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ARTICLE

pH- and Temperature-Responsive Aqueous Foams Stabilized by Hairy Latex Particles

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Syuji Fujii^{a*}, Ko Akiyama^a, Saori Nakayama^a, Sho Hamasaki^aShin-ichi Yusa^b and Yoshinobu Nakamura^{a,c}Received 00th January 2012,
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Polystyrene (PS) particles carrying pH- and temperature-responsive poly[2-(dimethylamino)ethyl methacrylate] (PDMA) hairs (PDMA-PS particles) were synthesized by dispersion polymerization. The diameter, diameter distribution, morphology, chemical composition and surface chemistry of the particles were characterized using scanning electron microscopy (SEM), elemental microanalysis, dynamic light scattering and zeta potential measurements. The hydrophilicity-hydrophobicity balance of the PDMA could be tuned by varying both pH and temperature and therefore these sterically-stabilized particles acted as doubly stimuli-responsive stabilizers for aqueous foams by adsorption and desorption to/from the air-water interface. At and above pH 6.0, in which range the PDMA hairs were either non-protonated or partially protonated, particle-stabilized foams were formed at both 23 and 55 °C. The foam prepared at 55 °C was the more stable of the two, lasting for at least 24 h, whereas the 23 °C foam destabilized within 24 h. SEM studies indicated that the particles adsorbed at the air-water interface as monolayers at 23 °C and as multilayers at 55 °C. At and below pH 5, in which range the hairs were cationic, hydrophilic and water-soluble, no foam was formed irrespective of temperature. Rapid defoaming could be induced by lowering the solution pH at both temperatures, due to rapid in situ protonation of the PDMA hairs, prompting the PDMA-PS particles to desorb from the air-water interface. The foaming and defoaming cycles could be repeated at least five times.

Introduction

Solid particles are known to stabilize foams by adsorbing to gas-liquid interfaces¹⁻⁷. Inorganic particles, such as silica⁸⁻¹¹, alumina^{12,13} and graphene¹⁴, as well as organic materials, including polymer particles¹⁵⁻²¹ and polymeric microrods²², and natural particles, such as bacterial cells²³ and aquatic hyphomycete spores²⁴, can all function as particulate foam stabilizers.

Controlling the stability of foams is crucial and the destruction of foams (defoaming) is often required in practical applications such as in the paper and oil industries²⁵. However, there are few examples of the in situ defoaming of particle-stabilized foams. It has been shown that magneto-responsive foams can be prepared using a mixture of Fe and hypromellose phthalate particles as the foam stabilizer, and such foams can be defoamed by the application of a magnetic field^{26,27}. It has also been demonstrated that the stability of foams can be controlled by tuning the hydrophilicity-hydrophobicity balance of the particle surfaces. This balance can be quantified by the contact angle, θ (measured through the aqueous phase)¹⁻⁷. Particles have been reported to best stabilize foams when θ is between 43 and 90°, such that the particles are partially wetted by both the gas and liquid phases²⁸. Conversely, the adsorption energy of

particles at the air-water interface with a contact angle near 0° is so low that the particles cannot form stable foams and aqueous particle dispersions are instead obtained. The contact angle of the particles and consequently the energy required to remove these particles from the air-water interface can be modified using a particulate foam stabilizer whose surface hydrophilic-hydrophobic balance can be controlled by external stimuli. Poly(acrylic acid)-stabilized polystyrene (PS) particles have been reported to act as a pH-responsive particulate foam stabilizer²⁹. Being stable solely under acidic conditions, such foams are destabilized by the addition of an aqueous alkaline solution; the poly(acrylic acid) on the PS particle surfaces is deprotonated and becomes hydrophilic as the pH is increased and the PS particles are desorbed from the air-water interface, which leads to defoamation. Recently, PS latex particles carrying pH-responsive poly[2-(diethylamino)ethyl methacrylate] (PDEA) hairs (PDEA-PS particles) have also been reported to work as both a pH-responsive particulate foam stabilizer and an acid-induced defoaming agent³⁰. In this system, foams are stable under basic conditions but are destabilized by the addition of acid.

In the present study, PS particles carrying poly[2-(dimethylamino)ethyl methacrylate] (PDMA) hairs (PDMA-PS

particles) were used as a particulate foam stabilizer sensitive to two stimuli: pH and temperature (Figure 1). Detailed characterizations of particle-stabilized foams were conducted with respect to their stability, structure and pH and temperature responses.

