Supporting Information

Tuning the thermal response of 3D-printed bilayer hydrogels *via* architectural control using binary ethanol-water solvent systems

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1 Analysis and Equations

1.1. Rhodamine B dye elution calculation

The concentration of dye in each aliquot was determined using a Cary 60 Ultraviolet-Visible (UV–Vis) spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

Equation (1) describes the change in rhodamine B dye concentration with time:[1]

$$\left(\frac{C}{C_0}\right) = t^{1/2}\sqrt{\frac{D}{h^2\pi}} \tag{1}$$

where C is the concentration of dye at time t in minutes; C_0 is the total concentration of dye in the original sample; D is the diffusion coefficient; h is the sample thickness. C/C_0 vs. $t^{1/2}$ was plotted to determine the diffusion coefficient from the slope over one hour. The values for C and C_0 as a function of time were obtained using the concentrations determined from the measured absorbance spectra obtained from UV-Vis spectroscopy. Briefly, a calibration curve of known concentrations of rhodamine B dye in deionized (DI) water was collected to correlate dye concentration with the absorbance of the 554 nm peak. Values of C were found by interpolating the calibration curve; C_0 was taken as the maximum value achieved by the eluted rhodamine B dye.

1.2. Crosslink Density Calculation

Crosslink density was determined using Equation (2)[2]

$$\nu = \frac{E'}{3RT} \tag{2}$$

where v is the crosslink density, E' is the plateau modulus as found through DMA analysis (**Figure S3**), R is the ideal gas constant (8.314 J kg^{-1} mol^{-1}), and T is an absolute temperature well into the plateau region.

1.3. Bilayer Modeling

The curvature of the hydrogels can be represented by the kinematic model of Timoshenko[3]

$$\Delta\kappa = \frac{\left(\frac{\Delta L_{active}}{L_{0,active}} - \frac{\Delta L_{passive}}{L_{0,passive}}\right) \times f(m,n)}{h} \text{ (mm}^{-1}\text{)} \quad (3)$$

where $\Delta\kappa$ is the change in curvature and h is the total layer thickness of the active (h_a) and passive (h_p) layers given by $h = h_a + h_p$. The function $f(m,n)$ is defined as

$$f(m,n) = \frac{6(1+m)^2}{3(1+m)^2 + (1+mn)\left(m^2 + \frac{1}{mn}\right)} \quad (4)$$

where m is the ratio of the layer thicknesses ($m = h_p/h_a$) and n is the ratio of the elastic moduli of the passive (E_p) and active (E_a) layer ($n = E_p/E_a$). Calculations and model fitting were performed using MATLAB (Mathworks) software.

2. Experimental results

Table S1. Amounts of added reagents for the 3D-printing resin for each polymer and solvent content.

Sample	Ethanol (mL)	Water (mL)	HEA (mL)	NIPAAm (g)	MBA (g)	TPO (g)
NIPAAm 100-0	10	0.0	0	18.4	0.26	0.60
NIPAAm 75-25	7.5	2.5	0	18.4	0.26	0.60
NIPAAm 50-50	5.0	5.0	0	18.4	0.26	0.60
HEA 100-0	10	0.0	19.6	0	0.026	0.60
HEA 75-25	7.5	2.5	19.6	0	0.026	0.60
HEA 50-50	5.0	5.0	19.6	0	0.026	0.60

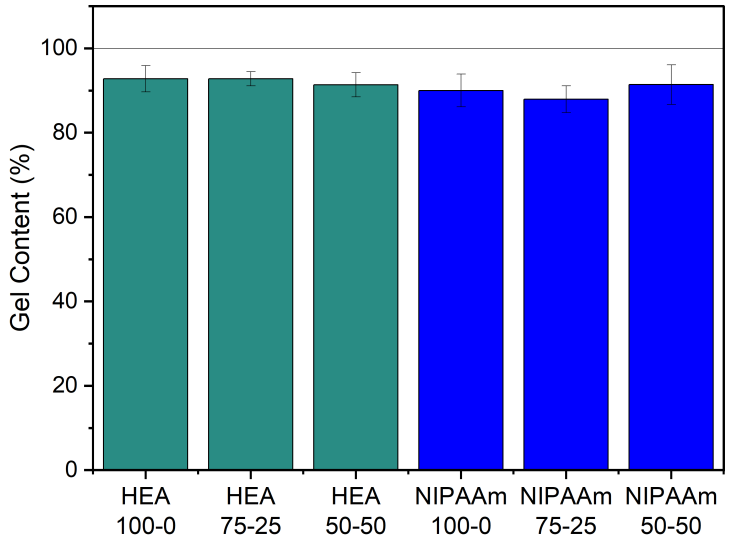

Figure S1. Measured gel content (%) of 3D printed pNIPAAm and pHEA gels prepared using 100-0, 75-25 and 50-50 ethanol-water binary solvent.

