



# Preparation and full characterization of cationic latex of styrene–butyl acrylate

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## ABSTRACT

Cationic latexes based on styrene and butyl acrylate using cetyl trimethyl ammonium bromide (CTAB) as surfactant were carried out using both batch and semicontinuous emulsion polymerization. Monomer conversion, particle size and its distribution,  $\zeta$  potential, latex surface tension were determined as function of CTAB levels. Evolutions of these properties were followed, and the results from batch compared to those from semicontinuous process. It was revealed that polymerization rate in batch process was enhanced with CTAB, and the polymerization rate was controlled by addition rate of the preemulsion in semi-continuous process. Molecular adsorption area of CTAB on latex particle surface was calculated, which showed clearly that  $\zeta$  potential and surface tension in the latex were directly related with surfactant adsorption on the particle surface. The molecular surface adsorption area of CTAB on latex particle could be used to explain the evolution of latex properties such as  $\zeta$  potential and latex surface tension.

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## 1. Introduction

Polymer latexes prepared through emulsion polymerization have a great variety of applications in textile and leather treatments, paper industry as well as paints and coatings industries. Interests in emulsion polymerization have shown constant increase since Harkins' theoretical modeling for emulsion polymerization in 1940s [1]. It is to note that, up to date, most of the studies on emulsion polymerization have been focused on systems with anionic surfactants and/or combination of anionic and non-ionic surfactants. It is the same for initiator systems, i.e. mostly anionic or non-ionic initiators have been used. The various latex particles thus produced are negatively surface charged. However, positively surface charged latex particles are also required in many cases such as oil-field drilling, paper industries [2–5] and other recently emerged areas [6–8]. Studies on cationic latexes are obviously far behind their industrial development, and relative reports are far fewer compared to those on anionic latexes, although Goodwin et al. [9] reported a detailed procedure for preparation of cationic polystyrene latex through emulsifier-free emulsion polymerization, which was then employed to prepare cationic latexes based on polystyrene or its copolymers for flocculation and retention of calcium carbonate in papermaking [10] and fiber coating [11]. Güven et al. [12] also claimed to have prepared monosized polystyrene nanoparticles using *N*-[3-(dimethylamino)propyl] methacrylamide combined with a cationic initiator 2,2'-azobis(2-methyl propanamide)

dihydrochloride (V-50). Cationic latexes using either styrene [13], or methacrylate [14] or butyl acrylate [15] with different vinyl containing quaternary ammonium monomer were also reported. In other studies, cationic surfactants such as dodecyl trimethyl ammonium bromide [16] and cetyl trimethyl ammonium bromide [17–19] (or chloride) were also used in preparation of cationic latexes. Recently these cationic latex particles have been also studied for various applications such as PS–carbon nanofiber nanocomposites [20] and biological purposes [6,19–21]. Voorn et al. [22] reported they have successfully achieved to control cationic charge densities on particles by adjusting the ratio between epoxy and amino groups through aminolysis of epoxy groups from copolymerized glycidyl methacrylate. Sui et al. [23] claimed they prepared polyelectrolyte complexes aggregates with pH-tunable solubility from a random copolymer of diallyldimethylammonium and acrylic acid (having a net positive charge as polycation) and poly(styrenesulfonate) as polyanion; whereas Schumacher et al. [24] also obtained stable cationic latexes by charge inversion of anionic styrene–acrylic copolymer latexes upon binding aluminum and ferric ions using a high-HLB non-ionic surfactant in order to keep a strong steric stability of the latex in the presence of high concentrations of multivalent counterions. Recently, a mathematical model for seeded cationic emulsion polymerization was developed [25], which the author claimed being able to predict the evolution of the monomer conversions, the thickness of the outer shell and the total surface charge density.

It is clear that interests in cationic polymer latexes have been in constant increase since 1990s, both fundamental and applied research are being reported. Nevertheless, there have no systematic studies on emulsion polymerization using cationic surfactant and

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initiator. In this paper, we have carried out a study on emulsion copolymerization of styrene (St) and butyl acrylate (BA) with cationic surfactant, cetyl trimethyl ammonium bromide (CTAB). A series of emulsion copolymerization of St–BA were carried out using CTAB as surfactant combined with anionic, non-ionic and cationic initiators. Polymerizations with varying amount of CTAB at different levels of diverse initiators were carried out. Monomer conversion, particle size and its distribution have been determined.

## 2. Experimental

### 2.1. Materials

Styrene (Chongyang Chemicals, Hubei, China) and butyl acrylate (Guoyao Chemicals Groups, China) were distilled under reduced pressure before use. Cetyl trimethyl ammonium bromide (CTAB), from Shanghai Chemical Reagents, and 2,2-azobis(2-amidinopropane) dihydrochloride (AIBA), from Beijing Institute of Chemical Engineering, were used as received. Ammonium persulfate (APS), from Jiangnan Chemicals Plant #2 in Shanghai, was re-crystallized before use. *tert*-Butyl hydrogen peroxide (BHPO) and sodium formaldehyde sulfoxylate (SFS) were used as received.

### 2.2. Polymerization and characterization

A typical recipe for the polymerization includes 70 g of water, 30 g of monomers with St/BA at molar ratio of 1.231 (50/50 by mass). 1.0 g of initiator (0.33% of the monomer weight) was used in all latex preparations, while the amount of surfactant was varied from 0.3% to 4.0% relative to the mass of the total monomers. Emulsion polymerization was conducted in a 250 ml four-necked glass flask through two different processes, i.e. batch and semi-continuous emulsion polymerizations. In batch, all ingredients, except the initiator (APS, AIBA or BHPO) and a small amount of water used to make the initiator solution, were first located into the reactor. The flask was nitrogen purged under stirring for 15 min to form an emulsion, and located immediately into a water bath at a set temperature. Except otherwise indicated, the polymerization was carried out at 70 °C. Initiator solution was injected into the flask shortly after the flask moved into water bath. When redox initiator was used, SFS solution was introduced into the reactor continuously during 2–3 h. The polymerization lasted 4–5 h.

