Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Rheological responses of microgel suspensions with temperature-responsive capillary networks

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Materials and Methods:

Materials Acrylamide (AAm, M_W = 71.08 g mol^{-1}) and N-isopropylacrylamide monomer (NIPAm, stabilized with 4-methoxyphenol, M_W = 113.16 g mol^{-1}) were purchased from Tokyo Chemical Industry (TCI) America. Rhodamine B (RhB), 2-Hydroxyethyl methacrylate (HEMA), N, N'-dicyclohexylcarbodimide (DCC), 4-dimethylaminopyridine (DMAP), dichloromethane, acetonitrile, ammonium persulfate (APS), N, N-methylenebisacrylamide (BIS), Irgacure-2959 (I-2959), and Span 80 were purchased from Sigma-Aldrich (St Louis, MO, USA). Mineral oil (light) was obtained from Thermo Fisher Scientific. All chemicals were used as received without further purification.

Preparation of PAAm microgel suspensions PAAm microgels were synthesized from water-in-oil emulsion drops. PAAm precursor solution was prepared by mixing a monomer (AAm, 0.65 M) and a crosslinker (BIS, 0.03 M) in deionized (DI) water using a vortex mixer (MX-S, Dlab, USA) until all chemicals dissolved at 23 °C. Similarly, a photo-initiator solution (2.5 M) is prepared by mixing APS in DI water. The aqueous solution was then obtained by mixing PAAm precursor solution (7.6 mL) and photo-initiator solution (2.5 M, 0.4 mL) by vortex mixing. The oil phase containing 40 mL mineral oil and surfactants (Span 80, 780 μL) was transferred to a 50 mL centrifuge tube (SPL Life Science Co., Ltd) and mixed using a vortex mixer. 8 mL of PAAm precursor solution was slowly added into the centrifuge tube and agitated manually. The mixed emulsion was transferred to a glass dish (Pyrex, 90 × 50 mm) and irradiated with UV light (Omnicure S2000, wavelength: 365 nm, Lumen Dynamics, Canada) at 300 mW cm^{-2} for 80 min. After polymerization, the crosslinked PAAm microgels were collected in a 50 mL centrifuge tube and rinsed three times with 40 mL mineral oil to remove the surfactants by vortex mixing for 1 min and centrifugation at 5000 rpm for 10 min. To determine the volume fraction of microgels,

the fully swollen microgels were frozen using liquid nitrogen and placed in a freeze-dryer (FreeZone 2.5, Labconco, USA) at 0.03 mbar and −80 °C for at least five days to fully dry the microgels. A white powder was obtained and thereafter protected from humidity until its utilization.

Optical microscopy (Eclipse Ni, Nikon, Japan) was used to characterize the size distribution of fully swelled microgels. The images were analyzed through NIS-Elements software and over 100 microgels for each dataset were measured. To clearly show the margin of microgels, a threshold plug-in in ImageJ was employed to process the optical micrographs. Coefficient of variation (CV) is used to quantify the polydispersity of fabricated PAAm microgels, where σ is the standard deviation and μ represents the mean.

$$CV = \frac{\sigma}{\mu}$$

Preparation of microgel-capillary suspensions PNIPAm precursor solution (10 mL) was employed as the capillary solution to PAAm microgel suspensions, which was prepared by mixing NIPAm (0.83 g), BIS (0.02 g), and I-2959 (0.04 g) in DI water using a vortex mixer. We first determined the molecular weight (M_W) of PNIPAm by synthesizing linear PNIPAm from the same molar ratio of the monomer and the initiator (4 wt%) as we originally employed in the capillary solution except for the photo-crosslinker. The dn/dc value is 0.1730 mL g^{-1},[1] and the concentration we use is 5.0 mg mL^{-1}. We conducted gel permeation chromatography (GPC) and the M_W of linear PNIPAm is 9.7 × 10^5 (± 18.1%) g mol^{-1} (Fig. S3). To obtain the molecular weight between crosslinks ($\bar{M}_c$) in crosslinked PNIPAm networks, we examined the volumetric equilibrium degree of swelling from a bulky PNIPAm hydrogel. To achieve a dried state, hydrogel samples are dried