To measure the gel content, cylindrical pNIPAAm and pHEA gels (1 mm × 7 mm) were printed. Upon post-curing, the mass of the gels was measured (w_1). The gels were then placed into 200-proof ethanol solution. Ethanol was refreshed (*i.e.,* the surrounding ethanol and the dissolved sol fraction were discarded, and new 200-proof ethanol added) every ~2.5 hours for four cycles. Finally, the hydrogels were dried in a vacuum oven (~30 °C) for 6 hours and weighed (w_2). The gel content was calculated as $\frac{w_2}{w_1} \times 100$.

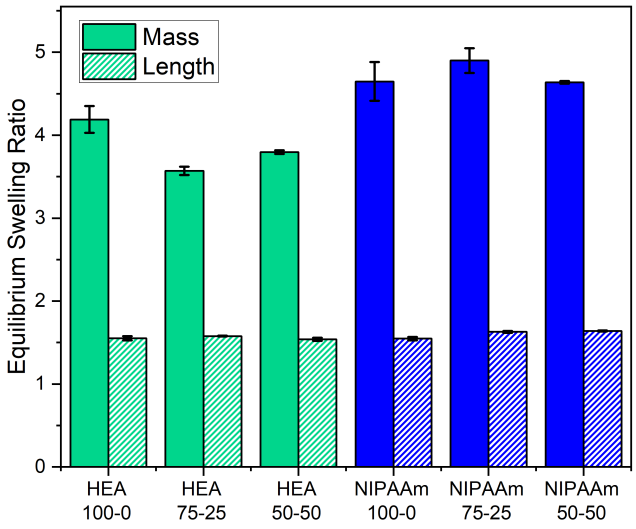

Figure S2. Equilibrium swelling ratio of printed pNIPAAm and pHEA 100-0, 75-25 and 50-50 hydrogels in DI water after a minimum of 24 hours.

Mass uptake is typically recorded as a measure of hydrogel swelling, but for interfacing into bilayer hydrogels, length swelling is an essential measure to ensure consistency (*e.g.,* flatness) in the bilayers.

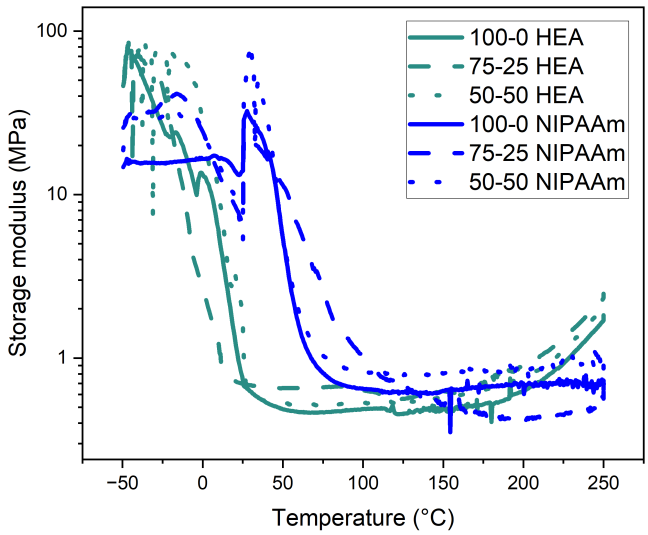

Figure S3. DMA of as-printed pNIPAAm and pHEA 100-0, 75-25 and 50-50 monolayer non-hydrated gels in compression mode.

While the decomposition temperature of pHEA and pNIPAAm have been reported in literature as 425 °C and 422 °C, respectively, we observed degradation at 300 °C. [4,5] Therefore, we limited our maximum measurement temperature to 250 °C. For our DMA analysis, first, to capture the glassy region of the networks, a temperature ramp from -50 °C to 25 °C at an amplitude of 0.05% strain was conducted. To capture the rubbery region of the networks, a second ramp from 25 °C to 250 °C at 0.05% strain was utilized. The plateau modulus was measured from the rubbery region of the networks.

