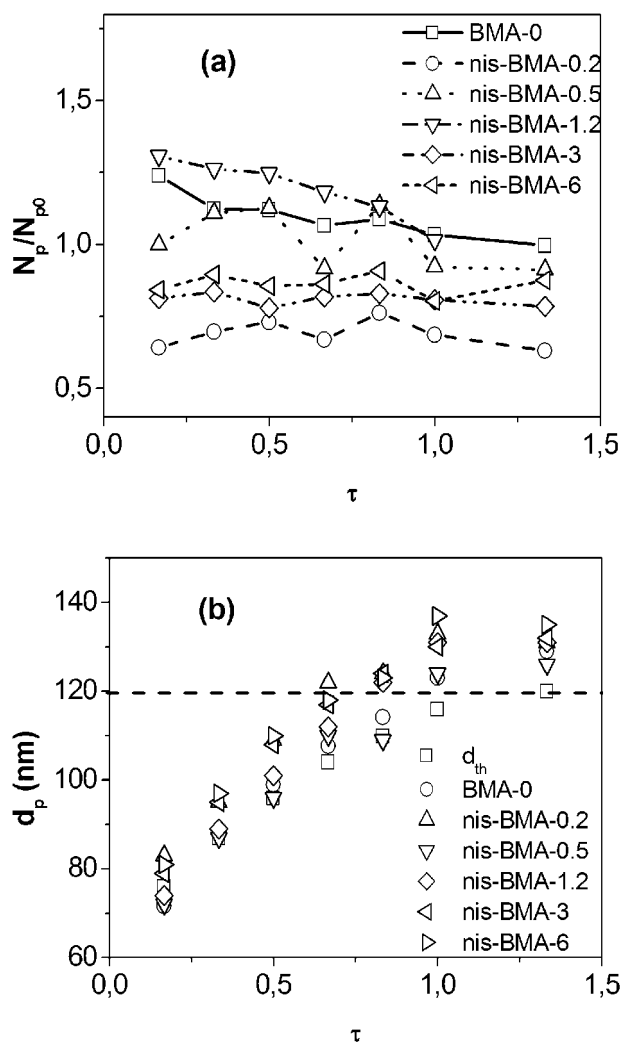


Figure 6 Evolution of (a) number of particles, and (b) particle diameter during the semi-continuous stage of the nis-BMA- K polymerizations.

ber of particles of the starting seed, N_{p0} . The experimental values for d_p were affected by a polydispersity within range of 0.001–0.069 and 0.009–0.070 for the nis-BMA and is-BMA runs, respectively.

The measured increase of particle size as a function of τ was always slightly larger than predicted, as shown in Figures 5(b) and 6(b). The deviations increased progressively throughout the feeding stage within a range of 0 ÷ 15 nm for the is-BMA runs and 0 ÷ 20 nm for the nis-BMA ones, leveling off at an excess of 10 nm at the end of the polymerization in the former. In fact the small but not negligible reduction of N_p caused by the repeated withdrawal of 1.5–3 vol% of the polymerization mixture throughout the feeding stage can account for such deviations. This was confirmed by control experiments where in the absence of external perturbations the experimental deviations $|d_s - d_{calc}|$ were well within the intrinsic instrumental accuracy of the measurement of $\sim \pm 3\%$.

Generally speaking, a larger-than-expected final particle size, that is a decreasing number of particles, may be associated to a supply of surfactant insufficient to maintain a constant surface coverage, resulting in some particle aggregation. Indeed, as illustrated in Figure 5(a), the is-BMA- K samples with $K \leq 3$ exhibit a nearly constant value of $N_p/N_{p0} \approx 1$, indicative of a well-controlled seeded polymerization process. Only in the case of is-BMA-6 was a broad and multimodal particle size distribution recorded at an earlier stage of polymerization, possibly as a result of secondary nucleation as the free surfactant concentration is raised beyond the CMC (see later).

