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ORIGINAL CONTRIBUTION

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Synthesis of polystyrene-based cationic copolymers and their colloidal properties in water

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Abstract A series of polystyrene-based cationic copolymers was synthesized by two different methods: (1) solution copolymerization of styrene and vinylbenzyl trimethylammonium chloride (VBTMAC) in ethanol, and (2) surfactant-free emulsion copolymerization of styrene and vinylbenzyl chloride in water followed by reaction with trimethylamine. The results indicated that the different synthesis methods would result in different polymer structures and, therefore, affect the solubility and colloidal properties of the copolymers in water. For the copolymers prepared by method 2, partial crosslinking was observed. The copolymers made by this method are almost water-insoluble. In contrast, the copolymers made from direct copolymerization of styrene and VBTMAC in ethanol are water-soluble or dispersible, but the solubility and the particle size of microaggregates formed by these copolymers in water strongly depend on charge density and temperature. One of the important results from this study is that uniform colloidal particles with a very small particle size (30–50 nm) can be obtained by dispersing polystyrene-based cationic copolymers in water without adding any surfactants.

Key words Cationic – Polystyrene copolymer – Colloid – Micelle – Microaggregate

Introduction

Cationic polymeric latexes have shown potential applications in many fields, including papermaking [1–6], paper coating [7, 8], and adhesion [9]. Recent studies [4–6] indicated that cationically charged polystyrene latexes could be used as effective papermaking retention aids or sizing agents. However, it was found that the particle size and charge density of the polymeric latex are two critical factors affecting the performance of the latex. As a papermaking retention aid or sizing agent, it was found [4–6] that the most effective particle size of these latexes is in the range 30–50 nm. Although emulsion polymerization is the most convenient technology for making uniform latexes, this method can generally produce only a cationic polystyrene latex with a particle size larger than 150 nm, which is not effective as a papermaking additive agent. In order to reduce the particle size, a microemulsion polymerization technique has to be employed [4–6]. Although the particle size of cationic polystyrene-based latex can be well controlled by microemulsion polymerization, the high surfactant consumption and the difficulty in latex clarification after polymerization are two major problems. Instead of directly synthesizing a latex using emulsion or microemulsion polymerization, it was shown in our previous study [6] that linear cationic polystyrene polymers obtained by solution polymerization of styrene and cationic vinylbenzyl trimethylammonium chloride (VBTMAC) monomers in ethanol could form stable colloidal aggregates in water with a particle size of 30–50 nm and a similar structure as cationic polystyrene latex. A previous study also indicated that these colloidal aggregates are effective papermaking retention aids and sizing agents.

It has been well known that charged copolymers with a hydrophobic backbone can form stable colloidal particles in water if the charge density and polymer structure are well controlled [10, 11]. Poly(styrene-*co*-VBTMAC) is a typical cationically charged hydrophobic copolymer. The hydrophobic polystyrene tends to aggregate and the hydrophilic VBTMAC tends to dissolve in water. As a result, this copolymer is expected to form stable colloids in water if the hydrophobic/hydrophilic forces are well balanced.

Poly(styrene-*co*-VBTMAC) copolymers have been synthesized previously via copolymerization of styrene and cationic monomers [9, 12], and via quaternization of the copolymer of styrene and vinylbenzyl chloride (VBC) with trimethylamine [9, 13–16]. This class of polymers has been studied as curing agents for epoxy resins [9], as catalyst-supporting agents [15, 16], and as antibacterial agents [12, 17]. However, the colloidal properties of these copolymers in water have not been reported in the literature. In this study, a series of poly(styrene-*co*-VBTMAC) copolymers with various charge densities was synthesized using two different methods. The relationship among the polymerization conditions, polymer structure, charge density, and the colloidal properties of copolymers in water was studied.

