

Durable Gelfoams Stabilized by Compressible Nanocomposite Microgels

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Experimental Procedures

Materials

N-isopropylacrylamide (NIPAm, purity 98%), *N,N'*-methylenebis(acrylamide) (BIS, 97%), styrene (99%), potassium peroxydisulfate (KPS, 95%), methacrylic acid (MAc, 99%), SDS (95%), and fumaric acid (FAc, 98%) were purchased from Wako Pure Chemical Industries, Ltd. A 0.5% stabilized aqueous solution of ruthenium tetroxide (RuO₄) was purchased from Electron Microscopy Sciences and used as received. For all experiments, water was distilled and then ion-exchanged (EYELA, SA-2100E1) before use.

Synthesis of core microgels

pNIPAm-based core microgels were synthesized by precipitation polymerization in water. A mixture of NIPAm, BIS, MAc, FAc, and water was poured into a 1 L three-neck round-bottom flask equipped with a mechanical stirrer, a condenser, and a nitrogen gas inlet. The monomer compositions are listed in Table S1. The monomer solution was heated to 70 °C under stirring at 250 rpm and then sparged with nitrogen gas for 30 min to purge any oxygen from the solution. KPS dissolved in 5 mL of water was injected into the flask to start the free-radical polymerization. The reaction was allowed to proceed for 4 h, before the microgel dispersion was allowed to cool to room temperature. The microgels were purified twice by centrifugation/redispersion with water using a relative centrifugal force of 70,000×*g*. The composition of each microgel is denoted with the letters 'N', 'F', and 'M', where N indicates pNIPAm, M indicates methacrylic acid, and F indicates fumaric acid.

Synthesis of solid microspheres

Polystyrene (PS) microspheres were prepared by soap-free emulsion polymerization. Initially, styrene (26.7144 g) and NIPAm (3.2258 g) dissolved in 280 mL of water was poured into a three-neck round-bottom flask equipped with a mechanical stirrer and a condenser. Then, the reaction mixture was heated to 70 °C in a temperature-controlled oil bath and sparged with nitrogen for 30 min to purge any dissolved oxygen from the solution. Then, the KPS initiator (2 mM) dissolved in 20 mL water was added to start the polymerization. The polymerization was allowed to proceed for 24 h under a nitrogen atmosphere, before the resulting microgel dispersion was cooled to room temperature in an ice bath. The obtained dispersions were purified twice by centrifugation/redispersion with water. To improve the foaming tendency of the polystyrene nanoparticles, 10 mol% of NIPAm was added before the addition of KPS.

Synthesis of core-shell particles

PS-core pNIPAm-shell microgels were synthesized by seeded precipitation polymerization in the presence of PS microspheres. The concentration of core particles was fixed at 1 wt.%. A monomer solution containing water (10 mL), NIPAm (95 mol%), and BIS (5 mol%) was poured into a four-necked round-bottom flask, and the solution was sparged for 30 min with nitrogen to purge any dissolved oxygen from the reaction medium. Then, the aqueous dispersion containing PS microspheres was added to the flask (final concentration: 1.0 wt.%). The initiator KPS (0.0162 g) dissolved in water (5 mL) was injected into the flask to start the polymerization, which proceeded for 4 h. The obtained dispersion was cooled to room temperature and purified by a centrifugation/redispersion. The obtained particles were denoted as PS-N particles. The shell thickness of PS-N particles (120 nm) was determined by dynamic light scattering (DLS).

Synthesis of nanocomposite (NC) microgels

An appropriate amount of ion-exchanged water was poured into a 200 mL three-necked flask, and residual oxygen was removed by nitrogen sparging. The aqueous solution was heated to 70 °C with constant stirring at 250 rpm. Then, the core-microgel dispersion (final solid content: 0.17 wt.%) was poured into the flask under a nitrogen atmosphere. Sufficient 1 M NaOH solution was added to the flask to adjust the pH of the system to ~10, before KPS (0.0271 g, 1 mM) dissolved in 5 mL of water was injected into the flask. Then, styrene monomer was added to start the polymerization. The polymerization was allowed to proceed for 24 h, before the resultant composite microgel dispersion was cooled to room temperature. The composite microgels were purified twice by centrifugation/redispersion with ionized water using a constant centrifuge force. In this manuscript, the composite microgels are denoted as Core-SZ, where Core denotes the core microgel, S indicates polystyrene, and Z indicates the styrene concentration during the seeded emulsion polymerization.