pH-responsiveness

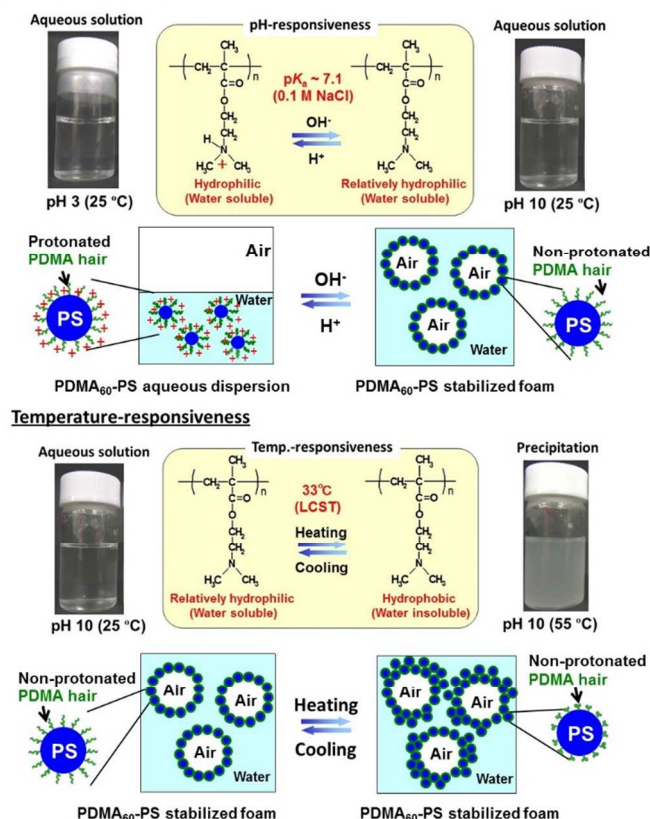


Figure 1. Application of PS particles carrying poly[2-(dimethylamino)ethyl methacrylate] (PDMA) hairs as a pH- and temperature-responsive particulate foam stabilizer. Digital camera images show aqueous solutions of PDMA homopolymer.

Results and discussion

The PDMA homopolymer is a weak polybase that is soluble in aqueous media below pH values of approximately 7 due to protonation of its tertiary amine groups. At pH 8 or above, the homopolymer has low or zero charge density and hydrogen bonding is solely responsible for its water solubility. Under these conditions, the neutral PDMA chains exhibit inverse temperature solubility, characterized by a lower critical solution temperature (LCST)^{31,32}. The LCST of PDMA ($M_n = 22,400$, $M_w/M_n = 1.67$; synthesized by free radical polymerization) in a 0.1 M NaCl aqueous solution (1.0 %) was determined to be 34.5 °C by measuring percent transmittance at 545 nm (see ESI).

The PDMA-PS particles used in this study were prepared by dispersion polymerization in isopropanol (IPA) using a PDMA macroinitiator as an inistab, based on the results of our previous study³³. Prior to purification, the milky-white IPA dispersion contained excess free PDMA macroinitiator as well as various by-products, and no foam was observed even after vigorous agitation. After four water-based centrifugation-redispersion cycles, the IPA had been completely replaced with water as the

dispersion medium. Figure 2 shows an SEM image of dried PDMA-PS particles that confirms their spherical morphology. The number-average particle diameter (D_n) and the associated coefficient of variation were estimated from this image to be 380 ± 70 nm and 18.1%, respectively. Laser diffraction particle size analysis indicated that the volume-average diameter (D_v) in IPA was 380 ± 170 nm, which is similar to the number average diameter. Elemental microanalysis determined that the percentage PDMA loading in the PDMA-PS particles was 2.86% by mass, based on a comparison of the nitrogen content of the particles to that of a PDMA homopolymer synthesized by free radical polymerization ($N = 0.24\%$ for the PDMA-PS particles and 8.40% for the PDMA homopolymer). The PDMA component is soluble in IPA, and therefore its presence on the PS particle surfaces should act as a colloidal protective layer and generate a stable dispersion of the PDMA-PS particles in the liquid, similar to the behavior of PDEA-PS particles³⁴. Assuming that all the PDMA chains are covalently bonded at the PS particle surfaces and that the PS particles have a D_n of 380 nm (determined from the SEM images), the area occupied by the PDMA chains at the surface of each particle was calculated to be 8.2 nm² from the elemental microanalysis results noted above³⁴ using a PS density value of 1.06 g/cm³³⁵. The square root of the occupied molecular area (2.9 nm) is comparable to the diameter of gyration (1.38 nm) of a PDMA chain (degree of polymerization = 60), indicating that the grafting density at the particle surface appears to have produced PDMA chains with random-walk configurations. This is noteworthy, since it is also possible for PDMA-PS block copolymers to form a mixed surface layer of PS and PDMA having a brush-type configuration³⁴.

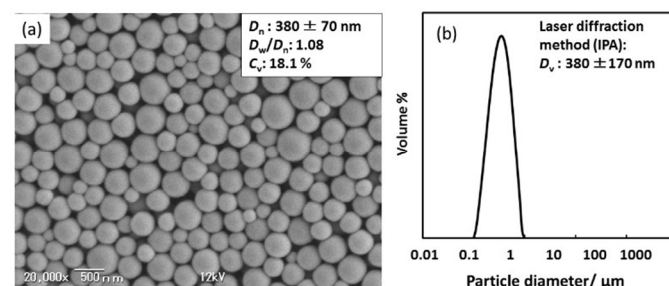


Figure 2. (a) SEM image and (b) laser diffraction particle size analysis data of PDMA-PS latex particles synthesized by dispersion polymerization. In (b) the PDMA-PS latex particles were dispersed in isopropanol.

