Styrylmethyl(trimethyl)ammonium Methacrylate Polyampholyte Latexes

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ABSTRACT: Monodisperse polyampholyte latexes that contain 25/23 and 29/18 mol % of polystyrylmethyl(trimethyl)ammonium and methacrylate groups were prepared by emulsion polymerization of vinylbenzyl chloride (VBC), *tert*-butyl methacrylate (tBMA), styrene, and divinylbenzene followed by stepwise conversion of the VBC and tBMA to cations and anions, respectively. As NaCl is added to aqueous dispersions, the polyampholyte latexes shrink up to 0.5 M and then swell up to 5 M NaCl, in which the particles are colloidally stable. The polyampholyte latexes also are colloidally stable in 1.2 M $BaCl_2$ solution. In contrast, the precursor quaternary ammonium chloride polyelectrolyte latexes coagulate rapidly in NaCl and $BaCl_2$ solutions.

Introduction

A polyampholyte has both positively and negatively charged groups bound to a single polymer chain.[1−3] Early research on synthetic polyampholytes was inspired by proteins, which have no net charge at the isoelectric point, are cationic at pH values below the isoelectric point, and are anionic at pH values above the isoelectric point. Typical of the first synthetic polyampholytes, aqueous solutions of copolymers of 2-vinylpyridine and methacrylic acid decreased in viscosity, and then the polymer precipitated as the pH increased to the isoelectric point. At higher pH, the polymer redissolved and the solution viscosity increased.[4] Although polyampholytes resemble polyelectrolytes, which have only one sign of charge, their behaviors in solution are quite different. A polyelectrolyte gives much higher viscosity in pure water, as the polymer chain expands due to intrachain electrostatic repulsion, than in salt solutions, where the conformation of the polymer chain contracts, as small solute ions screen the repulsions. A polyampholyte with balanced charge either has a globular conformation or precipitates in pure water and expands to a random coil with increased solution viscosity when electrolytes such as NaCl are added. This behavior has been called the “antipolyelectrolyte effect”.[1−3]

Polyampholytes can be classified by charge type according to whether the functional groups are strong or weak electrolytes: (1) weak/weak, such as amine/carboxylic acid, in which each component is ionic over only part of the pH range; (2) strong/strong, such as quaternary ammonium/sulfonate, in which both components are ionic over the entire pH range; (3) weak/strong; and (4) strong/weak.[1−3] The quaternary ammonium methacrylate polyampholytes described in this paper are strong/weak.

Polyampholytes can have many architectures. A linear polyampholyte can have alternating, random, or blocky cationic and anionic groups,[1−3,5−9] or it may be a block copolymer.[10−13] Linear polymers having zwitterionic repeat units are charge balanced polyampholytes.[14−17] The solution properties depend on both the charge type and the architecture. Alternating copolyampholytes are usually soluble in water at the isoelectric point, whereas random and blocky polyampholytes with balanced charge are insoluble in water and dissolve in electrolyte solutions.[5,6]

Polyampholyte hydrogels cross-linked with methylene bisacrylamide and with nearly balanced charge of amine and carboxylic acid groups,[18,19] or of sulfonate and quaternary ammonium groups,[20−22] behave as antipolyelectrolytes: They swell as electrolyte concentration increases. Charge balanced copolyampholytes containing >90 mol % of acrylamide do not swell as polyelectrolytes at low electrolyte concentration, whereas hydrogels with a large percent of ionic repeat units swell both at low and at high electrolyte concentrations.[21,23] Hydrogels formed from acrylic acid and 3-(*N*-methacrylamidopropyl)trimethylammonium chloride are still more complex and can exist in at least seven phases.[24]

Interest in cationic latexes as catalysts for organic reactions in aqueous dispersions prompted us to synthesize polyampholyte latexes, which also can be called microgels. For comparison with cationic latexes studied before, we wanted the cationic groups to be styrylmethyl(trimethyl)ammonium ions and the particles to be 100−200 nm in diameter.[25−28] A second objective was to obtain latexes that are colloidally stable in water at high salt concentrations, because previous cationic latexes coagulated at >0.5 M NaCl, rendering them less active catalysts.[25] Catalytic activity in common ambient environments, such as seawater, could be highly useful. Stability in electrolyte solutions also is important for applications in wastewater purification, lubrication, and drug delivery.

Previously, we reported polyampholyte latexes containing quaternary ammonium ions and either *p*-styrenesulfonate or vinylbenzylsulfonate ions.[29] However, none of those latexes were colloidally stable for long periods of time, probably due to nonuniform composition. Now we report the preparation and properties of monodisperse latexes containing styrylmethyl(trimethyl)ammonium chloride and methacrylic acid units in the 50/50 to 60/40 composition range. The new latexes expand as polyampholytes and are colloidally stable even in 5 M NaCl solution. A preliminary investigation of the catalytic activity will be reported elsewhere.[30]

Experimental Section

Materials. Sodium dodecyl sulfate (SDS), sodium bisulfite, potassium persulfate (KPS), *p*-toluenesulfonic acid (PTSA), 1,4-

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Table 1. Compositions of tBMA/VBC Copolymer Microgels

	weight of monomers, g			Cl^- anal.[a]		N anal.[b]
sample	styrene	VBC	tBMA	mmol/g	N^+ (mol %)[c]	N^+ (mol %)
25/25N	2.03	1.56	1.46	1.89	24.7	24.6
20/30N	2.02	1.82	1.14	2.12	28.6	29.1
30/20N	2.06	1.26	1.73	1.41	17.3	17.6

[a] Chloride-selective electrode. [b] Combustion. [c] The average repeat unit was calculated to be 126 g/mol (25/25N), 132 g/mol (20/30N), and 119 g/mol (30/20N) for determination of mol %.

dioxane, and aqueous 25 wt % trimethylamine (TMA) were used as received. The *m*/*p* mixture of vinylbenzyl chloride (VBC), styrene, divinylbenzene (DVB), and *tert*-butyl methacrylate (tBMA) monomers were distilled under vacuum and filtered through alumina. Water was deionized and treated with active carbon and had a conductivity of 0.65×10^{-6} ohm^{-1} cm^{-1} after exposure to air. Spectra/Por dialysis membrane with a molecular weight cutoff of 50 000 was washed with deionized water. Synthetic seawater ("Instant Ocean" from Aquarium Systems Co.) contained about 34 g L^{-1} of dissolved salts as chloride, 19 251 mg L^{-1}; sodium, 10 757; sulfate, 2659; magnesium, 1317; potassium, 402; calcium, 398; carbonate/bicarbonate, 192; strontium, 8.6; boron, 5.6; bromide, 2.3; iodide, 0.22; lithium, 0.18; and <0.5 of many other elements.