Field emission scanning electron microscopy (FE-SEM) characterization

The dried particles on a solid substrate were examined using a field emission scanning electron microscope (FE-SEM, Hitachi Ltd., S-5000, operated at 20 keV). The dispersions (1 μL) were dried on a PS substrate at room temperature (~25 °C). Prior to observation, the samples were sputtered with Pt/Pd (80 s, 6 Pa, 15 mA).

Transmission electron microscopy (TEM) characterization

In order to characterize the inner structure of nanocomposite microgels, ultra-thin cross section of nanocomposite microgels was evaluated with TEM (JEOL JEM-2100, operated at 200 kV). For sample preparation, lyophilized composite microgels were steamed for 30 min with RuO₄ vapor and mixed in epoxy matrices (EPON812, TAAB Laboratories Equipment). The matrices were heated to 70 °C for 24 h and sliced into ultrathin-cross sections.

Cryo-electron tomography (Cryo-ET) analysis

The composite microgels were observed in the hydrated state using cryo-EM. Aqueous samples of the nanocomposites (2.5 μL) were applied to R 1.2/1.3 Quantifoil grids (Quantifoil Micro Tools), which had been glow-discharged beforehand. The grids were then blotted and plunge-frozen using a Vitrobot, Mark IV (Thermo Fisher Scientific; 95% humidity; 4 °C; 4 s blotting time). The frozen hydrated grids were individually mounted onto a cryo-specimen holder (Gatan model 914) at liquid-nitrogen temperature and examined using a JEM2200FS electron microscope (JEOL Inc.) equipped with a field-emission electron source operated at 200 kV and an in-column (omega-type) energy filter operated in zero-energy-

loss mode with a slit width of approximately 20 eV. Images of the frozen hydrated microgels were recorded using a CMOS camera (DE-20, Direct Electron LP, San Diego) with a low electron dose of approximately $\sim 20 \text{ e}^-/\text{\AA}^2$ at a nominal magnification of 20,000 \times , corresponding to 2.73 \AA per pixel on the specimen. Alignment of the tilt series was performed using the etomo tomography processing software contained within the IMOD package.^[1] For preparing 3D segmentation images, intensity-based segmentation with manual supervision was performed. The image contrast was adjusted as needed to accurately segment the high-contrast areas corresponding to polystyrene.

Dynamic light scattering measurements

The hydrodynamic diameter (D_h) of the obtained particles was determined by dynamic light scattering (DLS; Zetasizer Nano S, Malvern). The measurements were performed at a scattering angle of 173 $^\circ$ in aqueous solutions. To determine the hydrodynamic diameter, the Stokes–Einstein equation was used (Zetasizer software v6.12). The thickness of the swollen hydrogel shell layer on the core surface was determined as $(D_{h,\text{core/shell@25 }^\circ\text{C}} - D_{h,\text{core@25 }^\circ\text{C}}) / 2$.

Electrophoretic mobility (EPM) measurements

The electrophoretic mobility (EPM) was evaluated using a Zetasizer NanoZS instrument (Malvern, Zetasizer software v. 4.20). For sample preparation, the ionic strength of the particle dispersion was adjusted to 1 mM using a NaCl solution. The EPM data correspond to an average of three independent measurements. Prior to all measurements, the samples were equilibrated for 600 s at the set temperature.

Preparation of particle-stabilized foams

Particle-stabilized foams were prepared by mixing 2 mL of the particle dispersion with an Ultra-Turrax T25 homogenizer at 3000–10000 rpm for 60 s. The obtained foams were examined by optical microscopy (LZ-LEDT, Kenis), and the bubble size was measured using the software ImageJ.

