

Emulsifier-Free Emulsion Polymerization of Styrene with 4-Vinylbenzoic Acid: Kinetics and Distribution of the Carboxyl Groups

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ABSTRACT: Carboxylated polystyrene particles were prepared by the batch emulsion polymerization of styrene (Sty) with 4-vinylbenzoic acid (VBA) in the absence of an emulsifier with $K_2S_2O_8$ as a free-radical initiator. The effect changes in the ratio of potassium hydroxide to VBA and the concentration of VBA to Sty on the kinetics, monomer conversion,

distribution of carboxyl groups, and particle size distribution were analyzed. The stability of the latices was evaluated.

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Key words: colloids; emulsion polymerization; micelles; particle size distribution; polystyrene

INTRODUCTION

Polymer latices with surface functional groups have received considerable attention because of their extensive applications, including synthetic rubbers, paints, adhesives, binders, additives in paper and textiles, leather treatment, impact modifiers, solid-phase flocculants, rheological modifiers, solid-phase supports in catalysis, chromatography, diagnostic assays, calibration standards, cell separation, drug-delivery systems, and electrooptics and nonlinear optics.^{1–9} Emulsifier-free emulsion polymerization (EFEP) is used widely to prepare polymers with a variety of functional groups, such as carboxylate,^{10–15} sulfonate,^{16,17} hydroxyl,^{18,19} aldehyde,^{20,21} amino,^{22,23} epoxy,^{19,24} vinyl,²⁵ sulfhydryl,²⁶ chloromethyl,^{27,28} active ester,^{29,30} ethylene urea,³¹ and cyano³² groups. Functionalized latices accessed through EFEP are prepared in the presence of either water-soluble surface active initiators^{33,34} or hydrophilic comonomers (with or without ions).³⁵ EFEP has special attractiveness in that the stabilizing species are formed *in situ* during the polymerization and useful merits such as the fact that high purity and monodisperse spherical latices are produced if the process is controlled in the proper way.^{36,37} Among the various functional-group latices, carboxylated latices belong to an interesting and important class of latices. In general, it is well known that the EFEP of oil-soluble monomers [mainly styrene (Sty)] with water-soluble comonomers (carboxylic acid monomers) has been widely

used to produce carboxylic acid containing polystyrene latices. The most frequently studied acid monomers copolymerized with Sty are itaconic acid (IA),³⁸ acrylic acid (AA),¹³ and methacrylic acid (MAA).¹⁴ These carboxylic acid monomers are often completely soluble in water. Ceska³⁹ copolymerized IA, AA, and MAA with Sty by EFEP in separate reactions and found that the copolymerization rates of Sty with the monomers increased in the order $IA < AA < MAA$. The rate increased as the hydrophobicity of the monomer increased. In this article, we present a study of the EFEP of Sty with 4-vinylbenzoic acid (VBA), with the objective of investigating the polymerization kinetics, conversion of the monomers, characterization of the particle (size and surface charge), carboxylic acid group distribution in the dispersion, and stability of the latices. The main advantage of VBA is that it is less soluble in water than acrylic monomers;⁶ that is, it has a more hydrophobic character. This should lead to better incorporation of the carboxylic acid moiety in the polymer particles and to less polyelectrolyte formation in the aqueous continuous phase. The achievement of such a goal would increase the stability of the particles and give the maximum number of functional groups on the surface for further functionalization of the particles. Also, the main purpose of this study was to find an alternative to the acrylate monomers used for the synthesis of carboxylic acid containing latex particles.

EXPERIMENTAL

Materials

Sty (Aldrich) was distilled over CaH_2 *in vacuo* to remove any trace of inhibitor and stored at $-20^\circ C$

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TABLE I
Recipes of the Surfactant-Free Emulsion Polymerization

Latex	Sty		VBA		VBA/Sty (mol %)	KOH (0.974N)		KOH/VBA (mmol/mmol)	Water (g)	KPS (g)	Water for KPS (g)
	g	mmol	g	mmol		g	mmol				
1	4.27	40.97	0.36	2.44	5.96	0.53	0.52	0.21	25.30	0.064	2.99
2	4.30	41.28	0.37	2.48	6.00	1.08	1.06	0.43	25.07	0.067	2.55
3	4.27	40.99	0.36	2.45	5.98	1.58	1.54	0.63	25.22	0.067	2.52
4	4.35	41.73	0.36	2.45	5.87	2.12	2.06	0.84	25.16	0.066	2.81
5	4.33	41.55	0.37	2.48	5.98	2.54	2.47	0.99	25.37	0.068	2.57
6	4.25	40.81	0.37	2.46	6.04	3.47	3.38	1.37	25.17	0.065	2.58
7	4.33	41.59	0.37	2.47	5.94	4.00	3.89	1.58	25.08	0.066	2.34
8	4.69	45.01	0.37	2.47	5.49	4.69	4.57	1.85	25.02	0.066	3.33
9	4.25	40.85	0.37	2.46	6.03	5.33	5.19	2.11	25.42	0.066	2.76
10	4.25	40.85	0.03	0.20	0.50	0.28	0.27	1.33	25.06	0.066	2.91
11	4.26	40.92	0.05	0.31	0.76	0.42	0.42	1.34	25.07	0.066	2.75
12	4.25	40.83	0.06	0.40	0.99	0.58	0.57	1.40	25.05	0.066	2.62
13	4.28	41.07	0.18	1.23	2.99	1.73	1.68	1.37	25.09	0.066	2.50
14	4.35	41.78	0.49	3.28	7.85	4.61	4.49	1.37	25.20	0.065	2.28
15	4.33	41.60	0.61	4.09	9.83	5.75	5.60	1.37	25.31	0.066	2.52
16	4.28	41.12	0.73	4.91	11.93	6.85	6.67	1.36	25.15	0.067	2.78