The experiments in which the nonionic surfactant was added in the second stage yielded more scattered data, meaning that the system appears to be more sensitive to the rate of supply of fresh surfactant during particle growth. The observed drift toward $N_p/N_{p0} < 1$ at longer relative times [Fig. 6(a)] and the lack of a clear correlation between the $N_p(t)$ data, spanning in the $1.3 < N_p/N_{p0} < 0.6$ range, and the corresponding K values do not allow exclusion of either secondary nucleation or some particle aggregation when Brij 58P was used.

To establish the main cause of such a different behavior, the time evolution of the surface tension (γ) was recorded for both the nis-BMA- X and the is-BMA- X lattices [Fig. 7(a, b)]. The experiments run with the addition of a large excess of surfactant ($K = 6$) led to a rapid drop of γ down to ~ 33 mN/m and 42 mN/m for SDS and Brij 58P, respectively, corresponding to concentrations of free surfactant at or above the CMC (34 mN/m for SDS and 43 mN/m for Brij 58P, from Fig. 1). Under these conditions, micellar nucleation can not be excluded, and indeed its occurrence in run is-BMA-6 was confirmed by DLS analysis, showing a multimodal particle distribution throughout the feeding stage. The lack of such secondary nucleation process in the nis-BMA-6 run could be explained by the same poorer nucleation efficiency of the nonionic surfactant discussed previously.^{11,19}

More generally, inspection of the plots shown in Figure 7 shows that three different situations can be identified: (1) at high K , the rate of surfactant addition exceeds the increase in surface area, leading to rapid surface saturation (nis-BMA-6, is-BMA-6 and is-BMA-3 at longer relative time); (2) at intermediate K , the surfactant addition rate nearly compensates the increase in surface area (nis-BMA-3, is-BMA-1.2 and is-BMA-0.8); and (3) at low K , the addition rate is insufficient to compensate for the increasing surface area and causes a drift toward higher γ , corresponding to progressive surfactant depletion from the particle surface (nis-BMA-0.2, 0.5, 1.2 and is-BMA-0.2).

In the intermediate case, the surface tension data indicate that at the given K , the supply of surfactant initially matches or is close to that required by the

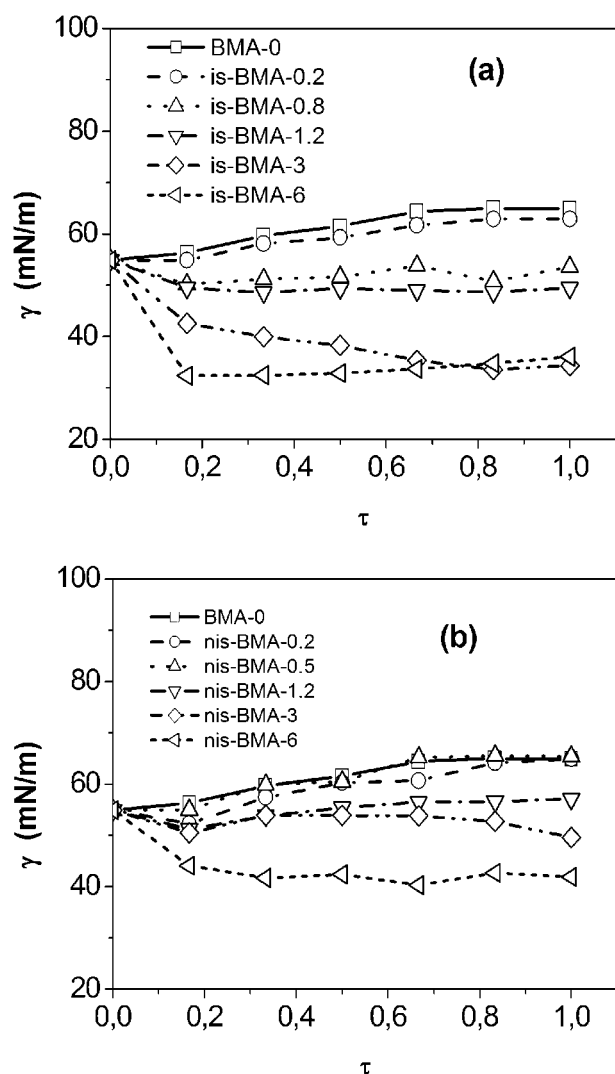


Figure 7 Evolution of the surface tensions (γ) versus relative time for (a) SDS and (b) Brij 58P addition.

