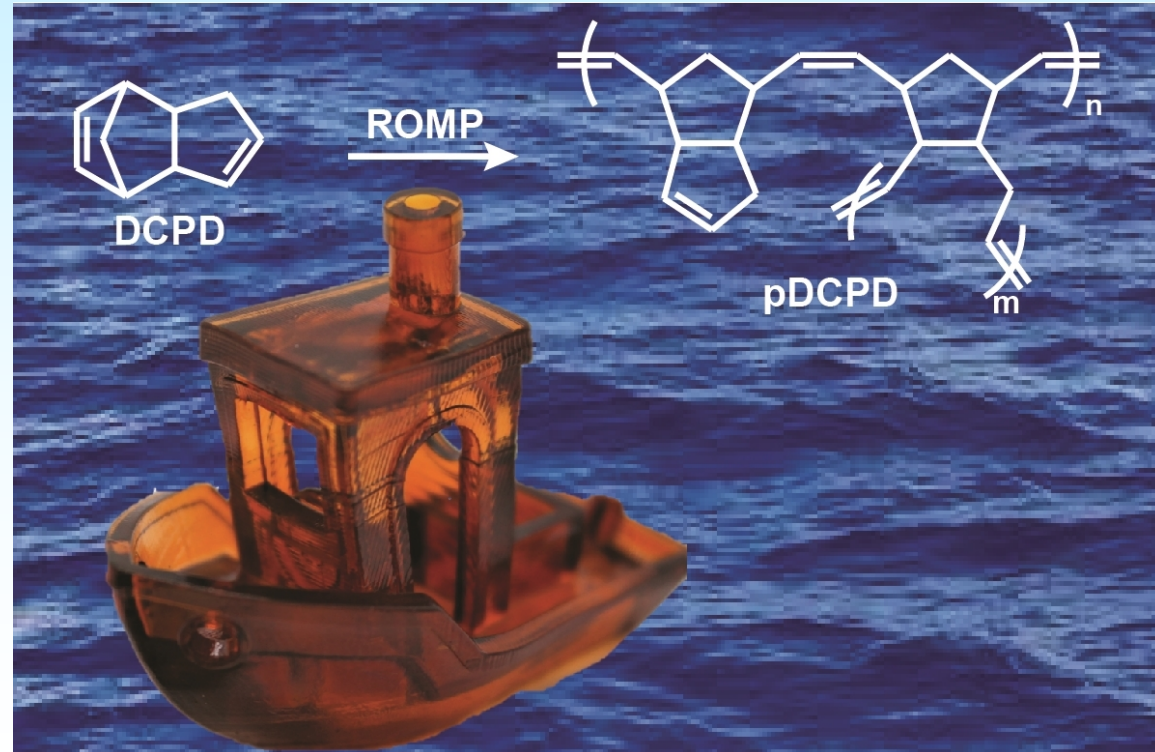


Alex Commisso, Samuel Leguizamon

Sandia National Laboratories, Albuquerque

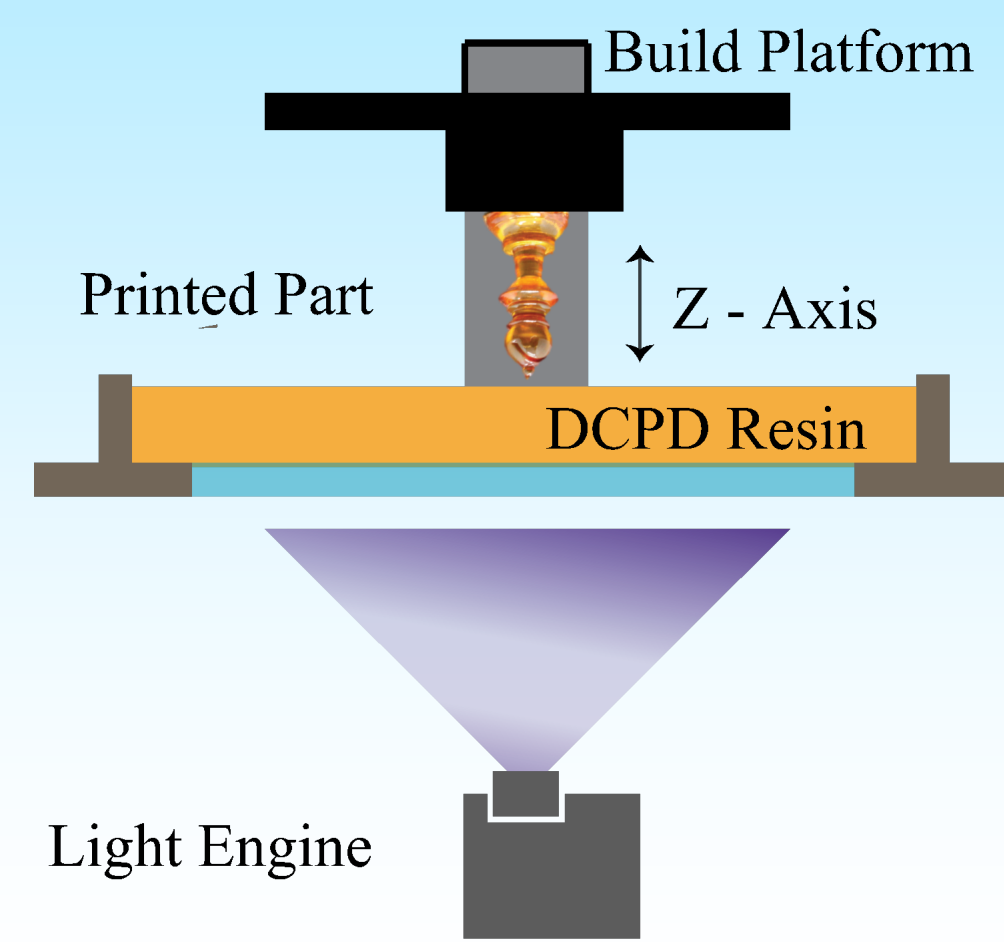
PhotoROMP for Additive Manufacturing

Photosensitization of ruthenium ROMP catalysts affords photoROMP rates of dicyclopentadiene (DCPD) appreciable to SLA AM