Characterization of the microgels at the air/water interface using a Langmuir trough

All compression isotherms were performed using a Langmuir trough (HBM 700LB, Kyowa Interface Science Co., Ltd., Japan) equipped with a Wilhelmy plate at 25 $^\circ\text{C}$. In order to adsorb the microgels at the air/water interface, 500 μL of a 0.2–1.0 wt.% microgel dispersion was first mixed with 500 μL of ethanol, and then the microgels, which were dispersed in a water/ethanol solution (1:1 volume ratio), spread over the air/water interface of the filled water. After 30 min, the equipped barrier was moved at a constant speed of 100 mm/min. The pH and ionic strength of the filled water were adjusted using HCl or NaOH and NaCl.

Dynamic viscoelastic measurements

The dynamic viscoelasticity of foams stabilized by unmodified and modified microgels were measured using a rheometer (MCR302e, Anton Paar). Approximately 1 mL of foam was used, and the strain dependences (0.01–100%) of the storage modulus (G') and loss modulus (G'') were measured at 25 $^\circ\text{C}$ and 10 s^{-1} using a plate (D-PP25/AL/S07).

Results and Discussion

Table S1. Monomer compositions and hydrodynamic diameter (D_h) derived from DLS measurements of the microgels used in this study. Poly(*N*-isopropyl methacrylamide) (pNIPMAm) microgels were used in a previous study^[2]

Code	Monomers (mol.%)					SDS (mM)	D_h 25 °C (nm)
	NIPAm	BIS	FAc	MAc	NIPMAm		
N(1)_440	99	1	—	—	—	0.2	436
N(1)_690	99	1	—	—	—	—	689
N(1)_1900	99	1	—	—	—	—	1895
N(5)	95	5	—	—	—	0.1	448
N(10)	90	10	—	—	—	0.1	382
NF	90	5	5	—	—	—	1310
NM	90	5	—	5	—	—	658
NMF	70	5	5	20	—	—	722
pNIPMAm ^[2]	—	10	—	—	90	2	224