increasing total particle surface area. The slight decrease of γ at longer τ is related to a progressive increase of concentration of free surfactant. To explain such behavior, one should take into account that the input of monomer and surfactant fed to the reactor scales with the particle volume under instantaneous conversion and constant N_p , whereas the request for additional surfactant scales with the particle surface area. As the result, since the surfactant/monomer feed ratio R is kept constant throughout the semi-continuous stage for practical reasons, the relationship tends to underestimate R at an early stage of feed addition and to overestimate it at a late stage.

To compensate for this drift, the constant parameter K in eq. (1) should rather be considered as a function of the final solids content and seed conditions, that is of the increase of particle size and of the corresponding surface area, $K = f(d_{\text{calc}} - d_s)$. This would allow us to obtain a more accurate estimate

of the instantaneous request of additional surfactant to maintain a constant surfactant coverage on the latex particle surfaces during the feed stage, resulting in nearly constant surface tension in the latex and thus stationary colloidal conditions. In practice, even with the most accurate calculations there will always be an upper and a lower limit for the colloidal stability of the growing latex particles unless a variable surfactant feed rate is adopted, and the proposed models²⁹ can only provide a predictivity tool for the suitable range of surfactant feed rate for a given monomer mixture, type of surfactant, final solids content, and seed conditions.

In our case, the above considerations can be discussed more quantitatively by considering the surface coverage ratio, defined as

$$\theta = \frac{A_t^S}{A_t^P}, \quad (4)$$

where A_t^P is the total surface area of the particles and A_t^S , the total surface area occupied by the surfactant molecules adsorbed onto the particle surface, was calculated as follows:

$$A_t^S = n_{\text{ads}}^S \cdot a^S \cdot N_A, \quad (5)$$

where N_A is the Avogadro constant, n_{ads}^S is the number of moles of surfactant effectively adsorbed, and a^S is the specific surface area occupied by a single surfactant molecule. An accurate measurement of a^S according to eq. (6) can be derived from the adsorption isotherms obtained, e.g., by the soap titration method, providing the surface excess concentration Γ_{ads} (roughly the number of moles per unit area) at the particle surface.³⁰ However, for the sake of simplicity, a^S was determined here by using for the surface excess concentration Γ_s the value obtained from the slope before CMC of the semi-logarithmic plots derived from those of Figure 1, according to eq. (6):³¹

$$a^S = \frac{10^{23}}{\Gamma \cdot N_A} \quad (6)$$

$$\Gamma = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln C} \right)_T, \quad (7)$$

where R is the gas constant, T is the absolute temperature, C is the surfactant concentration, and a^S is the specific surface area of the surfactant in the closely packed monolayer at the liquid-gas interface. The latter is obviously not an accurate estimate of the specific surface area of adsorbed surfactant molecules, a_{ads}^S ; nevertheless, it can still provide an unambiguous picture of the evolution of θ along with the particle growth during the semi-continuous stage of the polymerization. Indeed, values of a_{ads}^S ranging

from 0.47 to 0.63 nm² were found for SDS on poly(vinyl chloride), poly(styrene), and poly(butyl acrylate) lattices, as determined by adsorption isotherm at the polymerization conditions,^{22,32,33} whereas the experimental values in the present study were a^S (SDS) = 0.36 nm² and a^S (Brij 58P) = 0.70 nm². In the case of Brij 58P, the result is further affected by the mixed nature of the surfactant composition, since it was arbitrarily assumed in the calculation that all the SDS derived from the seed latex be adsorbed onto the particles, implying a corresponding reduction of the effective surface area available for Brij 58P. As discussed in the introduction,¹⁸ this is likely to be a somewhat loose approximation; in fact, in our experiments the initial seed had $\theta \approx 0.35$, and a fourfold increase in surface area such as that occurring upon increasing d_p from 60 to 120 nm at constant N_p , would imply as much as 9% of the total particle surface in the final nis-BMA latex is occupied by the SDS molecules from the seed.