in the oven at 50 °C to constant weight. The $\bar{M}_c$ values can be calculated by the following equation based on the phantom network model:[2]

$$\bar{M}_c = -\frac{(1-2/\varphi)V_1\rho_2 v_{2r}^{2/3} v_{2m}^{1/3}}{(\ln(1-v_{2m}) + v_{2m} + \chi v_{2m}^2)}$$

where φ is the functionality of the crosslinks (φ = 4), V_1 is the molar volume of the solvent (DI water, $V_1 =$ 18 g cm^{-3}), v_{2m} is the volume fraction of the polymer network in the swollen gel at the equilibrium state and χ is the polymer-solvent interaction parameter. The v_{2m} values were calculated from the following expression at swelling equilibrium where m_s (1.74 g) is the mass of the fully swelled hydrogel and m_d (0.23 g) is the mass of the hydrogel after drying. ρ_2 (1.33 g cm^{-3}) and ρ_1 (1.0 g cm^{-3}) are densities of the polymer network and solvent, respectively.

$$v_{2m} = \left[1 + \frac{(m_s/m_d - 1)\rho_2}{\rho_1}\right]^{-1}$$

The χ parameters of the hydrogels can be obtained experimentally:[3]

$$\chi = \frac{1}{2} + \frac{v_{2m}}{3}$$

The volume fraction of polymer network as prepared, v_{2r}, was calculated as:

$$v_{2r} = \left[1 + \frac{(m_r/m_d - 1)\rho_2}{\rho_1}\right]^{-1}$$

where m_r (1.30 g) is the mass of the as-prepared hydrogel. The calculated $\bar{M}_c$ value for the crosslinked PNIPAm from capillary solution is 12.1 × 10^3 g mol^{-1}.

Imaging of microgel-capillary suspensions To visualize the capillary networks between microgels, RhB was conjugated to HEMA for subsequent copolymerization with NIPAm. RhB

5.26 g (11 mmol), DCC 2.88 g (14 mmol) and DMAP 134 mg (1.1 mmol) was dissolved in CH_2Cl_2 (75 mL). HEMA 1.82 g (14 mmol) was then introduced to the solution at 0°C.[4] After 30 min, the ice bath was removed and the reaction mixture was stirred at room temperature for 16 h. After filtering off the byproduct dicyclohexylurea, the solvent was evaporated under reduced pressure. The residue was redissolved in 30 mL acetonitrile and the insoluble materials were filtered off. The capillary solution used for imaging is composed of RhB-HEMA and NIPAm at a molar ratio of 1:20. To mix the PAAm microgel suspension and the capillary solution, a Thinky planetary mixer (Thinky U.S.A., Inc.) was applied at 2000 rpm for 5 min. An inverted microscope (Olympus IX71) with an attached WeatherStation environmental chamber was used for fluorescent imaging (2D images). Images were captured using a CoolSnap HQ2 CCD camera (Photometrics) at 20 × magnification with Tetramethylrhodamine (TRITC) filter (excitation 555/28 nm and emission 617/73 nm). Leica STED Sp8 with Falcon microscope was employed for 3D confocal microscopic images and panoramic videos. Z-stack images (26 images over 15 μm) were taken and 3D-reconstructed using Leica LAS X and Arvis software.

Rheological measurements Rheological data was obtained using an ARG2 rheometer by TA instruments with a plate-plate parallel geometry (sandblasted, 40 mm diameter) and a gap of 500 μm. All the measurements were performed at 25 °C unless otherwise noted. The samples were first transferred onto the bottom plate of the rheometer using a spatula and then compressed by lowering the geometry. To determine the linear shear moduli, storage moduli G' and loss moduli G" of PAAm microgel suspensions, we performed the oscillatory frequency sweeps with frequencies from 0.001 Hz to 10 Hz at a low strain amplitude of 1%. Similarly, frequency sweeps ranging from 0.01 Hz to 100 Hz at strain of 1 % were conducted for microgel-capillary suspensions. To quantify the yield stress and confirm the linear viscoelastic region of each

