Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Supplementary Information

# Volumetric Additive Manufacturing of Shape Memory Polymers

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## Experimental

*General Considerations.*

1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TA-ICN), 2-methyl-4′-(methylthio)-2-morpholinopropiophenone or Irgacure 907, methylene chloride, isopropyl alcohol, and TEMPO were purchased from Sigma-Aldrich, and Tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (TME-ICN) was purchased from TCI America. Aluminum *N*-nitrosophenylhydroxylamine (ANPHA) was purchased from Gelest. All chemicals were used without further purification. Triethylene glycol diallyl ether (TEGDAE) was synthesized following previously published procedures.[1,2] Prior to use in photoresin, TEGDAE was filtered through activated carbon to remove any discoloration that could impact resin absorption. Dynamic Mechanical Analysis (DMA) was conducted on a Q800 DMA from TA instruments connected to an ACS-3 TA air chiller system.

*Thiol-ene Photoresin Formulation.*

Resin formulations were prepared as stoichiometric mixtures of TEGDAE:TA-ICN:TME-ICN with 1:1 molar ratios of vinyl:thiol functional groups, as seen in Table S1.[3] 10mM of I907 was added to enable photoinitiation. 23.5mM ANPHA and 0.1mM TEMPO were added as inhibitors to enable proper thresholding behavior and improved potlife for volumetric printing.

*Bulk Sample Preparation.*

Bulk samples for dynamic mechanical analysis were prepared by injection molding resin in DMA sample molds (dimensions 20×6×0.5 mm) and exposing to a 405 nm LED flood cure (UV Curing Chamber, XYZ Printing) at 18 mW/cm$^2$ for 20 min ($E_{abs}$ estimate 20,000 mJ/cm$^3$). Samples were heat treated for 1 hour at 120 °C to ensure complete conversion in UV-cured parts.

*DMA – Glass transition analysis.*

Using a thin film tensile clamp fixture, samples were cooled to 0 °C and then heated to 100 °C at a rate of 3 °C min$^{-1}$ with a constant strain applied of 1% at a frequency of 1 Hz. Glass transition temperature ($T_g$) testing was done in triplicate, and the average of those runs was used as the reference value for further SMP characterization.

*DMA– Shape memory analysis.*

Samples were a) heated from 20 °C or room temperature to 20 °C above $T_g$ (roughly 60 °C for both Th-b and Th-c, and so 60 ° C was used for both) at a rate of 3 °C min$^{-1}$ and kept isothermal for 5 min, (b) deformed under a ramped strain rate at the rate of 5% min$^{-1}$ up to 10 or 20% applied strain, (c) reduced to a temperature 20 °C below the $T_g$, after which the force was removed, and finally (e) reheated at 3 °C min$^{-1}$ to 20 °C above $T_g$. The test was repeated from step (b) over four cycles. Shape recovery was measured using the following equation:

$$R(\mathrm{N}) = \frac{\varepsilon_m - \varepsilon_p(\mathrm{N}_s)}{\varepsilon_m - \varepsilon_p(\mathrm{N}_i)} * 100\% \qquad (1)$$

Where $R$(N) is the shape recovery percentage for each shape memory cycle, N, $\varepsilon_m$ is the applied deformation strain, and $\varepsilon_p$ is the permanent deformation. $\varepsilon_m - \varepsilon_p(\mathrm{N}_s)$ corresponds to the change in strain of during shape recovery, and $\varepsilon_m - \varepsilon_p(\mathrm{N}_i)$ corresponds to the change in strain during programming. Ideally, for each cycle the value of $R$(N) should be 100%.[4]

*Rheological Tensile Testing.*

Tensile testing of the SMP samples was performed on a TA Instruments DHR-1 in tension mode. Samples were the same as that mentioned for DMA testing. Tests were performed above the $T_g$ at 60°C and tension was applied at a strain rate of 5% min$^{-1}$ until failure.

*Volumetric Additive Manufacturing.*

Readers may find information about volumetric dose calculations from our previous literature.[3] VAM prints were performed in a custom printer setup equipped with a 405 nm LED light engine (CEL5500 or 3DLP9000, Digital Light Innovations), with a telecentric lens and maximum intensity of 45 or 63.3 mW $cm^{-2}$ at the surface of the resin vial. The resin vial was mounted with a custom fixture to a rotational stage (HDR50, ThorLabs), and all prints were conducted with a rotation rate between 15 - 25 degree/s. Projection output was measured using a Si photodiode power meter, and spectral distribution (Figure S8) measured using a compact CCD spectrometer (PM100D with S120VC sensor, and CCS100, Thorlabs). Spectral information for the 3DLP9000 projector is given in the Supporting Information, and methods for calculating wavelength-dependent absorbed optical dose can be found in previous literature examples.[3]