Polymerization. A solution of 0.060 g of SDS in 20.0 mL of water was placed in a 100 mL three-necked round-bottomed flask that was equipped with a nitrogen inlet, a Teflon blade mechanical stirrer, and an addition funnel that also was equipped with a mechanical stirrer. A mixture of 0.12 g of SDS, 0.015 g of sodium bisulfite, 5.0 mL of water, and 5.0 g of a mixture of styrene, VBC, tBMA, and DVB (amounts are in Table 1) was placed in the addition funnel and stirred to form a preemulsion. The mixture in the flask was heated to 60 °C with stirring for 15 min under a stream of nitrogen, 0.50 g of the preemulsion was transferred to the flask, and 0.04 g of KPS and 0.005 g of sodium bisulfite were added to start polymerization. After an opaque latex formed (within 30 min), the rest of the preemulsion was added continuously over 60 min. The addition funnel was replaced by a condenser, and the mixture was stirred at 60 °C for 3 h. After cooling to room temperature, the dispersion was filtered through cotton to remove any solid coagulum. (Usually there was none.)

Quaternary Ammonium Chloride Latexes. The latex dispersion, 25 mL of water, and 17.0 g of 25 wt % aqueous TMA were placed in a 150 mL beaker and sealed in a stainless steel reactor. The mixture was held under pressure with magnetic stirring for 48 h with the reactor half immersed in a 60 °C oil bath. The excess TMA was evaporated by bubbling nitrogen through the mixture. The dispersion was dialyzed against deionized water for 1 week with frequent changing of the water and was ultrafiltered with stirring through a 0.1 μm cellulose acetate/nitrate membrane (Millipore) under 20 psi pressure of nitrogen. Water was added repeatedly to the dispersion until about 800 mL of filtrate was collected, and the filtrate had a constant conductivity of 1.5×10^{-6} ohm^{-1} cm^{-1}. The solids content was measured by evaporating separately three 1.00 mL aliquots of the dispersion at >100 °C to constant weight. The chloride ion content of the latex was determined by titration using an ion selective electrode.[25-27]

Polyampholyte Latexes. A mixture of 20 mL of dispersion (1.0 g of solids), 100 mol % of PTSA based on the tBMA content, and 2.0 g of 1,4-dioxane was held for 48 h under pressure in a stainless steel reactor at 120 °C. The latex was purified by dialysis and ultrafiltration as described for the quaternary ammonium chloride latexes.

IR Analysis. To determine the degree of hydrolysis of tBMA units after various reaction times, a 10 mL portion of the mixture was immediately frozen, the solvent was lyophilized, and the remaining solid was analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with Kubelka–Munk processing.

Titrations.[31-34] A 0.050 g sample of latex solid was diluted to 50 mL with water, purged with nitrogen, and stirred. Standard 0.048 M HCl solution (4.0 mL) was added, and the mixture was titrated with standard 0.050 M NaOH solution. Both conductivity and pH were measured 1.5–2.0 min after addition of each 0.1 mL of titrant.

Analysis of PTSA. A measured amount of the latex was placed in 4 M NaCl, and the pH was reduced to 2.5 with HCl to displace PTSA from the particles. The dispersion was ultrafiltered through a 0.1 μm membrane, and the particles were washed with water. The filtrate was diluted to a measured volume, and the concentration of PTSA was determined from its absorbance and the independently measured molar extinction coefficient of PTSA in water.

Colloid Stability. Dispersions containing 0.05% w/v particles had an initial turbidity at 546 nm of about 0.7 at room temperature (20–26 °C) in a 10 mm cuvette. The change of turbidity as a function of time was measured at various concentrations of $BaCl_2$ and NaCl.

In slow coagulation experiments, a 2 mL aliquot of the latex was mixed with 8 mL of the barium chloride solution, allowed to stand for 2 h, and sedimented gently in a benchtop centrifuge for 10 min. The supernatant was transferred to a cuvette, and the turbidity was measured. After 48 h the cuvettes were photographed.

In faster coagulation experiments, 2.4 mL of the NaCl solution was mixed with 0.6 mL of the latex dispersion, and the average turbidity at 540–550 nm was recorded continuously for 5 min with a diode array spectrophotometer. The initial slope of the graph of turbidity vs time was taken to be the initial rate of coagulation.

Coagulation kinetics in basic dispersions were determined by adding a known amount of NaOH to the dispersion and measuring the turbidity as described for NaCl solutions. The pH was measured at the end of the experiment.

