

Effects of Three Crosslinkers on Colored pH-Responsive Core–Shell Latexes

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ABSTRACT: Environmentally responsive hydrogels have become attractive research subjects for many applications. In this work, a series of pH-sensitive and color-changing nanoparticles (nanogels) with core–shell structures were synthesized. The cores were blue latex particles synthesized by a miniemulsion technique with styrene and methacrylic acid as monomers and Neozapon Blue 807 as a dye. The shell was a pH-sensitive polymer that was precipitation-polymerized onto the core from 2-(diethylamino) ethyl methacrylate with *N,N'*-methylenebisacrylamide, poly(propylene glycol) diacrylate, and divinylbenzene as crosslinking agents. In the resultant latexes, the color was

observed to change from deep blue to pale blue as the pH of the system was changed from a high of 10 to a low of 3. The synthesized latexes and particles (gels) were then characterized with an ultraviolet–visible spectrometer, dynamic light scattering, Fourier transform infrared, and nuclear magnetic resonance. Atomic force microscopy was also used to investigate the different morphologies of the particles after the synthesized latexes were dried at different pH values. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 4093–4099, 2008

Key words: hydrogels; emulsion polymerization

INTRODUCTION

Environmentally responsive systems (hydrogels, nanoparticles, and micelles) are a topic of ongoing interest. The properties of these systems, such as hydrophilicity, molecular shape, and morphology, can respond to environmental changes such as the temperature, pH value, and light. Thermally sensitive hydrogels, especially those based on poly(*N*-isopropylacrylamide), are the most widely studied systems.^{1–3}

pH-sensitive systems have been prepared from monomers with carboxylic acids or other functional groups that can be protonated and deprotonated at different pHs. Methacrylic acid (MAA) and acrylic acid have been used to synthesize alkali-swelling hydrogels.^{4–6} Several acid-swelling hydrogels have also been synthesized. There are two main categories of monomers used for acid-swelling hydrogel synthesis. The first category includes the weakly basic vinylpyridines, such as 2-vinylpyridine.⁷ The second category includes amine acrylates or amine methacrylates. Amalvy et al.⁸ synthesized and characterized

pH-responsive microgels based on 2-(diethylamino)ethyl methacrylate (DEAEMA). The gels became swollen at pHs above 7 and deswelled at pHs below 7. Amino-based monomers are also used to synthesize self-assembling micelles with other polymerization methods such as oxyanion-initiated polymerization⁹ and atom transfer radical polymerization.¹⁰

In this work, a series of color-changing pH-responsive hydrogels with a core–shell structure were synthesized. The cores were composed of blue polystyrene particles prepared by miniemulsion. The shell was poly[2-(diethylamino)ethyl methacrylate] (PDEAEMA) crosslinked with three types of crosslinkers: *N,N'*-methylenebisacrylamide (MBA), poly(propylene glycol) diacrylate (PPGDA), and divinylbenzene (DVB). These crosslinkers can be used to crosslink acrylate monomers and have different properties, such as water solubility and molecular length. The pH-responsive properties and the effects of the crosslinkers were investigated through various techniques.

EXPERIMENTAL

Materials

The materials used in this work included styrene (Alfa Aesar, Ward Hill, MA), MAA (Aldrich, St. Louis, MO), sodium dodecyl sulfate (SDS; Sigma), sodium metabisulfite (Aldrich), ammonium persulfate (APS; Acros Organics, Belgium), the nonionic surfactant Triton X-405 (Dow Chemical, Midland, MI), DEAEMA (Aldrich), MBA (Polysciences, Inc.,

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TABLE I
Summary of the Types and Amounts of the Crosslinkers and Particle Size Information for the Synthesized Latex

Sample	Crosslinker		Latex diameter (nm)		Volumetric swelling factor
	Type	Molar ratio to DEAEMA	pH 9	pH 6	
1	PPGDA	1.7×10^{-3}	243	1171	4.8
2	PPGDA	3.4×10^{-3}	312	1013	3.4
3	PPGDA	5.1×10^{-3}	290	722	2.5
4	MBA	8.5×10^{-4}	311	—	—
5	MBA	1.7×10^{-3}	306	1052	3.4
6	DVB	8.5×10^{-4}	299	735	2.4
7	DVB	1.7×10^{-3}	354	708	2

The average diameter of the blue core particles was 108 nm.