VAM builds were carried out with either a negative lens or a quartz cubic bath (Reflex Analytical Corporation) of index matching (IM) fluid to minimize the cylindrical distortion of the vial (03-339-26F, Fisher Scientific) on printing. Without the IM fluid bath or negative lens (or printing in air), a grid distortion would be present resulting in a focusing effects, impacting the geometry. With a negative lens or IM fluid, grid distortions are mitigated. Characterization of the index match and negative lens grid distortion is shown in Figure 8 and further details are available in previous literature.[5] Tripod prints were conducted with a negative lens, and the geometry oriented to minimize impact of grid distortion. A volumetric energy dose of 126 mJ $cm^{-3}$ resulted in extractable parts. When using an IM fluid bath, the fluid was made from a mixture of Bisphenol A (1 glycerol/phenol) diacrylate (BPA-GDA) and polyethylene glycol diacrylate (Mw 575, PEGDA) to create a refractive index of 1.55, in close agreement with the refractive index of the **Th-b** photoresin. Ultimately, we found a mixture of 18.5:1 BPA-GDA:PEGDA was best. Good agreement of refractive indexes between IM fluid and the resin in the vial enables monitoring of object curing using a shadowgraph with red light irradiation (see supplementary video S4). 3-arm gripper structures were printed for shape memory testing using these IM fluid conditions and **Th-b** photoresin. Heating VAM prints to 30 °C using a hot plate under the IM fluid bath results in qualitatively better prints by shadowgram, mitigating small refractive index changes from slight temperature variations that are normally present in these exothermic thiol-ene polymerizations. With or without heating, the calculated volumetric energy dose needed for curing with IM fluid was the same (127 mJ $cm^{-3}$). With this, we see the relative volumetric energy dose needed for extractable parts is conserved between both optical systems.

*Post Processing.*

Printed samples were extracted and washed with a mixture of methylene chloride and isopropyl alcohol. Samples were post cured first using 20 min of 405 nm flood cure. After photo-post cure, objects were place in an oven at 120 °C for 1 hour.

*Shape Memory testing of SMP self-standing tripod (standing-permanent, flattened-temporary) and 3-arm gripper (open-permanent, closed-temporary).*

The post-cured self-standing tripod was flattened between two glass slides with a silicone gasket spacer under heating on a hot plate set to 80 °C. Reheating the structure on the 80 °C hot plate, results in recovery of initial standing shape. The gripper was printed in the open conformation. After postcure, the open gripper was then heated in an oven to 80 °C. While hot, the gripper arms were closed around a small vase. The structure with the vase was placed in a refrigerator to fix it in its temporary position as the temperature cooled down. After cooling, the gripper and vase were subjected to a heat gun which surpassed the $T_g$, opened the gripper and dropped the vase, and recovered the part to its permanent shape. Videos of these SMP structure actuation are available in the supplementary information.

## Tables

**Table S1**. Resin formulations and their associated $T_g$'s. All formulations contain 1:1 molar equivalents of vinyl:thiol functional groups and include 10 mM Irgacure 907, 23.5 mM ANPHA, and 0.1 mM TEMPO.

| **Resin** | **Molar eq. of functional group TEGDAE: TA-ICN: TME-ICN** | **Molar eq. of monomer TEGDAE: TA-ICN: TME-ICN** | **Glass transition temperature (°C)** |
|---|---|---|---|
| Th-a | 0 : 1 : 1 | 0 : 1 : 1 | 55 |
| **Th-b[a]** | **0.1 : 0.9 : 1** | **0.15 : 0.9 : 1** | **39** |
| **Th-c[a]** | **0.15 : 0.85 : 1** | **0.22 : 0.85 : 1** | **37** |
| Th-d | 0.3 : 0.7 : 1 | 0.45 : 0.7 : 1 | 20 |
| Th-e | 0.5 : 0.5 : 1 | 0.75 : 0.5 : 1 | 1.1 |
| Th-f | 1 : 0 : 1 | 1.5 : 0 : 1 | -53[b] |

[a] All formulations previously characterized.[3] Bolded formulations were characterized further in this study and have updated average $T_g$'s.

[b] $T_g$ of Th-f below chilling capabilities of DMA. Estimate based on updated linear trend (supplementary figure S4).

