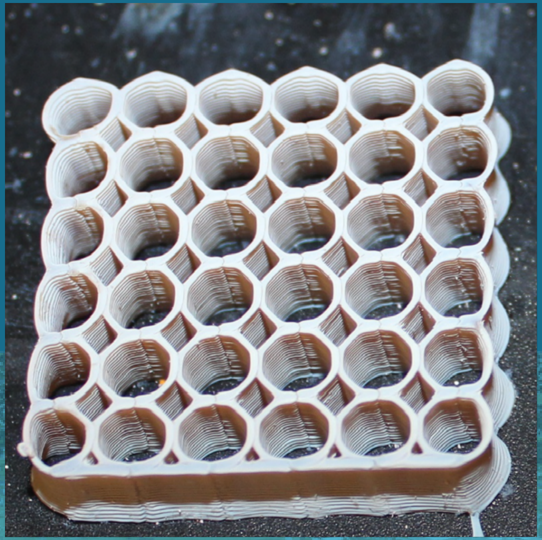
SAND2022-7647C

Sandia National Laboratories

Olefin Metathesis – Opening the Door to New Materials for Additive Manufacturing



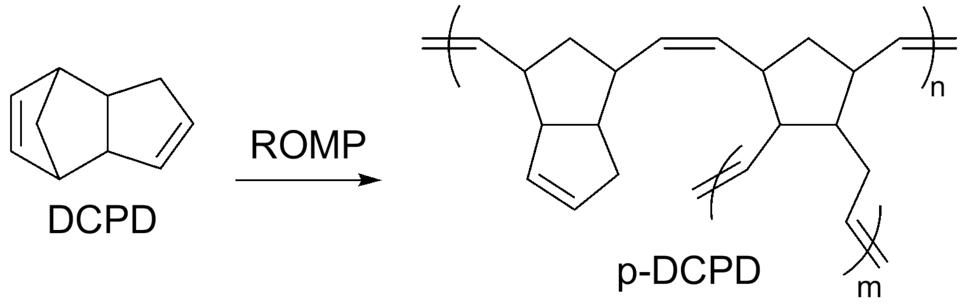
Samuel Leguizamon
Leah Appelhans
Jeffrey Foster
Brad Jones

June 22, 2022

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Photopolymerization for AM

- **Thermoset materials are conventionally formed through radical or cationic photopolymerization techniques**
- **Need for alternate mechanisms to expand library of AM thermosets**



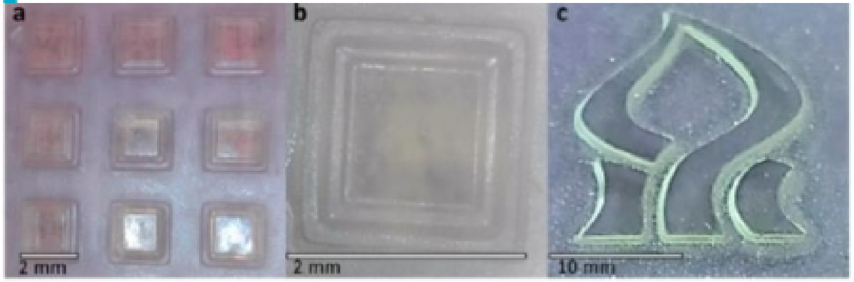
Ring-opening metathesis polymerization

- Tolerant to wide variety of functional groups
- Wide variety of monomers with useful mechanical, thermal, or di-electric properties
- Recent studies on depolymerizable monomers

Material	T_g (°C)	T_{max}(°C)	Elastic modulus (GPa)	Tensile strength, yield (MPa)	Strain at yield	Impact strength (J/cm)	Dielectric constant
pDCPD*	**150**	**190**	**2.1**	54	6%	**0.71**	2.50
Epoxy encapsulant*	100	120	**2.2**	46	20%	0.31	4.05
PU foam*	120	110	0.70	44	**350%**	**0.67**	**1.43**
Acrylate resin**	ca. 75	ca. 70	**2.2**	**65**	**<6%**	0.25	ca. 3

*Average values obtained from MatWeb database of material properties (http://www.matweb.com).
**(https://www.hubs.com/knowledge-base/sla-3d-printing-materials-compared).

Ring-opening Metathesis Polymerization (ROMP) and AM



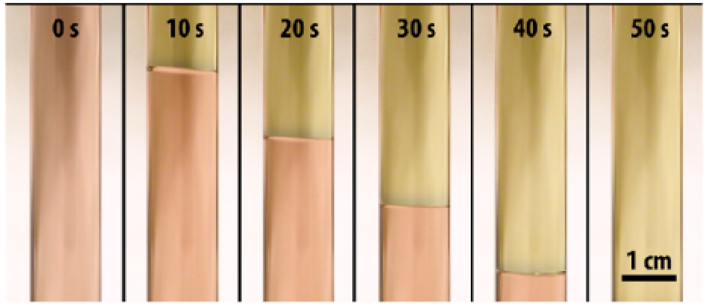
Eivgi et al. ACS Catal. 2020, 10, 2033−2038

Can we optimize photochemistry to adapt photoROMP for AM printing?

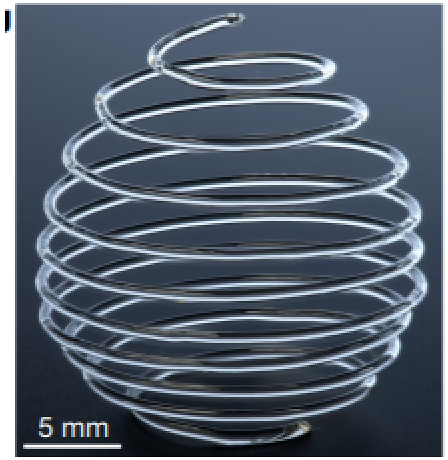
AM previously demonstrated using photoROMP

Limitations:

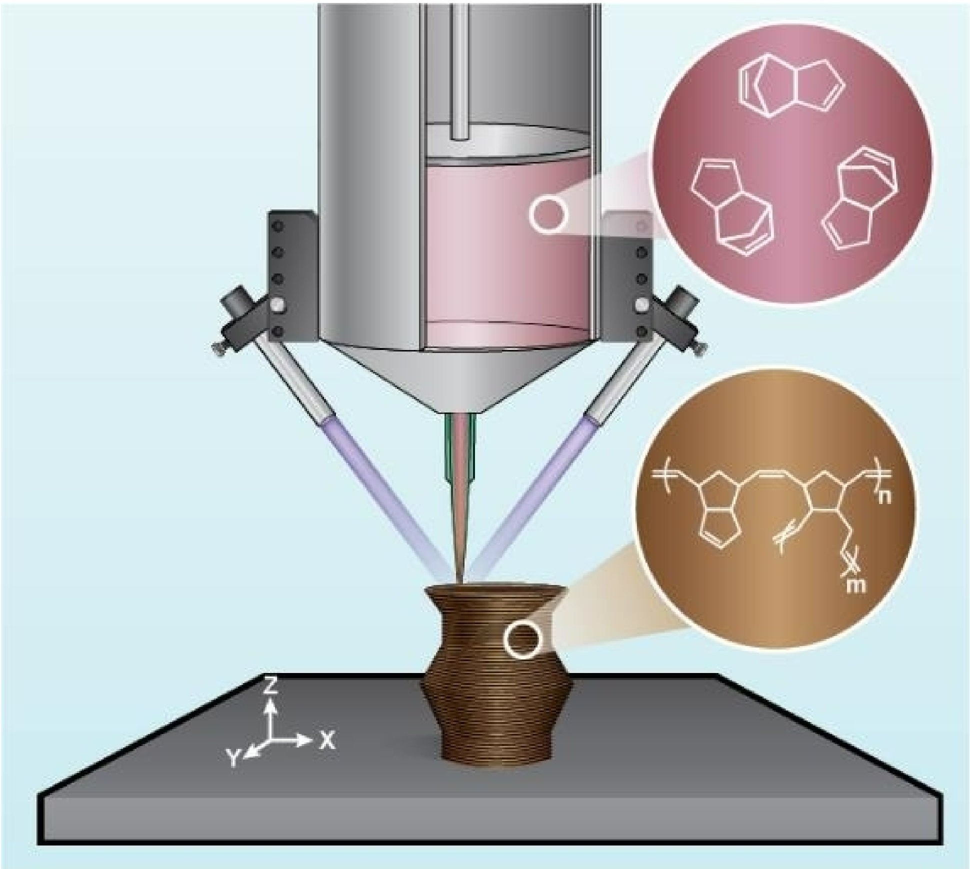
- *Sluggish polymerization rates*
- *Few available photo-latent catalysts*
- *Demonstrations limited to >5 layers*