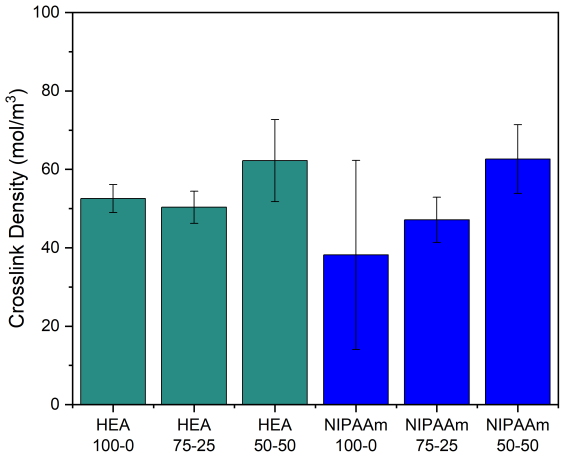

Figure S4. Calculated crosslink density of monolayer pHEA and pNIPAAm non-hydrated gels using Equation 2. For pHEA networks, the storage modulus at 120 °C was used to calculate the crosslink density. For the pNIPAAm networks, the storage modulus at 175 °C was used for crosslink density calculations. Error bars represent the standard deviation from three sample measurements.

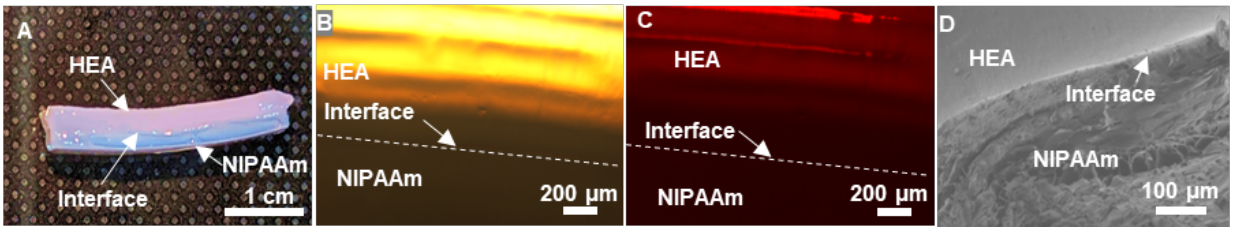

Figure S5. Interface and adhesion of layers in a 100-0 bilayer. A. Optical photograph of a rectangular 100-0 bilayer hydrogel with rhodamine B dyed pHEA layer and neat pNIPAAm layer. B. Darkfield micrograph of the 100-0 bilayer hydrogel showing a brighter pHEA layer and a darker pNIPAAm layer, with the interface between the two indicated by a dotted line. C. Corresponding epifluorescence optical micrograph of the bilayer hydrogel in **Figure S5B**, showing fluorescence of the pHEA layer, absence of fluorescence in the pNIPAAm layer, and the interface between the two layers indicated by a dotted line. The epifluorescence micrograph shows fluorescence only in the pHEA region, while the neat pNIPAAm layer does not fluoresce, indicating that the pHEA and pNIPAAm form discrete layers with a minimal amount of diffusion of pHEA into pNIPAAm in the bilayers during printing. D. Scanning electron microscopy (SEM) micrograph of a lyophilized 100-0 bilayer highlighting the smooth pHEA layer, porous pNIPAAm layer, and the distinct interface between the pHEA and pNIPAAm layers. The much smaller pHEA pores shown in **Figure 2** are not visible at this magnification.

To prepare 100-0 bilayer gels containing rhodamine B dye in the pHEA layer, first, 10 mL of HEA 100-0 was mixed with 200 µL of 0.2 mM Rhodamine dye and 3D-printed to form the first layer of the bilayer gel. The NIPAAm 100-0 solution was then added to the 3D printer resin vat and printed to form bilayer hydrogels. After post-curing for 15 minutes, the bilayer gel was placed in DI water for 24 hours for equilibration before imaging using a Leica DM2500 microscope (Leica-Microsystems, Germany) to obtain **Figures S5B-C**.