## Figures

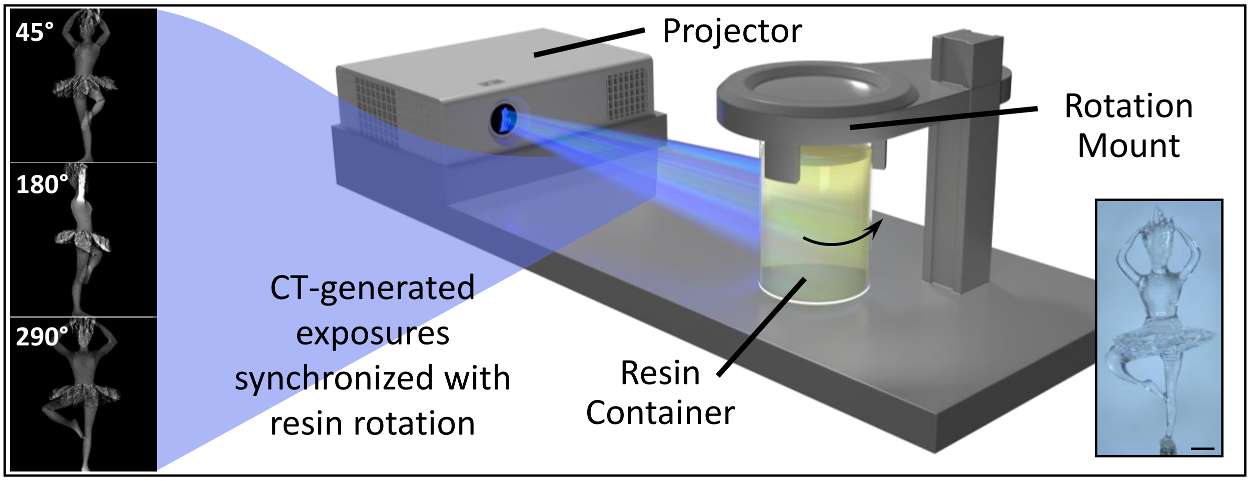
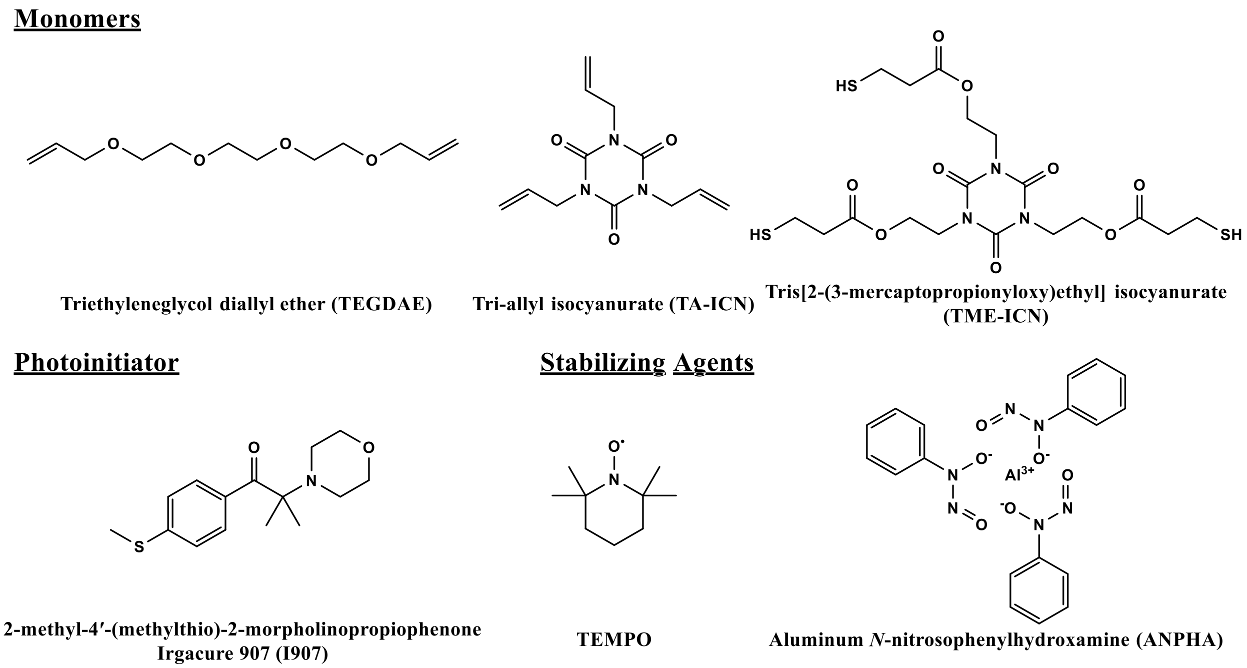


**Figure S1.** Schematic of VAM hardware configuration. The insets at left present example projections from different angles, resulting in the structure shown in the right inset. (Scale bar 2mm). Reused with permission from Cook et al.[3]



Triethyleneglycol diallyl ether (TEGDAE)

Tri-allyl isocyanurate (TA-ICN)

Tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (TME-ICN)

2-methyl-4′-(methylthio)-2-morpholinopropiophenone Irgacure 907 (I907)

TEMPO

Aluminum *N*-nitrosophenylhydroxamine (ANPHA)

