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SYNTHESIS, PURIFICATION AND CHARACTERIZATION OF CATIONIC LATICES PRODUCED BY THE EMULSION COPOLYMERIZATION OF STYRENE WITH 3-(METHACRYLAMIDINOPROPYL)TRIMETHYLAMMONIUM CHLORIDE

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Abstract—A study was made of the effect of varying the amount of 3-(methacrylamidinopropyl)trimethylammonium chloride (MAD) on the emulsion copolymerization of styrene and MAD with azo-bis(isobutyramidine hydrochloride) as initiator. The addition of MAD accelerated the polymerization and decreased the particle size. Cleaning of these latices in order to remove polyelectrolyte not incorporated in the latex particles was found to be tedious. Serum replacement, diafiltration and centrifugation appeared to be unsatisfactory since desorption of polyelectrolyte was still observed after standing or stirring. A combination of centrifugation and treatment with silica appeared to clean the latices to a satisfactory level (expressed as $[N^+] < 5 \times 10^{-7}$ mol/dm³). Surface charge density, as determined by conductometric acid–base titrations, rose slightly on increasing the initial MAD concentration. Shot-growth (two-step) emulsion polymerization or the use of a cross-linking agent (divinylbenzene) hardly affected the surface charge density.

INTRODUCTION

The immobilization of catalytic systems on insoluble supports has received considerable academic and industrial attention over the last few decades. Most of these investigations focused on organic supports that can be functionalized by chemical reactions [1, 2]. Generally, after immobilization the activities of intrinsically highly catalytic systems have been disappointing. In most cases this is due to mass transfer limitations to the support particles (interparticle diffusion) or within the particles (intraparticle diffusion). To overcome these problems, smaller nonporous particles are needed but a drawback of particle size is the need for more sophisticated techniques to purify the resulting products.

Emulsion polymerization offers the possibility of synthesizing these small, organic, nonporous particles in the submicron region. This polymerization technique also allows the synthesis of particles with narrow particle size distribution (monodispersity). Functionalization of these latices can then be achieved by emulsion polymerization in the presence of a functional monomer, a functional surfactant, a functional initiator or by post-polymerization modification [3].

In a conventional emulsion polymerization, latices are stabilized by surfactants. The removal of stabilizer after polymerization is difficult, and coagulation may result [4, 5]. In the case of surfactant-free emulsion polymerization of styrene, particles are stabilized by ionic initiator residues. Potassium persulphate as initiator has been studied extensively and was found

to give sulphate stabilized latices [4, 9]. In order to obtain a better control of both particle size and surface charge density, ionic comonomers can be used. Most studies have been concerned with the stabilization by anionic groups [10–14] introduced by sulphonate-containing monomers. Other types of ionic monomers frequently used are monomers containing carboxyl groups [15–20], and nonionic hydrophilic monomers like acrylamide and acrylamide derivatives [21–24]. Surprisingly, the use of cationic comonomers is less common [25–29]. The use of surfactant-like monomers has also been reported [30–32].

Our goal is to prepare stable cationic latices with high surface charge density as supports for cobalt(II)phthalocyanine-tetrasodiumsulphonate (CoTSPc). In this paper we describe the synthesis, purification and characterization of cationic latices prepared by emulsion polymerization of styrene in the presence of the functional cationic comonomer, 3-(methacrylamidinopropyl)trimethylammonium chloride (1, MAD) and azo-bis(isobutyramidine hydrochloride) (2, AIBA) as initiator (Scheme 1).