Experimental

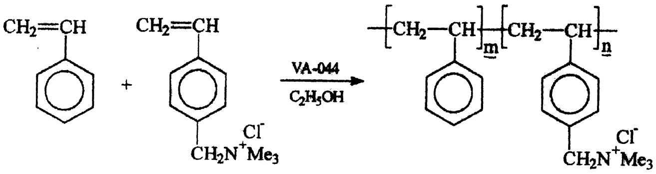
Materials

Styrene (Aldrich) was distilled under reduced pressure before use. VBC (meta and para mixtures, Aldrich) was purified by passing it through an activated neutral aluminum oxide (Aldrich) column. VBTMAC (meta/para 60/40, Acros Organics), trimethylamine (40% aqueous solution, Aldrich) and initiator 2,2′-azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride (VA-044, Wako Pure Chemicals) were used as received. Ethanol and tetrohydrofuran (THF) were analytical grade and were used as received.

Copolymer synthesis

Method 1: Solution copolymerization of styrene and VBTMAC

Direct copolymerization of two monomers in ethanol was used to synthesize the copolymers of styrene and VBTMAC as shown in Scheme 1.

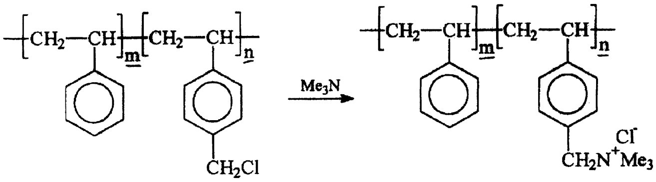


Scheme 1 Solution copolymerization of styrene and VBTMAC

A typical example is given as follows. A four-necked glass reactor equipped with a magnetic stirrer was filled with 150 ml ethanol, 108 mmol styrene and 12 mmol VBTMAC. The solution was flashed with nitrogen for 30 min and thermostated at 60 °C. After stabilization of temperature, 0.7 mmol VA-044 in 5 ml deionized water was added. The polymerization was carried out under nitrogen for 4 h with constant stirring. The mixture was then distilled under reduced pressure at 35 °C to give the cationic copolymer. The conditions used for the copolymerizations are given in Table 1.

Method 2: Quaternization of styrene-VBC copolymer using trimethylamine

The styrene-VBTMAC copolymers were also prepared by quaternization of styrene-VBC copolymer in THF using trimethylamine as a quaternization agent as shown in Scheme 2.



Scheme 2 Quaternization of poly(styrene-*co*-VBC)

The styrene-VBC copolymers were prepared by surfactant-free emulsion polymerization using a cationic initiator VA-044. In a typical surfactant-free emulsion polymerization of styrene and VBA, a four-necked glass

Table 1 Solution polymerization conditions for poly(styrene-*co*-VBTMAC)s and their colloidal properties

Sample	A	B	C	D	E
Styrene (mmol)	108	108	108	108	108
VBTMAC (mmol)	5.7	12	19	27	46
VA-044 (mmol)	0.7	0.7	0.7	0.7	0.7
Ethanol (ml)	150	150	150	150	150
VBTMAC ratio (mol%)[a]	5	10	15	20	30

[a] Based on the total feeding monomers

reactor equipped with a mechanical stirrer was filled with 150 ml deionized water, 150 mmol styrene and 16.7 mmol VBC. The solution was flashed with nitrogen for 30 min and thermostated at 60 °C. After stabilization of temperature, 0.83 mmol VA-044 in 5 ml deionized water was added. The polymerization was carried out under nitrogen with a stirring speed of 400 rpm for 4 h. The latex suspension was centrifuged (Beckman L-80 ultracentrifuge) at 8000 rpm for 30 min. The precipitates were then washed twice with ethanol and centrifuged again to remove excess monomers and other impurities. The isolated copolymers were dried under vacuum at room temperature. The polymerization conditions for the styrene and VBC copolymers are given in Table 2.