The degree of protonation of the amine groups (α) was calculated from Eq. 1, below.

$$\alpha = 1/(1 + 10^{pH-pK_a}) \quad (1)$$

Here pK_a is the proton dissociation constant of the amine group. Figure 3 shows the relationship between α and pH, calculated on the basis of Eq. 1 and using a pK_a value of 7.1 (0.1 M NaCl) as determined by acid-base titration. This plot shows the dependence of the α value on pH, especially under conditions in which the pH and pK_a are close to one another, although it should be noted that these α values are rough estimates. In reality, closely positioned dissociable groups will affect one another and the dissociation curve will be less steep³⁶⁻³⁸.

The zeta potentials and hydrodynamic diameters (D_h) of the PDMA-PS particles were measured at pH 3 and 10. At pH 3, the zeta potentials were positive at 25 and 55 °C and had values

of 30.5 and 28.0 mV, respectively, indicating that the particle surfaces had a cationic character due to protonation of the tertiary amine groups on the PDMA hairs. The D_h values at pH 3 were determined to be 500 and 494 nm at 25 and 55 °C, which are in reasonably good agreement with the diameters estimated by SEM analysis. The zeta potential at pH 10 was 0.1 mV at 23 °C, a value that results from deprotonation of the PDMA hairs. Under the same conditions, the D_h was 494 nm with a narrow particle size distribution, suggesting that the PDMA-PS particles were dispersed due to the significant water-solubility of the PDMA hairs even in their non-protonated form, such that they acted as a colloidal stabilizer. In contrast, at pH 10 and 55 °C, the PS particles were observed to flocculate to form precipitates which could be seen on visual observation. In alkaline media above the LCST, the amine groups were not protonated and the PDMA stabilizer therefore collapsed on the particle surface in the aqueous media, leading to flocculation of the PDMA-PS particles. The aqueous electrophoresis studies confirmed that the surface charge density on the PDMA-PS particles varied with pH and, more importantly, this zeta potential result indicated that the hydrophilicity-hydrophobicity balance could be tuned by changing the pH. Thus, the particles were much more hydrophilic in acidic media due to the protonated PDMA hairs and less hydrophilic in basic media due to deprotonation of the PDMA. Therefore, it is important to consider the relationship between the pH of the aqueous dispersion and the degree of protonation of the amine groups on the PDMA chains.

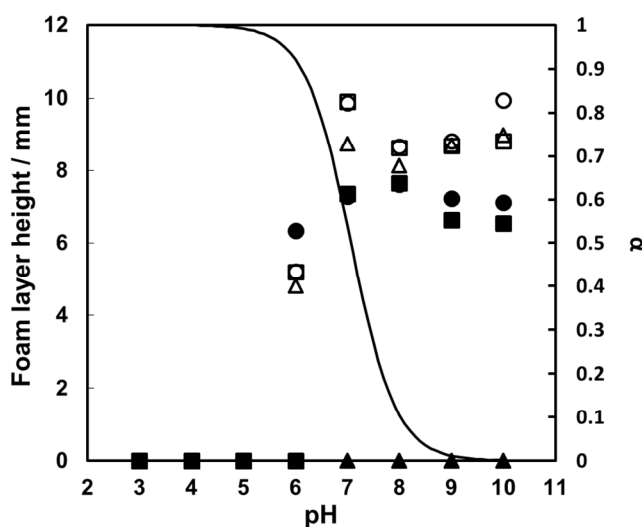


Figure 3. pH- and temperature-dependent behavior of foams prepared using the PDMA₆₀-PS latex particles (5.0 wt%, 0.1 M NaCl). Height of the foam layer versus pH of the aqueous dispersion recorded at different times: immediately after preparation (●, ○), after 1 hour (■, □) and after 24 hours (▲, △). (●, ■, ▲) 23 °C and (○, □, △) 55 °C. Line indicates degree of ionization of dimethylamino group of PDMA versus pH (0.1 M NaCl).

Foam stability depends on the wettability of the particles at the air-water interface. Therefore, we expected that the behavior of foams stabilized with these PDMA-PS particles would change significantly depending on both pH and temperature. To evaluate foamability and foam stability, the height of the foam layer was measured after agitating glass vessels containing aqueous dispersions of the PDMA-PS latex particles (0.1 M

NaCl, 5.0 wt%) at different pH values and at 23 or 55 °C (Figure 3 and ESI).

