

Supporting Information

4D printable tough and thermo-responsive hydrogels

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Figure S1 to S10

Other Supplementary Materials for this manuscript include the following:

Movies S1 to S6

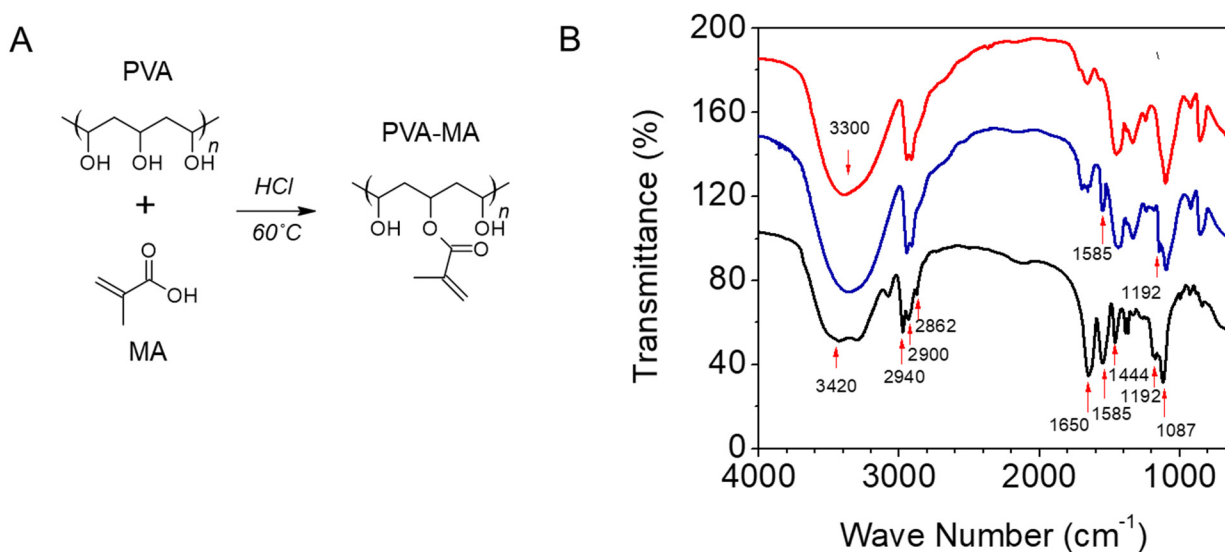


Figure S1. A) Synthesis route of PVA-MA from poly(vinyl alcohol) (PVA) and methacrylic acid (MA). B) FTIR spectrum of the pristine PVA (red), PVA-MA (blue) and PVA/(PVA-MA)-g-PNIPAM hydrogel (black). 3420 cm⁻¹ (N-H in NIPAM groups), 3300 cm⁻¹ (broad peak indicating the O-H in PVA), 2940 cm⁻¹ (C-H in PVA), 2900 cm⁻¹ (C-CH₂ in methacrylate groups), 2862 cm⁻¹ (C-CH₃ in methacrylate and NIPAM groups), 1650 cm⁻¹ (C=O in NIPAM groups), 1585 cm⁻¹ (C=C in methacrylate groups), 1444 cm⁻¹ (C-H in methacrylate and NIPAM groups), 1192 cm⁻¹ (C-O-C between PVA and methacrylate groups), 1087 cm⁻¹ (C-O-H in PVA). When comparing PVA (red) and PVA-MA (blue), we could see the peaks at 1192 cm⁻¹ and 1585 cm⁻¹ which corresponds to the formation of ester bond and the grafted MA containing C=C bond.