Robertson et al.
ACS Macro Lett., 2017, 6, 6

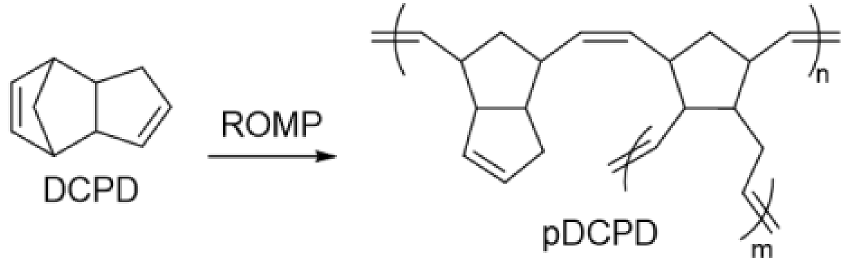


Robertson et al.
Nature, 2018, 557, 223

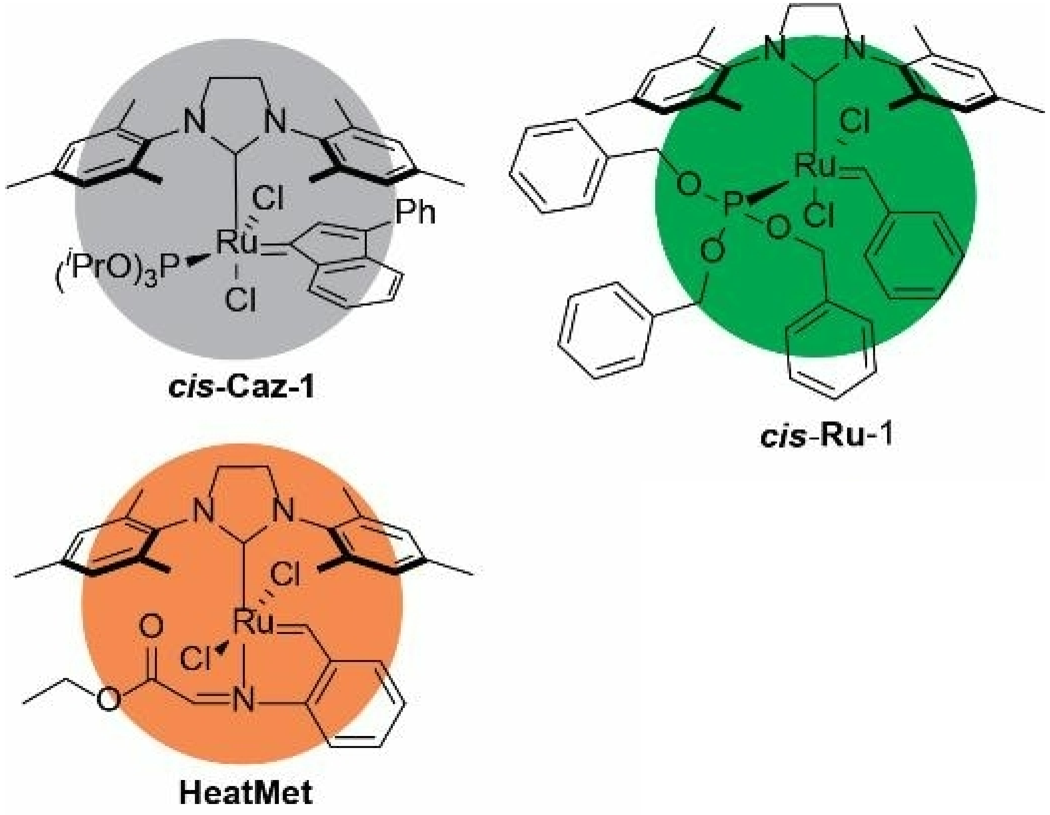


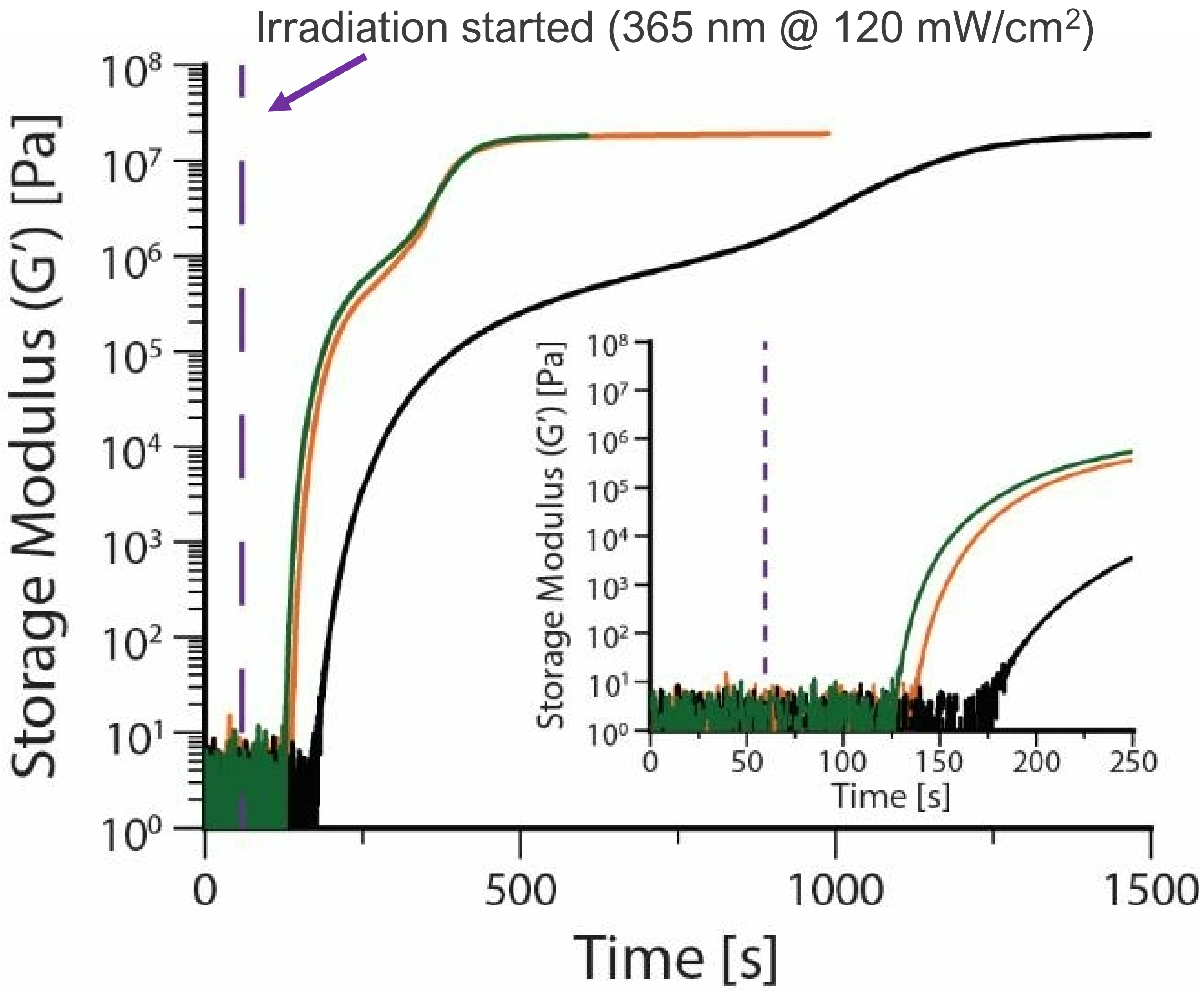
Leguizamon, S. C.; Cook, A. W.; Appelhans, L. N. *Chemistry of Materials* **2021,** *33* (24), 9677-9689.

PhotoROMP AM

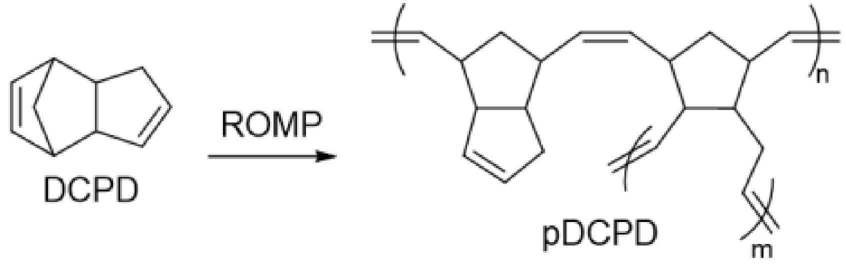


- **Access to wide-range of metathesis-active monomers**
- **Potential for rapid printing rates**