Figure 3 shows the height of the foam layer as a function of the pH of the aqueous dispersion, immediately after preparation and at various times afterwards (see also ESI). The height of the foam layer was defined as the distance between the foam/dispersion boundary and the three phase contact line of the air, glass and foam. At and above pH 6.0 and at 55 °C, the foams were stable for at least 24 h, although the height gradually decreased with time due to water drainage and partial coalescence of air bubbles. At 23 °C, foams were also formed at and above pH 6.0, although these foams disappeared within 24 h. At pH 6.0, foam stability was lower than at pH \geq 7.0 and the foam collapsed within 1 h. Interestingly, foamability at 55 °C was lower than that at 23 °C at pH 6.0. The possible reason for this phenomenon is an increase in the degree of protonation of amine groups of PDMA at pH 6.0 (near pK_a value) resulting in increased particle hydrophilicity at higher temperature³⁹. The foam stability was higher at 55 °C than at 23 °C, since the surfaces of PDMA-PS particles carried dehydrated PDMA hairs at 55 °C and were thus more hydrophobic, resulting in an increased adsorption energy at the air-water interface and consequently greater foamability and foam stability⁴⁰. No foam could be prepared at low pH values (e.g. 3.0, 4.0 and 5.0), at which the particles were covered with cationic PDMA hairs at both temperatures.

It has been demonstrated that the PDMA-PS particles could work as a particulate emulsifier for *n*-hexane/water emulsion and an emulsion phase inversion occurred from oil-in-water at low temperatures to water-in-oil at higher temperatures³⁹. In our foam system, a phase inversion from air-in-water to water-in-air never occurred and foam were prepared at high temperature without fail. The difference in foam and emulsion systems should be observed due to a difference in wettability for the PDMA-PS particles to air and the oil: the PS particles with dehydrated PDMA hairs can be preferentially wetted by the oil but not air (dehydrated PDMA hairs is still hydrophilic against air which could be considered to be the most hydrophobic oil.).

It has been reported that the air-water interface is negatively charged^{41,42}, therefore, positively charged particles are expected to adsorb to the interface and thus stabilize foams²¹. However, the cationic PDMA-PS hairy particles were not found to stabilize foams at and below pH 5.0, at which value the PS particles would have had protonated, water-soluble PDMA hairs. One possible factor preventing the adsorption of the cationic PDMA-PS particles may have been an image charge effect at the air-water interface. If a charge, Q , is located in an aqueous medium with a dielectric constant larger than that of air, an image charge, Q' , is present and may be calculated using the following equation⁴³⁻⁴⁶.

$$Q' = -\left(\frac{\epsilon_a - \epsilon_w}{\epsilon_a + \epsilon_w}\right)Q \quad (2)$$

where ϵ_a and ϵ_w are the dielectric constants of air and water, respectively. Assuming that $\epsilon_a = 1$ and $\epsilon_w = 78$, then Eq. 2 gives Q' as $0.957Q$. It follows that image charges of the cationic PDMA-PS particles will be present that have the same sign and almost the same charge⁴⁷. It has been calculated that one PDMA-PS particle will have 3.2×10^6 amine groups (see ESI), which should lead to strong electrostatic repulsion from the interface. This repulsive image force overcomes the attractive interaction between the anionic air-water interface and the

cationic PDMA-PS particles and, as a result, the PDMA-PS particles cannot adsorb at the air-water interface. Recently, it was theoretically and experimentally demonstrated that positively charged particle adsorption to the negatively charged oil-water interface from aqueous phase is suppressed due to image charge effect, which prevents the formation of particle-stabilized emulsion⁴⁸. Another factor responsible for the lack of adsorption of the PDMA-PS particles could be an entropic effect associated with the counter anions present in the vicinity of the protonated PDMA hairs. When the PDMA-PS particles carrying solvated PDMA hairs approach the air-water interface, the entropies of the PDMA hairs and the counter anions decrease (in other words, the number of possible configurations of the PDMA hairs is reduced and the space in which the counter anions can situate themselves decreases), which is unfavorable with regard to the Gibbs free energy of the system. Based on all the above observations, the significant influence of pH on the foamability of these aqueous particle dispersions is similar to the effect of pH on foams stabilized by PDEA-PS latex particles³⁰.

The structures of the particle-stabilized foams were observed using an optical microscope at 25 °C (Figure 4). Agitation of a pH 3.0 aqueous dispersion of the PDMA-PS particles did not result in any foam, but rather imparted Brownian motion to the particles (Figure 4a). At and above pH 6.0, particle-stabilized polydisperse bubbles and free colloiddally stable PDMA-PS particles were observed, indicating that a slightly hydrophobic surface is sufficient for the particles to adsorb at the air-water interface. The foam was composed of spherical and near-spherical bubbles with sizes ranging from *ca.* 60 μm to a few mm (Figures 4b-f).