EXPERIMENTAL PROCEDURES

Emulsion polymerization

Styrene (Merck) and divinylbenzene (DVB; 65 wt% divinylbenzene isomers, 30 wt% ethylvinylbenzene isomers; Merck) were distilled before use. AIBA (Polyscience) was used as purchased. MAD (Merck) was received as a 50% aqueous solution. The inhibitor was removed by extraction with diethylether. The remaining solution was flushed with N₂ and stored at –18°. A double-wall all-glass reactor, thermostated at 60° and equipped with a mechanical stirrer, was filled with 350 ml of distilled deoxygenated water and

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Scheme 1. Structure of MAD (1) and AIBA (2).

flushed with argon for 20 min. Styrene (30 g) was then added to the reactor and after 5 min the desired amounts of MAD and AIBA were added together with 50 ml of water. The emulsion polymerization was carried out under argon and the stirring speed was maintained at 300 rpm. Each polymerization was stopped after *ca* 16 hr and the product was filtered through glass wool to remove any possible coagulum. All concentrations are based on the water volume.

Shot-growth experiments. The first step was identical to S2 (see Table 2), i.e. 400 ml water, 30 g styrene, 0.5 g MAD and 0.5 g AIBA. A second batch of monomers was added after 3 hr (6 g styrene, 150 mg AIBA, a varying amount MAD and 50 ml of water).

For kinetic experiments, samples were taken in order to monitor conversion and the polymerization was stopped by the addition of hydroquinone-monomethylether. After evaporation of the volatile components by heating at 90° and drying of the sample under reduced pressure, the styrene conversion was determined by weight.

Cleaning procedure

The latex (≈ 100 ml) was centrifuged twice (20,000–30,000 rpm for 30 min, Centrikon T-2060), decanted, redispersed in water and then treated with 2–5 g silica (Merck, Kieselgel 60 for column chromatography, 63–200 μm). After each treatment, the silica was filtered off on a paper filter. Silica treatment, followed by filtration was repeated twice. The latex was subsequently centrifuged twice before rinsing with aq. NaOH (pH = 11) in a serum-replacement cell provided with a 50 nm polycarbonate membrane (Nucleopore). After the passage of at least 15 cell volumes of diluted base, the cell was flushed with at least 20 cell volumes of deionized water followed by titration of the latex.

VIS spectra were recorded on a Hewlett–Packard diode array 8451A spectrophotometer using a 1 cm cell. Average particle size and polydispersity were determined by Scanning Electron Microscopy (SEM).

Titration

An amount of latex was weighed and, where necessary, water was added to make up to a volume of 25 ml. The latex solution was flushed with argon for at least 30 min. The inert atmosphere was maintained during the titration. The latex was titrated with 0.001 N HCl solution. The conductivity was monitored using a Radiometer CDM80 conductivity meter. The surface charge density was calculated from latex solid contents and titration data.

RESULTS AND DISCUSSION

Kinetics of emulsion polymerization

Surfactant-free emulsion copolymerization with ionic comonomers is not as straightforward as it may seem, particularly because of the great difference between water-solubility of the two monomers. In a classical emulsion polymerization, i.e. the polymerization of a scarcely water-soluble monomer (e.g. styrene) in the presence of a water-soluble initiator and a surfactant, the kinetics may be described by the Smith–Ewart theory [32]. The most important mechanistic difference between a classical and a surfactant-free emulsion polymerization is the nucle-

ation stage, the so-called stage I. In the case of conventional emulsion polymerization, particles may originate from monomer-swollen micelles activated by initiator radicals (micellar nucleation). Particle production stops when all surfactant molecules have been adsorbed on the already existing particles. This is the end of stage I. In the case of a surfactant-free emulsion polymerization, e.g. copolymerization of the scarcely water-soluble styrene with the water-soluble MAD, the homogeneous nucleation mechanism is likely to occur [26, 34]. Thermal decomposition of the water-soluble initiator starts copolymerization of MAD with styrene in the water phase. Copolymerization in the water phase proceeds until the oligomer:

- (i) is captured by already existing particles;
- (ii) reaches a critical chain length after which it will "precipitate" to form a primary particle; or
- (iii) terminates before it can be adsorbed or can nucleate [35].

These processes are dependent on the solubility (hydrophobic–hydrophilic balance) of the formed oligomer, the capturing ability of the already existing particles and the rate of termination of the oligomers in the water phase. Primary particles coalesce to larger particles until their surface charge provides sufficient colloidal stability. Particle production stops when all oligomeric radicals are captured by already existing stable particles before nucleation can occur.

