Supporting Information

Processable and controllable all-aqueous gel based on the high internal phase water-in-water emulsions

EunSuk Lee[1], YoungSeon Jo[1], YeRin Kim[1], Hojoon Yoon[1], SeoYoung Choi[1], Baekmin Q. Kim[2], Subeen Kim[3] and KyuHan Kim[1]*

[1]Department of Chemical and Biomolecular Engineering, SeoulTech, Seoul, 01811, Republic of Korea

[2]Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, 19104, USA

[3]Department of Chemistry, Northwestern University, Evanston, Illinois, 60208, USA

*Correspondence to: kyuhankim@seoultech.ac.kr

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Materials and methods

Construction of phase diagram

Determining phase density: Phase densities for constructing phase diagrams were determined using pycnometers (10 ml, DAIHAN scientific). Two empty pycnometers were labeled as 1, 2 and weighed as M_1, M_2. After distilled water (DI water) was added to each pycnometer, the pycnometers were reweighed as M'_1, and M'_2 to calculate their volume using the well-known density of DI water. (calculated using the following equation, $\rho_{water} \times V_i = M'_i - M_i$) After dissolving 1.8618 g of polyethylene glycol (PEG, M_w= 20k, Sigma-Aldrich), and 2.5076 g of dextran (DEX, M_w= 40k, Sigma-Aldrich) in 20 mL DI water and allowing for phase separation, specific amounts of the PEG-rich phase, and DEX-rich phase were separately added into pycnometers 1 and 2, and the total mass of each pycnometer was weighed as M_{PEG}, M_{DEX}. The density of each rich phase was computed using the following equation ($\rho_{Polymer} \times V_i = M'_{polymer} - M_i$). The density of each phase was calculated to be 1.0208 g/ml for the PEG-rich phase and 1.0876 g/ml for the DEX-rich phase.

Constructing phase diagram: A phase diagram of the aqueous two-phase systems (ATPSs) with PEG and DEX was constructed through turbidity titration experiments.[1] 3 ml of PEG and DEX solution at a concentration capable of phase separation was prepared in a 15 ml tube, and centrifuged using a centrifuge (Cef-8, DAIHAN scientific) at 4500 rpm for 10 minutes to confirm phase separation. Then, the dilution process of adding 0.1 ml of DI water to the above solution, mixing, and centrifuging was repeated until phase separation does not occur even after centrifugation. The composition of the solution was calculated from the mass of DEX, PEG and DI water except for the mass of the last added DI water. (The mass fraction of each polymer is expressed as X and Y in the equation below.) The above experimental process was repeated for 16 solutions of PEG and DEX with different concentrations to obtain each composition, and using the obtained compositions, the equation for the binodal curve ($Y = c_1 e^{c_2 X^{0.5} + c_3 X^3}$ [1]) was obtained by a curve fitting.

Estimation of various interactions at the water-water interface

Capillary interaction: When the radius of particles is less than 5 μm, the capillary interaction between two particles was given by $F = -2\pi\gamma Q_1 Q_2 / L^2$ ($r_k \ll L, Q_k = R_k \sin(\alpha_k + \psi_k)\sin\psi_k$), where γ, Q, L, and R represent the interfacial tension, capillary charge, distance between particles, and radius of particle,

respectively. To express the maximum capillary interaction between two identical particles, it was assumed that the value of Q_k is equal to R from the inequality, $\sin(\alpha_k + \psi_k)\sin\psi_k \leq 1$, resulting in $F_{MAX} = -2\pi\gamma R^2/L$. Accordingly, the maximum magnitude of pressure induced by capillary interaction can be simply expressed by F_{MAX}/R^2, which results in $P_{MAX} = -\dfrac{2\pi\gamma R^2}{LR^2} \sim 1 \, kPa$.

Depletion attraction: The ideal value of the depletion pressure was calculated from osmotic pressure which is represented by the common equation, $\Pi = CRT$, where C, R, and T represent the molarity of DEX or PEG dispersed in the solution, the universal gas constant, and the absolute temperature in Kelvin, respectively. The molarity, calculated from the masses of DEX, PEG, and water in the mixture system, was substituted into the above equation, and as a result, the ideal value of the depletion pressure, $P_{ideal} = 16.8 \, kPa$.

On the other hand, in the real case, the osmotic pressure value was obtained by measuring the osmolality of each phase using an osmometer (Osmomat 030-D, Gonotec), and 50 µL each of the DEX-rich phase and the PEG-rich phase were used for this purpose. As a result, the osmolality of the PEG-rich and the DEX-rich phases were measured as 171 mOsm/kg and 120 mOsm/kg, respectively. Theses measured values were then converted to kPa unit (PEG-rich phase: 371 kPa, DEX-rich phase: 253 kPa). Then, the depletion pressure of the total mixture was estimated as $P_{real} = 16.8 \, kPa$, based on the averaged osmotic pressure of the two phases.

Synthesis of polymeric particles

PS particle Synthesis: Polystyrene (PS) particles were synthesized by dispersion polymerization.[3] Prior to the reaction, styrene (≥99%, Sigma-Aldrich) was passed through a column packed with aluminum oxide (Sigma-Aldrich) to remove reaction inhibitors, and other reagents were used without further purification. 10.0 g of Styrene, 1.5 g of poly(vinylpyrrolidone) (PVP40, M_w= 40k, Sigma-Aldrich), 0.2 g of 2,2-azobis(2-methylpropionitrile) (AIBN, 98%, JUNSEI) and 100.0 g of absolute ethanol (99.5%, DAEJUNG) were added to a 250 mL three-neck reaction flask. The reactor was immersed in an oil bath and reacted by stirring using a hot plate stirrer. The reaction solution was deoxygenated with nitrogen gas while slowly heating to 70 °C for 30 minutes at a stirring speed of 200 rpm. Then, when the temperature reached 70 °C, the injection of nitrogen gas was stopped and the reaction was performed for 12 hours. The obtained polystyrene particles were filtered/washed with ethanol after removing unreacted monomers

with methyl alcohol (99.8%, DAEJUNG), and then dried in a vacuum oven at 60 °C for 12 hours.

Density of polystyrene particles: Through the experiment for determining the density of each phase, the densities of the PEG-rich phase and DEX-rich phase were confirmed to be 1.02 g/ml and 1.08 g/ml, respectively. To determine the density of the synthesized polystyrene particles, two aqueous PEG and DEX solutions with 7.64 % and 10.29 %, respectively were prepared first, and then, the polystyrene particles were dispersed in the PEG solution with 1 w/v%. Subsequently, each solution was poured into a 1.5 ml tube at a 1:1 ratio and centrifuged at 12000 rpm for 10 minutes. After the centrifugation, it was observed that polystyrene particles were preferentially located at the water-water interface and formed a thin film (Fig. S3C), which strongly indicates that the density of the PS particle ranges from 1.02 g/ml to 1.08 g/ml.

PS-COOH particle Synthesis: Carboxyl polystyrene particles (PS-COOH) were synthesized by dispersion polymerization.[4] 1.44 g of poly(vinylpyrrolidone) (PVP55, Sigma-Aldrich, M_w= ~55k), 0.45 g of Triton X-100 (TX100, Sigma-Aldrich), 2.55 g of DI water, 48.45 g of ethanol, 9 g of Styrene and 0.36 g of AIBN were added to a 500 mL three-neck reaction flask. After a homogeneous solution was formed at room temperature, the solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 minutes. Then the flask was placed in a 70 °C oil bath and stirred mechanically at 150 rpm. 1.08 g of acrylic acid (AA, 99%, Sigma-Aldrich), 9 g of Styrene, 48.45 g of ethanol, and 2.55 g of DI water were introduced to a 250 ml three-neck flask. Then the AA solution was deoxygenated by bubbling nitrogen gas at 70 °C for 30 minutes. After the polymerization reaction had proceeded for 1 hour, the hot AA solution was added into the reaction flask. The reaction continued for 16 hours, followed by a cooling process for 30 minutes. After washing with ethanol and DI water, PS-COOH could be obtained after the drying process.

The morphology of particles (PS, PS-COOH) was characterized using a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) at a voltage of 10.0 kV.

Particle surface modification EDC coupling reaction

Polymeric chains were affixed to the surface of colloidal particles via EDC reaction[5]. The experimental details are indicated below. A MES buffer solution was first prepared by dissolving 0.1 M 2-(N-Morpholino)ethanesulfonic acid hydrate (MES hydrate, ≥99.5%, Sigma-Aldrich) in DI water and the pH of the buffer solution was adjusted to 6.0 with 0.1 N Sodium hydroxide (NaOH, DAEJUNG). 0.1 g of

carboxyl silica particles (SP-COOH, 0.5 μm or 1 μm, Polysciences) or carboxyl polystyrene particles (PS-COOH) were dissolved in 2.5 mL MES buffer solution. Subsequently, 0.0383 g of N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC, ≥99.0%, Sigma-Aldrich) was added and reacted for 30 minutes to activate the carboxyl group, and then 0.023 g of N-hydroxysuccinimide (NHS, 98% Sigma-Aldrich) was also added and reacted for 1 hour.