In semicontinuous process, a preemulsion was prepared prior to polymerization, which was made in 2 steps. 85% of the total surfactant and 28% of the total water for the polymerization were first introduced in a container and agitated at 800 rpm for 10 min so that to obtain a homogeneous solution, the monomers were then added under stirring and the system kept stirred for another 15 min to make a preemulsion. A quarter of the preemulsion along with 65% of the total water and 15% of surfactant were introduced into the glass reactor as the initial charge. The reactor was then located into a water bath pre-heated to 70 °C. AIBA solution, the initiator, was also prepared with the rest of the water (7% of the total), and a third of the solution was injected by a syringe to start the polymerization. It took usually 5 min to observe a tint blue occurring in the reactor, indicating formation of latex particles. The 3 quarters of the preemulsion and 2/3 of the initiator solution were then started to be added at constant rates 20 min after injection of the initiator solution. The addition time lasted in general 4 h. Upon completion of these additions, the system was cooked at the polymerization temperature under same stirring rate for another 1 h to chase the residual monomers.

During the polymerization, samples were taken in order to follow the evolutions of monomer conversion and particles size.

$\zeta$  Potential of the particles, number average particle size and size distribution were determined using Malvern Nano-ZS light scattering instrument. Particle size of selective samples were also examined using transmission electron microscopy (TEM, JEM-100CX-II, Hitachi, Japan) with phosphotungstic acid (2%) as the staining agent. Monomer conversion was determined gravimetrically, and samples occasionally checked by gas chromatograph (Shimadzu GC-14C, Japan), the two results were in good agreement with the highest deviation of  $\pm 3.0\%$ .

### 2.3. Calculations of particle number and surfactant molecular adsorption area

The mass of each particle ( $M$ , g) is obtained by Equation (1):

$$M = \frac{4\pi}{3} \times \left(\frac{D_p}{2}\right)^3 \times \rho \times 10^{-21} = \frac{\pi D_p^3 \rho}{6} \times 10^{-21} \quad (1)$$

where  $\rho$  is the density of the polymer ( $\text{g}/\text{cm}^3$ ), and  $D_p$  the average particle size expressed in nm. Knowing the solid content ( $S$ ) in 1 g of latex, the number of particles per liter of latex ( $N_p$ ,  $\text{L}^{-1}$ ) is calculated by Equation (2):

$$N_p = \frac{S}{M} \times 10^3 = \frac{6S}{\pi D_p^3 \rho} \times 10^{24} \quad (2)$$

The surface area of each individual particle ( $S_i$ ,  $\text{nm}^2$ ) is estimated by Equation (3):

$$S_i = 4\pi \times \left(\frac{D_p}{2}\right)^2 \quad (3)$$

The total surface of all the particles per liter of latex ( $S_t$ ) is therefore:

$$S_t = N_p \times S_i \quad (4)$$

With  $C$  denoted as the molar concentration of the surfactant in the latex, and CMC its critical micelle concentration, and  $N_A$  the Avogadro number, the molecular adsorption area ( $S_a$ ,  $\text{nm}^2$ ) of the surfactant molecules on the particle surface can be therefore estimated by Equation (5):

$$S_a = \frac{S_t}{(C - \text{CMC}) \times N_A} \quad (5)$$

CMC of CTAB was determined through du Nouy method using Powrreach tentiometer JK99B (Zhongcheng, Shanghai). A series of CTAB solutions with different known accurate concentrations were first prepared. The solutions were equilibrated overnight at 20 °C, and the surface tension was measured in a double walled container with circulating water of 20 °C. 3 Readings were recorded and the data reported were averaged. A CMC of  $5.3 \times 10^{-4}$  mol/L was obtained, in the same range with those reported values of  $4.8 \times 10^{-4}$  [26],  $8.0 \times 10^{-4}$  [27], or  $8.4 \times 10^{-4}$  mol/L [28], which were usually effected at 25 °C. Another series of data of the molecular adsorption area (denoted as  $S_b$ ) of the surfactant on the particle surface was also obtained using the amount of surfactant molecules freely dissolved in the aqueous phase (described as CTAB in the serum, i.e. those not adsorbed on the particle surface) instead of CMC. To obtain this amount of CTAB in the serum, the objective latex was frozen overnight, thawed at room temperature and centrifuged at 12,000 rpm for 30 min to get a clear supernatant (latex serum), the surface tension of the serum was measured and the concentration of CTAB was obtained from a curve of surface tension versus CTAB concentration, established prior to the test.

**Table 1**  
Influence of initiator type on latex properties.

Initiator	Conversion (%)	$D_p$ (nm)	PDI	$\zeta$ (mV)
AIBA	98.4	68.0	0.086	+76.4
APS	97.6	123.0	0.168	+43.1
Redox	81.6	72.0	0.080	+53.5

### 3. Results and discussion

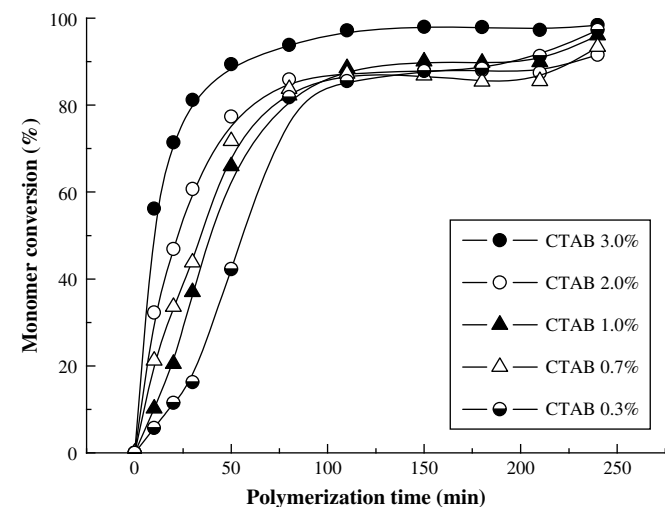
#### 3.1. Emulsion polymerization using initiators bearing different charges

Keeping CTAB as surfactant at 3.0% relative to the weight of total monomer amount, 3 parallel experiments were carried out using either cationic initiator AIBA, or anionic APS or non-ionic redox system (BHPO-SFS), particle size and  $\zeta$  potential of the latex were measured, results summarized in Table 1.