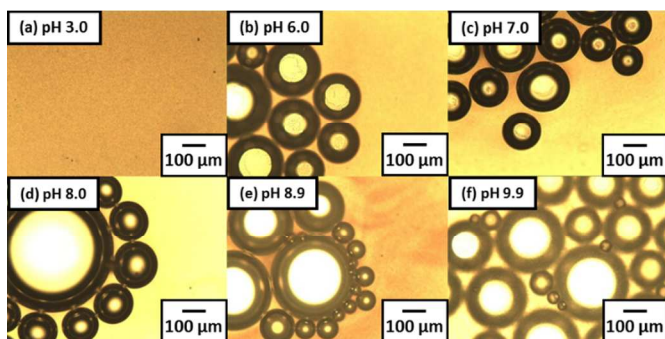


Figure 4. Optical microscopy images of foams formed at pH values between 3.0 and 9.9 in the wet state immediately after preparation.

The foams prepared at and above pH 6 at 23 and 55 °C were stable and retained their three-dimensional structures even after drying. Some coalescence occurred, but visual inspection indicated that the bubble size distribution was not changed significantly by the drying process. The microstructures of the dried particle-stabilized foams were investigated in more detail using SEM (Figures 5 and 6).

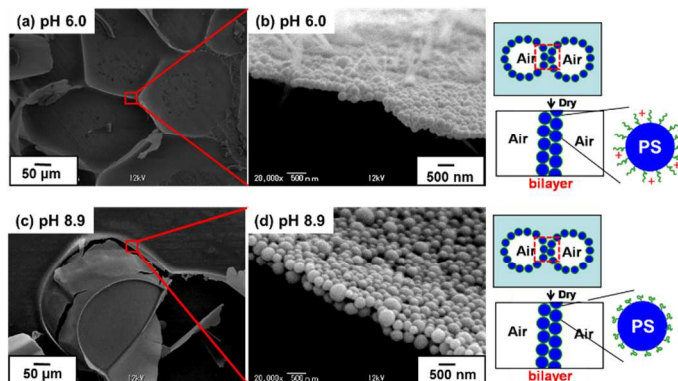


Figure 5. SEM images of foams stabilized with PDMA-PS latex particles (5.0 wt%, 0.1 M NaCl) at 23 °C and at (a, b) pH 6.0 and (c, d) pH 8.9. Images (b) and (d) are magnified sections of (a) and (c), respectively.

Figure 5 shows SEM images of the particle-stabilized foams prepared at pH values of 6.0 and 8.9 at 23 °C. At both pH values, particle bilayers were observed, suggesting that air bubbles were stabilized by PDMA-PS particle monolayers. The PDMA hairs were evidently water-soluble over a wide range of pH at 23 °C and the PDMA-PS particles, which were dispersed in aqueous media, presumably adsorbed to the air-water interface as a monolayer and stabilized the air bubbles. The widespread formation of particle bilayers strongly suggests that most of the wet air bubbles were stabilized by monolayers of adsorbed particles, and that these monolayers were forced together to form bilayers during water drainage from the foams. Similar results were reported by Fujii et al.^{19,20} and by Dupin et al.⁴⁹. There is, however, little evidence for the exquisite long-range ordering of latex particles in the latex layers, as observed by Fujii et al.^{19,20}. The lack of long-range order is presumably related to the somewhat higher polydispersities obtained for the PDMA-PS particles used in the present work; the coefficient of variations were 18.1% for the PDMA-PS particles compared to *ca.* 5% for the PS particles used in the previous studies^{19,20}.

Figure 6 shows SEM images of dried foams prepared at 55 °C using the PDMA-PS particles at pH 6.0 and 8.9 and also dried at 55 °C. Focusing on the top surfaces of the dried bubbles confirmed the presence of the PDMA-PS particles. A relatively smooth surface, in which the PDMA-PS particles were nearly close-packed, was evident in samples from both pH systems (Figure 6). The internal particle microstructures were also examined after rupturing the dried foam. In the case of the foams prepared at pH 6.0, well-defined particle bilayers were again observed in most cases (Figure 6b). For the foams prepared at pH 8.9, latex multilayers (2-5 layers) were observed (Figure 6d), which suggests that flocculated PDMA-PS particles stabilized the air bubbles.

The effect of temperature on the microstructures of the particle-stabilized foam was also investigated. This experiment was conducted at pH 9, at which foam could be formed at both 25 and 55 °C (Figure 7). The foam was initially prepared at 25 °C and then dried at the same temperature. As already observed, a bilayer composed of the PDMA-PS particles was observed in SEM images (Figures 7a, b). The aqueous foam prepared at 25 °C was then heated to 55 °C and agitated using a touch mixer. SEM images of the foam dried at 55 °C indicated the formation of multilayers of the particles (Figures 7c, d). This result demonstrates that the PDMA-PS particles that lost colloidal

stability due to the dehydration of their PDMA hairs at 55 °C (above the LCST) underwent flocculation in the aqueous media and were adsorbed to the surfaces of the bubbles previously stabilized with PDMA-PS particle monolayers. The foam was subsequently cooled to 25 °C and again agitated. Interestingly, the majority of the observed coatings consisted of PDMA-PS particle bilayers (75 %), while fewer multilayers were seen (25 %) (Figures 7e, f). Evidently, the PDMA-PS particles initially adsorbed to the bubble surfaces as multilayers were re-dispersed into the aqueous media as single particles carrying solvated PDMA hairs, leaving particle monolayers on the bubble surfaces.

