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Control of Charge Densities for Cationic Latex Particles

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ABSTRACT: We report a systematic investigation, together with a new method, on controlling cationic charge densities of latex particles. A covalently bonded charge density up to 100 μequiv/g was achieved on the basis of copolymers of glycidyl methacrylate (GMA) and butyl methacrylate (BMA) by either surfactant-free or nonionically stabilized emulsion polymerization, followed by the aminolysis of epoxy groups into quaternary ammonium groups. The cationic charge density was successfully controlled by adjusting the ratio between epoxy and amino groups. It was found that the formation of disadvantageous water-soluble polyelectrolytes was negligible. Cationic charges were also introduced to latex particles by using cationic azo initiators and/or copolymerization with cationic or amine-containing comonomers, but colloidal titrations showed that controlled formation of highly charged cationic latex particles without the formation of water-soluble polyelectrolytes was only achievable for the aminolysis approach.

1. Introduction

Latex particles bearing functional groups find numerous applications varying from additives for paint formulations to binding materials for biological molecules. Functional groups on the surface of latex particles commonly used are carboxyl, hydroxyl, amine, or quaternary ammonium groups. The quaternary ammonium group provides the latex with a permanent cationic charge capable of binding latex particles with anionic materials like paper fillers[1] or nucleotides.[2] High surface charge densities of the latexes are required to generate a strong attractive force between two different particles. The charges on the latex particles are generally formed by using cationic surfactants or the copolymerization of hydrophilic, charged monomers with hydrophobic monomers. Several studies have appeared describing the emulsion copolymerization of hydrophobic and hydrophilic monomers.[3−6]

An often used approach for the formation of these cationic latex particles is the use of cationic surfactants like cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB).[7−9] Nevertheless, this approach has a disadvantage that charges are not covalently bound to the latex particles and, furthermore, control of charge density is not easily achieved. For many applications, like in biomedicine, small mobile charged species are a major disadvantage. Therefore, cationic charges have been incorporated into latexes by using cationic azo initiators.[10,11] Decomposition of these water-soluble initiators forms one or more charged radicals, capable of creating at most two charges per polymer chain. In the case of surfactant-free emulsion polymerizations of nonionic monomers, these initiator fragments are the only contributors to the electrostatic stabilization and charge formation of the latex particles.

During the past decade, polymerization in the presence of quaternary ammonium functionalized monomers also enabled the formation of particles with a higher surface charge density.[12] Moreover, surfactant-free copolymerizations of these monomers with conventional monomers reduced the final latex particle size enormously compared to homopolymer latex particles of the conventional monomers.[13,14] The addition of a cationic monomer in the second step of a two-step growth emulsion polymerization will enable the buildup of cationic charge at the surface of the latex particle. Several studies have appeared describing the copolymerization of styrene and an amine-containing monomer.[15,16] These monomers can be protonated at low pH and are readily copolymerized with styrene.[17] All of the mentioned polymerizations and conversion reactions lead to the formation of charged latex particles. However, the presence of ionic comonomers or highly water-soluble amino monomers leads to a broad particle size distribution and the formation of water-soluble polyelectrolytes. An alternative approach for the formation of cationic latexes is via the conversion of an amide group into primary and tertiary amines using either Hofmann or Mannich reaction.[18] However, both reactions were accompanied by hydrolysis, which led to the formation of amphoteric latex particles.

Almost all of the research on cationic latex particles has been focused on surfactant-free emulsion polymerizations. Clean latexes do not have the problem of removing stabilizers, which often leads to coagulum formation. On the other hand, multistage processes for cationic latex formation in the presence of seed particles or the copolymerization procedure do not normally form latex particles with a diameter smaller than 50 nm (nanosized particles). Instead, tailoring emulsion polymerizations in the presence of functional monomers and surfactants will enable the formation of latexes with small particle sizes.

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Table 1. Recipes for Preparation of Cationic Latexes from Cationic Initiators

	IRC		feed[a]				initiator	
entry	monomer	mass [g]	monomer	mass [g]	NDM [g]	water [g]		mass [g]
A1−2	iBMA	1.00	iBMA	8.00	0.06	124	V-50	X[b]
A3−4	iBMA	1.00	iBMA	8.00	0.05	121	VA-44	Y[b]
A11−12[c]	iBMA	1.00	iBMA	8.00	0.05	120	V-50	X[b]

[a] Feed of monomer at a rate of 0.01 mL min^{-1}. [b] Amount of initiator was varied. [c] Surfactant-stabilized emulsion polymerization, 6−8 wt % of NP3070 (based on monomer) added.

Table 2. Typical Polymerization Recipes for Cationic Latexes with Cationic Monomers

	IRC		feed[a]						
entry	monomer	mass [g]	monomer	mass [g]	NDM [g]	water [g]	ethanol [g]	V-50 [g]	NP3070 [g]
B1	iBMA	0.25	iBMA	8.00	0.06	135		0.41	
B2−4	MAPTAC/iBMA[b]	0.25	MAPTAC/iBMA[c]	7.13	0.09	140	5.1	0.43	
B5−7	MATMAC/iBMA[b]	0.25	MATMAC/iBMA[c]	7.13	0.09	145	5.1	0.42	
B11	iBMA	0.25	iBMA	8.00	0.06	135		0.40	2.0
B12−14	MAPTAC/iBMA[b]	0.27	MAPTAC/iBMA[c]	7.13	0.09	144	5.1	0.43	2.1
B15−17	MATMAC/iBMA[b]	0.27	MATMAC/iBMA[c]	7.13	0.09	145	5.1	0.43	2.1

[a] Feed of monomer at a rate of 0.01 mL min^{-1}. [b] Weight ratio between cationic monomer and iBMA is 1/10. [c] Feed contains 0−5 wt % cationic monomer.

In this article, we present a systematic investigation, as well as a new method, on controlling the covalently bonded cationic charges in latex particles. Clean latexes were prepared by surfactant-free emulsion polymerization and nanosized latex particles were synthesized in the presence of nonionic surfactants. Our first approach was the charge formation by using two different cationic initiators. Second, we have used different comonomers such as cationic comonomers and amine-containing comonomers. The ionic comonomers already carry a cationic charge, and charges can be introduced to amino-monomers via protonation. Finally, the emulsion copolymerization of glycidyl methacrylate with butyl methacrylate led to epoxy-containing latex particles. The epoxy groups were converted into quaternary ammonium groups to obtain positively charged particles. The amount of charges present at the surface of the latex particles and final latex particle size of all three approaches were studied.

