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Submicrometer-sized polystyrene (PS) particles carrying poly[2-(diethylamino)ethyl methacrylate] (PDEA) hairs (PDEA-PS particles) were synthesized by free radical dispersion polymerization. The hydrophilicity-hydrophobicity balance of the PDEA could be tuned by varying temperature at near neutral pH (a lower critical solution temperature of PDEA at pH 6.86, 41 °C) and therefore these sterically-stabilized particles acted as temperature-sensitive stabilizers for aqueous foams. At 25 °C, where the PDEA hairs were hydrated and PDEA-PS particles were colloidally stable in aqueous media, foam was formed which coalesced with time and the size of the bubble increased. At 40 and 45 °C, where the PDEA hairs were partially non-hydrated and PDEA-PS particles were close to flocculation or weakly flocculated, foams were formed and bubble coalescence and size increase speeds were slower than those observed at 25 °C. At and above 50 °C, where the PDEA hairs were non-hydrated and PDEA-PS particles were non-hydrated and PDEA-PS particles were formed. Scanning electron microscopy studies indicated that the particles mainly adsorbed at the air-water interface as monolayers at 25 °C and as multilayers at and above 40 °C. The foam stability and structure could be controlled by changing the temperature.

Introduction

There have been increasing interests in stimuli-responsive polymer particles because of their diverse possible applications, such as catalyst supports¹⁻³, smart particulate emulsion⁴⁻⁷/foam⁸⁻¹⁰/liquid marble¹¹⁻¹⁵ stabilizers, and novel electrical and optical devices¹⁶⁻¹⁸. Especially, temperature-responsive (e.g. poly(N-isopropyl acrylamide)¹⁹⁻²²) and pH-responsive (e.g. poly(methacrylic acid)²³) polymer particles have been extensively studied. Moreover, double stimuli-responsive polymer particles are of increasing interest, because some applications might require an independent response to several factors. In order to obtain double stimuli-responsive polymers, a temperature-responsive monomer is often copolymerized with a pH-responsive one. Under this situation, polymers synthesized from N,N-dialkylaminoethyl methacrylates obtain lots of interests, because they show temperature and pH double stimuli-responsive character in aqueous media. A wellstudied example of this type of polymer is poly(N,N-

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Figure 1. Application of PS particles carrying poly[2-(diethylamino)ethyl methacrylate] hairs (PDEA-PS particles) as a temperature-sensitive particulate foam stabilizer.

dimethylaminoethyl methacrylate)²⁴⁻²⁹. Recently, poly(N,N-diethylaminoethyl methacrylate) (PDEA) was found to be responsive to temperature as well as $pH^{30,31}$, although PDEA was believed to be responsive only to pH for a long time period: PDEA shows lower critical solution temperature (LCST) at near neutral pH.

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Polystyrene (PS) latex particles carrying PDEA hairs (PDEA-PS particles) have been reported to work as both a pH-responsive particulate foam stabilizer and an acid-induced defoaming agent⁹. Being stable under basic conditions, such foams are destabilized by the addition of an aqueous acid solution. The PDEA on the PS particle surfaces is protonated and becomes hydrophilic as the pH is decreased below pK_a 7.6 (0.1 M NaCl) and the PS particles are desorbed from the air-water interface, which leads to defoamation. Herein, we focus on temperature-sensitive character of PDEA and describe the temperature-sensitive foams stabilized with the PDEA-PS particles (Figure 1). Particularly, effects of temperature on foam stability and structure are extensively characterized.