emulsion formulation, we measure the shear stress with shear rates covering 100 s^{-1} to 0.001 s^{-1}. As control groups, the frequency sweep and strain sweep of the capillary solution are performed (Fig. S7). The shear moduli and viscosity of the PNIPAm precursor remain in small values compared with microgel suspensions, which cancels the possibility that the rheological change is because of the overlay of microgel suspensions and a capillary solution. Frequency sweeps and amplitude and oscillation tests were conducted using the same batch of microgel suspensions for consistency. Oscillation temperature ramp was performed at a ramp rate of 2 °C/min from 25 °C to 45 °C after the polymerization of the capillary solution to determine the rheological response of temperature-responsive capillary bridges.

Contact angle measurements The contact angles of mineral oil and PNIPAm precursor solutionon PAAm layers were measured by Goniometer (Ramé-Hart Model 200). The same PAAm precursor for the synthesis of microgels was applied to cast PAAm layers. The PAAm precursor was injected in between two glass slides with Kapton films of 0.1 mm functioning as the spacer. The prepared PAAm layers were transferred to the petri dish and swelled in DI water overnight before being used for the measurements. 15 μL droplets of the test liquids were deposited onto the PAAm layer surface using a microsyringe (Gilmont). The reported values for contact angles are averaged over at least three independent measurements.

3D extrusion printing Microgel-crosslinked capillary networks were printed by extrusion using a 3D printer (BioX, Cellink). Microgel-capillary suspensions (Φ= 0.17) were transferred to the 3 mL syringes and centrifuged at 2000 rpm for 3 min to remove the air bubbles from the ink. The ink was placed in the extrusion carriage of the 3D printed and printed on a glass slide using a 22-gauge needle (inner diameter 0.41 mm) at 20 mm s^{-1} deposition rate with a pneumatic pressure of 30 kPa for printability assessment. The schematic image of the 3D extrusion process is displayed

in Fig. 4a. The printed structures were then transferred to a homemade transparent humid box to prevent drying out during UV irradiation (365 nm). The printed complex structures were photo-crosslinked by a UV intensity of 100 mW cm^{-2} for 20 min (Omnicure) (Fig. 4e).

Preparation of the casted PNIPAm, PAAm, and PAAm microgel/PNIPAm layers We used a sandwich molding method for the casting of PNIPAm, PAAm, and PAAm microgel/PNIPAm layers. The PAAm precursor was prepared by the same recipe used for the synthesis of PAAm microgels. The PNIPAm precursor was prepared by the same composition as the capillary solution. Microgel-capillary suspensions with Φ_{PNIPAm} of 0.17, 0.26, 0.44, and 0.87 were also prepared. Precursors and suspensions were injected in between two glass slides, with the other two glass slides functioning as a spacer of 1 mm. Molded precursors and suspensions were polymerized and crosslinked with a UV intensity of 100 mW cm^{-2} for 20 min. After that, the layers were transferred to petri dishes filled with DI water and swelled overnight at 23 ^{o}C and then heated to 50 °C for 5 hours to finish isotropic free swelling and deswelling. Linear swelling and linear deswelling ratios were calculated based on the measured lateral length via a caliper.

Statistical Analysis Data is presented as mean ± standard deviation (SD). A minimum of three tests were performed for rheological measurements and swelling and deswelling ratio to ensure that the results reported were significant.