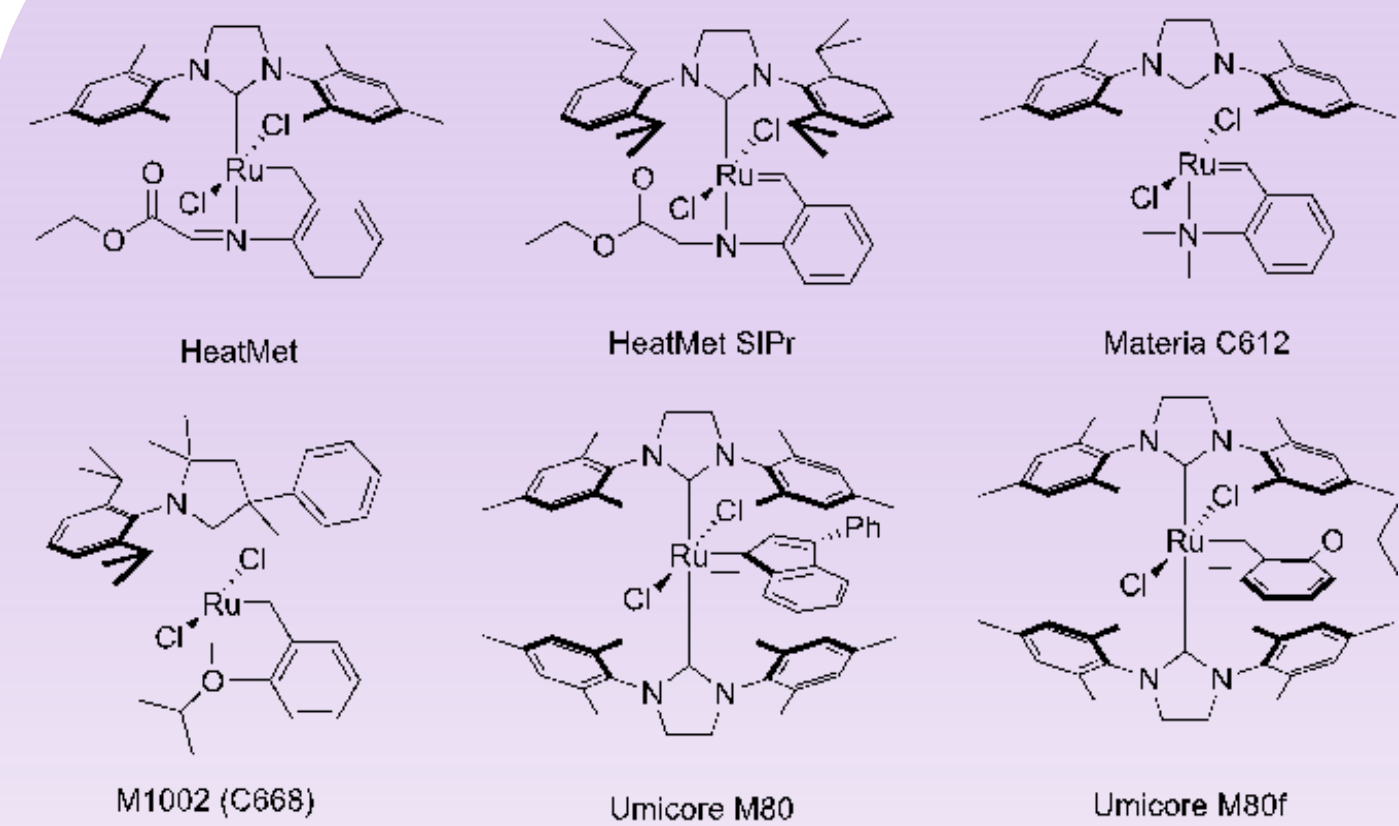


Leguizamon, S. C.; Appelhans, L. N. et al. *Macromolecules* **2022**, 55, 18, 8273–8282