**Figure S2.** Chemical structures of compounds used in this study.

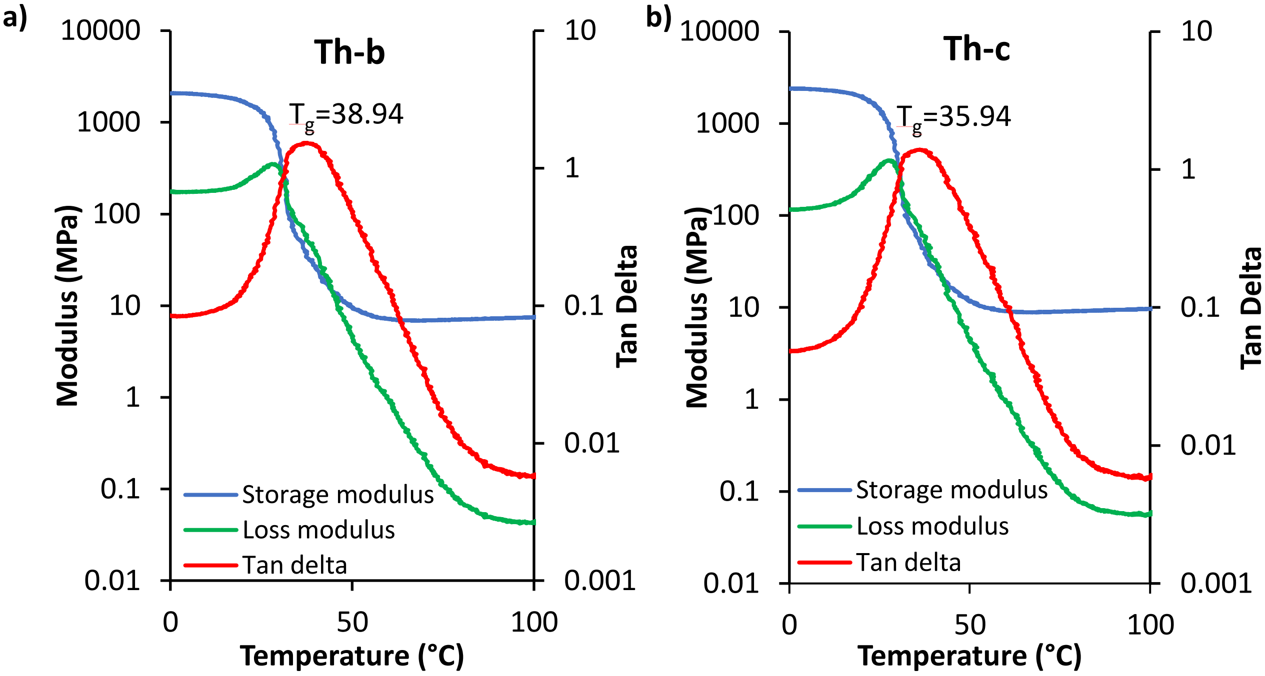


**Figure S3.** a) Representative DMA curve of a Th-b sample (0.1:0.9:1 TEGDAE:TA-ICN:TME-ICN wrt to functional group). b) Representative DMA curve of a Th-c sample (0.15:0.85:1 TEGDAE:TA-ICN:TME-ICN wrt functional group). Blue curves denote storage modulus, green the loss modulus, and red is the tan delta. The peak of the tan delta was assigned as the $T_g$ for each run. An average of three runs was used to denote the $T_g$ of Th-b (39 °C) and Th-c (37 °C) formulations in Table S1.

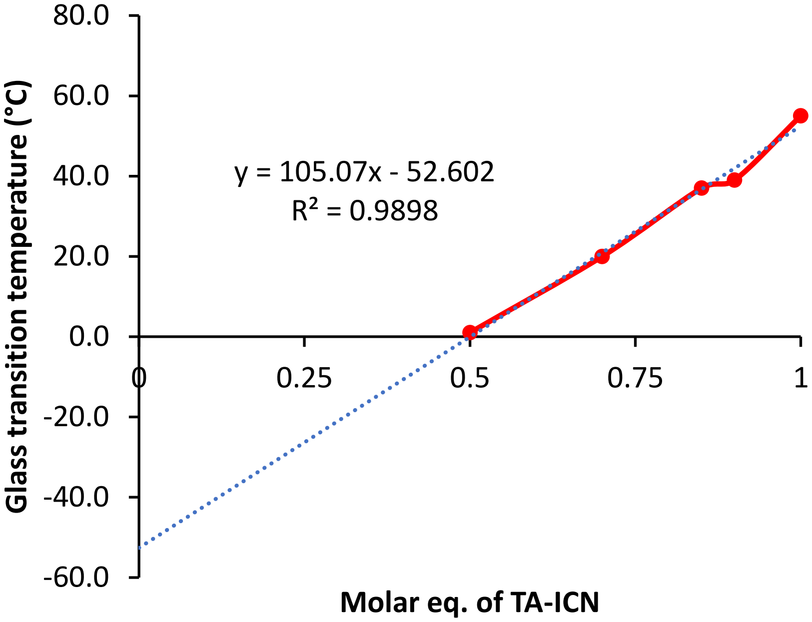


**Figure S4.** Updated trend of thiol-ene resin formulations glass transition temperatures with respect to the molar equivalents of TA-ICN (1:1 vinyl to thiol molar ratio). As the amount of TEG-DAE increases, and TA-ICN decreases, the glass transition temperature drops, with an estimated minimum of -53 °C.