PEG chain-attached silica particles: Using methoxypolyethylene glycol amine (mPEG-NH_2, M_w= 5k / 10k, Sigma-Aldrich), the surface modification of silica particles was conducted. The reaction solution was prepared by mixing the activated SP-COOH (0.5 μm or 1 μm) and mPEG-NH_2 in the buffer solution at various mass ratios (1:X) and reacted overnight at 37 °C. After washing with DI water, the samples of PEG chain-attached silica particles (SP-PEG) could be obtained through a vacuum-drying process. To compare the effect of the molecular weight of the attached polymer chains on the colloidal particles, different molecular weights of mPEG-NH_2 (M_w= 750 / 2k, Sigma-Aldrich) were also applied in the same method using a fixed mass ratio of particle to polymer chain (1 : 0.1).

Zeta potential measurement: To confirm the change of degree of surface modification, zeta potential analysis was conducted with a zeta potential analyzer (ELSZ-2000ZS, Otsuka electronics). Here, to achieve a better accuracy of zeta potential measurements, 0.5 μm-silica particles were used as a model system for the emulsifier of W/W emulsions, and the change in the degree of surface modification is indirectly identified. Here, the surface modification of 0.5 μm-silica particles conducted with various mass ratios of the 5k-PEG chain to the particles of 0.001, 0.01, 0.1, 1, respectively. Additionally, the surface modification of 0.5 μm-silica particles also conducted with various mass ratios of the 10k-PEG chain to the particles of 0.01, 0.1, 1, respectively. Prior to the measurement, all samples were dispersed in DI water at a concentration of 0.1wt%.

DEX chain-attached silica particles: To synthesize DEX chain-attached silica particles, an amine group was attached to DEX.[6] 10 g of DEX in 70 ml dimethyl sulfoxide (DMSO, ≥99.9%. Sigma-Aldrich) was mixed with a solution of 2 g 1,1′-Carbonyldiimidazole (CDI, Sigma-Aldrich) in 5 ml DMSO, and the activation reaction proceeded at 50 °C for 15 minutes. Subsequently, 5 ml ethylenediamine (≥99%, Sigma-Aldrich) was added, and the mixture was stirred for 18 hours at 50 °C. Using a dialysis tube [avg. flat width 23 mm (0.9 in.), MWCO 14000, 99.99% retention, Sigma-Aldrich], the reaction solution was dialyzed in running water for 24 hours, and additionally dialyzed twice for 1.5 hours with DI water (3 L). Then, amino-DEX was recovered through freeze drying. The reaction solution was prepared by mixing the activated SP-COOH (1 μm) and amino-DEX in the buffer solution at the mass ratio (1:0.1) and reacted

overnight at 37 °C. After washing with DI water, the samples of DEX chain-attached silica particles (SP-DEX) could be obtained through a vacuum-drying process.

PVA chain-attached silica particles: The reaction solution was prepared by mixing the activated SP-COOH (1 μm) and polyvinyl alcohol (PVA, M_w= 30~70k, Sigma-Aldrich) in the buffer solution at the mass ratio (1:0.1) and reacted overnight at 37 °C. After washing with DI water, the samples of PVA chain-attached silica particles (SP-PVA) could be obtained through a vacuum-drying process.

PEG chain-attached PS particles: The reaction solution was prepared by mixing the activated PS-COOH and mPEG-NH_2 (M_w= 5k) in the buffer solution at the mass ratio (1:0.1) and reacted overnight at 37 °C. After washing with DI water, the samples of PEG chain-attached polystyrene particles (PS-PEG) could be obtained through a vacuum-drying process.

Observation of W/W interface

1.8618 g of PEG, and 2.5076 g of DEX were dissolved in 20 mL of DI water. The mixture solution was transferred to the cuvette and left to stand until phase separation was complete. Then, 10 μL of the particle solution where silica particles (SP, 1 μm, Polysciences) were dispersed in DI water at a concentration of 10 wt% was injected into the air/water interface of the solution. After the particles had sunk due to gravity and were absorbed at the water/water interface by the interfacial tension of the system, the behavior of the particles at the water/water interface could be observed using a custom-built lateral-view microscope. The experiments were conducted similarly for SP-COOH, SP-PEG, SP-DEX, and SP-PVA.

Preparation of W/W emulsion

Formation of W/W Emulsions: For the preparation of the emulsion, PEG and DEX were dispersed in DI water at concentrations of 15.70 wt% and 20.05 wt%, respectively, using a vortex mixer (MaXshake™VM30, DAIHAN Scientific). Colloidal particles were dispersed in the PEG solution in various fractions of 1-5 w/v% based on the total volume of the emulsion. W/W Pickering emulsions were formed in a vial (Each PEG/DEX solution was added in a 1:1 volume ratio) through a homogenizer (HG-15D, DAIHAN Scientific) at different rpms from 2,000 to 20,000 for 3 minutes. In addition, the internal phase volume fraction ($\varphi_{DEX-rich}$) of the W/W emulsion was calculated as the volume of the phase-separated DEX-rich phase divided by the total volume of the emulsion.

Stability of W/W emulsion under various pH conditions: To test the emulsion stability over a wide range of pH, the pH was adjusted by adding 0.1 M HCl and NaOH to the initial PEG and dextran solution. 5 w/v% SP-PEG particles were then added to form an emulsion using a homogenizer at 11000 rpm for 3 minutes (see Figure S18).

Optical microscope imaging: After homogenization, images of the emulsion in the glass vial were taken at various magnifications using the lateral-view optical microscope to observe the stability of the emulsion over time and the high internal phase emulsion (HIPE) structure. The size of the droplets within the emulsion was quantified by measuring the size of > 100 droplets using the software Image J.

Fluorescence microscope imaging: To visualize the dispersed phase, the DEX-rich phase, in the W/W emulsions, 0.05 w/v% of fluorescein isothiocyanate–dextran (FITC-dextran, M_w= 40k, Sigma-Aldrich) was added to the DEX solution before emulsifying the emulsion. Using an upright optical microscopy (BX53M, Olympus) with a fluorescence filter cube (Excitation: 455–495 nm/emission: 505–555 nm, TLV-U-FF-FITC, Olympus) and a camera (KSS3-10S camera, Korea LABTECH), the morphology of W/W emulsions were identified. As a result, the fluorescent DEX-rich phase retained its green coloration, while the PEG-rich phase exhibited no fluorescence and appeared dark.

Preparation of All-aqueous gels

The entire process for preparing all-aqueous gels was indicated as follows.[7]

Formation of W/W HIPEs containing monomers: The PEG stock solution was prepared by dissolving 7.64 wt% of PEG in DI water, dispersing 5k-PEG chain-attached colloidal particles (SP-PEG and PS-PEG) at concentrations of 1 and 5 w/v%. Subsequently, 7 wt% of acrylic acid (monomer), 2.5 wt% of N,N′-methylenebisacrylamide (MBAam, 99%, Sigma-Aldrich, crosslinker), and a radical photo-initiator were added to the solution. Here, lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP, ≥95%, Sigma-Aldrich), which is a photo-initiator, was added in a ratio of 1.30 mol% relative to acrylic acid. The DEX stock solution was prepared by dissolving 10.29 wt% of DEX in DI water. All stock solutions were made at final concentrations. The prepared PEG and DEX aqueous solutions were combined in a vial and stirred with a homogenizer at 11,000 rpm for 3 minutes (min) to form W/W HIPEs, which were then left in a darkroom until a stable structure was observed (~30 min). Furthermore, to demonstrate versatility, different types of hydrophilic monomers, such as acrylamide (≥99%, Sigma-Aldrich) and polyethylene glycol diacrylate (PEGDA, M_w= 700, Sigma-Aldrich) were added to form a w/w HIPE stabilized with

SP-PEG particles (5k-PEG chain attached) at 5 w/v %.

Formation of all-aqueous gels: Subsequently, the W/W HIPEs (containing monomers) were photopolymerized by exposure to 700 W UV light for 30 min using a UV curing machine (RX-CB1500D-DJT, Raynics). To clearly observe the internal structure of the all-aqueous gels, 0.05 w/v% of FITC-labeled dextran (displaying green luminescence with excitation/emission wavelengths of 495/525 nm) was initially dissolved in the DEX-rich phase, and the internal structures were thoroughly investigated. In addition, 0.001 w/v% of rhodamine 6G (displaying green luminescence with excitation/emission wavelengths of 530/552 nm) which was initially dissolved in the PEG-rich phase, was also utilized to clearly observe the interconnectivity of the all-aqueous gels. Then, optical (Differential Interference contrast, DIC), fluorescence and Z-stacked 3D images were captured by a confocal microscopy (LSM 800 Bio, Carl Zeiss) and analyzed using the ZEN software.

Drying of all-aqueous gels: After curing the W/W HIPEs, they were frozen with liquid nitrogen and freeze-dried for 48-72 hours in a freeze dryer (FDU-1200, Sunileyela) to remove the internal phase. Furthermore, the morphologies of all-aqueous gels were characterized by using a scanning electron microscope (SEM, Tescan VEGA3) at a voltage of 15.0 kV. Prior to observation, all samples were completely dried and sputter-coated with platinum.