Vat polymerization

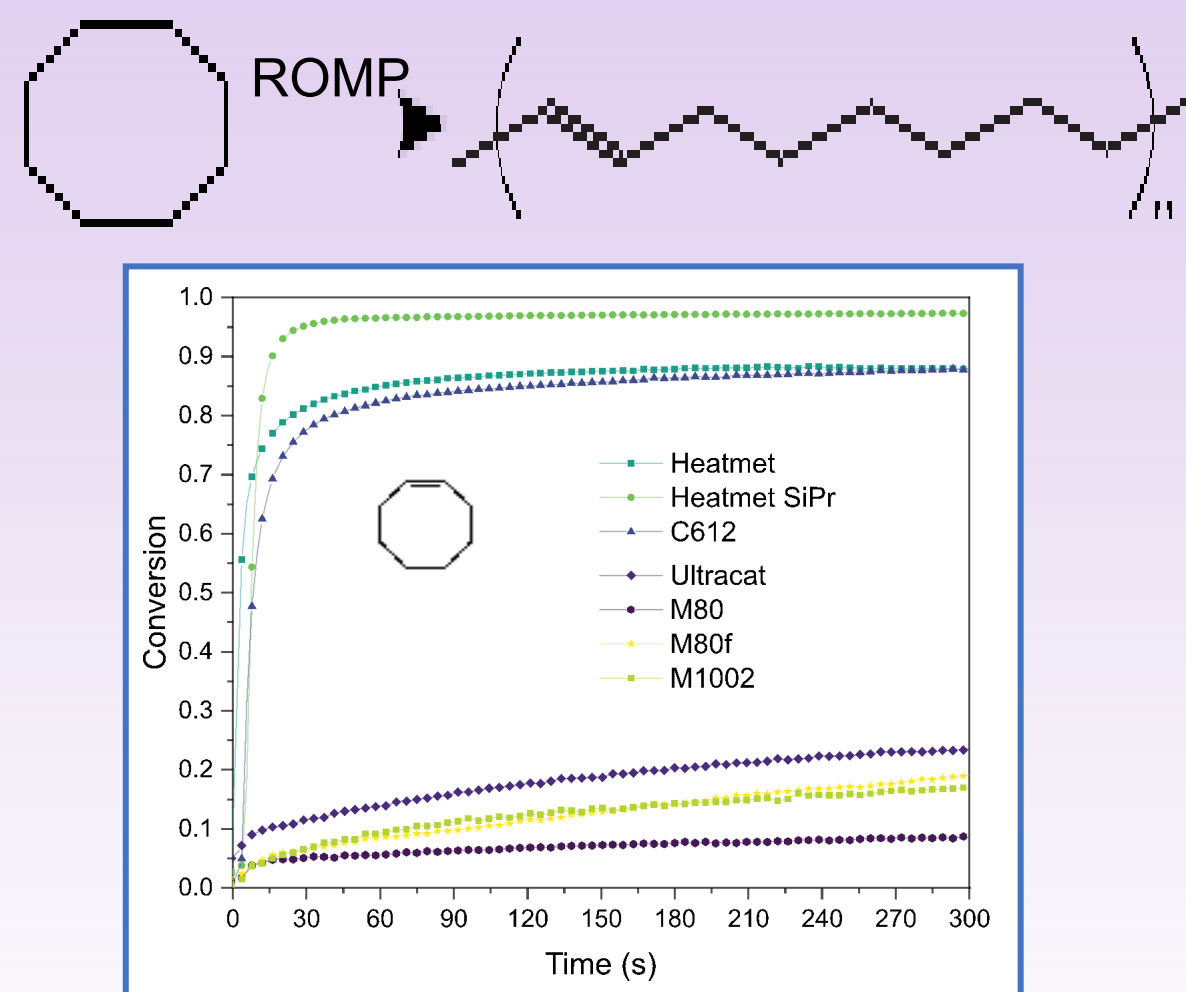


PhotoROMP of *cis*-cyclooctene



PhotoROMP system

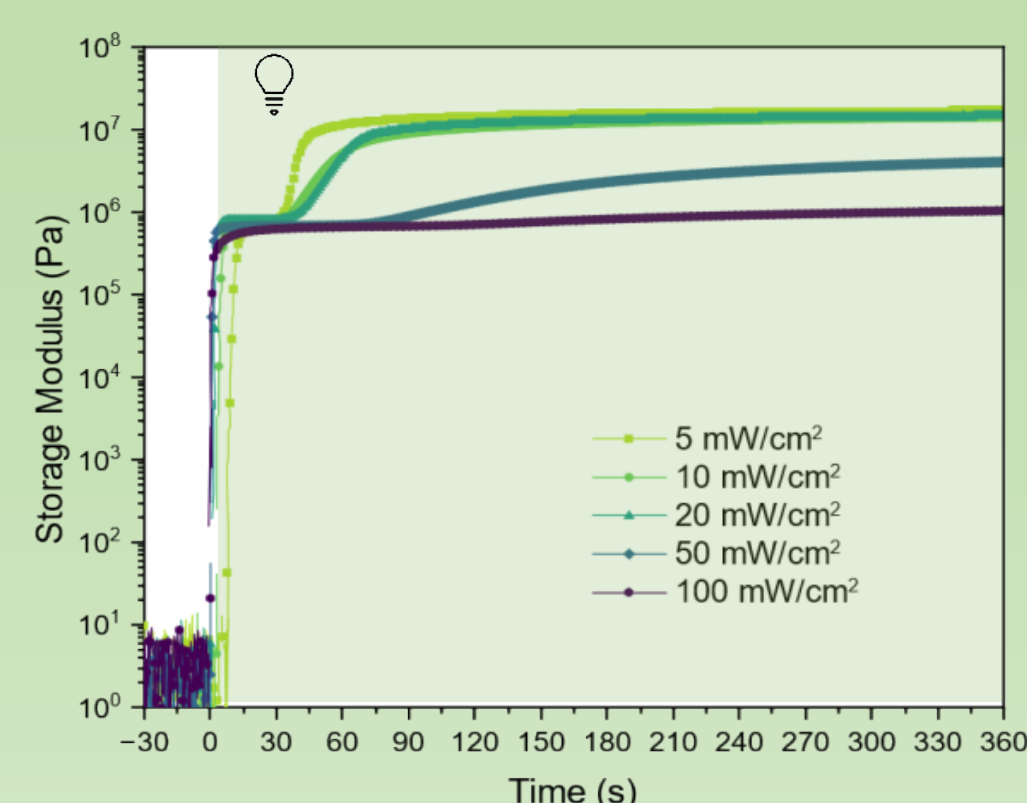
- 10,000:1 mol. equiv. monomer/catalyst
- 0.5, 1 wt. equivalent ITX, EDAB to Heatmet