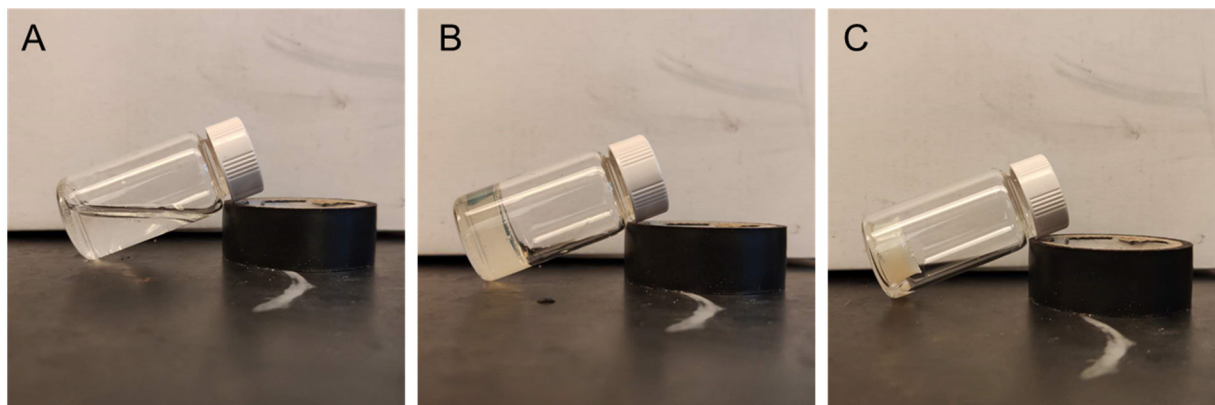


Figure S2. A) 10% PVA-MA, 0.5% TPO-Li dissolved in water. B) PVA-MA hydrogel obtained after UV irradiating the precursor in A. C) Toughened PVA-MA hydrogel after salting out in 1M Na_2SO_4 solution for 5 hours.

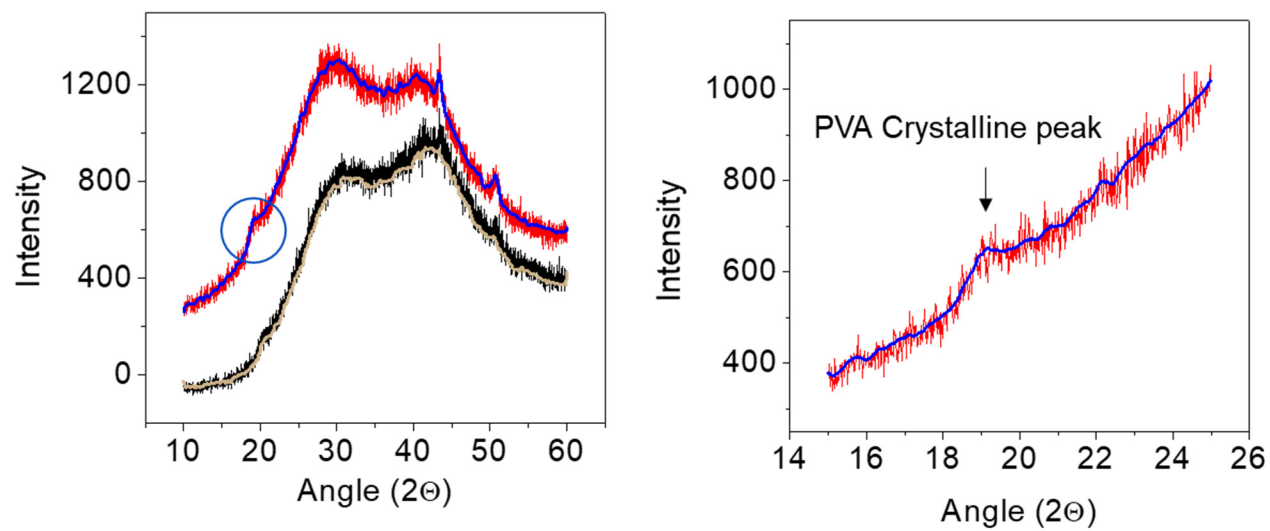
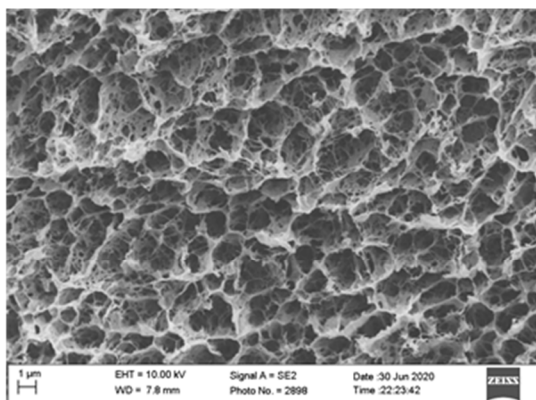
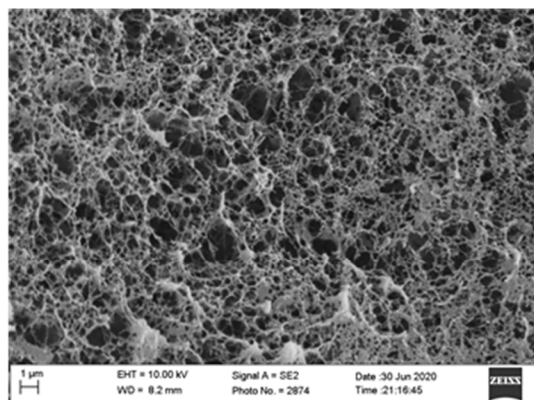


Figure S3. XRD pattern of PVA/(PVA-MA)-g-PNIPAM hydrogel before (black) and after (red) toughening by salting out treatment.