The chloromethyl groups in the copolymers were treated with large molar excess (~tenfold) of trimethylamine, calculated from the amount of VBC added in the polymerization. The dry poly(styrene-*co*-VBC) was dissolved in THF (10 wt%) in a round-bottomed flask with a magnetic stirrer. Excess aqueous trimethylamine was added and the flask was sealed and gently agitated with a magnetic stirrer.

For the copolymers with low VBC contents (samples F and G in Table 2), the copolymers were THF-soluble both before and after quaternization using trimethylamine. For these copolymers, the quaternization reaction was carried at room temperature for 24 h, then the solvent was evaporated and the product was dried under vacuum at 40 °C.

For the copolymers with high VBC contents (samples H, I-1, I-2, and J in Table 2), the copolymer precipitated from THF during quaternization. However, these high-charged copolymers are ethanol-soluble. For these polymers, the THF was poured out after precipitation and 20 ml ethanol was added followed by tenfold excess of aqueous trimethylamine. The quaternization reaction was continued in ethanol for another 24 h. Afterwards, the excess of trimethylamine was removed by purging the mixture with nitrogen. The solvent was distilled and the product was dried under vacuum at 40 °C for characterization.

Table 2 Emulsion copolymerization conditions for poly(styrene-*co*-VBC)s

Sample	F	G	H	I-1	I-2	J
Styrene (mmol)	150	150	150	150	150	150
VBC (mmol)	3.1	7.9	17	27	27	64
VA-044 (mmol)	0.76	0.79	0.83	0.88	0.88	1.1
H_2O (ml)	150	150	150	150	150	150
Temp. (°C)	60	60	60	50	60	50
VBC ratio (mol%)[a]	2	5	10	15	15	30

[a] Based on the total feeding monomers

Characterization of the copolymers and colloids

IR and NMR spectroscopy

IR spectra were recorded on a Nicolet 550 FTIR spectrometer using KBr discs. ^{13}C NMR spectra were recorded on a Bruker 400 MHz DMX NMR spectrometer with high concentration solutions of copolymers in $CDCl_3$. The chemical shift was calibrated using $SiMe_4$.

Light-scattering spectroscopy

The particle size of the cationic polymeric aggregates was determined by photon-correlation spectroscopy at 25 °C using a Malvern Zetasizer 3000 (10 mW 633 nm He-Ne laser at 90°). *Z*-average particle size was calculated by computer using Contin analysis software.

Colloid titration

The charge density of the cationic polymers in water was determined by colloid titration. One drop of 0.5% toluidine blue-O (Aldrich) solution was added to a 10 ml 100 mg/l sample. The mixture was titrated to the colorimetric end point with 0.0001 N potassium polyvinyl sulfate (PVSK, Nalco). It should be noted that some copolymers could not form a true solution in water. Therefore, the charge density of these copolymers measured by colloid titration can only represent the apparent charge density of colloidal aggregates in water.

Results and discussion

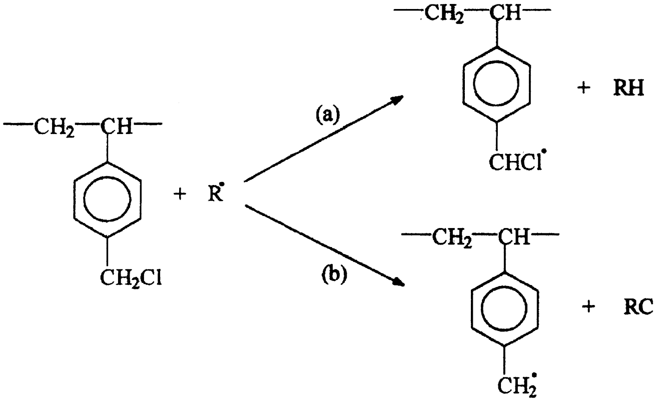
Cationic copolymers synthesized by solution polymerization (method 1)