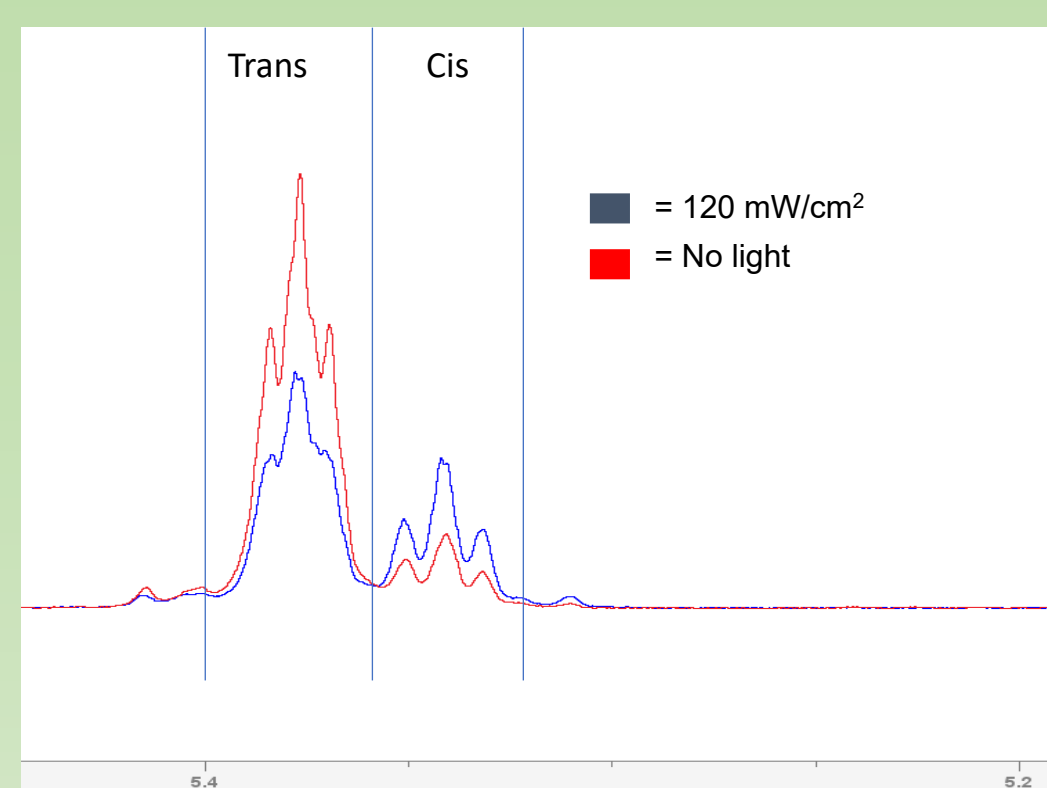
Catalyst Conc.	0.005 mol%	0.01 mol%	0.02 mol%	0.04 mol%
10 mW/cm ²				
100 mW/cm ²				

Catalyst choice and concentration affect activity, potlife, and mechanical properties.
Heatmet is ideal for rapid printing at a concentration of 0.01-0.02 mol%

In Situ Modulation of Polymer Crystallinity

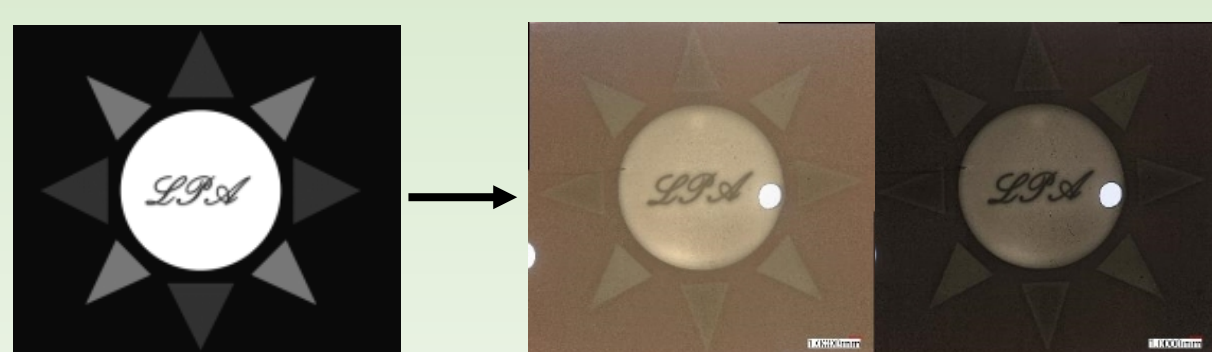


Crystallization kinetics (second increase in modulus) strongly dependent on light intensity