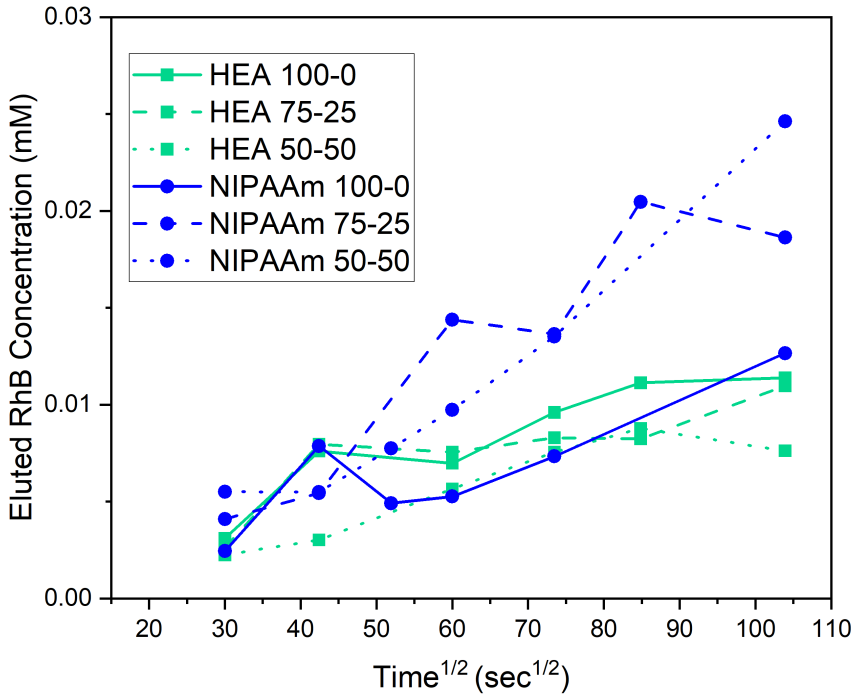

Figure S6. Concentrations of Rhodamine B dye eluted from pHEA and pNIPAAm hydrogels (100-0, 75-25 and 50-50 ethanol-water) over one hour.

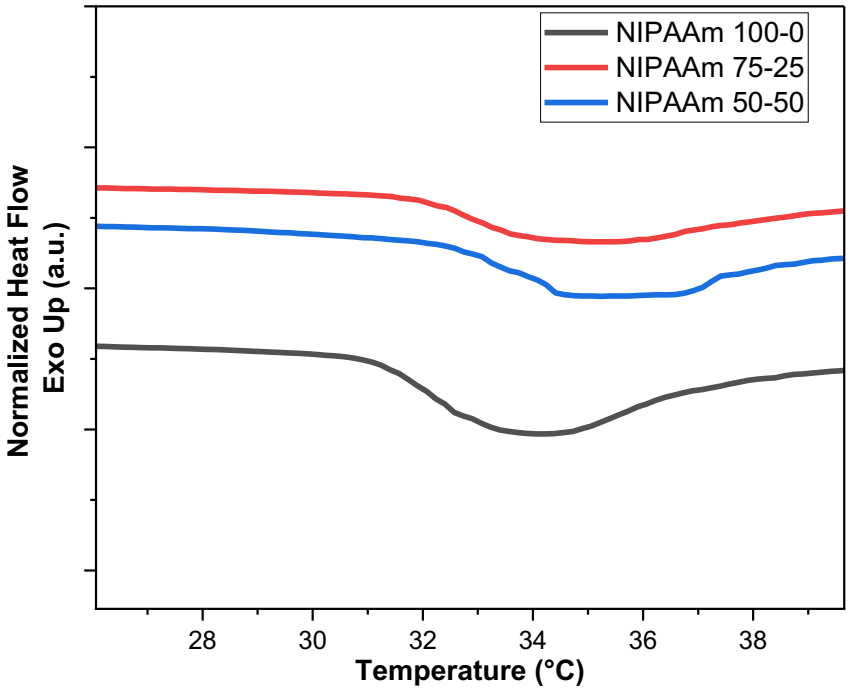

Figure S7. Representative DSC heating first trace of pNIPAAm hydrogels (100-0, 75-25 and 50-50 ethanol-water). Curves are shifted vertically to individually represent each curve. Each tick mark on the normalized heat flow (y-axis) represents a 0.15 W g^{-1} increment.