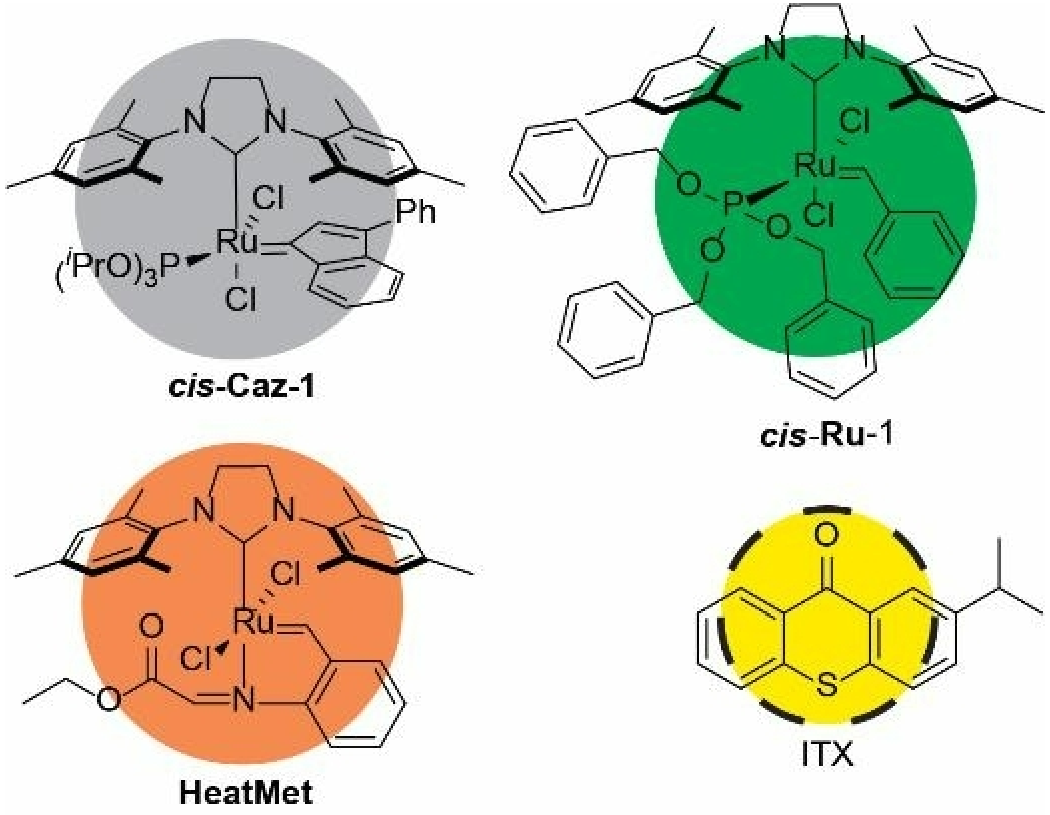


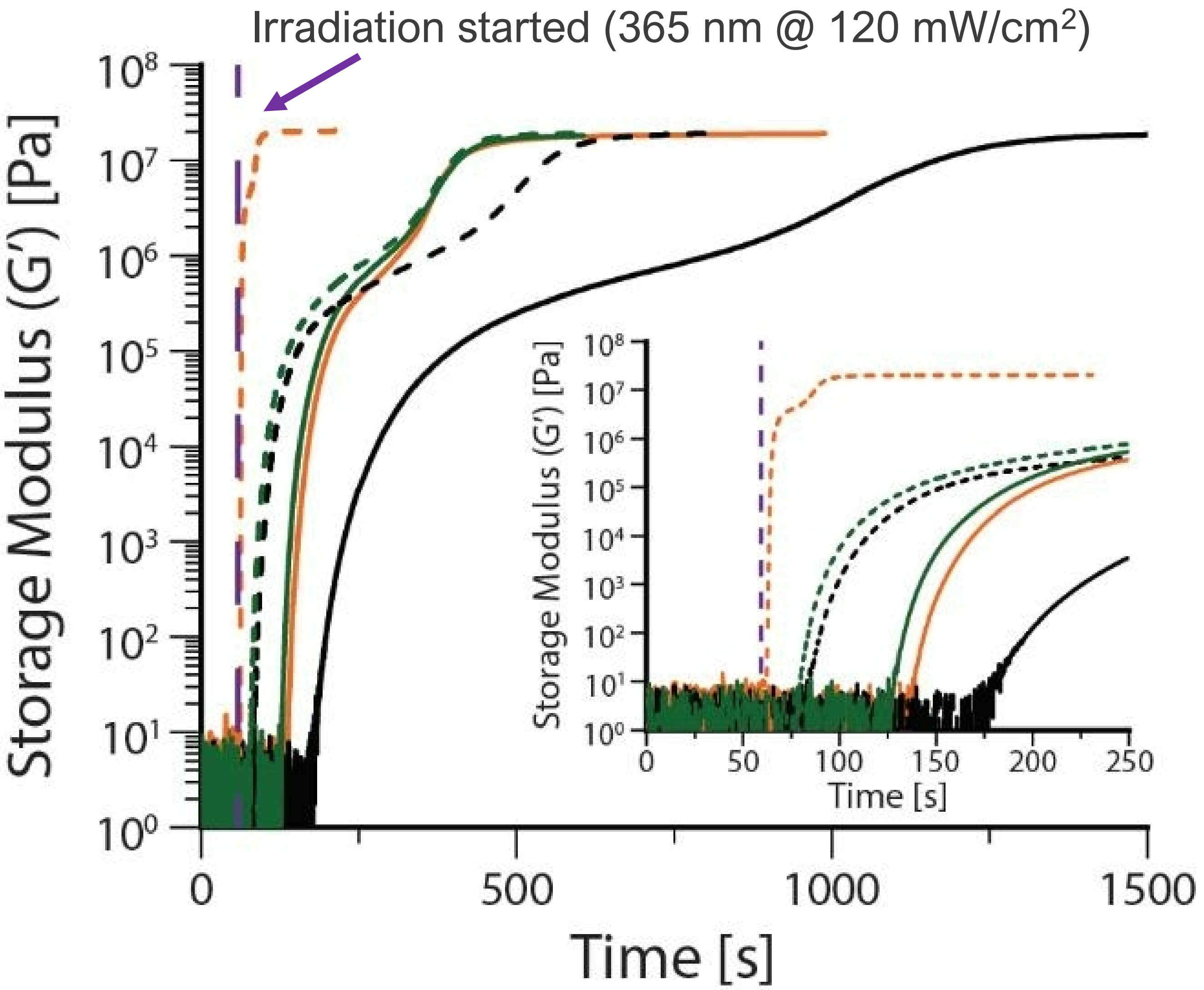


PhotoROMP AM

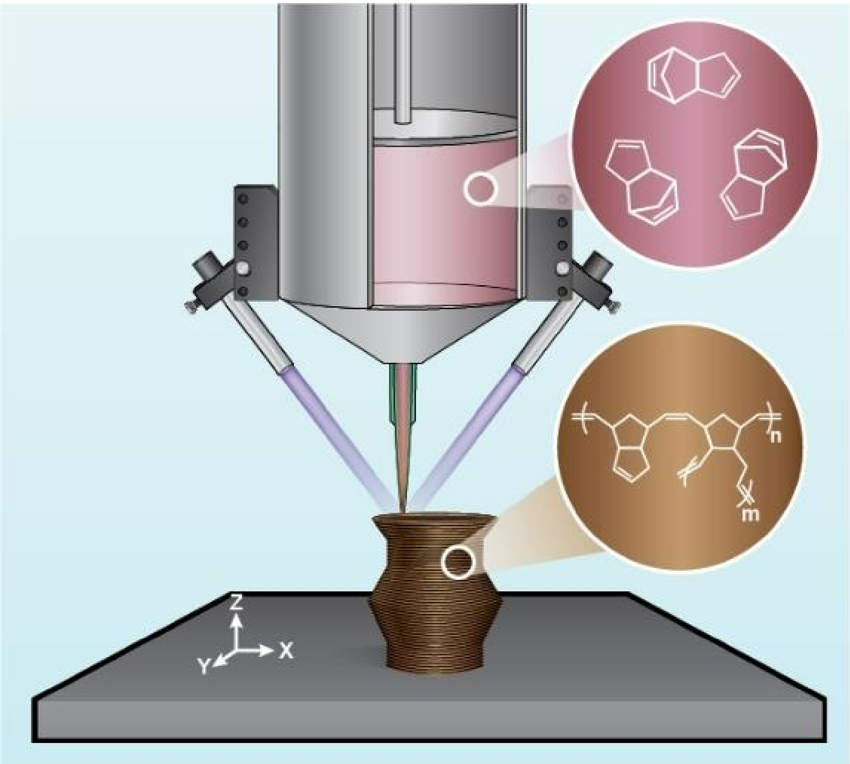


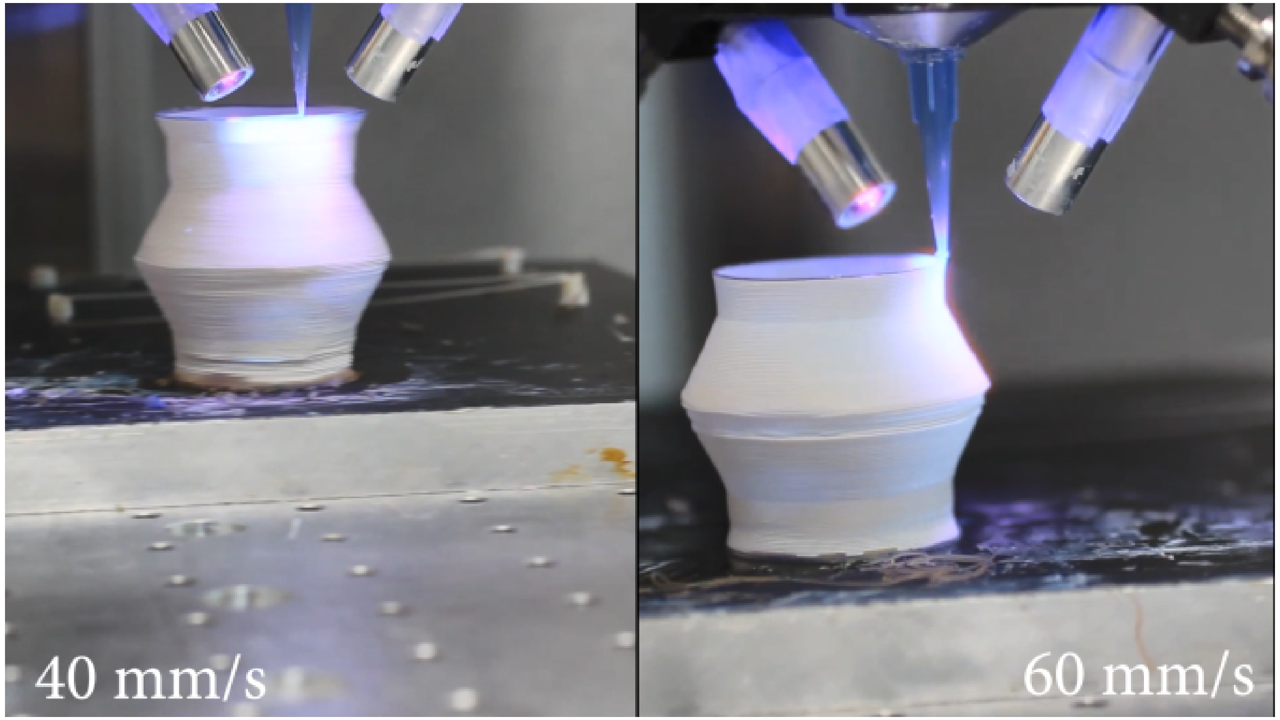
- **Access to wide-range of metathesis-active monomers**
- **Potential for rapid printing rates**