Supplementary Figures

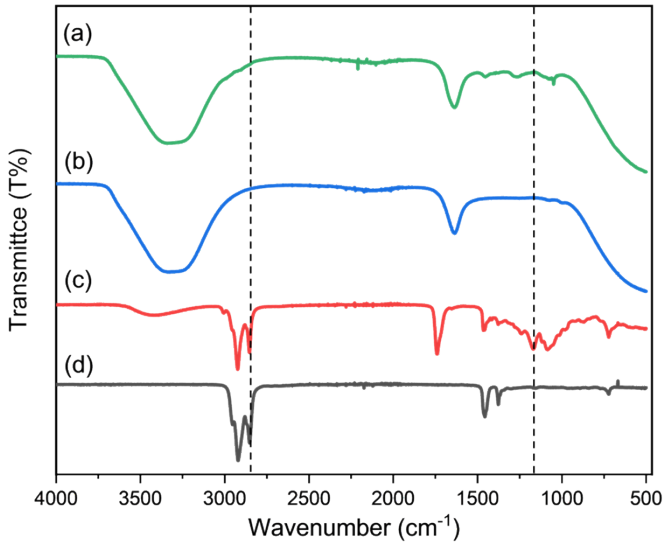

Fig. S1 FTIR spectra of (a) PAAm microgel suspension after oil washing once, (b) PAAm microgel suspension after oil washing three times, (c) Span 80, and (d) mineral oil.

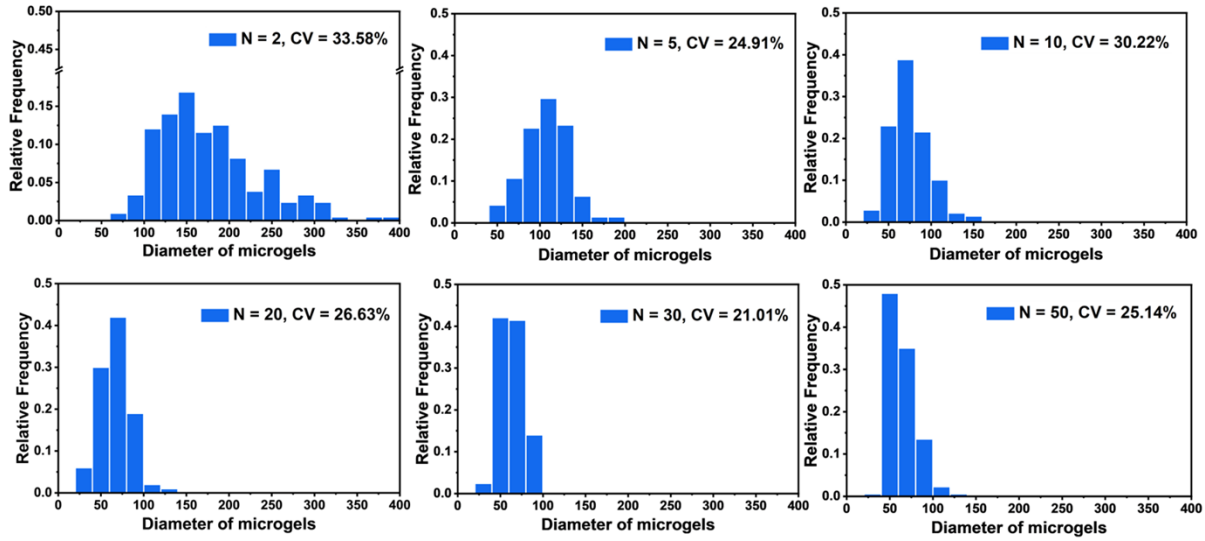

Fig. S2 Size distribution and coefficient of variation (CV) of PAAm microgels with the different number of agitations (N).

