Preparation and Characterization of Imidazole-Functionalized Microspheres

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ABSTRACT: The preparation of imidazole-functionalized latex microspheres by a two-stage emulsion copolymerization process and their characterization are reported on. Emulsifier-free emulsion copolymerization of styrene (St) and 1-vinyl imidazole (VIMZ) exhibited bimodal particle size distributions caused by secondary homogeneous nucleation process. However, secondary nucleation can be avoided by using cetyltrimethylammonium bromide (CTAB) as a stabilizer at a concentration below its cmc (critical micelle concentration). This would result in the formation of monodisperse latex particles. The final particle size diameter depended on the concentration of CTAB as well as the amount of VIMZ. To control the amount of the functional imidazole groups on the latex particle surfaces, independent of the latex diameters, without secondary nucleation of particles, the seeded emulsion copolymerization of styrene and VIMZ was explored as a second-stage polymerization at different concentrations and ratios of monomers in the presence of the previously prepared monodisperse poly(styrene-co-1-vinyl imidazole) seed latex particles. The concentration of imidazole functional groups on the surface of the latex particles could also be varied through the rearrangement of hydrophilic imidazole groups by varying the second-stage monomer addition process such as the utilization of monomer-swollen seed particles or a shot addition of monomers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5753–5762, 2006

Key words: imidazole-functionalized latex microspheres; two-stage emulsion copolymerization process; cetyltrimethylammonium bromide

INTRODUCTION

Water-soluble functional polymers have been used to remove heavy metal ions from wastewater.[1] In the same way, functional ligands present in polymer microspheres can also selectively bind to a specific metal ion present in water and such ion-exchange polymer beads are commercially available. Moreover, the colloidal characteristics of microspheres including their high surface-to-volume ratios, their dispersibility in a liquid medium, and their uniformity in size have extended their application to the biomedical area including bioseparations,[2] immunoassay diagnostics,[3,4] and drug delivery systems.[5] Recently, the fabrication of functionalized particles have been extensively explored to prepare optical and optoelectrical devices.[6] Particularly for optical applications, particle monodispersity is a key requirement, since it simplifies the interpretation of the optical properties without needing to take the particle size distribution into account. In many cases, the desired optical properties are obtained by preparing regularly ordered uniform particles. The assembly of particles can be achieved by varying the surface properties of the particles.[7] In addition, controlling the surface properties of model latex particles independent of particle size is required to prepare such particles.

Incorporation of functional groups on the surface of latex particles can be achieved simply by the emulsion copolymerization of hydrophobic monomers along with comonomer(s) containing hydrophilic functional groups. The hydrophilic nature of the functional monomers leads to the segregation of the functional groups in the outer shell of the resulting latex particles near the particle–water interface. As a result, the particles maintain their colloidal stability by either electrostatic repulsion or steric stabilization, resulting from the hydrophilic comonomer-rich polymer chains that cover the hydrophobic core particles. A number of hydrophilic comonomers have been used to prepare functional particles including (meth)acrylic acid,[8] glycidyl methacrylate,[9] vinyl pyridine,[10] and N-isopropylacrylamide.[7] However, problems may arise when trying to incorporate a large density of functional groups primarily at the particle surfaces: homopolymerization or copolymerization may occur in the aqueous phase rather than on the particle surface, because functional monomers are often highly water-soluble. This undesired polymerization can result in the formation of water-soluble polymer in the aqueous phase that could adsorb

TABLE I
Experiments for Batch Emulsifier-free Emulsion Copolymerization of Styrene (St) and 1-Vinyl Imidazole (VIMZ) Using Cationic Initiator, 2,2′-Azobis[2-amidinopropane]dihydrochloride (V-50)

Sample ID	St (g)	VIMZ (g)	V50 (mM)	Deionized Water (g)
E05	7.0	0.35	10.0	63.0
E10	7.0	0.70	10.0	63.0
E30	7.0	2.10	10.0	63.0

Batch polymerization carried out at 70°C for 18 h in a stirred reactor.

on the particle surface, resulting in particle flocculation as well as the formation of particles with a broad particle size distribution. The distribution of functional comonomers in latex particles depends on their hydrophilicity.[8,10] Even if the functional comonomers reside primarily in the particles and not in the aqueous phase, it may be possible that the functional comonomers might not be distributed homogeneously throughout the particles, and thus, their concentration can differ in the radial direction of the latex particles as well.

Seeded emulsion polymerization can be considered as a suitable process for the growth of particles,[11] the formation of a new thin functional shell layer on seed particle surfaces,[12] and formation of nonspherical morphologies[13] caused by phase separation during the polymerization. As an example of the growth of a sulfonate-rich polymer shell on the surface of polystyrene latex particles, Kim et al. used shot-growth emulsion copolymerization,[14] while Tamai et al. used seeded semicontinuous polymerization.[15] The shot-growth emulsion copolymerization may be more

effective to incorporate higher amounts of functional groups primarily on the particle surfaces because in the case of the seeded semibatch polymerization, a significant amount of functional groups could be buried inside the particle and inaccessible. It is important for the shell growth process to result in an enrichment of functional groups on the particle surface without any secondary nucleation. Kim et al.[14] reported that the shot-growth reactions should be carried out at a conversion of 85–95% of the first-stage reaction, before adding the second-stage monomers in one discrete shot; otherwise, secondary nucleation could occur during the shot-growth stage.

Macromolecules incorporating 1-vinylimidazole (VIMZ) and its derivatives are of great interest due to the possibilities for the preparation of new materials to exhibit ion-exchange properties[16–21] via complex formation with various metal ions such as Hg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, V^{3+}, Cr^{3+}, and Fe^{3+}. In addition, it has been suggested that imidazole-containing macromolecules could be employed as a carrier agent for protein separations.[22,23] For these reasons, copolymerizations of VIMZ with many different monomers have been reported, including styrene,[24] vinyl acetate,[24] methyl methacrylate,[24] ethyl methacrylate,[25] acrylonitrile,[26] sodium styrene sulfonate,[27] acrylamide,[28] and acrylic acid.[29]

Herein is described the synthesis and characterization of a series of latex particles that have a uniform particle size, but possess different amounts of imidazole groups on the latex particle surfaces. A two-stage emulsion copolymerization process, including a seed-stage reaction and a functionalized shell growth stage reaction, was used to prepare these particles.