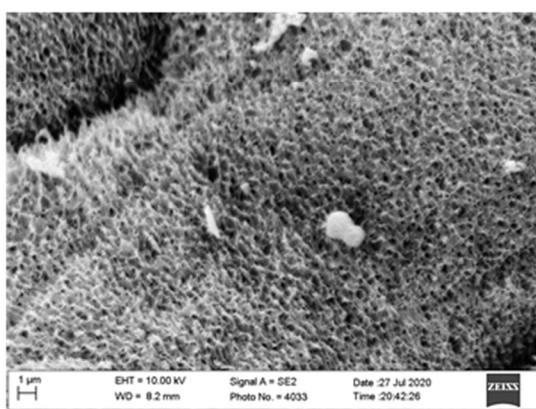
A PVA-MA:PVA ratio 3:7



B PVA-MA:PVA ratio 5:5



C PVA-MA:PVA ratio 7:3



D PVA-MA:PVA ratio 10:0

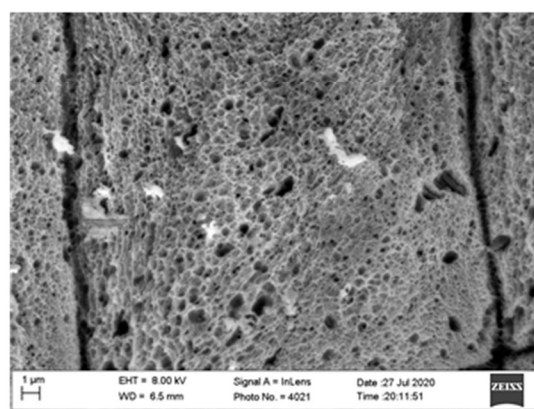


Figure S4. Microstructure of the PVA/(PVA-MA)-g-PNIPAM hydrogels with different PVA to PVA-MA ratios. The hydrogels were toughened in 0.5 M Na₂SO₄ solution, washed and then freeze-dried. The pore size decreased with increasing PVA-MA content.

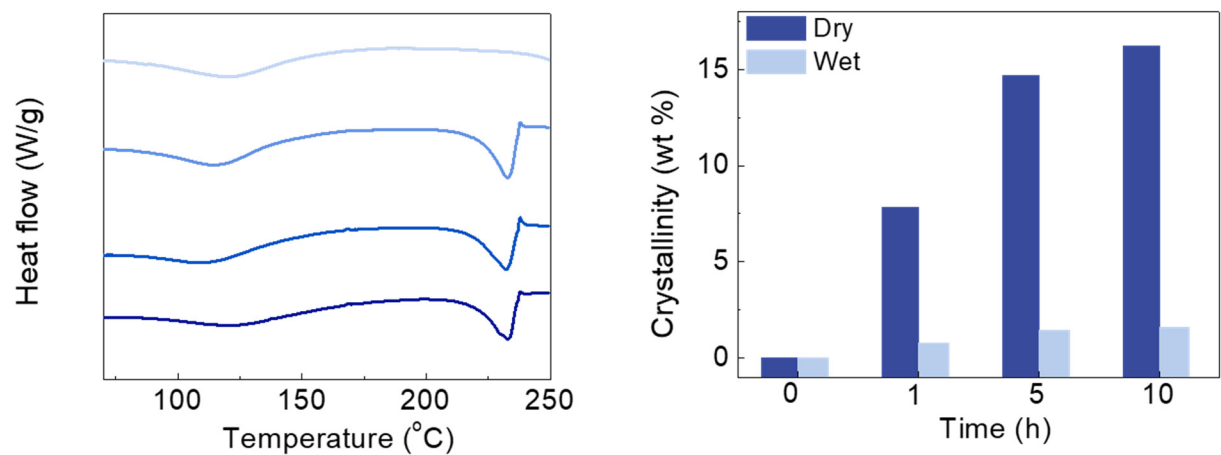


Figure S5. DSC characterization of the 5P_5P-MA hydrogel with increasing salting out time. The crystallinity of the hydrogel increased with salting-out time.

