Supplementary Material for "Thermal response of multi-layer UV crosslinked PEGDA hydrogels"

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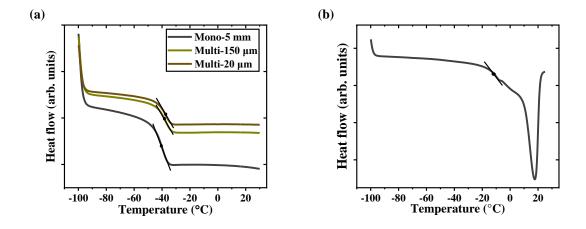


Fig. S1: (a) Thermogram of multi-20 μm (blue line, top spectrum), multi-150 μm (red line, middle spectrum) and mono-5 mm (black line, bottom spectrum) PEGDA hydrogel second heating from -100 $^{\circ}$ C to 25 $^{\circ}$ C, at 10 $^{\circ}$ C min-1 (before swelling in D₂O) with glass temperatures recorded between -41 $^{\circ}$ C and -43 $^{\circ}$ C. (b) Thermogram of PEGDA monomer, second heating from -100 $^{\circ}$ C to 25 $^{\circ}$ C, at 10 $^{\circ}$ C min⁻¹. Glass transition for PEGDA monomer recorded at -15.38 $^{\circ}$ C.

The equilibrium water content (EWC) was calculated using the equation

$$EWC = (M_S - M_d)/M_S \qquad \text{(Eq.S 1)}$$

M_s is the weight of the hydrogel at time t, and M_d is the dry weight of the hydrogel [18].

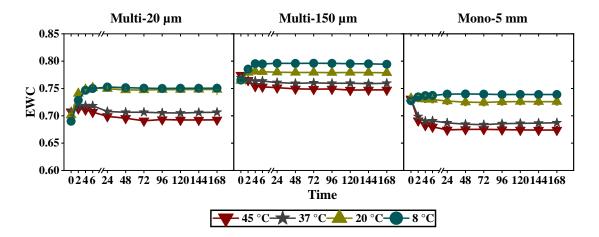


Fig. S2: EWC of multi-20 and 150 μ m and mono-5 mm PEGDA hydrogel samples, both stored at 8, 20, 37 and 45 °C in DI water for 168 hours (7 days) measured at predetermined time points immediately after printing (0 hrs). Error bars represent standard deviation from the mean n= 4 and n= 3 for multi-layered and monolithic independent samples, respectively. Some error bars are not visible as they are smaller than the data point symbols. All lines are guide to the eye only.

To calculate the lateral and axial strain ($\left|\epsilon_{W,L,H}\right|$ the following set of equations were used.

First, the percentage width, length and height change was calculated for each sample.

$$|\varepsilon_{\mathrm{Wn}}| = \left| \frac{\mathrm{W_t - W_0}}{\mathrm{W_0}} \right| \times 100$$
 (Eq.S 2)

$$|\varepsilon_{Ln}| = \left| \frac{L_t - L_0}{L_0} \right| \times 100$$
 (Eq.S 3)

$$|\varepsilon_{Hn}| = \left| \frac{H_t - H_0}{H_0} \right| \times 100$$
 (Eq.S 4)

 W_t , L_t and H_t and, W_0 , L_0 and H_0 were the width, length and height at time t (24 hours) and immediately after printing.

The Normalised dried weight (NDW)

$$NDW = (\overline{M}_{d0})/M_d$$
 (Eq.S 5)

The average dried weights of the samples (\overline{M}_{d0}) was calculated and compared to the dried weight (M_d) of each individual hydrogel which were stored for 168 hrs, at each temperature.

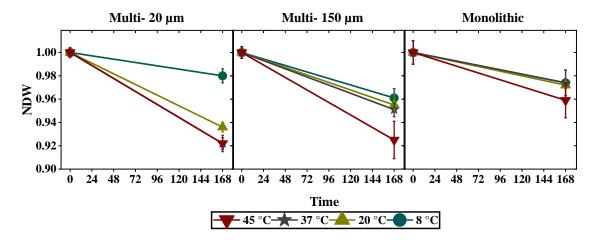


Fig. S3: NDW of multi-20 and 150 μ m and mono-5 mm PEGDA hydrogel samples measured for all samples stored at 8, 20, 37 and 45 °C. Error bars represent standard deviation from the mean n= 3, 4 and 3 for monolithic, multi-layered 150 and 20 μ m layer thickness, respectively. Some error bars are not visible as they are smaller than the data point symbols. All lines are guide to the eye only.