TABLE II
Recipes for Batch Emulsion Copolymerization of Styrene (St) and 1-Vinyl Imidazole (VIMZ) Using Cationic Initiator, 2,2′-Azobis[2-amidinopropane]dihydrochloride (V-50) in the Presence of Cetyltrimethylammonium Bromide (CTAB)

Sample ID	St (g)	VIMZ (g)	V50 (g)	CTAB (mM)	Deionized water (g)
C00-04	7.0	0.00	0.172	0.4	63.0
C00-06	7.0	0.00	0.172	0.6	63.0
C01-04	7.0	0.07	0.172	0.4	63.0
C01-06	7.0	0.07	0.172	0.6	63.0
C03-04	7.0	0.21	0.172	0.4	63.0
C03-06	7.0	0.21	0.172	0.6	63.0
C03-12	7.0	0.21	0.172	1.2	63.0
C03-20	7.0	0.21	0.172	2.0	63.0
C05-04	7.0	0.35	0.172	0.4	63.0
C05-06	7.0	0.35	0.172	0.6	63.0
C10-IG	7.0	0.70	0.172	–[a]	63.0
C10-04	7.0	0.70	0.172	0.4	63.0
C10-06	7.0	0.70	0.172	0.6	63.0
R03-12	30.0	0.90	0.735	1.2	270.0
R05-06	30.0	1.50	0.735	0.6	270.0

Batch (bottle) polymerization process was carried out at 70°C for 18 h.
[a] In the case of C10-IG, 0.1 wt % (based on water) of Igepal CO-880 was used as stabilizer instead of CTAB.

TABLE III
Experiments (V150 Series) for the Second-Stage Polymerization Using
R03-12 as Seed Particles

Sample ID	R03-12 latex (g)[a]	Styrene (g)	VIMZ (g)	V50 (g)	Deionized water (g)
V150-A	50	1.0 (swell)	0.0	0.0245	9.0
V150-B	50	1.0 (swell)	0.4	0.0245	9.0
V150-C	50	1.0	0.4	0.0245	9.0
V150-D	50	1.0 (swell)	0.4 (swell)	0.0245	9.0

[a] The solids content of R03-12 was 9.74 wt % and its number–average particle diameter (D_n) from TEM was 150 nm.

EXPERIMENTAL

Materials

Styrene monomer (St; 99%, Fisher Scientific Company, Pittsburgh, PA) was distilled in the presence of cuprous chloride (97+%, Sigma Aldrich, Milwaukee, WI) at a reduced pressure of 35 mmHg and 50°C to eliminate inhibitors. 2,2′-Azobis[2-methylpropionamidine] dihydrochloride (V-50; Wako, Richmond, VA) and Igepal CO880 (Rhone-Poulenc, Cranbury, NJ) were used as received. Cetyltrimethylammonium bromide (99+%, CTAB) were used as received (Sigma Aldrich, Milwaukee, WI). 1-Vinylimidazole (99+%, VIMZ; Sigma Aldrich, Milwaukee, WI) was used after cleaning by using inhibitor-removing columns.[30]

Latex synthesis

A series of batch (bottle) emulsion copolymerizations of styrene and VIMZ were carried out using V-50 as a cationic initiator in a stirred reactor at 70°C for 18 h to develop a recipe that may be used to prepare uniform latex particles by using emulsifier-free emulsion copolymerization as shown in Table I. The emulsion copolymerizations of St and VIMZ were also carried out in the presence of emulsifier as shown in Table II. For this purpose, all ingredients are added into a 200-mL bottle and then the bottle was purged with nitrogen for 1 min. Right after this, the bottle prepared was capped and then tumbled at 70°C and a speed of 30 rpm for 18 h. Samples C03-12 and C05-06 exhibited a narrow particle size distribution, which will be discussed later. Samples C03-12 and C05-06 were repeated to prepare the seed particles on a large scale (i.e., R03-12 and R05-06, respectively) to study the imidazole-functionalized shell growth reaction. In some samples shown in Table II, the resulting particles were not stable so as to form coagulum in the bottle, which will also be discussed later. The seed latex particles obtained from samples R03-12 and R05-06 were filtered to remove the coagulum (13.7 and 6.0 wt %, respectively) and the solids contents of the filtered R03-12 and R05-06 were 9.74 wt % and 9.24 wt %, respectively.

Several modes of monomer addition (without using any additional surfactants in the second-stage reaction) were explored to determine the conditions necessary for the effective incorporation of the imidazole groups onto the surface of seed particles, as shown in Table III. The solids content of the seed particles, R03-12, was 9.74 wt %. The number–average diameter (D_n) was 150 nm as measured by TEM, and the coefficient of variation in the number–average diameter was 8.9%. For V150-A, the seed latex particles were swollen with 1.0 g of styrene monomer in a tumbler at 25°C and a speed of 30 rpm for 24 h and the initiator solution (0.0245 g of V50 and 9.0 g of water) was subsequently added. In the case of V150-B, 0.4 g of VIMZ was added into the styrene-swollen seed latex particles before the polymerization was initiated. In the case of V150-C, all of the second-stage monomers were added just before the second-stage polymerization process was begun. Finally, V150-D used the seed particles swollen with all of the second-stage monomers. The second-stage polymerizations were carried out at 70°C for 20 h using the bottle polymerization process as described earlier in Table II.