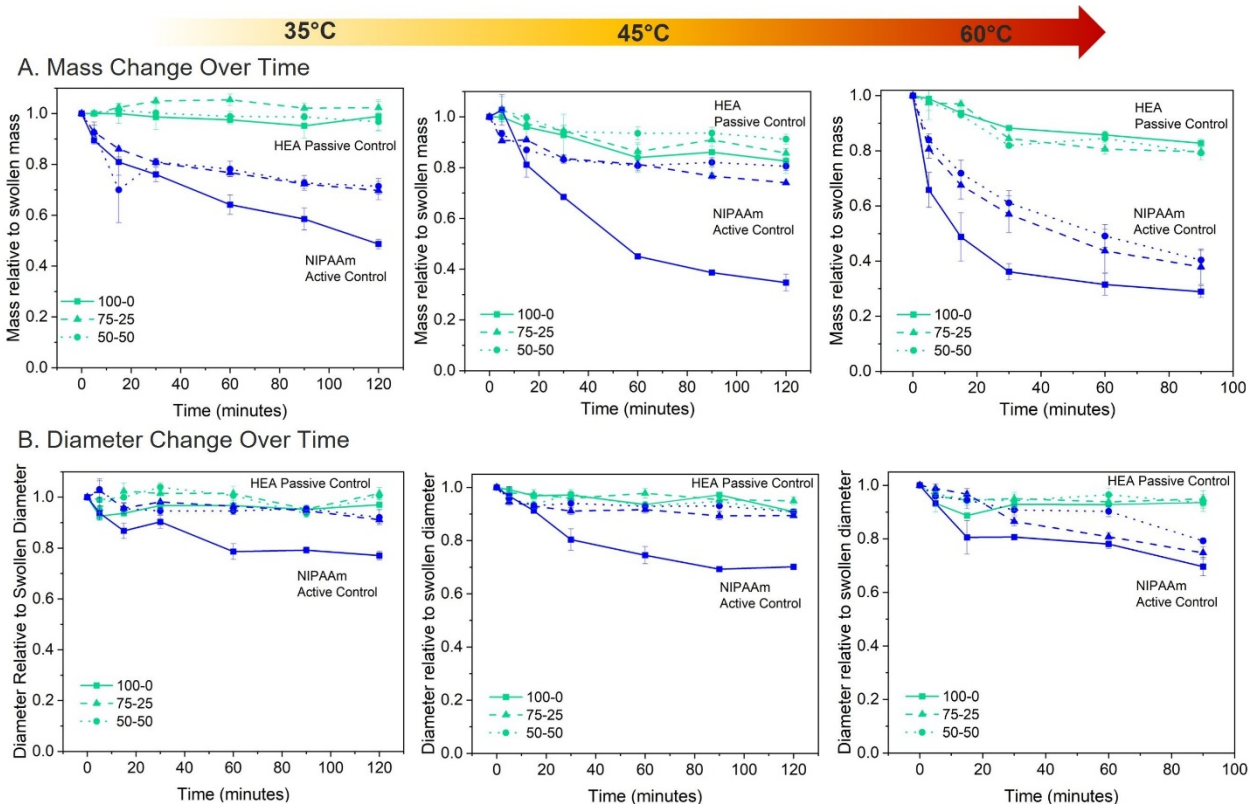

Figure S8. A. Ratio of measured mass of cylindrical hydrogels to equilibrium swollen mass during heating in a water bath at 35, 45, and 60 °C. B. Ratio of measured diameter of cylindrical hydrogels to equilibrium swollen diameter during heating in a water bath at 35, 45, and 60 °C. Solid lines connect data points from NIPAAm and HEA 100-0 hydrogels, dashed lines connect data points from NIPAAm and HEA 75-25 hydrogels, and dotted lines connect data points from NIPAAm and HEA 50-50 hydrogels.