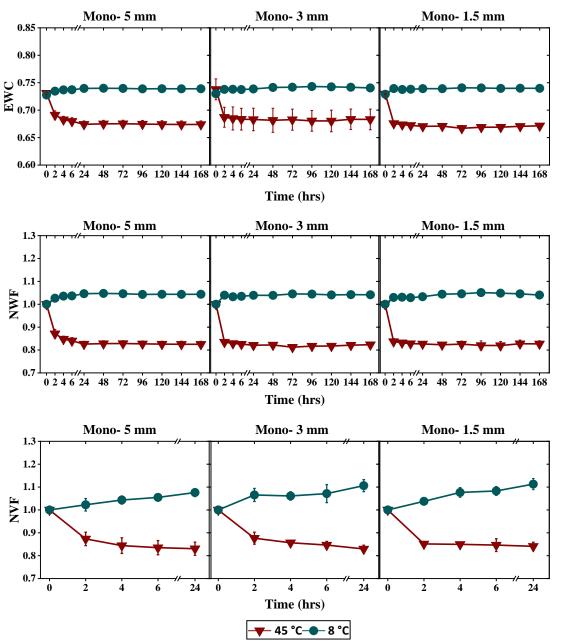


Fig. S4: EWC, NWF and NVF of mono-5, 3 and 1.5 mm thicknesses PEGDA hydrogel samples, stored at 8, 20, 37 and 45 °C in DI water for 168 hours (7 days) measured at predetermined time points immediately after printing (0 hrs). Error bars represent standard deviation from the mean n= 3. Some error bars are not visible as they are smaller than the data point symbols. All lines are guide to the eye only.

Calculating the depth of crosslinking:

First, prepolymer solutions with 1.8 and 9 mg/mL concentration of QY photoabsorber were separately prepared. Then, a treated coverslip glass was placed at the bottom of the vat. The prepolymer solution of one concentrations was poured into the vat and filled almost half of the vat volume. Then, the prepolymer solution was exposed to the same UV light with an equivalent dose of 120 mJ/cm² (light intensity 20 mW/cm² for a period of 6s). The crosslinked hydrogel layer was attached to the coverslip glass, due to being covalently bonded to it. The coverslip glass was attached on a right angle glass prism and the thickness of the crosslinked hydrogel layer was measured using an optical microscope. The thickness of the layer would indicate the crosslinking depth for each concentration.

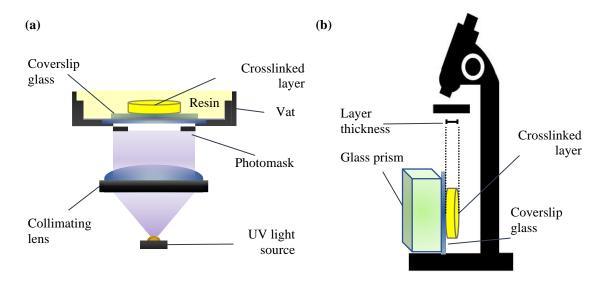


Fig. S5: Schematic of **(a)** setup for fabricating single layer hydrogels on coverslip glass, **(b)** Use of optical microscope for determining depth of UV light penetration for pre-polymer solutions with various QY photoabsorber concentrations.

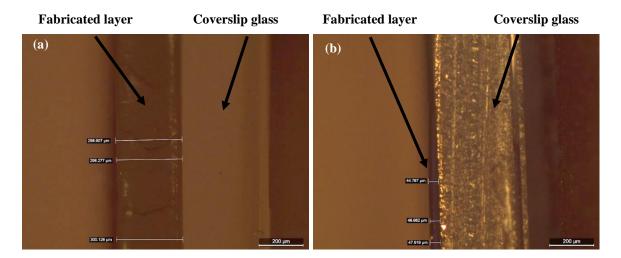


Fig. S6: Microscopy images of the fabricated single layers for pre-polymer solution with **(a)** 1.8 mg/mL and **(b)** 9 mg/mL, of QY photoabsorber concentrations.