Particle Sizes. TEM. One drop of 1% solids latex was placed on a Formvar-coated Cu grid, excess latex was removed by touching it with filter paper, and the grid was dried in air. The grid was treated with one drop of 1% uranyl acetate solution for 1 min and dried as before. Diameters of 75 nonaggregated particles were measured from the micrograph negative using an optical microscope with a calibrated stage. Magnifications were typically 10 000× by TEM and 10× by optical microscopy. Weight- and number-average particle sizes were calculated as before.[27]

Dynamic Light Scattering (DLS). Latexes were diluted 1000-fold with water or standard NaCl solution at 20 °C, and scattered light intensity from an argon laser at 488 nm was measured at an angle of 90° using a Brookhaven Instruments BI-200SM goniometer and BI-9000AT multi-τ digital correlator. Assuming the particles were hard spheres, the hydrodynamic radius (R_h) was calculated from the diffusion coefficient via the Stokes–Einstein equation,

$$R_h = kT/6\pi\eta D \tag{1}$$

where k is the Boltzmann constant, T is absolute temperature, η is the viscosity of the medium, and D is the diffusion coefficient of the particle. The viscosities and refractive indices of NaCl solutions were estimated from linear plots of literature values of the property at 20 °C[35] vs NaCl concentration.

Results

Latex Synthesis. The general strategy for synthesis of polyampholyte latexes is shown in Scheme 1. *tert*-Butyl methacrylate (tBMA) is the precursor of anionic units, vinylbenzyl chloride (VBC) is the precursor of cationic units, styrene is an inert monomer, and ≤1% divinylbenzene (DVB) is the cross-linker. Our first aim was a polyampholyte having a small excess of quaternary ammonium ion sites to act as a catalyst. Our second aim was a latex that contained equal amounts of methacrylate and quaternary ammonium ion units

Table 2. Elemental Analyses of tBMA/N$^+$ Copolymer Microgels (wt %)

sample	C	H	N	O^a	Cl
25/25N					
$[C_8H_8]_{0.50}$ $[C_{12}H_{18}NCl]_{0.25}$ $[C_8H_{14}O_2]_{0.25}$	76.91	8.61	2.49	5.69	6.31
experimental	74.04	8.59	2.34	9.71	5.32
experimental water (3.96%)	77.55	8.47	2.45	5.96	5.57
20/30N					
$[C_8H_8]_{0.50}$ $[C_{12}H_{18}NCl]_{0.30}$ $[C_8H_{14}O_2]_{0.20}$	76.72	8.54	2.92	4.44	7.38
experimental	72.96	8.83	2.75	8.30	7.16
experimental water (2.98%)	76.21	8.73	2.87	4.71	7.48
30/20N					
$[C_8H_8]_{0.50}$ $[C_{12}H_{18}NCl]_{0.20}$ $[C_8H_{14}O_2]_{0.30}$	75.91	7.88	2.33	7.98	5.90
experimental	73.66	8.82	1.98	10.96	4.58
experimental water (4.16%)	76.21	9.13	2.05	7.87	4.74

[a] By difference between 100% and the sum of percents of the other elements.

Table 3. Elemental Analyses of the Polyampholyte Microgels (wt %)

sample	C	H	N	O	Cl	other^a
PA2525						
$[C_8H_8]_{0.50}$ $[C_{12}H_{18}NCl]_{0.25}$ $[C_4H_6O_2]_{0.25}$	75.94	7.97	2.77	6.32	7.00	
experimental	73.36	7.94	2.60		0.00	16.10
PA2030						
$[C_8H_8]_{0.50}$ $[C_{12}H_{18}NCl]_{0.30}$ $[C_4H_6O_2]_{0.20}$	75.96	8.04	3.16	4.82	8.01	
experimental	71.97	8.19	2.68		0.29	16.87

[a] Calculated by difference between 100% and the sum of percents of the other elements.

Scheme 1

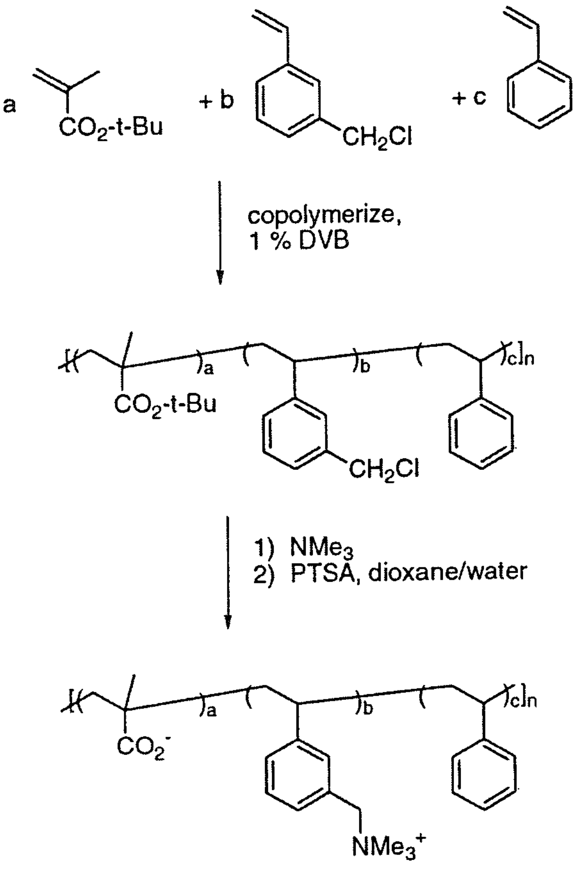


Table 4. Carboxylate and *p*-Toluenesulfonate Contents of the Polyampholyte Microgels

	COOH (mol %)		PTSA (mol %)	
sample	DRIFTS	conductivity	conductivity	UV−vis
PA2525	22.5	23	3.1	3.2
PA2030	17.5	19	6.5	6.8

to investigate swelling of the particles under varied conditions. We obtained stable latexes from the monomer mixtures listed in Table 1, which were designed to give 25/25, 20/30, and 30/20 mol % of methacrylate/quaternary ammonium ion repeat units.

Reaction of the chloromethyl groups of the tBMA/VBC/styrene latexes with trimethylamine formed quaternary ammonium chloride latexes, as shown by disappearance of the 1265 cm^{-1} IR band of the chloromethyl group. The latexes were thoroughly dialyzed and ultrafiltered to remove low molar mass and soluble polymeric impurities. Elemental analytical data are shown in Table 2. We attribute the excess oxygen to the presence of 3−4% water in the samples. The mole percents of quaternary ammonium chloride groups determined by (a) titration of chloride ion using an ion selective electrode and (b) combustion elemental analysis for nitrogen, agreed to within 0.5 mol % of N$^+$ units (Table 1). Both analyses indicated slightly fewer quaternary ammonium chloride groups than expected from the mixture of monomers.