Warrington, PA), PPGDA (Aldrich), and DVB and Neozapon Blue 807 dye (a copper phthalocyanine dye; BASF, Germany). All chemicals were used as received. De-ionized (DI) water was used throughout the research.

Preparation of the polystyrene core by miniemulsion polymerization

A monomer solution composed of 17 g of styrene, 1 g of MAA, and 2 g of Neozapon Blue 807 was added to 160 mL of distilled water containing 0.4 g of SDS and 0.4 g of Triton X-405. After mechanical stirring for 10 min at a speed of 400 rpm, the emulsion was homogenized at 18,000 rpm with an Ultra Turrax T18 homogenizer (IKA, Works Inc., Wilmington, NC) for 20 min.

The resulting miniemulsion was transferred to a 500-mL kettle equipped with a paddle stirrer, a nitrogen bubbler, and a reflux condenser. While being stirred at 150 rpm, the emulsion was heated under nitrogen to 45°C with a water bath. An initiator solution of 0.8 g of APS and 0.65 g of sodium metabisulfite in 20 mL of water was then added separately to the reactor at 0.1 mL/min with a KDS model 200 syringe pump (KD Scientific, Inc., Holliston, MA). After completion of the initiator feed, the polymerization was continued for another 2 h. The total polymerization time was 7 h. The yield was 95%. The resultant latex was purified by dialysis against distilled water for 3 days with Spectra/Por 1 membrane tubing (molecular weight cutoff: 6–8000, Spectrum Laboratories Inc., Rancho Dominguez, CA) to remove all surfactants, ions, and other initiator residues.

Preparation of the pH-sensitive shell

A polystyrene core solution (0.25 g of polymer solids) and de-ionized water to a total weight of 98 g were charged to a 500-mL kettle equipped with a mechanical stirrer, a nitrogen tube, and a reflux condenser. The pH was adjusted to 10 with 1M sodium hydroxide. The kettle was then put in a 70°C water

bath under a nitrogen purge. DEAEMA (30 g), various amounts of crosslinkers (see Table I), and 0.15 g of SDS were mixed in 250 g of water, and the pH was adjusted to 10 with NaOH. The mixture was homogenized at 6000 rpm for 10 min to form a pre-emulsion. APS (0.2 g) was dissolved in 25 g of water, and the pH was adjusted to 10. An 18-mL APS solution was added to the kettle at a speed of 0.1 mL/min. Five minutes after the initial APS addition, the pre-emulsion was added to the kettle over the course of 3 h by a MasterFlex monomer pump (Cole-Parmer Instrument Company, Vernon Hills, IL). The yield for this step of polymerization was 99%.

Characterization

¹H-NMR spectra were recorded in D₂O with a Mercury Innova (Palo Alto, CA) 200-MHz spectrometer. The samples were prepared by drying *in vacuo* at room temperature followed by redispersion in D₂O with an ultrasonic cleaner. The pH was adjusted with a deuterium chloride and sodium hydroxide solution (D₂O as a solvent). The particle size was measured with a Microtrac (North Largo, FL) UPA150 particle size analyzer. Solution transmission was measured on a DU-64 spectrophotometer (Beckman Coulter, Inc., Fullerton, CA) at a wavelength of 830 nm with the temperature controlled by a water circulator. Atomic force microscopy (AFM) images were obtained in the tapping mode with a standard NFESP silicon cantilever (length: 215–235 nm; spring constant: 3 N/m; resonance frequency: ca. 59–69 kHz; VEECO Probes, Camarillo, CA) in a Dimension 3000 scanning probe microscope (Digital Instruments, Woodbury, NY). The samples for AFM were prepared as follows: two drops of the latex were placed in 20 g of water, and then one drop of this diluted latex was put on a glass slide and air-dried.

RESULTS AND DISCUSSION

Synthesis of the pH-responsive core-shell hydrogel

The synthesis procedure is illustrated in Figure 1.