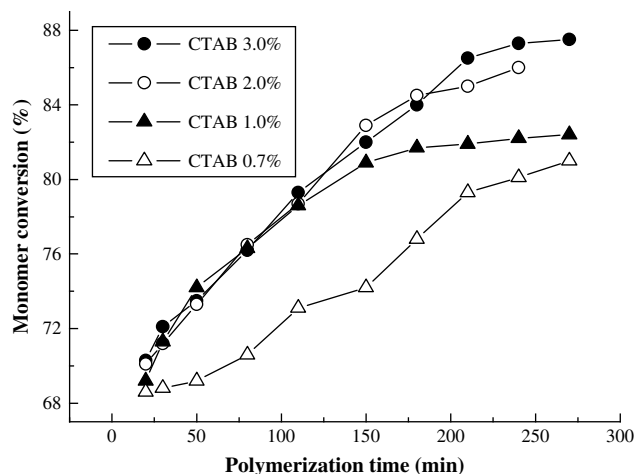
As one would have expected, the  $\zeta$  potential of particles was function of the initiator. Highest  $\zeta$  potential was observed with positively charged AIBA initiator, lowest  $\zeta$  potential with negatively charged APS, and the latex prepared with charge-free BHPO situated in between the two. Knowing that surfactant CTAB is positively charged, these observations seem expected. This indicated that cationic latex particles were better stabilized when initiator bearing the same charges was used. Smaller particle size was detected when compared to the same latex prepared using an initiator bearing opposite charges to the surfactant molecules.

#### 3.2. Kinetics of emulsion polymerization on batch and semicontinuous processes

In earlier studies on preparation of cationic latex using quaternary ammonium as the surfactant, it has been reported that stable cationic latex could be obtained only with cationic surfactant with one alkyl group with carbon numbers higher than 14, and the emulsification ability increased with carbon number in the alkyl chain length [14,29]. These reports revealed that the polymerization did not proceed well when using dodecyl benzyl dimethyl ammonium chloride, where the monomer conversion was never reached 30%, and serious latex flocculation occurred in all runs with surfactant amounts up to 3.0%. In this study, CTAB was therefore chosen as surfactant and cationic AIBA as the initiator.



**Fig. 1.** Dependence of monomer conversion on CTAB amount and variation of monomer conversion with polymerization time in batch process.



**Fig. 2.** Dependence of monomer conversion on CTAB amount and variation of monomer conversion with polymerization time in semicontinuous process.

In order to investigate the influence of surfactant CTAB on polymerization process and kinetics, samples were taken during polymerization and monomer conversions measured. The results are depicted in Fig. 1 for batch and in Fig. 2 for semicontinuous process.

From Fig. 1, it was clearly seen that, in runs with higher CTAB, monomer conversions were higher, particularly in the early stage of polymerization. The lowest conversion among all runs was observed with 0.3% CTAB. This was not unexpected because more CTAB would form more particles, and so to have higher polymerization rate. The monomer conversion showed a high rate of polymerization in the first 90 min followed by a plateau region, where the polymerization rate was obviously slowed down. For semicontinuous process given in Fig. 2, monomer conversion was expressed as the converted monomers relative to those added to the reactor at time of sampling. Since 25% of the total monomers was initially charged and allowed to polymerize for 20 min. before start of preemulsion addition, at this time about 70% of the monomers in the initial charge was polymerized regardless of the CTAB levels. This indicated that the polymerization time of 20 min for the initial charge was adequate, during which a great part of the charged monomers were polymerized. This monomer conversion corresponded to about 17–18% if based on the total monomers at end of the polymerization. The profile of conversion-time curves in semicontinuous was different from batch. The polymerization rate and monomer conversion were nearly constant during the whole polymerization process, and for the 3 runs with high CTAB levels, the curves in Fig. 2 overlapped in the first 2 h of polymerization, which was a clear indication that the polymerization was controlled here by monomer addition rate. An obvious lower polymerization rate was observed after 2 h of polymerization for the run with 1.0% of CTAB, which was believed to be owing to the monomer accumulation with continuous preemulsion addition, because the number of the particles in these runs were fewer than those in the run with 3.0 wt% of CTAB as one could expect. The lowest polymerization rate was observed in the run with 0.7% of CTAB, which was likely due to a dual effect of monomer starvation as in the other runs and the lowest CTAB level. The low CTAB level would lead to a smaller number of particles, and therefore to a significant decrease in polymerization rate.

#### 3.3. Evolution of particle size during polymerization

Particle size was also determined for latex samples during polymerization, size evolutions in batch and semicontinuous

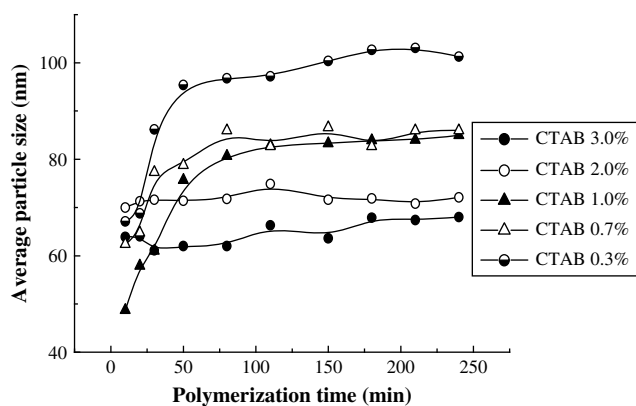


Fig. 3. Evolution of particle size in runs with different CTAB by batch process.