The effect of MAD concentration on the styrene conversion as a function of time is shown in Fig. 1. An increase of the initial MAD concentration accelerates the rate of styrene conversion. Since the rate of polymerization is affected by the number of particles, the particle size of the resulting latices was measured as a function of the MAD concentration (Fig. 2). Indeed, the particle size drops on increasing the MAD concentration: it will be shown below that this is due to the increase of surface charge density.

To eliminate any possible influence of (very small concentrations of) polyelectrolyte in the commercially available MAD, unquaternized amine was treated with iodomethane. The ammonium salt thus formed appeared to be free of polyelectrolyte, and increased particle size in emulsion copolymerization

Fig. 1. Effect of MAD concentration on the styrene conversion. *, [MAD] = 0 mol/dm³; □, [MAD] = 2.8×10^{-3} mol/dm³; △, [MAD] = 5.7×10^{-3} mol/dm³ (for other experimental conditions see Fig. 2).

Fig. 2. Effect of MAD concentration on the particle size [styrene] = 0.72 mol/dm^3 , [AIBA] = $4.6 \times 10^{-3} \text{ mol/dm}^3$, $T = 60^\circ$.

with styrene, compared with MAD under identical experimental conditions. In order to determine whether the origin of this unexpected phenomenon was due to the absence of polyelectrolyte or to the introduction of iodide, two emulsion polymerizations were carried out in the presence of MAD, one in the presence of NaCl and the other in that of equimolar NaI. The conversion versus time curves (Fig. 3) clearly show that the retardation of styrene conversion is not caused by the presence of low concentrations of polyelectrolyte, but stems from the presence of the iodide salt. We are not aware of any publication reporting this effect. It appears that iodide reacts as a radical scavenger, thereby reducing the overall efficiency of the initiator and resulting in an increase of particle size. This effect is still under investigation.

Latex purification

Earlier work in our laboratory showed that the CoTSPc-catalysed thiol oxidation in the presence of cationic polymer is dependent on the linear charge density on the backbone of the polyelectrolyte. In this line of thought, the catalytic activity of the latices will also be affected by its surface charge density. It is therefore necessary to determine the surface charge density of the produced latices.

Because of the very great difference between the partition coefficients of the monomers, the formation of free water-soluble polyelectrolyte (i.e. copolymer of styrene and MAD not anchored onto the latex particles) is likely to occur. In order to determine the surface charge density reliably, these polymeric side products, together with low molar mass contaminants, must be removed prior to surface charge determination.

In addition, the CoTSPc catalytic system is extremely susceptible to very low concentrations of cationic polymer. We have found that, for the present homopolymer (PMAD), the thiol oxidation is affected at free polyelectrolyte levels corresponding to $[N^+] = 10^{-6} \text{ mol/dm}^3$ [36]. In order to measure the true activity of the immobilized PMAD/latex system only, it is thus essential to clean the latex to such an extent as to obtain a polyelectrolyte concentration of the serum of the latex lower than

$[N^+] = 10^{-6} \text{ mol/dm}^3$. Aiming at the detection of extremely low concentrations of cationic polymer, we developed a VIS spectrophotometric method based on the occurrence of the dimeric or monomeric structure of CoTSPc in the presence or absence of these charged polymers, respectively [37, 38]. Because of the very high extinction coefficient of CoTSPs and to the clear difference between the VIS spectra of these two structures, this technique provided an excellent and sufficiently sensitive method for determining trace amounts of polycations.

As a result of the smaller particle diameter, purification of the latex requires more sophisticated cleaning techniques than those available for resin particle cleaning. El-Aasser reviewed various latex-cleaning techniques [39], e.g. dialysis, ion-exchange [4], serum replacement [40, 41], microfiltration [42] and diafiltration [43]. Low molar mass impurities can generally be removed by one of these methods. On the other hand, the removal of polyelectrolyte by one of these methods will usually be more difficult [44].