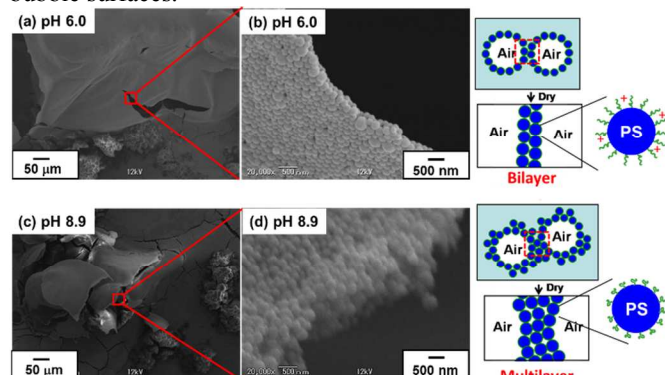


Figure 6. SEM images of foams stabilized with PDMA-PS latex particles (5.0 wt%, 0.1 M NaCl) at 55 °C and at (a, b) pH 6.0 and (c, d) pH 8.9. Images (b) and (d) are magnified sections of (a) and (c), respectively.

Finally, based on our observations of the pH-dependent particle-stabilized foams prepared in the batch mode, we investigated the possibility of inducing defoaming of a particle-stabilized foam by subsequent pH adjustment (Figure 8). For this purpose, a particle-stabilized foam was prepared at pH 9 and allowed to stand for 10 minutes, after which it was rapidly (within 1 minute) defoamed (or coalesced) by lowering the pH value of the aqueous phase to 4 by the addition of a small volume of concentrated aqueous HCl, followed by vigorous agitation with a touch mixer. This experiment was performed at both 23 and 55 °C. The observed defoaming presumably occurred because the PDMA-PS particles acquired a highly hydrophilic surface in situ as the PDMA hairs were protonated. Therefore, the PDMA-PS particles were no longer adsorbed at the air-water interface and thus detached from the interface, leading to disruption of the foam and phase separation to form a macroscopic air phase and an aqueous dispersion of PDMA-PS particles. This foaming-defoaming cycle was readily reversible over at least five sequential trials, with essentially equivalent amounts of foam obtained on each agitation. The foam heights measured for the 55 °C system were always higher than those of the 23 °C sample, showing that the PS particles carrying dehydrated PDMA hairs at 55 °C functioned as a more effective foam stabilizer compared to the same particles at 25 °C.

The encapsulation of air bubbles in water using stimulus-responsive latex particles in this manner may have potential applications in food manufacturing, cosmetic formulations and personal care products.

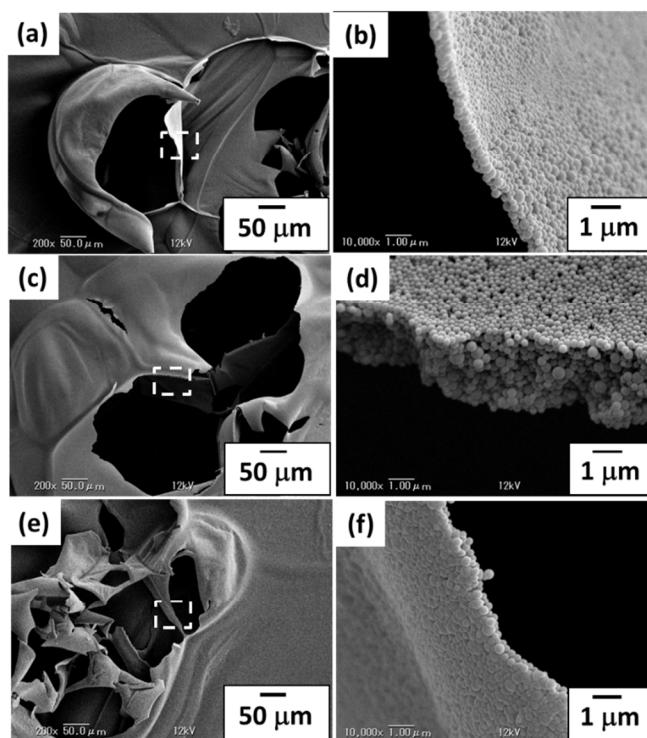


Figure 7. SEM images of foams stabilized with PDMA-PS latex particles (5.0 wt%, 0.1 M NaCl): (a, b) after agitation at pH 9 and 25 °C, (c, d) after agitation of the foam shown in (a, b) at pH 9 and 55 °C and (e, f) after re-agitating the foam shown in (c, d) at pH 9 and 23 °C. Images (b, d and f) are magnified sections of (a, c and e), respectively.