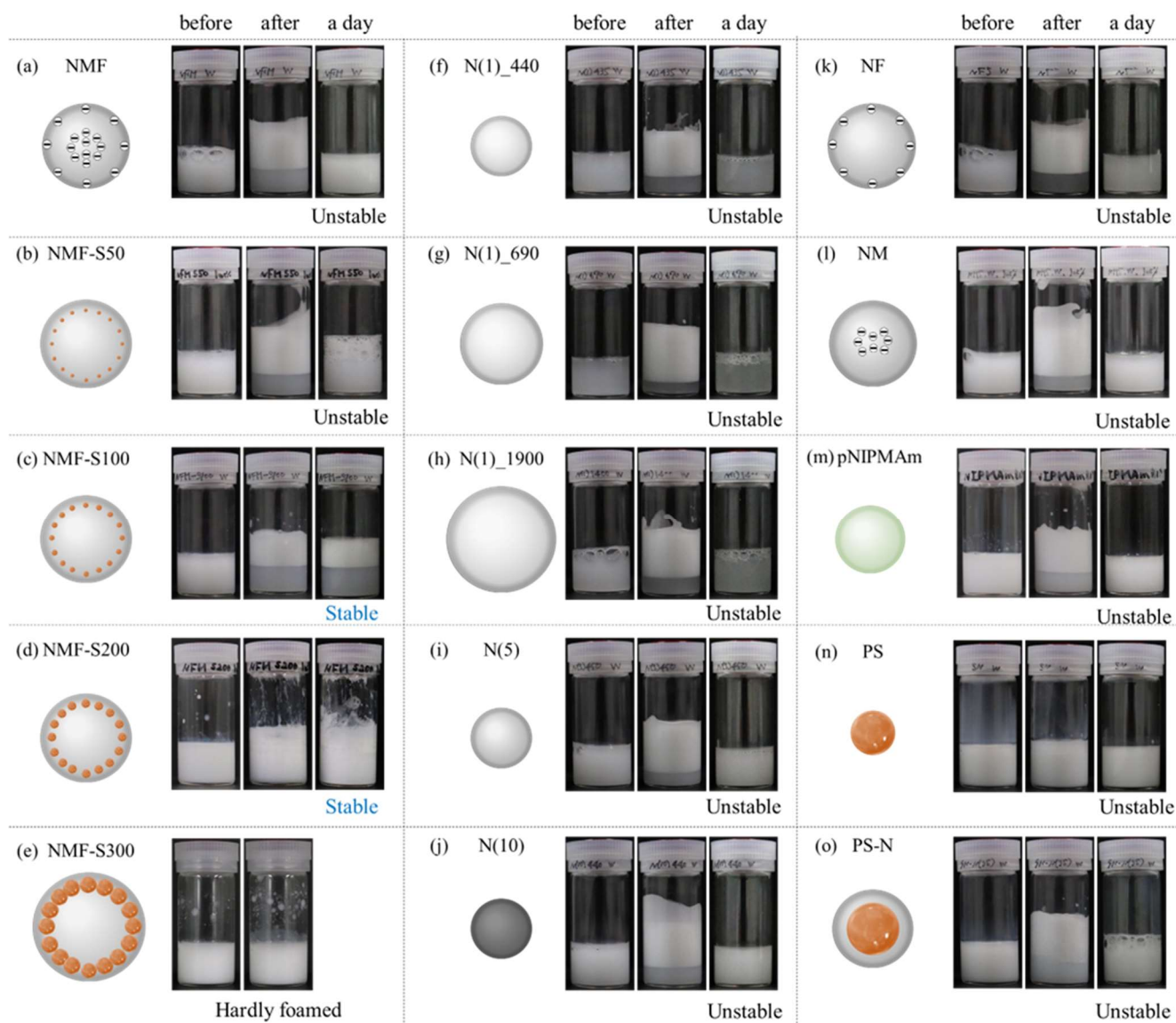


Figure S1. Foaming tests and characterization of foam stability using various types of unmodified microgels, modified NC microgels, solid microspheres, and core-shell microgels. (a) NMF, (b) NMF-S50, (c) NMF-S100, (d) NMF-S200, (e) NMF-S300, (f) N(1)_440, (g) N(1)_690 (h) N(1)_1900, (i) N(5), (j) N(10), (k) NF, (l) NM, (m) pNIPMAm, (n) PS, and (o) PS-N. All foams were prepared by mixing 1 wt% colloid dispersion at 10,000 rpm for 1 min at room temperature (25 °C). The foams were stored at room temperature for 1 day.

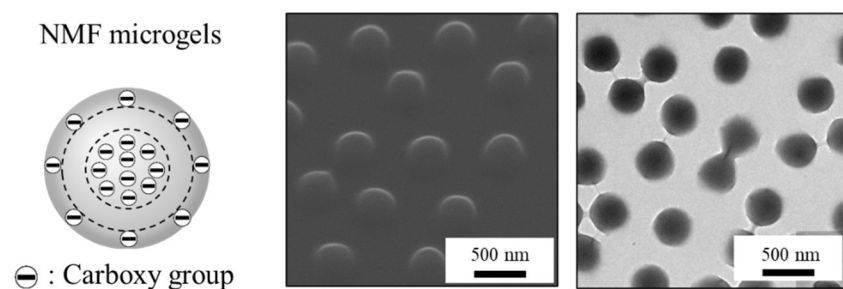


Figure S2. Schematic illustration, SEM image, and TEM image of NMF microgels.