The often used ion-exchange method alone is known to be insufficient to clean latices from polyelectrolyte [41, 45]. Moreover, the purification of the commercially available ion-exchange resin itself, i.e. the removal of charged polymeric contaminants, is laborious. We therefore purified polystyrene latices, stabilized by a block copolymer of styrene and quaternized 4-vinylpyridine, by using the ion-exchange method followed by serum replacement [38]. In that case, the combination of these two techniques appeared to be sufficient to cleanse the latex of polymeric contaminants. Unfortunately, this cleaning method was not satisfactory in all cases. Before developing a cleaning technique by ourselves, we tested three well-known purification methods for cleaning MAD stabilized polystyrene latices, viz. serum replacement, diafiltration and ultracentrifugation.

In the case of the serum replacement, Ahmed *et al.* [40] showed that the removal of salt from a diluted latex-containing low molar mass electrolyte is somewhat slower than expected theoretically implying interaction of the electrolyte with the polymer particle. It can be expected that in the present case, where interaction of polymeric contaminants with the latex

Fig. 3. Effect of the presence of iodide on the polymerization rate of styrene. [MAD] = $1.15 \times 10^{-2} \text{ mol/dm}^3$; [NaCl] = [NaI] = $1.0 \times 10^{-2} \text{ mol/dm}^3$; Δ , NaCl; *, NaI (for other experimental conditions see Fig. 2).

is very likely, the cleaning process will be even more time consuming. Indeed we observed that the cleaning procedure could take days or weeks, depending on the water flow through the cell and on the conditions used during the emulsion polymerization, i.e. the concentration of the charged monomer. The total volume of cleaning water ranged between 30 and 100 times the cell volume before the polyelectrolyte concentration in the effluent of the serum replacement cell was less than 5×10^{-7} mol/dm³ as determined by the CoTSPc-VIS method.

Diafiltration, a technique very similar to serum replacement was also investigated. Instead of pumping water through the cell containing a latex solution, the latex is continuously circulated in a tangential flow pattern through channels over a membrane by the use of a pump, and, shear-induced coagulation may occur. In our case, this method did not appear to be faster than the serum-replacement technique as was claimed by others [42] and indeed, in some cases coagulation was observed.

Latices cleaned by serum replacement and diafiltration were tested by stirring a dilute latex solution for 15 min at 2600 rpm at 25°, simulating the experimental conditions of the thiol oxidation. The resulting solution was centrifuged and the serum tested for the presence of polyelectrolyte by the CoTSPc-VIS method. In latices cleaned by serum replacement or diafiltration, unacceptably high levels of polyelectrolyte appeared to be desorbed after stirring. Apparently, both techniques purified the latex to such an extent as to leave some polyelectrolyte adsorbed to the latex surface. This polyelectrolyte desorbs so slowly that its concentration in the effluent is too low to be detected by the CoTSPc-VIS method ($[N^+] < 5 \times 10^{-7}$ mol/dm³). If, however, these cleaned latices were left to stand for approximately one week, or were subjected to vigorous stirring, the sera of the latices were found, after centrifugation, to contain detectable concentrations of polyelectrolyte.

Some authors claim the "complete" removal of polymeric contaminants by centrifugation [15, 24, 31]. We also tried to clean latices this way, i.e. repeated centrifugation, followed by decantation and redispersion in water. Unfortunately, even after six centrifugations, the serum of the resulting latex still