2. Experimental Section

Materials. Butyl methacrylate (BMA, Aldrich), isobutyl methacrylate (iBMA, Rohm), and glycidyl methacrylate (GMA, Aldrich) were purified by slowly passing through an inhibitor removing-column (hydroquinone remover, Merck) and, prior to polymerization, were distilled under reduced pressure. Ionic monomers methacrylamidopropyl trimethylammonium chloride (MAPTAC, ATOFINA) and methacrylatoethyl trimethylammonium chloride (MATMAC, ATOFINA), and amine-containing monomers 2-(dimethylamino)ethyl methacrylate (DMAEMA, Aldrich) and *N*-[3-(dimethylamino)propyl]methacrylamide (DMA, Aldrich) were used as received. Water-soluble cationic azo initiators VA-44 (2,2′-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride) and V-50 (2,2′-azobis(2-methylpropionamide) dihydrochloride) [recrystallized from water−acetone (50/50, w/w)] were kindly provided by Wako Chemicals GmbH. Polymeric surfactant Emulan NP3070, an alkylphenol poly(ethylene oxide), was kindly provided by BASF AG Ludwigshafen and used as received. All other chemicals were used without further treatment unless stated otherwise. Control of molecular weight was provided by the addition of a chain transfer agent (CTA), *n*-dodecyl mercaptan (NDM, Aldrich). Hydroquinone (Aldrich) was used to short-stop the reaction before conversion determination. Ethanol from Bisolve AR-grade was used to dissolve the cationic monomers. Trimethylamine (TMA, Aldrich), tetramethylammonium chloride (TMAC, Aldrich), NaCl (0.1 M, Aldrich), and hydrochloric acid (HCl, Merck) were used as received. Double deionized water (DDI) was obtained from a Milli-Q water system (Millipore) with a resistivity of 18.3 MΩ cm.

Synthesis of Latex Particles with Cationic Initiators. Semicontinuous or starved-feed emulsion polymerization used for the preparation of nanosized latex particles is detailed elsewhere.[19] Emulsion polymerizations were performed in a 250 mL three-neck round-bottom flask. The reactor was equipped with an argon inlet, a reflux condenser with an outlet to a bubble counter, a thermometer, and a septum through which the monomer feed was added to the reaction mixture using a Metrohm Dosimat 776 autotitrator. A typical polymerization procedure is described as follows (entry A11, Table 1). The initial reactor charge (IRC) was a microemulsion (average droplet size: 15 nm, as determined by dynamic light scattering, DLS; more details about DLS are given below) consisting of 120 g of deionized water, 0.05 g of NDM, 0.8 g of NP3070 surfactant, and 1.0 g of iBMA. Argon was bubbled through the reactor for 45 min under constant agitation at 800 rpm. After this, the reactor was heated to 60 ± 1 °C with an oil bath, followed by the addition of an aqueous solution of the initiator (0.5 g V-50 dissolved in 4.5 g of deionized water) to initiate the polymerization. 5 min after the initiator was added the monomer was fed at a rate of 0.01 mL min^{-1} with vigorous stirring. After the addition was complete, the flask was kept at 60 °C for another 2 to 4 h.

Synthesis of Cationic Latex Particles with Cationic Comonomers. All polymerizations were conducted under identical conditions, using the same setup and procedure as described above. The reactor was initially charged with deionized water, CTA, and ionic comonomer (and surfactant for the nonionically stabilized polymerization). Argon was bubbled through the reactor for 45 min under constant agitation at 800 rpm. After this, the reactor was heated to 60 ± 1 °C with an oil bath. An aqueous solution of the initiator (V-50) was added to the reactor and the monomer feed was started. Table 2 lists the recipes of the polymerizations performed. The ionic monomers MAPTAC and MATMAC were obtained as an aqueous solution of 75 wt %. To feed them together with iBMA to the reactor, they were first stripped from water. The resulting liquid monomer was subsequently dissolved in ethanol together with iBMA and fed to the reactor at the desired speed.

Emulsion copolymerization with amine-containing monomers. All polymerization reactions were conducted under identical conditions, using the same setup and procedure as described above. Deionized water, surfactant when ap-

Table 3. Polymerization Recipes for Cationic Latexes with Amine-Containing Monomers

	IRC		feed[b]					
entry	monomer[a]	mass [g]	monomer	mass [g]	NDM [g]	water [g]	V-50 [g]	NP3070 [g]
C1−3	DMA	*X*	iBMA/DMA	*A*/*B*	0.07	110	0.5	
C4−6	DMAEMA	*Y*	iBMA/DMAEMA	*C*/*D*	0.07	110	0.5	
C21	DMA	*X*	iBMA/DMA	*A*/*B*	0.06	109	0.5	2.0
C22	DMAEMA	*Y*	iBMA/DMAEMA	*C*/*D*	0.07	110	0.5	2.0

[a] Amino monomer content varies from 0.2 to 10 mol %, based on the total monomer amount. [b] Variable amount of monomer in the feed added at a constant rate of 0.01 mL min^{-1}.

Table 4. Recipes for Preparation of Epoxy-Containing Latex Particles

	IRC		feed[a]					
entry	monomer	mass [g]	monomer	mass [g]	NDM [g]	water [g]	V-50 [g]	NP3070 [g]
G2A	BMA	0.5	GMA/BMA	2.08/4.86	0.06	156	0.50	
G2B	BMA	0.5	GMA/BMA	4.17/3.08	0.05	156	0.48	
G2C	BMA	0.5	GMA/BMA	6.25/1.29	0.06	156	0.48	
G3	BMA	0.5	GMA/BMA	2.08/4.86	0.06	155	0.51	3.0
G4	BMA	0.5	GMA/BMA	4.17/3.08	0.05	159	0.50	3.3
G5	BMA	0.5	GMA/BMA	6.25/1.29	0.06	152	0.46	3.0

[a] Feed of monomer at a rate of 0.01 mL min^{-1}.

plicable, monomer, and CTA were charged to the reactor, as listed in Table 3. The reaction temperature was controlled at 60 °C. In the feed the ratio of iBMA to amino monomer was varied, denoted as *A*/*B* or *C*/*D*, although the total amount of monomer feed was always 8 mL. After the emulsion polymerization was complete, the latex was titrated to pH = 3 with HCl to protonate the amino moieties.

Emulsion Copolymerization with Glycidyl Methacrylate. The epoxy-containing latex particles were prepared by starved-feed emulsion polymerization using the same setup as described earlier. A mixture of deionized water, surfactant when applicable, monomer, and CTA was added to the reactor as initial charge. Table 4 summarizes the ingredients used for the polymerization. The feed of monomer consisted of GMA and BMA at different molar ratios. V-50 was used as initiator and the polymerizations were performed at 60 °C. After polymerization an extensive period of dialysis was performed to remove excess surfactant in latexes when nonionic surfactant was used. Conversion of the epoxy into quaternary ammonium groups was carried out by the addition of equimolar amounts of TMA and HCl and a catalytic amount of TMAC to a diluted dispersion of epoxy-containing latex particles. After the addition the temperature was increased to 70 °C to speed up the conversion.

Characterization and Colloidal Properties. Overall monomer conversion was determined gravimetrically. Conductivity of the reaction mixture was determined with a Radiometer CDM80 conductometer. For surfactant-free latexes, three cycles of centrifuging the latex particles, decanting the supernatant, and redispering the sediment were performed to clean the latex particles from absorbed species that could influence the measurements. Medicell dialysis tubing (9 in. Dia 36/32 in. (28.6 mm), MWCO 12−140000 Da) was used for the dialysis of the latex particles. Latexes were cleaned against double deionized water (DDI) and the conductivity of the water was checked until the conductivity was almost identical to that of the DDI water.

The ζ potential and its dependence on pH were determined on a Malvern Zetasizer Nano ZS instrument. The ζ potential was calculated from the electrophoretic mobility (μ) using the Smoluchowski relationship, $\zeta = \eta\mu/\epsilon$, where $\kappa a \gg 1$ (where η is the viscosity, ϵ is the dielectric constant of the medium, and κ and a are the Debye−Hückel parameter and the particle radius, respectively). The pH of the latexes was adjusted by adding either HCl or NaOH using a Mavern MPT2 autotitrator.