All polymerizations were carried out at 60°C with mechanical stirring (600 rpm) for 24 h.

under an inert atmosphere before use. VBA was obtained from Lancaster (Karlsruhe, Germany), the water-soluble free-radical initiator $K_2S_2O_8$ (KPS) was obtained from Aldrich (Steinheim, Germany), and both were used as received. All of the polymerizations were carried out with water, which was deionized and subsequently purified by a Millipore water purification system (Schwalbach, Germany) (CPMQIK05D2 MilliQ Plus 185).

Polymerization

The emulsion polymerizations were carried out in batch mode. The different formulations and reaction conditions applied in this study are presented in Table I. The reaction vessel used was a 100-mL, three-necked, glass, round-bottom flask equipped with a mechanical stirrer, a condenser, and an inert-gas (argon) inlet. The mixture was heated at 60°C in an oil bath and deoxygenated by argon bubbling before the addition of the initiator solution. After the temperature reached 60°C, a solution of KPS in approximately 2.5 mL of deoxygenated water was added quickly by injection. All polymerizations were carried out for 24 h.

Latex characterization

The overall conversion of the monomer was evaluated with a conventional gravimetric procedure. Samples of known mass were withdrawn periodically from the reaction flask with a hypodermic syringe, discharged into a flask, and immediately chilled in a liquid nitrogen bath to inhibit further polymerization. After the samples were freeze-dried

in vacuo, the residual mass (also including solid monomeric VBA) was determined. The particle size was determined with a Malvern Zeta Sizer 5000 (Worcestershire, UK) with dynamic light scattering (DLS). Transmission electron microscopy (TEM) was performed on some of the selected polymeric latices. The latices were cleaned by diafiltration with Millipore centrifuge filtration units [Ultrafree-15, molecular weight (MW) = 100,000 g/mol]; about 15 mL of each latex sample was centrifuged in one unit for 60 min. The solid residue was diluted again with water, and the centrifugation repeated. To remove all adsorbed oligomers, initiator fragments, and electrolytes that could influence the results of the surface-charge titration data and the physicochemical properties of the latex, as highlighted by Kamel et al.,⁴⁰ the cleaning cycles were repeated three times. The carboxyl group distribution on the surfaces of the particles was evaluated by conductometric titration of the purified latices (Conductometer 660 with a Pt electrode, Dosimat 655, and Potentiograph, all from Metrohm, Herisau, Switzerland). For the titration, a known mass of clean latex (ca. 1.0–1.5 g) was diluted with 5 mL of H_2O . Before the titration was started, the conductivity of the dispersion was adjusted to 2.5–3.0 mS/cm with KCl. Then, the pH was increased, if necessary, to 12 with a 0.1N potassium hydroxide (KOH) solution (Titrisol, Merck, Darmstadt, Germany). The mixture was then bubbled with inert gas (N_2) for 1 h, and the titration was started with 0.1N HCl solutions (Titrisol, Merck). The back-titration was carried out with a 0.1N KOH solution (Titrisol, Merck). The titration speed was 0.1 mL/min. The carboxyl group in the aqueous medium was also evaluated with the aqueous medium col-

lected from the cleaning cycle of the latex with the help of conductometric. Buried carboxylic groups (B) were calculated with the following equation

$$B = A - (E_{\text{sur}} + E_{\text{aq}})$$

where A is the amount of total carboxylic groups in the latex system, E_{sur} is the evaluated amount of carboxyl groups on the surface of the latex (by titration), and E_{aq} is the evaluated amount of carboxyl groups in the aqueous medium (by titration). We studied the stability of the latex against the electrolytes by pouring a 50- μL dispersion into 1 mL of CaCl_2 or KCl solutions of different concentrations. The storing of 1 mL of the dispersions for 24 h at -20°C and then thawing at room temperature tested the freeze-thaw stability of the latices. This cycle was repeated three times.

RESULTS AND DISCUSSION

Kinetics and conversion

Conversion-time curves for the emulsion polymerization of Sty with VBA at different KOH concentrations are shown in Figure 1. The polymerization rate increased with the concentration of KOH and reached a plateau when the KOH concentration was identical to the VBA concentration (stoichiometric conditions). Increasing the concentration of KOH above this value did not change the polymerization rate considerably. Conversion-time curves for the polymerization of Sty with VBA with a range of monomer feed ratios at a molar ratio of KOH to VBA of 1.3 are shown in Figure 2. The polymerization rate increased with increasing VBA content up to a value of 3 mol % and remained constant from 3 to 12 mol % VBA.