Table S2. Monomer composition, hydrodynamic diameter (D_h), and electrophoretic mobility (EPM) of the microgels used in this study.

code	temp. °C	D_h nm		EPM $\times 10^{-8} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$		Swelling ratio ^a
		pH = 3	pH = 10	pH = 3	pH = 10	
NMF	25	572 ± 6.9	N.A.	-0.77 ± 0.03	-2.27 ± 0.08	4.4
	70	355 ± 11	582 ± 37	-3.78 ± 0.08	-3.80 ± 0.08	
NMF-S100	25	543 ± 3.3	922 ± 14	-1.48 ± 0.10	-2.27 ± 0.04	3.9
	70	476 ± 2.0	750 ± 5.3	-3.62 ± 0.06	-3.69 ± 0.09	
NMF-S200	25	678 ± 11	863 ± 10	-1.78 ± 0.06	-2.28 ± 0.05	2.3
	70	600 ± 8.0	793 ± 13	-3.21 ± 0.03	-4.68 ± 0.17	
NMF-S300	25	932 ± 6.9	917 ± 8.9	-2.17 ± 0.07	-2.44 ± 0.03	1.0
	70	917 ± 2.9	927 ± 2.3	-3.87 ± 0.04	-4.65 ± 0.07	

^a Swelling ratio was defined as volume (pH = 10, 70 °C) / volume (pH = 3, 70 °C).

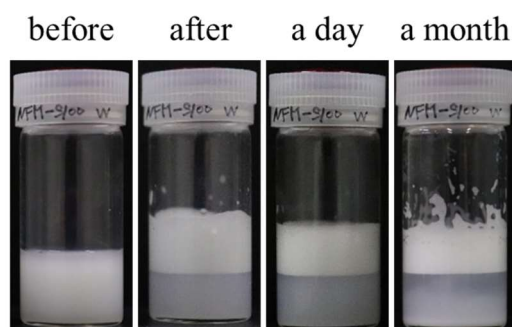


Figure S3. Photograph of NC-MSFs using NMF-S100 as a stabilizer. The foam was prepared by mixing 1 wt.% colloid dispersion at 10,000 rpm for 1 min at room temperature (25 °C). The obtained NC-MSFs were stable for at least one month after preparation.