Rheological properties of all-aqueous gels: The rheological properties of the all-aqueous gels were measured using a rheometer (MCR 302, Anton Paar) with parallel plate geometry (1 mm gap, 25 mm diameter), where different all-aqueous gels were prepared by adjusting the monomer concentration (3, 7, 10 wt%). Prior to the rheological measurement, the all-aqueous gels were loaded onto the bottom plate of the rheometer using a micropipette. The shear moduli at a fixed frequency (1 Hz) are then measured with various strain amplitudes ranging from 0.1 to 1000%. In addition, for the spreadability test, 0.3 mL of each sample with different monomer concentrations of 3, 7, and 10 wt% is loaded onto the fiber-based substrate (polyester/cotton blend, 7.5 × 4 cm) a using a micropipette. The spreadability of each sample is then tested by forming a thin film on the substrate using a spatula.

Molecular release measurements of all-aqueous gels: The all-aqueous gel containing FITC-Dextran (0.5 mg/ml) in the dispersed phase was initially stored in a vial and then, an additional 4000 µL DI water was gently poured to the top of the all-aqueous gels. The UV absorbance of the bulk water phase to which fluorescent molecules were released from the all-aqueous gel along a concentration gradient was measured over time (15 min, 30 min, 60 min, 180 min, 300 min, 1080 min) using a UV/VIS spectrometer

(UV-2700i, Shimadzu), and the concentration of released molecules was further calculated based on a standard calibration curve.

Viscosity measurement of various aqueous solutions: Using a rheometer (MCR 302, Anton Paar) with parallel plate geometry (1 mm gap, 25 mm diameter), the viscosity of different aqueous solutions of polymers that can form aqueous two-phase systems (ATPSs): 3 wt% and 7.5 wt% gelatin solutions, 7.64 wt% and 20 wt%-PEG solutions, and 10.29 wt% and 20 wt%-DEX solutions were measured. Prior to the viscosity measurement, the sample solutions were loaded onto the bottom plate of the rheometer using a micropipette. Shear rates ranged from 0.1 to 1000 1/s, and all solutions were measured at 25°C.