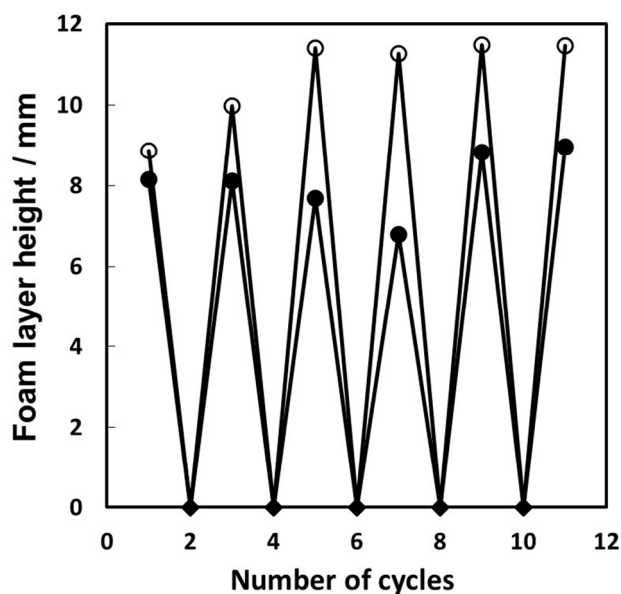


Figure 8. Height of the foam layer versus the number of pH cycles at: (●,○) pH 9 and (◆,◇) pH 4. Filled and empty symbols indicate 23 and 55 °C data. HCl and NaOH were used to adjust the pH of the aqueous media. These data indicate the reversible foaming and defoaming of a mixture of air and an aqueous PDMA-PS dispersion by varying pH.

Experimental

Materials. Styrene, 2-(dimethylamino)ethyl methacrylate (DMA; 98%), isopropanol (IPA; purity 99%) and aluminum oxide (activated, basic, Brockmann 1, standard grade, ~150 mesh, 58 Å) were purchased from Sigma-Aldrich. Styrene was treated with basic alumina to remove the inhibitor and then stored at -18 °C prior to use. 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086) was provided by Wako Chemicals. NaCl (99.5%), NaOH (98%) and an aqueous HCl solution (37%) were purchased from Sigma-Aldrich. A PDMA macroinitiator with a degree of polymerization of 60 (the degree of polymerization of the PDMA chain beside the central azo group) was synthesized by atom transfer radical polymerization, as reported previously⁵⁰. Deionized water (<0.06 µS cm⁻¹, Advantec MFS RFD240NA: GA25A-0715) was used in all work.

Synthesis of PDMA-PS latex particles

Dispersion polymerization of styrene (25.0 g) was performed in batch mode at 80 °C using the PDMA macroinitiator (4.64 g, 2.40×10^{-4} mol) and VA-086 initiator (0.623 g, 2.16×10^{-3} mol), applying a PDMA-to-VA-086 molar ratio of 10/90. The number-average molecular weight (M_n) of the PDMA macroinitiator was determined to be 21,500 and 19,400 by gel permeation chromatography (GPC) and ¹H nuclear magnetic resonance (¹H NMR), respectively, which accorded well with the theoretical value of 19,362 g/mol. The molecular weight distribution (M_w/M_n) was determined to be 1.12 by GPC. Styrene, PDMA macroinitiator and VA-086 were added to IPA (250 mL) in a one-necked 500 mL flask with a magnetic stir bar and the mixture was vigorously stirred at room temperature until all the compounds were dissolved, after which the solution was degassed using a nitrogen purge. Polymerization was initiated by placing the flask in an oil bath (80 °C), and was allowed to proceed for one week with continuous stirring at 300 rpm under a nitrogen atmosphere. Successive centrifugation-redispersion cycles were used to purify the resulting latex, with each supernatant being decanted and replaced with IPA (3 cycles; 5000 rpm, 30 min.) and then deionized water (4 cycles; 15,000 rpm, 30 min.). A Hitachi CF16RX II centrifuge with a Hitachi T15A 36 rotor was used.

GPC and NMR measurements

GPC measurements were performed using a Jasco RI-2031 Plus refractive index detector together with a Jasco PU-8020 pump and a Shodex OHpak SB-804 HQ column (exclusion limit ~107) working at 40 °C and a mobile phase flow rate of 0.6 mL/min. A 0.3 M Na₂SO₄ aqueous solution containing 0.5 M acetic acid was used as the eluent. The values of M_n and M_w/M_n were determined based on calibration with standard poly(2-vinyl pyridine) samples. ¹H NMR spectra were obtained with a Bruker DRX-500 spectrometer operating at 500.13 MHz.