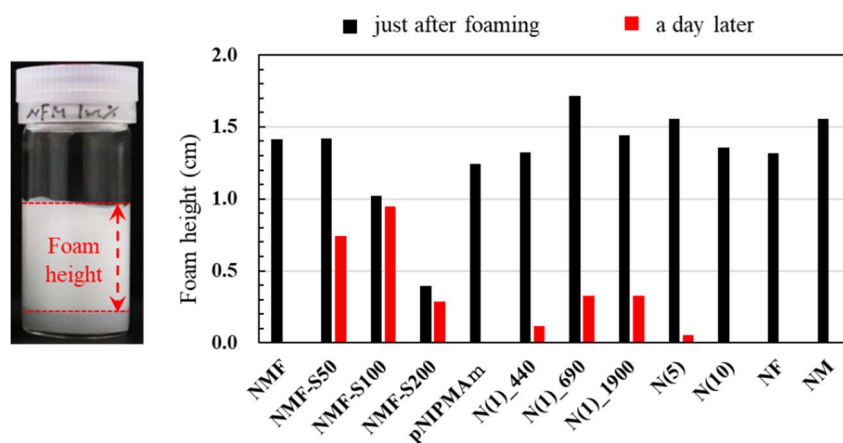
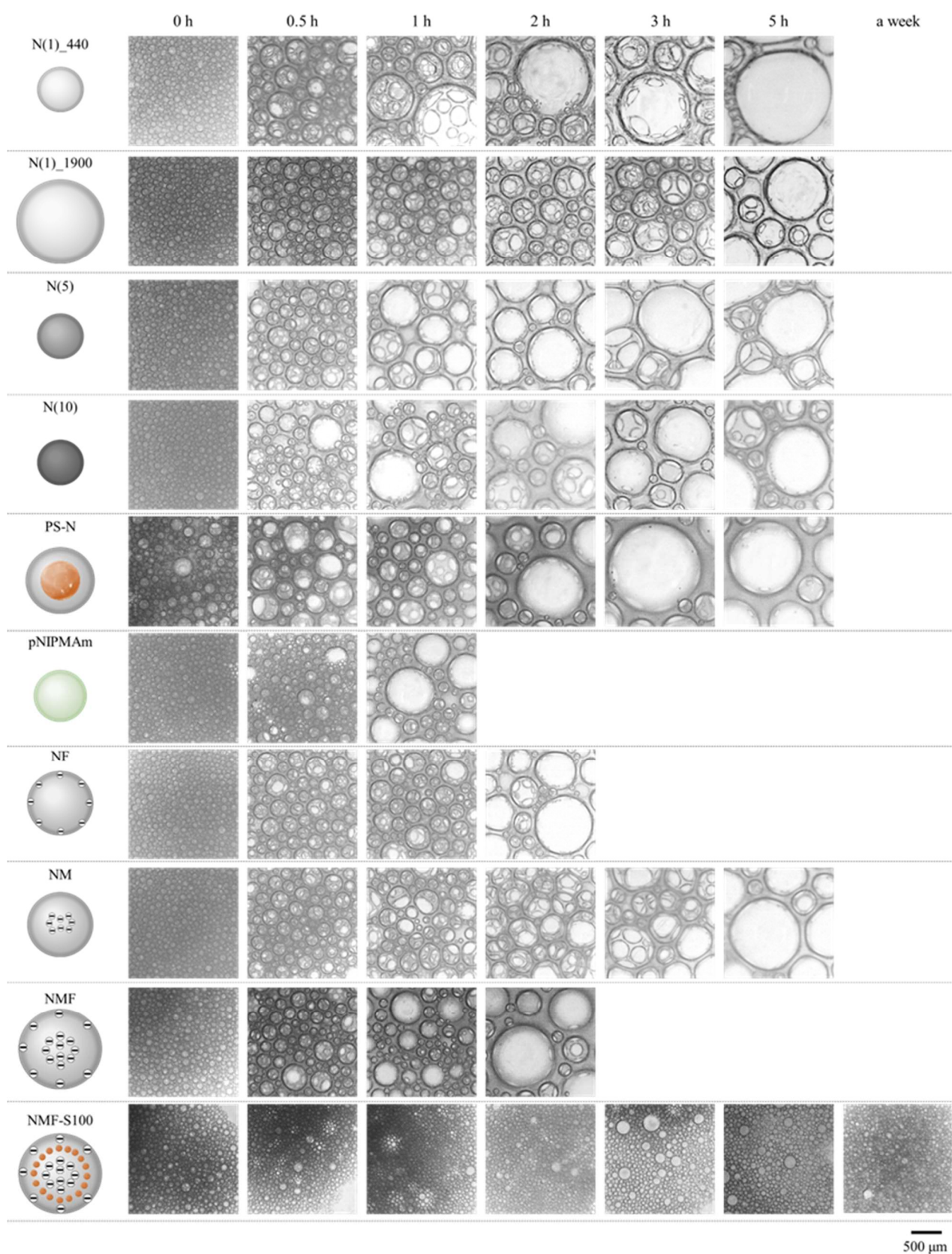


Figure S4. Foam height immediately after production and after 1 day, calculated from the images in Figure S1.



500 μm

Figure S5. Time-dependence of gas bubbles stabilized by unmodified and decorated microgels observed by optical microscopy.



Figure S6. Foaming test and characterization of foam stability with various types of microgels, NC microgels, and solid microspheres under different pH conditions (pH = 3 or 11). All foams were prepared by mixing 1 wt.% colloid dispersion at 10,000 rpm for 1 min at room temperature (25 °C). The foams were stored at room temperature for 1 day. The time-dependence of the foam diameter was also characterized using an optical microscope. Foams stabilized by NC microgels (NFM-S100) showed high storage stability regardless of the pH value of the solution.