Size exclusion chromatography (SEC) experiments were carried out on a Waters GPC instrument equipped with a Waters model 510 pump and Waters model WISP 710 autoinjector, using a Polymer Laboratories PLgel guard precolumn (50 × 7.5 mm) followed by four mixed-B (300 × 7.5 mm) columns. The polymer samples were dissolved in stabilized THF (1 mg/mL). For detection a model 410 RI detector was used.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Advanced Q100. The temperature gradient was −20 to 150 °C at a rate of 10 °C min^{-1}; the step change in the heat flow during the second heating run was used to determine the glass transition temperature.

The average particle size and particle size distribution were determined by means of dynamic light scattering (DLS) performed on a Malvern 4700 light scattering instrument equipped with a Malvern Multi-8 7032 correlator at a scattering angle of 90° at 21 °C. A JEOL 2000 FX transmission electron microscope was used for the particle size analysis. Latex samples of 0.05 wt % were air-dried on a 400-mesh copper grid with a Formvar supported film. Cryo-TEM analysis was performed with a Philips TEM CM12 transmission electron microscope. 3 μL of dispersion was placed on a carbon coated lacy substrate supported by a TEM 300 mesh copper grid (Ted Pella). Excess of sample was blotted with filter paper and the resulting thin film was vitrified in liquid ethane at its melting temperature using a Vitrobot vitrofication robot.

Charge densities of latex particles and water-soluble polyelectrolytes were determined by colloid titration.[4,20,21] In the case of surfactant-free latexes, the latexes were centrifuged using a Mistral 3000E at 3000 rpm for 12 h. The supernatant was then decanted and the particles were redispersed in DDI water. This procedure was repeated two more times. For nonionically stabilized latexes, the latexes were extensively dialyzed against DDI water; the permeant water containing the excess surfactant and, possibly, water-soluble polyelectrolyte was collected. Cleaned latex particles and collected supernatant/permeant water were titrated with 1.0 and 0.1 mM poly(vinyl sulfate, potassium salt) (Aldrich). Toluidine blue-O (Aldrich) was used as an indicator to determine the end point.[21] The charge densities of polymer latexes and water-soluble electrolyte from the titration are presented as microequivalents per gram (N_m). For latex particles, the surface charge density is also expressed as microequivalents per m^2 of particle surface (N_c); $N_c = 10^4 N_m D\rho/6$, where D (cm) is the diameter of latex particles, and ρ is the density of particle (about 1.05 g/cm^3 for acrylic polymers).

3. Results and Discussion

3.1. Cationic Charge Control by Initiator. Cationic latex particles were prepared by surfactant-free

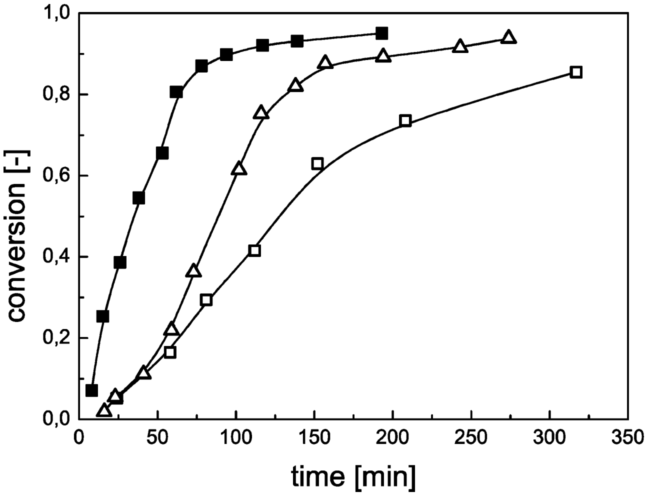


Figure 1. Monomer conversion curves for surfactant-free batch emulsion polymerizations of iBMA at different temperatures in the presence of VA-44 (■ at 60 °C) and V-50 (Δ at 60 °C and □ at 50 °C).

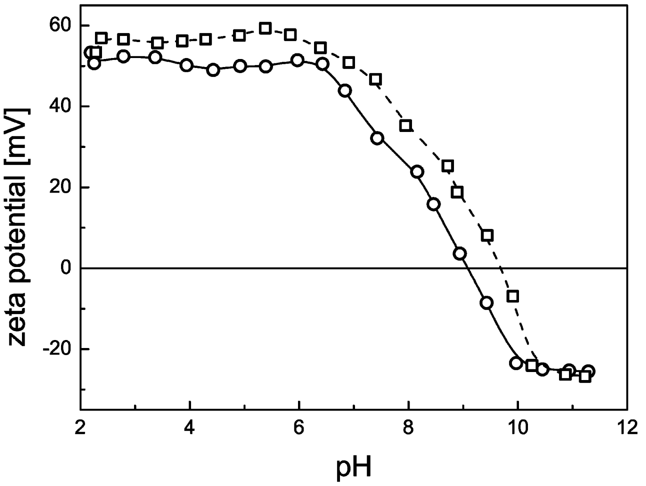


Figure 2. ζ potential variation as a function of the pH for entries A2 and A4, V-50 (□) and VA-44 (○), respectively.

starved-feed emulsion polymerizations at different temperatures. The polymerization recipes are given in Table 1. Two different initiators were used for the preparation of cationic polymer latexes, imidazolin VA-44 and amidino V-50.

Figure 1 shows that a maximum monomer conversion of approximately 95% was attained for a batch emulsion polymerization initiated by both initiators at 60 °C. Although the final conversion at this temperature is almost the same, the time to reach the final conversion is about 100 min longer for V-50. This difference is in accordance to the different decomposition rate constants for VA-44 (13.5×10^{-5} s^{-1}) and V-50 (3.2×10^{-5} s^{-1}) at 60 °C, as provided by the manufacturer of the initiators.

Cationic charge on the latex particles was only obtained by the covalently bonded amidino groups originated from V-50 and the imidazolin groups from the VA-44 initiator. The electrokinetic behavior was studied by measuring ζ potential of the systems as a function of pH at a constant electrolyte concentration (0.1 M NaCl). ζ potential values remained constant over a wide pH range up to pH = 6; slightly higher absolute values for V-50-initiated latexes were observed (Figure 2). The neutralization of the cationic initiator groups at a pH higher than 9 is common for these cationic initiators, which is in contrast to anionic persulfate initiated latexes that have a negative ζ potential over the whole pH range.[22] Hydrolysis of the amidino and imidazolin groups and formation of carboxylic surface groups might explain the negative values.[23] The isoelectric point (iep) is around pH = 9.7 for the V-50-initiated latex, consistent with the reported values by Sauzedde et al.,[17] and pH = 9 for the VA-44-initiated latex.

For surfactant-free emulsion polymerizations the increase in initiator concentration resulted in the formation of polymer latexes with lower molecular weights and a decrease in the particle size (from almost 250 nm to less than 200 nm, Table 5). This decrease in particle size can be explained by the increased stability of the particles as a result of the increasing number of the cationic initiator fragments at the end of the chains. Further, the increase of the initiator concentration led to higher ζ potential values and a significant rise in surface charge density up to a value of 47 μequiv/g (Table 5).