Given the above assumption, the concentration of free surfactant throughout each polymerization was calculated for both type of experiments from the γ values measured on each aliquot of latex withdrawn during the semi-continuous stage, using the calibration curves reported in Figure 1(a, b).

The surface coverage ratio was higher than 0.5 for is-BMA-6, is-BMA-3, and nis-BMA-6 (Fig. 8); in all remaining cases, θ remained below the initial value of 0.35 (that of the seed latex) and decreased slightly throughout the feed addition, with the exception of nis-BMA-3. The situation where $\theta \geq 0.5$ is consistent with a system highly saturated with surfactant,³⁴ where secondary nucleation cannot be excluded due to a micellar mechanism or to effective stabilization of homogeneously nucleated primary particles against flocculation onto the larger preexisting ones. However, the experimental data discussed before on the evolution of particle size and number of particles suggest that secondary nucleation should be excluded in the case of is-BMA-3 and nis-BMA-6. In fact, even at $\theta \geq 1$ the particle size distribution was narrow and monomodal, and the dimensionless N_p/N_{p0} ratio was nearly constant at about or slightly less than 1. Such behavior, however, is not surprising when considering that nonionic surfactants have a poorer nucleating efficiency than ionic surfactants, and indeed secondary nucleation did occur in is-BMA-6.

In contrast, the polymerizations with $K \leq 1.2$ led to a progressive decrease of θ , a condition potentially conducive to particle aggregation due to colloidal instability of surface-depleted particles. The surface coverage ratio decreased from the initial $\theta = 0.35$ to the lowest range at 0.1 ÷ 0.15 in two cases ($K \leq 0.5$) with Brij 58P, but only at the lowest content of SDS ($K = 0.2$). However, from the data presented in Figures 5 and 6, particle aggregation seems to take

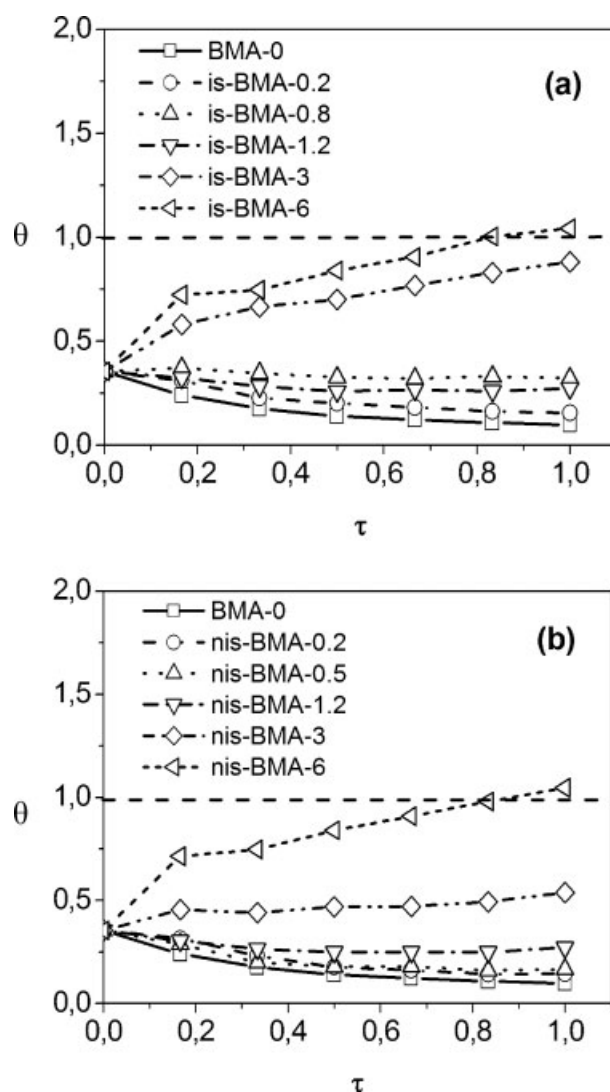


Figure 8 Surface coverage ratio versus relative time for (a) is-BMA-K, and (b) nis-BMA-K polymerizations.

place to an appreciable extent only in the nis-BMA-K runs. Once more, the different mechanism of stabilization of nonionic and ionic surfactants can be claimed to explain the poorer behavior of Brij 58P.