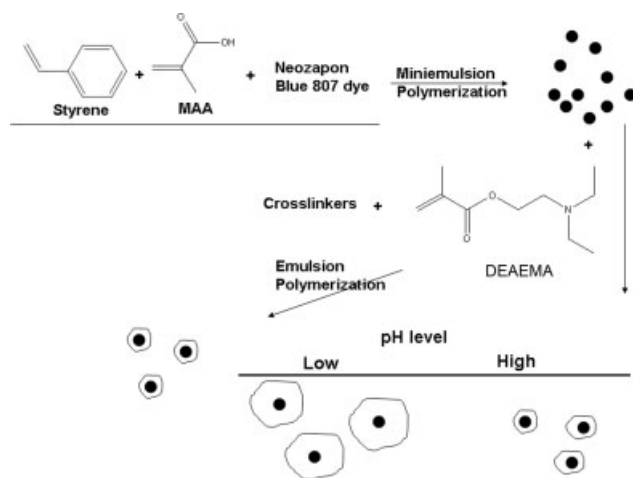
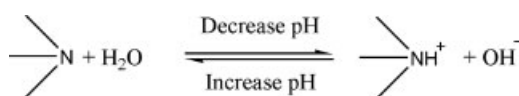


Figure 1 Illustration of the synthesis procedure.

In the first step, carboxylated blue polystyrene latex was synthesized with a miniemulsion polymerization technique. The synthesis step and process have been discussed in detail elsewhere.¹¹ After dialysis, the product of the miniemulsion polymerization was deep blue in color with a peak particle size of approximately 108 nm. These polystyrene particles were used as the core in the preparation of core-shell particles by the emulsion polymerization of DEAEMA and crosslinkers. At a high pH, the resulting PDEAEMA shell was hydrophobic and shrank around the blue core in water. At a low pH, the PDEAEMA shell was hydrophilic and swelled because of the protonation and deprotonation of the amino functional group (see Scheme 1).

The structural integrity of the core-shell particle was imparted by light crosslinking of the shell with three different difunctional monomers. The success of the shell preparation step was evidenced by the increase in particle size after the second step of polymerization. The results of particle size measurements are given in Table I. The partial NMR spectrum (solvent: D₂O) is shown in Figure 2. At a low pH, the NMR peaks are all sharp and visible because the outer shell is soluble under acidic conditions. As the pH increases, the outer shell becomes more and more hydrophobic, and the NMR peaks are smaller and smaller. Also, peak b, assigned to 6 aza-methylene protons, shifts from a lower concentration to around 3.1 ppm, and peak a, assigned to 6 methyl protons, shifts from a lower concentration to around 1.2 ppm because of the protonation of the tertiary amino groups in PDEAEMA. Similar shifts have



Scheme 1

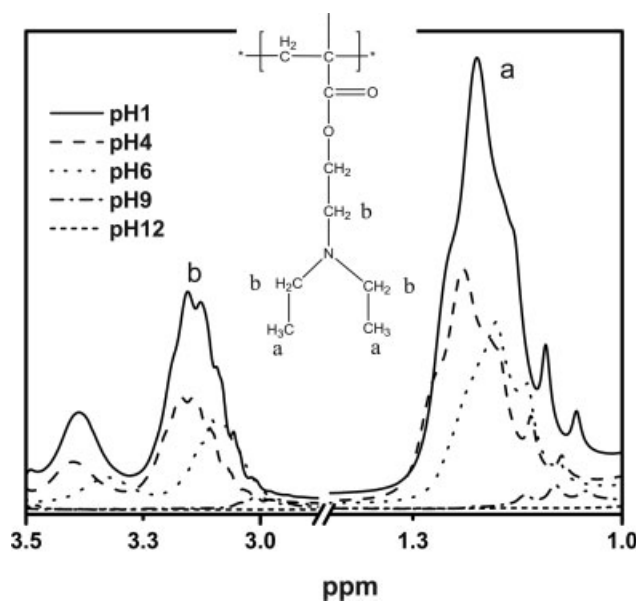


Figure 2 Specific peak changes in the NMR spectra of sample 1 at different pH values.

been reported for 2-(dimethylamino) ethyl methacrylate based triblock copolymers.¹²

Three crosslinkers were used in the research. As the amount of each crosslinker increased, the swelling factor decreased, as expected. Aside from sample 4, each sample showed a reversible color change with a change in pH. Because of the lower crosslink density of sample 4, the outer shell coalesced to form a white cotton precipitate as the pH changed from low to high. Samples 1, 5, and 7 have the same molar ratio of crosslinker to monomer. The color changes of samples 1, 5, and 7 at different pHs are shown in Figure 3 (note: there were some symbols on the bottles of sample 1 and 3; they were written with black markers and had no significant effect on the colors of the dispersions).

Although the amount of crosslinker in the monomer feed was very small, it had a significant effect on the properties of the final latex. Little color change was observed for sample 7. This was true of samples 3 and 6 also. These three samples had a much smaller volumetric swelling factor than the other samples.