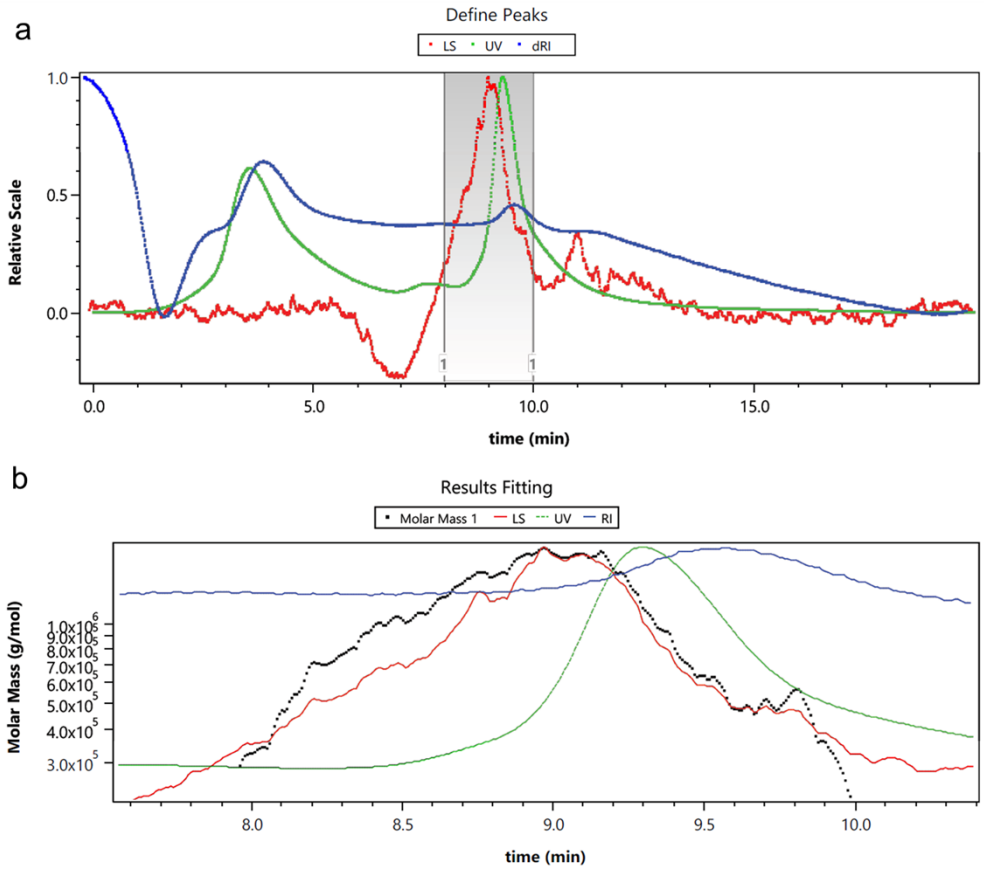

Fig. S3 The gel permeation chromatography (GPC) curve of the linear PNIPAm of 4 wt% I-2959 (same feed ratio between monomer and initiator in the crosslinkable PNIPAm precursor). (a) Calibration curves of peaks from evaporative light scattering (LS), UV, and differential refractive index (DRI) detectors. (b) Molecular mass fitting from LS, UV, and RI detectors.

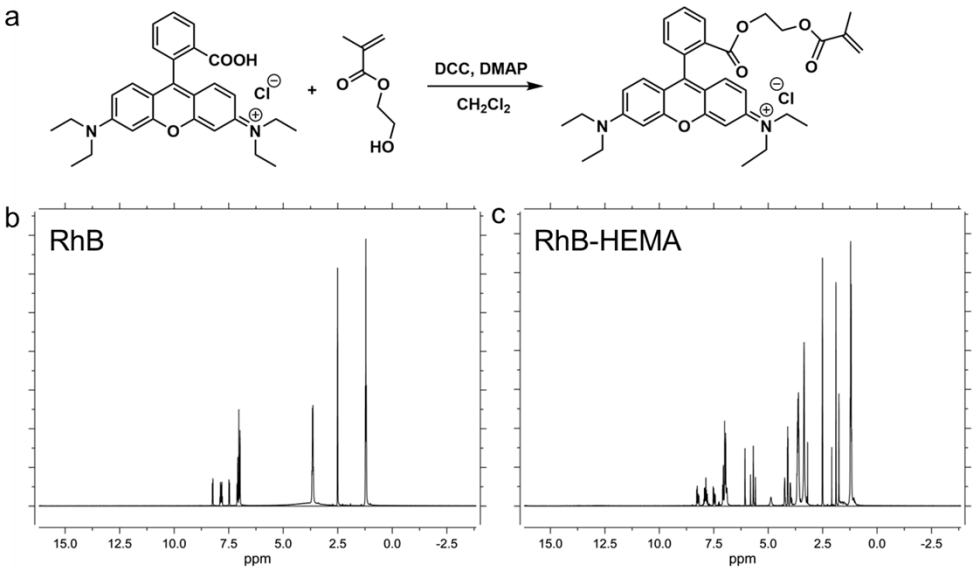

Fig. S4 (a) Synthesis of RhB-HEMA. (b and c) ^{1}H NMR spectra of (b) RhB and (c) prepared RhB-HEMA, respectively.