For latex series (V195) that have the same particle diameters, but different surface functional groups, the density of imidazole groups at the surface was varied using different ratios of second-stage monomers as shown in Table IV, and the second-stage monomers were added in the same way as for V150-C. The solids content of the seed particles, R05-06, was 9.24 wt % and the number–average diameter was 195 nm as measured by TEM. The coefficient of variation in the number–average diameter was 5.5%.

Characterization

The particle sizes of the resulting latex particles were examined by transmission electron microscopy (TEM) using a Philips 420T (Eindhoven, The Netherlands) instrument operated at an accelerating voltage of 80 kV. The particle size distribution was characterized using the coefficient of variation based on the number–average particle diameter (σ/D_n, i.e., standard deviation (σ) divided by the number–average diame-

TABLE IV
Experiments (V195 Series) for the Second-Stage Reaction
Using R05-06 as Seed Particles

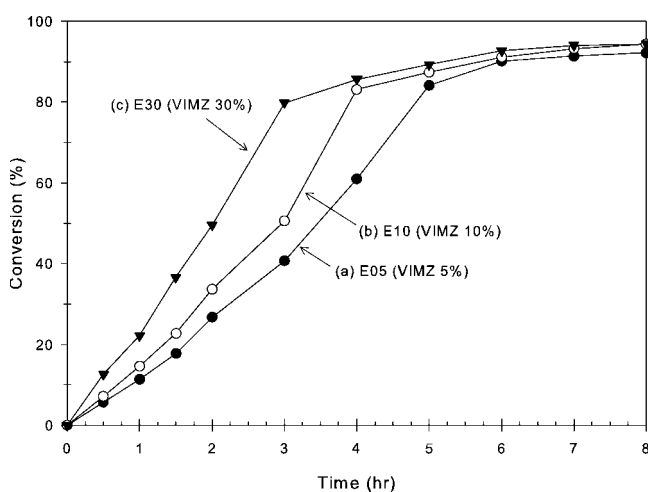| Sample ID	R05-06 latex (g)[a]	Styrene (g)	VIMZ (g) (wt %)[b]	V50 (g)	Water (g)
V195-A	50	1.4	0.0 (0)	0.0245	9.0
V195-B	50	1.2	0.2 (14.3)	0.0245	9.0
V195-C	50	1.0	0.4 (28.6)	0.0245	9.0
V195-D	50	0.6	0.8 (47.1)	0.0245	9.0

[a] Solids content of R05-06 was 9.24 wt % and its number–average particle diameter (D_n) as determined from TEM was 195 nm.
[b] Amount of VIMZ is based on the total amount of monomers in the second-stage polymerization (wt %).

ter, D_n) and, of course, lower values indicate a narrower particle size distribution. The amount of coagulum resulting from the colloidal instability of the resulting latex particles was obtained by filtering the latex through a nylon mesh with a pore size of 100 μm and weighing the collected coagulum.

The number of imidazole groups on the latex particle surface was determined by conductometric titration, and the latex particles for this purpose were cleaned using the serum replacement technique.[31] Conductometric titrations were carried out using 100 mL of the cleaned and diluted latex (with 0.5 wt % solids) at room temperature under an inert argon atmosphere. Approximately 1.5 mL of 0.0202N sodium hydroxide aqueous solution was added to the diluted latex, so that the pH of the emulsion was 10–11 and all of the imidazole functional groups would be deprotonated. Subsequently, a forward titration was carried out by adding 0.02N hydrochloric acid aqueous solution to the diluted latex with continuous stirring.

RESULTS AND DISCUSSION

First-stage reaction (seed-stage reaction)

Emulsion copolymerizations of styrene and different concentrations of VIMZ monomer (in the absence of any emulsifier) were carried out ranging from 5 to 30% based on the weight of styrene (Table I) using V-50 as a cationic initiator. As shown in Figure 1, the polymerization rate increased with increasing concentration of the functional comonomers, VIMZ, and the slope of all time-conversion curves increased gradually with the conversions up to 80%. For the conventional emulsion polymerization of styrene, according to Harkins,[32] the important site of particle nucleation is the monomer-swollen emulsifier micelles. However, the particle nucleation site of the emulsion copolymerization may be the aqueous phase in the absence of emulsifier.[33] The water-solubility of growing oligoradicals reached the critical level for precipitation, and then, particles are nucleated. Therefore, the more water-soluble oligo-
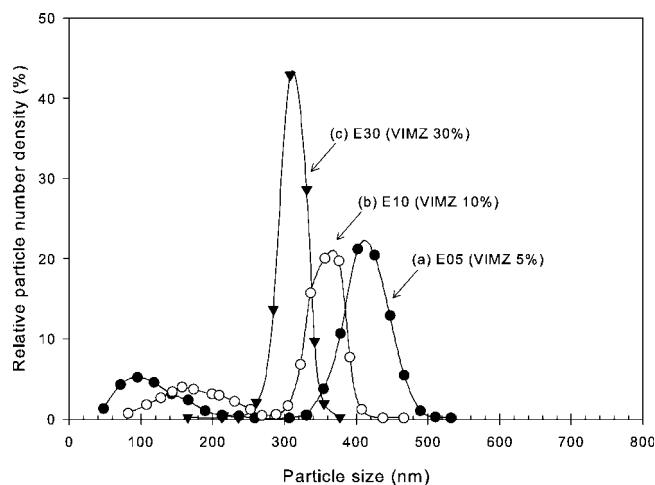

Figure 1 Conversion-time curve for the emulsifier-free emulsion copolymerizations of styrene and 1-vinyl imidazole (VIMZ): (a) 5 wt % VIMZ, (b) 10% VIMZ, and (c) 30% VIMZ based on the amount of styrene, as described in samples E05, E10, and E30 in Table II, respectively.