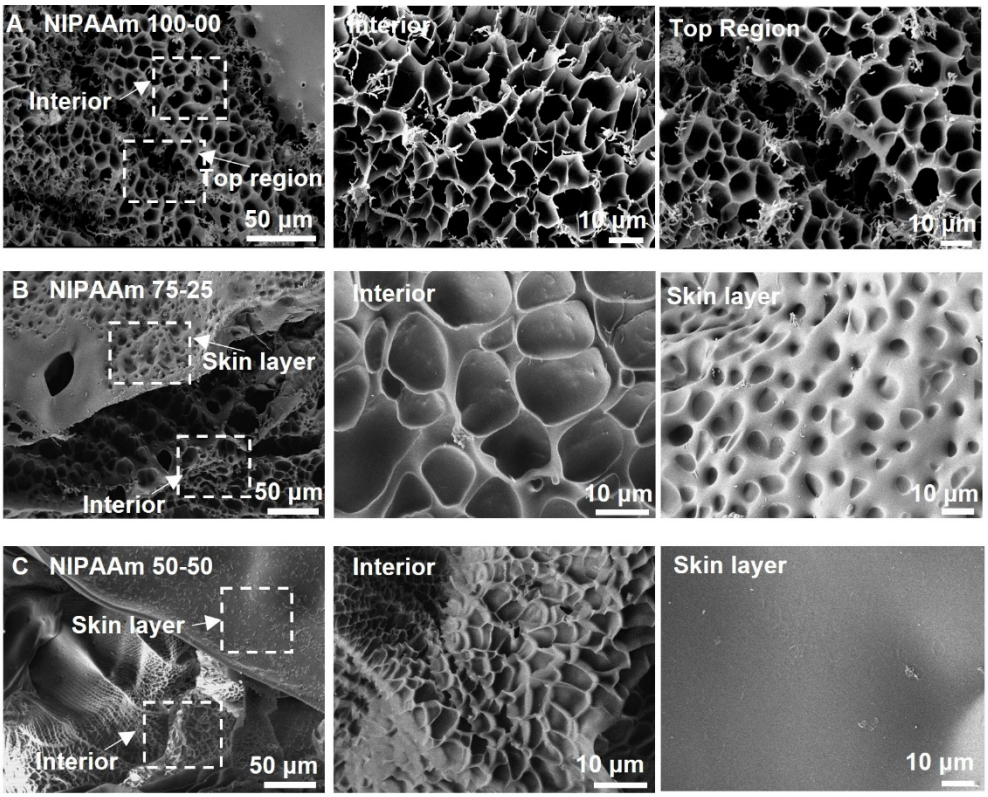

Figure S9. SEM micrographs of NIPAAm 100-0, NIPAAm 75-25, and NIPAAm 50-50 hydrogels after exposure to 60 °C water for 30 min. A. Left: Zoomed-out SEM micrograph of the NIPAAm 100-0 hydrogel after exposure to 60 °C for 30 min, with dotted inset boxes denoting the top layer and interior having porous structure. Middle: Zoomed-in view of the porous interior layer indicated in the zoomed-out view on the left-side SEM micrograph, and Right: zoomed-in image of the exterior top layer of the NIPAAm 100-0 hydrogel. B. Left: Zoomed-out SEM micrograph of the NIPAAm 75-25 hydrogel after exposure to 60 °C water for 30 min with inset, dotted boxes denoting the location of the skin layer on the exterior and the porous layer in the interior; Middle: Zoomed-in view of the porous interior indicated in the zoomed-out view on the left-side SEM micrograph, and Right: Zoomed-in view of the skin layer shown in the zoomed-out view on the left-side SEM micrograph. C. Left: Zoomed-out SEM micrograph of the NIPAAm 50-50 hydrogel after exposure to 60 °C for 30 min, with dotted inset boxes denoting the skin layer on the exterior

and the porous layer in the interior, Middle: Zoomed-in view of the porous interior layer indicated in the zoomed-out view on the left-side SEM micrograph, and Right: zoomed-in image of the exterior skin layer of NIPAAm 50-50 hydrogel.