Ultraviolet-visible (UV-vis) light transmission

The UV-vis absorption spectra of a polystyrene dispersion, blue latex dispersion, and dye-toluene solution are shown in Figure 4.

From Figure 4, it can be seen that the dye had a strong absorption at wavelengths between 600 and 700, whereas polystyrene had no absorption in this area. These absorption peaks were also observed for the blue latex dispersion synthesized by miniemulsion

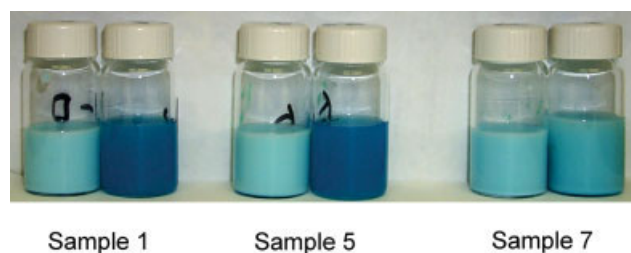


Figure 3 Color changes of samples 1, 5, and 7 at different pH values (the sample on the left had a pH of 9; the sample on the right had a pH of 3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymerization. In this research, the pH-sensitive outer shell of the synthesized latex particles (gels) changed from hydrophilic to hydrophobic as the pH changed from low to high. This transition caused the turbidity changes of the dispersion. To cancel the absorption changes of the dye as the pH and outer shell changed, the transmission at 830 nm was chosen as an indication of the turbidity of the dispersion.

Figure 5 shows the pH and transmission changes of sample 1 as a 0.1N HCl solution was added.

In almost all previous studies of environmentally sensitive hydrogels, the relationship between the hydrogel properties and environmental changes (temperature, pH, etc.) were investigated and reported. However, in this research, we noticed that the buffer behavior of the pH-sensitive outer shell and the dependence of the properties of the core-shell hydrogels on pH are not straightforward. From Figure 5, we can see that when a small amount of HCl was added to the dispersion, the pH decreased dramatically, but the transmission was hardly affected. This was because the amino group on PDEAEMA had not begun to undergo protonation and HCl itself had little effect on the transmission of

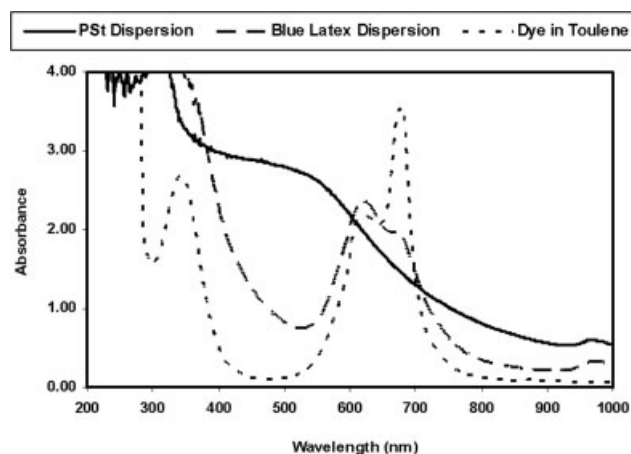


Figure 4 UV-vis spectra of the polystyrene (PSt) dispersion, blue latex dispersion, and dye solution in toluene.

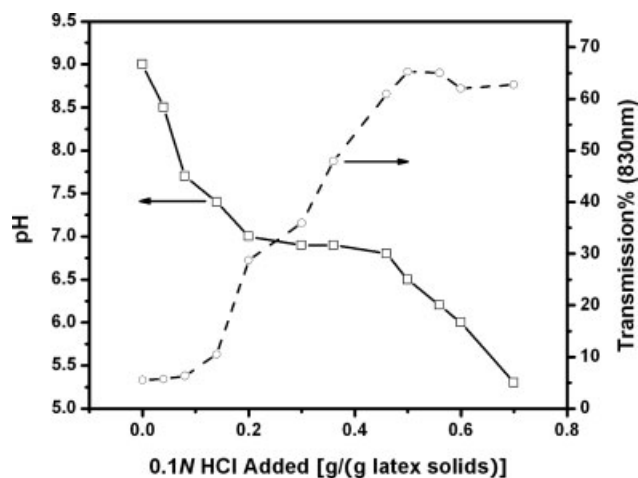


Figure 5 Effect of HCl on the pH and transmission of sample 1.