The effect of the increasing initiator concentration on the particle size for nonionically stabilized latex particles is given in Figure 3. Conditions for these experiments were such that the ionic strength of the latexes was not controlled by the addition of salt. It is clearly shown in Figure 3 that there is an obvious decrease in the final latex particle size from 55 to 20 nm, as a result of the increased initiator concentration. The contribution of the ionic groups to the stability of the latex particles is significant. Increasing the concentration of initiator for the surfactant-stabilized latex particles also led to an increase in ζ potential as observed for the surfactant-free latexes (Table 5). But the ζ potential is much lower than the surfactant-free latexes, probably due to the shielding of the charged groups by the surfactant molecules. To reveal the real particle surface charges, surface charge density titrations were carried out. It is clear that the surface charge density increased as a result of the increasing amount of charged initiator fragments bonded to the latex particles, also demonstrated in Figure 3.

In summary, the control of surface charge density has been successfully shown by the covalent bonding of cationic initiator fragments onto latex particles. Latexes with a surface charge density of 10−55 μequiv/g can be obtained by varing the initiator concentration. Furthermore, the charge control was similar for the surfactant-free and the nonionically stabilized nanosized latexes, and the increased initiator concentration effectively reduced the particle size for both latexes.

3.2. Cationic Charge Control via Cationic Monomers. Incorporation of charged monomeric units can significantly increase the amount of charges on a polymer latex particle. To increase the particle surface charge density to higher values than that with only cationic initiators, two approaches were attempted: using cationic comonomers or using amine-containing monomers. Copolymerizations of these two types of monomers with iBMA were performed in the presence of nonionic surfactants and by surfactant-free emulsion polymerization. The main advantage of surfactant-free emulsion polymerization is that it does not require intensive cleaning steps as compared to conventional emulsion polymerization with surfactants. However, nanosized particles were never obtained for surfactant-free latexes. It is possible to obtain nanosized latexes

Table 5. Influence of Initiator Concentration on Properties of Cationic Latexes from Cationic Initiators

entry	initiator [× 10^{-3} mol L^{-1}]	D_p[b] [nm]	PDI	convn (%)	ζ-potential [mV]	$N_{m,p}$[c] [μequiv/g]	$N_{c,p}$[d] [μequiv/m^2]	M_w [×10^3]
A1	14.8	247	0.24	94	18.3	11.7	0.50	212
A2	33.6	198	0.16	93	54.5	43.1	1.45	168
A3	13.9	239	0.18	95	21.0	13.9	0.58	207
A4	34.3	191	0.19	95	56.7	47.3	1.57	162
A11[a]	8.6	44.5	0.17	92	4.8	25.3	0.20	287
A12[a]	41.7	19.3	0.22	94	22.5	55.1	0.19	259

[a] Surfactant-stabilized latex particles. [b] *Z*-average particle diameter determined by DLS. [c] Surface charge density of polymer particles in μequiv/g ($N_{m,p}$). [d] Surface charge density of polymer particles in μequiv/m^2 ($N_{c,p}$).

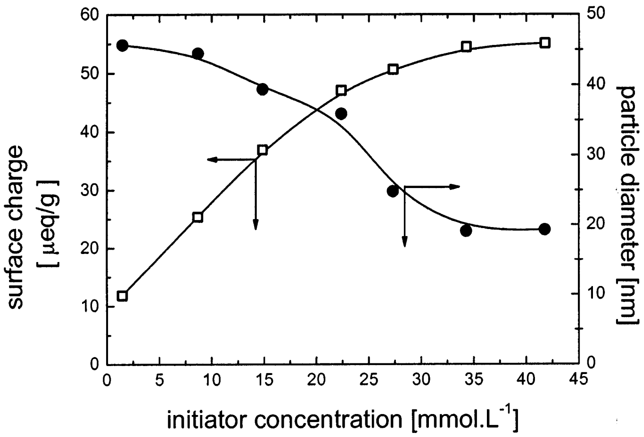
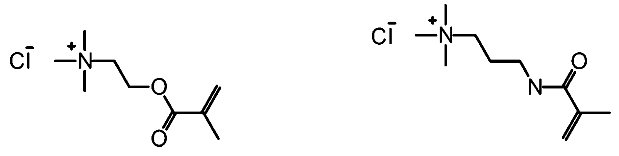


Figure 3. Surface charge and particle diameter (measured by DLS) against V-50 initiator concentration for cationic PiBMA latex particles from nonionically stabilized emulsion polymerization performed at 60 °C.



MATMAC **MAPTAC**

Figure 4. Structures of MATMAC and MAPTAC.

by using surfactant, but multiple dialyses are needed to remove excess surfactant.

3.2.1. Ionic Monomer Copolymerization. Two cationic monomers commonly used for the preparation of cationic latexes are MATMAC and MAPTAC (Figure 4). Both monomers were used to prepare stable polymer latex particles by starved-feed emulsion polymerization. The feed ratio of cationic monomer was varied from 0 to 5 wt % based on the total monomer composition. Increasing the concentration above 5 wt % did not result in higher charge densities; however, the content of water-soluble polyelectrolyte did increase.

In Table 6, various properties of polymer latexes are presented. For comparison, a surfactant free polymerization of iBMA initiated by V-50 was also performed (entry B1). The cationic charge provided only by the initiator fragments led to latex particles with a cationic charge density of 33 μequiv/g. Compared to entry B1, the introduction of only 0.2 mol % (based on the total monomer amount) of cationic monomer loaded as initial reactor charge (B2 and B5) showed already a remarkable difference in particle size and the amount of charges formed on the latex particles (Table 6). Increasing the amount of ionic comonomer in the polymerization recipe resulted in the latex particles with an increased amount of surface charge density. Meanwhile, the higher surface charge density also rendered the latex particles with greater stability. (Note: the amount of cationic monomer should not be too high; otherwise destabilization of latex due to bridging flocculation would occur.) By using the cationic monomers a significant reduction of the particle diameter was found compared to surfactant-free emulsion polymerizations without using ionic comonomers (Table 5). However, a particle size below 89 nm was not achieved.

On the other hand, when 5 mol % of cationic monomers in the feed was used, the particle size PDI increased up to 0.35, and the charge density of water-soluble polyelectrolyte also increased significantly, up to 77 μequiv/g for entry B7 (Table 6). The marked increase in PDI is indicative of the formation of large particles via bridging flocculation due to the existence of a large amount of water-soluble polyelectrolyte.[26]

Observation with DLS of the two latex systems produced from different cationic monomers showed only minor differences in the final latex particle sizes. MATMAC-based particles were marginally smaller than the MAPTAC-based latex particles, which is in agreement with a previous study.[10] The overall monomer conversion in the case of MAPTAC was slightly lower than for MATMAC. It was also found that the emulsion polymerization in the presence of MATMAC produced slightly higher amounts of water-soluble polyelectrolytes. Despite these marginal differences, the lack of kinetic parameters of these two cationic monomers makes it very difficult to justify any kinetic difference between them. Because of the complexity of the emulsion copolymerization, a more detailed investigation is needed to reason the kinetic difference, which is outside of the scope of this research.