Characterization of PDMA-PS particles

Chemical composition of the PDMA-PS particles
CHN elemental microanalyses were carried out using a CHN-Corder MT-5 (Yanaco, Japan). The PDMA loading of the PDMA-PS particles was determined by comparing the nitrogen content of the particles to that of a PDMA homopolymer prepared by free radical solution polymerization.

Aqueous electrophoresis and dynamic light scattering

Zeta potentials were calculated from the electrophoretic mobility of solutions, using a Malvern Zetasizer Nano ZS. Measurements were conducted at pH 3 and 10 with dispersions diluted by adding NaOH,

starting from an initial pH of 3. Zeta potentials were determined by averaging the results of five runs at each pH value. Following electrophoretic mobility measurements at each pH, dynamic light scattering of the aqueous PDMA-PS dispersion was conducted using the same instrument at a scattering angle of 173°. Three measurements were made at each pH.

Foam preparation

Sufficient NaCl was added to a 5.0 wt% aqueous dispersion of PDMA-PS latex particles so as to obtain a 0.1 M NaCl solution, such that NaCl was used as the background electrolyte. The solution pH was adjusted as required by the addition of concentrated aqueous solutions of either HCl or NaOH, after which 5.00 g of this aqueous latex dispersion was placed in a glass vessel (13.5 mL) with a screw cap and then agitated using a touch mixer (Tube Mixer Trio TM-1F, As One) for 1 min at 2500 rpm at 23 or 55 °C. Prepared foams were stored at either 23 or 55 °C. Foam heights were measured using a ruler; the foam height was determined to be 0 mm when a planar interface was visible between the aqueous dispersion and the air surface.

Characterization of foams

Digital camera

Photographs of samples in glass vials were acquired with a digital camera (GX200, Ricoh).

Optical microscopy

The aqueous foams were placed on a microscope slide and observed using an optical microscope (Shimadzu Motic BA200) fitted with a digital camera system (Shimadzu Moticom 2000).

Scanning electron microscopy

Scanning electron microscopy (SEM; Keyence VE-8800, 12 kV) studies were conducted on dried samples sputter-coated (Elionix SC-701 Quick Coater) with Au. The number-average diameter of the PDMA-PS particles ($n = 100$) was determined from SEM observations.

Conclusions

Submicrometer-sized PS particles carrying PDMA hairs were successfully synthesized by dispersion polymerization, and their size, size distribution, and chemical composition were well characterized. The performance of the PDMA-PS latex particles as a pH- and temperature-responsive particulate foam stabilizer was evaluated. The PDMA-PS particles were able to stabilize aqueous foams at and above pH 6.0, whereas no foam was formed at and below pH 5.0, at both 23 and 55 °C. The critical minimum pH required for stable foams was closely correlated with the pK_a value of 7.1 (0.1 M NaCl) of the PDMA chains. The particle-stabilized foams were stable and retained their three-dimensional structures even after drying. SEM examination of the dried foams suggested that flocculated PDMA-PS particles were adsorbed at the air-water interface for the foam prepared at 55 °C. In the case of the foam prepared at 23 °C, well-defined particle bilayers, similar to those reported previously for sterically/charge stabilized particles^{19,20}, were observed. This observation indicates that the bubbles were stabilized with PDMA-PS particle monolayers adsorbed at the air-water interface. Defoaming was achieved simply by decreasing the pH of the system at both 23 and 55 °C.

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Notes and references

^a Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, 5-16-1 Omiya, Asahi-ku, Osaka 535-8585, Japan.

^b Graduate School of Engineering, University of Hyogo 2167 Shosha, Himeji, Hyogo 671-2280, Japan.

^c Nanomaterials Microdevices Research Center, Osaka Institute of Technology, 5-16-1 Omiya, Asahi-ku, Osaka 535-8585, Japan.

Electronic Supplementary Information (ESI) available: Details on the calculation of amine group numbers on the PS particles, the temperature-sensitive behavior of PDMA as demonstrated by percent transmittance measurements and the pH and temperature doubly dependent behavior of foams as indicated by digital camera images. See DOI: 10.1039/b000000x/

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- Note that surface tension of water decreased from 71.99 mN/m to 67.10 mN/m with an increase of temperature from 25 °C to 55 °C [N. B. Vargaftik, B. N. Volkov and L. D. Voljak, *J. Phys. Chem. Ref. Data* 1983, **12**, 817], which should lead to an decrease of adsorption energy of the particles at the air-water interface [S. Levine, B. Bowen and S. J. Partridge, *Colloids Surf.* 1989, **38**, 325.]. It is therefore clear that the dominant influence of temperature is in reducing the

degree of hydration of the PDMA hairs on the PS particles to such an extent that the PDMA-PS particles can adsorb to air-water interface.

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Graphical Abstract for Soft Matter manuscript:

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by S. Fujii et al.

(corresponding author: Dr. S. Fujii; syuji.fujii@oit.ac.jp)