Figure 2 Particle size distributions of poly(styrene-*co*-VIMZ) latexes prepared by emulsifier-free emulsion copolymerization of styrene and 1-vinyl imidazole (VIMZ) as measured by TEM: (a) 5 wt % VIMZ, (b) 10% VIMZ, and (c) 30% VIMZ based on the amount of styrene, as described in samples E05, E10, and E30 in Table II, respectively.

radicals generated by adding more water-soluble monomers can expect to form more primary particles and result in the fast rate of polymerization.

Ohtsuka et al. studied the emulsion copolymerization of styrene and 4-vinyl pyridine (4VP) in the absence of emulsifiers at different values of pH.[10] The rate of the emulsifier-free emulsion copolymerization of styrene and 4VP under acidic conditions was faster than under basic conditions. Under acidic conditions, most of the pyridine groups present in 4VPs would be protonated and highly water-soluble, so that cationic 4VP would react with water-soluble initiator radicals to produce water-soluble oligoradicals. When the highly water-soluble monomers are exhausted, the majority of monomer consumed would become the styrene monomer, and thus, the polymerized styrene fraction in the growing radicals would increase. As a result, the hydrophilicity of growing radicals would sharply decrease and then precipitate.

Imidazole is a stronger base than pyridine and their pK_b are reported to be 7.05 and 8.95, respectively.[34] The nitrogen in the imine position of imidazole ring can be easily protonated[35] and complexed with metals.[20,21] The successive complexation constant of copper(II) with poly(vinylimidazole) was measured by spectrophotometric analysis and the complex existed as a form of metal complex with monoligand to multiligands.[36] Significant amounts of imidazole in VIMZ could be protonated analogous to the case with 4VP and become highly water-soluble even at a neutral polymerization pH, around 7. The protonated VIMZ reacts with water-soluble initiator preferentially to form water-soluble surface-active oligoradicals, which grow to a certain critical size and then precipitates to form particles. This type of particle formation by coagulative nucleation is well-known as the homogeneous nucleation process.[37]

Figure 2 shows that the latex particles with narrow particle size distribution were formed only at the highest concentration of VIMZ in our experimental ranges; otherwise, the emulsifier-free emulsion copolymerization of styrene and VIMZ led to the formation of a bimodal particle-size distribution. To clarify this, TEM images were investigated as a function of conversion, as shown in Figure 3. Secondary
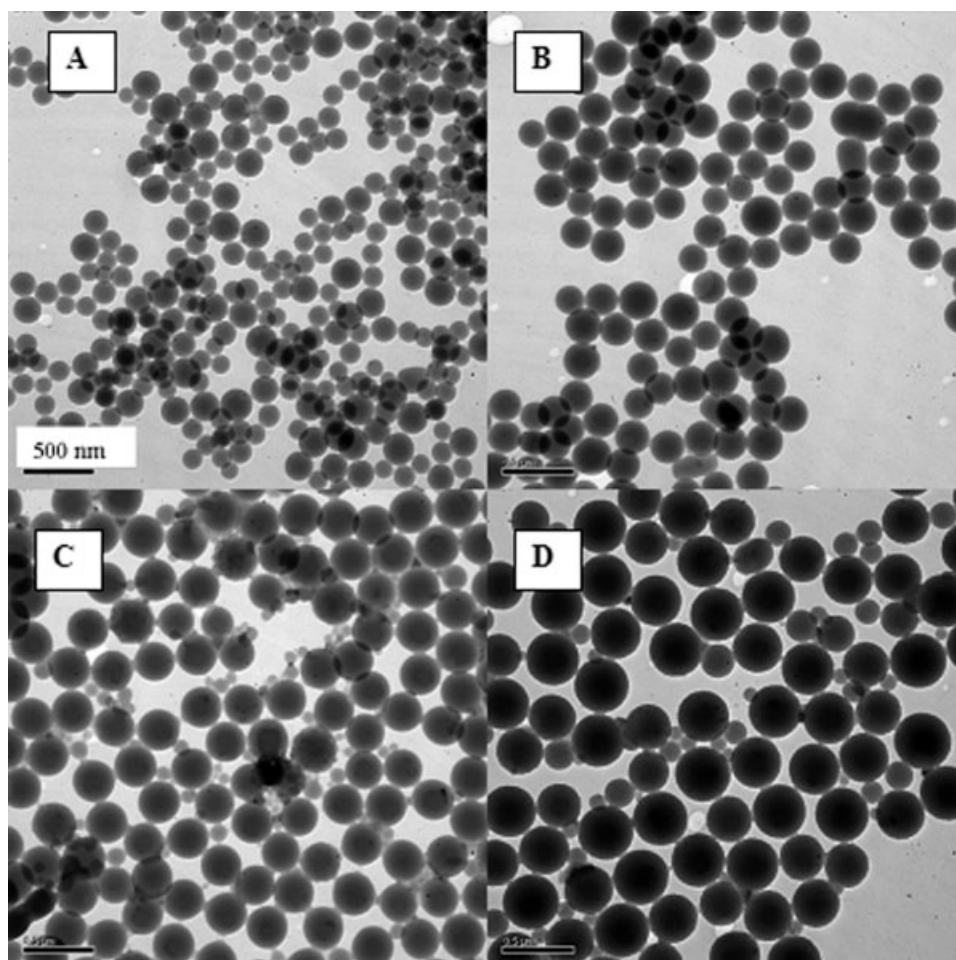
Figure 3 TEM micrographs of latexes resulting from the emulsifier-free emulsion copolymerization of St and VIMZ (10% VIMZ based on styrene, sample E10 in Table II) at various conversions: A, 7.2%; B, 22.7%; C, 50.6%; and D, 94.3%.
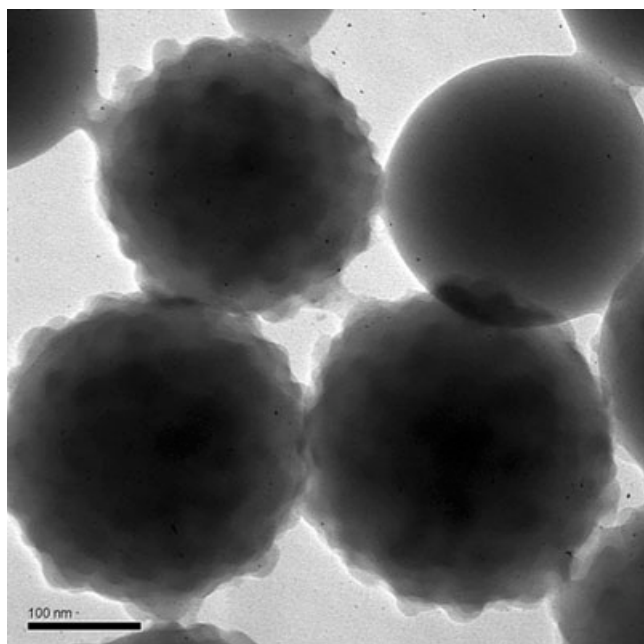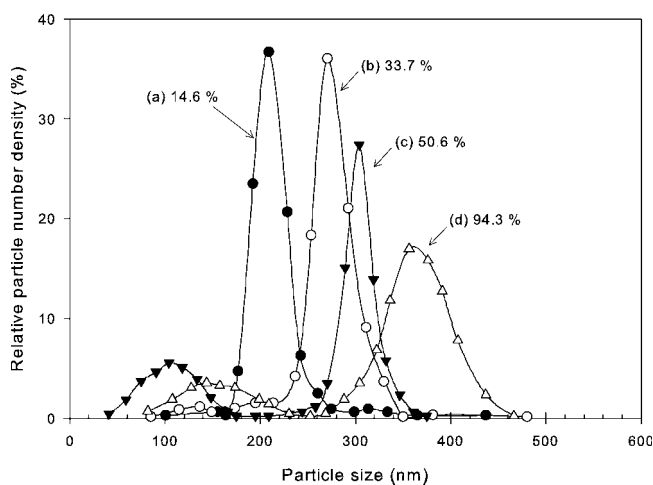
Figure 4 TEM micrograph of latexes resulting from the emulsifier-free emulsion copolymerization of St and VIMZ (10% VIMZ based on styrene, sample E10 in Table II) at conversion = 33.7%.