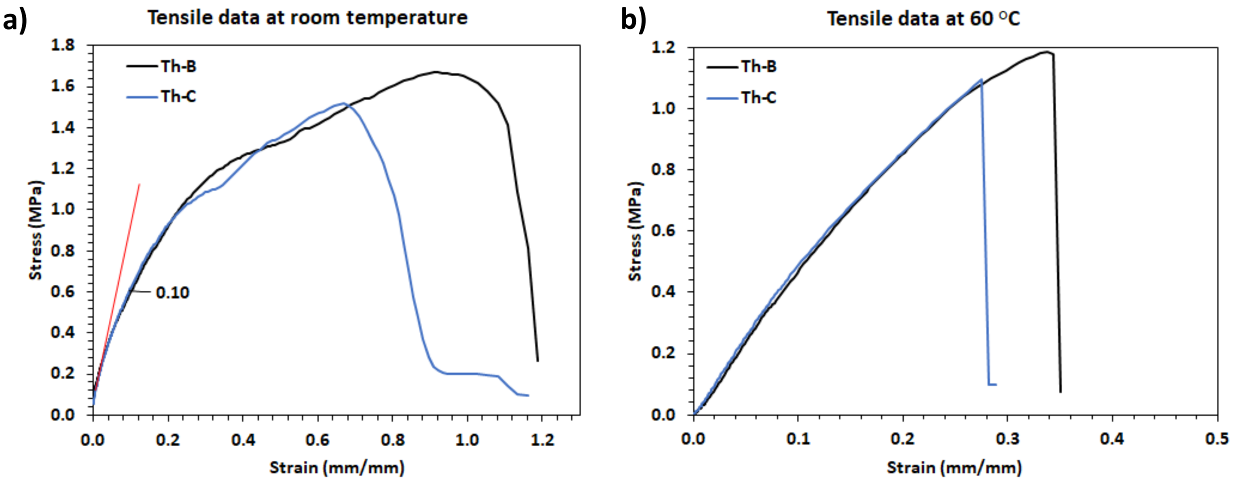


**Figure S5.** Representative tensile data of Th-b (black) and Th-c (blue) samples conducted at a) room temperature (approximately 20 °C), and b) 60 °C. The red line visible in a) denotes the linear elastic modulus, resulting in an elastic limit of roughly 5% strain. Samples were bulk cast DMA rectangles matching the geometry for SMP cyclic testing, and tensile tests were done using a rheometer with controlled temperature chamber. Note that **Th-b** has a higher elongation-to-break at both temperatures tested.

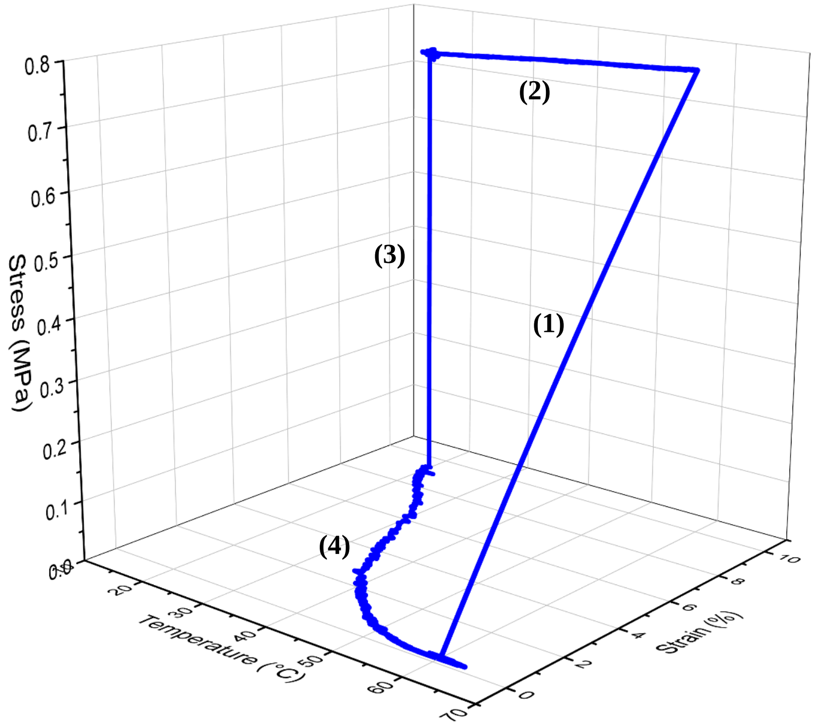


**Figure S6.** Representative diagram of the second cycle of a controlled strain shape memory DMA test of Th-c resin at 10% deformation strain. Numbers 1-4 correspond to the four main steps of testing: 1) Samples were heated to 60 °C, roughly 20 °C above their $T_g$, While heated, they were elongated to 9.4 or 18.4% strain, 2) They were held at these deformation strains while cooled to 20 °C, roughly 20 °C below their $T_g$, 3) the force was released, and 4) they were heated above their $T_g$ in a stress-free state, undergoing shape recovery.