processes are shown in Figs. 3 and 4, respectively. For batch process, the particle size in later stage of polymerization, i.e. after 50 min, was in good agreement with classical emulsion theory, namely, the particle size in final latex was decreased with increase in CTAB concentration. And thus the latex done with 3.0% of CTAB was found to have the smallest particle size and that with 0.3% of CTAB the largest, in good agreement with the results shown in Fig. 1. It is to note that the particle size in the three runs with lower CTAB (1.0% and below) was in constant ascending in the initial stage (<50 min polymerization time); meanwhile the particle size in the runs with higher CTAB (3.0%, 2.0%) were quite constant, despite increase in monomer conversion. These are common observations in emulsion polymerization, because at lower CTAB concentration, particles are not fully covered by surfactant molecules. With particle growth, particle aggregation or coagulation would occur in an early stage so that to reduce the total particle interface, leading to therefore an increase in particle size. This increase will cease once all monomer droplets disappear and all monomers molecules redistributed among all the particles to form the monomer-swelled particles, corresponding to the end of the Interval I according to Smith–Ewart theory [30,31]. Whereas at higher surfactant concentration, all or most of the primary particles are well covered by surfactant molecules from the beginning of the polymerization, particle aggregation, if any, is very limited compared to the cases where very little surfactant is used, which implies that the Interval I in emulsion polymerization is reached sooner with more surfactant used. The particle size would be quite constant once the Interval I is over

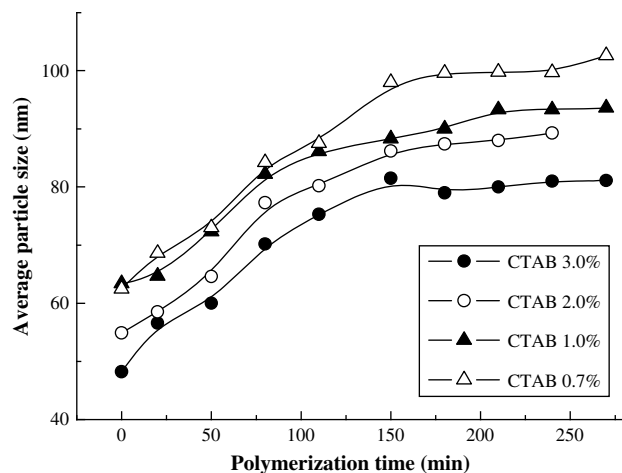


Fig. 4. Evolution of particle size in runs with different CTAB by semicontinuous process.

because it is widely accepted that the main locus of monomer polymerization is inside of the particles, and in the subsequent Interval II the only particle size change is the volume change owing to monomer to polymer conversion. The observations in Fig. 3, i.e. an increase in the particle size in the early stage of the polymerization was observed in the runs with lower CTAB and the particle size remained relatively constant in the runs with higher CTAB, can be well explained by the classical theory of emulsion polymerization.

From Fig. 4, where particle size evolutions in runs with different CTAB by semicontinuous process were given, a quite different profile was observed compared to that observed in Fig. 3 for batch process. A gradual increase in particle size was seen in all runs regardless of the CTAB levels, which is common for semicontinuous emulsion polymerization [32,33] when monomer feed rate is slower than polymerization rate while surfactant concentration is above its CMC, as is the present case. Under such circumstance, particles are well stabilized and the polymerization of the introduced monomers contributes to particle growth. As to the difference in the particle size in runs with different CTAB levels, i.e. particle size observed was in the reverse order of the CTAB levels as seen in batch process (Fig. 3), it can be understood in the same way as described for batch process.

#### 3.4. Evolutions of $\zeta$ potential and surface tension during batch emulsion polymerization

It is to note that all latex samples were diluted to solids of 0.10% prior to test of  $\zeta$  potential, because  $\zeta$  potential was dependent on latex solids as shown in Fig. 8. Evolutions of  $\zeta$  potential of latex particles and surface tension of latexes during polymerization with different CTAB by batch process are depicted in Fig. 5. Basically, evolution of  $\zeta$  potentials of all latex particles in batch process was characterized by a high value at early stage of polymerization, followed by a sharp decrease. This decrease was believed to be due to growth of latex particles. At starting, CTAB were assumingly presented under 4 different forms, namely, CTAB molecules dissolved in aqueous phase, empty CTAB micelles, CTAB micelles with solubilized monomers, and CTAB adsorbed on monomer droplets, among which CTAB in the last item should be negligible compared to CTAB monomer micelles, particularly for the present system because of sparse water solubility of St and BA [31]. According to emulsion polymerization theory, the main loci of monomer polymerization are inside the micelles with solubilized monomers, thus turning these monomers-containing micelles into primary particles, which, with polymerization proceeding, would quickly become surfactant scanty due to particle growth. To keep the particles stabilized, CTAB molecules initially used in empty micelles first and those on the surface of monomer droplets secondly, along with monomers, would diffuse to the surface of the surfactant deficient primary particles due to thermodynamic driving force. The classical theory predicts also that monomer droplets disappear at around 30% of conversion of monomers. The disappearance of the monomer droplets is a turning point with regard to the availability of the surfactant molecules in the system. Before this point, there are surfactant molecules “in stock” for particle growth, i.e. those in free micelles or adsorbed on monomer droplets, which are available for the growing particles; whereas after this point, the only surfactant molecules in the aqueous phase to supply for particle growth are those remained in equilibrium, of which the amount depends on the extent of the polymerization in a given run. In principle, the particles surface coverage by surfactant will become lessened with continuing particle growth after this point.  $\zeta$  Potential should be concomitantly decreasing since the charge density on the particle surface should be declining with lessened charge. This was exactly the case observed in Fig. 5A, where  $\zeta$  potential was