Results and discussion

In order to check the temperature-sensitive character of PDEA, percent transmittance (%T) values for the aqueous buffered solution of PDEA macroinitiator (0.1 wt%; a polymerization degree of the PDEA chain beside the central azo group, 60), which was used for synthesis of PDEA-PS latex particles (see Experimental), were measured between 25 and 60 °C (Figure 2). In the case of pH 6.86 buffered aqueous solution system, %T values were 100 % at and below 41 °C, and sharply dropped down to near 0 % at 48 °C: 85.5 % of diethylamino groups in PDEA is calculated to be deprotonated at pH 6.86. The PDEA precipitated in the aqueous medium due to dehydration, which led to milky-white dispersion. It was confirmed that pH values were 6.86 and 6.84 at 25 and 60 °C, respectively, and there was little change in pH values under the measurement conditions. From these results, LCST of PDEA at pH 6.86 was determined to be 41 °C. On the other hand, %T values were almost 100 % between 25 °C and 60 °C for the pH 4.01 aqueous buffer (see Figure 2). At pH 4.01, nearly 100 % diethylamino groups in PDEA are protonated and hydrated PDEA showed high solubility in aqueous media.

The PDEA-PS particles used in this study were prepared by dispersion polymerization in isopropanol (IPA) using a PDEA



Figure 2. Temperature dependence of percent transmittance of PDEA macroinitiator aqueous solution (0.1 wt%) at pH (\blacktriangle) 6.86 and (\Box) 4.01.

9000 25 8000 Hydrodynamic diameter / nm 20 7000 Zeta potential / mV 6000 15 5000 4000 10 3000 2000 5 1000 0 0 20 30 40 50 60 Temperature / °C

Figure 3. Temperature dependence of (\blacktriangle) zeta potential and (\blacklozenge) hydrodynamic diameter of PDEA-PS latex particles for aqueous dispersion (0.03 wt%) at pH 6.86.

macroinitiator as an inistab, based on the results of our previous study9. Prior to purification, the milky-white IPA dispersion contained excess free PDEA macroinitiator as well as various byproducts, and no foam was observed even after vigorous agitation. Scanning electron microscopy (SEM) images of dried PDEA-PS particles obtained after purification using IPA and water confirmed their spherical morphology. The number-average particle diameter (D_n) and the associated coefficient of variation were estimated from the SEM images to be 410 ± 250 nm and 14.1 %, respectively. Laser diffraction particle size analysis indicated that the volume-average diameter (D_v) in IPA was 670 ± 220 nm, which is similar to the D_n . Elemental microanalysis studies determined that the PDEA loading percentage in the PDEA-PS particles was 2.78 % by mass, based on a comparison of the nitrogen content of the particles to that of a PDEA homopolymer synthesized by free radical polymerization (N = 0.21 % for the PDEA-PS particles and 7.55 % for the PDEA homopolymer). The PDEA 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 PDEA-PS particles in the liquid. Assuming that all the PDEA chains are covalently bonded at the PS particle surfaces and that the PS particles have a D_n of 410 nm (determined from the SEM images), the area occupied by the PDEA chains at the surface of each particle was calculated to be 9.16 nm² from the elemental microanalysis results noted above using a PS density value of 1.06 g/cm^{3 32} (see ESI). The square root of the occupied molecular area (3.03 nm) is larger than the diameter of gyration (1.38 nm) of a PDEA chain (degree of polymerization = 60), indicating that the grafting density at the particle surface appears to have produced PDEA chains with random-walk configurations. This is noteworthy, since it is also possible for PDEA-PS block copolymers to form a mixed surface layer of PS and PDEA having a brush-type configuration³³.

The aqueous electrophoresis studies conducted at pH 6.86 confirmed that surface charge density on the surface of the PDEA-PS particles is not sensitive against temperature and zeta potentials were near +15 mV in a temperature range between 25 and 60 °C (Figure 3).

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Figure 4. Temperature-dependent behavior of foams prepared using PDEA-PS latex particles (10 wt%, pH 6.86). (a) Photograph of vessels taken at different times after homogenization of the aqueous dispersions with air at different temperatures. (b) Height of the foam layer as a function of temperature of the aqueous dispersion recorded at different times: immediately after preparation (\Box), after 24 h (\blacksquare) and after 1 week (\blacktriangle).