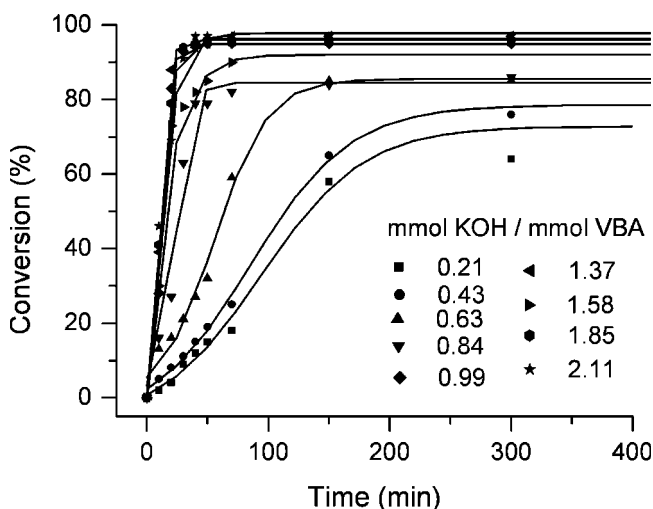


Figure 1 Conversion-time curves for the emulsion polymerization of Sty with VBA at different KOH concentrations.

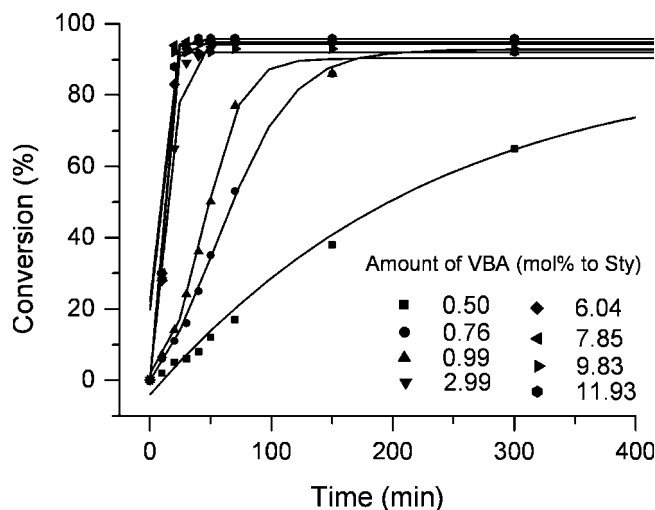


Figure 2 Conversion-time curves for the emulsion polymerization of Sty with VBA with a range of monomer feed ratios.

Several mechanisms for particle nucleation and growth in EFEP systems have been proposed. Fitch and Tsai⁴¹ proposed a homogeneous nucleation mechanism for the formation of particles. According to this theory, oligomeric radicals are formed in the aqueous phase in the initial stage of polymerization. These oligomers precipitate after attaining a certain critical MW and act as primary particles. In the presence of a water-soluble initiator such as KPS, a poorly water-soluble monomer such as Sty is initiated and polymerized in the aqueous phase to produce oligomeric radicals with sulfate end groups. These species can then act as oligomeric surfactants and form micelles.⁴² Sty, when copolymerized with an ionic comonomer, is sometimes suggested to follow the micelle nucleation mechanism or a combination of the micelle and precipitation mechanisms.^{35,43}

The kinetic data shown in Figures 1 and 2 suggest that for the Sty-VBA system, it is possible to propose different polymerization mechanisms depending on the degree of neutralization of VBA and the ratio of VBA to Sty, which is similar to the analysis presented in the literature for acrylic monomers.^{10,39,44} The conversion curves for ratios of KOH to VBA greater than 0.99 and for higher VBA feed ratios (>1 mol % relative to Sty) suggested that the amphiphilic VBA probably acted as a classical surfactant. The polymerization mechanism was that of a batch emulsion polymerization with an amount of surfactant above the critical micelle concentration (cmc) to follow a micellar nucleation mechanism. In this case, the Sty monomers entered into the micelles, and polymerization happened inside the micelles to produce particles with carboxylic groups of VBA located at the particle-water interface. When the KOH to VBA ratios were 0.84 and 0.63 or when the VBA