Emulsion polymerization has been employed for the copolymerization of styrene and ionic comonomers [9, 12, 18–20]. However, because styrene is water-insoluble but ionic monomers are water-soluble, the copolymer prepared by emulsion polymerization may contain two different fractions, i.e., one has a high styrene content and another has a high ionic monomer content. This phenomenon has been reported by Kim et al. [20] for a styrene and sodium styrene sulfonate system. In order to prepare homogenous random poly(styrene-*co*-VBTMAC)s with different charge densities, the solution polymerization was explored in this study. It should be noted that although solution polymerization may overcome the problems that occurred in emulsion polymerization, it is difficult to find a good solvent for the copolymers with various ratios of styrene and VBTMAC because the solubility of polystyrene and polyVBTMAC are significantly different in most solvents. In this study, different solvents, including dioxane, THF, ethanol, and their mixtures were first tested. The primary results suggested that among the solvents examined in this study, ethanol is the best solvent for poly(styrene-*co*-VBTMAC) if the molar ratio of VBTMAC in the copolymers is in the range 10–30%. Although it is well-known that polystyrene is insoluble in ethanol, a clear solution was obtained during polymerization for all the copolymers listed in Table 1 except sample A (5 mol% VBTMAC based on total monomers in the feeding solution). The increase in the solubility of polystyrene-based copolymer in ethanol results from the introduction of charged units into the polymer backbone. During the synthesis of sample A, small amounts of precipitates that were soluble in THF were found. This is probably due to the low cationic monomer ratio in this copolymer, thus reducing the solubility of the copolymer in ethanol.

Cationic copolymers synthesized by quaternization (method 2)

In addition to the direct polymerization of styrene and VBTMAC in ethanol, an alternative method that involves quaternization of copolymer poly(styrene-*co*-VBC) with trimethylamine was also studied. In this method, poly(styrene-*co*-VBC)s with different VBC ratios were first synthesized by emulsion polymerization, then the poly(styrene-*co*-VBC)s were further modified with trimethylamine to give cationically charged poly(styrene-*co*-VBTMAC)s.

The solubility of the poly(styrene-*co*-VBC) copolymers was first examined. Because both polystyrene and polyVBC are THF-soluble polymers, it was expected that copolymers of styrene and VBC should also be THF-soluble. However, it was found that the copolymers of styrene and VBC could not be totally dissolved in THF. It was also found that the solubility of poly(styrene-*co*-VBC) decreased as the content of VBC was increased. The polymerization temperature also significantly affected the copolymer solubility, i.e., the solubility was much lower for the copolymers made at 60 °C compared to those made at 50 °C. The unusual solubility of the copolymers in their good solvent (THF) may suggest that the copolymers were partially crosslinked during the polymerization. It is believed that the crosslinking is through a chain-transfer reaction between living polymer radicals and chloromethyl groups, which was reported by Verrier-Charleux et al. [21] in emulsion polymerization of VBC. According to their study, two possible radical-transfer reactions, in which hydrogen or chlorine is abstracted from the chloromethyl group, may occur (Scheme 3). They further suggested that path (a) was more favored than path (b) by calculating the bond disassociation energy. Furthermore, the presence of the chlorine atom could also stabilize the ϕ-CHCl$^\bullet$ radical, which makes hydrogen abstraction more favorable. Obviously, all these chain transfers will result in a crosslinking polymer. Because the chain-transfer reaction strongly depends on the copolymerization temperature, the degree of crosslinking and the solubility of the copolymers in their good solvent should also be a function of the polymerization temperature, i.e., the higher the temperature, the higher the crosslinking degree and the lower the solubility of the copolymers.