Hydrolysis of the *tert*-butyl esters with 1 mol equiv of *p*-toluenesulfonic acid in water containing 10 wt % 1,4-dioxane formed methacrylic acid units. The dioxane was needed to swell the particles. Attempted hydrolyses using mineral acids were incomplete. The 25/25N and 20/30N latexes produced colloidally stable polyampholytes, but the 30/20N latex coagulated. Elemental analyses of the stable polyampholyte latexes PA2525 and PA2030 are reported in Table 3. Since little or no chlorine remained, the samples must have contained some other anion, such as *p*-toluenesulfonate, in addition to the methacrylate ions, as counterions for the quaternary ammonium ions. The disappearance of the *tert*-butyl ester IR band at 1726 cm^{-1} and the appearance of a carboxylate ion band at 1566 cm^{-1} were followed by DRIFTS and were quantitated by normalizing the 1726 cm^{-1} peak area from the Kubelka−Munk function to the areas of peaks at 1495 and 1454 cm^{-1}. The results are reported in Table 4.

The acidic groups in the polyampholyte latexes were analyzed by conductometric and potentiometric titrations.[31−34] The sample was converted completely to acidic form by addition of a known amount of HCl and then titrated with standard NaOH. Figure 1 shows the

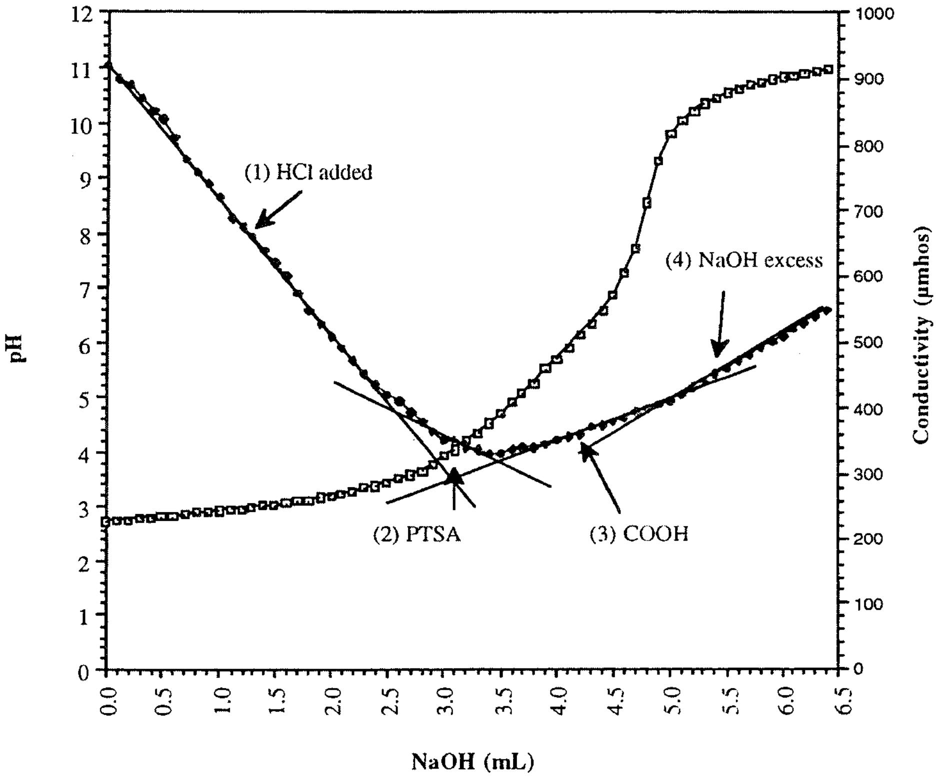


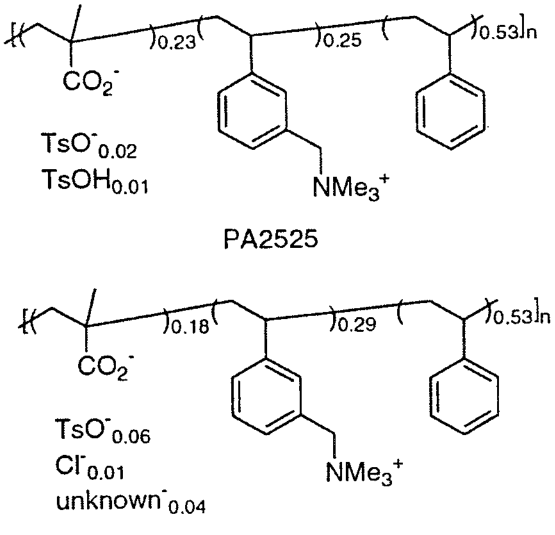
Figure 1. Conductivity/pH titration of PA2525 microgel.

titration curves of PA2525. In region 1 the conductivity decreases due to replacement of protons from HCl by sodium ions, which have a lower equivalent conductance than protons. We attribute the lesser negative slope in region 2 to neutralization of *p*-toluenesulfonic acid in the pH range 3.4−4.6, the positive slope in region 3 to deprotonation of carboxylic acid groups in the pH range 4.6−10.1, and the greater slope of region 4 to excess NaOH. The break points in the conductivity plots give the amounts of NaOH required to consume each type of acid present. The analyses for carboxylic acid groups by DRIFTS and by conductometric titration agreed to within 8% relative to the average value for both polyampholyte latexes (Table 4).