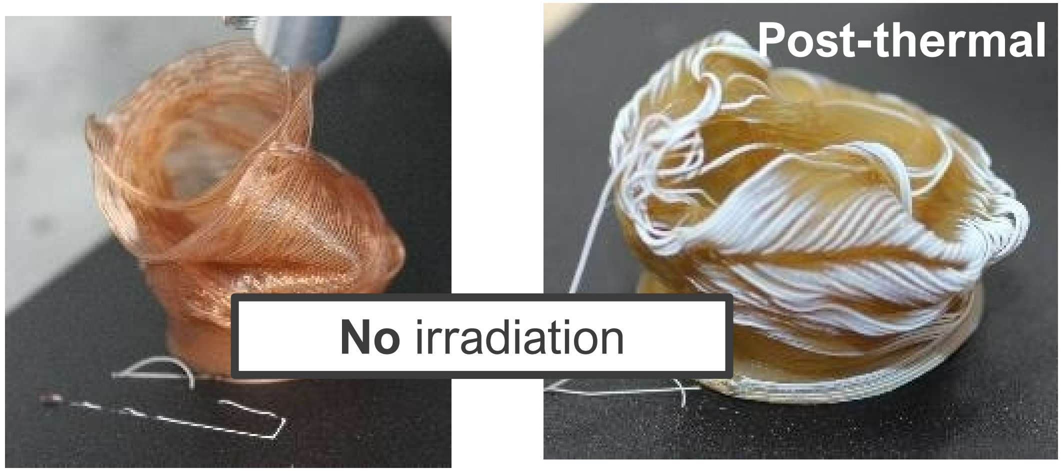


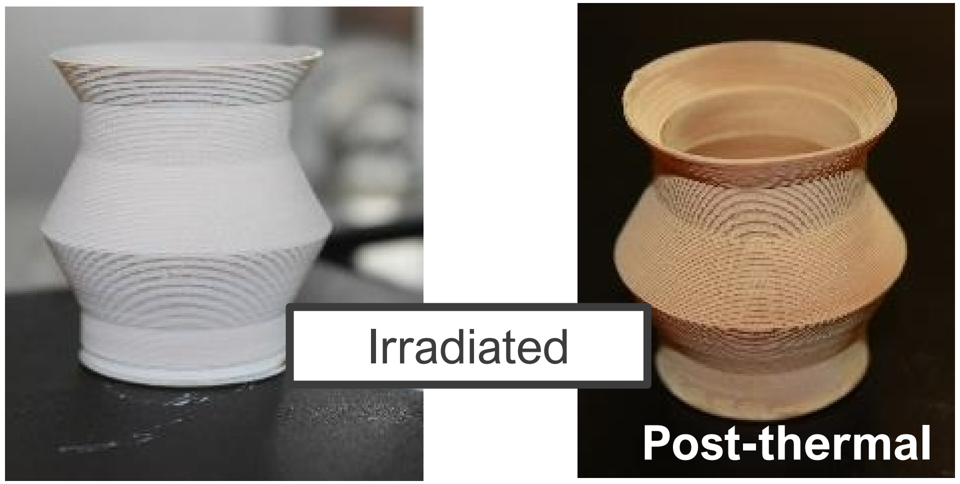


DIW AM of ROMP-based Resin

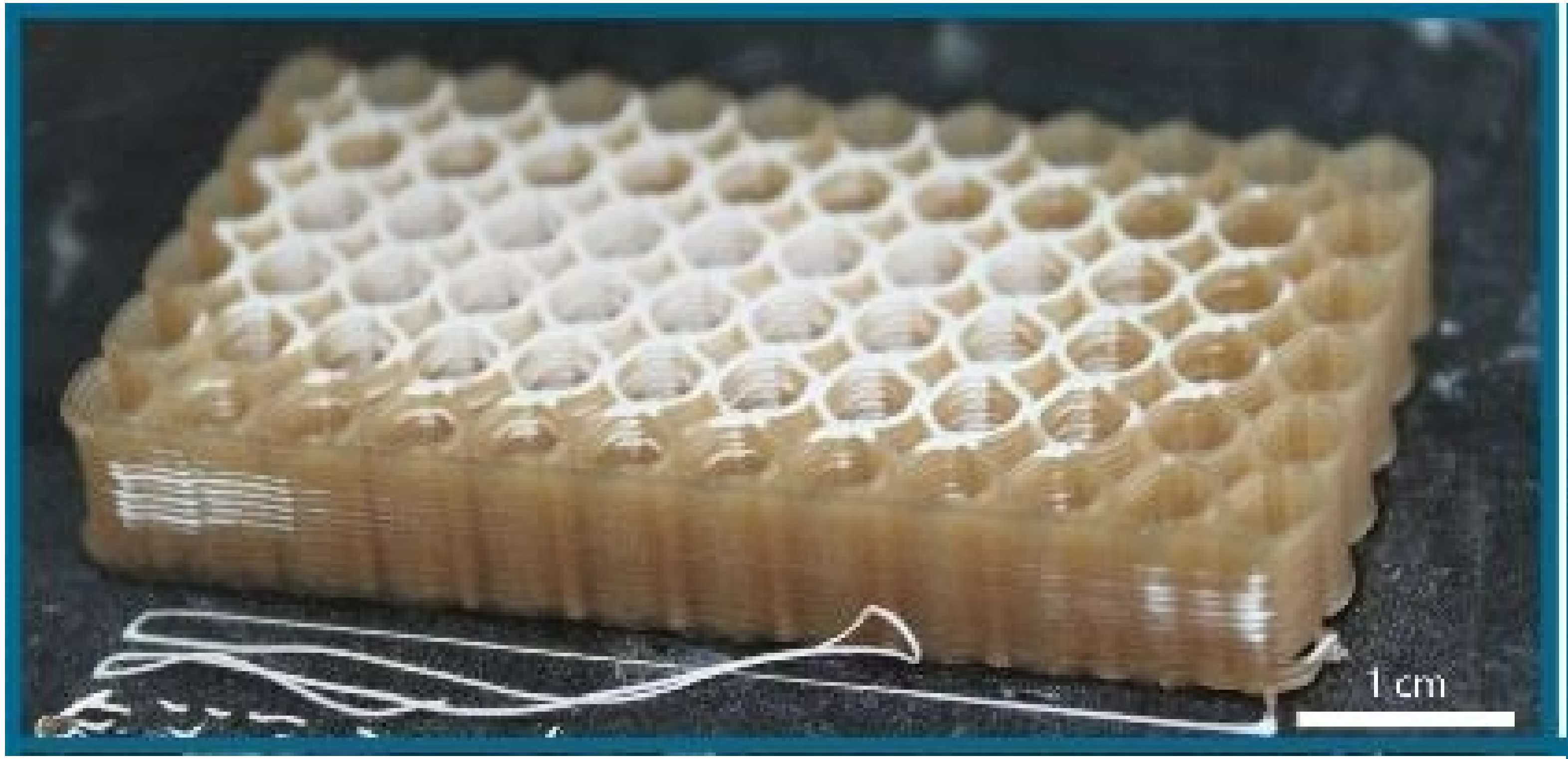


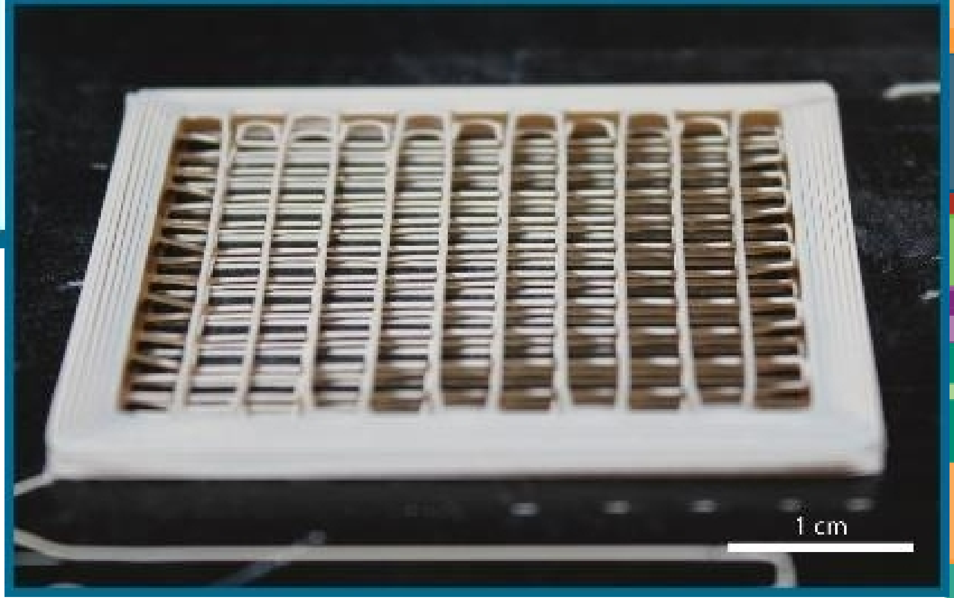


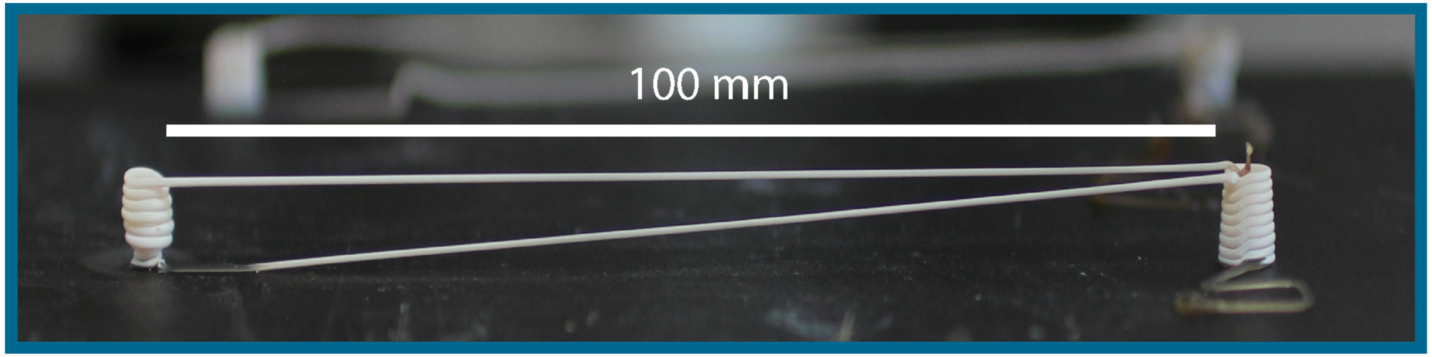




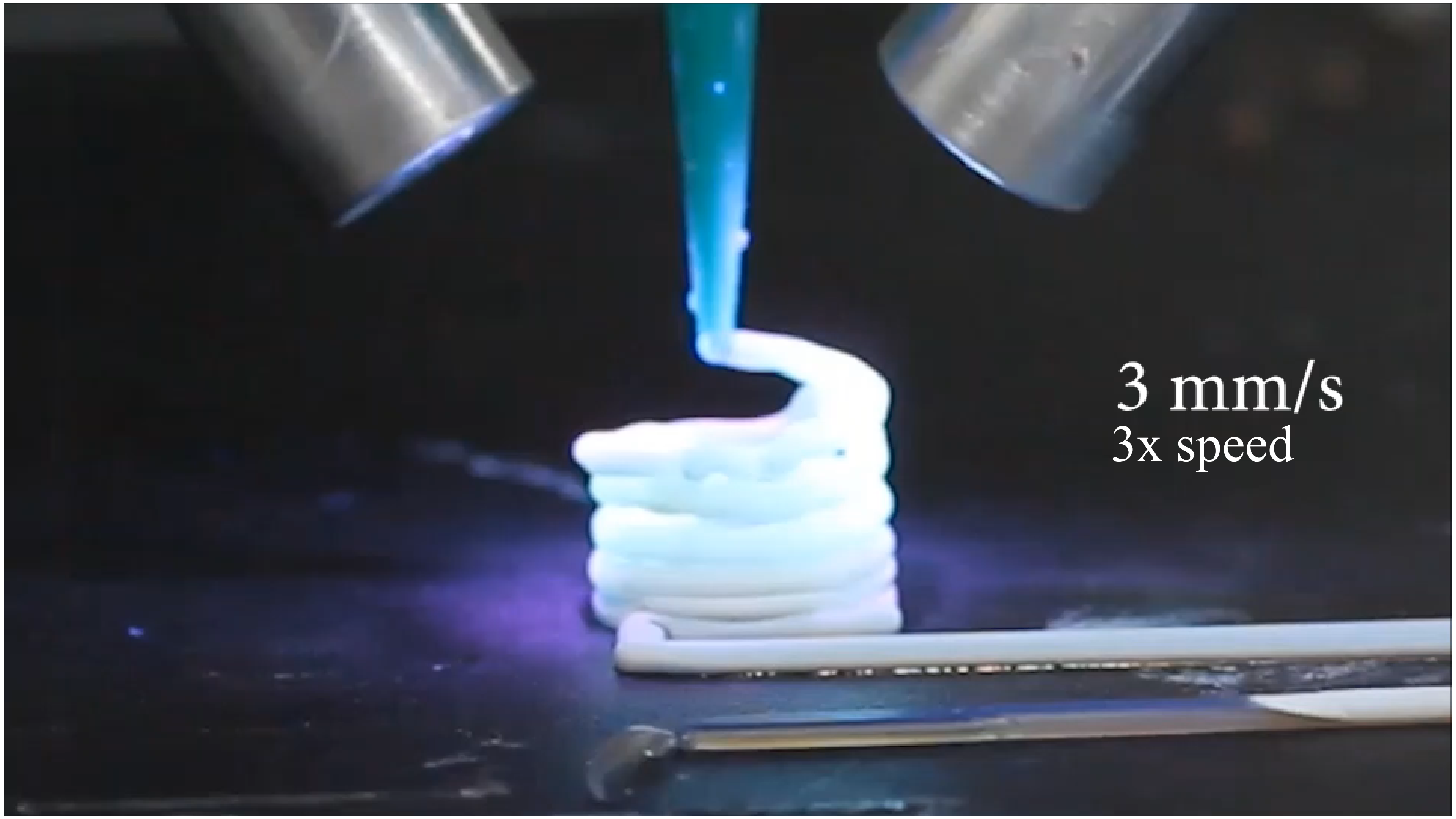
DIW AM of ROMP-based Resin



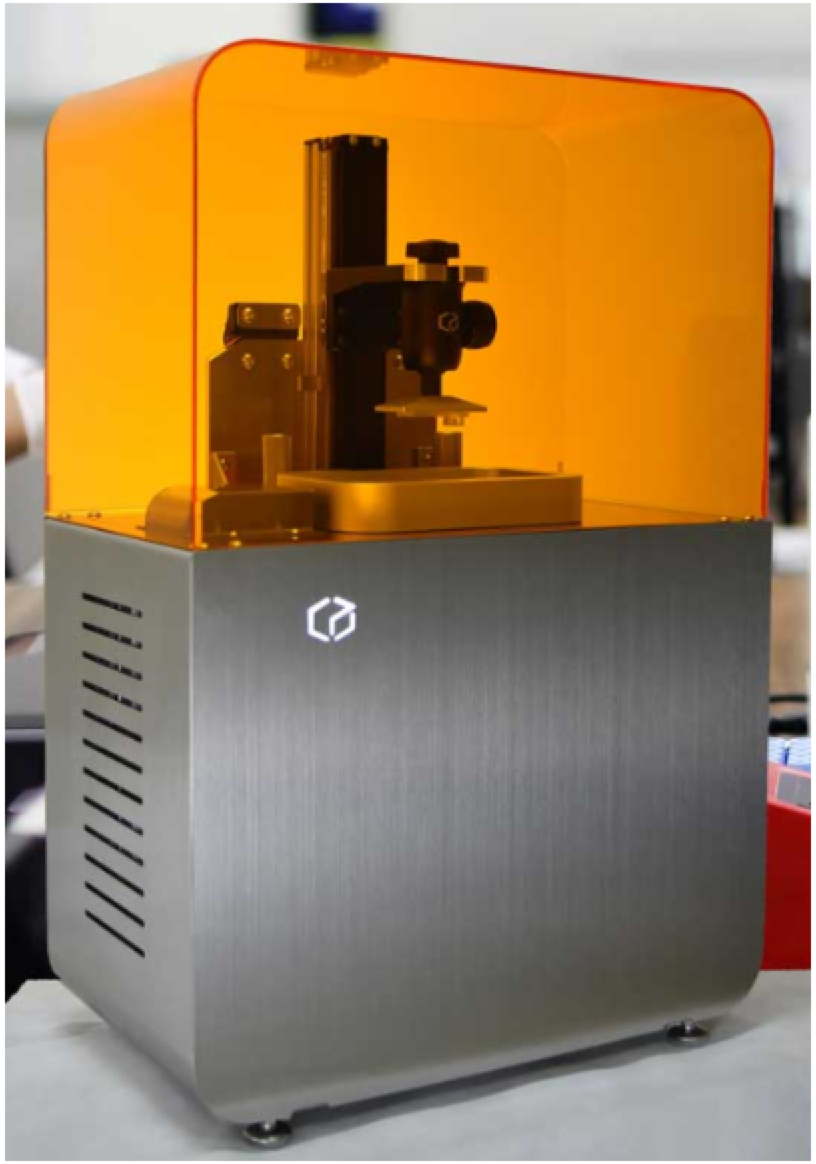




DIW AM of ROMP-based Resin

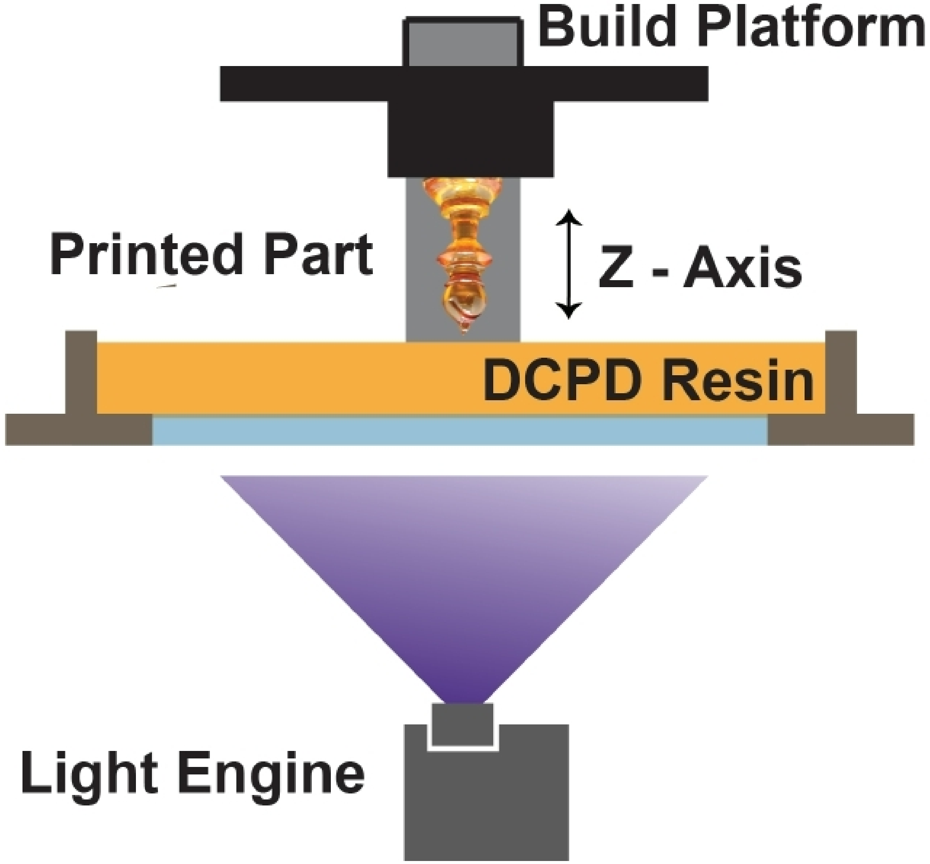


Stereolithography AM of pDCPD

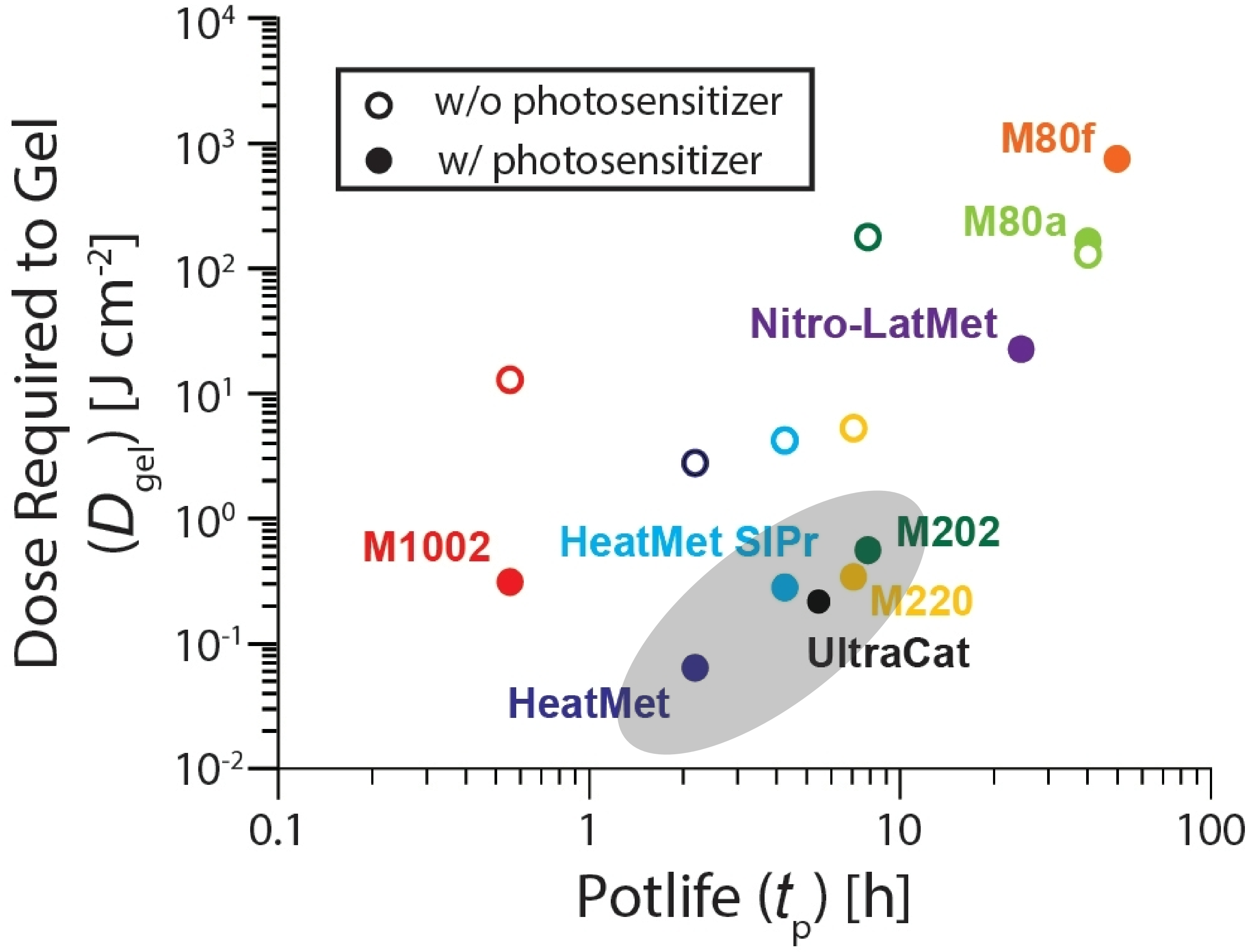


https://www.kudo3d.com/micro/

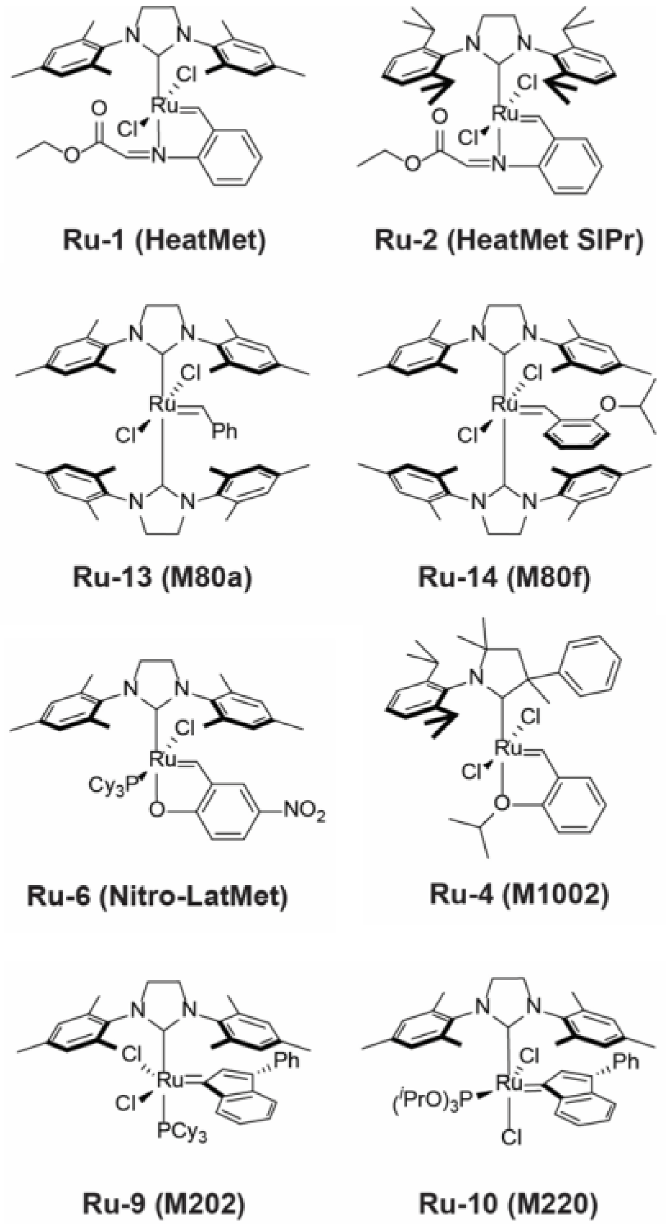
- Adapt DIW formulations for SLA printing
- SLA enables higher resolution and more complex geometries
- Use commercial SLA printer



Stereolithography AM of pDCPD



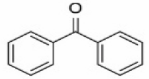
Survey of Catalysts



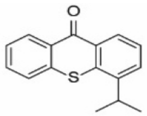
Stereolithography/Digital Light Processing AM

Survey of Photosensitizers

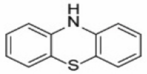
Benzophenone
E_T = 285 kJ mol^{-1}



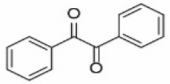
2-Isopropylthioxanthone
(ITX)
E_T = 255 kJ mol^{-1}



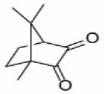
Phenothiazine
E_T = 253 kJ mol^{-1}



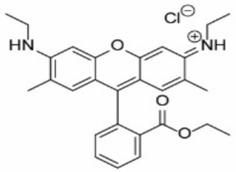
Benzil
E_T = 223 kJ mol^{-1}