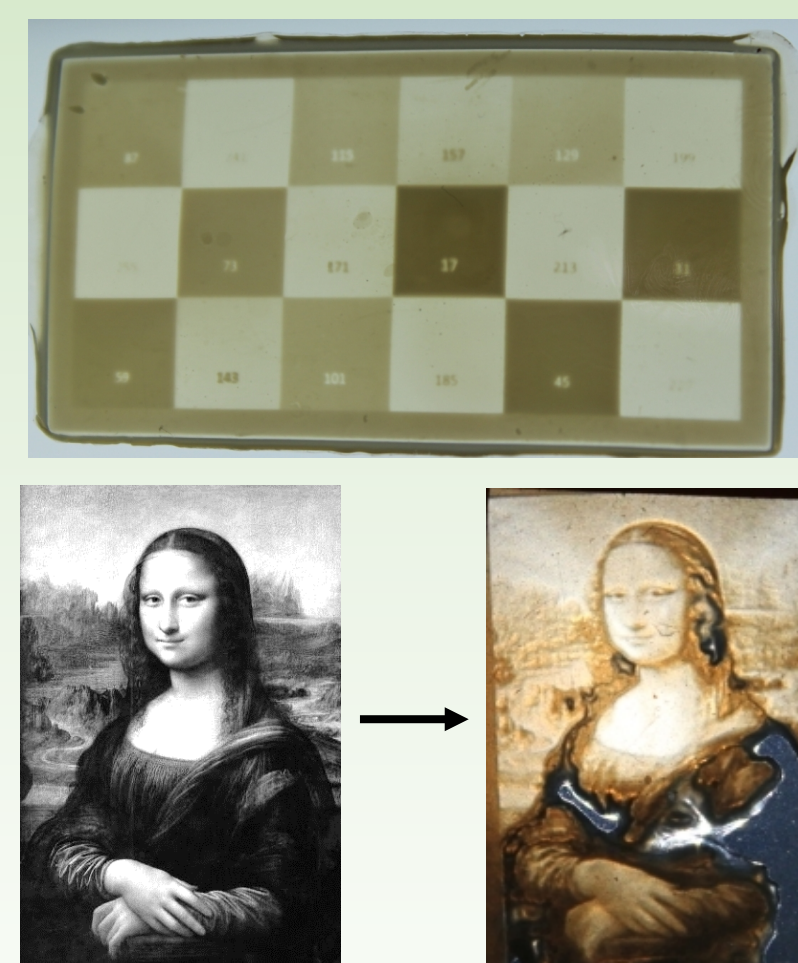
Higher intensity of light = higher cis polymer content

Greyscale Lithography

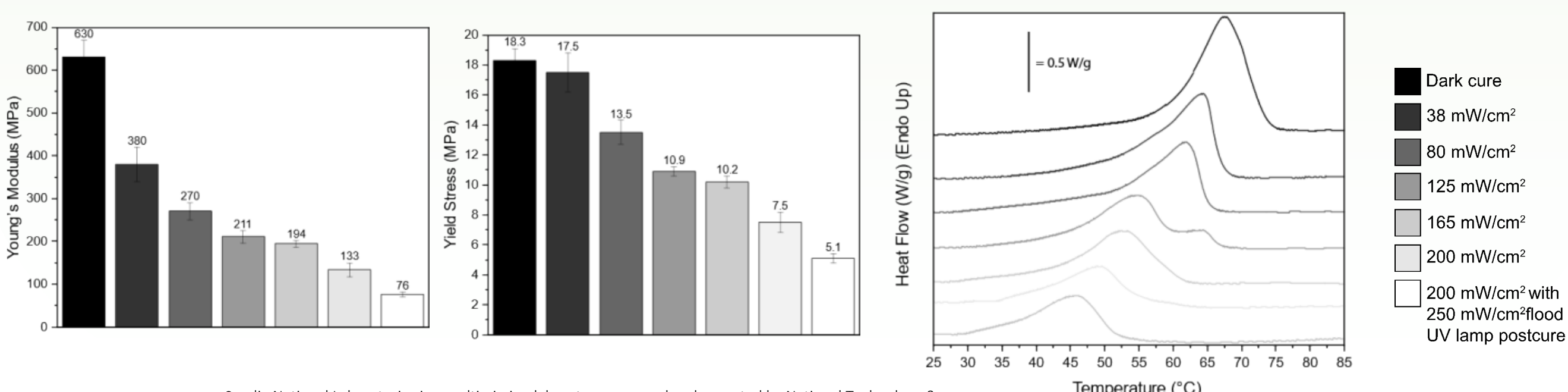


Area	Light Intensity (mW/cm ²)
Sun - center	100
Sun - lighter rays	50
Sun - darker rays	22
Sun - letters	10

Full greyscale range affords printing of extremely intricate designs



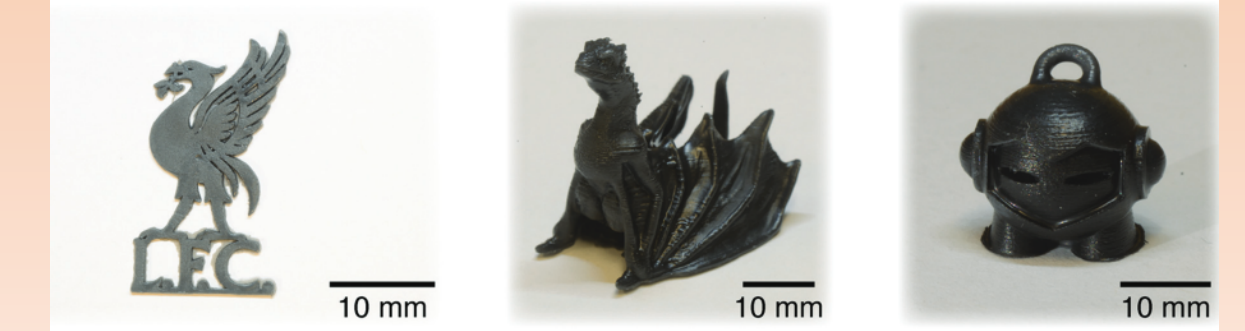
Greyscale Printing Mechanical Properties