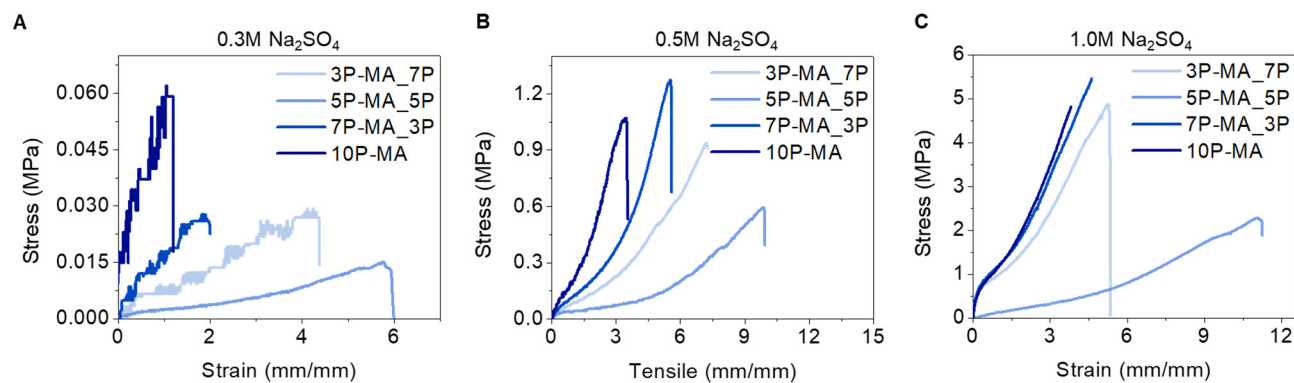


Figure S6. Stress-strain curves of PVA/(PVA-MA)-g-PNIPAM hydrogels with different PVA-to-PVA-MA ratios and toughened in different concentrations of Na_2SO_4 solutions. The 5P-MA_5P hydrogel toughened in 0.5 M Na_2SO_4 presented the optimum overall mechanical and responsive performance.

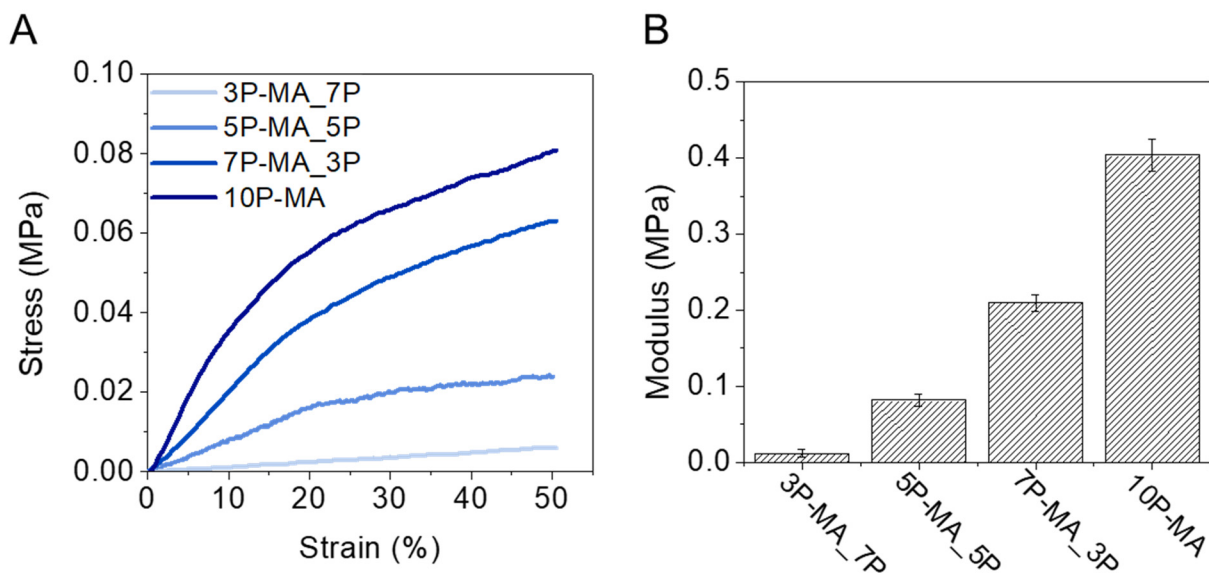


Figure S7. A) Stress-strain curves of the as-printed hydrogels with various PVA / PVA-MA ratios in the strain range of 0-50%. B) Corresponding modulus extrapolated from the linear regions of the stress-strain curves in A. According to “Flory rubber elastic theory”, during elastic deformation of polymers, the crosslinking density is proportionally correlated with the elastic modulus of the polymer.