the dispersion. When the pH of the dispersion decreased to around 7.6, the transmission began to increase dramatically; this indicated that protonation of the amino group had begun. After the pH dropped below 7.6, the extra hydrogen ions added by the HCl solution started to be associated with the amino group because of the equilibrium shown in Scheme 1. During this stage, all hydrogen ions added (from HCl) were associated with the amino groups, so the hydrogen concentration in the dispersion did not change; thus, the pH remained constant. However, the protonation of the amino groups still went on as HCl was added, and the protonation made the PDEAEMA outer shell more soluble and swell; thus the transmission of the dispersion was still increasing, and the color of the dispersion continued to change. After this stage, when more HCl solution was added, all amino groups were protonated, and the outer shell did not change anymore; thus, the pH started to drop, but the transmission became stable. The samples with different crosslinkers showed similar buffer behavior (Fig. 6).

Figure 7 shows the effect of the crosslink density on the transmission. The transmittance changed dramatically as the pH was decreased. Sample 1, which had the lowest crosslink density, had the most dramatic increase in transmittance, whereas sample 3, which had the highest crosslink density, had a much smaller change in transmittance as the pH changed. The transmittance measured here represents only that of the outer shell because the core particles did not change much as the pH changed. The transmittance increase was caused by the swelling and deswelling of the outer shell. The blue color of the core could be seen when the transmittance increased sufficiently. For the visual effect, samples 1 and 2 showed apparent color changes with a change in the pH, but sample 3 did not.

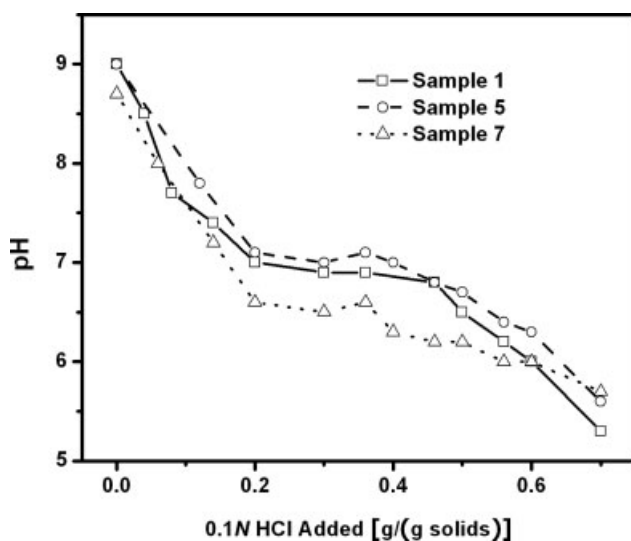


Figure 6 Buffer behavior of the samples with different types of crosslinkers.

The photograph in Figure 3 illustrates the effects of the crosslinker types on the color changes of the latex at different pHs; Figure 8 shows the effects of the crosslinker types on the transmittance of the latex.

From Figure 8, we can see that the transmittance of sample 1 with PPGDA as the crosslinker showed a dramatic change, whereas sample 7 with DVB as the crosslinker experienced little transmission change, with a pH change. From Table I, we can see that sample 7 had the smallest crosslinker volumetric swelling factor. Consequently, the crosslinkers had a very large effect on the swelling ability of the pH-sensitive core-shell particles, thus affecting the transmission of the samples. From the volumetric swelling factor in Table I, it is reasonable to assume

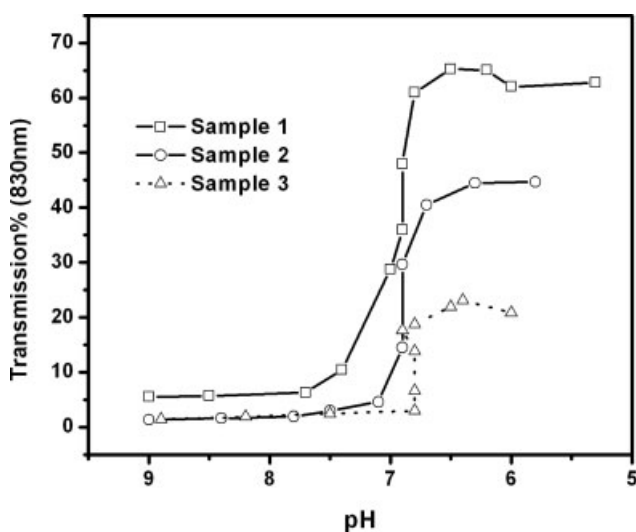


Figure 7 Effect of the crosslink density on the transmission of the dispersion.