nucleation can be observed during the polymerization that resulted in a bimodal particle size distribution at the end of the polymerization. As a result of the homogeneous nucleation process, the nucleated particles would possess hydrophilic surfaces derived predominantly from VIMZ monomer. Any hydrophobic growing radicals generated after the VIMZ monomers were exhausted would not adsorb easily on the hydrophilic surface of previously nucleated particles. As a result, the secondary nucleation of particles might be possible. For instance, a secondary crop of particles were observed to be adsorbed on the previously generated latex particles at a conversion of 33.7%, as shown in Figure 4. After this conversion, the newly formed particles could result in a bimodal particle-size distribution. Figure 5 shows that the shape of the particle size distribution changes from a narrow distribution to a bimodal form as the polymerization proceeds.

When at least 30 wt % of VIMZ (based on styrene monomer) was used, a narrow particle size distribution was obtained. Using this latex as the seed particles in a second-stage polymerization in an attempt to vary the concentration of imidazole groups on the surface may not be feasible because the seed particles would already possess a high concentration of functional groups on the surface. For example, the surface density of imidazole groups at the surface of the cleaned E30 latex particles and the packing area of imidazole were determined to be 2.1 μeq/m^2 and 80.3 Å^2/imidazole, respectively. The uncleaned E30

latex particles sedimented in 1 day, although the latex could be redispersed by a weak shear force. However, after extensive cleaning of the latex, using several ion exchange cycles followed by serum replacement, the latex particles became very stable in water and their ζ-potential was found to be 29.6 ± 4.2 mV (characterized using a Penkem model 501 Lazer Zee Meter) at a pH of 7. This observation implies that significant amounts of VIMZ are polymerized in the water phase to form water-soluble polymers, which can cause the particles to be flocculated by bridging. The existence of significant amounts of water-soluble polymers in the water phase can be supported by elemental analysis (characterized by GALBRAITH Laboratories) of cleaned E30 latex particles, which showed that cleaned E30 contained only 5% of VIMZ monomers based on the dried polymer weight. The theoretical amount of VIMZ should have been 23 wt % if all of the VIMZ monomers had polymerized and had been incorporated into the latex particles.

Our objective in this work was to prepare the uniform latex particles with different amounts of imidazole functional groups present on the latex particle surfaces. For this purpose, it was necessary to generate seed particles that had a uniform particle size and a low surface density of imidazole groups present on the latex particle surface prior to the second-stage polymerization where the amount of functional monomers may be varied over a wide range, independent of the particle size. Thus, preparation of the seed particles in the absence of VIMZ was indicated. However, a certain amount of hydrophilic comonomer in the seed-stage polymerization reaction can help to incorporate a large amount of hydrophilic comonomer onto the surface of the seed particles

Figure 5 Number–average particle size distributions of latex particles resulting from the emulsifier-free emulsion copolymerization of St and VIMZ (10% VIMZ based on styrene, sample E10 in Table II) at various conversions.
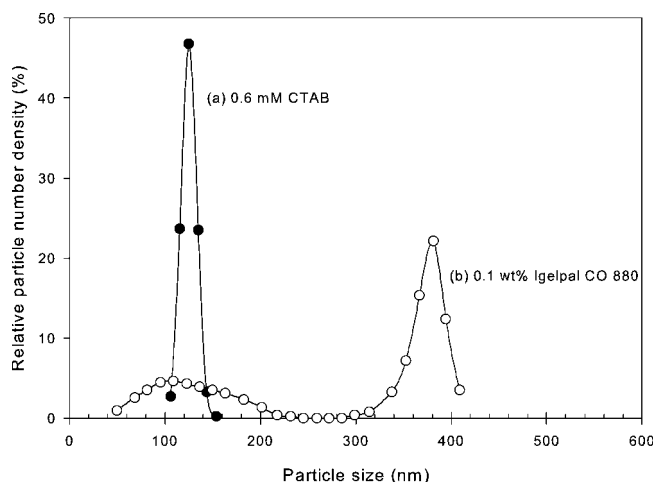
Figure 6 Particle size distributions resulting from the emulsion copolymerization of styrene and 1-vinyl imidazole (10 wt % based on styrene) as determined by TEM in the presence of: (a) 0.6 mM CTAB (sample C10-06, Table II) and (b) 0.1 wt % Igepal CO880 (sample C10-IG, Table II).