The variation of initiator concentrations showed unexpected behavior as the initiator concentration was increased from 12 to 40 mmol L^{-1}. Instead of lowering the particles size with increasing initiator concentrations for entries B4 and B7, an increase was observed from 109 to 133 nm and 89 to 121 nm, respectively. A possible explanation could be that the presence of a high concentration of water-soluble monomers and an increased radical concentration in the water phase could lead to a higher termination rate in the water phase.[24,25] This resulted in fewer nuclei and subsequently an increase in polymer particle size. High particle size PDIs were also observed as a result of the higher initiator concentrations. Another possible cause for the formation of larger particles could be due to bridging flocculation as a result of the increased concentration of water-soluble polyelectrolyte, as discussed earlier.

Nanosized cationic charged latex particles were synthesized by the starved-feed emulsion polymerization using a nonionic surfactant according to entries B11–17 in Table 2. With the addition of the surfactant, most of the latex particles had a particle diameter smaller

Table 6. Characteristics of Cationic Polymer Latexes from Surfactant-Free Emulsion Copolymerization of iBMA and Cationic Monomers

entry	cationic monomer in IRC	feed M+/iBMA [mol/mol]	convn[a] (%)	$N_{m,w}$[b] [μequiv/g]	$N_{m,p}$[c] [μequiv/g]	$N_{c,p}$[c] [μequiv/m^2]	D_p[d] [nm]	PDI	ζ-potential [mV]
B1			97		32.8	1.13	198	0.11	54.5
B2	MAPTAC	0/100	81	0.7	42.7	1.06	143	0.19	58.3
B3	MAPTAC	3/97	85	11.3	65.5	1.34	117	0.16	68.6
B4	MAPTAC	5/95	83	69.5	93.1	1.77	109	0.35	76.6
B5	MATMAC	0/100	91	0.9	44.9	1.08	138	0.14	57.4
B6	MATMAC	3/97	89	13.8	69.8	1.36	112	0.18	73.9
B7	MATMAC	5/95	90	76.6	98.4	1.53	89	0.25	81.4

[a] Final overall monomer conversion determined gravimetrically. [b] Charge density of water-soluble polyelectrolyte formed during polymerization. [c] Surface charge density of polymer latex particles. [d] *Z*-average particle diameter determined by DLS.

Table 7. Characteristics of Cationic Polymer Latexes from Nonionically Stabilized Emulsion Polymerization of iBMA and Cationic Monomers

entry	cationic monomer in IRC	feed M+/iBMA [mol/mol]	convn (%)	$N_{m,w}$[a] [μequiv/g]	$N_{m,p}$[b] [μequiv/g]	$N_{c,p}$[b] [μequiv/m^2]	D_p[c] [nm]	PDI	ζ-potential [mV]
B11			78	-	46.8	0.20	24.2	0.16	8.8
B12	MAPTAC	0/100	70	0.6	42.2	0.22	30.2	0.24	13.4
B13	MAPTAC	3/97	72	19.8	61.7	0.29	27.3	0.13	25.7
B14	MAPTAC	5/95	70	72.7	91.8	0.41	25.7	0.17	32.2
B15	MATMAC	0/100	82	1.8	43.4	0.25	32.9	0.18	14.9
B16	MATMAC	3/97	74	20.6	67.5	0.32	27.5	0.11	27.7
B17	MATMAC	5/95	72	72.1	96.6	0.41	24.6	0.17	35.1

[a] Charge density of water-soluble polymer. [b] Surface charge density of polymer particles. [c] *Z*-average particle diameter determined by DLS.

Table 8. Characteristics of Cationic Polymer Latexes from Surfactant-Free Emulsion Copolymerization of iBMA and Amine-Containing Monomers

entry	monomer[a]	feed M/iBMA [mol/mol]	convn (%)	$N_{m,w}$ [μequiv/g]	$N_{m,p}$ [μequiv/g]	$N_{c,p}$ [μequiv/m^2]	D_p[b] [nm]	PDI	ζ-potential [mV]
C1	DMA	0/100	93	2.4	23.8	0.68	165	0.13	28.1
C2	DMA	5/95	94	8.7	46.7	0.99	122	0.19	49.9
C3	DMA	9/91	91	18.3	75.9	1.28	97	0.18	72.8
C4	DMAEMA	0/100	90	4.9	21.2	0.66	178	0.21	26.0
C5	DMAEMA	5/95	92	10.6	40.5	0.98	139	0.09	45.4
C6	DMAEMA	9/91	92	21.5	69.4	1.34	111	0.16	70.3

[a] IRC contains 0.2 wt % of amino monomer. [b] *Z*-average particle diameter determined by DLS.

than 30 nm (Table 7). With the increasing comonomer content an increase of the ζ potential was observed. However, the ζ potentials were much lower than those of the corresponding surfactant-free latexes (Table 6), due apparently to the shielding effect of the nonionic surfactant. The colloidal titration revealed that the actual amount of charges present at the particle surface for surfactant-stabilized latexes is comparable to the surfactant-free latexes. Similar to the surfactant-free latexes, for nanosized latexes a large amount of water-soluble polyelectrolytes (up to 73 μequiv/g) was produced as a result of a relatively high content of cationic monomers (entries B14 and B17).

3.2.2. Amine-Containing Monomer Copolymerization. Formation of cationically charged latex particles is feasible by the emulsion copolymerization of iBMA and amine-containing monomers, followed by protonation of the tertiary amine groups. For the protonation it is needed to adjust the pH of the medium to 3. At the start of the reaction, the initiator was added, and the amino monomer present in the reactor formed water-soluble oligomers. The oligomers formed precursors for the following polymerization with iBMA. The control of surface charge density was first investigated by increasing monomer concentration in the feed with a constant amount (0.2 wt %) of amino monomer in the IRC. Increasing the amount of monomer in the feed to a total cationic comonomer concentration of 10 mol % resulted in the latex particles with a higher surface charge density compared to the particles produced without any amine-containing comonomers. As can be seen in Table 8, a maximum surface charge density of 76 μequiv/g was obtained for the copolymerization of DMA and iBMA. Furthermore, there was a gradual increase in the amount of water-soluble polyelectrolyte with the addition of both amine-containing comonomers. Nevertheless, the formation of water-soluble polyelectrolyte was significantly reduced compared to the copolymerizations with ionic monomers (Table 6).

A prominent characteristic for the copolymerization in the presence of amine-containing or cationic comonomers is the decrease in particle size with increasing amount of these comonomers. The particle size decreases drastically as a result of the incorporation of charged groups into the polymer particles, which provides the particles with higher colloidal stability. No large difference in the latex final particle size was observed for the DMEAMA- and DMA-based latex particles.