Supporting Figures
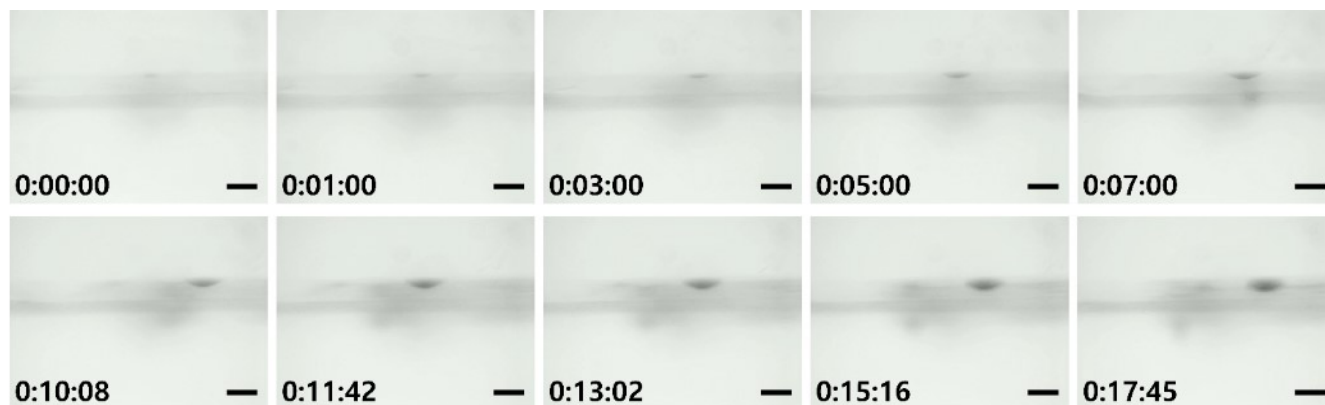
Figure S1. The behavior of silica particles (SP) at the water-water interface (PEG 7.64 wt%/DEX 10.29 wt% system, Top: PEG-rich phase/Bottom: DEX-rich phase) was observed through a horizontal microscope. Time is indicated in hours:minutes:seconds. At the water-water interface, silica particles form aggregates due to depletion force within the first 1 hour. The size of all particles is 1 μm, and the scale bar is 1000 μm.
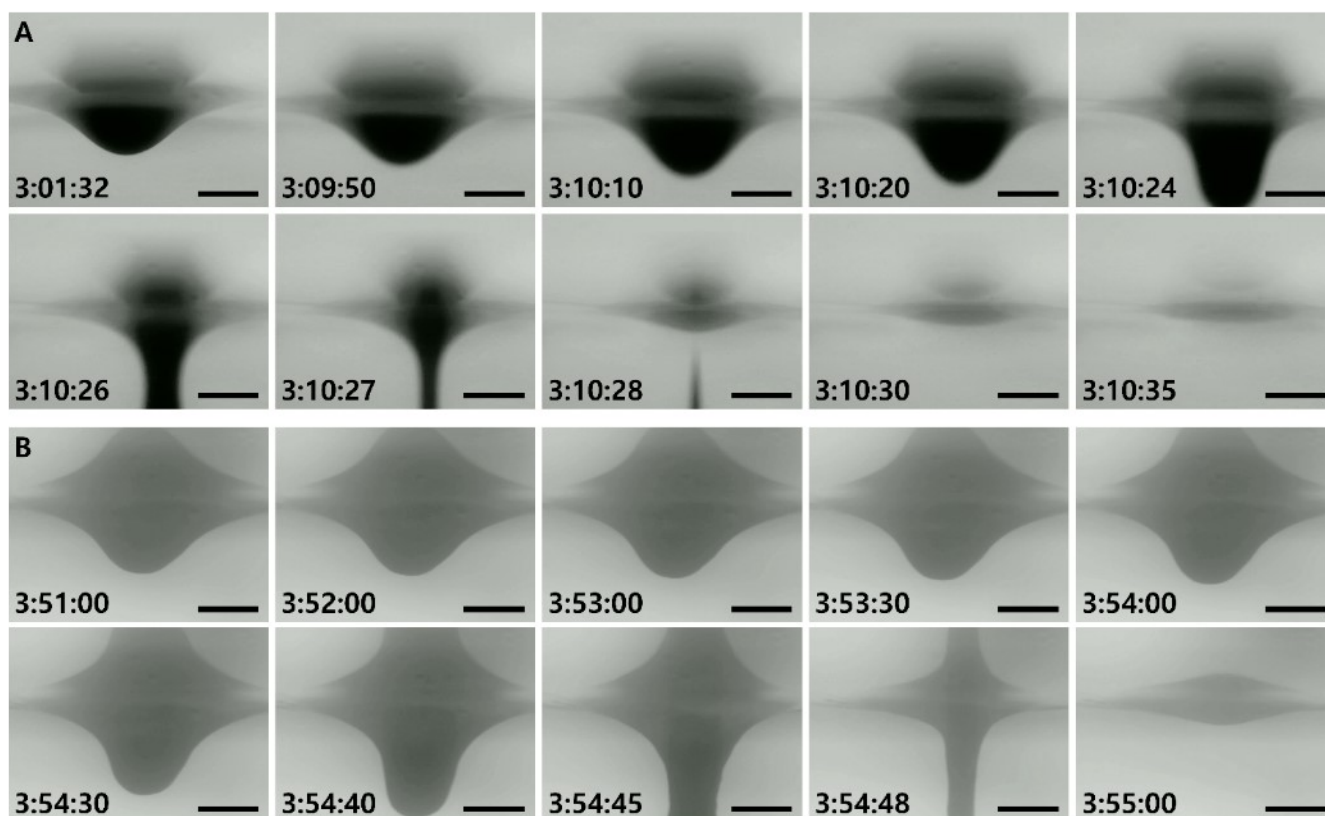
Figure S2. The behavior of colloidal particles at the water-water interface (PEG 7.64 wt%/DEX 10.29 wt% system, Top: PEG-rich phase/Bottom: DEX-rich phase) was observed through a horizontal microscope. Time is indicated in hours:minutes:seconds. A) For pure silica particles (SP), complete desorption from the interface can be observed approximately within 30 seconds after the considerable shape change of particle aggregates is observed. B) For carboxyl silica particles (SP-COOH), it takes a bit longer to observe particle aggregates than for pure silica. However, it can be observed that particle aggregates are completely desorbed from the interface within approximately 1 minute after the significant shape change is observed. The size of all particles is 1 μm, and the scale bar is 500 μm.
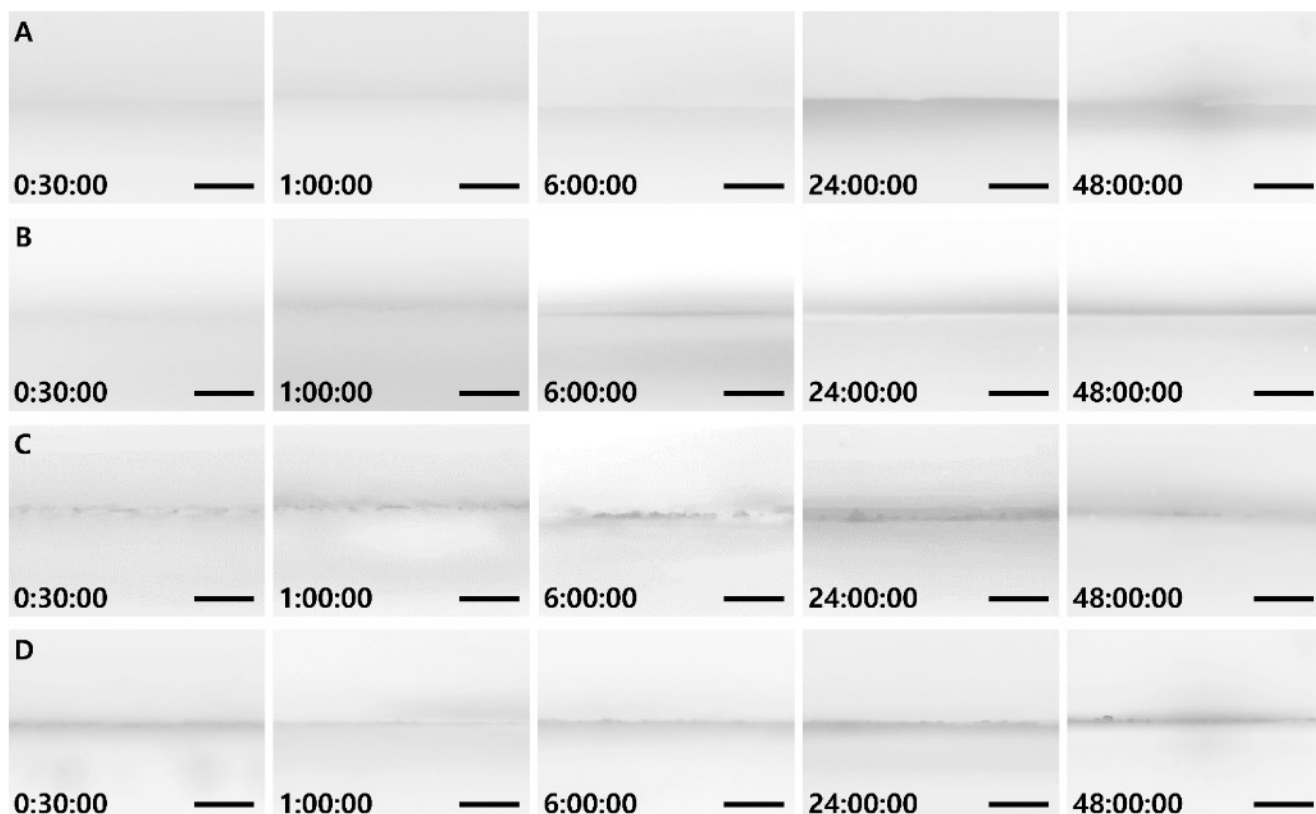
Figure S3. The behavior of silica particles with different degrees of 5k-PEG chain attachment to the surface was observed at the water-water interface (PEG 7.64 wt%/DEX 10.29 wt% system, top: PEG-rich phase/bottom: DEX-rich phase) was observed through a horizontal microscope. Time is indicated in hours:minutes:seconds. A) Silica particles whose surfaces are modified with the mass ratios of 0.001. B) Silica particles whose surfaces are modified with mass ratios of 0.01. C) Silica particles whose surfaces are modified with mass ratios of 0.1. D) Silica particles whose surfaces are modified with mass ratios of 1. All silica particles modified with several different mass ratios of 5k-PEG chains are stable at the water-water interface for at least 48 hours. The size of all particles is 1 μm, and the scale bar is 500 μm.
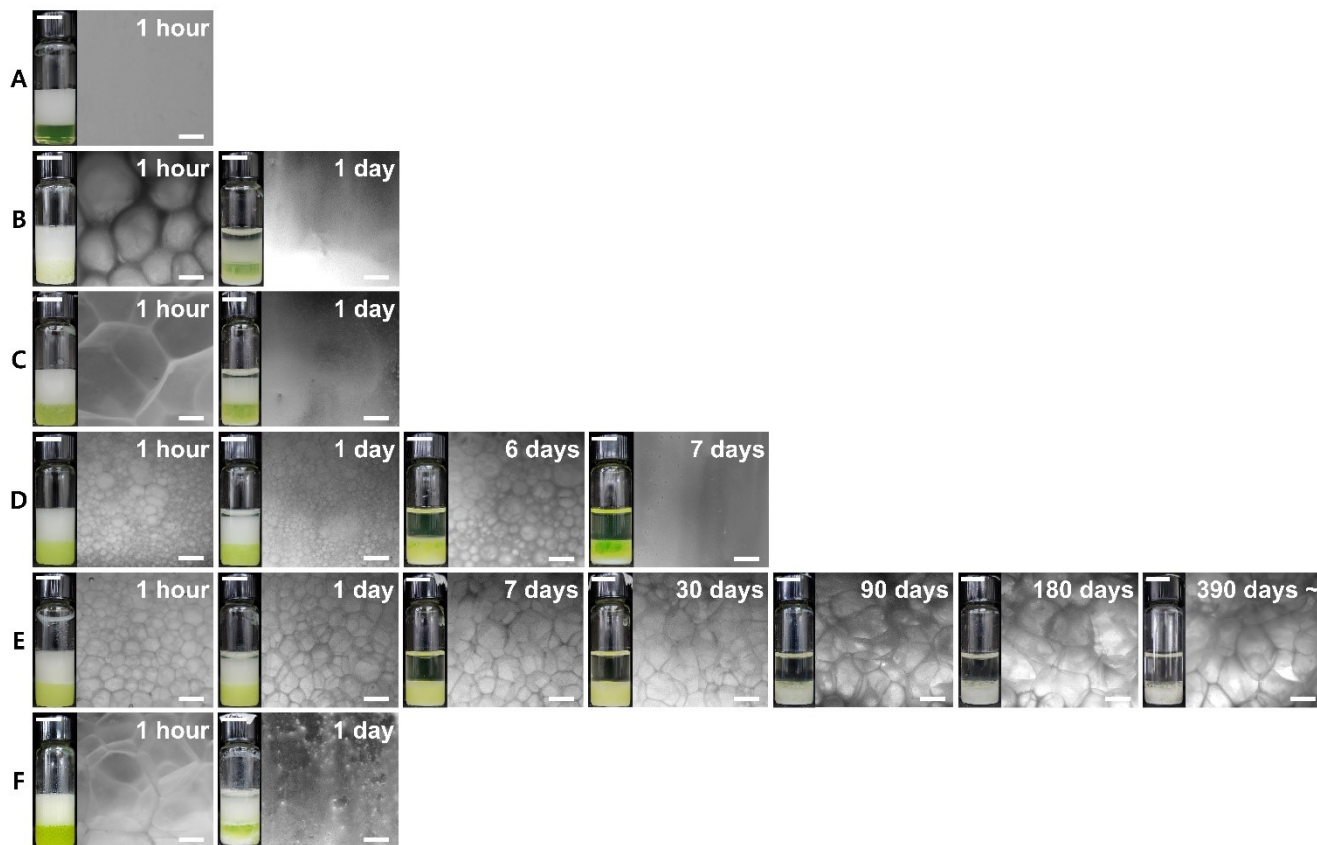
Figure S4. Macroscopic and microscopic images of W/W HIPEs over time. All W/W HIPEs with SP (A), SP-COOH (B), and SP-PEG(C, D, E, F) are emulsified at a fixed particle concentration of 5 w/v% and a fixed homogenizing speed of 11000 rpm. The upper phase in macroscopic images is the remaining PEG-rich phase, and the lower phase is the phase of W/W HIPE. Scale bars in macroscopic images and optical microscopic images taken from the horizontal microscope are 1 cm and 500 μm, respectively. A) W/W HIPEs whose surfaces are stabilized with pure silica particles phase-separate within minutes. B) W/W HIPEs with carboxyl silica particles phase-separate within a few hours. C) W/W HIPEs with the silica particles whose surfaces are modified with mass ratios of 0.001 phase-separate within a few hours. D) W/W HIPEs of silica particles whose surfaces are modified with mass ratios of 0.01 phase-separate within 7 days. E) W/W HIPEs of silica particles whose surfaces are modified with mass ratios of 0.1 remain stable even after 390 days. F) W/W HIPEs of silica particles whose surfaces are modified with mass ratios of 1 phase-separate within 1 days.
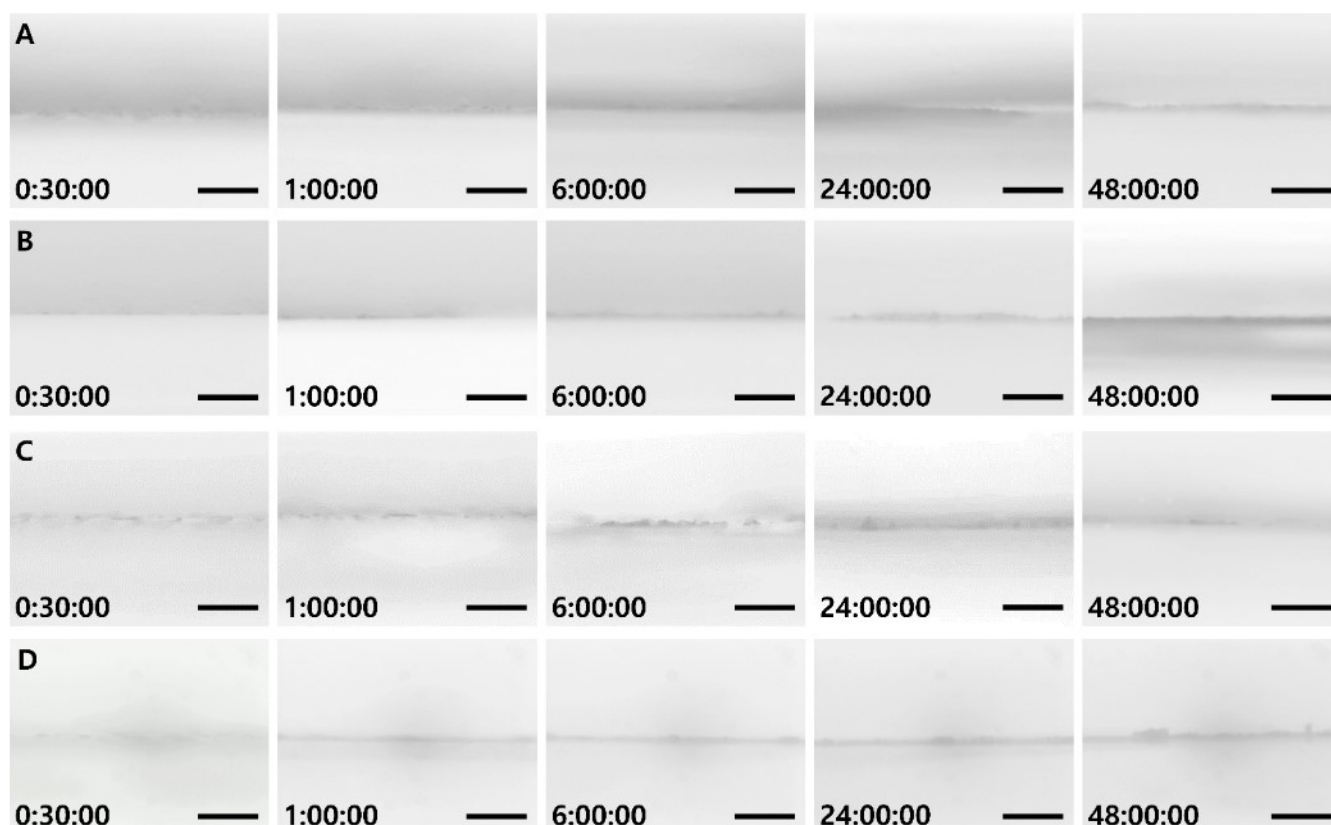