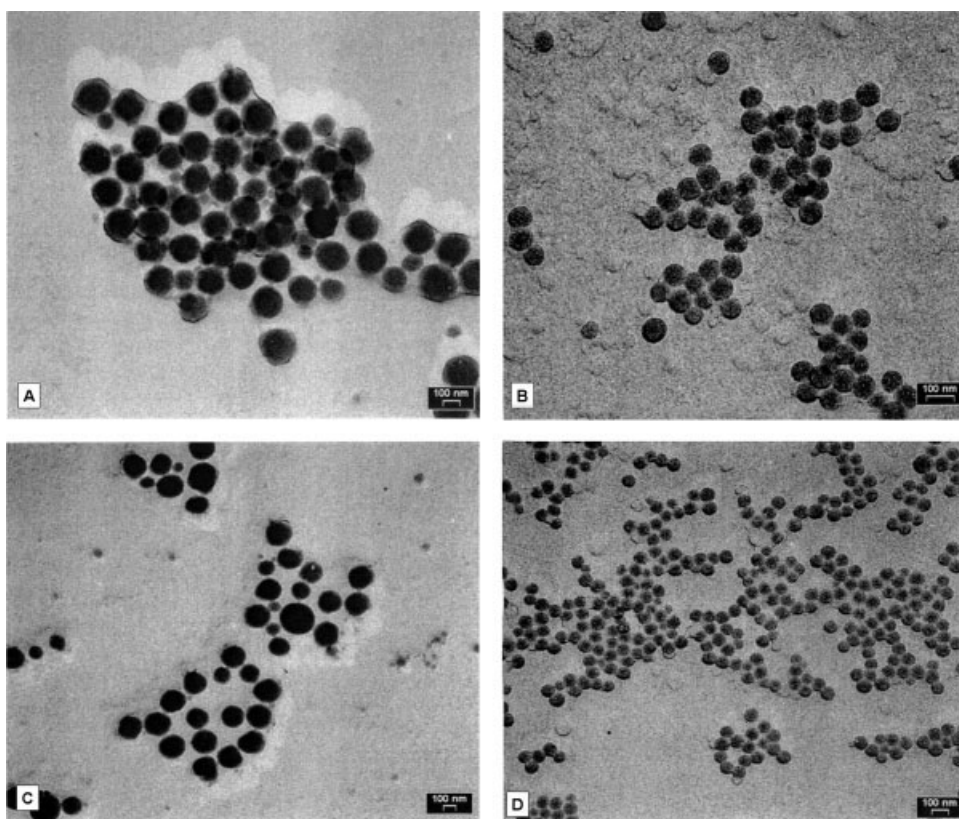


Figure 3 TEM pictures of representative latices: (A) latex 4, prepared at KOH/VBA = 0.75 : 1; (B) latex 5, prepared at KOH/VBA = 1 : 1; (C) latex 10, prepared at 0.5 mol % VBA/Sty; and (D) latex 13, prepared at 3 mol % VBA/Sty.

levels were 0.76 and 0.99 mol % (relative to Sty), the KPS was decomposed thermally into primary radicals to induce the polymerization of VBA in preference to Sty in the aqueous phase. Because Sty is sparingly water-soluble, very few molecules of Sty were polymerized in this stage of the polymerization. The oligomers formed, which were amphiphilic in nature, likely acted as emulsifiers. At a concentration equal to their cmc, these species probably formed micelles and followed a micellar nucleation mechanism. These micelles were the primary particles. At the stage of particle growth, Sty monomers swelled the primary particles, and the polymerization proceeded inside the particles. Particle growth then took place by the polymerization of Sty monomers exclusively inside the particles until the Sty droplets disappeared. The polymer particles were stabilized by the VBA oligomers and the Sty–VBA oligomers located at the particle–water interface. A different conversion curve for the lowest VBA feed ratio (0.5 mol % relative to Sty) suggested that the polymerization of Sty occurred at an almost constant rate up to a conversion of 65%. During the next stage, the polymerization occurred very slowly. This behavior suggested that a homogeneous polymerization reaction took place in the aqueous phase, as proposed by Fitch and Tsai.⁴¹ However, the conver-

sion curves for the KOH/VBA ratios of 0.43 and 0.21 possibly followed a combination of both a micellar and a homogeneous nucleation mechanism, as the systems had the lowest amount of neutralized VBA. This could have produced oligomeric surfactants that formed micelles above the cmc to follow a micellar nucleation mechanism, and possibly, the oligomers were precipitated after a critical MW was attained in the aqueous phase to follow a homogeneous nucleation mechanism.

Average particle size

The size of the particles was measured by DLS, and they were directly visualized by TEM. TEM images of some representative latices are shown in Figure 3. It is clear that uniform spherical particles were formed in the latex prepared at a KOH/VBA of 1 (latex 5) and for the latex prepared at 3 mol % VBA when the KOH/VBA ratio was 1.3 (latex 13). Figure 4 shows the average particle sizes (DLS studies) of the polymers prepared with different ratios of KOH to VBA. The size of the particles had its minimum value when the molar ratio of KOH to VBA was unity. However, when the ratio of KOH to VBA was less than 1 or greater than 1, the particle size increased. Thus, the particle size changed remark-

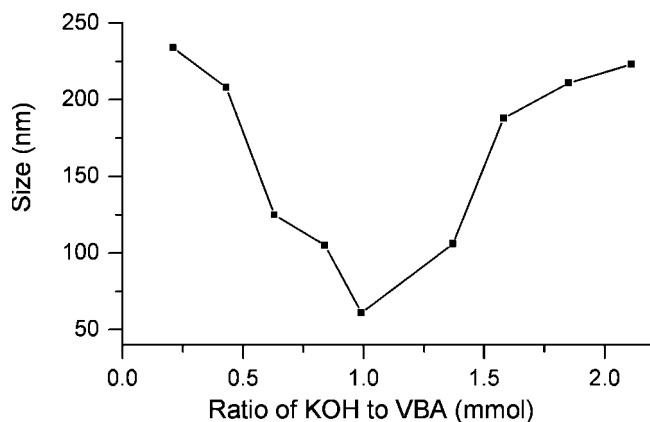


Figure 4 Average size of the particles obtained with different KOH/VBA ratios.

ably with the degree of neutralization, which meant that the number of particles formed in the polymerization system was dependent on the degree of neutralization. Alternatively, the ionic strength could have played an important role here. As all VBA molecules were neutralized, the added KOH increased the ionic strength of the system, and this increased the cmc of the amphiphilic oligomers and reduced the stability of the primary particles. That meant that the number of primary particles was diminished, and the average size of the polymer particles increased with increasing ionic strength of the aqueous phase.^{45,46}

Figure 5 shows the change in the average size (DLS studies) of the particles formed under a range of monomer feed conditions and at a constant ratio of KOH to VBA. As shown in the curve, the particle size decreased as the concentration of VBA increased up to a value of 1 mol %. For higher VBA concentrations, the particle size remained relatively constant. A possible explanation was the polymerization of VBA in the aqueous layer. The excess of VBA could form water-soluble polyelectrolytes, so the number of primary particles did not increase substantially (see the next section), and the particle size remained almost constant. Table II shows the average particle size of different latices.