Scheme 3 Crosslinking mechanism of poly(styrene-VBC)

In addition to the crosslinking reaction, partial hydrolysis of VBC may also occur during copolymerization. The hydrolysis of VBC has been reported previously by Verrier-Charleux et al. [21]. However, the high-resolution ^{13}C NMR spectroscopy recorded by copolymers G, H, and I-1 in CDCl$_3$ shows no hydroxymethyl peak at 65 ppm (Fig. 1), which indicates

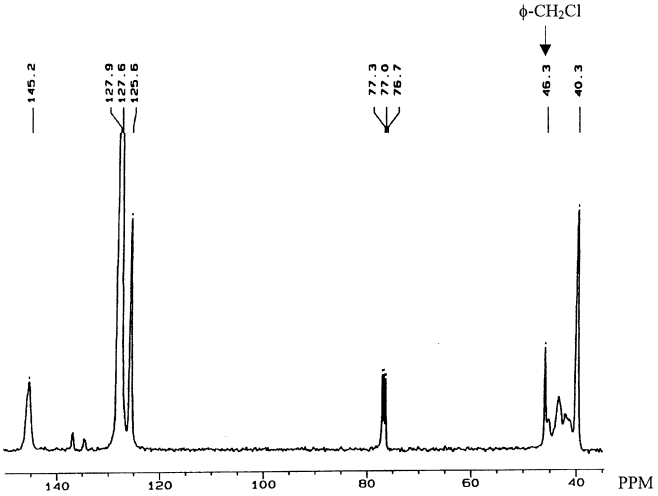


Fig. 1 ^{13}C NMR of poly(styrene-*co*-vinylbenzyl chloride) (sample H) in CDCl$_3$ at 25 °C

that hydrolysis of the chloromethyl group is negligible for the copolymers prepared in this study.

Although THF is a good solvent for both styrene homopolymer and styrene-VBC copolymer, it may not be a good solvent for styrene-VBTMAC copolymer because cationically charged polyVBTMAC has a low solubility in organic solvents. This was confirmed by the precipitation of the copolymers H, I, and J (VBTMAC contents are larger than 15 mol% for these copolymers) during the quaternization reaction. It should be noted that the chloromethyl groups in the copolymer may not fully react with trimethylamine if the copolymer is precipitated from the solution. In order to fully functionalize all the VBC repeat units with trimethylamine groups, the precipitated copolymer from THF was isolated and then dissolved in ethanol, followed by further reaction with trimethylamine. The completion of the conversion was proved by the disappearance of the CH_2Cl band (1265 cm^{-1}) in the IR spectra.

Because the copoly(styrene-*co*-VBTMAC)s contain a water-insoluble styrene backbone and different contents of cationically charged VBTMAC, the copolymers can be either water-soluble or insoluble depending on the charge density, molecular weight, and structure. Similar to other amphiphilic copolymers, it is expected that poly(styrene-*co*-VBTMAC) can form colloidal stable aggregates in water if the hydrophobicity and hydrophilicity are well-balanced.

The solubility of the copolymers prepared by method 1 is different from that of the copolymers prepared by method 2. For example, the copolymers prepared by solution polymerization (method 1) could be easily dissolved or dispersed in water if they contained a reasonable amount of cationic monomer, but the copolymers made using method 2 were almost water-insoluble except for highly charged samples with 30 mol% VBTMA in feeding monomers. The significant difference in the solubility between the copolymers made from two different methods may be due to two reasons. First, as discussed above, the copolymers from quaternization of poly(styrene-*co*-VBC) were partially crosslinked. Obviously, the crosslinking of the copolymers will reduce their solubility in water. Second, the copolymers made from quaternization may have a higher molecular weight than those made from solution polymerization because emulsion polymerization was employed in the first stage of the polymer preparation. It is well-known that emulsion polymerization usually results in a relatively high molecular weight polymer. Unfortunately, we could not successfully measure the molecular weight of the copolymers because the copolymers have different charge densities, which will significantly affect the molecular weight measurement using common methods such as viscosity and gel permeation chromatography.