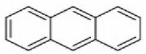
Camphorquinone
(CQ)
E_T = 216 kJ mol^{-1}



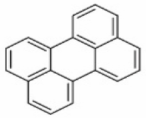
Rhodamine 6G
E_T = 190 kJ mol^{-1}



Anthracene
E_T = 177 kJ mol^{-1}

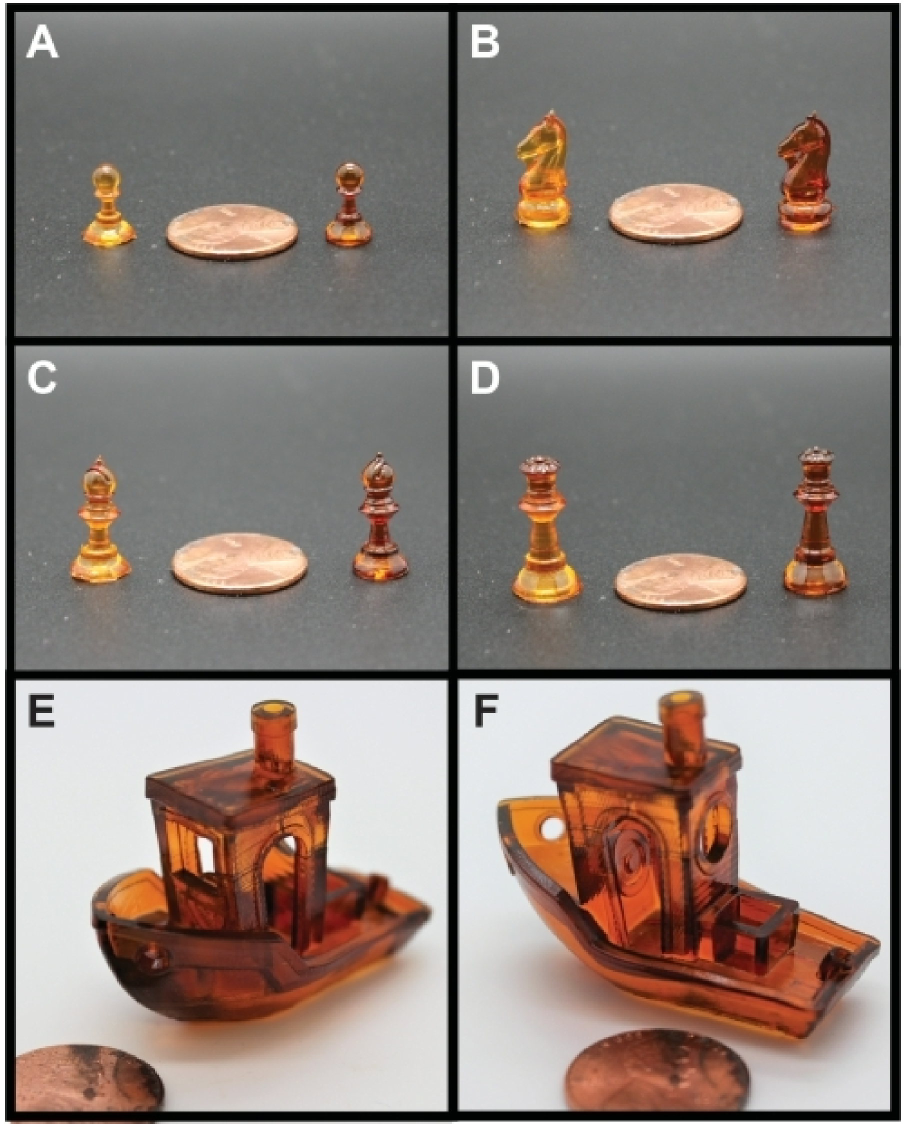


Perylene
E_T = 148 kJ mol^{-1}



Photosensitizer	Irradaition Wavelength (λ) [nm]	Extinction Coefficeint (ε) [L mol^{-1} cm^{-1}]	Norbornene Conversion at t_{172} [%]	Dose Required to Gel (D_{gel}) [J cm^{-2}]
—	365 nm	—	0.2	3.2
	405 nm	—	4.0	6.2
	475 nm	—	1.5	25.5
	525 nm	—	3.2	—
Benzophenone	365 nm	90	63.3	1.2*
	405 nm	5	1.3	—
2-Isopropylthioxanthone (ITX)	365 nm	4300	62.9	0.2
	405 nm	960	55.0	0.9
Phenothiazine	365 nm	400	58.5	1.0
	405 nm	8	0.8	3.2
Benzil	365 nm	65	62.7	0.1
	405 nm	8	67.4	0.1
	475 nm	3	15.3	1.6
Camphorquinone (CQ)	365 nm	3	34.1	2.9
	475 nm	42	62.2	0.4
Rhodamine 6G	365 nm	2374	2.8	3.8
	525 nm	22900	1.2	—
Anthracene	365 nm	2270	0.1	3.5
	405 nm	5	0.2	8.4
Perylene	365 nm	3270	0.0	6.0
	405 nm	17100	0.0	8.2

Stereolithography AM

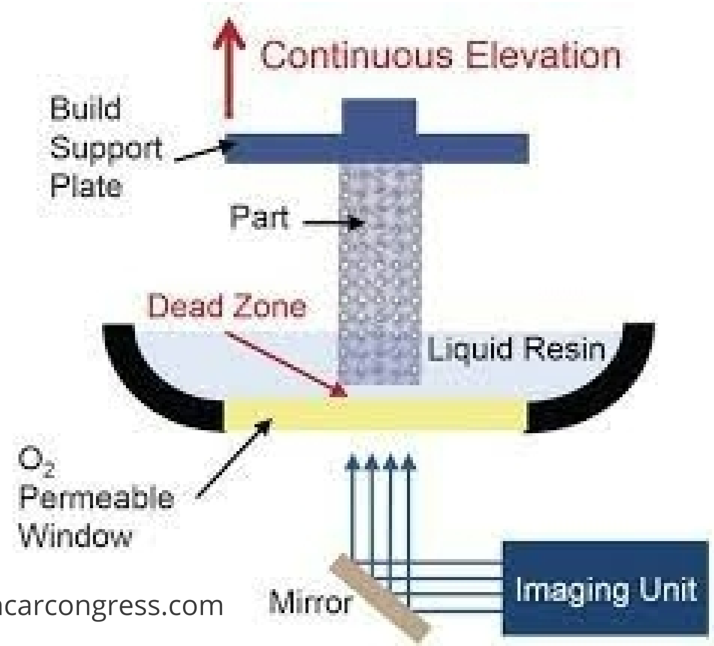


Potlife is still an issue – requiring resin replacement mid-build during large builds

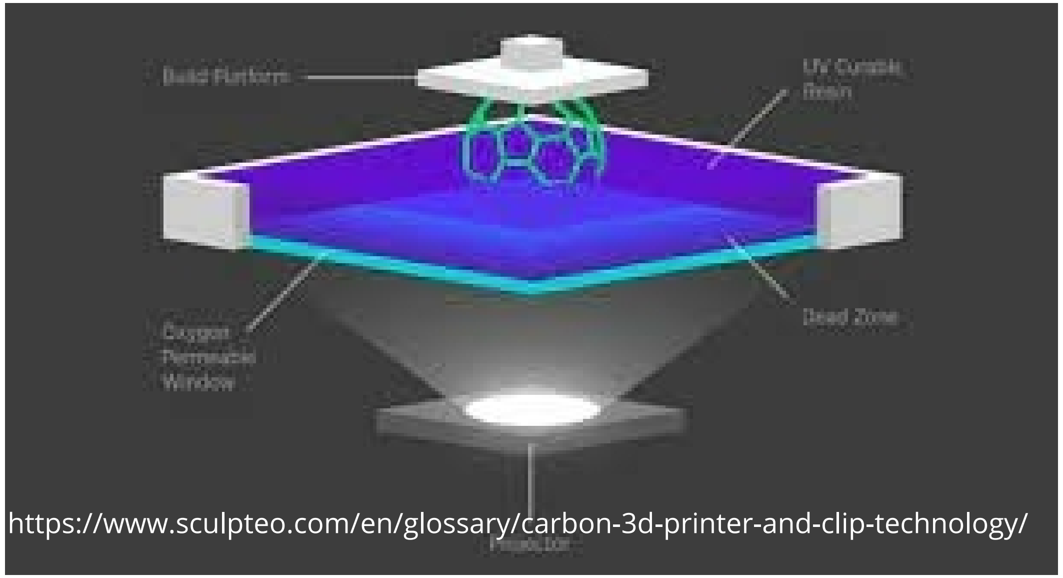
Solution: Continuous SLA AM

SWOMP: Selective Wavelength Olefin Metathesis Polymerization

CLIP:

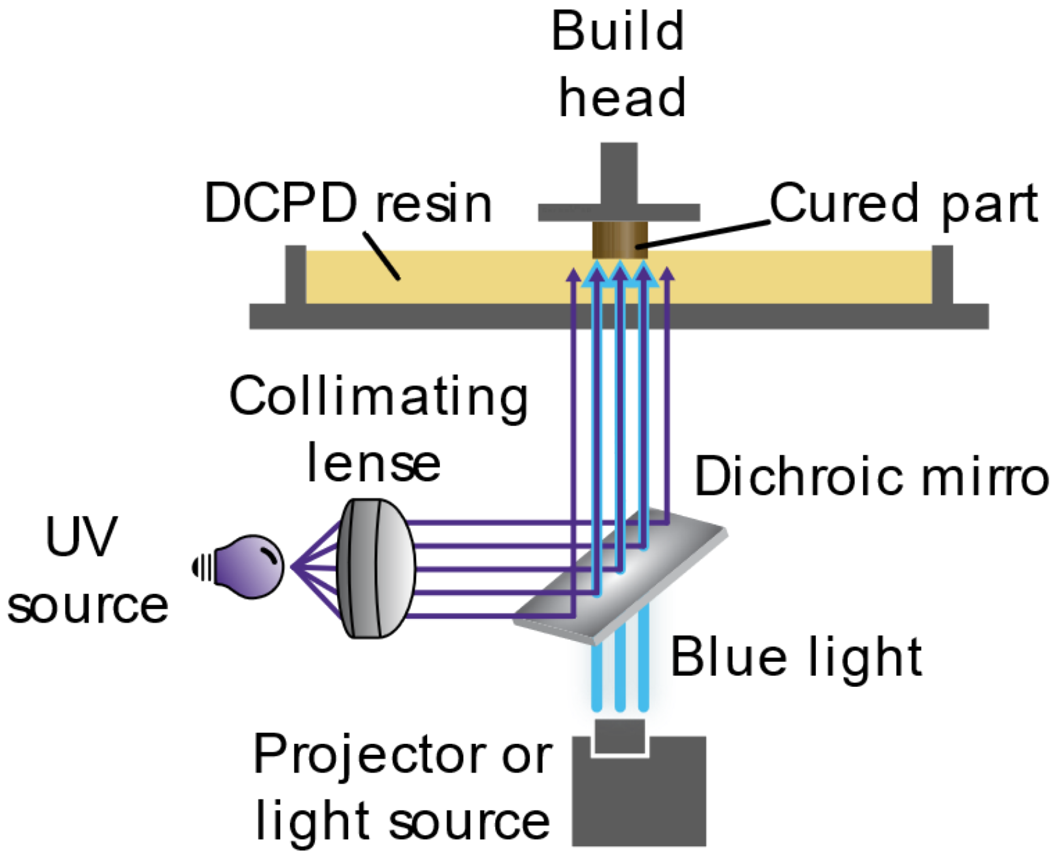


https://www.greencarcongress.com



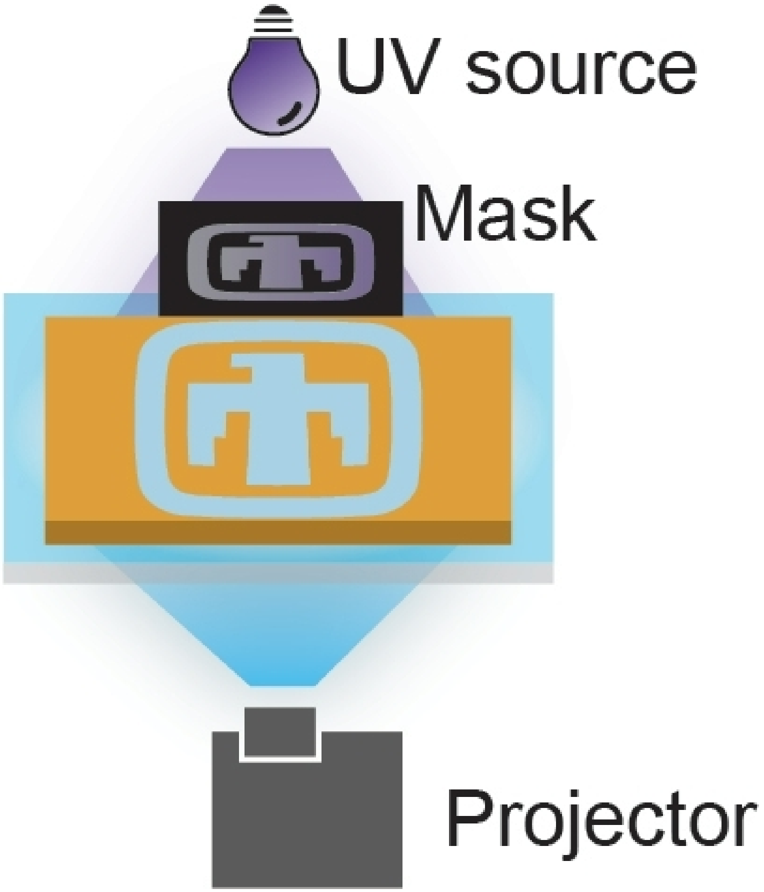
https://www.sculpteo.com/en/glossary/carbon-3d-printer-and-clip-technology/

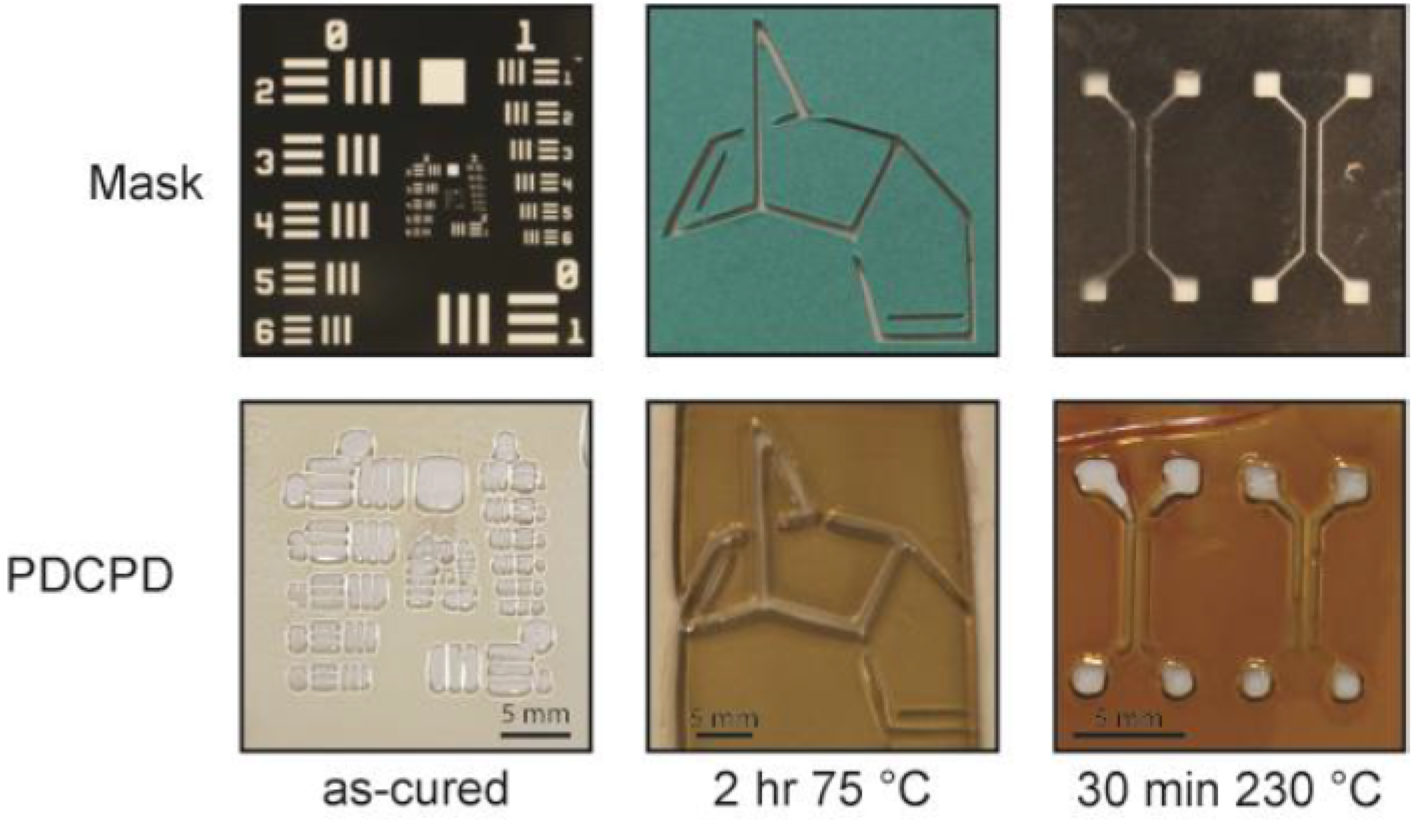
Two wavelengths –**one initiates** and **one inhibits**



J. C. Foster, A. W. Cook, N. T. Monk, B. H. Jones, L. N. Appelhans, E. M. Redline and S. C. Leguizamon, *Advanced Science*, 2022, **9**, 2200770.