Hydrodynamic diameters (D_z) were measured as approximately 520 nm at and below 39 °C with narrow particle size distributions (Figure 3), which suggests a high degree of PDEA-PS latex particle dispersion due to the hydrated water-soluble character of the PDEA hair acting as a colloidal stabilizer. The zeta potentials of the PDEA-PS particles were too low for the particles to disperse stably in the aqueous media, and therefore steric stabilization mechanism due to hydrated water-soluble PDEA hair should work for the colloidal stability: Note that zeta potentials of > approximately +30mV and < approximately -30 mV are required for the colloidal particles to disperse stably in aqueous media via electrostatic stabilization mechanism³⁴⁻³⁶. Between 41 °C and 45 °C, D_z were measured to be 550-600 nm, which were a little bit larger than those measured at and below 39°C and should indicate partial flocculation of the PDEA-PS particles occurred. This temperature range where the partial flocculation occurred correlated well with that where the PDEA started to precipitate in pH 6.86 buffered aqueous solution (Figure 2). Above 45 °C the PS particles were flocculated to higher

extent, as indicated by a significant increase in the apparent particle diameters (above micrometer size) and diameter distributions (Figure 3). Above LCST, the PDEA stabilizer precipitated in the aqueous media and the PDEA-PS particles lost colloidal stability, which led to flocculation of the particles. Adjusting the temperature back to 25 °C from 60 °C led to redispersion of the PDEA-PS latex particles.

Foamability and foam stability are dependent on the wettability of the particles at the air-water interface⁸⁻¹⁰; therefore, it was expected that the behaviour of foams stabilized with these PDEA-PS particles would change significantly at temperature close to the LCST in the bulk aqueous dispersion. To evaluate foamability and foam stability, the height of foam layer was measured after homogenizing aqueous dispersions of the PDEA-PS latex particles (10.0 wt%, pH 6.8 buffered dispersion) at different temperatures (Figure 4). In a temperature range investigated in this study (25-55 °C), foams were formed after mixing the latex with air. Their heights immediately after preparation were almost the same between 25 °C and 55 °C,



Figure 5. OM images of foams stabilized with PDEA-PS particles (10 wt%, pH 6.86) prepared at temperatures of (a, f) 25 °C, (b, g) 40 °C, (c, h) 45 °C, (d, i) 50 °C, and (e, j) 55 °C. Figs. (f-j) are magnified images of Figs. (a-e), respectively. Arrows in Figs. (i, j) indicate flocs.



Figure 6. Photographs of PDEA-PS particle-stabilized foams (a, c) before and (b, d) after drying on a glass substrate. Foams were prepared and dried at temperatures of (a, b) 50 °C and (c, d) 25 °C.

and tended to increase gradually above 45 °C (Figure 4a). At 25 °C, bubbles coalesced with time and size of the bubble increased and the number of bubbles decreased. At 40 and 45 °C, bubble coalescence and size increase were observed, whose speeds were slower than those observed at 25 °C. At and above 50 °C, no distinct coalescence of bubbles was observed and foams kept their cream-like character for at least 1 week. Figure 4b shows the height of the foam layer, defined as the distance between the foam/dispersion boundary and the three phase contact line of air, glass and foam, as a function of the temperature of the aqueous dispersion, immediately after preparation and for some time afterwards. The height gradually decreases with time due to water drainage and coalescence of air bubbles at and below 45 °C. It appears that stable foams, whose heights are almost the same for 1 week, are formed under conditions where particles are heavily flocculated in bulk (at and above 50 °C). These results indicated that the surface of PDEA-PS particles is relatively hydrophilic at and below 45 °C and adsorption energy at air-water interface is lower than those at and above 50 °C, which should lead to desorption of the particles, followed by coalescence/defoamation. On the other hand, the particle surface is hydrophobic at and above 50 °C and the adsorption energy of the particles at the interface is high enough to obtain stable foams.