The influence of cationically charged VBTMAC on the solubility of the copolymers prepared using method 1 is shown in Table 3. It can be seen that the solubility of the copolymers in water consistently increases as the content of VBTMAC is increased. For example, samples A, B, and C (with 5, 10, and 15 mol% VBTMAC in feeding monomers, respectively) are not water-dispersible at 40 °C. However, at the same temperature, sample D (with 20 mol% VBTMAC in feeding monomers) could be dispersed in water and formed a stable colloidal dispersion. Light-scattering measurements indicated that the particle size of polymeric aggregates formed at 40 °C is 51 nm for this sample. It was also found that the colloidal particle was very stable (no particle aggregation was found after half a year). The formation of these colloidal aggregates is not surprising because the van der Waals forces between hydrophobic polystyrene backbones promote aggregation, while the electrostatic repulsion forces between cationically charged VBTMACs protect the aggregates from unlimited growth of the particles. As a result, stable colloids were formed. When the feeding fraction of VBTMAC is further increased to 30 mol% (sample E), the copolymer can be fully dissolved in water to give a true solution at 25 °C. These results suggest that the solubility of these copolymers increases with increase in charge density.

The influence of temperature on the solubility of poly(styrene-*co*-VBTMAC) in water is interesting. It can be seen from Table 3 and Fig. 2 that the solubility of all the copolymers in water increases as the temperature is increased. For example, samples C and D formed stable

Table 3 Influence of dispersion temperature on cationic particle size[a]

Sample	Particle size (nm)							
	25 °C	40 °C	60 °C	70 °C	75 °C	80 °C	90 °C	100 °C
A	–	–	–	–	–	47	41	40
B	–	–	–	–	56	47	30	30
C	–	–	92	34	+	+	+	+
D	–	51	+	+	+	+	+	+
E	+	+	+	+	+	+	+	+

[a] Solution was prepared by mixing 1 g copolymer in 1 l water for 1 h at the fixed temperature, then the solution was cooled to room temperature. The particle size was measured at 25 °C. "–" indicates unstable dispersion, "+" indicates full dissolution

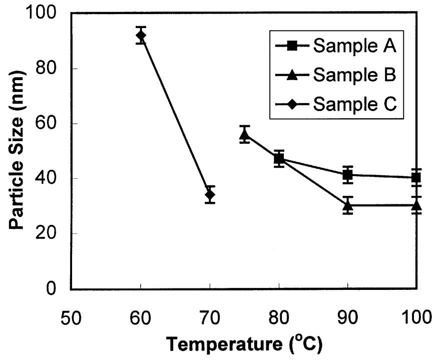


Fig. 2 Particle size as a function of dispersion temperature

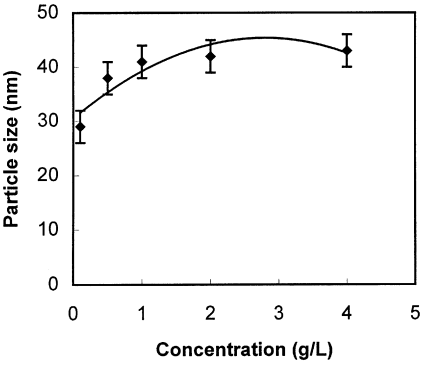


Fig. 3 Particle size (sample A) as a function of dispersion concentration. The colloid dispersions were prepared in boiled water

colloidal dispersions in water, but they were fully dissolved when the temperature was increased to 75 and 60 °C, respectively.

It was found that not only the solubility of the copolymer but also the particle size of the colloidal dispersion was significantly affected by temperature. Light-scattering measurements indicated that the particle size decreased as the temperature increased. This is consistent with the solubility of copolymers in water. The general conclusion from Table 3 and Fig. 2 is that as the temperature is increased, the solubility of the copolymer also increases, which results in a decrease in the particle size of colloidal aggregates.