contained, at least for our catalytic systems, unacceptably high levels of polyelectrolyte. The technique is also very laborious. This cleaning method clearly demonstrated the effect of ionic strength of the serum on the desorption rate of polyelectrolyte (Table 1). As can be seen from Table 1, the CoTSPc-VIS method suggested, after one centrifugation of the latex, the absence of free polyelectrolyte (both samples A and B). Much to our surprise, after redispersion of the remaining solid in pure water followed by a second centrifugation, the CoTSPc-VIS method indicated the presence of polyelectrolyte (both samples A and B). After redispersion of the solid in a salt solution (0.1 M KNO₃) and subsequent centrifugation, the CoTSPc-VIS method again suggested the absence of polyelectrolyte (sample A), while the serum, after redispersion of the same solid in pure water, followed by centrifugation, contained polyelectrolyte according to our detection method (sample B). These findings are in good agreement with the theoretical considerations put forward by Hesselink [46]. The effect that the adsorption isotherm of charged polymers onto charged surfaces is determined by a coulombic and a nonionic adsorption term. If the charges have the same sign, as in our case, the latter must predominate, otherwise no adsorption would occur (the coulombic term has a negative effect on the adsorption isotherm due to the identical sign of the charges). Addition of salt will decrease the desorption rate as a result of a decrease in the electrostatic repulsion between the polyelectrolyte and the charged latex surface.

From all these attempts to clean the cationic latices, it became clear that, after using one of the known purification methods, the cleaned latices will contain unacceptably high levels of polyelectrolyte. For this reason, it was necessary to develop a method to clean latices to such an extent as to render polymer colloids suitable for the support of CoTSPc in catalytic systems.

It was found in our laboratory that cationic polymers like 2,4-ionene adsorb strongly to silica. Following this line of thought, we also tried to purify the cationic latices by this adsorption medium. In order to reduce simultaneously the amount of soluble charged polymer and the ionic strength of the latex solution, the latex was centrifuged twice before treatment with silica. Figure 4 shows the effect of silica treatment on the presence of polyelectrolyte in the sera of these latices, as determined by the CoTSPc-VIS method. A treatment with silica consists of shaking the latex with silica for at least 12 hr, followed by filtration. Curve A shows the presence of polyelectrolyte in the serum after two centrifugations (presence of dimeric structure of CoTSPc at 630 nm). Curve B clearly shows that after one treatment with silica the serum still contained polyelectrolyte. Curves C and D show that after 2 and 3 treatments of latex with silica the serum contained polyelectrolyte at concentrations below 5×10^{-7} mol N⁺/dm³ (monomeric structure of CoTSPc at 660 nm). To rid the latex of any possible further impurities undetectable by the CoTSPc-VIS method, the latex was centrifuged twice after being treated with silica. Most important of all, the sera of the latices remained free of polyelectrolyte after stirring at 2600 rpm for

Table 1. Effect of ionic strength on the desorption of polyelectrolyte as measured by the occurrence of monomeric or dimeric structure of CoTSPc in the sera of the precipitated latices

Number of centrifugations	Serum of sample A	Serum of sample B
1	— ^a	—
2	+ ^b	+
3	—	+
4	+	+

^a — = absence of polyelectrolyte according to CoTSPc-VIS method.

^b + = presence of polyelectrolyte according to CoTSPc-VIS method.

Sample A: (1) centrifugation, (2) redispersion in distilled water followed by centrifugation, (3) redispersion in 0.1 M KNO₃ followed by centrifugation and (4) redispersion in distilled water followed by centrifugation. Sample B: as sample A, except for step (3) where distilled water was used instead of 0.1 M KNO₃.

Fig. 4. The effect of cleaning latex with silica in the presence of polyelectrolyte in the serum. (A) After two centrifugations, (B) one treatment with silica followed centrifugation, (C) two treatments with silica followed by centrifugation and (D) three treatments with silica.

15 min, nor could any polyelectrolyte be detected in the sera after the latex was left to stand for more than one week. The major difference between this cleaning technique and the common techniques is that, in the former case, the desorption of polyelectrolyte from the latex surface is enhanced by the addition of another strongly absorbing material during the collision of latex particles with the silica spheres whereas, in the traditional cleaning techniques, the desorption is purely controlled by the adsorption-desorption equilibrium. The disadvantage of adding strongly adsorbing material is that in a few cases coagulation of the latex was observed during the cleaning process, probably initiated by the adsorption of cationic particles on the silica surface.