The *p*-toluenesulfonate groups in the latexes were analyzed also by UV absorbance of the ultrafiltrate from the latex after addition of HCl and 4 M NaCl to displace the *p*-toluenesulfonic acid. The UV and conductometric analyses for *p*-toluenesulfonate are reported in Table 4 and agree to within 5% of the average values.

Summaries of the compositions of the polyampholyte latexes are shown in Scheme 2. The data are averages of the two methods of analysis of methacrylate and *p*-toluenesulfonate. An unknown anion for charge balance is included in the results for PA2030, and *p*-toluenesulfonic acid is included to account for sulfur in excess of the amount of *p*-toluenesulfonate anion needed for charge balance in the results for PA2525.

Scheme 2



Latex Stability. Stabilities of both the quaternary ammonium chloride and the polyampholyte lateses were examined turbidimetrically in $BaCl_2$ solutions by a method modified from the literature.[36] Results are presented for the quaternary ammonium chloride latex 20/30N in Figures 2 and 3. The results for the latex 25/25N were identical. Figure 2 shows a sharp increase in turbidity at $[BaCl_2] > 0.3$ M due to slow coagulation and loss of turbidity at $[BaCl_2] > 0.8$ M due to precipitation of the coagulum. Figure 3 shows the results photographically. In contrast, the corresponding polyampholyte latex PA2030 was completely stable in 1.2 M $BaCl_2$ solution after 6 months, as shown in Figures 4 and 5. We attribute the small decrease of turbidity at >0.5 M shown in Figure 4 to increase of the refractive index of the aqueous phase with increasing concentration of $BaCl_2$.

A rapid increase of turbidity of the quaternary ammonium chloride latex 20/30N at [NaCl] > 0.7 M is shown in Figure 6, and photographs of the samples are shown in Figure 7. In contrast, polyampholyte latex PA2030 was completely stable in 4 M NaCl solution (and so was PA2525). An example up to 3.3 M NaCl is shown in Figure 8.

Polyampholyte latexes PA2030 and PA2525 responded differently to increasing pH because of their

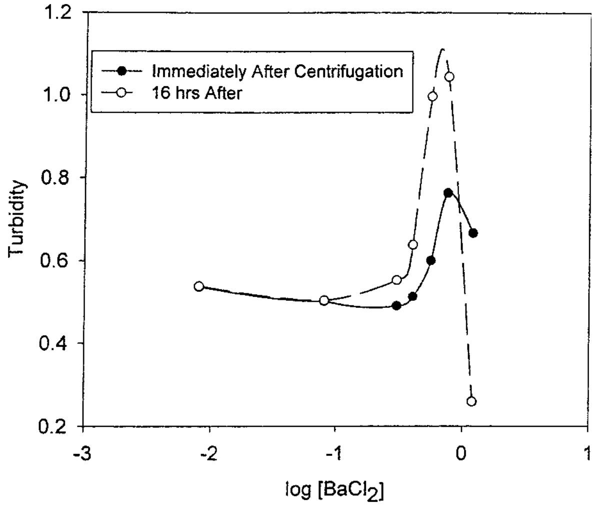


Figure 2. Turbidity of the 20/30N microgel in $BaCl_2$.

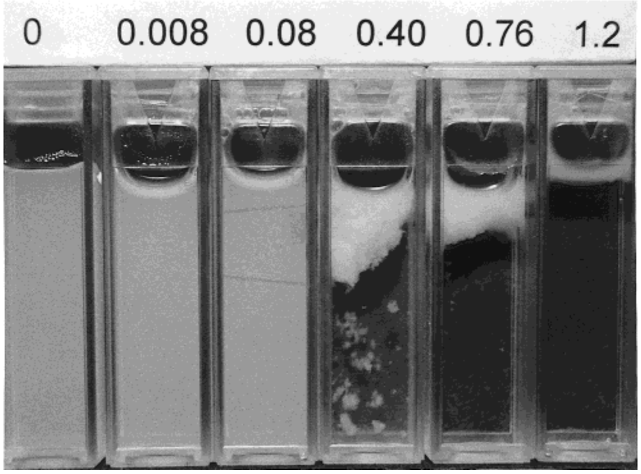


Figure 3. Effect of $BaCl_2$ concentration (M) on the 20/30N microgel after 48 h.

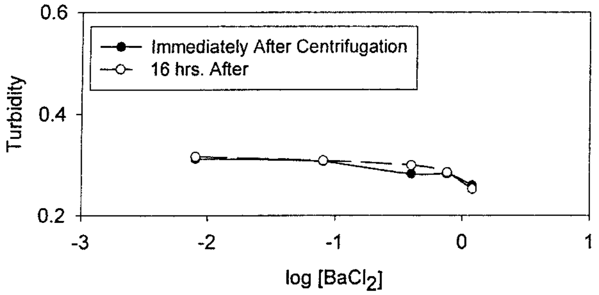


Figure 4. Turbidity of the PA2030 microgel in $BaCl_2$.

different ratios of fixed charges, 18/29 and 23/25 COO^-/N^+, respectively. PA2030, which always had an excess of positive charge, was stable in solutions up to pH 11.3 with no added electrolyte other than NaOH, whereas PA2525, which had excess positive charge at neutral pH due to incomplete ionization of carboxylic acid groups, coagulated slowly at pH 9.4 and rapidly at pH 9.9, where the latex had little or no net charge, as shown in Figure 9. However, when PA2525 was placed first into 4 M NaCl, in which it was stable, and then made basic with NaOH to pH 10.6, where the carboxylic acid groups are fully ionized, the turbidity did not change. Thus, PA2525 is more stable in basic 4 M NaCl than in basic solutions of lower electrolyte strength.