because the hydrophilic interface layer of the seed particles can decrease the interfacial tension, leading to fast copolymerization predominantly on the surface of seed particles.[33] The relatively fast polymerization rate of a hydrophilic monomer in emulsion polymerization using water-soluble initiators can bring about the secondary nucleation of new particles instead of the desired particle growth, which also depends on the number of seed particles.[14] In our experiments, latexes prepared in the absence of VIMZ exhibited very broad particle size distributions; the coefficients of variation on the number–average diameter were 17.3% and 19.1% at 0.4 and 0.6 mM of CTAB, respectively, which is below its critical micelle concentration (cmc), where homogenous nucleation would be dominant. It was reported that the cmc of CTAB is 0.92 and 1.08 mM at 23 and 41°C, respectively.[38]

A conventional emulsion copolymerization utilizing CTAB and Igepal CO-880 surfactants was evaluated with the objective of preparing particles with a narrow size distribution using 10 wt % VIMZ (based on the amount of styrene present in the first seed-stage reaction), as shown in Figure 6. In both cases, the surfactants used were at a concentration below their cmc. The addition of a small amount of nonionic emulsifier, Igepal CO-880, resulted in the formation of a latex with a bimodal particle size distribution as described earlier for the emulsifier-free emulsion copolymerization of styrene with small amounts of VIMZ. However, the addition of small amounts of cationic surfactant, CTAB, resulted in the formation of latex particles with a narrow size distribution.

The dependence of the particle size on the amount of VIMZ was investigated at a CTAB concentration of 0.6 mM, as shown in Figure 7. When the amount
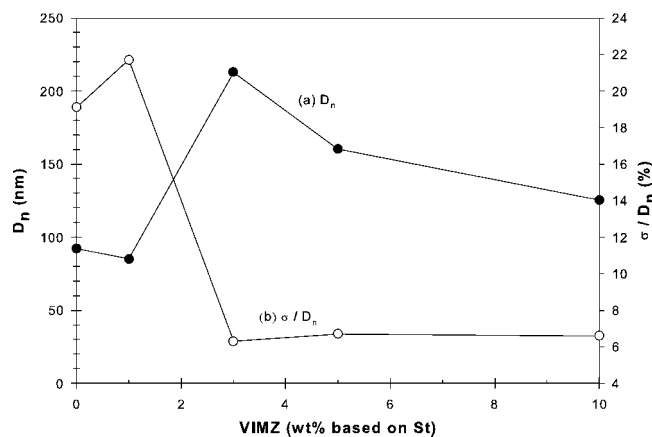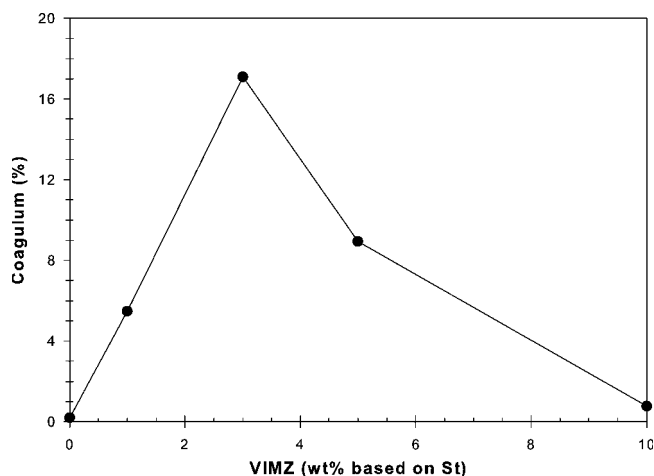

Figure 7 Effect of the amount of VIMZ at [CTAB] = 0.6 mM on: (a) the number–average latex particle diameter (D_n) as measured by TEM, and (b) the coefficient of variation (σ/D_n).

of VIMZ was increased from 0 to 1 wt %, the particle size decreased slightly and the particle size distribution was quite broad. The particle size increased sharply at a VIMZ concentration of 3 wt % and after that, the particle size decreased, while still maintaining a narrow size distribution as the amount of the VIMZ was increased. The dependence of particle size on the amount of CTAB was then explored at a constant amount of VIMZ (3 wt %), as shown in Figure 8. The particle size decreased as the amount of CTAB increased and narrow size distributions were also maintained until the concentration of CTAB reached 1.2 mM. At 2 mM CTAB, latexes with a broad particle size distribution were obtained. Even a CTAB concentration of 1.2 mM, which we believe is slightly higher than the cmc, produced a uniform particle size distribution. The cmc of an ionic surfactant has a minimal value (cmc*) occurring at a tem-
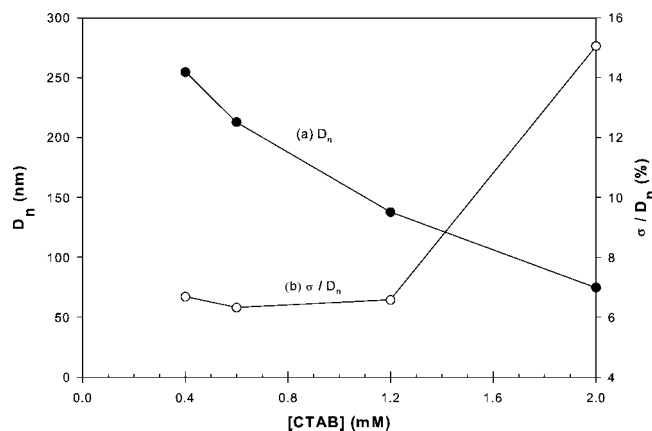
Figure 8 Effect of the concentration of CTAB at 3 wt % VIMZ on: (a) the number–average latex particle diameter (D_n) as measured by TEM and (b) the coefficient of variation (σ/D_n).