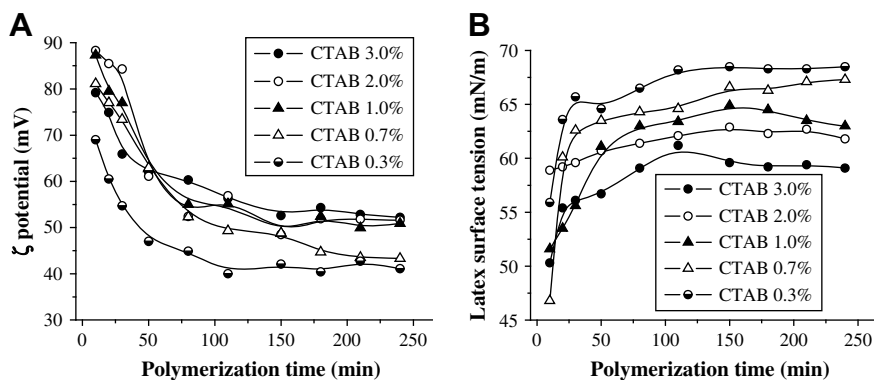


Fig. 5. Evolutions of  $\zeta$  potential (A) and latex surface tension (B) in batch process with different CTAB levels.

decreasing, and this decrease occurred earlier with lower CTAB level, because more supplementary CTAB was available in runs with higher surfactant. A close examination on the figure also revealed that the starting points of the sharp decrease in lower CTAB runs (0.3 and 0.7%) coincided to about 30% monomer conversion shown in Fig. 1. This may be taken as an indication that the classical emulsion polymerization theory, established based on polymerization using anionic surfactants, may well apply to this present system. Once monomer droplets disappeared, particles were assumed to be constituted by polymer and monomers, and monomer conversion was continued inside the particles, particle size would remain unchanged (Fig. 3), or even slightly decreased owing to a higher polymer density than its monomer. By consequence, the  $\zeta$  potential remained relatively constant afterwards as was observed in Fig. 5A.

In Fig. 5B was also presented variation of latex surface tension along the whole batch polymerization process. As mentioned above, the surfactant coverage on latex particles became more deficient with particle growth and monomer conversion, and so was the surfactant concentration in the surrounding aqueous phase, which entrained the rapid increase in latex surface tension as shown in Fig. 5B. This increase was quickly slowed down after about 30 min of polymerization, which was in accordance with shortage in surfactant supply. The relatively stable surface tension after 50 min of polymerization in Fig. 5B corresponded to the plateau region in  $\zeta$  potential in Fig. 5A and could be described based on the same mechanisms.

### 3.5. Evolutions of $\zeta$ potential and surface tension in latexes from semicontinuous process

In Fig. 6 were displayed the evolutions of  $\zeta$  potential and surface tension in polymerization through semicontinuous process. The

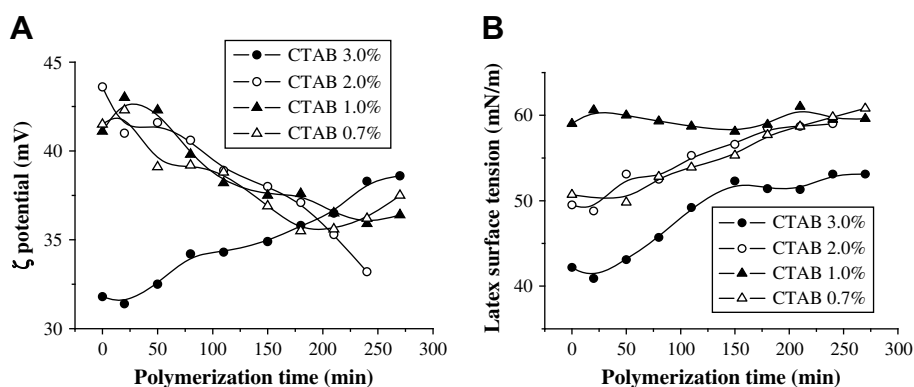


Fig. 6. Evolutions of  $\zeta$  potential (A) and latex surface tension (B) in semicontinuous process with different CTAB levels.

dependence of  $\zeta$  potential on CTAB level was much more complex than in batch process. First observation was that the initial  $\zeta$  potential in the run with 3.0% of CTAB was the lowest among all the runs, which was believed to be a reflection of increase in CTAB concentration in the aqueous phase rather than an adsorption of more CTAB on latex particles, namely, a higher concentration of CTAB molecules in the aqueous phase may cause this observation. From a theoretical viewpoint,  $\zeta$  potential is electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words,  $\zeta$  potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle [34]. Therefore, its value depends on the charge density on the particle surface and the charge level in the bulk aqueous surrounding, and will be lowered when the concentration of surfactant is increased once the particle surface coverage by surfactant molecules is saturated. This may explain the lowest initial  $\zeta$  potential in the run with 3.0% of CTAB. The lowest latex surface tension observed in the same latex (Fig. 6B) supports also a higher CTAB concentration in the aqueous phase. The lower initial  $\zeta$  potential in the run with 3.0% of CTAB, compared to those with 2.0% and 1.0% of CTAB, in batch process shown in Fig. 5 could also be understood in the same way.

As to the evolution of the  $\zeta$  potentials during polymerization, Fig. 6A showed clearly that  $\zeta$  potential was in constant decrease in the three runs with lower CTAB levels (2.0%, 1.0% and 0.7%), similar to latexes of batch process (Fig. 5), whereas the  $\zeta$  potential in the latex done with 3.0% of CTAB was in constant increase. In this semicontinuous polymerization, there was a redistribution of CTAB molecules between latex surface and water phase upon their addition into the reactor with preemulsion. With particle growth, more surfactant molecules were needed to assure the particle

**Table 2**  
Influence of CTAB on emulsion polymerization and latex properties.

Run <sup>a</sup>	CTAB <sup>b</sup> (%)	Solids (%)	Conversion (%)	$D_p$ (nm)	PDI <sup>c</sup>	$\zeta^d$ (mV)	$\sigma$ (mN/m)
B1	0.3	26.89	96.00	101.3	0.041	41.1	68.5
B2	0.7	28.22	98.74	82.0	0.058	43.3	68.3
B3	1.0	27.60	97.34	81.0	0.067	50.9	63.0
B4	1.5	28.27	97.34	77.9	0.046	50.4	62.3
B5	2.0	29.68	99.08	72.1	0.032	52.2	61.8
B6	2.5	27.98	98.73	67.6	0.085	54.0	60.3
B7	3.0	29.50	98.51	67.0	0.118	52.2	59.4
B8	3.5	27.65	92.85	66.9	0.155	52.4	52.2
B9	4.0	29.20	95.20	65.0	0.174	53.1	52.3

<sup>a</sup> Cationic AIBA as initiator, 0.1 g, 0.33% of the monomer mass.