Figure 7. SEM images of foams stabilized with PDEA-PS latex particles (10 wt%, pH 6.86) prepared at temperatures of (a, f, k) 25 °C, (b, g, l) 40 °C, (c, h, m) 45 °C, (d, i, n) 50 °C and (e, j, o) 55 °C. Figs. (a-e) depict surface morphology of the foams, and Figs. (f-j) depict ruptured foam section. Insets in Figs. (a-e) show magnified images. Figs. (k-o) show magnified images of Figs. (f-j), respectively.

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Figure 8. (a-c) OM and (d-i) SEM images of foams stabilized with PDEA-PS latex particles (10 wt%, pH 6.86): (a, d, g) after agitation at pH 6.86 and 25 °C, (b, e, h) after agitation of the foam shown in (a, d, g) at pH 6.86 and 50 °C and (c, f, i) after reagitating the foam shown in (b, e, h) at pH 6.86 and 25 °C. Insets in Figs. (a-c) show magnified images. Figs. (g-i) show magnified images of Figs. (d-f), respectively.

The microstructures of the particle-stabilized foams were investigated just after preparation using optical microscope (OM) in detail. At 25 °C, where the PDEA-PS particles could be stably dispersed in the aqueous media, particle-stabilized polydisperse bubbles and free colloidally stable PS particles were observed (see Figure S1). The foam is composed of near spherical and nonspherical bubbles with sizes ranging from ca. 30 to 1430 μ m (D_n, 400±270 µm), as shown in an OM image presented in Figure 5a. Bubble surface was smooth and no flocs of the PDEA-PS particles were observed (Figure 5f). At and above 40 °C, where the particles are close to/weakly/heavily flocculated in the aqueous media, polydisperse bubbles (size range from ca. 10 to 230 µm) with near spherical and non-spherical morphologies were observed (Figures 5b-5e). It is worth noting that flocculated PDEA-PS particles adsorbed at the bubble surfaces and flocculated particles in the continuous aqueous media were clearly observed at 50 and 55 °C (white arrows in Figures 5i and 5j indicate large flocs, see also Figure S2). The difference in bubble size at lower and higher temperatures should correlate with adsorbability of the PDEA-PS particles to air-water interface, which is affected by entropies of PDEA hairs and the counter anions present in the vicinity of the partially protonated PDEA hairs as well as hydrophilic-hydrophobic balance of the particle surface. When the PDEA-PS particles carrying hydrated PDEA hairs approach to the air-water interface, the entropies of the PDEA hairs and the counter anions decrease (in other words, the number of possible configurations of the PDEA hairs is reduced and the space in which the counter anions can situate themselves decreases), which is unfavourable with regard to the Gibbs free energy of the system. This lower adsorbability of the PS particles carrying hydrated PDEA hairs to the interface should lead to larger bubble size in comparison with PS particles carrying nonhydrated and shrinked PDEA hairs.