Thermoplastic Additive Manufacturing

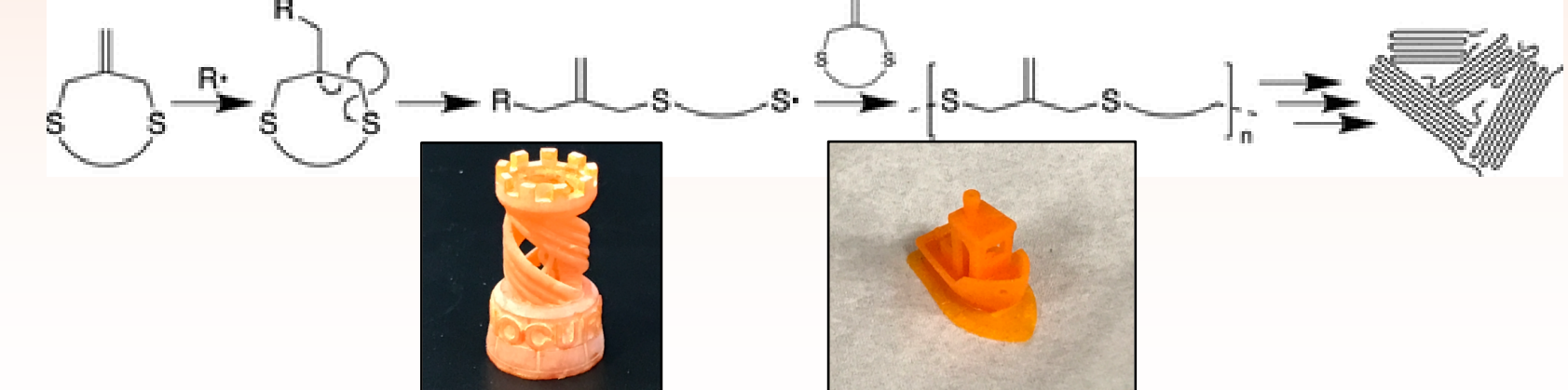
SLA AM is typically restricted to non-processable thermosets but thermoplastics offer processability and greater properties but few examples exist beyond thiol-enes

Thiol-enes – exceptional mechanical properties but poor interlayer adhesion



Alim, M. D.; Bowman, C. N. et al. *Mater. Horiz.*, 2020, 7, 835-842

Cyclic Allylic Sulfides – Improved interlayer adhesion but lesser mechanical properties



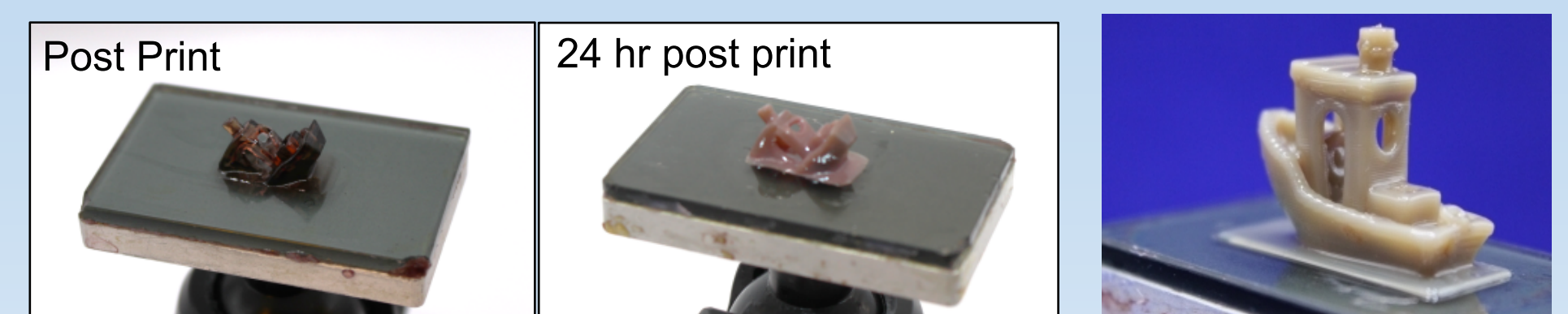
Commisso, A. J.; Scott, T. F. et al. *Chem. Mater.* 2023, 35, 10, 3825–3834

Challenges

- Rapid photopolymerization
- Shape fixity
- Sufficient mechanical properties
- Interlayer adhesion

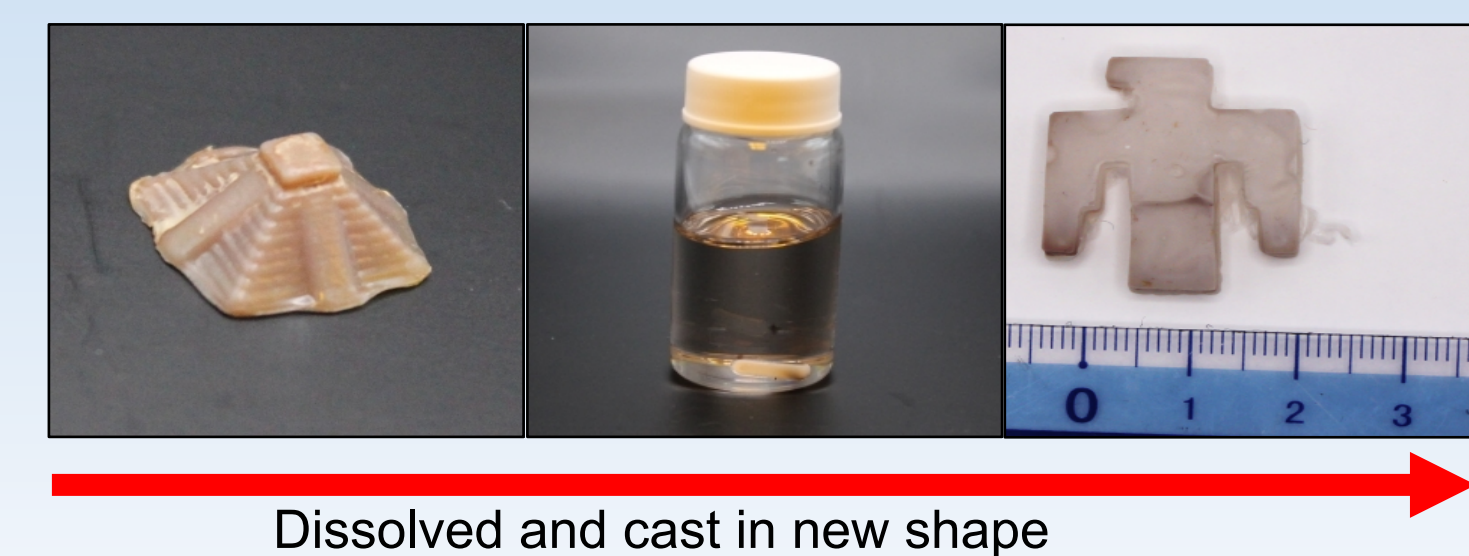
DLP Printing of Thermoplastic *cis*-cyclooctene