<sup>b</sup> CTAB% by mass with regard to the mass of total monomers.

<sup>c</sup> Particle size dispersity index, PDI = 0 for monodisperse latex particles.

<sup>d</sup>  $\zeta$  Potential and surface tension  $\sigma$  of latex determined at 0.1% solids.

stability, and this was supplied by freshly added CTAB in the pre-emulsion. There are two possibilities for  $\zeta$  potential to decrease: the freshly added CTAB is less than the amount needed to maintain a same surface coverage with particle growth, or newly added CTAB was dissolved more in water phase than adsorbed on particle surface when particle surface was fully CTAB covered because the potential between the charge on particle surface and that in surrounding medium would be lessened as discussed above; and an increase in  $\zeta$  potential ought to be detected only if the newly added CTAB was more adsorbed on particle surface in comparison with those dissolved in water phase. Taking into account of the evolution of the surface tension of the latex, which was in regular increase with polymerization as displayed in Fig. 6B, it could be concluded that the particle surface coverage in the runs with 2.0% or lower level of CTAB was going down with polymerization; while for the run with 3.0% of CTAB, the surface coverage may be kept nearly constant, and only CTAB concentration in the water phase was going down owing to the presence of CTAB in excess at beginning of the polymerization. This interpretation could explain all the results displayed in Fig. 6. In addition, the evolution of latex surface tension shown in Fig. 6B was in the same direction of the evolution observed in batch process (Fig. 5B), although here this increase was much more moderate compared with batch process. This different observations in  $\zeta$  potential and surface tension of latex in semi-continuous latexes revealed that  $\zeta$  potential was a more sensitive element, which described better what was happening in the latex than the surface tension could do.

### 3.6. Latex property dependence on CTAB surfactant level

A series of latexes with different CTAB content were carried out using batch process, properties of the final latexes were determined and collected in Table 2.

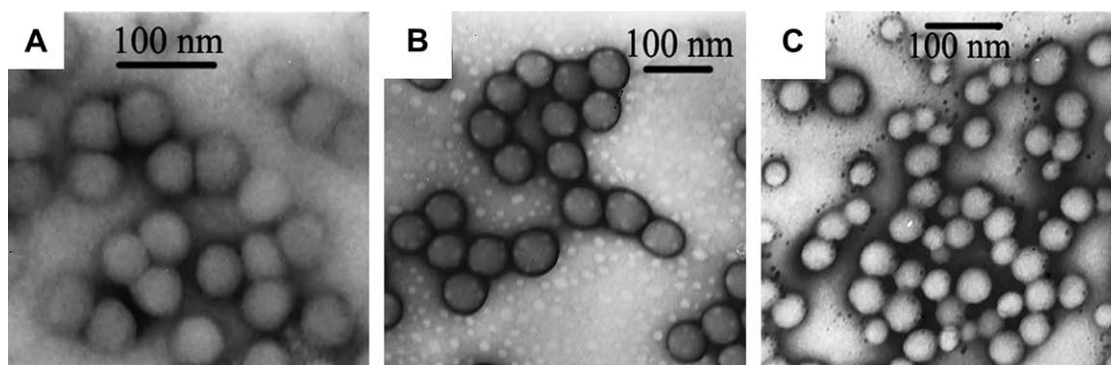
It is seen from Table 2 that particle diameter  $D_p$  displayed a quite regular decrease with increase in CTAB. This decrease was much less significant than usually observed in emulsion polymerization using anionic surfactant. Interestingly, the particle size distributions were all reasonably narrow except for the samples with high CTAB levels, where a slightly broader PDI was observed (CTAB  $\geq$  3.0%). In order to have a visual examination on the particle size and size distribution, TEM pictures of the samples B1 (0.3% CTAB), B3 (1.0% CTAB) and B7 (3.0% CTAB) are given in Fig. 7, which clearly showed a broader particle size distribution in sample B7, in accordance with the results in Table 2.

In Table 2,  $\zeta$  potential of the latex particles was showing a regular increase with CTAB up to 3.0%, after which it remained relatively constant. The regular increase in  $\zeta$  potential with increase in CTAB when CTAB was below 3% was due to presence of more CTAB adsorbed on latex particle surface. At low concentration, increased CTAB was mainly adsorbed onto the particle surface, contributing to an increase in  $\zeta$  potential; further increase in CTAB would not contribute to  $\zeta$  potential increase once the particle surface was saturated by surfactant, thus leading to a relative constant  $\zeta$  potential as seen in Table 2. In accordance with  $\zeta$  potential, the surface tension of the latexes,  $\sigma$ , was in gradual decline with increase in CTAB, which was an indication of presence of more CTAB in aqueous phase of the latexes.

### 3.7. Latex $\zeta$ potential and mechanisms of CTAB adsorption

Further study revealed that  $\zeta$  potential was function of polymer latex solids as shown by data in Fig. 8.

$\zeta$  Potential evolution for the three samples displayed in Fig. 8 was characterized by a common feature: with latex solids decreasing by gradual dilution,  $\zeta$  potential was relatively constant when the solids was above 20%, it ascended to a higher value when



**Fig. 7.** TEM micrographs of latex particles prepared with varied CTAB levels. (A) Latex B1, CTAB 0.3%; (B) latex B3, CTAB 1.0%; (C) latex B7, CTAB 3.0%.