Number of particles

A plot of the change in the number of polymer particles formed as a function of the KOH/VBA ratio is shown in Figure 6. The number of particles increased considerably with increasing degree of neutralization, and the number of particles reached a maximum at a KOH/VBA molar ratio of 1. At higher molar ratios, the number of particles decreased. These results were expected; the neutralization of the carboxylic acid monomer (VBA) had a greater effect on the formation of particles. In this polymerization

system, growing radicals formed in the aqueous phase were composed of VBA and Sty. The effect of the degree of neutralization of the carboxylic acid monomer on the formation of particles may have been predominantly due to a change in the hydrophilic nature of the growing radicals formed in aqueous phase, which governed the number and size of particles.⁴⁴

Figure 7 shows the number of polymer particles formed under a range of monomer feed conditions. Increasing the VBA feed ratios from 0.5 to 3 mol % led to a remarkable increase in the number of particles formed. At even higher feed ratios (>3 mol %), the number of particles decreased until the VBA content reached about 10 mol %; thereafter, the number of particles increased again as the VBA content was raised to about 12%. From these results, the role of VBA in the formation of particles may be described as follows. In a polymerization where the VBA feed ratio was between 0.5 and 3 mol %, the formation of particles was attributed predominantly to the precipitation of growing radicals formed in the aqueous phase. With increasing concentration of VBA, the cmc of the surface active species was reached, and in the system, the number of primary particles did not increase anymore. The number of particles decreased as VBA increased in the range 3–10 mol %, and this could have meant that the excess of VBA was attached on the surface of the primary particles (as a polyelectrolyte) and did not contribute to the formation of other primary particles in the aqueous phase. In the polymerization involving 11.9 mol % VBA, the increase in the number of particles was attributed predominantly to the initiation of the polymerization in the micelles and to the precipitation of growing radicals in the aqueous layer to form

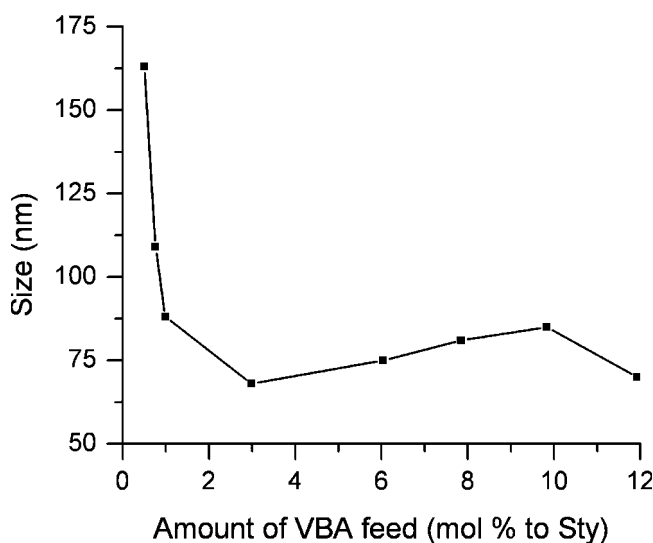


Figure 5 Average size of the polymer particles formed under a range of monomer feed conditions.

TABLE II
Average Particle Sizes After Polymerization

Latex	KOH/VBA (mmol/mmol)	Average particle size (nm) in H ₂ O	Latex	VBA (mol % to Sty)	Average particle size (nm)
1	0.21	234	10	0.50	163
2	0.43	208	11	0.76	108
3	0.63	125	12	0.99	88
4	0.84	105	13	2.99	68
5	0.99	61	6	6.04	75
6	1.37	75	14	7.85	81
7	1.58	188	15	9.83	85
8	1.85	211	16	11.93	70
9	2.11	223			

primary particles. This hypothesis was supported by the observed increase in the rate of polymerization with increasing VBA concentration.

Distribution of carboxyl groups

The effect of the degree of neutralization of VBA on the distribution of carboxyl groups in the system is shown in Figure 8. The fraction of carboxyl groups localized on the surface of the particles increased slightly, and buried carboxyl groups decreased slightly with increasing KOH/VBA ratio from 0.2 to 0.6. However, a decrease in the number of surface carboxyl groups was observed for KOH/VBA ratios of 0.8–1.3. An increase in the number of carboxyl groups on the surface was again noted for KOH/VBA ratios ranging from 1.5 to 2. The distribution of the carboxyl groups was determined predominantly by the hydrophilic character of the comonomer. With increasing degree of neutralization of VBA, that is, increasing KOH/VBA ratio, more molecules were soluble in water, and the number of aqueous oligom-

ers was increased. With increasing pH, the neutralized VBA molecules were found in the aqueous layer (KOH/VBA ratio = 0.6–1) or on the surface of the particles (KOH/VBA ratio = 1–1.6), due to their higher affinity for the water than for the hydrophobic Sty.^{11,47,48}

Figure 9 shows the effect of the variation of the monomer feed ratio on the distribution of carboxyl groups at a constant KOH/VBA molar ratio (1.3). At very low concentrations of VBA (0.5–3 mol %), carboxyl groups were found on the surface of the particles. An increased VBA concentration did not imply an increased percentage of carboxylic groups on the surface. The excess of VBA (3–12 mol %) was buried in the interior of the particles.