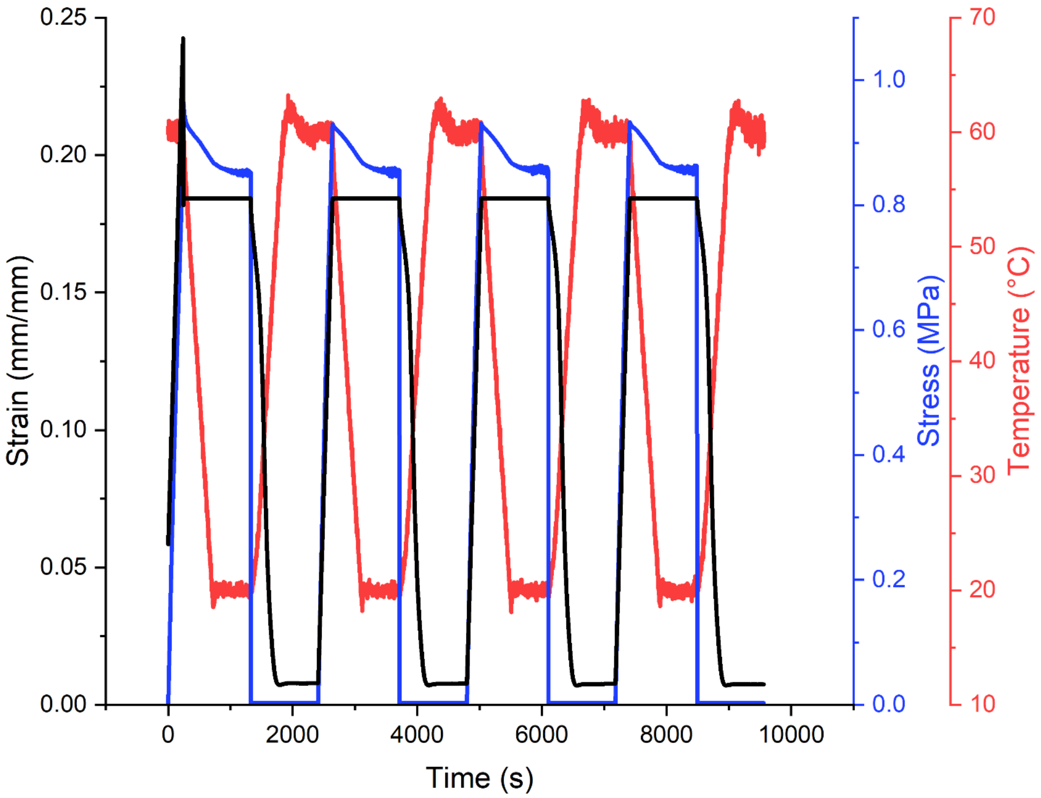


**Figure S7.** DMA shape memory cycling at 20% deformation strains in bulk casted rectangular samples of **Th-b** formulation. Programming 20% strain elongation for deformation results in a real held strain of 18.4%. Strain (black) and Stress (blue) are represented on the primary axis, and temperature (red) is on the secondary axis. **Th-b** polymer shows 96% shape recovery in the first cycle and 100% shape recovery in the remaining three cycles.