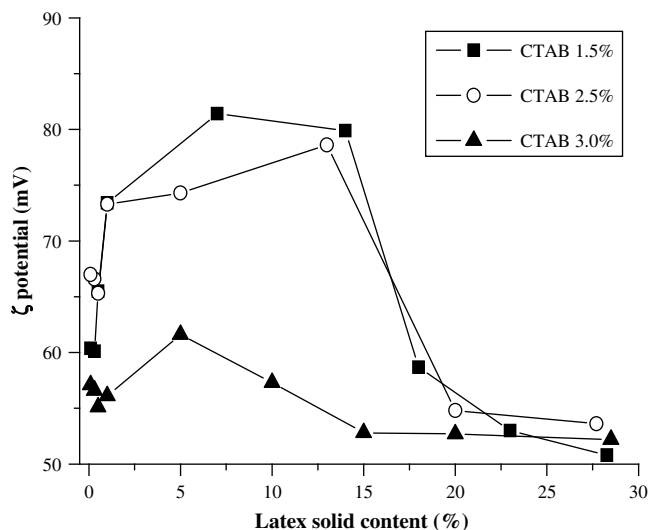


Fig. 8. Dependence of  $\zeta$  potential on latex solids in latexes prepared with different CTAB levels.

further diluted to solids between 15% and 1% depending on CTAB content in the original latex, followed by a sharp descent,  $\zeta$  potential reached finally to a constant value. At high solids ( $\geq 20\%$ ), CTAB was in excess and its concentration far above its CMC (determined to be of  $5.3 \times 10^{-4}$  mol/L), the aqueous surrounding of the particles was rich of CTAB micelles and molecules so that the  $\zeta$  potential was low. Upon addition of water to lower the solids, CTAB concentration in aqueous phase was decreasing through simple dilution while CTAB adsorbed on particles surface were not significantly affected because CTAB concentration was still above or close to its CMC, this ought to lead to an increase in  $\zeta$  potential as observed when the solids were varied between 20% and 15% for the 2 samples with CTAB  $\leq 2.5\%$ . The same was observed for the solids between 15% and 5% for the sample with 3.0% CTAB. However, with further dilution of the latex, this increase should reach its maximum at one point, where molecules of CTAB in aqueous phase and those adsorbed on particle surface were approaching to its critical equilibrium. Starting from this point, when going to higher solids (with less water added), micelles were present and shortage of CTAB due to dilution was supplied through disappearance of CTAB micelles,  $\zeta$  potential was not that sensitive with addition of water, namely, it was relatively constant; whereas going to lower solids with further dilution, CTAB micelles were to disappear, individually molecules dissolved in water started to decrease in

a perceptible manner because no micelles were present to supply the need of CTAB due to this dilution, and part of the CTAB adsorbed on particles surface started to desorb, which should contribute to decrease  $\zeta$  potential. This would occur at or around the CMC of the CTAB. From Table 3, where concentrations of CTAB corresponding to latex solids for the run with 1.5% of CTAB were given, it can be seen that CTAB concentration went below its CMC at about 1.0% of latex solids. The sharp decline in  $\zeta$  potential in Fig. 8 was in good agreement with this interpretation. It is obvious that the evolution of  $\zeta$  potential was narrowly related to CTAB concentration. With latex prepared using higher CTAB, this variation in  $\zeta$  potential should be less pronounced, because reduction in CTAB concentration with latex dilution was lessened at same latex solids in comparison with those done with lower CTAB levels. This could serve to understand the much lessened variation of  $\zeta$  potential in the sample done with 3.0% of CTAB. With further dilution and thus further desorption of CTAB from particle surface, it is easy to conceive that a decrease in  $\zeta$  potential was expected to occur. And at the last stage of latex dilution to very low solids, most of the CTAB, initially adsorbed on latex particle surface was desorbed. The residual minimal CTAB on particle surface became hard to be desorbed, so that the  $\zeta$  potential became again relatively stable as was the case when latex solids were below 0.5%. This was exactly what observed in Fig. 8.

To further confirm these observations and provide more support for the proposed mechanisms of the evolution of CTAB adsorption and desorption, single CTAB molecule adsorption area on the particle surface was calculated and its evolution following latex dilution along with  $\zeta$  potential and latex surface tension is presented in Table 3.

The CTAB molecular adsorption area was calculated based on latex solids, particle size, particle polymer density ( $1.07 \text{ g/cm}^3$  used) and CTAB concentration. According to the way CTAB adsorbed on particles was calculated as described in experimental section, two series of CTAB molecular adsorption areas,  $S_a$  and  $S_b$ , are given in Table 3.  $S_a$  was calculated using CMC of CTAB ( $5.3 \times 10^{-4}$  mol/L) for all latexes when CTAB concentration was superior to its CMC (solids  $\geq 2.18\%$ ), and assumed that all CTAB was adsorbed on particle surface once its concentration was inferior to its CMC (solids  $\leq 1.02\%$ ). For  $S_b$ , the entry "CTAB in serum" (data row 7 in Table 3) was subtracted from CTAB in latex (data row 2) in order to estimate the amount of CTAB absorbed on particle surface.

$S_b$  values indicated clearly that molecular adsorption area at higher solids (also high CTAB concentration) was relatively constant and varied slightly between 4.70 and 5.00  $\text{nm}^2$ ; a more pronounced increase was observed with continuous latex dilution; and interestingly, these  $S_b$  values became again stable once the concentration

Table 3  
Evolution of cationic latex properties with 1.5% of CTAB with latex dilution.