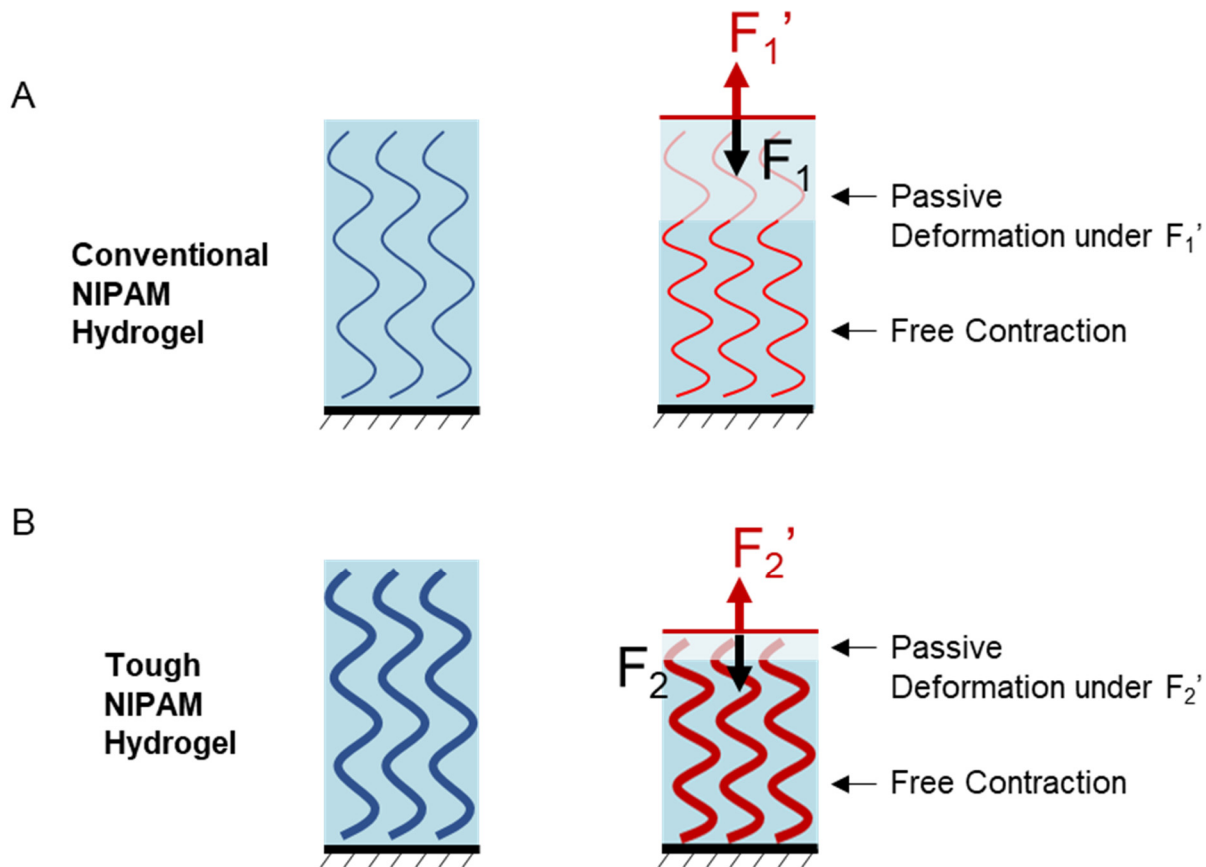


Figure S8. Illustration of contraction under constraint of a conventional PNIPAM hydrogel (A) compared with tough PVA/(PVA-MA)-g-PNIPAM hydrogel (B). When the hydrogel contracts to deliver force F to external objects, it also experiences an equivalent counter-force F' from the external object. For the soft conventional PNIPAM hydrogel, while the hydrogel contracts significantly without external force / constraint, the contraction is limited when there is external force / constraint due to the large passive deformation created by F_1' . The deliverable force F_1 is low in this case as the hydrogel itself could not tolerate high force and would relax the tensile by deformation. In contrast, for the tough PNIPAM hydrogel, the free contraction is comparable to that of the conventional PNIPAM hydrogel. However, the tough PNIPAM hydrogel could tolerate high force and shows small passive deformation. Thus, the tensile is not relaxed and the deliverable force F_2 is increased.

