Supporting Information

Moldable High Internal Phase Emulsion Hydrogel Objects from Non-Covalently Crosslinked Poly(*N*-Isopropylacrylamide) Nanogel Dispersions

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EXPERIMENTAL SECTION

Materials.

N-Isopropylacrylamide (NIPAm), *N,N'*-methylenebis(acrylamide) cross-linker (BIS), and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich and used as received. Ureido-pyrimidinone (UPy) functionalized poly(ethylene glycol) methacrylate (PEGMA) macromonomer and Rhodamine B piperazine methacrylamide were synthesized by the method as described in our previous study.[1, 2] Hostasol dye was kindly donated by the Prof. Haddleton's group. All other chemicals were analytical grade and used without further purification. Deionized water was used in all experiments.

Preparation of non-covalently crosslinked nanogel particles.

NIPAm (0.20 g), water (30.0 ml) and SDS (8.6 mg) were placed into a 50 ml round-bottom flask. This mixture was purged with N_2 for 15 min, and then heated to 70 ^{o}C. After an additional 15 min, 1.5 ml of UPy functionalized PEGMA macromonomer solution (dissolved in chloroform, concentration: 0.10 g/ml) was injected, and then KPS (0.01 g) dissolved in 1.0 ml of pure water was immediately added to initiate the reaction. The polymerization was allowed to proceed under a N_2 atmosphere for 10 h. The resulting nanogel dispersion was filtered through filter paper to remove any coagulum, and then purified by dialysis for one week against deionized water (twice daily changes of water) to remove surfactant and unreacted monomer. To prepare fluorescence-tagged nanogel particles, 1 mg of Rhodamine B piperazine methacrylamide was used as a comonomer during the polymerization. Average size of the nanogel particles is around 160 nm at 25 ^{o}C.

Preparation of HIPE-hydrogels stabilized by nanogel particles and guest molecule loading.

The HIPE-hydrogels were prepared by shearing a mixture of 2.4 ml of hexane and 0.6 ml of nanogel particle dispersion (varied particle concentration: 0.5 wt%, 1 wt%, 2 wt%, 5 wt%) for 2 min with an Ultra Turrax T25 homogenizer at 11,300 rpm. To investigate the dye release profile from the HIPE-gel, Sudan III was added into the hexane organic phase (concentration: 0.1 mg/ml) during the preparation of the HIPE-hydrogel. After the mechanical shearing, the obtained emulsion gel was freeze-dried. The freeze-dried material was then immersed into 5 ml of water. Sodium dodecyl sulfate (concentration: 0.6 mg/ml) was used to stabilize the Sudan III solids released from the HIPE-gels. Sudan III dispersion was taken out every 5 min and replaced by 5 ml of fresh water. After three times, the system was then allowed to proceed heating (50 ^{o}C, 2 min) and cooling (room temperature, 10 min) program. All the obtained Sudan III dispersion was dried at 60 ^{o}C, then redissolved into 3 ml of ethanol, which was then conducted on UV-Vis spectrometer to determine the concentration of the released Sudan III.

Characterization.

Average particle sizes of the nanogel particles were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano instrument. HIPE hydrogels were transferred onto silica wafers and dried over night at room temperature or freeze-dried and then coated with Au before taking images on a Zeiss Supra 55VP FESEM microscope. Confocal imaging was performed on a Zeiss LSM 510 confocal microscope. Lasers with wavelengths of 514 nm and 488 nm were used to excite rhodamine labeled nanogel particles and hostasol in hexane, respectively. Rheological experiments were taken at 25 ^{o}C on a Malvern Kinexus Rheometer using a parallel-plate geometry. The gap width between the plates was 1 mm. In each measurement, the applied strain was maintained at a constant value of 1% within the linear viscoelastic range, which was determined by strain sweeps. The temperature was set to ±0.01^{o}C in accuracy by using a Julabo machine. The controlled release analysis of dye molecules was performed on a Perkin Elmer Lamda-45 UV-Vis spectrometer.