Besides increasing the amino monomer amount in the feed we have also investigated the effect of increasing the amount of DMA or DMAEMA in the initial reactor charge. For these polymerizations only iBMA was fed to the reactor over time. It was observed that the surface charge density of latex particles increased as the amino monomer amount in the IRC increased from 0 to 10 mol

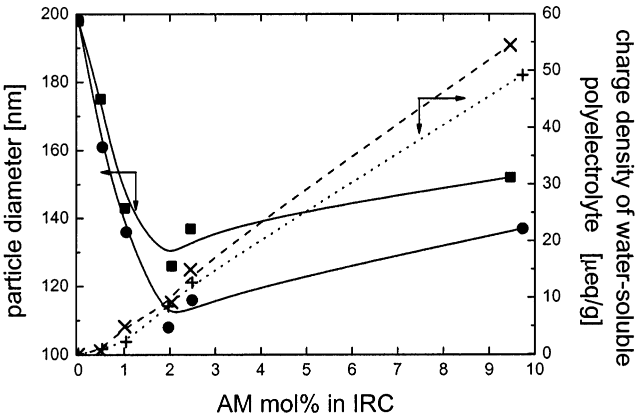


Figure 5. Latex particle size and charge density of water-soluble polyelectrolyte vs the concentration of amino monomer in IRC for surfactant-free emulsion polymerization: DMAEMA, D_p determined by DLS (■) and $N_{m,w}$ (×); DMA, D_p(●) and $N_{m,w}$(+).

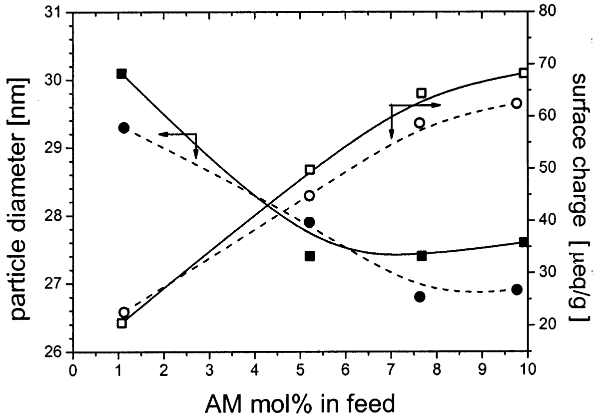


Figure 6. Latex particle size and particle surface charge density vs concentration of amino monomer in the feed for nonionically stabilized emulsion polymerization: DMA, D_p determined by DLS (■) and $N_{m,p}$(□); DMAEMA, D_p(●) and $N_{m,p}$(○).

%. However, the effect on the increase of the particle surface charge density was much smaller than observed for the addition of amino monomers via the feed: a maximum of only 47.4 µequiv/g was obtained for DMA-based latexes. Furthermore, the formation of water-soluble polyelectrolytes was enormously increased; for instance, in the case of DMAEMA-based latexes, the maximum charge density of water-soluble polyelectrolyte was 54.4 µequiv/g (Figure 5), as opposed to 21.5 µequiv/g (Entry C6, Table 8) when the amino monomer was added in the feed. As also shown in Figure 5, a decrease of particle size from 200 to 103 nm was observed upon increasing the amount of DMAEMA in the IRC. Further increasing the amine-containing monomer concentration up to a total concentration of 10 mol % led to an increase in the final latex particle size and a broader size distribution. The increase of latex particle size is again very likely due to the bridging flocculation, as a consequence of the formation of a large amount of water-soluble polyelectrolytes.

Nonionically stabilized emulsion polymerizations were also conducted to check the influence of the surfactant on the particle size and surface charge densities of the resulted nanosized latexes. The recipe used for the polymerization is listed in Table 3 (entries C21−22). Figure 6 does not show a significant decrease of the final latex particle size as a result of the increased content of amine-containing monomer in the feed compared to the surfactant-free polymerizations. Similar to the surfactant-free polymerizations reported in Table 8, an increase in the surface charge density was observed for the surfactant-stabilized nanosized latexes as the content of the amino monomer increased in the monomer feed (Figure 6); meanwhile, the surface charge density increased to about 70 µequiv/g, accompanied however by the formation of a large amount (55 µequiv/g) of water-soluble polyelectrolytes.

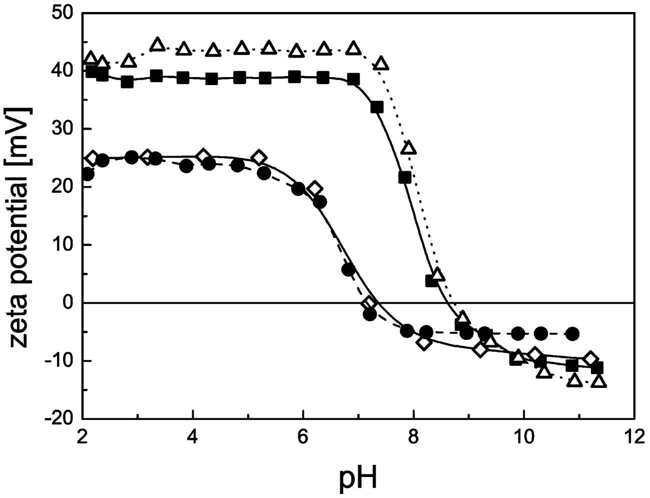
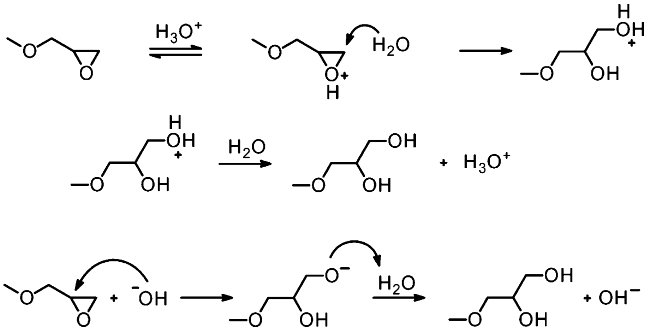


Figure 7. ζ potential as a function of pH for nonionically stabilized nanosized latexes based on DMA (●) and DMAEMA (◇) and for surfactant-free latexes based on DMA (■) and DMAEMA (△).

Electrokinetic measurements were performed on the cationic latex particles from amine-containing comonomers produced either by surfactant-free or nonionically stabilized emulsion polymerization at a constant ionic strength (addition of 0.1 M NaCl) with varying pH. All the investigated latexes were prepared by adding 1 wt % of amino monomer in IRC. No further addition of amino monomer was used throughout the polymerization. For both amino monomers, the isoelectric point for the nonionically stabilized latexes was at pH = 7, significantly lower than the iep (pH = 8.6) for the surfactant-free latexes, as illustrated in Figure 7. This iep shift may be attributed to the strong charge shielding by the nonionic surfactant. The nonionic surfactant (NP3070) used here contains poly(ethylene oxide) segments, and the formation of multiple H-bonding between the O atoms in NP3070 and the N-centered cations $\equiv N^{+}-H$ is very likely. The formation of similar H-bonds between ammonium ions and polyether has been reported in the literature.[27,28] As a consequence, these H-bonded cations would not be "seen" by counterions (such as HO^{-}) during the course of ζ potential measurements, leading to the iep shift toward lower pH.

From the experiments on emulsion copolymerizations of both ionic and amine-containing comonomer with iBMA we can conclude that the charge control of highly charged cationic latex particles is possible. The copolymerizations of iBMA and amino comonomers DMA or DMEAMA led to the formation of charged particles. However, latex particles with a cationic charge density higher than 90 µequiv/g can only be obtained when using ionic monomers MAPTAC and MATMAC. Nevertheless, by using either ionic or amine-containing comonomers for the charge control of cationic latex particles, a large amount of disadvantageous water-

Scheme 1. Acid and Base Catalyzed Hydrolysis of Glycidyl Methacrylate[35]



soluble polyelectrolytes was also formed. This effect was more pronounced for the ionic monomers than for the amino monomers. The existence of nonionic surfactants in nonionically stabilized nanosized latexes showed no significant effect on the maximum surface charge density compared to the surfactant-free latexes.