Control on the final particle size of is-BMA and nis-BMA lattices

To test the effectiveness and versatility of eq. (1), a set of polymerizations was carried out using the values of $K = 0.8$ for SDS and $K = 1.2$ for Brij 58P and by varying the amount of monomer fed to the reactor to result in a range of final particle sizes, i.e., 120, 140, or 160 nm (see first column of Table III). The polymerization procedure was the same as that adopted for the is-BMA-K and nis-BMA-K runs. The seed was prepared *in situ* at $\sim 5\%$ solids, using the same formulation as in is-S-4.1 to produce particles with $d_s \approx 60$ nm. The recipe for the following semi-continuous stage

TABLE III
Final Particle Diameter of BMA Latices Prepared in the Presence of Different Types of Surfactant

Run ^a	Seed				Semi-continuous stage				Final latex		
	Latex (mL)	BMA (g)	N_{p0} (10^{17} L ⁻¹)	d_p (nm)	BMA (g)	H ₂ O (mL)	SDS (mmol L ⁻¹)	Brij 58P (mmol L ⁻¹)	d_{calc} (nm)	d_{exp} (nm)	PD
i-120	28.4	1.4	4.6	58	8.6	13	11	—	112	116	0.005
ni-120	28.4	1.4	4.6	58	8.6	13	—	4.8	112	119	0.019
i-140	21.1	1	3.0	64	9.0	20	12	—	138	134	0.010
ni-140	21.1	1	4.2	61	9.0	20	—	5.3	132	136	0.012
i-160	21.1	1	3.3	64	14.0	45	11	—	158	177	0.028
ni-160	21.1	1	3.9	62	14.0	45	—	4.9	153	176	0.013

^a Total concentrations of initiator and buffer, including the contribution from the seed: KPS = 2 mmol L⁻¹, (NH₄)₂CO₃ = 5 mmol L⁻¹.

was adjusted to ~ 20% solids, where the seed polymer accounted for 6.25–14 wt % of the total polymer in the final latex, that is, depending on the final target particle diameter. The amount of surfactant to be added, and thus the surfactant/monomer feed ratio, was also obtained from eq. (1) based on the targeted final particle size. The actual average particle diameters expected for the final latex, d_{calc} , and the experimentally measured ones, d_{exp} , are reported in Table III; the former was calculated in each run based on the DLS data from the seed (d_s , and thus N_{p0}) and on the amount of monomer fed to the reactor.

The batch polymerizations carried out to prepare the “in situ” seeds for each individual run gave quite reproducible results, with nearly constant average particle size. Irrespective of the nature of the surfactants used in the following semi-continuous stage, the distribution of the particle diameters in the final latex was also monomodal and narrow.

From the dimensionless N_p/N_{p0} ratios plotted as a histogram in Figure 9, one can clearly see that the deviations from the ideal case ($N_p/N_{p0} = 1$) are always larger for the ni-X samples than for the corresponding i-X ones, with the lower figures of the former

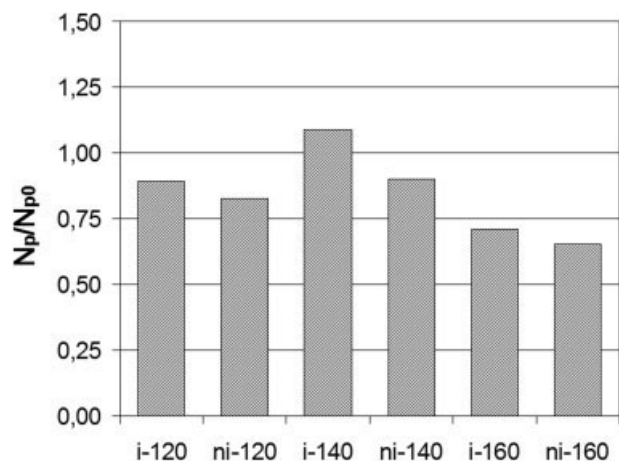


Figure 9 Final N_p/N_{p0} ratio for the BMA latices stabilized by either ionic or nonionic surfactant and targeted at different particle sizes.