These particle-stabilized foams were stable and retained their threedimensional structure even after drying (Figure 6), and few bubbles were broken during/after evaporation of the aqueous phase overnight at ambient temperature^{37,38}. Very little coalescence occurred and visual inspection indicated that the bubble size distribution was almost unchanged during/after drying. It is worth noting that foams prepared at 25 °C kept their three-dimensional structure even after/during drying and remained stable at least 2 years, although they defoamed with time in wet state. Figure 7 shows SEM images of the foams dried at temperatures where they are formed. Focusing on the top surface of the dried foams confirmed formation of netshaped pattern with sizes of several hundreds micrometer and near ten micrometer. These sizes accorded well with those of bubbles. Magnified SEM images confirmed the presence of the PDEA-PS particles which were near close-packed for all the systems. After rupture of the dried foam using a knife, the internal microstructure can be investigated. For the foams prepared at 25 °C, well-defined particle bilayers were widely formed (Figure 7f). The formation of the PDEA-PS particle bilayers should indicate that air bubbles were mainly stabilized by monolayers of adsorbed particles. During water drainage from the drying foams, these monolayers are presumably contacted together to form bilayers. Similar bilayer formation mechanism was proposed in the previous studies^{9,37,38}. In some cases, particle monolayers were observed, which should be formed at the top surface of a dried foam that was directly exposed to bulk air phase and was not overlapped with other bubble surfaces. Degree of particle ordering in the particle layers was lower than those observed in our previous studies^{37,38}. The lack of long-range order observed in the present study should be due to the somewhat higher polydispersities in size obtained for the PDEA-PS particles; the coefficient of variations were determined to be 14.1 % for the PDEA-PS particles and approximately 5 % for the latex particles used in the previous studies^{37,38}. For the foams prepared at and above 40 °C, particle multilayers (3-12 layers) were mainly observed (Figures 7g-7j), which should suggest that the flocculated PDEA-PS particles are adsorbed to air-water interface to stabilize air bubbles. The multilayer thickness was estimated to be ca. 1-5 µm from SEM image analysis, which was smaller than the PDEA-PS floc size observed in OM images (ca. 10 µm at 55 °C). Therefore, there is a possibility that water drainage during drying partially breaks the PDEA-PS particle flocs adsorbed to the bubble surface, which leads to thinner foam layer thickness than expected. Another possibility can be raised that the particle flocs on the bubble surface were compressed into a near close-packed arrangement during the water drainage/evaporation of water.

The effect of external temperature stimulus on the microstructures of the particle-stabilized foam was also investigated (Figure 8). The foam was initially prepared at 25 °C and then dried at the same temperature. As already observed, polydisperse aqueous bubbles with diameters ranging from approximately 30 to 1000 μ m (D_n , 410±280 µm) were observed just after preparation (Figure 8a) and bilayers composed of the PDEA-PS particles were mainly observed for the dried foams in SEM images (Figures 8d). The aqueous foam prepared at 25 °C was then heated to 55 °C and agitated using a homogenizer. OM studies confirmed aqueous bubbles with $D_{\rm n}$ of 70 ± 30 µm, which is the similar size with those directly prepared from aqueous dispersion of PDEA-PS particles at 55 °C (Figure 8b). These results indicated that the bubbles prepared at 25 °C were divided into smaller bubbles during agitation at 55 °C. SEM images of the foam dried at 55 °C indicated the preferential formation of multilayers of the particles comparing to bilayers (Figure 8e). This result should demonstrate that the PDEA-PS particles that lost colloidal stability due to the dehydration of their PDEA hairs at 55 °C underwent flocculation in the aqueous media and were adsorbed to the fresh air-water surfaces formed during homogenization. There should be another possibility for the colloidally unstable particles/flocs adsorb to the as-formed bubble surfaces covered by

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PDEA-PS particle monolayer. The foam was subsequently cooled to 25 °C and again agitated. Interestingly, bubble size was determined to be 80 \pm 30 μ m just after preparation, which was similar to those formed at 55 °C and smaller than those originally formed at 25 °C. These results should indicate that affinity of the particles for airwater interface, rather than adsorption energy (the energy needed for the particle to desorb from the interface), determined the bubble size. More interestingly, the majority of the foam walls consisted of PDEA-PS particle bilayers, while a few multilayers were observed (Figure 8f). Evidently, the PDEA-PS particles initially adsorbed to the bubble surfaces as multilayers at 55 °C were re-dispersed into the aqueous media as single particles carrying solvated PDEA hairs, leaving particle monolayers on the bubble surfaces. The foam obtained at 25 °C after a temperature cycle between 25 and 55 °C coalesced with time and the size of the bubble increased.

Encapsulation of air bubbles in aqueous media utilizing stimuliresponsive polymer particles in this manner may have potential applications in cosmetic formulations, food manufacturing and personal care products.