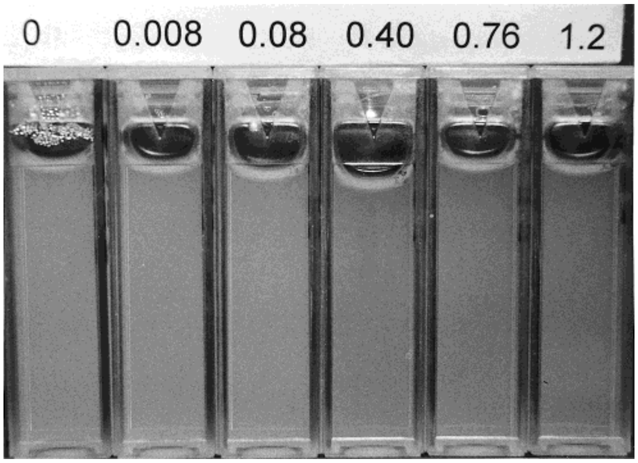


Figure 5. Effect of $BaCl_2$ concentration (M) on the PA20/30 microgel after 48 h.

Latex stabilities were tested also in synthetic seawater, because of our interest in using them as catalysts in common ambient environments. Neither the quaternary ammonium chloride nor the polyampholyte latexes coagulated immediately. After 1 week the turbidity of the quaternary ammonium ion latexes increased, and after 4 weeks they precipitated. The polyampholyte latexes were completely stable under the same conditions.

Particle Sizes. Measurements by TEM, which are reported in Table 5, showed that all of the latexes had diameters of 140−160 nm in dry form and polydispersities (weight-average/number-average diameters) of $d_w/d_n = 1.02-1.04$. The hydrodynamic diameters (d_h) at high dilution in pure water were much larger than the diameters of dry particles and are reported along with the swelling ratios $(d_h/d_n)^3$ in Table 5.

The hydrodynamic diameters varied markedly with NaCl concentration, as shown in Figures 10 and 11. Starting in pure water, both the quaternary ammonium chloride and the polyampholyte latexes shrink substantially with added NaCl up to 0.01 M and continue to shrink in NaCl up to 0.5 M. We attribute the shrinkage to the osmotic transfer of water from the latex to the NaCl solution. Further increases in NaCl concentration from 1.0 to 5.0 M swell the polyampholytes markedly.

Discussion

The solution properties of linear polyampholytes and the swelling properties of polyampholyte gels depend greatly on the charge balance, the mole percent of charged units, and the polymer architecture.[6−9] Alternating, random, zwitterionic, and block copolyampholytes all have different properties. Our microgels were prepared by emulsion copolymerization of lipophilic monomers. Assuming that the amount of monomers consumed in the aqueous phase is negligible and that all of the monomers polymerize, the architectures can be discussed in terms of copolymer reactivity ratios determined from solution and bulk polymerizations. Data are not available for tBMA, but methyl, ethyl, and *n*-butyl methacrylate (M_1) copolymerize with styrene (M_2) with $r_1 \sim r_2 \sim 0.4-0.5$ and with *p*-chloromethylstyrene (M_2) with $r_1 \sim 0.4$ and $r_2 \sim 0.9-1.5$.[37] Similarly for styrene (M_1) and *p*-chloromethylstyrene (M_2), $r_1 \sim 0.6$ and $r_2 \sim 1.1-1.6$.[37] Therefore, the polymer from a terpolymerization of a 25/25/50 mixture of tBMA/VBC/styrene (*p*-VBC = *p*-chloromethylstyrene) tends to have

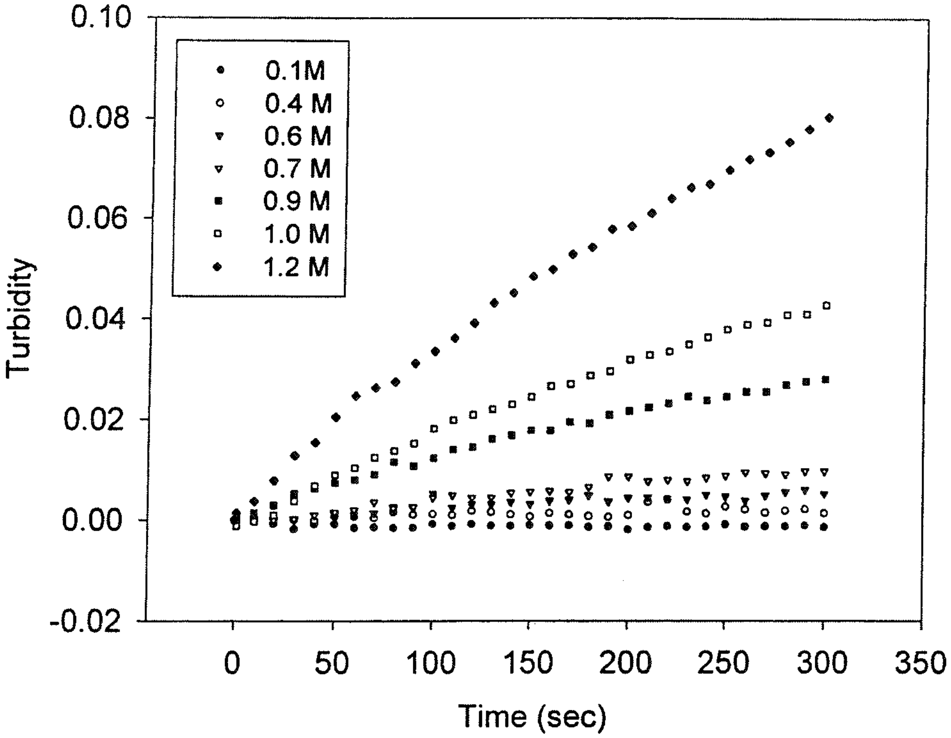


Figure 6. Coagulation kinetics of the 20/30N microgel in NaCl solutions.