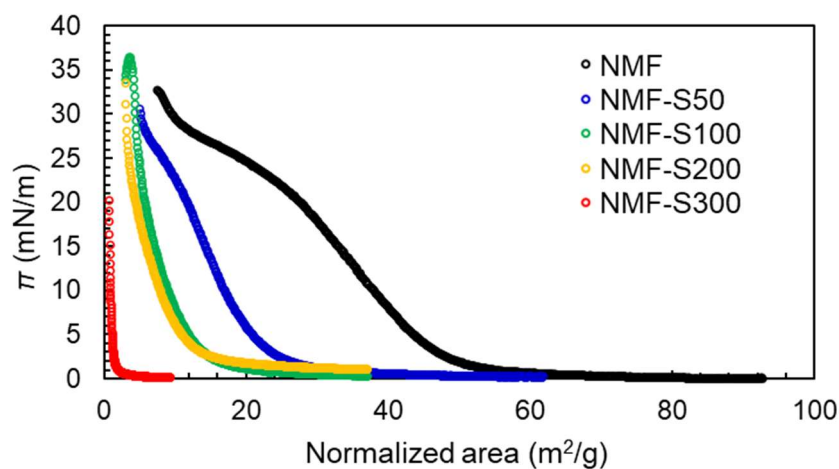


Figure S7. Compression isotherms for different microgels obtained from a Langmuir trough. The normalized area was defined as (interfacial area (m^2) / weight of microgel spread at interface (g)). All experiments were performed at the air/water interface at 25 °C and pH = 3.

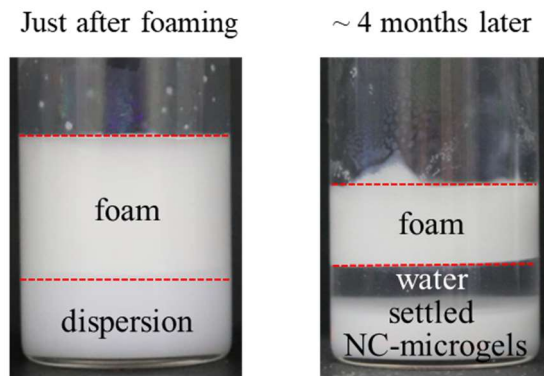


Figure S8. Photograph of NC-MSFs using NMF-S100 as a stabilizer. The foam was prepared by mixing 3.3 wt.% colloid dispersion at 10,000 rpm for 1 min at room temperature (25 °C). The obtained NC-MSFs were stable for at least 4 months after preparation.

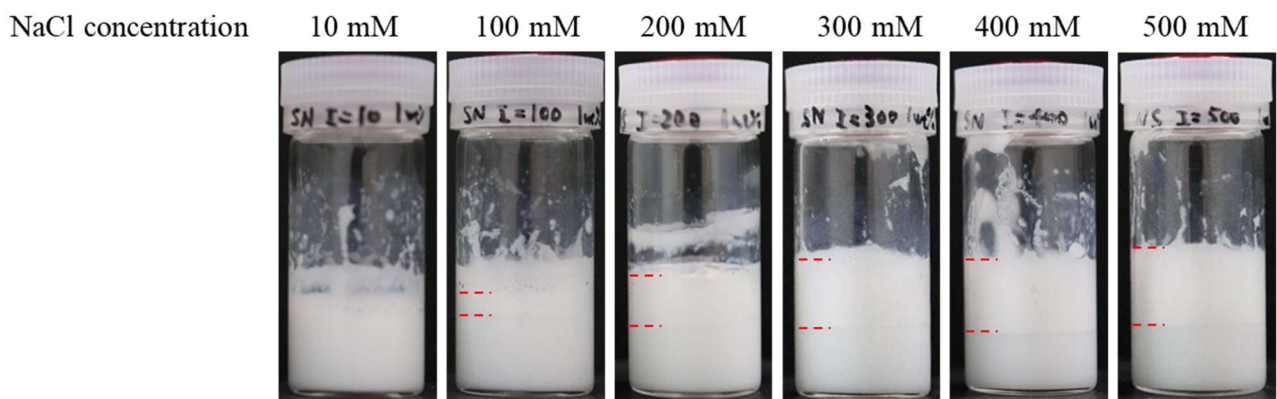


Figure S9. Photograph of PS-stabilized foams with different ionic concentrations. All foams were prepared by mixing 1 wt% colloid dispersion at 10,000 rpm for 1 min at room temperature (25 °C). NaCl promoted the particle adsorption to the air/water interface by decreasing the zeta potential of the PS particles as reported in ref [3].