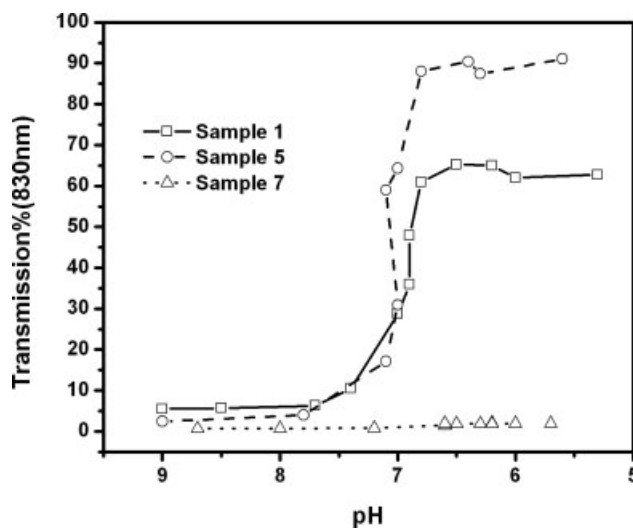


Figure 8 Effect of different crosslinkers on the transmission of the latex.

that the swelling ability of the pH-sensitive core-shell hydrogels was related to the distance between the two double bonds on the crosslinker molecules. In this way, we can explain that although the crosslink density was the same for samples 1, 5, and 7, sample 1 had a much larger volumetric swelling factor than the other two samples because the distance between two double bonds on the PPGDA molecules is much longer than that of the other two crosslinkers.

AFM

The morphology of pH-sensitive core-shell hydrogel particles after drying was observed by AFM. The samples were prepared at different pHs. HCl and ammonium hydroxide were used to adjust the pH of the sample as they did not leave any trace on the sample after drying. Figures 9 and 10 show the film or particles formed at different pHs on glass slides.

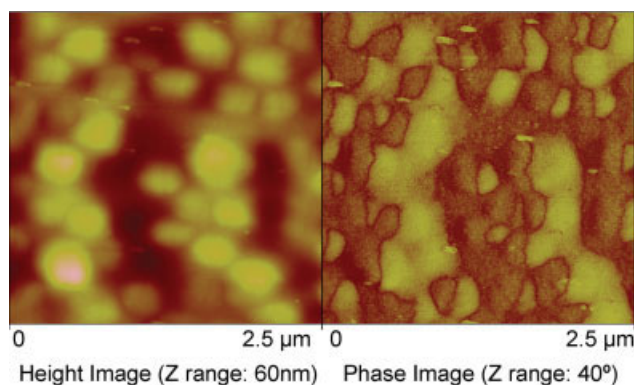


Figure 9 AFM images of sample 1 dried at pH 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The sample in Figure 9 was dried at a pH of 3, whereas the sample in Figure 10 was dried at a pH of 10. By comparing these two pictures, we can see that the size of the particles in Figure 9 was smaller than that of the particles in Figure 10. The hydrodynamic particle size of the synthesized pH-sensitive particles was more than 1 μm for sample 1, but the particles shown in Figure 9 were much smaller. This was due to the shrinkage of the outer shell after evaporation of the water. Another interesting phenomenon is that the outer shell formed a film, whereas the core particles distributed within it caused the observed raised areas. In the height image of Figure 9, the height of these raised locations is low (<50 nm) compared to the shrunken particle size (ca. 250 nm). The morphology of the particles cannot be identified from the phase image in Figure 9. The pH-sensitive outer shell was very soft at room temperature compared to the core particles because the glass-transition temperature (T_g) of the outer shell, composed of PDEAEMA, was only 16°C ,⁸ but T_g of the core, which was poly(styrene-co-methacrylic acid), was around 100°C . Also, at a low pH, the outer shells loosely surrounded the core particles as the outer shells were lightly crosslinked and highly swollen; as a result, the shell very easily coalesced and formed a film, whereas the core particles would not coalesce.