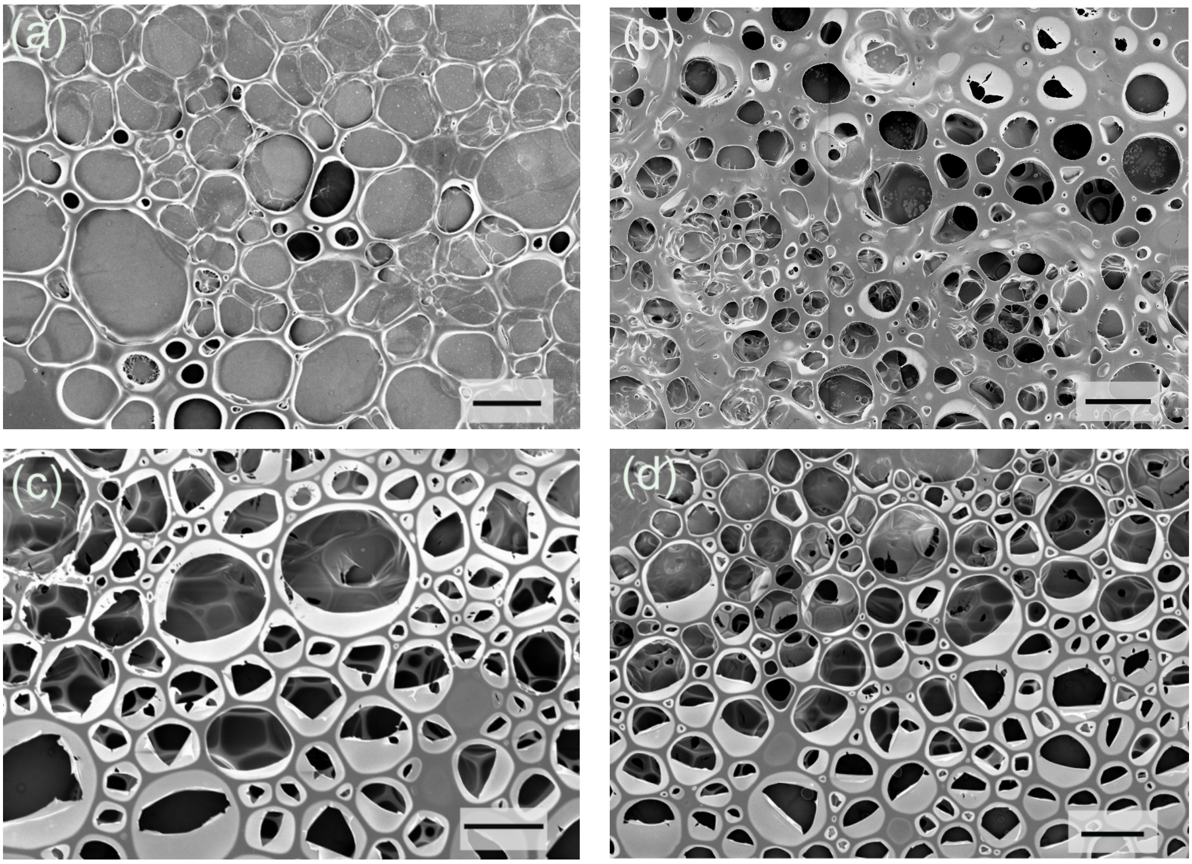

Fig. S1 SEM images of HIPE-hydrogels dried in air with different concentrations of the nanogel particles in the original water phase (0.5wt%, 1wt%, 2wt%, 5wt%), all scale bars: 20μm.

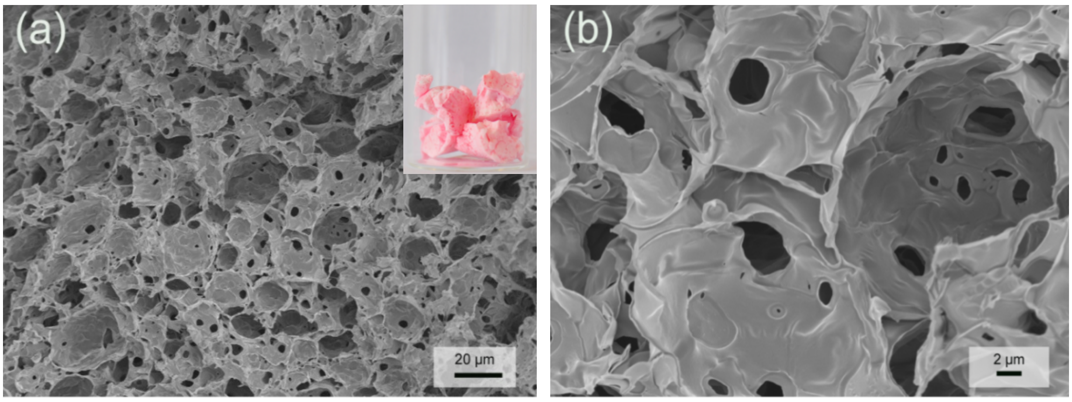

Fig. S2 (a) SEM image of internal fracture surface of HIPE-hydrogels (2 wt% of nanogel particles in water phase) after freeze drying, insert: macroscopic appearance, (b) enlarge observation.

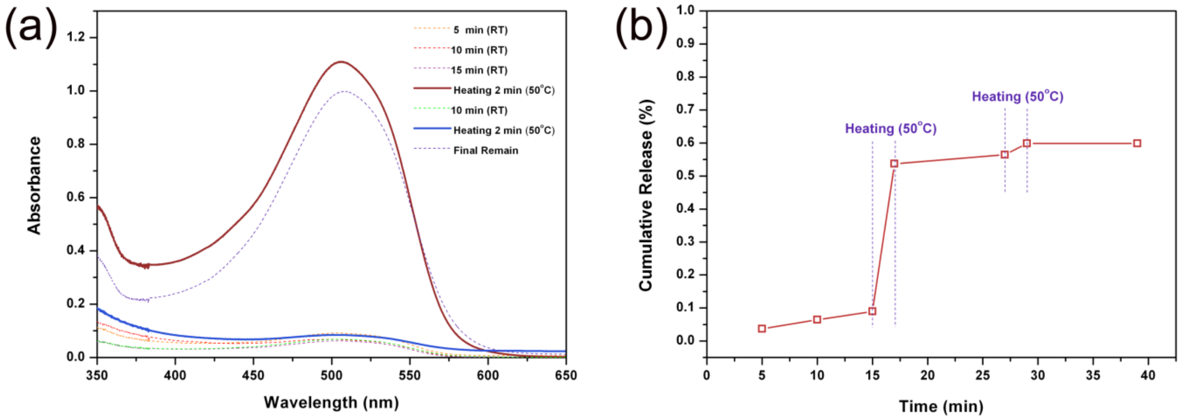

Fig. S3 (a) UV-Vis absorbance of released Sudan III in ethanol in several cooling and heating cycles; (b) cumulative release profile of Sudan III dye against time.

References

1. Y. Chen, N. Ballard, F. Gayet and S. A. F. Bon, *Chem. Commun.*, 2012, **48**, 1117-1119.
2. Y. Chen, S. T. Jones, I. Hancox, R. Beanland, E. J. Tunnah and S. A. F. Bon, *ACS Macro Letters*, 2012, **1**, 603-608.