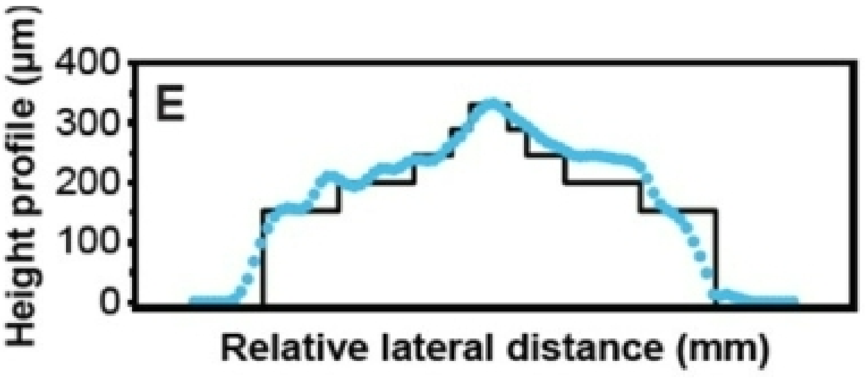
SWOMP

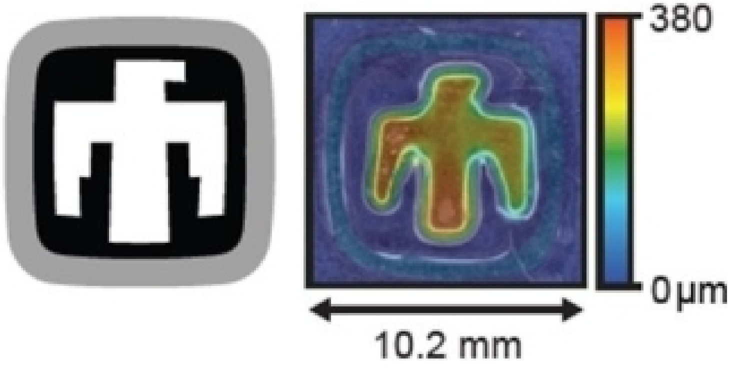

UV source
Mask
Projector


Mask
PDCPD
5 mm
5 mm
5 mm
as-cured
2 hr 75 °C
30 min 230 °C

SWOMP

Single exposure designed topography

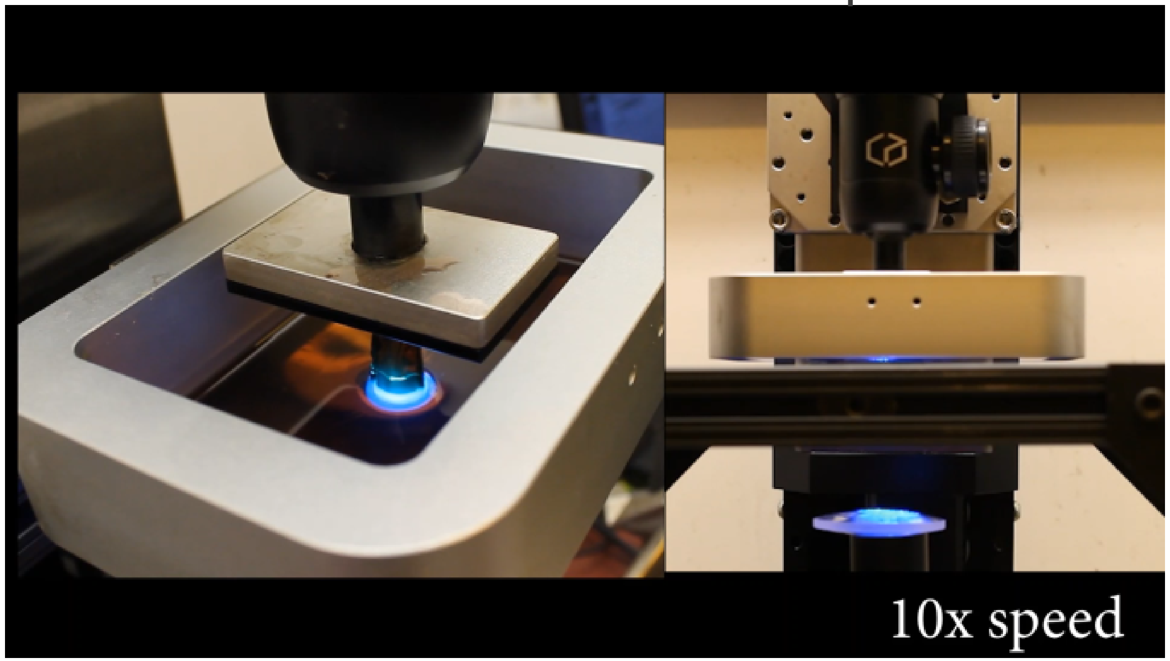




Continuous SLA printing: printed using a custom-built dual-wavelength printer

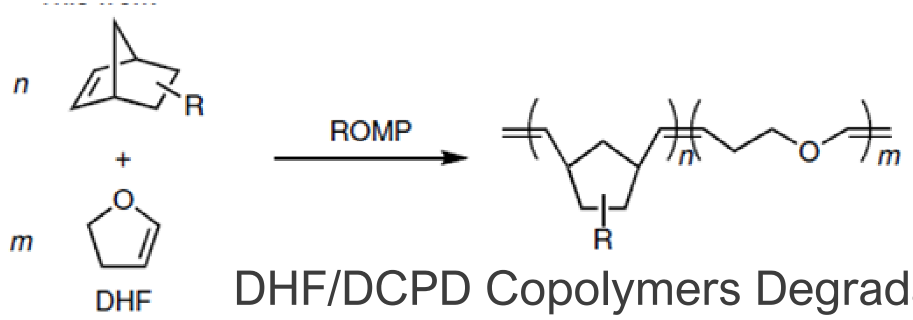
Thunderbird printed at 36 mm/h z-speed

Printed at 180 mm/h z-speed

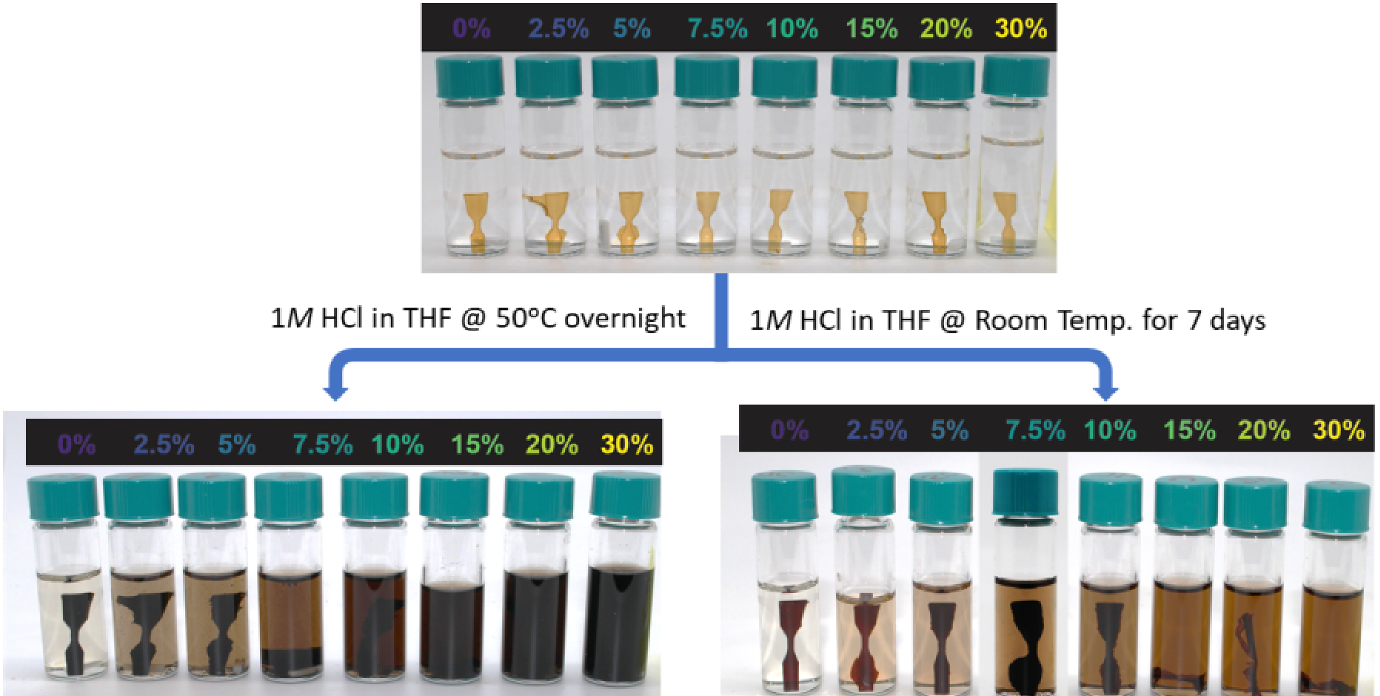


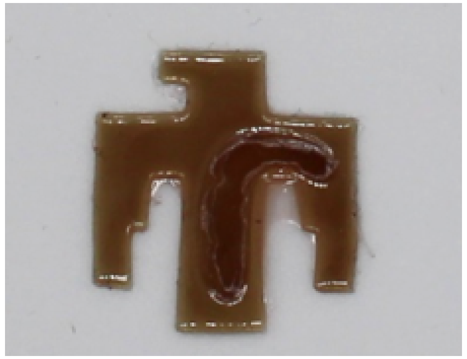
Depolymerizable pDCPD - Sustainability Thrust

Yan Xia, et al.; Nature Chemistry (14) 53–58 (2022)

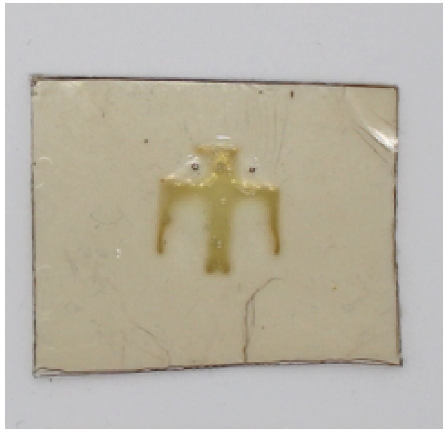


DHF/DCPD Copolymers Degradation





Step 1
Photopattern a thunderbird from DHF/DCPD (15/85 mol/mol)



Step 2
Photopolymerize a film of pDCPD (no DHF) around thunderbird

Step 3
Etch away thunderbird in 1*M* HCl in THF @ 50°C for 10 minutes

Acknowledgements

Thanks to:

Jeffrey Foster

Leah Appelhans

Brad Jones

Adam Cook

Nick Monk

Liz Zapien

Dept. 1853

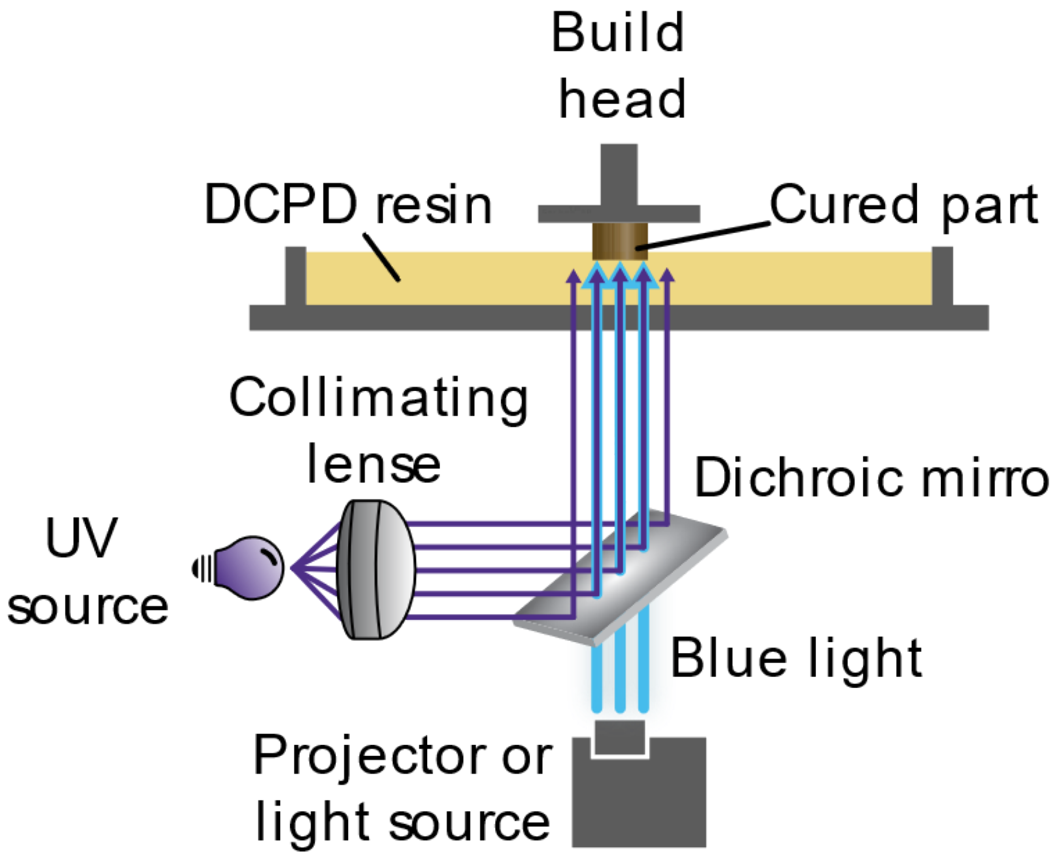
$$$ NNSA NA – 115 Additive Manufacturing Development Program

ExEx LDRD Project # 224701

Leguizamon, S. C.; Cook, A. W.; Appelhans, L. N. *Chemistry of Materials* **2021,** *33* (24), 9677-9689.

Foster, J. C.; Cook, A. W.; Monk, N. T.; Jones, B. H.; Appelhans, L. N.; Redline, E. M.; Leguizamon, S. C., *Advanced Science* **2022,** *9* (14), 2200770.

SWOMP: Selective Wavelength Olefin Metathesis Polymerization



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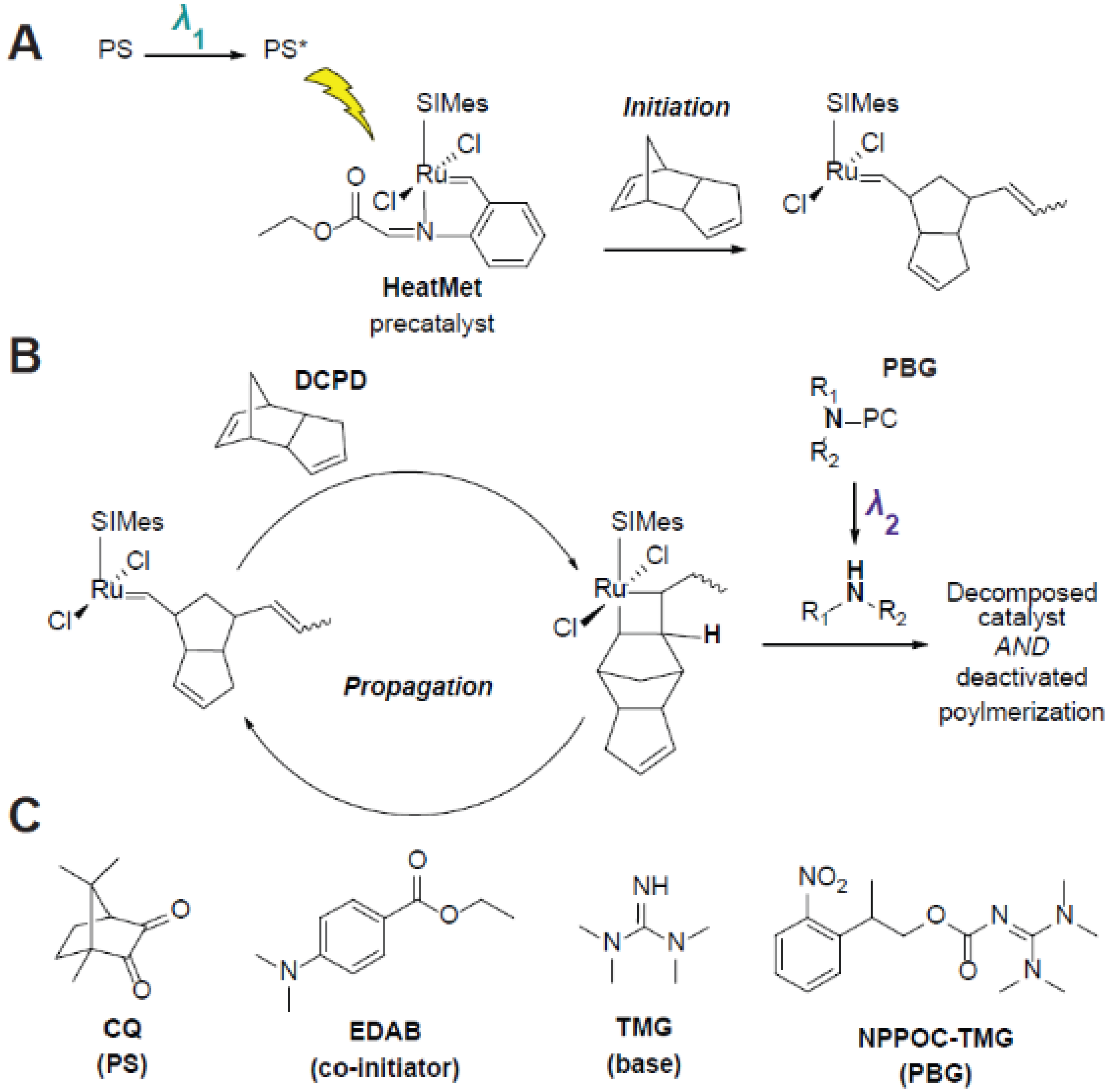
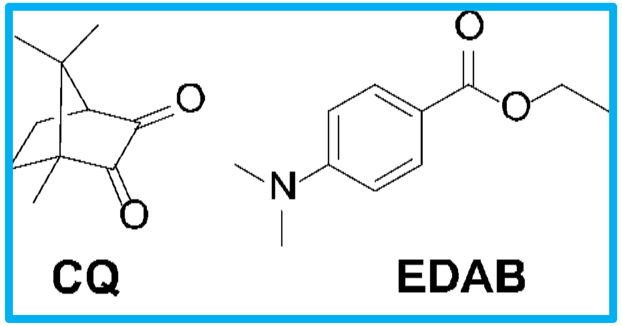
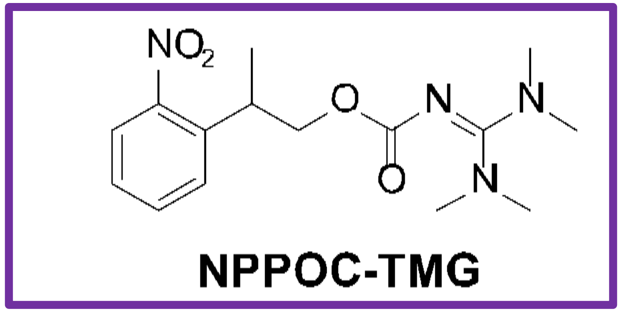
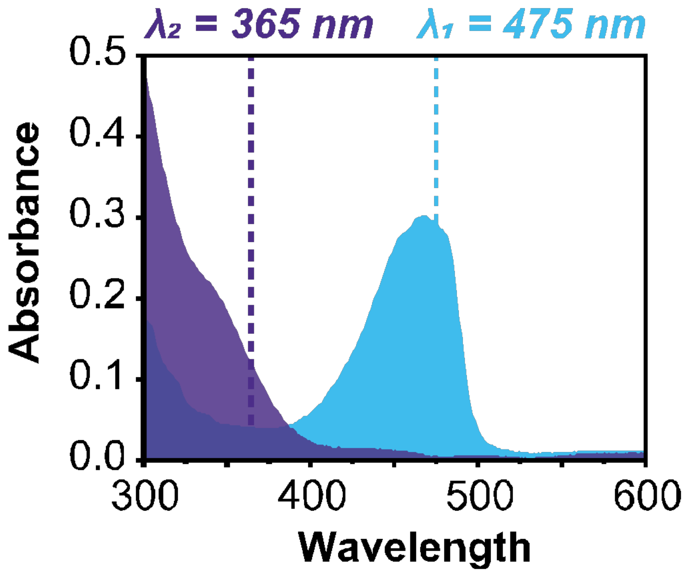
Two wavelengths –one initiates and one inhibits