Figure S5. The behavior of silica particles modified with different molecular weights of PEG chain was observed at the water-water interface (PEG 7.64 wt%/DEX 10.29 wt% system, top: PEG-rich phase/bottom: DEX-rich phase) through a horizontal microscope. Time is indicated in hours:minutes:seconds. A) Silica particles whose surfaces are attached with 750-PEG chain. B) Silica particles whose surfaces are attached with 2k-PEG chain. C) Silica particles whose surfaces are attached with 5k-PEG chain. D) Silica particles whose surfaces are attached with 10k-PEG chain. For all particles whose surfaces were attached by polymeric chains with various lengths, no significant particle aggregations were observed even after 48 hours, and accordingly, no particle desorption was observed as well. The size of all particles is 1 μm, and the scale bar is 500 μm.
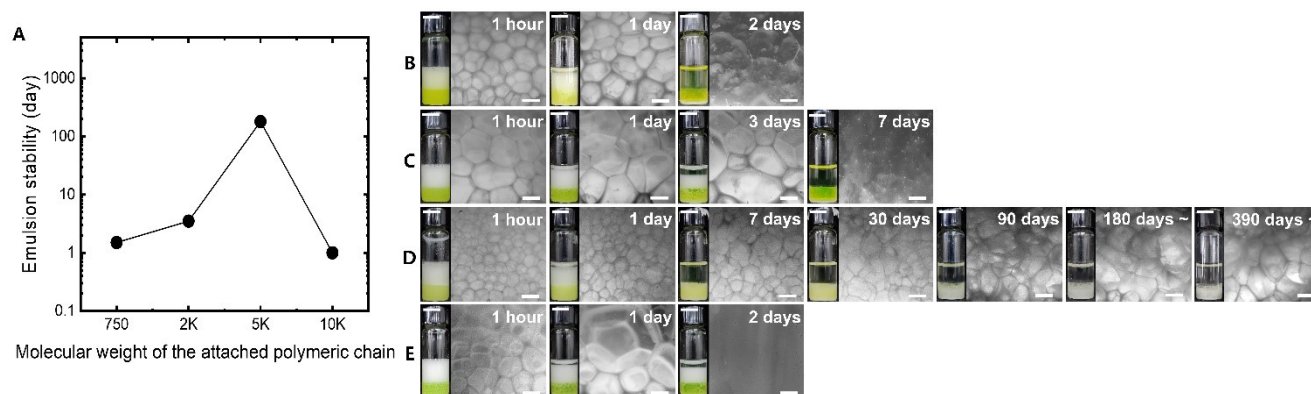
Figure S6. A) A graph indicating the change in the duration of stability of W/W emulsions depending on the surface modification with different lengths of PEG chains at the fixed mass ratio of 0.1 (750, 2k, 5k, and 10k). As a result, 5k-PEG with the mass ratio of 0.1 seems to provide the most effective stabilization of particles at the interface under the given experimental conditions. B)-E) Macroscopic and microscopic images of W/W HIPEs over time. All W/W HIPEs with SP-PEG are emulsified at a fixed particle concentration of 5 w/v% and a fixed homogenizing speed of 11000 rpm. The upper phase is the remaining PEG-rich phase, and the lower phase is the phase of W/W HIPE. Scale bars in macroscopic images and optical microscopic images taken from the horizontal microscope are 1 cm and 500 μm, respectively. B) W/W HIPEs of silica particles whose surfaces are attached with 750-PEG chain phase-separate within 2 days. C) W/W HIPEs of silica particles whose surfaces are attached with 2k-PEG chain phase-separate within 4 days. D) W/W HIPEs of silica particles whose surfaces are attached with 5k-PEG chain remain stable even after 390 days. E) W/W HIPEs of silica particles whose surfaces are attached with 10k-PEG chain phase-separate within 2 days.
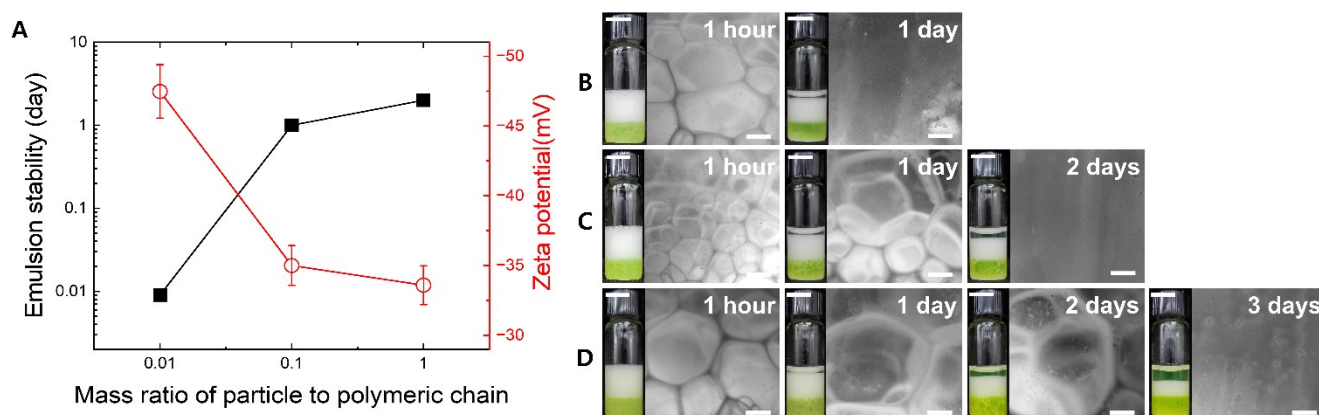
Figure S7. A) A graph indicating the change in the duration of stability of W/W emulsions and the zeta potential of silica particles depending on the particle surfaces modified with different mass ratios of 10k-PEG chains to the particles (0.01, 0.1, and 1). The magnitude of zeta-potential in 10k-PEG gradually decreases with increasing the mass ratio from 0.01 to 1, and the magnitude values are considerably greater than those of 5k-PEG at the same mass ratios of 0.01, 0.1, and 1, which strongly indicates that there are not enough 10k-PEG chains attached to the particle surface at the mass ratio of 1. B-D) Macroscopic and microscopic images of W/W HIPEs of 10k-PEG chain-attached silica particles whose surface is modified with different mass ratios of 0.01 (B), 0.1 (C) and 1 (D) over time. B) W/W HIPEs of silica particles whose surfaces are attached by 10k-PEG with the mass ratios of 0.01 phase-separate within a few hours. C) W/W HIPEs of silica particles whose surfaces are attached by 10k-PEG with the mass ratios of 0.1 phase-separate within 2 days. D) W/W HIPEs of silica particles whose surfaces are attached by 10k-PEG with the mass ratios of 1 phase-separate within 3 days. All W/W HIPEs with SP-PEG are emulsified at a fixed particle concentration of 5 w/v% and a fixed homogenizing speed of 11000 rpm. The upper phase in the macroscopic images is the remaining PEG-rich phase, and the lower phase is the phase of W/W HIPE. Scale bars in macroscopic images and optical microscopic images taken from the horizontal microscope are 1 cm and 500 μm, respectively.