Rapid polymerization rates afford DLP prints in 5 – 10 minutes (~z = 1 cm)



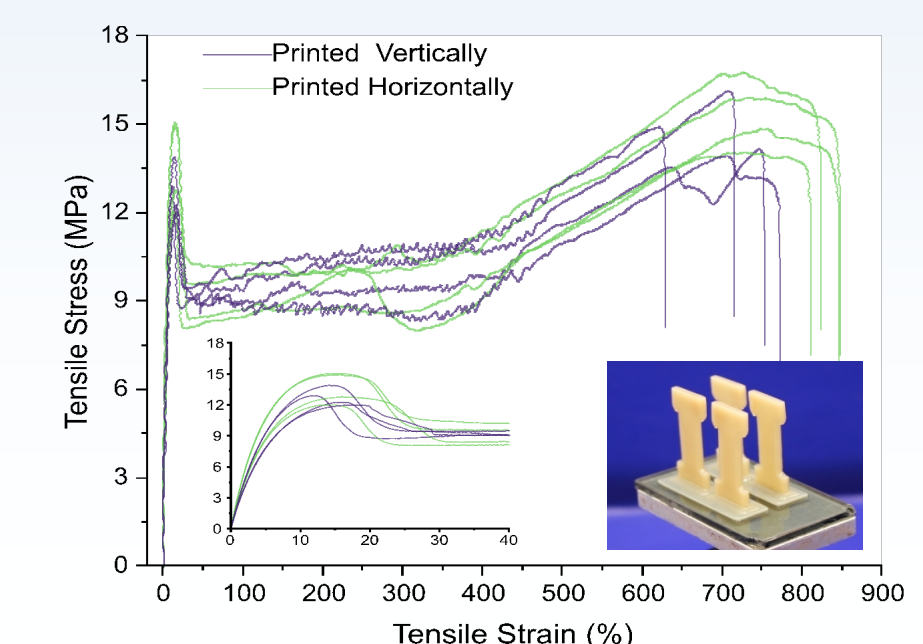
Reprocessable prints

- Solid prints soluble in toluene, chloroform, THF etc.
- Solvent casting allows for reprocessing of unused prints/supports