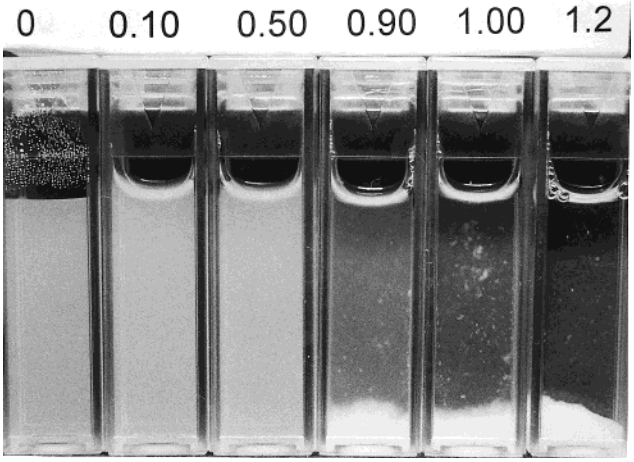


Figure 7. Effect of NaCl concentration (M) on the 20/30N microgel after 48 h.

alternating styrenic and methacrylic units, polymer formed early is somewhat rich in VBC, and polymer formed late is richer in styrene and tBMA. Compared with previous polyampholytes, the distributions of charged units in our polyampholyte latexes most nearly resemble those of the copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and 2-(methacryloyloxyethyl)trimethylammonium chloride (MADQUAT) that were prepared in inverse microemulsions, in which $r_1 = 0.8$ and $r_2 = 1.9$.[38] The copolymers from inverse microemulsions have been separated into AMPS-rich and MADQUAT-rich fractions.[7] In copolymerizations DVB polymerizes moderately faster than styrene to form an inhomogeneous distribution of cross-links. Thus, the quaternary ammonium units of our polyampholytes tend to be in more highly cross-linked regions of the particles than are the methacrylate units.

We are not aware of any other charged latexes that are colloidally stable in 5 M NaCl solution, although steric stabilization by adsorbed or grafted poly(ethylene oxide) is often effective at high electrolyte strength. The stability is likely related to the increasing hydrodynamic diameters of the polyampholytes with increasing NaCl concentration. As shown in Figure 11, <0.1 M NaCl at neutral pH osmotically shrinks the particles because of Donnan exclusion of Na^+ ions from the gel, which contains an excess of N^+ cations relative to methacrylate anions. As NaCl concentration increases up to 0.5 M, Na^+ and Cl^- ions penetrate the particles and become counterions to the fixed carboxylate and quaternary ammonium ions. Table 6 reports the intraparticle concentrations of N^+ and COO^- ions, which were calculated at varied NaCl concentrations from the

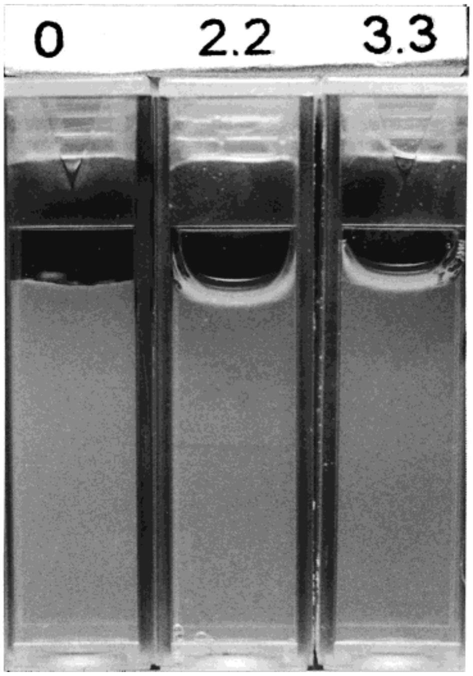


Figure 8. Effect of NaCl concentration (M) on the PA2030 microgel after 48 h.

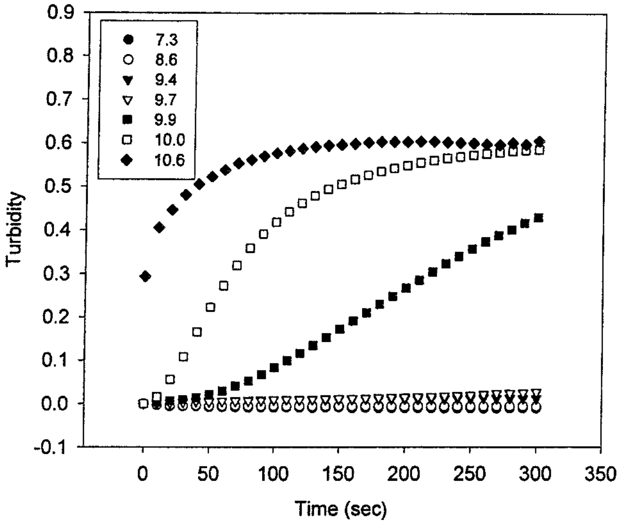


Figure 9. Coagulation kinetics of the PA2525 microgel at varied pH.

Table 5. Sizes and Swelling of Microgels in Water[a]

	TEM		DLS	swelling factor
sample	d_w	d_w/d_n	d_h	$(d_h/d_n)^3$
2030N	153.4	1.021	226.8	3.5
2525N	156.1	1.034	210.5	2.7
3020N	156.3	1.017	193.4	1.9
PA2030 ($18O^-/29N^+$)	149.5	1.026	220.2	3.6
PA2525 ($23O^-/24N^+$)	139.9	1.042	212.7	4.0

[a] In pure water with no added electrolytes. pH before dilution ranged from 6.4 to 5.5. d_w and d_n are the weight- and number-average diameters, and d_h is the hydrodynamic diameter (in nm).