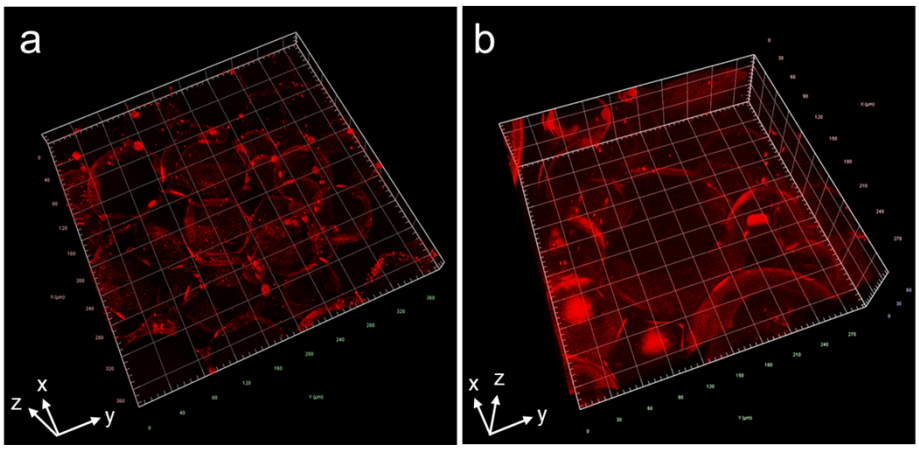

Fig. S5 3D confocal microscopic images of microgel-capillary suspensions with (a) $\Phi_{PNIPAm} =$ 0.04 and (b) $\Phi_{PNIPAm} =$ 0.17.