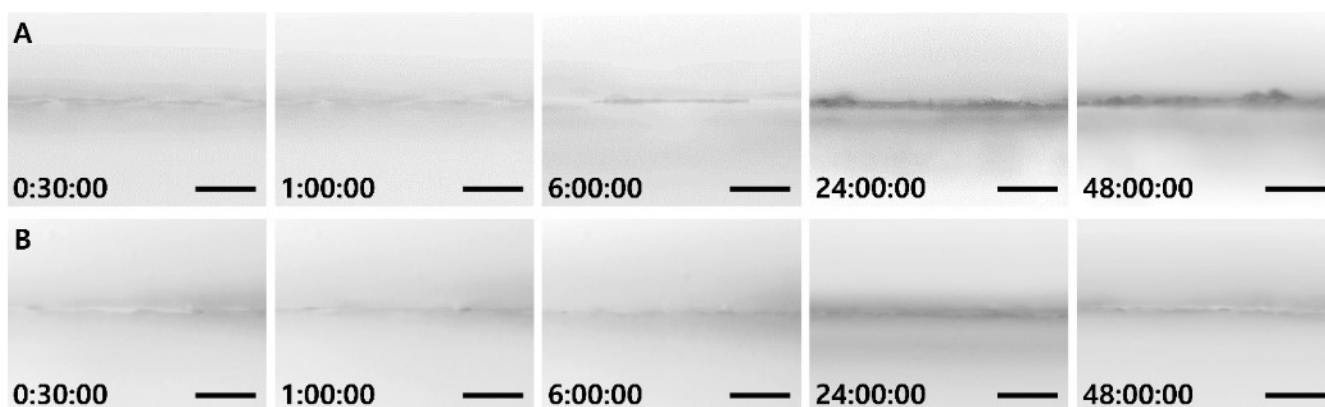
Figure S8. The behavior of colloidal particles whose surface is attached with other polymeric chains at the water-water interface (PEG 7.64 wt%/DEX 10.29 wt% system, Top: PEG-rich phase/Bottom: DEX-rich phase) was observed through a horizontal microscope. Time is indicated in hours:minutes:seconds. A) DEX chain-attached silica particles (SP-DEX). B) PVA chain-attached silica particles (SP-PVA). For all particles whose surfaces were attached with polymeric chains, no particle aggregations were observed even after 48 hours, and accordingly, no particle desorption b was observed as well. The size of all particles is 1 μm, and the scale bar is 500 μm.
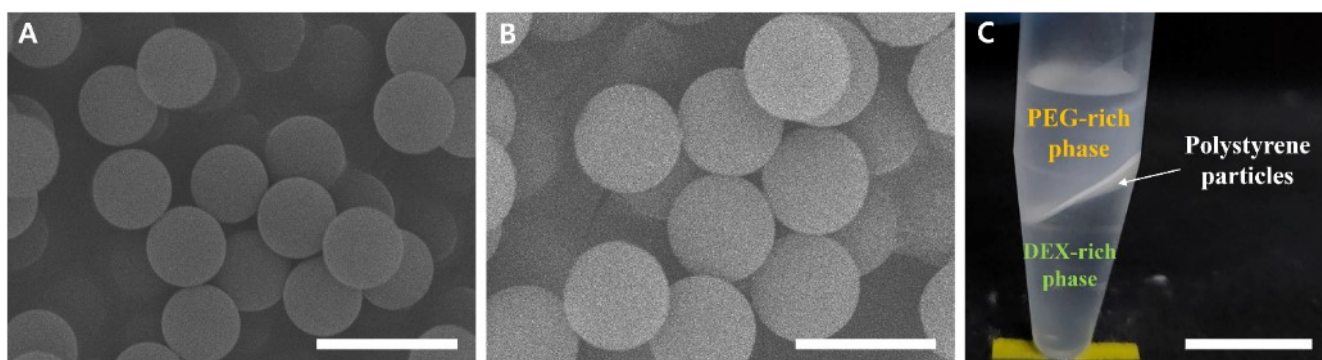
Figure S9. A) The SEM image of bare polystyrene (PS) particles. An average diameter is about 1.7 μm. B) The SEM image of carboxyl polystyrene (PS-COOH) particles whose average diameter is about 2.3 μm. C) The macroscopic image of polystyrene particle solution (1 w/v%) containing 7.64 wt% of PEG and 10.29 wt% of DEX after the centrifugation process [12000 rpm (rcf: 9659 x g) for 10 minutes]. Scale bar of macroscopic image is 1 cm. PS particles are preferentially located between the two aqueous phases, which strongly indicates that the density of synthesized PS particle ranges between 1.021 (density of the PEG-rich phase) and 1.088 (density of the DEX-rich phase). To obtain SEM (Scanning electron microscope) images, all samples were coated with platinum before taking images. All scale bars for SEM images are 3 μm.
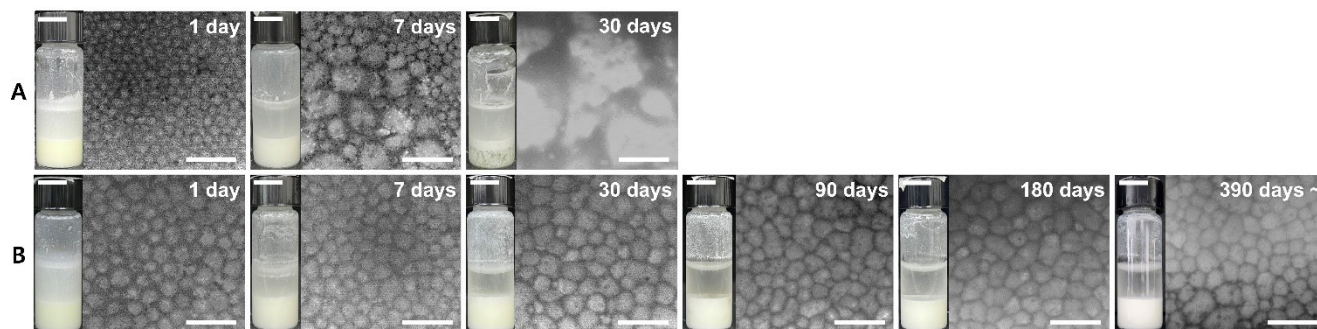
Figure S10. Macroscopic and microscopic images of W/W HIPEs over time. All W/W HIPEs with pure PS particles (A) and PS-PEG particles (B) are emulsified at a fixed particle concentration of 5 w/v% and a fixed homogenizing speed of 11000 rpm. The upper phase in the macroscopic images is the remaining PEG-rich phase, and the lower phase is the phase of W/W HIPE. (A) The structural change of W/W HIPEs stabilized by Pure PS particles with time. 24 hours after the emulsification, the W/W Pickering emulsion where dispersed droplets with a diameter of ~ 100 μm are observed, as shown in the Left. It seems to be somewhat stable for up to a week, but after a week, the HIPE began to be destabilized rapidly, and collapses within a few weeks. (B) The structural change of W/W HIPEs stabilized by PS-PEG particles. W/W HIPEs with PS-PEG particle remain stable even after 390 days.
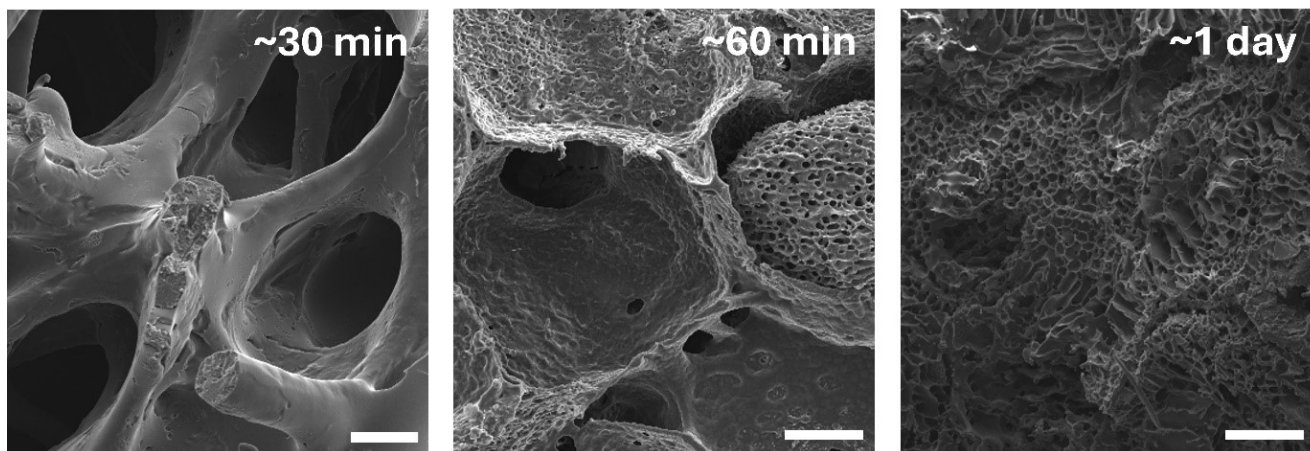
Figure S11. SEM image of freeze-dried all-aqueous gels as a function of waiting time between emulsification and polymerization. All gels were polymerized by photopolymerization at three different waiting times after emulsion formation. The images show that polymerized structures in the dispersed phase become more prominent with longer waiting times. To enhance visualization via SEM, all samples were platinum-coated. The scale bar in each image represents 100 μm.
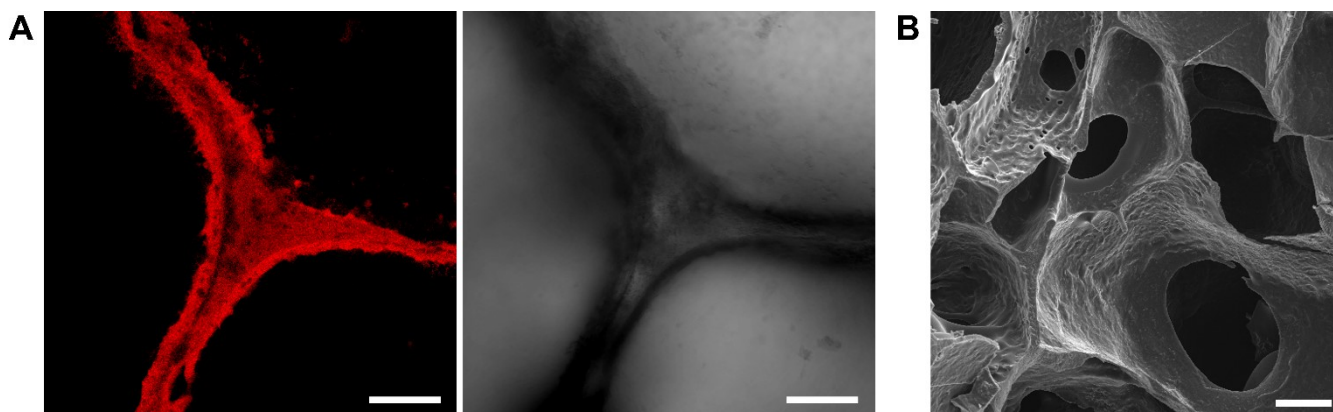