Latex characterization

Only a few techniques and few data appear to be available to characterize surface charge densities of cationic latices [26,47]. We tried to determine the surface charge by potentiometric titration of the latex with silver nitrate immediately after the silica cleaning procedure. All ammonium groups on the surface of the latex particles should have chloride as counterion. It was found that the surface charge density of various latices thus determined showed no relation to the initial MAD concentration. We therefore tried another, although more time-consuming technique, viz. replacement of the counterion with hydroxide by the serum replacement technique, rinsing the latex with dilute sodium hydroxide solution ($\text{pH} \approx 11$). This was followed by extensively washing of the latex with pure water to remove excess of base and by subsequent conductometric acid-base titration of the resulting latex. The surface charge densities so determined showed a satisfactory relation to the MAD content and were quite different from those determined by the silver nitrate method. These experiments suggest that cleaning of latices with silica replaces the chloride ion by an unknown counterion that does not precipitate on the addition of silver nitrate.

Figure 5 shows a typical titration curve of a latex, containing hydroxide as counterion. At first the

Fig. 5. Conductivity as a function of the amount of acid added to latex S2 $[\text{HCl}] = 0.001 \text{ mol/dm}^3$, 0.321 g (solid) in 25 ml water.

conductivity of the latex solution hardly changes on the addition of the hydrochloric acid (0.001 mol/dm^3) indicative of the reduced mobility of the counterion. When all the hydroxide ions have been replaced, the conductivity rises steeply as a result of the excess of acid. The number of basic groups on the particle surface can be calculated from the intersection of these two lines. The results of the titration are shown in Fig. 6 and Table 2. It can be seen that the surface charge density increases slightly on raising the initial MAD concentration confirming the conversion-time curves. Considering the high affinity-type adsorption isotherm of polymers [46], it seems reasonable to assume that, during the emulsion polymerization, polyelectrolyte is adsorbed by the growing particles and, in consequence, increases the colloidal stability of the growing particles. On further increasing the comonomer (MAD) concentration, more MAD-rich copolymer or even homopolymer formation is likely. The presence of more polyelectrolyte may result in:

- (i) bridging between particles resulting in a broadening of the particle size distribution (D_w/D_n);
- (ii) continuous formation of primary particles resulting in a heterodisperse latex system.

Fig. 6. Surface charge density ($\mu\text{mol/m}^2$) as a function of the initial MAD concentration.

Table 2. Particle size distribution and surface charge density of the latex particles at different MAD concentrations

	10 ³ [MAD] (mol/dm ³)	<i>D_n</i> (nm)	<i>D_w</i> / <i>D_n</i>	Surface charge density	
				(μmol/g)	(μmol/m ²)
S0	—	760	<i>h</i> ^d	8.67 ^a	—
S1	2.8	317	1.02	— ^b	— ^b
S2	5.7	236	1.01	25.8	1.06
S3	14.2	156	1.02	34.5	0.94
S4	28.3	159	1.01	45.4	1.26
S5	56.6	162	1.06	54.5	1.54
S6	84.9	151	1.09	80.6	2.13
SDVB1 ^c	5.7	239	<i>h</i> ^d	18.9	—
SDVB2 ^c	5.7	238	<i>h</i> ^d	19.3	—

^aLatex cleaned by serum replacement, followed by AgNO₃ titration.^bNot determined.^cSDVB1 = 1% techn. DVB, SDVB2 = 3% techn. DVB.^dHeterodisperse.[AIBA] = 4.6×10^{-3} mol/dm³, [styrene] = 0.72 mol/dm³ and *T* = 60° (see Experimental Procedures).

The formation of nonanchored polyelectrolyte may be decreased by reducing the critical chain length of the growing water-soluble oligomeric radical. A possible way to reduce the critical chain length without affecting the charge density is the addition of the cross-linking agent (DVB). Moreover, the cationic charges anchored this way are chemically truly bonded to the latex particles. The results in Table 2 clearly show that the surface charge density decreases on the addition of DVB (compare S2 with SDVB1 and SDVB2). Moreover, the addition of cross-linker caused a broadening of the particle size distribution. Apparently, cross-linker addition causes a dual particle-formation mechanism.