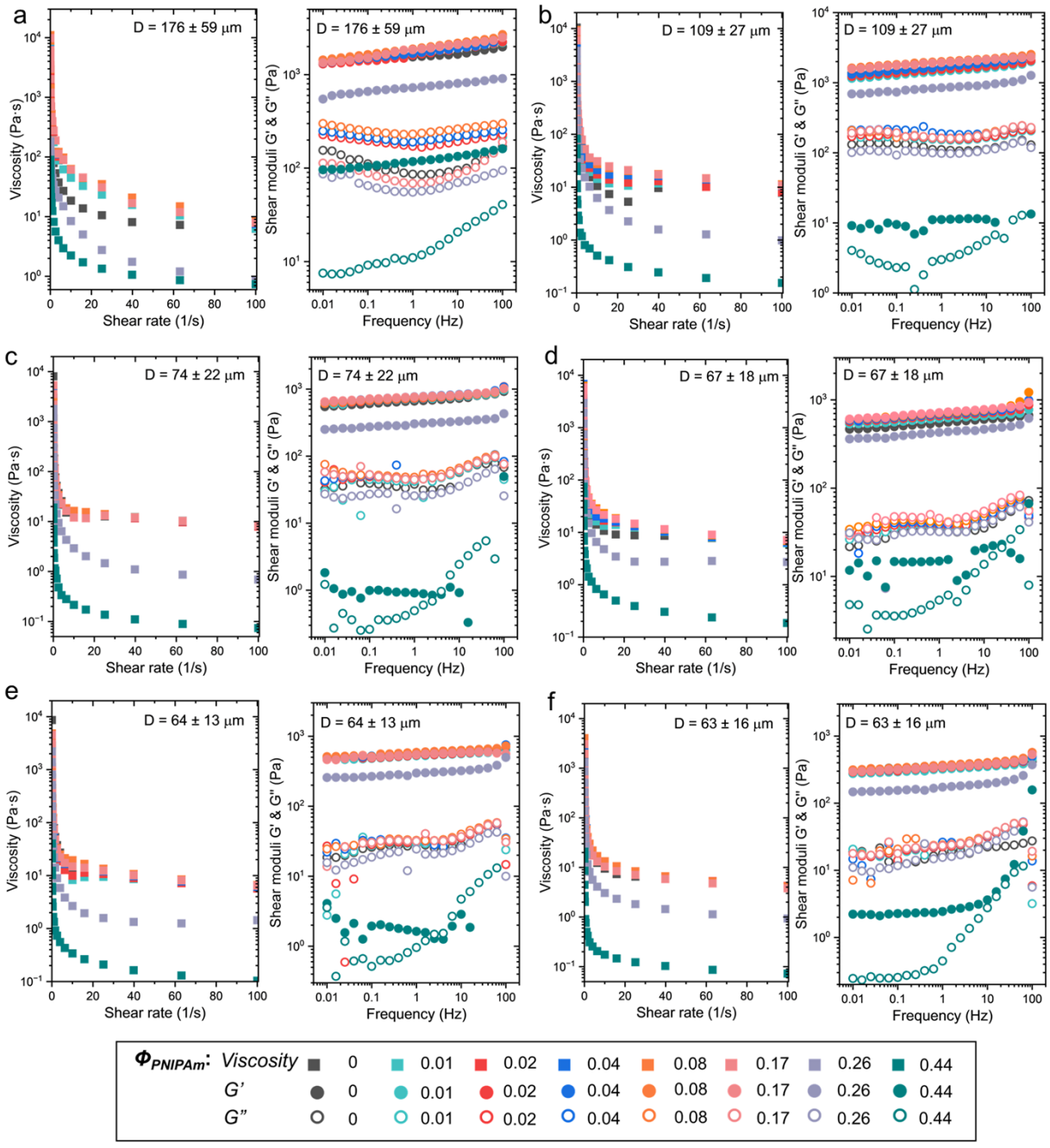

Fig. S6 Frequency sweep and strain sweep of microgel-capillary suspensions with different D and Φ_{PNIPAm}.

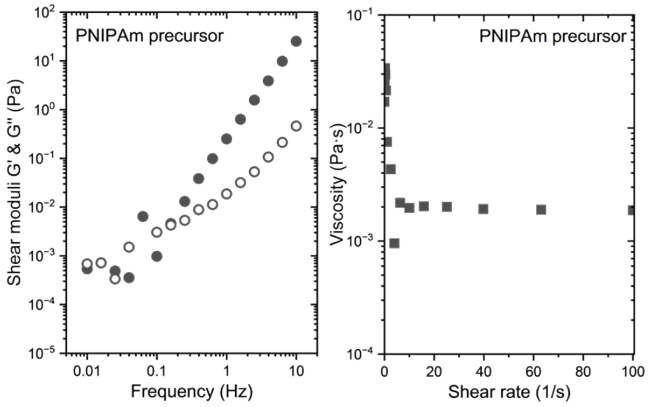

Fig. S7 Frequency sweep and strain sweep of the PNIPAm precursor used as the capillary solution.

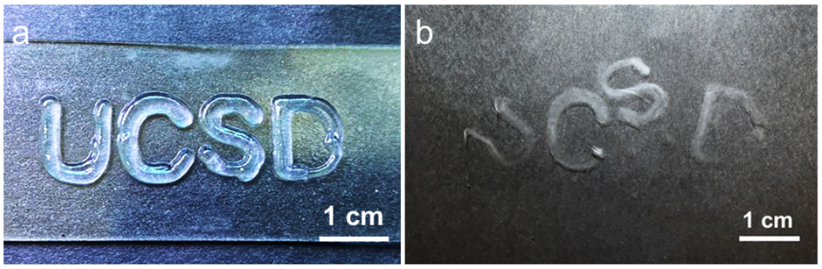

Fig. S8 Top view of the as-printed and cured freestanding "UCSD" letters after immersing in DI water for 24 hours.