Figure 9 Dependence of the amount of coagulum on the amount of VIMZ at [CTAB] = 0.4 mM. The amount of coagulum was weighed and determined based on the total amount of monomers used in a recipe.

perature T^*. The cmc at various temperatures was reported to depend on cmc*, T/T^*, and the heat capacity for micellization and the cmc* and T^* of CTAB are reported as 0.88 mM and 302.1 K, respectively.[39] Lee measured the cmc of CTAB at a range of temperatures from 17 to 41°C and showed that the cmc initially decreased with increasing temperature and then increased after 20°C which is close to the reported T^* of CTAB.[38] Many ionic surfactants were reported to exhibit this type of temperature dependence of cmc over a range from 0 to 75°C.[39,40] The cmc of CTAB is expected to be higher at a reaction temperature (70°C), compared with the cmc at room temperature which is close to T^*, and thus, 1.2 mM can still be below the cmc of CTAB at a polymerization temperature of 70°C. Moreover, the concentration of CTAB in the aqueous phase could be lower than its cmc due to the depletion of surfactant caused by the adsorption of the surfactant on the monomer droplets.

When the concentration of CTAB is below its cmc, latex particle formation should occur via homogenous nucleation as is the case in emulsifier-free emulsion copolymerization. Homogeneous nucleation is not confined only to the precipitation of growing radicals to form nuclei, but also includes the aggregation of nuclei that were previously generated.[37] The rapid increase in the volume of too many nuclei leads to their aggregation and, consequently, to a decrease in the number of particles at a certain point in the polymerization, i.e., limited aggregation occurs. When the amount of VIMZ is <3 wt %, the nuclei generated from the precipitation of growing radicals in the homogeneous nucleation process would be stabilized by the CTAB present. However, after this point, there are too many nuclei generated

with too large a surface area to be stabilized by the existing amount of CTAB. In addition, an increase in the hydrophilicity of the particle surface would also decrease the amount of CTAB adsorbed on the polymer particles, and thus, the stability offered by CTAB would be limited. As a result, limited aggregation would be more dominant at this point. Figure 9 shows that the amount of coagulum, obtained from the emulsion copolymerization of styrene and VIMZ at a [CTAB] of 0.4 mM, was the highest at 3 wt % VIMZ at which point the particle size increased sharply (as shown in Fig. 7), indicating the presence of particle aggregation. Figure 10 shows that the amount of coagulum can be reduced by increasing the amount of CTAB, even if limited adsorption of CTAB might occur on the hydrophilic surface of nucleated particles.

Functional shell growth stage reaction

Seeded emulsion copolymerizations of styrene and VIMZ were carried out in the presence of the previously-prepared uniform poly(styrene-*co*-VIMZ) latex particles to vary the surface densities of imidazole groups present on the latex surface independently of the particle size. Table V gives the density of functional group present on the latex particle surfaces as a function of the monomer addition method (Table III). The final number–average particle diameters (D_n) of V150-B, C, and D were the same, i.e., 166 nm within a deviation of 0.5 nm. These latex particles were grown identically in size starting from the R03-12 latex seed particles (D_n = 150 nm) by using the same amount of second-stage monomers, but a different monomer addition method. The particle size of V150-A was slightly smaller, 159.8 nm, because a
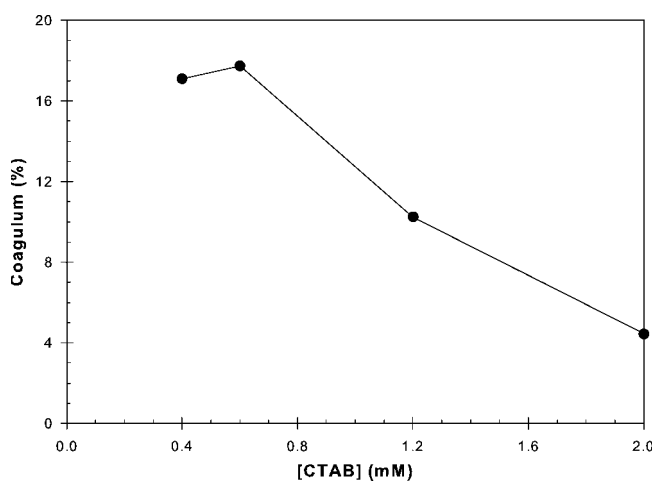
Figure 10 Dependence of the amount of coagulum on the concentration of CTAB at [VIMZ] = 3 wt %. The amount of coagulum was weighed and determined based on the total amount of monomers used in a recipe.

TABLE V
**Characterization of the V150 Latex Particles**

Batch no.	D_n (nm)	σ/D_n (%)	σ_C (μeq/m^2)	Å^2/Imidazole
Seed (R03-12)	150.0	8.9	0.77 ± 0.05	215.4
V150-A	159.8	6.5	0.90 ± 0.04	185.4
V150-A$_{THEO}$[a]			0.67 ± 0.04	
V150-B	166.4	7.2	1.58 ± 0.05	105.6
V150-C	166.0	6.2	1.65 ± 0.02	100.4
V150-D	166.2	5.2	1.53 ± 0.05	108.7

[a] Theoretical value of surface imidazole density (σ_C) of V-150 A = (σ_C of R03-12) × [(D_n of R03-12)/(D_n of V150-A)]^2.

lower amount of second-stage monomer was used. Importantly, no matter what method of monomer addition was used, the particle size distributions of all the resulting latex particles were narrow. These results indicate that there was no secondary nucleation. Instead, the mode of monomer addition was expected to affect the location of hydrophilic groups on the surface of the particle.