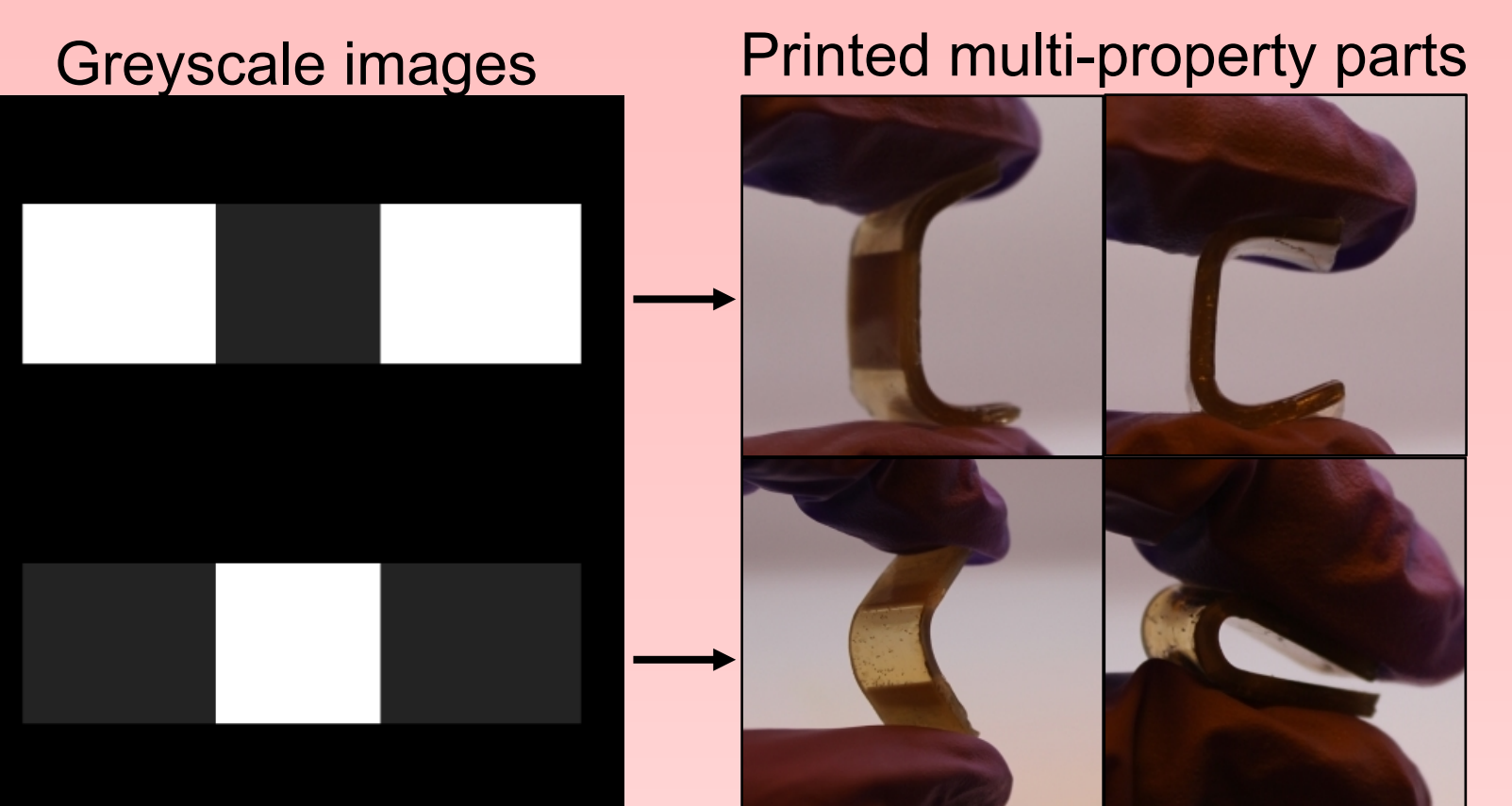
Improved interlayer adhesion

- Similar modulus and yield stress observed for both printed orientations
- Significant necking over 600% strain when printed vertically and tested perpendicular to weaker adhesion points

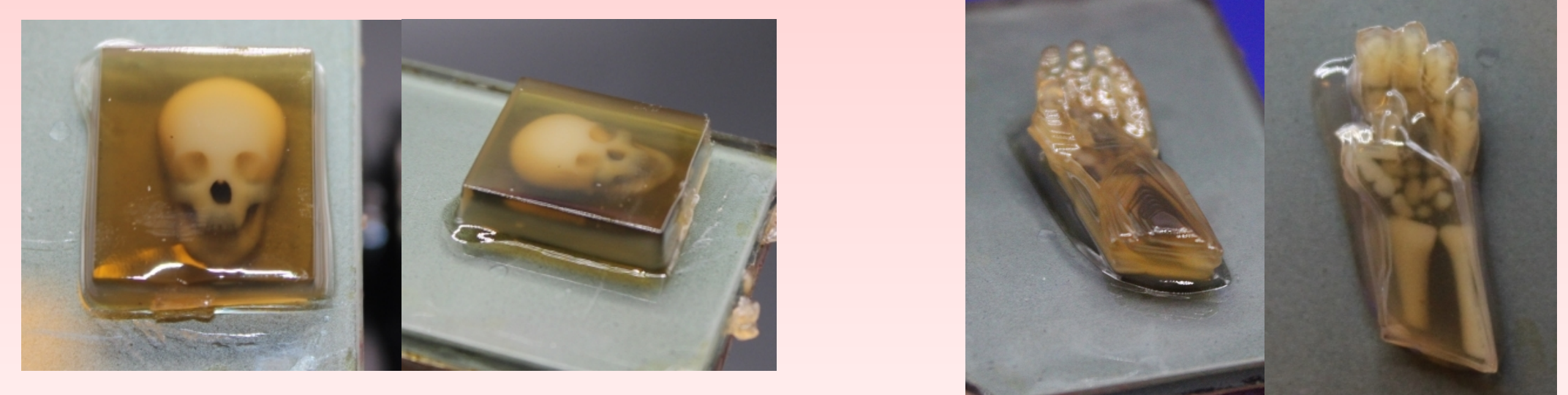


3D Greyscale Additive Manufacturing

Three-dimensional control of properties from a single pot affords endless mechanical optimization



Single Pot Multi-property 3D prints

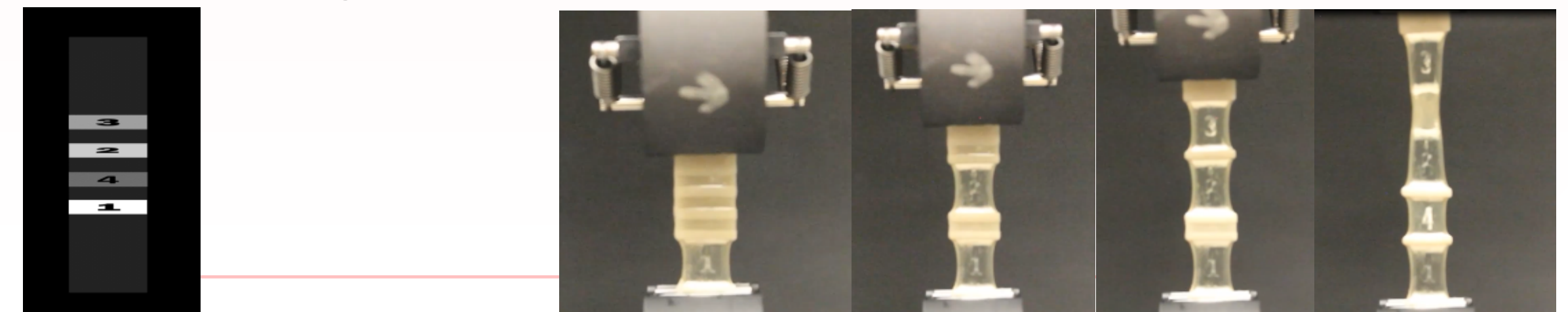


Selective Tensile Straining

Equal Modulus Soft Regions



Gradient Modulus Soft Regions



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