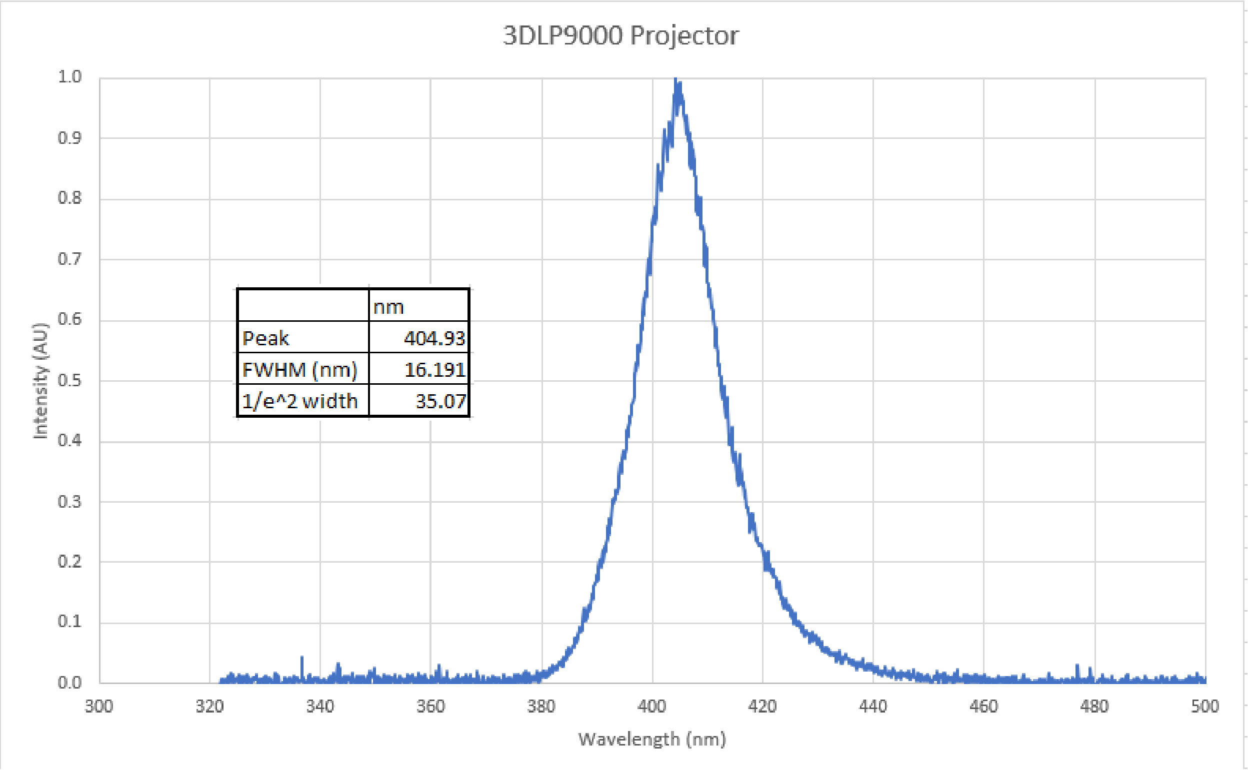


**Figure S8.** Spectral window of 3DLP9000 projector used in VAM printing. LED peak at 405 nm.

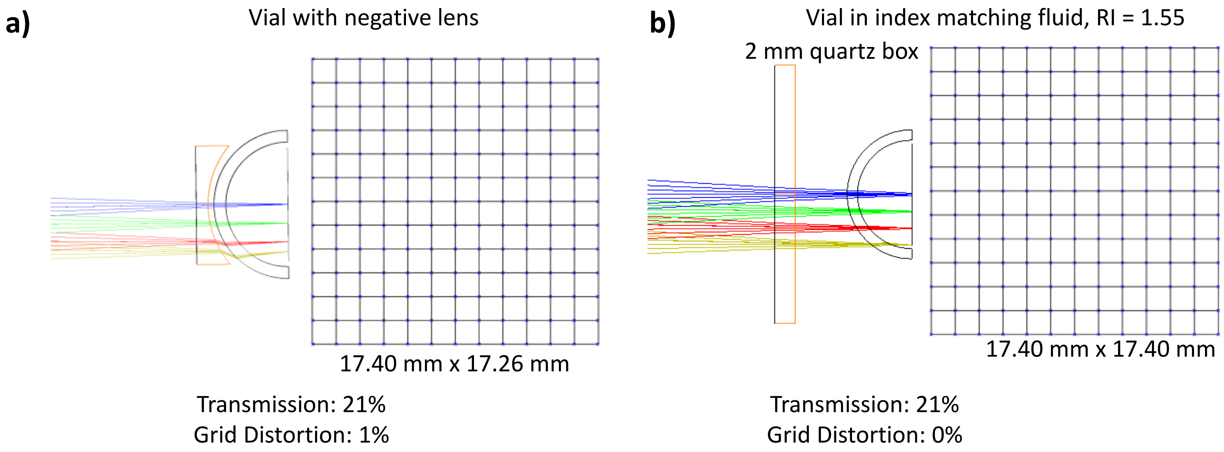


**Figure S9.** a) Zemax analysis of projection through negative Achromatic lens into a cylindrical vial of resin. b) Zemax analysis of projection through a square container of index matching fluid matching the refractive index of resin in the cylindrical resin vial (RI = 1.55). Addition of IM fluid (or negative lens) removes all (or nearly all) grid distortion and focusing effects of the cylindrical vial.