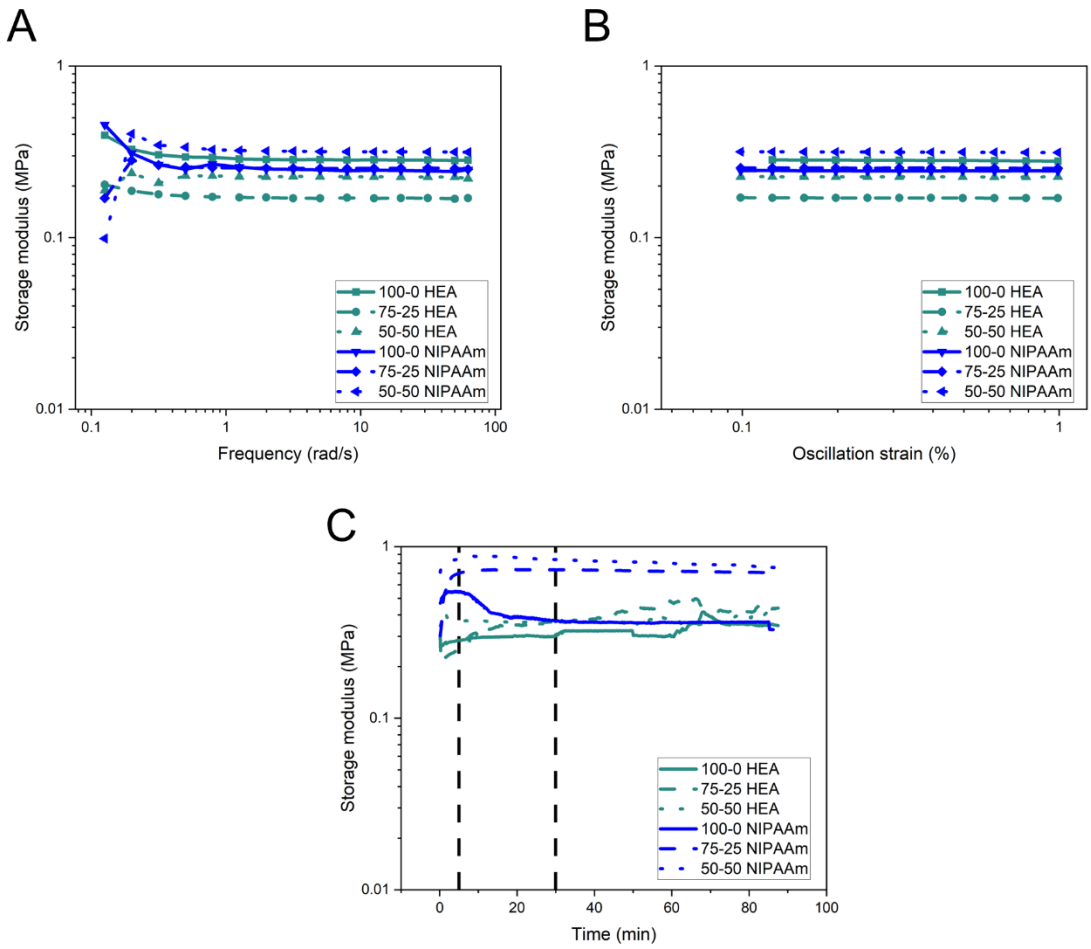

Figure S10. Immersion DMA plots of pNIPAAm and pHEA hydrogels (100-0, 75-25 and 50-50 ethanol-water). A. Frequency sweep, B. Oscillation strain sweep, and C. Isothermal time sweep at 60°C over 90 min. The dotted line at 5 min represents the first measured point of contraction in **Figure S8** and the dotted line at 30 min represents the time corresponding to the data in **Figure 3**.