Experimental

Materials

Styrene, *N*,*N*-(diethylamino)ethyl methacrylate (DEA; 99 %), 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 %), HCl aqueous solution (37 %) and ammonia aqueous solution (28 %) were purchased from Sigma-Aldrich. Buffer solutions with pH 6.86 and 4.01 (pH standard solution) were purchased from Horiba Ltd. A PDEA-based macroinitiator with a degree of polymerization of 60 (the polymerization degree of the PDEA chain beside the central azo group) was synthesized by atom transfer radical polymerization, as reported previously⁹. Deionized water (<0.06 μ S cm⁻¹, Advantec MFS RFD240NA: GA25A-0715) was used.

Synthesis of PDEA-PS latex particles

Dispersion polymerization of styrene was performed in batch mode at 80 °C using the PDEA-based macroinitiator (5.45 g, 2.40×10⁻⁴ mol) and VA-086 initiator (0.623 g, 2.16×10⁻³ mol) as described previously⁹; the PDEA macroinitiator was used as an inistab (initiator + colloidal stabilizer) and the molar ratio of PDEA macroinitiator and VA-086 was 10/90. A number-average molecular weight of the PDEA-based macroinitiator was determined to be 22,500 and 23,100 by gel permeation chromatography (GPC) and ¹H nuclear magnetic resonance (¹H NMR), respectively. The molecular weight distribution (M_w/M_n) was determined to be 1.08 by GPC. Styrene, PDEA-macroinitiator and VA-086 were added to IPA (250 mL) in a one-necked 500 mL flask with a magnetic stirrer bar. This reaction mixture was vigorously stirred at room temperature until dissolution was completed, and was then degassed using a nitrogen purge. Polymerization was commenced after placing the flask into an oil bath (80 °C), and was allowed to proceed for 1 week with continuous stirring at 300 rpm under a nitrogen atmosphere. Successive centrifugation-redispersion cycles were used to purify this latex, with each supernatant being decanted and replaced with IPA (5 cycles; 4,600 rpm, 30 min.), deionized water (5 cycles;

10,000 rpm, 30 min.) and then buffer solution (3 cycles; 10,000 rpm, 30 min) using a centrifuge (Hitachi CF16RXII type centrifuge with a Hitachi T15A 36 rotor). After the fifth centrifugation-redispersion cycle using IPA, the supernatant was examined using ultraviolet-visible spectroscopy (Agilent 8453, Agilent Technologies) in order to check the removal of impurities such as non-adsorbed free PDEA macroinitiator and its by-products.

Characterization of PDEA-PS particles

CHN elemental microanalysis and ¹H NMR measurement were conducted using dried PDEA-PS particles obtained from aqueous dispersion of the PDEA-PS particles (non-buffered), and aqueous electrophoresis and dynamic light scattering were conducted using buffered aqueous dispersion. Laser diffraction particle size analysis was conducted using IPA dispersion of the PDEA-PS particles.

Chemical composition of the PDEA-PS particles

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

Particle size analysis

Size and size distribution of the PDEA-PS particles were determined using a laser diffraction particle size analyser (Malvern Mastersizer 2000) equipped with a small volume sample dispersion unit (Hydro 2000SM; *ca.* 150 mL including flow cell and tubing), a HeNe laser (633 nm), and a solid-state blue laser (466 nm). The stirring rate was adjusted to 2,000 rpm. The mean particle diameter was taken to be the volume mean diameter (D_v), which is mathematically expressed as $D_v = \Sigma D_i^4 N_i / \Sigma D_i^3 N_i$, where D_i is the diameter of individual particles and N_i is the number of particles corresponding to the specific diameter. The resulting data are presented as mean diameter with standard deviation.