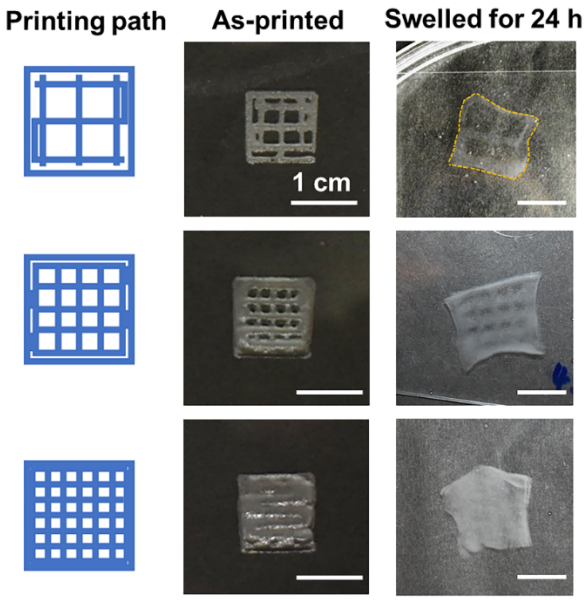

Fig. S9 Printing path and photographs of as-printed microgel-capillary suspensions and crosslinked microgel-capillary networks with infill densities of 25%, 45%, and 65%. Scale bar = 1 cm.

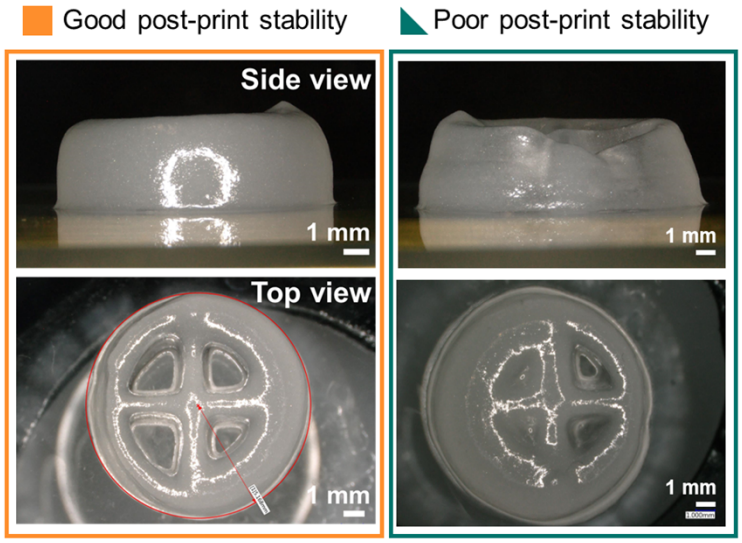

Fig. S10 Side and top-view optical images of the printed 3D multi-layered cylinder lattices showing good post-print stability and poor post-print stability. The structure collapse of the printed 3D lattices happened within 30 min after printing is defined as poor post-print stability.

Supplementary Videos:

Video S1: Video demonstrates the 3D extrusion printing of PAAm microgel suspension ink, in which letters "UCSD" is printed out.

Video S2: Video demonstrates 3D extrusion printing of microgel-capillary suspension ink, in which a lattice cylinder structure is printed out with the dimension of 5 mm in radius and 3 mm in height.

Video S3: Video demonstrates the 3D extrusion printing of PAAm microgel suspension ink, in which a lattice cylinder structure is printed out with the dimension of 5 mm in radius and 3 mm in height.

Video S4: Video demonstrates the panoramic presentations of Fig. 3d to visualize the capillary bridges between microgels.

References

1. G. Zhang and C. Wu, *Journal of the American Chemical Society*, 2001, **123**, 1376-1380.
2. T. Caykara, S. Kiper and G. Demirel, *European Polymer Journal*, 2006, **42**, 348-355.
3. S. Champ, W. Xue and M. B. Huglin, *Polymer*, 2001, **42**, 6439-6445.
4. Z. Gan, J. Ju, T. Zhang and D. Wu, *Journal of Nanomaterials*, 2011, **2011**, 753705.