The surface density of imidazole groups of V150-A can be lower than that of the seed latex particles (R03-12) if the total surface area would only be increased by the growth of particles, maintaining a constant number of imidazole groups on the surface and rearrangement of the surface groups did not take place. The theoretical value for V150-A was 0.67 μeq/m^2, as calculated in V150-A$_{THEO}$ (see footnote to Table V for the calculation). However, the surface charge density of imidazole groups of V150-A latex particles grown only from styrene-swollen R03-12 was determined to be 0.90 μeq/m^2, which is greater than that of the seed particles (0.77 μeq/m^2), indicating that the imidazole groups had undergone surface rearrangement. When the hydrophobic styrene monomer swells the latex particles, the internal viscosity should be lowered and the glassy polymeric chains should become mobile at the reaction temperature. Since the particles were plasticized by the hydrophobic styrene monomer, some of the previously-buried hydrophilic moieties would be expelled to the surface of the particles. As a result, a rearrangement of the hydrophilic surface groups would take place, thus increasing the surface charge density. On the other hand, when the VIMZ monomer was added into the seed particles swollen with styrene, VIMZ added in the second-stage reaction might diffuse into the particles and be buried due to the lowered internal viscosity of the particles. In the same way, when the particles were grown from the seed particles swollen with both styrene and VIMZ, more of the VIMZ could be buried. However, since VIMZ is hydrophilic, it would be preferentially located close to the water phase, and not inside the particle. This hypothesis is supported by the observation that the surface charge density of V150-C prepared without monomer-swelling was the greatest.

Since the seeded emulsion polymerization of styrene and VIMZ using the poly(styrene-co-VIMZ) seed particles exhibited no secondary nucleation during the functional shell growth stage, the second-stage reactions were carried out by adding all of the second-stage monomers in the presence of R05-06 seed particles in an attempt to vary the number of imidazole groups present on the latex particle surface. Since there was a possibility for surface rearrangement of hydrophilic surface groups depending on the method of monomer addition, the seed particles were used without any monomer-swelling. The amount of VIMZ was varied from 0 to 47.1% (based on the amount of total second-stage monomer). In this way, latexes V195-A, B, C, and D were prepared successfully, with almost the same particle diameter, but with different surface imidazole densities, as shown in Figure 11. The surface imidazole density of the seed latex particles (R05-06) was determined to be 1.34 μeq/m^2 by conductometric titration. When styrene was added directly to the seed particles without monomer-swelling as in the case of V200-A, the surface imidazole density was decreased to 1.04 μeq/m^2 because particles only grew in size and a rearrangement of the hydrophilic surface groups was not significant. When only the styrene was added in the presence of styrene-swollen seed latex particles, the rearrangement of hydrophilic surface groups occurred, as previously discussed in the case of V150-A. Also, the imidazole surface density dramatically increased with an increase in the ratio of VIMZ to styrene in the second-stage monomer mixture. The resulting particles were of identical diameter and the coefficient of variations (σ/D_n) was within 5%, indicating that secondary nucleation did not occur. The imidazole surface density of V195-D,
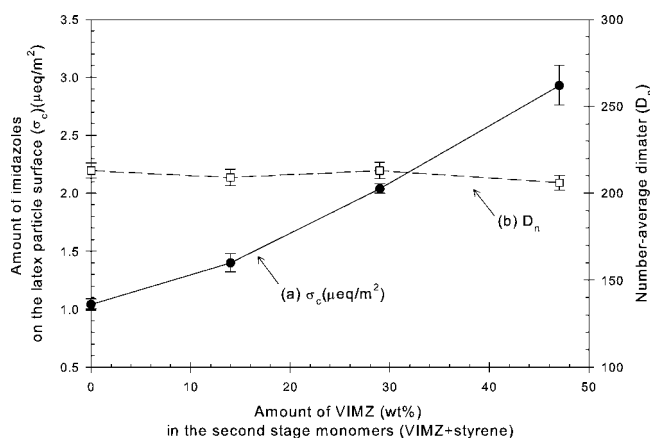
Figure 11 Dependence of the amount of VIMZ in the second stages monomers on: (a) the surface imidazole density (σ_C) and (b) the number–average diameter (D_n) of the resulting latex particles. R05-06 latex particles were used as seed particles (Table IV).

where the highest amount of VIMZ was used in this work, was 2.93 µeq/m^2, and the packing area per imidazole group was calculated to be 56.8 Å^2/imidazole.

CONCLUSIONS

Imidazole-functionalized latex particles can be prepared by two-stage emulsion copolymerization, where the particle size and surface charge can be controlled independently. In the case of the emulsifier-free emulsion copolymerization of styrene and VIMZ, secondary nucleation of particles was observed, in particular, when small amounts of VIMZ were used. The particles formed by secondary nucleation were initially adsorbed on the existing particles, and then grew to exhibit a bimodal particle size distribution at the end of reaction. When CTAB was used as stabilizer at a concentration below its cmc, a uniform particle size distribution was obtained. In addition, at least 3 wt % of VIMZ based on styrene was required to avoid a broadening in the particle size distribution. The amount of coagulum can be reduced by increasing the amount of stabilizer as well. The number of imidazole groups can be varied by adding different ratios of styrene and VIMZ in the presence of seed particles. A series of latex particles could be prepared with an almost identical diameter, but different surface charge densities. In particular, the method of monomer addition in the second stage resulted in the possible rearrangement of hydrophilic imidazole groups present on the latex particle surfaces, but no secondary nucleation process was observed even at the highest loading level of VIMZ. Controlling the surface properties of uniform latex particles independent of particle size can be expected for the preparation of model latex particles possibly for use in biomedical application or in optical devices.

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