Figure S12. CLSM (A, left), DIC (A, right) and SEM (B) images of the internal structures of all-aqueous gels prepared with W/W HIPEs containing 5 w/v% SP-PEG. Upon detailed examination of sliced all-aqueous gels with SP-PEG at 5 w/v%, potentially leading to completely separate droplets are frequently observed in CLSM images. However, upon additional evaporation applied to the gels, pore throats are frequently observed in the polymer support, as shown in SEM image. This suggests that sufficient interconnectivity between the pores may occur due to shrinkage of the polymeric support during the water evaporation process. All scale bars are 100 μm.
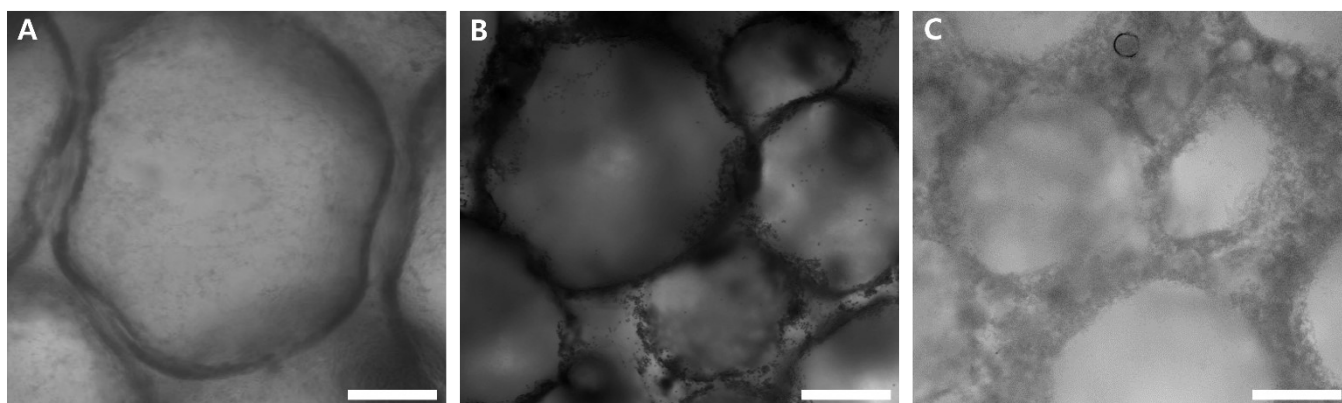
Figure S13. DIC images of all-aqueous gels prepared from W/W HIPEs stabilized with 5k-PEG chain-attached colloidal particles. A) All-aqueous gel based on W/W HIPE containing 1 w/v% SP-PEG. B) All-aqueous gel based on W/W HIPE containing 1 w/v% of PS-PEG. C) All-aqueous gel based on W/W HIPE containing 5 w/v% of PS-PEG. As increasing the concentration of PS particle, an excessive abundance of PS particles is primarily observed in the continuous phase. All scale bars are 100 μm.
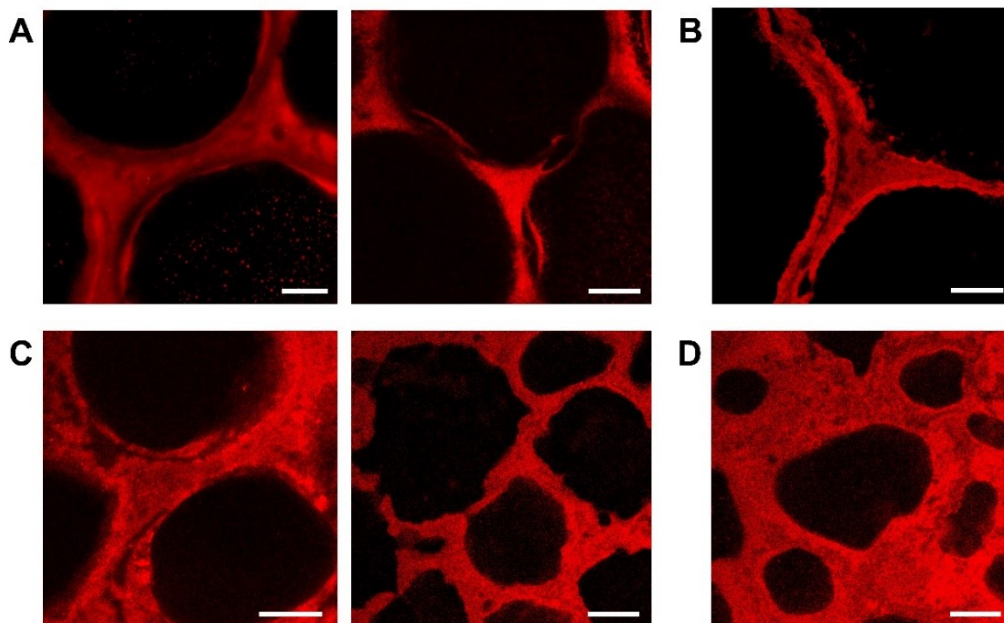
Figure S14. CLSM images of all-aqueous gels with regulated interconnectivity under different conditions. A) All-aqueous gels containing 1 w/v% SP-PEG. Interconnectivity was controlled by sedimentation time of ~15 min (left, closed cell) and ~30 min (right, open cell) for each dispersed droplet. B) All-aqueous gel containing 5 w/v% SP-PEG (sedimentation time of ~30 min). Formed a closed structure with thick polymer walls throughout. C) All-aqueous gel containing 1 w/v% PS-PEG. Interconnectivity was controlled by sedimentation time of ~15 min (left, closed cells) and ~30 min (right, partially open cells) for each dispersed droplet. D) All-aqueous gel containing 5 w/v% PS-PEG (sedimentation time of ~30 min). Very thick polymer walls throughout, forming a closed structure. All all-aqueous gels were labeled with rhodamine 6G in the continuous phase. All scale bars are 100 μm.
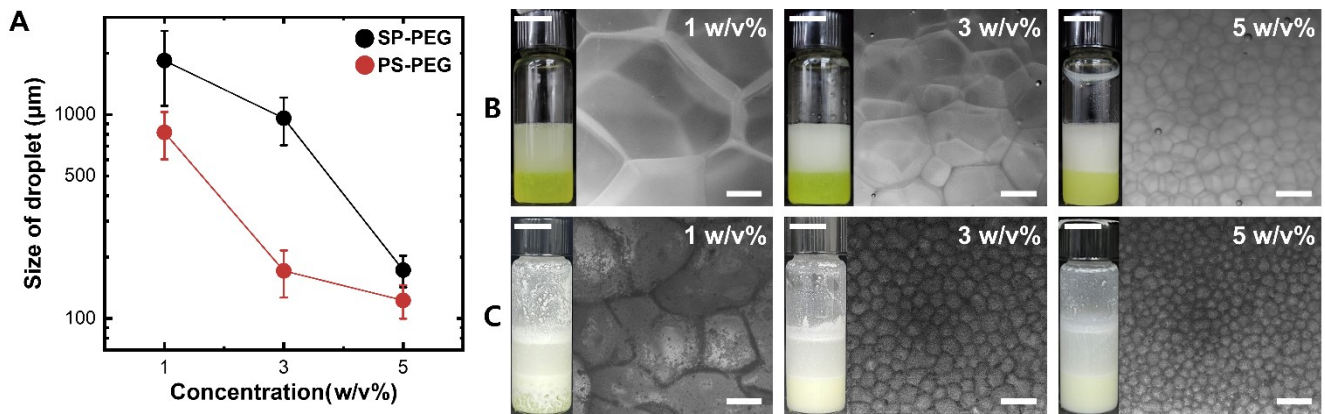
Figure S15. W/W HIPEs with varying a concentration of 5k-PEG chain attached particles (1, 3, 5 w/v%). All W/W HIPEs were emulsified at a fixed homogenizing speed of 11000 rpm. The upper phase in the macroscopic images is the remaining PEG-rich phase with some colloidal particles that are not participated in the emulsification, and the lower phase is the W/W HIPEs. A) The change in the droplet size of the W/W HIPE with varying concentrations of SP-PEG and PS-PEG. The droplet sizes of the HIPEs with SP-PEG and PS-PEG are measured at 1 hour and 24 hours after the emulsifications, respectively. B) Images of the W/W HIPEs with SP-PEG taken at 1 hour after the emulsification. C) Images of the W/W HIPEs with PS-PEG taken at 24 hours after the emulsification. Scale bars in macroscopic images and optical microscopic images taken from the horizontal microscope are 1 cm and 500 μm, respectively.
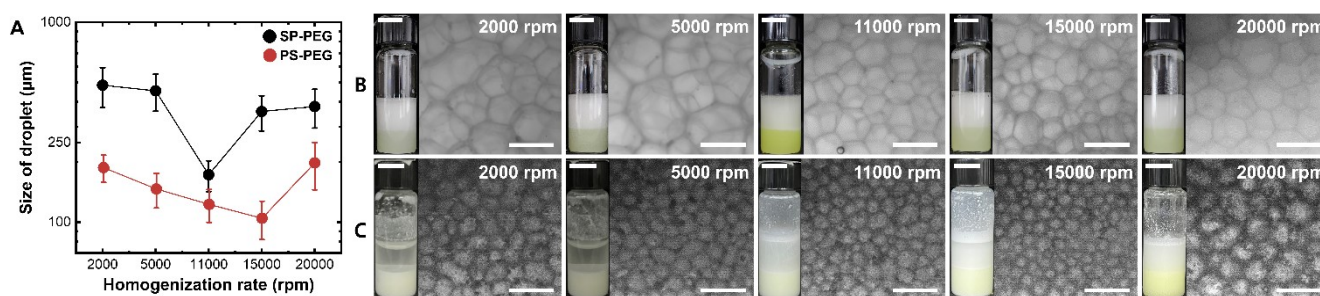