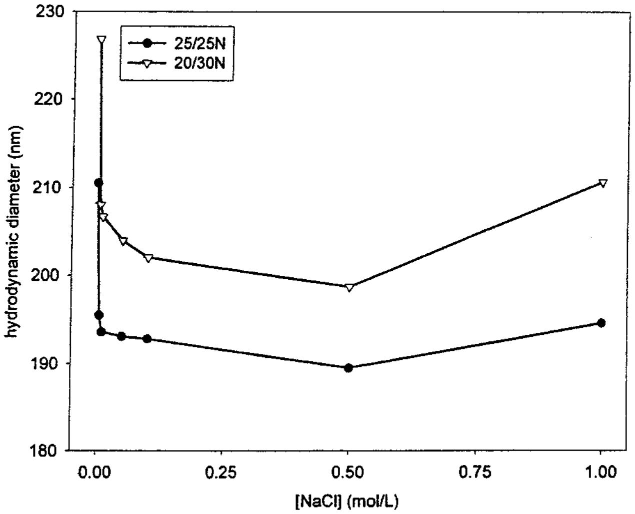


Figure 10. Effect of NaCl concentration on the hydrodynamic diameters of the 25/25N and 20/30N microgels.

swelling ratios of the polyampholytes (Table 5) and the ion contents (Scheme 2). The external Na^+ and Cl^- concentrations are about the same as the internal N^+ and COO^- concentrations at 0.5−1.0 M NaCl. At >1 M NaCl, hydrated Na^+ and Cl^- ions osmotically swell the polyampholyte particles. If the concentrations of ions inside the particles are approximately the same as those outside at high NaCl concentrations, the composition of the gel phase is not much different from that of the solution phase. Consequently, the effective Hamaker constant of the particle is similar to that of the solvent, and there is little van der Waals attraction between the swollen particles.[39] This explanation has been offered before for the stability of microgel particles that are much more swollen than our polyampholytes.[39,40] Polyampholyte chains extending into the solution may provide additional electrosteric stabilization. The swelling of the polyampholyte microgels in NaCl solutions is analogous to the "antipolyelectrolyte" effect demonstrated for blocky copolyampholytes that were prepared in inverse microemulsions from NaAMPS and MADQUAT.

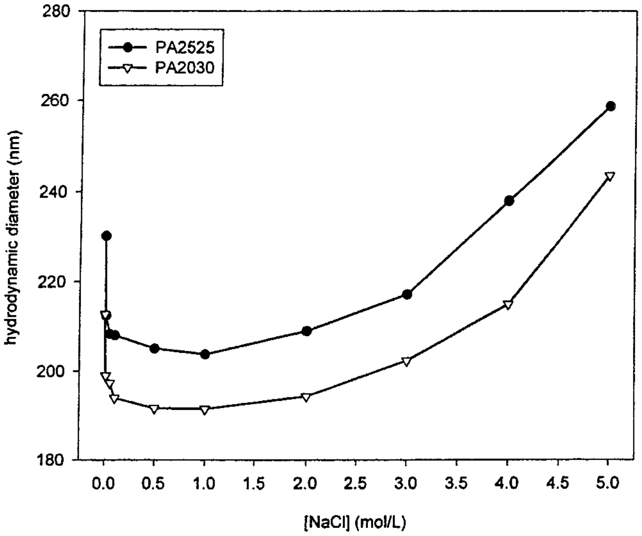


Figure 11. Effect of NaCl concentration on the hydrodynamic diameters of the PA2525 and PA2030 microgels.

Table 6. Molar Internal Concentrations of Fixed Ions in the Polyampholytes at Varied External NaCl Concentrations

	PA2525		PA2030	
NaCl (M)	N^+	COO^-	N^+	COO^-
0.0	0.64	0.61	0.75	0.46
0.01	0.66	0.62	1.00	0.62
0.05	0.68	0.64	1.04	0.64
0.10	0.68	0.64	1.09	0.67
0.50	0.70	0.66	1.14	0.70
1.0	0.72	0.68	1.14	0.70
2.0	0.68	0.64	1.09	0.67
3.0	0.60	0.57	0.92	0.57
4.0	0.46	0.43	0.80	0.49
5.0	0.35	0.34	0.56	0.34

The properties of our quaternary ammonium methacrylate latexes differ from those of copolyampholyte gels that were prepared from NaAMPS and MADQUAT with 1.4−5.0% methylenebisacrylamide in inverse microemulsions.[41] The NaAMPS/MADQUAT microgel particles had varied shapes and sizes, whereas the quaternary ammonium methacrylate microgels are spherical and more nearly monodisperse. The NaAMPS/MADQUAT microgel particles with balanced charge flocculated below a certain electrolyte concentration, as expected by analogy to the corresponding soluble polymers.[41] In contrast, our microgels remain dispersed at neutral pH at all NaCl concentrations due to excess positive charge. The charge balanced polyampholyte PA2525 at pH ≥ 9.9 without added NaCl also flocculates. Above a critical concentration of electrolyte required for stability, the sizes of the NaAMPS/MADQUAT microgel particles were insensitive to electrolyte concentration and did not depend on the amount of cross-linker, whereas our particles continue to swell with increasing NaCl concentration and remain swollen when charge is balanced in a pH 10.6 and 4 M NaCl solution. Most of the differences between the N$^+$/methacrylate and the NaAMPS/MADQUAT microgels can be attributed to strong/weak vs strong/strong electrolyte units, but the swelling behavior of the NaAMPS/MADQUAT microgels is puzzling. Better knowledge of the distributions of cross-links and of the ionic repeat units would help the understanding of the properties and facilitate the design of new microgels to have desired swelling behavior.

Conclusions

Polyampholyte latexes of low polydispersity containing 25/23 and 29/18 mol % of polystyrylmethyl(trimethyl)ammonium and methacrylate groups were prepared by surfactant-free emulsion polymerization of vinylbenzyl chloride, *tert*-butyl methacrylate, styrene, and divinylbenzene followed by stepwise conversion of the VBC and tBMA to cations and anions, respectively. The microgels behave as "antipolyelectrolytes" in water by swelling with increasing concentrations of added salts. They are colloidally stable at NaCl concentrations up to 5 M, which makes them candidates for applications in catalysis, water purification, and drug delivery. Their catalytic activity for decarboxylation of 6-nitrobenzisoxazole-1-carboxylate is reported elsewhere.[30]

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