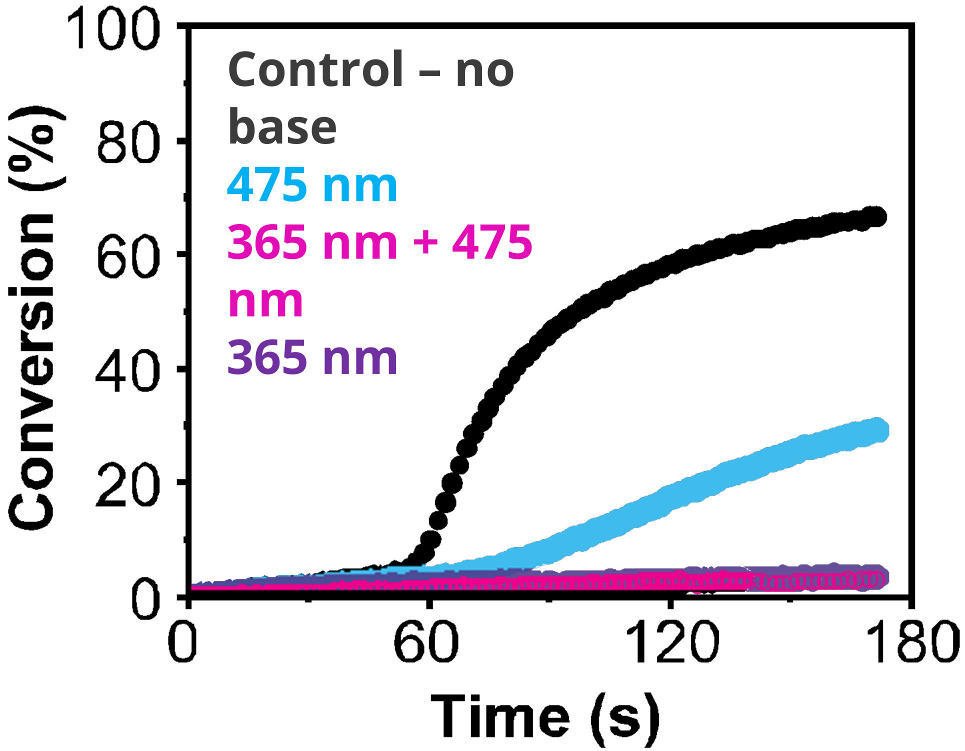


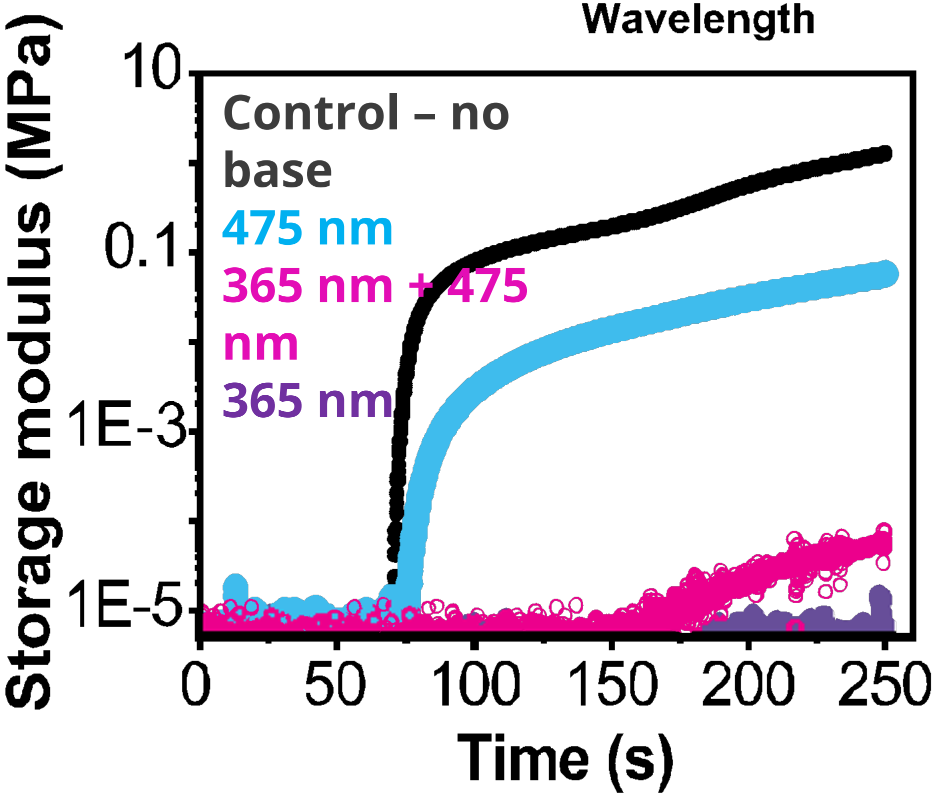
SWOMP


CQ
EDAB


NPPOC-TMG

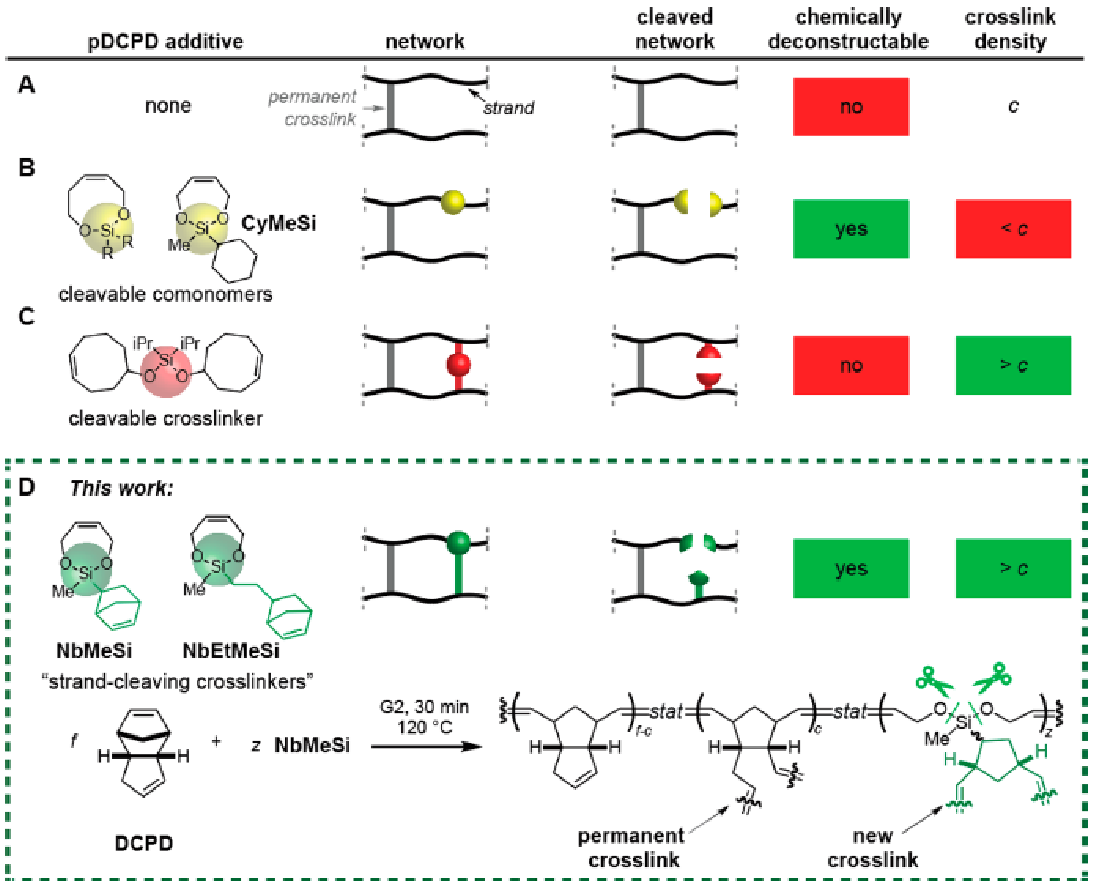

λ₂ = 365 nm
λ₁ = 475 nm
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
300
400
500
600
Wavelength


Conversion (%)
0
20
40
60
80
100
0
60
120
180
Time (s)
Control – no base
475 nm
365 nm + 475 nm
365 nm


Storage modulus (MPa)
10
0.1
1E-3
1E-5
0
50
100
150
200
250
Time (s)
Control – no base
475 nm
365 nm + 475 nm
365 nm

Depolymerizable pDCPD - MSRF Sustainability Thrust

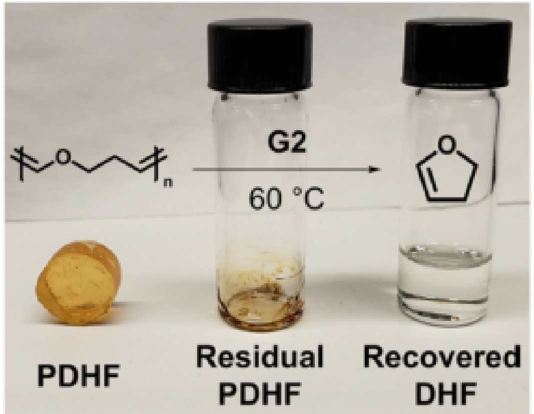
Jeremiah Johnson Group (MIT):



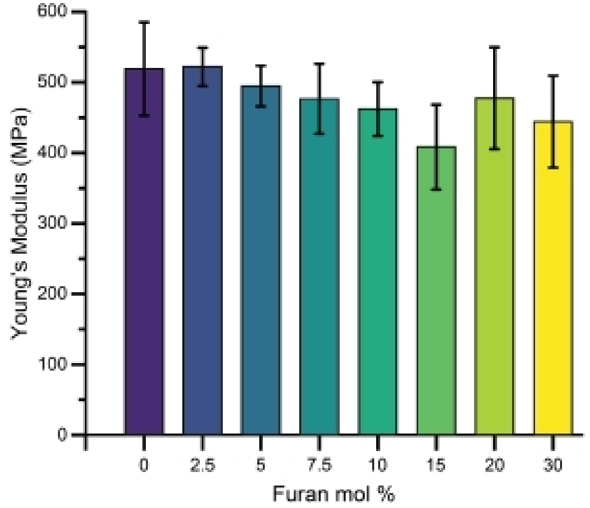
J. A. Johnson, et al.; *ACS Macro Lett*. 2021, 10, 805-810

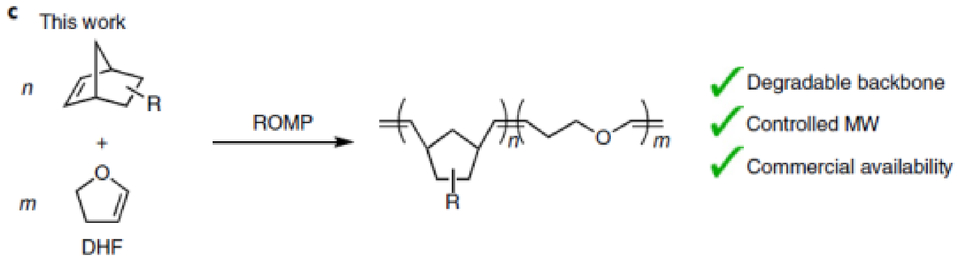
- Requires synthesis of monomers
- Poor monomer shelf life
- Facile degradation in TBAF
- pDCPD double bonds still active for recycling/upcycling

Yan Xia Group (Stanford):



Yan Xia, et al.; *J. Am. Chem. Soc.* 2020, 142, 3, 1186 –1189





Yan Xia, et al.; Nature Chemistry (14) 53–58 (2022)

- DHF (dihydrofuran) is commercially available
- Stable monomer
- Facile degradation in acid
- pDCPD double bonds still active for recycling/upcycling