Amount of charge

By knowing the average size of the latex particles and thus its surface area and the conductometrically accessible surface carboxylic acid, one can readily calculate the amount of surface-charge density. Figure 10

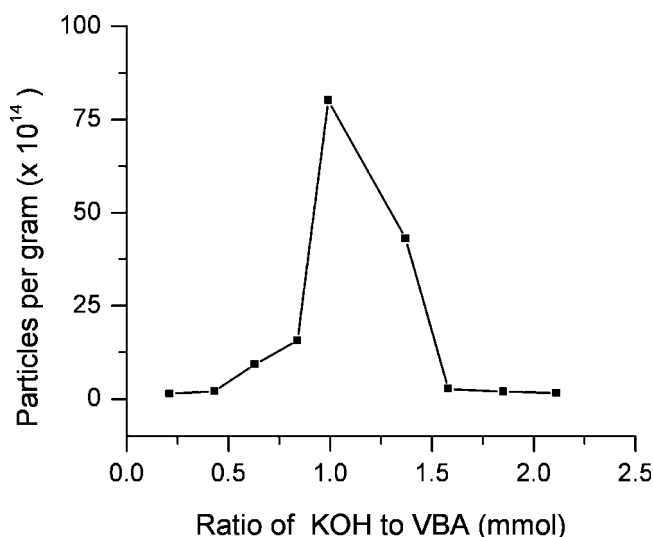


Figure 6 Number of polymer particles obtained with different KOH/VBA ratios.

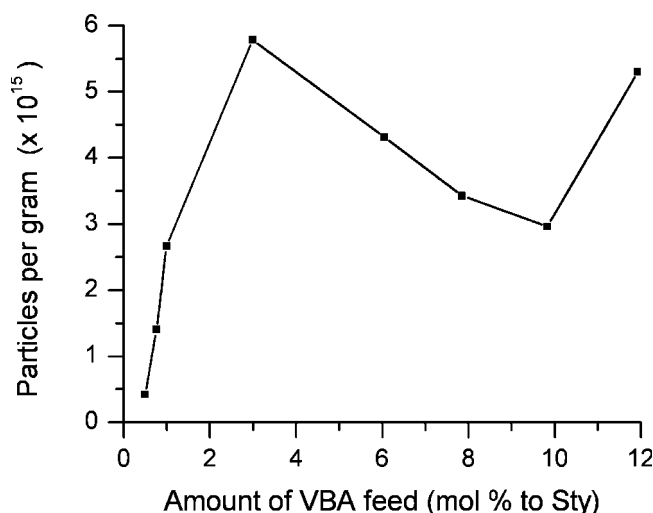


Figure 7 Number of polymer particles formed under a range of monomer feed conditions.

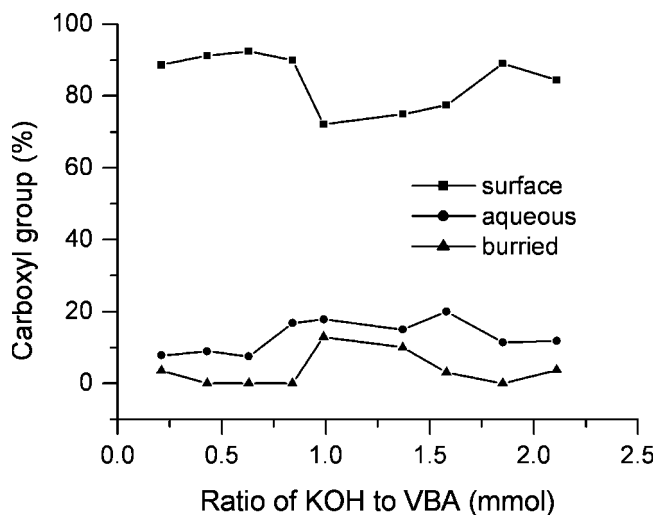


Figure 8 Distribution of the carboxylic acid groups at the surface of the polymeric particles, in the interior of the polymeric particles, and in the aqueous layer after polymerization as a function of the charging of the molar ratio of KOH to VBA.

shows the surface-charge density after the polymerization of VBA with Sty at different pH values (different amounts of KOH). The surface charge density decreased as the KOH/VBA molar ratio increased in the range 0.2–1.0, and a minimum value was reached. After this minimum, the surface concentration increased as the molar ratio was raised further. This resulted from the more hydrophilic character of the neutralized VBA molecule. Also, for the titration of the polymer dispersions prepared at KOH/VBA molar ratios of up to 1.0, different amounts of KOH were needed than of HCl solution