3.3. Cationic Charge Control via Post-Modification of GMA/BMA Copolymer Latexes. We have shown the cationic charge control by emulsion copolymerization with ionic or amine-containing comonomers, but a drawback of this approach is the formation of undesired water-soluble polyelectrolytes and the appearance of secondary nucleation, giving rise to a broad particle size distribution. A process to obtain cationic charges on latex particles without the formation of the water-soluble polyelectrolytes is the post aminolysis of epoxy-containing latex particles. Cationic latexes can be obtained by converting the epoxy group into a quaternary ammonium group via aminolysis.

Stable and un-cross-linked epoxy-containing particles were synthesized by the copolymerization of butyl methacrylate (BMA) with glycidyl methacrylate (GMA) by nonionically stabilized and surfactant-free emulsion polymerization at 60 °C. The recipes of several polymerizations are given in Table 4.

A prerequisite for the free radical polymerization of GMA is the near neutral pH condition, under which the polymer latex systems are produced, preventing the ring opening of oxirane.[29] Hydrolysis of the epoxy group takes place under acidic or basic conditions. After ring-opening, the intermediate will react further with water (a weak nucleophile) to form 1,2-dihydroxypropyl methacrylate (Scheme 1). This product is able to react with GMA, producing a difunctional methacrylate[30−32] and giving rise to cross-linking.[33,34]

The build-in of the GMA units in the copolymers by surfactant-free emulsion polymerization (entries G2A, G2B, and G2C) was verified by DSC analysis. The T_g of the GMA/BMA copolymer increased from 27 °C for the composition of 28/72 (mol/mol) to 43 °C for the composition of 78/22 (mol/mol). The ζ potential measurements of the unmodified copolymer latex particles showed no significant difference compared to the P(iBMA) particles (see section 3.1). Both particles are cationically charged by the presence of the amidino group of the initiator.

Surfactant-free and surfactant-stabilized latexes were dialyzed before the post modification of the epoxide unit was performed. Conversion of the surface epoxy into a quaternary ammonium groups by the addition of HCl, TMA, and a catalytic amount of TMAC is depicted in Scheme 2.[36] The conversion rate is temperature dependent. Therefore, the reaction was conducted at 70 °C, just below the cloud point temperature of the nonionic surfactant, for a period of 72 h.

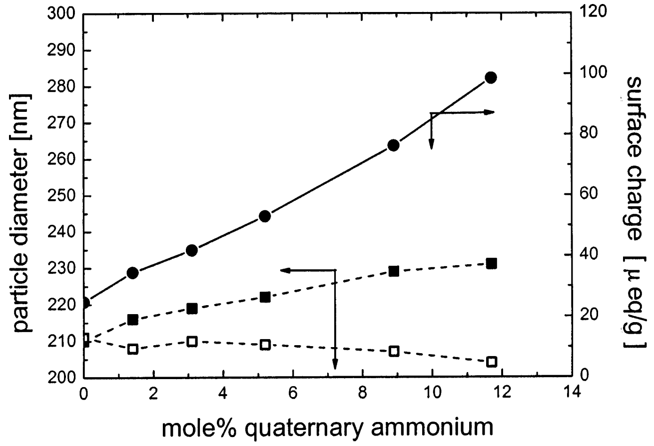


Figure 8. Particle size by DLS and particle surface charge density for GMA/BMA copolymer latex (entry G2A) from surfactant-free emulsion polymerizations: (■) particle size of latex after aminolysis; (□) particle size of the same latex treated with 0.1 M NaCl; (●) evolution of surface charge density with increasing amount of quaternary ammonium groups.

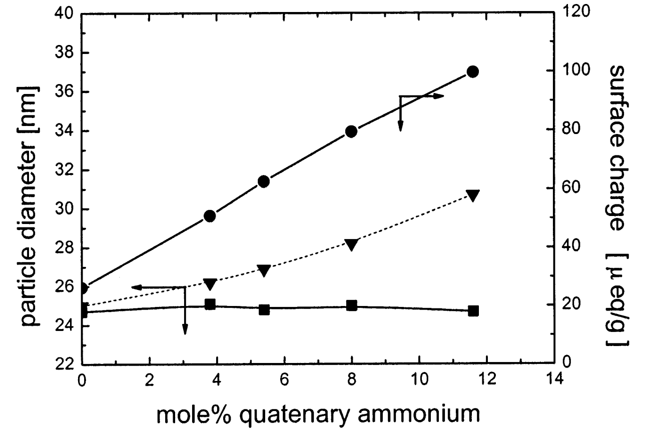
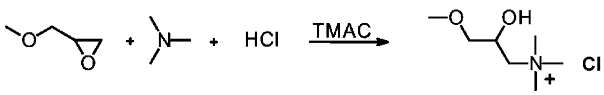


Figure 9. Particle size by DLS and particle surface charge density for GMA/BMA copolymer latex (entry G3) from nonionically stabilized emulsion polymerizations: (▼) particle size of latex after aminolysis; (■) particle size of the same latex treated with 0.1 M NaCl; (●) evolution of surface charge density with increasing amount of quaternary ammonium groups.

Scheme 2. Conversion of Epoxy Group into a Quaternary Amine Catalyzed by Tetramethyl Ammonium Chloride



The epoxy groups at the surface would react first and the reaction gradually proceeded to the interior of the particle. For all the GMA copolymers the conversion of more than 12 mol % epoxy groups, based on the total amount of BMA and GMA present, into quaternary ammonium groups led to the formation of a complete transparent aqueous solutions of cationic GMA/BMA copolymer. Stable latex particles were preserved when the concentration of TMA and HCl was decreased and less hydrophilic quaternary ammonium groups were formed. As shown in Figures 8 and 9, as the amount of quaternary ammonium varied, the surface charge density of the particles could be tuned in a wide range of

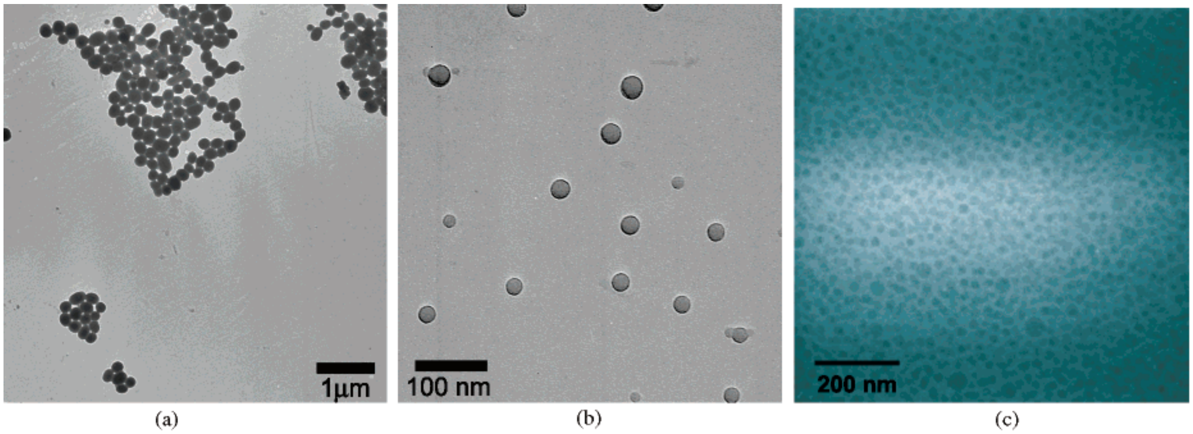


Figure 10. TEM micrographs of GMA/BMA polymer particles: (a) surfactant-free latex with 78/22 (mol/mol) GMA/BMA (entry G2C); (b) Nonionally stabilized particles with 78/22 (mol/mol) GMA/BMA (G5); (c) Nonionally stabilized particles with 28/72 (mol/mol) GMA/BMA (G3), observed by cryo-TEM.