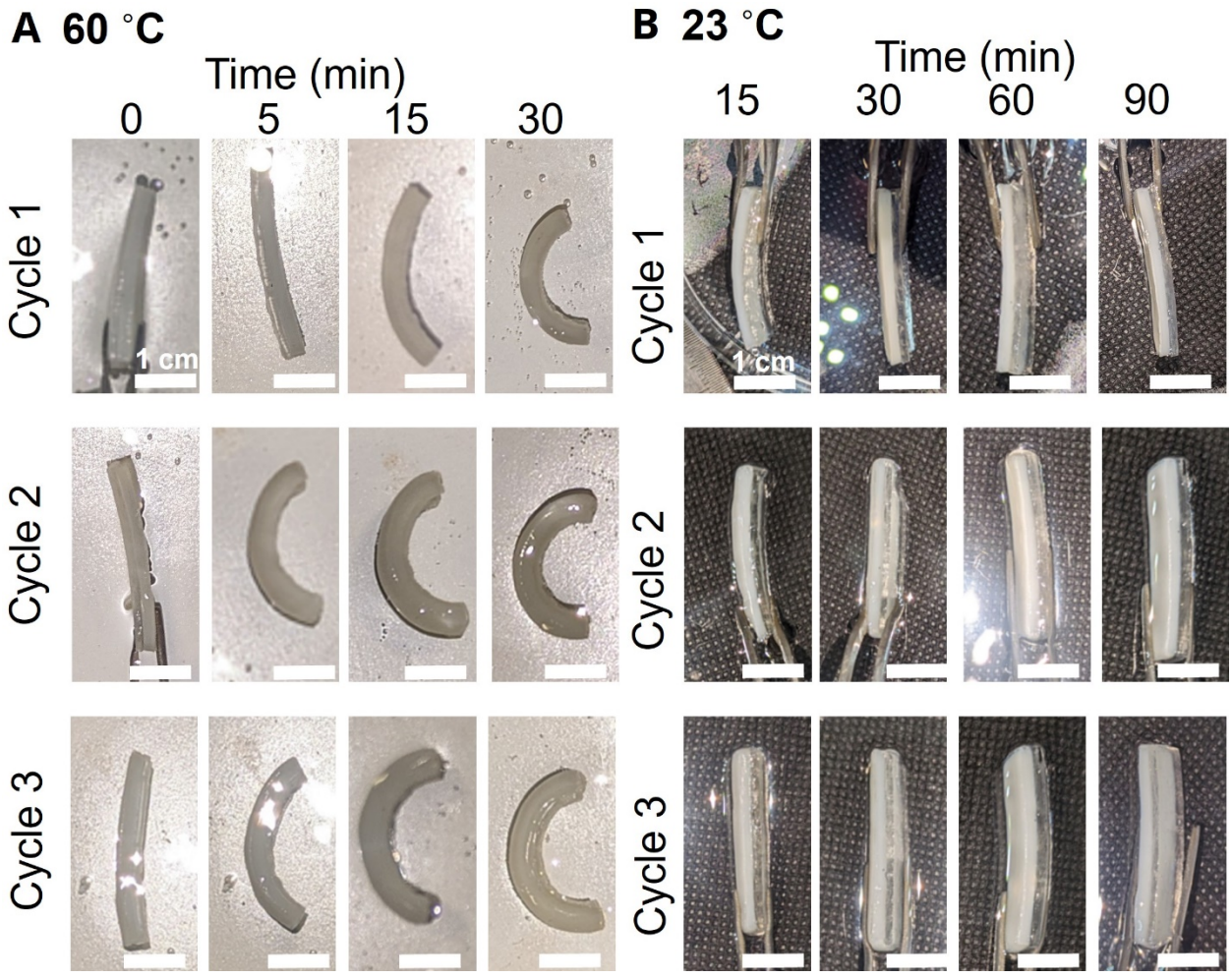

Figure S11. Reversible thermal actuation of a 50-50 bilayer hydrogel over 30 min. Photographs of A. Left to Right: 50-50 bilayer hydrogel immersed in 60 °C water at specific time intervals of 0, 5, 15 and 30 minutes and B. Left to Right: The same bilayer hydrogel removed from 60 °C water and immersed in room temperature (~25 °C) water at specific time intervals of 15, 30, 60, and 90 minutes. All scale bars in A and B are 1 cm.

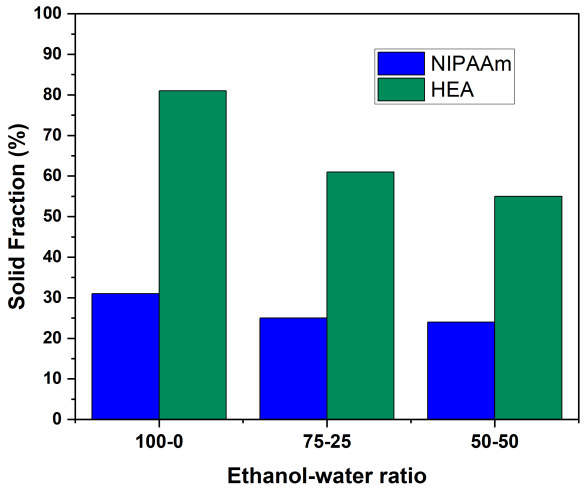

Figure S12. Comparison of solid fraction of pNIPAAm and pHEA hydrogels. The solid fraction was calculated by thresholding the SEM images in **Figure 2** using ImageJ.

References

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