Although many articles have been published on surfactant-free emulsion polymerization in the presence of an ionic comonomer, only few studies report surface charge densities. A review is given in Table 3. We emphasize that the different cleaning techniques used in these studies, together with the different extents of cleaning, will certainly affect the reported surface charge densities. In the case of emulsion polymerization of styrene with butyl acrylate and methylacrylic acid [15], the authors in fact suggest the incomplete removal of adsorbed polyelectrolyte.

The surface charge densities as given in Table 2 constitute cationic monomeric units and initiator residues at the ends of polymeric chains that have not been buried. Since immobilization of the slightly acidic protonated initiator residues ($pK_a \approx 12.5$ [48, 49]) on the latex surface will certainly decrease its pK_a [25], a difference in basicity between two types of cationic groups both having a hydroxide as the counterion was to be expected. [50]. The titration curve (Fig. 5), however, clearly demonstrates that this distinction cannot be made. Although the concentration of initiator residues at the latex surface cannot be determined, an estimate can be made. Even at low MAD concentrations ([MAD] = 5.66×10^{-3} mol/dm³), the polymerization is completed within 3 hr (see Fig. 1) meaning that *ca* 30% of the initiator has thermally decomposed ($k_d(\text{AIBA}) = 3.22 \times 10^{-5}$ sec⁻¹, at 60° [51]). From the polymerization conditions, as given in Experimental Procedures, the maximum charge density per unit of weight due exclusively to initiator residues can now be calculated. They amount to 37 μmol/g. It must be noted that this can only be the case if all decomposed

initiator radicals induce polymerization, *no* free polyelectrolyte is formed and *no* initiator residues are being buried in the latex particles. Clearly, these prerequisites do not hold in the present case; the efficiency of the initiator will be less than unity (for solution polymerization this value usually ranges between 0.6–1 [52]), polyelectrolyte is formed and initiator residues will be buried inside latex particles. Assuming an efficiency of 0.7, the maximum concentration of initiator molecules at the latex surface is 26 μmol/g. The surface charge density of S0 is much lower than this theoretical value ([MAD] = 0, Table 2. It should be noted that the reaction time in this case was much longer than 3 hr). Liu *et al.* reported a surface charge density to AIBA residues of 10.3 μmol/g in the case of EMVPB (total charge density is 15.3 μmol/g, see Table 3).

Although the addition of charged comonomer results in latices having a higher solid content and a greater surface charge density than in the absence of ionic monomer, the surface charge may be further increased by the so-called seeded-growth method and shot-growth emulsion polymerization. The difference between these two methods is that in the latter case, a second charge of monomer is added to the emulsion while the first charge is still reacting. In a seeded-growth experiment the latex (seed) is purified before a second emulsion polymerization is carried out. It is claimed that a better morphology as well as an increase of surface charge density [45, 54] can be achieved in the case of the shot-growth method compared with the seeded-growth technique [53]. This phenomenon has been explained by a difference in swelling behaviour between a purified (i.e. monomer free) and nonpurified latex [53, 55, 56] or by the presence of oligomeric radicals in the slightly monomer-swollen particles [57, 58]. The results of the shot-growth method are given in Table 4. The experimental conditions used during the first charge of the shot-growth reaction were identical to those used to synthesize latex S2 (see Table 2 and Experimental Procedures). After 3 hr (conversion > 80%), a second charge of monomer, comonomer, initiator and water is added. It can be concluded that the surface charge

Table 3. Surface charge densities of several latices produced by surfactant-free emulsion polymerization in the presence of an ionic comonomer

System	<i>D</i> (nm)	Surface charge density	
		(μmol/g)	(μmol/m ²)
STY/NaSS ¹⁰	236	21.2	0.87
STY/BuAc/MAA ¹⁵	272	15.7	0.75
STY/BuAc/MAA ¹⁵	208	104.9	3.82
STY/NaSS ⁴⁰	165	35.2	1.02
STY/NaVTS ⁴⁰	84	36.1	0.53
BuAc/AA ⁵⁹	67	93.0	1.09
STY/EMVPB ²⁶	390	15.3	1.05
STY/DVPM ²⁶	280	19.7	0.97
STY/AMPS ¹³	280	40.7	1.99
STY/TMA ⁶⁰	120	56.4	1.18
STY/MAD (S6)	151	80.6	2.13