Latex properties	28.27	21.27	14.01	7.00	4.37	3.27	2.18	1.02	0.50	0.30	0.10
Latex solids (%)	28.27	21.27	14.01	7.00	4.37	3.27	2.18	1.02	0.50	0.30	0.10
CTAB in latex ( $10^{-4}$ mol/L $\text{H}_2\text{O}$ )	176.00	120.00	71.3	32.9	20.04	15.00	10.01	4.41	2.18	1.31	0.452
Latex surface tension (mN/m)	62.30	63.56	69.98	81.42	60.58	60.76	61.00	73.17	65.60	60.78	60.65
$\zeta$ Potential (mV)	50.4	53	79.9	81.4	77.7	76.6	72.7	73.4	65.5	60.1	60.36
Number of particles ( $N_p$ , $10^{18}/\text{L}$ )	7.23	4.96	2.99	1.38	0.84	0.62	0.41	0.185	0.092	0.055	0.018
Serum properties after latex freezing and centrifugation											
Serum surface tension (mN/m)	34.09	35.23	36.12	38.43	–	43.24	–	49.57	54.45	57.74	58.95
CTAB in serum ( $10^{-4}$ mol/L $\text{H}_2\text{O}$ )	6.14	5.77	5.56	4.91	–	3.59	–	2.15	1.25	0.71	0.25
Calculated data											
Total particle surf. ( $10^3 \text{ m}^2/\text{L H}_2\text{O}$ )	48.04	32.95	19.87	9.17	5.58	4.12	2.72	1.23	0.613	0.367	0.122
$S_a^a$ ( $\text{nm}^2$ ) (using CMC)	4.67	4.77	5.00	5.52	6.31	7.19	9.62	4.63	4.67	4.65	4.49
$S_b^b$ ( $\text{nm}^2$ ) (using CTAB in serum)	4.70	4.79	5.02	5.44	–	5.99	–	9.03	10.39	10.16	10.13

<sup>a</sup>  $S_a$ , CTAB molecular adsorption area calculated using its CMC as CTAB amount dissolved in water phase for latex with solids above 2.18% (when CTAB concentration was above CMC) and assuming all CTAB adsorbed on latex particles for the rest of the 4 latexes; and  $S_b$ , calculated using data in the row "CTAB in serum", the experimental CTAB concentration detected in latex serum.

of CTAB was below its CMC, i.e.  $5.3 \times 10^{-4}$  mol/L, starting at solids = 1.02%. Comparing  $S_a$  values with those of  $S_b$ , different evolution profile was observed: (1) At high CTAB concentration at same latex solids (also same CTAB total concentration),  $S_a$  values were very similar, indicating that CTAB in aqueous phase was fully saturated; (2) At lower CTAB concentrations but still superior to its CMC (solids > 1.02%), both  $S_a$  and  $S_b$  were increasing with latex dilution, implying that amount of CTAB adsorbed on particle surface was decreasing. The more pronounced increase in  $S_a$  than in  $S_b$  indicated that CTAB concentration in aqueous phase started to decrease with latex dilution before CMC being reached, as shown the entry CTAB in serum in the table; (3) Once CTAB concentration was below its CMC, these two values of molecular adsorption areas became significantly diverged depending on the ways they were calculated.  $S_a$  values, based on assumption that all CTAB molecules were adsorbed on particle surface, were very similar to those at high CTAB concentration; whereas  $S_b$  values became much larger, indicating less CTAB adsorbed on particle surface. The quite identical  $S_b$  when CTAB was below its CMC indicated that these were firmly adsorbed CTAB molecules, which were not desorbing any more from the particle surface with latex dilution. From the ways these molecular adsorption areas were obtained, it was appropriate to conclude that  $S_b$  values were more reliable, because it was obtained based on the experimental data of CTAB concentration in aqueous phase. And in addition, the abrupt decrease observed in  $S_a$  values when latex was diluted to solids below 1.02%, implying more CTAB absorbed once CTAB concentration was below its CMC, was also not conceivable. These results clearly indicated that  $\zeta$  potential and surface tension in the latex were directly related with surfactant adsorption on the particle surface. The molecular surface adsorption area of CTAB on latex particle surface could be used to explain the evolution of latex properties such as  $\zeta$  potential and latex surface tension.

It is to point out that, molecular adsorption areas of CTAB thus determined were larger than those reported by Landfester et al. [17] in miniemulsion polymerization, which gave this adsorption area varying between  $2.02 \text{ nm}^2$  (for a latex prepared using 10 mM of CTAB, AIBN as initiator and with particles diameter of 116 nm) and  $1.12 \text{ nm}^2$  (for a latex with 20 mM of CTAB, with particles diameter of 89 nm), because those data were obtained with the simplistic assumption that all or most surfactant molecules were located at the particle surface.

#### 4. Conclusions

Emulsion copolymerization of St/BA at 50/50 monomer composition by weight was carried out with cetyl trimethyl ammonium bromide (CTAB) as surfactant at levels varied from 0.3% to 4.0% relative to monomer amount using batch and semicontinuous processes. For batch process, a high polymerization rate was observed in the first 90 min. For semicontinuous process, a relatively constant polymerization rate was observed during the whole process of polymerization due to monomer starvation imposed by slow addition rate of monomer preemulsion. With increase in CTAB, particle size in final latex was slightly decreased, latex particles are quite monodisperse in latexes with CTAB of up to 3.0% in batch

prepared latexes; whereas in semicontinuous latexes a similar decrease in final particle size was detected, the particle growth period was obviously extended. As to the  $\zeta$  potential of the latex particles, a slight increase was observed with increase in CTAB, and the surface tension of the latexes was increasing in accordance with the observed decrease in  $\zeta$  potential. It was found that  $\zeta$  potential of the particles depended on latex solids. Upon water addition into the latex for dilution, this  $\zeta$  potential past through a maximum at about 80 mV and decreased finally to a relatively constant values around 60 mV when latex solids were reduced to a level equal to or lower than 1.0%. When anionic initiator was used instead of positively charged CTAB,  $\zeta$  potential in final latex was much lower than that in latex done with cationic initiator; while  $\zeta$  potential in latex prepared with charge-free redox initiator was in between those prepared using with CTAB and ammonium persulfate.

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