Percent transmittance (%T) measurements

%T values of the aqueous solution for PDEA macroinitiator were recorded on a UV-Vis spectroscopy (Agilent 8453, Agilent Technology) using a 1.0 cm path length quartz cell at various temperatures.

Aqueous electrophoresis and dynamic light scattering

Zeta potentials were calculated from the electrophoretic mobility, measured using a Malvern Zetasizer Nano ZS. Measurements were conducted as a function of temperature with buffered aqueous dispersions (0.02 w/v%, pH 6.86 and 4.01) by gradually increasing temperature, starting from an initial temperature of 25 °C. Zeta potentials were averaged over 5 runs at each temperature. The variance was typically smaller than 2 mV. Following electrophoretic mobility measurements at each temperature, dynamic light scattering of the aqueous PDEA-PS dispersion was conducted using the same instrument at a scattering angle of 173° to obtain hydrodynamic diameters. Three measurements were made at each temperature.

¹H NMR

¹H NMR spectra were recorded in CDCl₃ for the PDEA-based macroinitiator and PDEA-PS latex particles using a Jeol EX-270 NMR spectrometer.

Foam preparation

5.00 g of the buffered aqueous latex dispersion (10 wt%) was placed in a glass vessel (13.5 mL) with a screw cap and then homogenized using a homogenizer (T25 digital ULTRA-TURRAX, IKA) for 1 min at 20,000 rpm at 25, 40, 45, 50 and 55 $^{\circ}$ C. Foams were prepared and stored at temperature at which the foams were prepared. Foam heights were measured using a ruler.

Characterization of foams and aqueous dispersions

Digital camera

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

Optical microscopy

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

Conclusions

The PDEA-PS particles, whose surface hydrophilicityhydrophobicity balance could be tuned by varying temperature at pH 6.86, can work as a temperature-sensitive foam stabilizer. At 25 °C, where the PDEA hairs were hydrated and PDEA-PS particles were colloidally stable in aqueous media, PDEA-PS particle-stabilized foam was formed, which coalesced with time and the size of the bubbles increased. At 40 and 45 °C, where the PDEA hairs were partially non-hydrated and PDEA-PS particles were close to flocculation or weakly flocculated, foams were formed and bubble coalescence and size increase speeds were slower than those observed at 25 °C. At and above 50 °C, where the PDEA hairs were non-hydrated and the PDEA-PS particles were heavily flocculated in aqueous media, the more stable cream-like foams whose volume were almost the same for 1 week were formed. SEM studies indicated that the particles mainly adsorbed at the air-water interface as monolayers at 25 °C but as multilayers at and above 40 °C. The foam stability and structure could be controlled by changing the temperature.

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References

- S. Pathak, M. T. Greci, R. C. Kwong, K. Mercado, G. K. S. Prakash, G. A. Olah and M. E. Thompson, *Chem. Mater.*, 2000, 12, 1985.
- Y. Mei, G. Sharma, Y. Lu and M. Ballauff, *Langmuir*, 2005, 21, 12229.
- Y. Mei, Y. Lu, F. Polzer and M. Ballauff, *Chem. Mater.*, 2007, 19, 1062.

2006, 22, 7512.