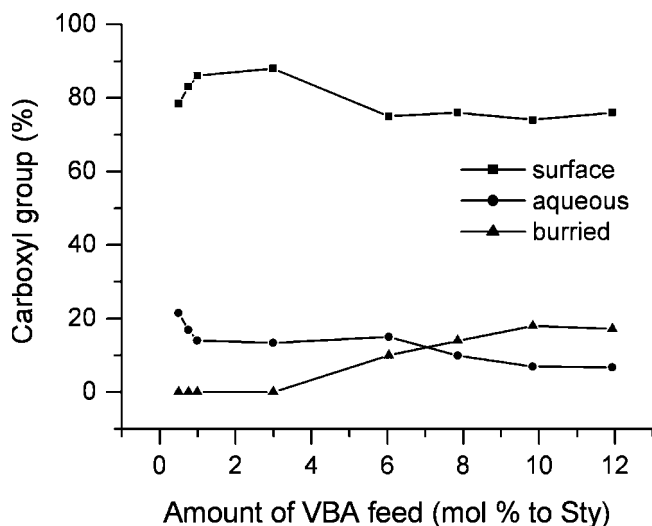


Figure 9 Distribution of the carboxylic acid groups at the surface of the polymeric particles, in the interior of the polymeric particles, and in the aqueous layer after the polymerization under a range of monomer feed conditions.

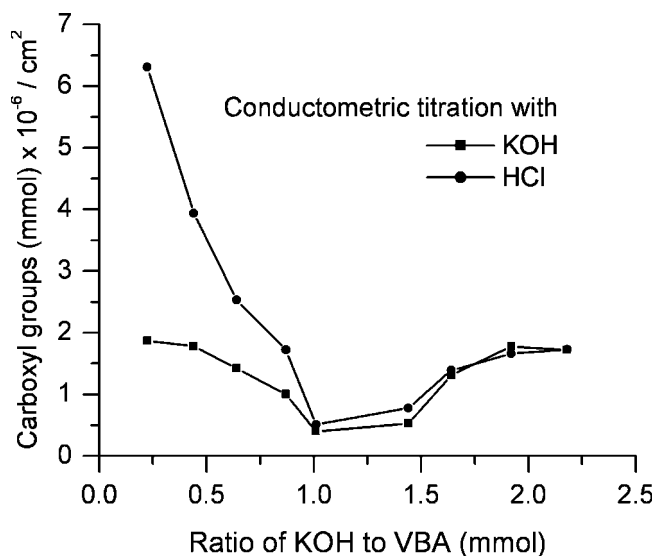


Figure 10 Surface charge density after the polymerization as a function of the changing molar ratio of KOH to VBA.

for the back-titration. This could be explained with the model proposed by Hoy.¹² In this model; the particles are surrounded with a hydrophilic shell formed of many layers of hydrophilic groups. As the KOH titration occurs, the charge at the surface of the particles increases, and the dense shell structure is loosened due to the electrostatic repulsion of the COO⁻ groups. As this process is very slow, not all of the carboxylic acid groups can be titrated during the timescale of the KOH titration. This neutralization occurs during the period of equilibration before of the start of the HCl titration. As explained earlier,

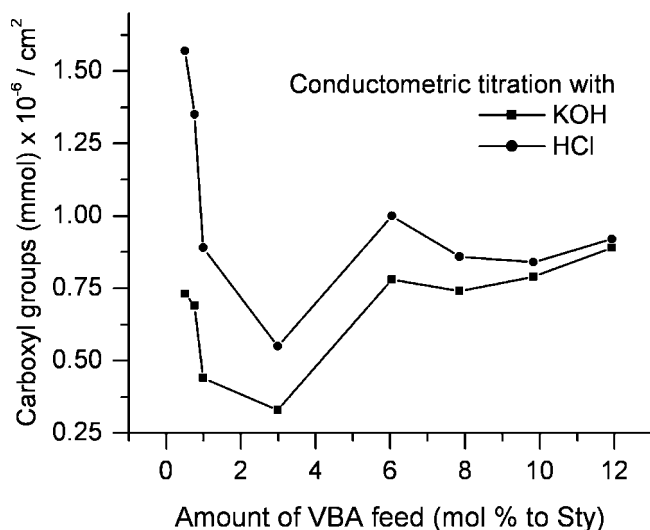


Figure 11 Surface charge density of the polymer particles as a function of the monomer feed ratio after the polymerizations.

TABLE III
Stability of the Latexes Synthesized with Different Amounts of KOH in Different Concentrations of KCl Solution

KOH/VBA (mmol/mmol)	Latex	KCl solution (N)								
		First day			Second day			Third day		
		0.1	1.0	2.5	0.1	1.0	2.5	0.1	1.0	2.5
0.21	1	-	-	-	-	-	-	-	-	-
0.43	2	+	-	-	+	-	-	+	-	-
0.63	3	+	+	+/-	+	+	+/-	+	+	+/-
0.84	4	+	+	+	+	+	+	+	+	+
0.99	5	+	+	+	+	+	+	+	+	+
1.37	6	+	+	+	+	+	+/-	+	+	+/-
1.58	7	+	+	+	+	+	+	+	+	+
1.85	8	+	+	+	+	+	+	+	+	+
2.11	9	+	+	+	+	+	+	+	+	+

- = unstable; + = stable.

with increasing hydrophilic character of the monomer, more of the monomer was bonded near or in the aqueous layer. Therefore, for polymerizations carried out at a basic pH (KOH/VBA > 1.2 mmol/mmol), the surface densities of the carboxyl groups calculated by KOH and HCl titrations were equal.