The sample in Figure 10 was prepared at a pH of 9. The particles are apparent in both the height image and phase image. At a high pH, the outer shell collapsed to surround the core particles to form whole large particles. Because the T_g of the outer shell was lower than room temperature, many particles stuck together; however, the outer shell did not form an even film. The height of these particles was much larger than the height of the raised locations in Figure 9, and the particles can be identified clearly from the substrate even in the phase image of Figure 10. The sizes of the particles shown in

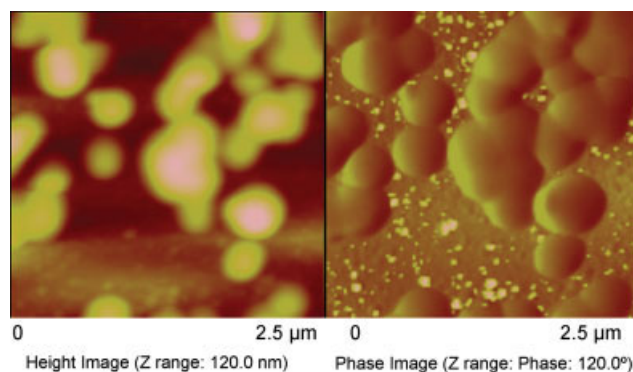


Figure 10 AFM images of sample 1 dried at pH 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

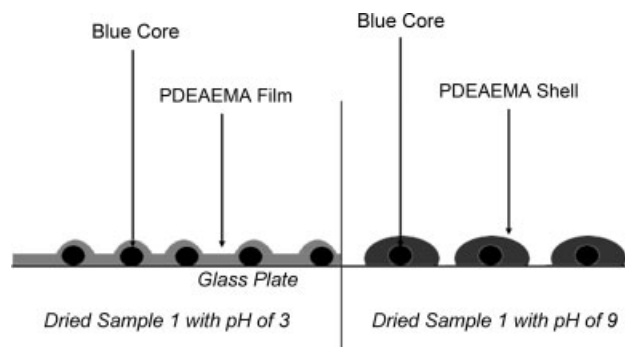


Figure 11 Illustration of the dried particle morphology in samples dried at different pH values.

Figures 10 were all larger than those measured by dynamic light scattering because the particles flattened as the sample was dried. A model in Figure 11 is proposed to describe the morphology of the dried samples.

CONCLUSIONS

pH-sensitive, color-changing latexes were prepared by the precipitation of PDEAEMA on the surface of blue polystyrene core particles synthesized by mini-emulsion polymerization. The outer shell of the resultant latexes changed from hydrophobic to hydrophilic as the pH changed from high (9) to low (3). The transition pH was between 7 and 8 for all latexes synthesized. The color of the latexes changed as the transition occurred. At a low pH, the outer shell was hydrophilic, swollen, and transparent, allowing the color of the blue core particles to be seen; at a high pH, the outer shell was hydrophobic and collapsed around the core particles. This caused the latexes to turn pale and white.

The pH-responsive properties of the synthesized latex particles were investigated by dynamic light scattering, NMR, visible light transmittance at 830 nm, and AFM. Buffer behavior was found for all samples when the pH was adjusted from high to low by the addition of 0.1N HCl. Within the range of the amounts of HCl solution added, the pH of the latex did not change, although the color and transmittance continued to change because of the existing equilibrium shown in Scheme 1.

Three types of crosslinkers (PPGDA, MBA, and DVB) were used during the polymerization. Although small amounts of crosslinkers were used, they had a great impact on the swellability of the outer shell and therefore affected the color-changing ability and range over which the transmittance would change with pH. At the same crosslink density for samples 1, 5, and 7, sample 7 (crosslinked by DVB) particles had the smallest volumetric swelling

factor; thus, as the pH changed, the color of the latex did not change significantly, and the transmittance changed much less than that of samples crosslinked by PPGDA and MBA. The swellability may be linked to the chain length between two double bonds on the crosslinker molecules. The crosslink density also affected the swellability of the outer shell. The higher the crosslink density was, the smaller the volumetric swelling factor was, and, consequently, a smaller change in color and transmittance was observed.

AFM pictures at different sample pHs showed the different morphologies of the particles. At a low pH, the outer shell was hydrophilic and formed an even film with core particles distributed in it when dried. Because of this, the raised locations in the height image have a very low height, and no particles can be identified in the phase image. For the samples prepared at a high pH, the outer shell was hydrophobic and collapsed around the core particles to form whole hydrophobic particles when dried. Although these particles tended to stick together,

they can be identified in both the height and phase images in Figure 10.

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