Figure S16. W/W HIPEs with varying homogenizing speeds (2000, 5000, 11000, 15000, 20000 rpm). All W/W HIPEs are emulsified at a fixed particle (5k-PEG chain attached particles) concentration of 5 w/v%. The upper phase in the macroscopic images is the remaining PEG-rich phase with colloidal particles that are not participated during the emulsification, and the lower phase is the W/W HIPEs. A) The change in the droplet size of the W/W HIPEs with varying the homogenization rate. The droplet sizes of the HIPEs with SP-PEG and PS-PEG are measured at 1 hour and 24 hours after the emulsifications, respectively. We investigated the effect of homogenization rate on droplet size, finding that higher energy initially reduces droplet size by increasing the total interfacial area. Droplets remain stable once particles fully cover this interface; otherwise, partial coverage can lead to coalescence into larger droplets. For SP-PEG particles, droplet size decreased with increasing energy up to 15,000 rpm, beyond which an excessively large interface led to rapid coalescence, resulting in larger droplets. PS-PEG particles, with a density balanced between the two aqueous phases, effectively stabilized droplets up to 15,000 rpm but also showed increased droplet size at 20,000 rpm due to similar stabilization limits. B) Macroscopic and microscopic images of the W/W HIPEs with SP-PEG taken 1 hour after the emulsification. C) Macroscopic and microscopic images of the W/W HIPEs with PS-PEG taken 24 hours after the emulsification. Scale bars in macroscopic images and optical microscopic images are 1 cm and 500 μm, respectively.
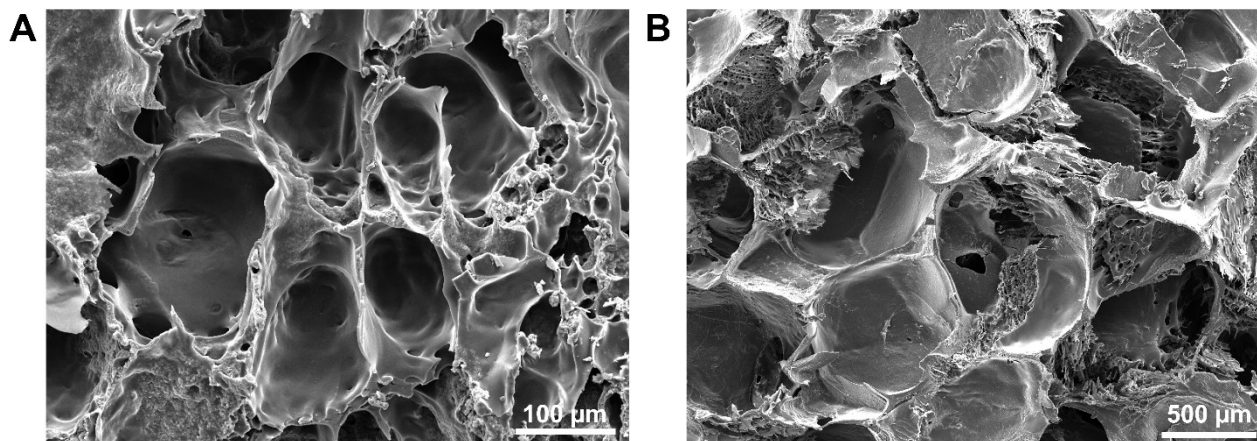
Figure S17. SEM images of polymeric supports prepared by freeze-drying all-aqueous gels made of different monomers (acrylamide, PEGDA). All all-aqueous gels with SP-PEG are emulsified at a fixed particle concentration of 5 w/v% and a fixed homogenizing speed of 11000 rpm. A) All-aqueous gel polymerized with acrylamide. B) All-aqueous gel polymerized with PEGDA. All samples were completely freeze-dried for 48 hours and sputter-coated with platinum.
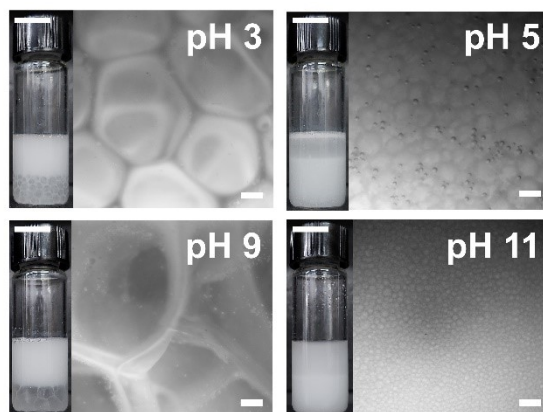
Figure S18. Macroscopic and microscopic images of W/W emulsions with varying pH. All emulsions were pH-adjusted with 0.1 M HCl and NaOH, and the particles utilized 5 w/v% SP-PEG. All emulsions were stable for at least 1 hour. Scale bars in macroscopic images and optical microscopic images are 1 cm and 500 μm, respectively.

Supplementary Movie 1. Spreading the all-aqueous gel containing 3 wt% monomer and 5 w/v% PEG-chain attached silica particles using spatula as a thin film on fiber-based plates.

Supplementary Movie 2. Spreading the all-aqueous gel containing 7 wt% monomer and 5 w/v% PEG-chain attached silica particles using spatula as a thin film on fiber-based plates.

Supplementary Movie 3. Spreading the all-aqueous gel containing 10 wt% monomer and 5 w/v% PEG-chain attached silica particles using spatula as a thin film on fiber-based plates.

Supporting Table

Table S1. Table adjusting the interconnectivity of all-aqueous gels under different conditions. At a particle concentration of 1 w/v %, the interconnectivity can be controlled by particle type and time conditioning. However, at 5 w/v %, a closed structure is formed regardless of time conditioning.

Type	PEGylated silica particles (SP-PEG)			PEGylated polystyrene particles (PS-PEG)		
Concentration	1 w/v %	5 w/v %		1 w/v %		5 w/v %
Sedimentation time	~15 min	~30 min	~30 min	~15 min	~30 min	~30 min
Inter-connectivity	Closed cell	Open cell	Closed cell	Closed cell	Partially open cell	Closed cell

Supporting References

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