Figure 11 shows the surface charge density of the polymers prepared with different amounts of VBA. We observed two different curves for the HCl and KOH titrations, but as the concentration of VBA in the system increased, the difference between the two curves was reduced. At low VBA concentrations, all of the VBA was dissolved in the aqueous layer; the polymerization started in the aqueous phase, and hydrophilic oligomers were formed. These VBA-rich oligomers could act as surfactants and stabilize the Sty particles. During the next step of the polymerization process, the oligomers were bonded at the surface of the growing polystyrene particles. At a higher concentrations of VBA, these species acted as normal molecular surfactants and were localized only at the surfaces of the final polymer particles. At VBA concentrations between these two extremes, the poly-

merization took place in both fashions, that is, through hydrophilic oligomers and molecular VBA surfactants. The differences between the HCl and KOH titration curves became less pronounced and the surface charge increased with a higher amount of VBA in the polymerization system.

Stability

Stability of the purified functionalized latices was observed in the presence of CaCl₂ and KCl solutions. All of the latices were unstable even in the 0.1N CaCl₂ solutions; however, they were stable in the 2, 1, and 0.1N KCl solutions. This effect was explained by consideration of the coordination of the carboxylate groups present on the surfaces of the particles with the metal ions. Ca²⁺ could saturate two charges on the particle surface, whereas K⁺ could saturate just one, and if the charge on the surface was lower, particles could coagulate more easily. The second effect may have been due a certain amount of bridging between the particles caused by the divalent Ca²⁺.⁴⁹ The third effect was the ionic

TABLE IV
Stability of Latexes Synthesized with Different Amounts of VBA in Different Concentrations of KCl Solution

VBA (mol % to Sty)	Latex	KCl solution (N)								
		First day			Second day			Third day		
		0.1	1.0	2.5	0.1	1.0	2.5	0.1	1.0	2.5
0.50	10	-	-	-	-	-	-	-	-	-
0.76	11	+/-	+/-	-	+/-	+-	-	-	-	-
0.99	12	+	+	+/-	+	+	+/-	-	-	-
2.99	13	+	+	+/-	+	+	+/-	+	+	+/-
6.04	6	+	+	+	+	+	+/-	+	+	+/-
7.85	14	+	+	+	+	+	+	+	+	+
9.83	15	+	+	+	+	+	+	+	+	+
11.93	16	+	+	+	+	+	+	+	+	+

- = unstable; + = stable.

strength of the medium, which was higher for divalent ions. In media with higher ionic strengths, the diffuse layer of the particle was smaller; the particles could come nearer to one other and coagulate more readily. Tables III and IV shows the stability of the purified latices produced with different molar ratios of KOH to VBA and VBA feed ratios at a constant molar ratio of KOH to VBA in KCl solutions of different concentrations, respectively. When the molar ratio of KOH/VBA was 0.21, the latex was unstable at all KCl concentrations. This was due to the low surface concentration of carboxylate groups at the shear plane. However, the stability increased with increasing KOH/VBA molar ratio. In the KCl solutions, the dispersions showed an increased stability with higher amounts of VBA; that is, as the amount of carboxylic groups increased, the charge density on the surface increased. Also, the formation of VBA polyelectrolytes anchored onto the particles may have also enforced the stabilization of the colloids produced because of the increased steric hindrance of approaching particles.

The freeze-thaw stability of the purified latices was judged as follows. The latices were frozen at -20°C for 24 h, and then, the frozen latices were kept at room temperature until they thawed. Tables V and VI show the freeze-thaw stability of the latices; an increasing ratio of KOH to VBA and an increasing amount of VBA in the polymeric system increased the stability. However, the stability was reduced by an increase in the ionic strength of the dispersion when the KOH concentration was higher (Table V).

CONCLUSIONS

The amount of neutralized VBA in the EFEP had a profound influence on the Sty-VBA copolymerization. Increasing the concentration of KOH adding up to an equimolar amount of VBA increased the rate

TABLE V
Freeze-Thaw Stability of Latexes Synthesized with Different Amounts of KOH

Latex	KOH/VBA (mmol/mmol)	First day	Second day	Third day
1	0.2	–	–	
2	0.4	+	–	
3	0.6	+	–	
4	0.8	+	–	
5	1	+	–	
6	1.3	+	–	
7	1.5	+	+	+/-
8	1.75	+	+	+/-
9	2	+/-	–	–

– = unstable; + = stable.

TABLE VI
Freeze-Thaw Stability of Latexes Synthesized with Different Amounts of VBA

Latex	VBA (mol % to Sty)	First day	Second day	Third day
10	0.5	–		
11	0.75	–		
12	1	–		
13	3	–		
6	6	+	+/-	
14	8	+	+	+/-
15	10	+	+	+
16	12.5	+	+	+

– = unstable; + = stable.

of conversion. However, higher concentrations of KOH did not increase the conversion rate further. The rate of conversion was also influenced by the molar ratio of VBA in the feed; increasing the amount of VBA up to 3 mol % relative to Sty increased the rate conversion. Higher molar ratios of VBA did not influence the conversion rate further. This could be explained with different polymerization mechanisms, for example, micelle and precipitation nucleation mechanisms. As the polymerization mechanism was different depending on the ratios of KOH to VBA and the amount of VBA feed in the polymerization system, all other properties of the latices, such as stability, surface charge, and particle size, were influenced. This method represents an attractive alternative to conventional AA-containing particles prepared by emulsion polymerization.

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