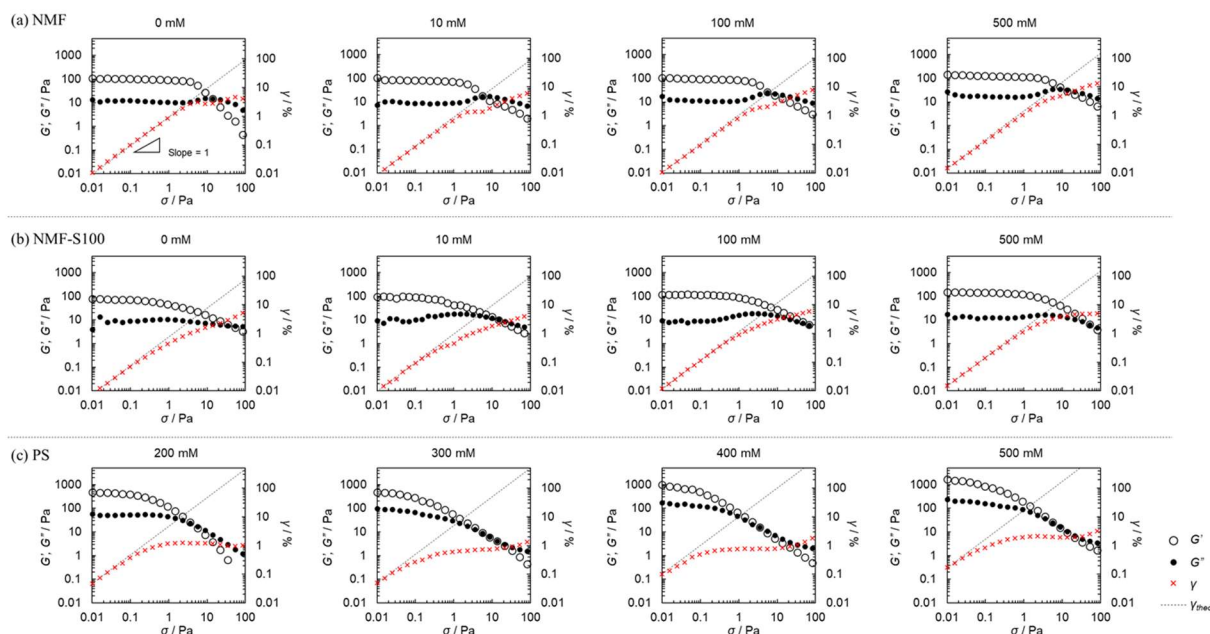


Figure S10. Strain dependence of the storage modulus (G'), loss modulus (G''), and shear stress (σ) of particle-stabilized foams with different NaCl concentrations. (a) NMF, (b) NMF-S100, and (c) PS. All foams were prepared by mixing 1 wt.% colloid dispersion at 10,000 rpm for 1 min at room temperature (25 °C). The yield point was defined as the point at which $\log \gamma$ and $\log \sigma$ deviated from a linear relationship as reported.^[4]

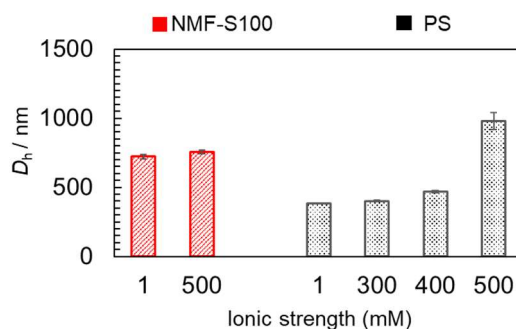


Figure S11. D_h derived from DLS measurements of NMF-S100 and PS with different NaCl concentrations. PS aggregated when the NaCl concentration was 400 mM or higher.

Supplementary Movies

Movie S1. Desorption of microgels from the air/water interfaces of gas bubbles.

Movie S2. Tilt series of cryo-ET of NMF-S100 nanocomposite microgels.

Movie S3. Tilt series of cryo-ET of NMF-S300 nanocomposite microgels.

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