indicating a generally poorer effectiveness of the non-ionic surfactant as stabilizer against particle aggregation.

When considering the influence of the target particle size, the N_p/N_{p0} ratio remains close to one for the i-120 and i-140 latices, whereas comparatively larger deviations are observed for i-160 latices. Apparently, in the latter case, particle aggregation begins to become no longer negligible, possibly occurring at the early stage of the feed addition in which the particle surface can become surfactant-depleted. In fact, in the latter case, as the result of the different scaling factors for the surfactant and monomer feeds, a comparatively lower surfactant/monomer feed ratio was adopted to achieve a similar surface coverage ratio in the final particle. Indeed, the range of suitable K values had been defined based on the experimental data from latices with particles of ~ 120-nm diameter, and it has been shown that a surfactant/monomer feed ratio \pm optimized for a given target particle size will result in a progressive increase of θ as the particle size increases well beyond that. For the same reason, if the \pm is calculated based on a final particle size (and thus $\Delta A/A_s$) much larger than the one used to determine the optimal K value, one can expect that the growing particle will be surfactant-depleted at the early stage of the feed.

CONCLUSION

The effectiveness of two surfactants, the anionic SDS and the nonionic Brij 58P, in stabilizing colloidal behavior during the seeded semi-continuous starved-feed emulsion polymerization of BMA was studied as a function of the surfactant/monomer feed ratio \pm . The corresponding amount of surfactant, S , was set according to the simple semi-empirical relationship of eq. (1) containing the adjustable parameter K .

Coagulation was never observed with either surfactant within the range $0 \leq K \leq 6$. However, particle size analysis and the particle number density N_p calculated therefrom showed that some particle

aggregation did generally occur in the case of Brij 58P, whereas a nearly constant N_p throughout the polymerization was measured when using SDS. More generally, the K values suitable to achieve a good control over the colloidal properties of the growing latex particles were in a lower range when using SDS ($0.2 \leq K \leq 1.2$) than in the case of Brij 58P ($0.5 \leq K \leq 3$). It can be concluded that colloidal particles stabilized by the ionic SDS are more tolerant than those stabilized by Brij 58P toward a reduction of surface coverage, which may result in aggregation due to a depletion mechanism. The opposite situation holds when an excess of surfactant is present (here at $K \geq 3$), since secondary nucleation due to stabilization of newly generated primary particles can take place with a comparatively lower concentration in excess of the CMC, when using SDS.

The results of a series of polymerizations to produce particles with a range of different sizes showed that adoption of the same K value optimized for a given particle size can result in progressive loss of colloidal stability as the target particle size increases. This is because if the final particle size is much larger than the seed, the given \pm (calculated based on the optimized K value) is likely to be insufficient to ensure that at the early stage of particle growth a sufficient amount of surfactant is added to compensate for the increase of surface area.

In fact, the true key parameter that should remain nearly constant to maintain the colloidal stability is the surface coverage ratio θ . At a given K (constant \pm) and starting typically from a seed with a high θ value, owing to the different scaling factors of \pm and ΔA the instantaneous θ is likely to decrease or even undergo a minimum at the early stage of the feed addition, then growing progressively to reach the target θ value. The larger the difference in size between the seed and the final particle, the lower the minimum θ that could be reached during the semi-continuous stage. For a more general approach the optimal K value should therefore be considered as a tool to estimate the corresponding θ from eq. (4), which in turn could be used to design a step-wise reduction of \pm ensuring a nearly constant θ throughout the feeding stage.

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