It should be noted that the temperatures indicated in Table 3 and Fig. 2 were the temperatures used for copolymer solution preparation rather than particle size measurement. In this study, all the particle sizes were measured at room temperature. It is very interesting that although some samples could not be dissolved in water at room temperature, once they formed a colloidal dispersion at high temperature they remained as a colloidal stable dispersion even though the temperature was reduced to room temperature. This phenomenon suggests that at low temperature, the copolymer chains entangled each other in the solid state and a high solvation energy is needed to dissolve the copolymer. However, when the temperature is increased the thermodynamic energy of polymer chains increases, resulting in an increase in the solubility of the copolymers in water. When the thermodynamic energy, van der Waals forces, and electrostatic repulsion forces are balanced, stable colloids are formed. However, when the temperature is lowered, the electrostatic repulsion forces between the colloidal particles provide a high energy barrier between the particles, which protects the coagulation of the colloidal particles. As a result, stable colloidal suspensions can be obtained through this temperature change cycle.

The dependence of particle size of aggregates on the copolymer concentration for sample A is shown in Fig. 3. It can be seen that the particle size increases as the copolymer concentration is increased.

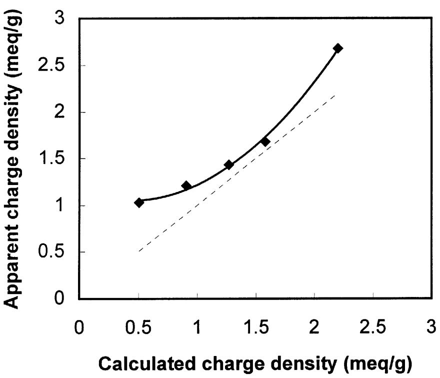


Fig. 4 Correlation between apparent charge density (*full line*) and theoretical charge density calculated from feeding initiator and monomers (*dotted line*)

Theoretically, the charge density of the copolymers can be calculated using the following equation by assuming that the conversion of the monomers is 100% during the copolymerization.

$$\rho = \frac{M_{\mathrm{VBTMAC}} + M_{\mathrm{initiator}}}{W_{\mathrm{VBTMAC}} + W_{\mathrm{styrene}} + W_{\mathrm{initiator}}} , \qquad (1)$$

where M and W are the molar number and weight of the monomer or initiator in the feeding solutions, respectively. It can be seen from Fig. 4 that the apparent charge density is slightly higher than theoretical volume, particularly at low VBTMAC feeding ratio. Two possible reasons may be attributed to this result. First, the reactivity ratio of VBTMAC in ethanol may be higher than that of styrene. Second, because the copolymers had limited solubility in water, the titration was conducted in a colloidal suspension rather than in a true solution. This suggests that the charge density obtained from colloid titration in this study should represent a surface charge of microaggregates of the copolymers rather than that of true polymers. Because the cationically charged VBTMAC and initiator repeat units prefer to stay on the surface of the microaggregates and styrene repeat units prefer to stay in the core of the microaggregates, the colloid titration result may not be the same as the true charge density in the copolymer chains.

Conclusions

Cationically charged poly(styrene-*co*-VBTMAC)s with different charge densities may be synthesized by quaternization of poly(styrene-*co*-VBC) copolymer with trimethylamine and by direct polymerization of styrene and VBTMAC in ethanol. However, the two methods result in different copolymer structures. The copolymers made by quaternization of poly(styrene-*co*-VBC) were partially crosslinked, and they are almost water-insoluble. In contrast, the copolymers made from direct copolymerization of styrene with VBTMAC in ethanol can be dissolved or dispersed in water, but the solubility and colloidal particle size strongly depend on the charge density and the temperature used for colloid preparation.

The aggregates formed by poly(styrene-*co*-VBTMAC)s have a very small particle size (30–50 nm) compared to those of cationically charged polystyrene latexes made from emulsion polymerization (>150 nm). No surfactant is needed for preparing these very small and uniform colloidal particles.

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