Table 9. Characteristics of Cationic Polymer Latexes from Emulsion Copolymerization of BMA and GMA, Followed by Aminolysis

entry	GMA/BMA [mol/mol]	$M_w \times 10^{-3}$ [g/mol]	convn [wt %]	D_p[b] [nm]	PDI	$N_{m,w}$[a] [μequiv/g]	$N_{m,p}$[a] [μequiv/g]	$N_{c,p}$[a] [μequiv/m^2]	ζ-potential [mV]
G2A	28/72	268	83	210	0.12		68.4	2.50	56.4
G2B	54/36	242	78	207	0.09	0.11	72.6	2.62	67.3
G2C	78/22	259	84	214	0.10	0.19	71.8	2.68	69.5
G3	28/72	314	86	24.8	0.13	0.14	79.5	0.34	28.2
G4	54/36	357	83	25.1	0.11	0.18	78.1	0.34	27.9
G5	78/22	349	71	24.6	0.11	0.12	80.6	0.35	29.7

[a] Charge densities are obtained from latexes with 8 mol % of epoxy groups aminolyzed. [b] *Z*-average particle diameter determined by DLS.

30 to 100 μequiv/g for cationic latexes from both surfactant-free and nonionically stabilized emulsion polymerization, even though the particle size differs a lot (210 and 25 nm, respectively). The presence of the hairy polyelectrolyte (chains containing quaternary ammonium) did enlarge the hydrodynamic diameter (measured by DLS) of the latex particles slightly as can be seen in Figures 8 and 9. Addition of 1 mL of 0.1 M NaCl was used to collapse the layer of polyelectrolyte on the particle surface to determine the actual particle size, which revealed the actual particle size of the modified latex particles was about 205 nm for the surfactant-free latex and 25 nm for the nonionically stabilized latex, respectively, as also shown in Figures 8 and 9.

Figure 10 shows TEM micrographs of the GMA/BMA copolymer particles prepared by both surfactant-free polymerization and in the presence of the nonionic surfactant. As can be seen, the surfactant free latexes have a particle size of approximately 180 nm, while the nanosized polymer latexes (G5 and G3), produced in the presence of the nonionic surfactant, have an average particle size of 22 nm. The particle sizes obtained from TEM are in good agreement with the DLS results (Table 9).

Table 9 summarizes the particle diameters, surface charge densities of the final latex particles, and the content of water-soluble polyelectrolyte formed during the conversion. The measurements indicate that almost no water-soluble polyelectrolytes (<0.2 μequiv/g) were formed as a result of the aminolysis procedure. When the concentration of TMA and HCl was increased, the amount of water-soluble polyelectrolyte increased only slightly until the point (about 12 mol % of epoxy groups aminolyzed, based on the total amount of BMA and GMA) at which all the polymer chains became water-soluble. For both surfactant-free and nonionically stabilized latex particles the polydispersity index is around 0.1, lower than that for the cationic latexes prepared from the emulsion copolymerization of either cationic monomer or amine-containing monomer (Tables 6−8), which is likely due to the absence of water-soluble polyelectrolyte for the modified GMA/BMA copolymer latex (bridging flocculation is then prevented). The isoelectric point for the modified GMA/BMA copolymer latex (entry G2A, Figure 11) was determined to be 10.2, slightly higher than that for the P(iBMA) latex with a cationic charge solely from the initiator (entry A2).

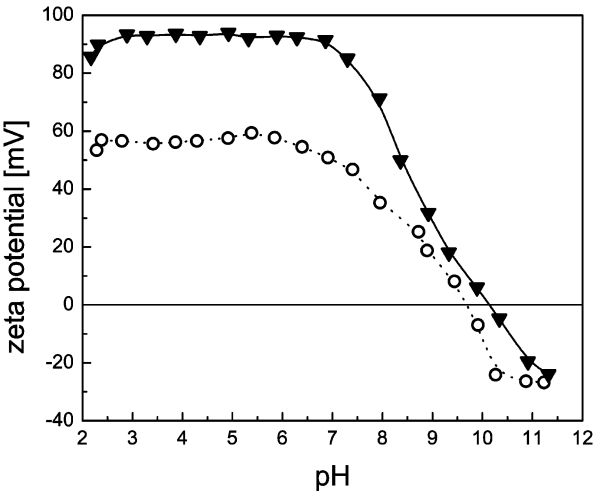


Figure 11. ζ potential vs pH curves for latex particles from surfactant free emulsion polymerization: (○) amidino stabilized P(iBMA) latex, entry A2; (▼) GMA-BMA copolymer latex after aminolysis (11.7% of epoxy group reacted), entry G2A.

In summary, the cationic charge control of latex particles by aminolysis of epoxy groups on the surface of latex particles showed to be a successful approach.

The maximum cationic charge density of 100 μequiv/g is comparable to values reported in the literature by using cationic comonomers.[4,13,15,25] Good control of the surface charge density was obtained with the negligible formation of water-soluble polyelectrolytes. The approach is applicable for both surfactant-free and nonionically stabilized emulsion polymerizations.

4. Conclusions

In this article we have described a systematic investigation, as well as a new method, on controlling surface cationic charge densities of latex particles in the range of 10−100 μequiv/g.

The surfactant-free emulsion polymerizations initiated by cationic initiators enable the formation of cationic latex particles (100−250 nm in diameter) with moderate charge densities. By adjusting the initiator concentration in the recipe a maximum charge density of 55 μequiv/g can be reached. Copolymerization of iBMA and ionic or amine-containing monomers renders polymer particles with a much higher cationic charge density up to 97 μequiv/g. By variation of the concentrations of ionic monomer or amine-containing monomer, a good control of charge density is possible. However, in both cases the formation of disadvantageous water-soluble polyelectrolytes is significantly increased. Finally, the aminolysis of the epoxy group at the surface of BMA/GMA copolymer latex particles results in the formation of highly charged (up to 100 μequiv/g) cationic latex particles with negligible formation of water-soluble polyelectrolytes. The charge formation can be easily controlled by varying the extent of conversion of epoxy groups into quaternary ammonium groups. This two-step approach proves to be most successful one in producing highly charged cationic latexes.

By using a nonionic surfactant, all three above-mentioned methods have been successfully used to obtain nanosized (20−40 nm), cationic latex particles. The surface charge densities can be controlled in a similar way to the surfactant-free emulsion polymerizations.

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