STY, styrene; BuAc, butyl acrylate; MAA, methylacrylic acid; NaSS, sodium styrene sulphonate; NaVTS, sodium vinyltoluene sulphonate; AA, acrylic acid; EMVPB, 1-ethyl 2-methyl 5-vinylpyridinium bromide; DVPM, 1,2-dimethyl 5-vinylpyridinium methylsulphate; AMPS, 2-acrylamido-2-methyl propane sulphonic acid; TMA, *N*-trimethyl *N*-ethyl methacrylate ammonium iodide.

Table 4. Surface charge density of latices produced by the shot-growth method

Latex ^a	10 ³ [MAD] (mol/dm ³)	D (nm)	D _w /D _n	Surface charge density	
				(μmol/g)	(μmol/m ²)
SG1	12.6	220	1.01	26.0	1.00
SG2	25.2	204	1.02	28.8	1.03
SG3	50.3	214	1.01	32.6	1.22
SG4	75.5	218	1.16	30.9	1.18

^aExperimental details are given in Experimental Procedures.

density increases slightly by using the shot-growth technique. For high concentration of MAD, the resulting latex had a higher polydispersity. The production of latices with a relatively high polydispersity by the addition of a second charge at low conversion 50%) agrees closely with the findings of Sakato [45].

From the batch and shot-growth experiments (Tables 2 and 4), it can be concluded that in both cases the addition of comonomer slightly increases the surface charge density. Increasing the comonomer concentration will increase the total surface (as a result of particle-size reduction) and therefore more comonomer can be built in (increase of total charge per unit of weight, μmol/g). We postulate that MAD can be built into the latex surface only up to a certain level of charge density. As soon as this level is reached, the incoming comonomer-rich oligomeric radicals are prevented from entering and inducing polymerization in the particles as a result of coulombic repulsion. The shot-growth experiments confirm this view. The quasi indifference of surface charge densities presented in Table 3 to changing the comonomer, despite the great difference between ionic comonomers and the various experimental conditions used to prepare these functionalized latices, can also be understood on these grounds.

A possible alternative route for synthesizing highly charged latices and simultaneously avoiding the formation of free polyelectrolyte is the post polymerization method [3]. However, some drawbacks are introduced by this technique:

- (i) large (unstable) particles are produced in the case of surfactant-free emulsion copolymerization of a hydrophobic monomer;
- (ii) large quantities of comonomer are buried inside the polymer particles and thus are unavailable for functionalization; and
- (iii) functionalization may be incomplete as a result of the formation of highly charged surface during the modification.

CONCLUSION

3-(Methacrylamidinopropyl)trimethylammonium-chloride (MAD) can be used as a comonomer in the emulsion polymerization of styrene with AIBA as initiator. Increasing comonomer concentration appeared to increase the conversion rate of styrene, an effect which can be attributed to particle size reduction. Since the latices will be used as a support for CoTSPc, a catalyst in the thiol oxidation, and since this catalytic system is extremely sensitive to low concentrations of free polyelectrolyte, the latices must be thoroughly cleaned prior to use in the catalytic reaction. Conventional purification techniques like

serum replacement, diafiltration and centrifugation were found to be insufficient and continuous desorption could be observed on standing or after stirring. Centrifugation of latices, followed by treatment with silica, was found to clean the latices to such an extent as to lead to serum-containing polyelectrolyte concentrations lower than $[N^+] < 5 \times 10^{-7}$ mol/dm³. Surface charge density as determined by conductometric acid-base titrations increased on increasing MAD concentration. Addition of a cross-linking agent (DVB) decreased the surface charge density and broadened the particle size distribution. So-called shot-growth emulsion polymerization hardly increased the surface charge density.

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