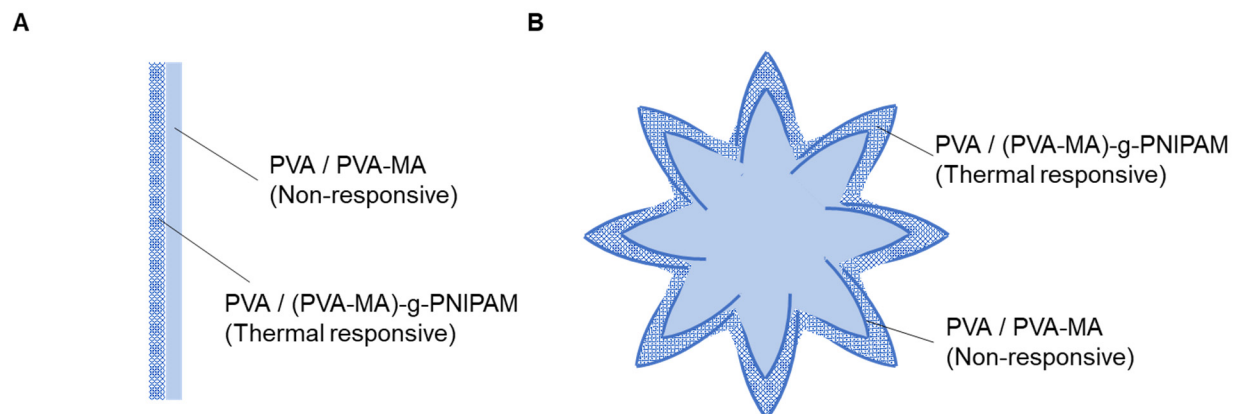


Figure S9. Illustration of the bilayer actuator designs.

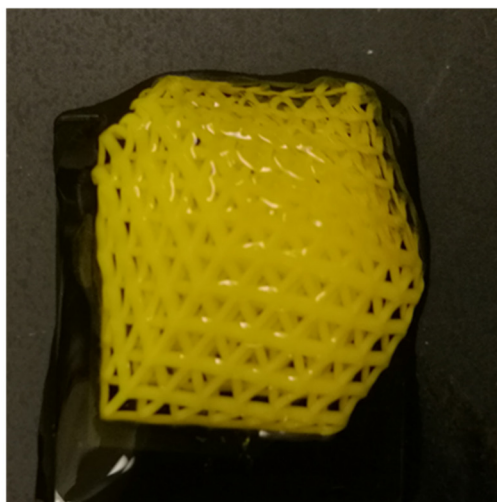
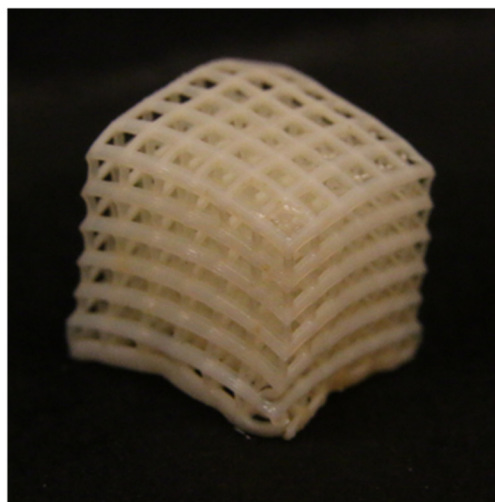
A**B**

Figure S10. Printed simple cubic lattice of PVA/(PVA-MA)-g-PNIPAM hydrogel before (A) and after (B) the toughening treatment by salting-out. These lattices were originally weak and collapsed in air in the as printed state (A) but became capable of self-supporting their own weight and retain the designed structure as a stand-alone architecture in air after toughening in 0.5 M Na_2SO_4 (B).