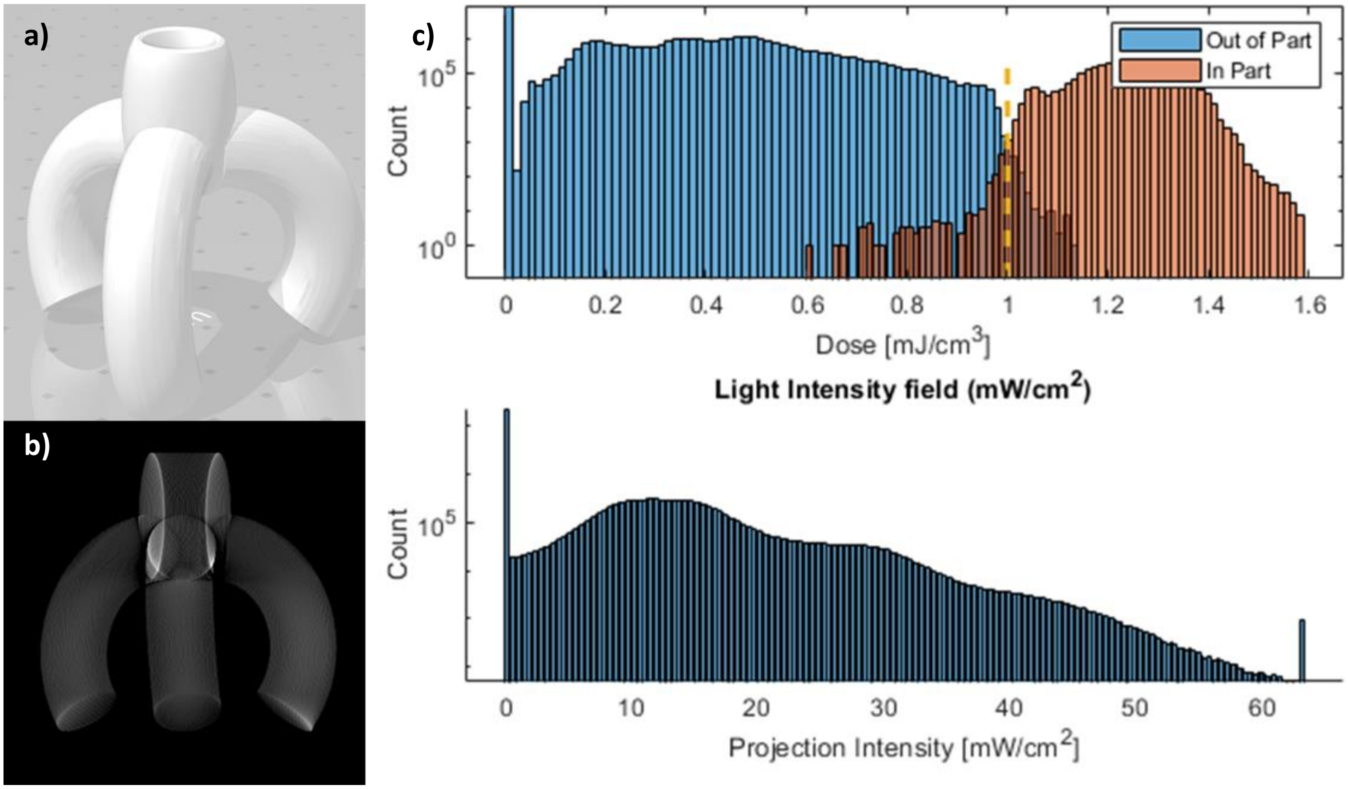


**Figure S10.** a) Image of STL of 3-arm gripper. b) Representative projected image for a single angle to reconstruct the gripper. c) In Part/ Out of Part histogram with critical volumetric dose set to 1 mJ cm$^{-3}$ s$^{-1}$. Printed parts had an estimated volumetric dose of 192 mJ cm$^{-3}$.

## Video Descriptions.

**Video S1.** SMP behavior observed in a bulk-cast rectangular sample of **Th-b**.

**Video S2.** Thermal actuation of self-standing tripod SMP structure printed via VAM using **Th-b** photoresin. Structure was programmed to a flattened temporary shape. Upon stress-free heating on an 80 °C hot plate, the tripod recovered to standing over the span of two minutes.

**Video S3.** Thermal actuation of a bio-inspired 3-arm gripper structure printed via VAM using **Th-b** photoresin. The permanent shape of the gripper was the open state, and the gripper was thermally programmed to close in and hold a small vase. Upon reheating in a 60 °C oven in a stress-free state, the gripper quickly releases the vase within seconds.

**Video S4.** Video of red light shadowgram used to monitor thiol-ene polymerization during VAM printing. 3-arm gripper was printed using the tomographic reconstruction visible in Figure S10. Video is 3x print speed (192s print time).

## Supplementary References.

1. J. V. Crivello, K. D. Jo, *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 1473.
2. A. Rusli, W. Cook, G. G. Liang, *Eur. Polym. J.* 2011, **47**, 1785.
3. C. C. Cook, E. J. Fong, J. J. Schwartz, D. H. Porcincula, A. C. Kaczmarek, J. S. Oakdale, B. D. Moran, K. M. Champley, C. M. Rackson, A. Muralidharan, R. R. McLeod and M. Shusteff, *Adv. Mater.*, 2020, **32**, 2003376.
4. M. Behl and A. Lendlein, *Materials Today*, 2007, **10**, 20–28.

5. B. D. Moran, E. J. Fong, C. C. Cook and M. Shusteff, in *Emerging Digital Micromirror Device Based Systems and Applications XIII*, SPIE, 2021, **11698**, 8–15.