38. S. Fujii, P. D. Iddon, A. J. Ryan and S. P. Armes, Langmuir,

- ARTICLE
- 4. S. Fujii, E. S. Read, S. P. Armes and B. P. Binks, *Adv. Mater.*, 2005, **17**, 1014.
- S. Fujii, Y. Cai, J. V. M. Weaver and S. P. Armes, J. Am. Chem. Soc., 2005, 127, 7304.
- T. Ngai, S. H. Behrens and H. Auweter, *Chem. Commun.*, 2005, 3, 331.
- 7. W. Richtering, Langmuir, 2012, 28, 17218.
- B. P. Binks, R. Murakami, S. P. Armes, S. Fujii and A. Schmid, Langmuir, 2007, 23, 8691.
- S. Fujii, M. Mochizuki, K. Aono, S. Hamasaki, R. Murakami and Y. Nakamura, *Langmuir*, 2011, 27, 12902.
- 10. S. Fujii, K Akiyama, S. Nakayama, S. Hamasaki, S. Yusa and Y. Nakamura, *Soft Matter*, 2015, **11**, 572.
- D. Dupin, S. P. Armes and S. Fujii, J. Am. Chem. Soc., 2009, 131, 5386.
- 12. S. Fujii, S. Kameyama, S. P. Armes, D. Dupin, M. Suzaki and Y Nakamura, *Soft Matter*, 2010, **6**, 635.
- S. Fujii, M. Suzaki, S. P. Armes, D. Dupin, S. Hamasaki, K. Aono and Y. Nakamura, *Langmuir*, 2011, 27, 8067.
- 14. D. Dupin, K. L. Thompson and S. P. Armes, *Soft Matter*, 2011, 7, 6797.
- K. Ueno, G. Bournival, E. J. Wanless, S. Nakayama, E. C. Giakoumatos, Y. Nakamura and S. Fujii, *Soft Matter*, 2015, DOI: 10.1039/C5SM01584G.
- 16. S. Tsuji and H. Kawaguchi, Langmuir, 2005, 21, 8439.
- 17. H. Kawaguchi, Prog. Polym. Sci., 2000, 25, 1171.
- 18. J. H. Holtz and S. A. Asher, Nature, 1997, 389, 829.
- 19. R. H. Pelton and P. Chibante, Colloid Surface, 1986, 20, 247.
- K. S. Oh, J. S. Oh, H. S. Choi and Y. C. Bae, *Macromolecules*, 1998, **31**, 7328.
- D. Duracher, A. Elaissari, F. Mallet and C. Pichot, *Macromol. Symp.*, 2000, 150, 305.
- 22. S. Tsuji and H. Kawaguchi, Langmuir, 2004, 20, 2449.
- 23. H. He, L Li and L. J. Lee, Polymer, 2006, 47, 1612.
- 24. F. Schacher, M. Ulbricht and A. H. E. Müller, *Adv. Funct. Mater.*, 2009, **19**, 1040.
- K. Yamada, M. Shibuya, C. Takagi and M. Hirata, J. Appl. Polym. Sci., 2006, 99, 381.
- Y. Shen, F. Zeng, S. Zhu and R. Pelton, *Macromolecules*, 2001, 34, 144.
- V. Bütün, S. P. Armes and N. C. Billingham, *Polymer*, 2001, 42, 5993.
- F. A. Plamper, A. Walther, A. H. E. Müller and M. Ballauff, Nano Lett., 2007, 7, 167.
- 29. T. Matsumoto, K. Nakamae, M. Okubo, M. Sue, M. Shimao and M. Komura, *Kobunshi Ronbunshu*, 1974, **31**, 669.
- A. Schmalz, M. Hanisch, H. Schmalz and A. H. E. Müller, *Polymer*, 2010, **51**, 1213.
- T. Thavanesan, C. Herbert and F. A. Plamper, *Langmuir*, 2014, 30, 5609.
- 32. J. Brandrup, E. H. Immergut and E. A. Grulke, Polymer Handbook, 4th ed. Wiley, New York, 1999.
- S. Fujii, M. Suzaki, Y. Nakamura, K. Sakai, N. Ishida and S. Biggs, *Polymer*, 2010, **51**, 6240.
- 34. S. Ross and R. F. Long, Ind. Eng. Chem., 1969, 61, 58.
- 35. T. M. Riddick and L. A. Ravina, Ind. Eng. Chem., 1970, 62, 70.
- 36. S. Ross, Ind. Eng. Chem., 1970, 62, 73.
- S. Fujii, A. J. Ryan and S. P. Armes, J. Am. Chem. Soc., 2006, 128, 7882.
- 8 | J. Name., 2012, **00**, 1-3

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