



*Exceptional service in the national interest*

# ADDITIVE MANUFACTURING OF DECONSTRUCTABLE, RECYCLABLE, PDCPD THERMOSETS VIA PHOTOROMP

*Towards Sustainable, Generation-Invariant Additive  
Manufacturing of High Performance Thermosets*

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*Albuquerque, NM, USA*

Thursday, December 5, 2024

Printing and Sustainability

2024 MRS Fall Meeting and Exhibit, Boston, MA, USA



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# SUSTAINABILITY IN ADDITIVE MANUFACTURING

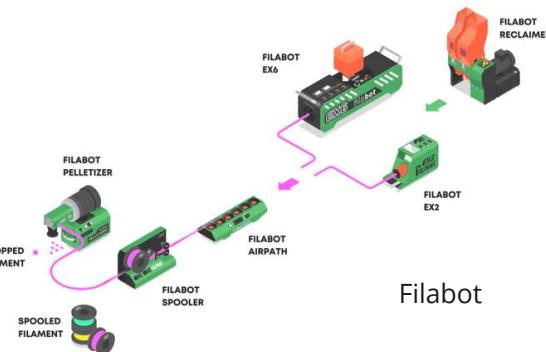
- Plastic pollution is an ongoing global challenge
- Need sustainability in polymer manufacturing
- Also true for additive manufacturing
- Thermoplastics can be reprocessed
- Thermosets, by nature, are difficult to recycle

**Need sustainable additive manufacturing of thermosets**



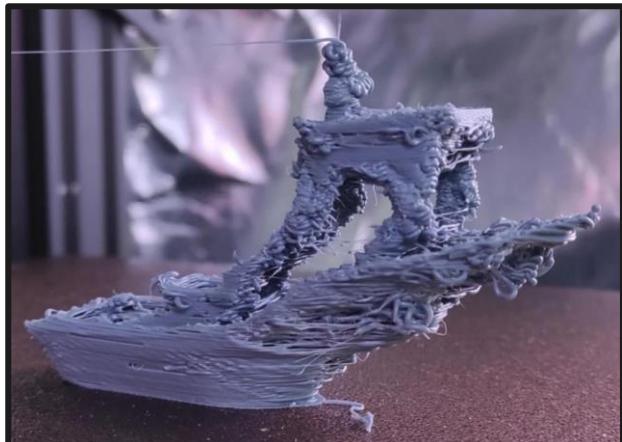
Printerior

**FDM filament recycling**

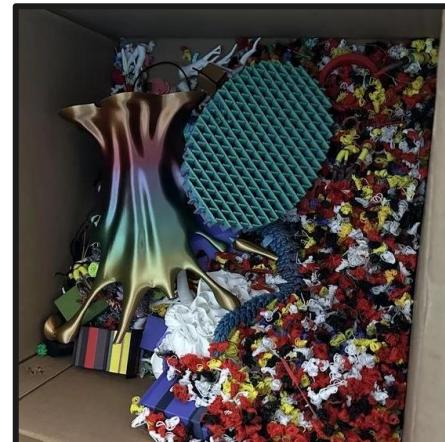


Filabot

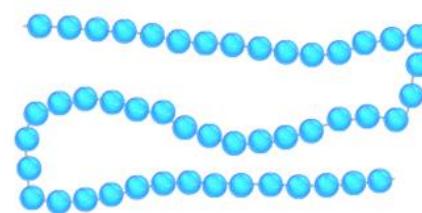
**Failed prints**



**Supports and other waste**



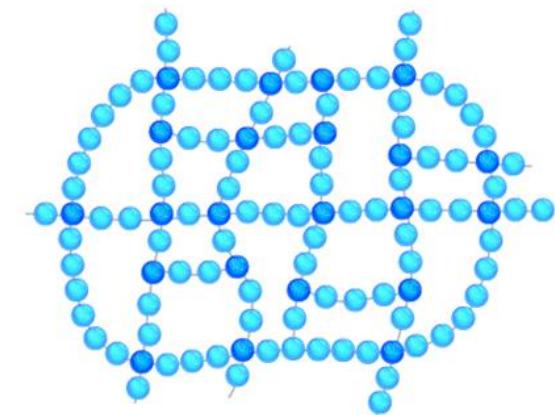
3Dprinting community, Reddit



**THERMOPLASTICS**

HP Maufacturing

**VS.**



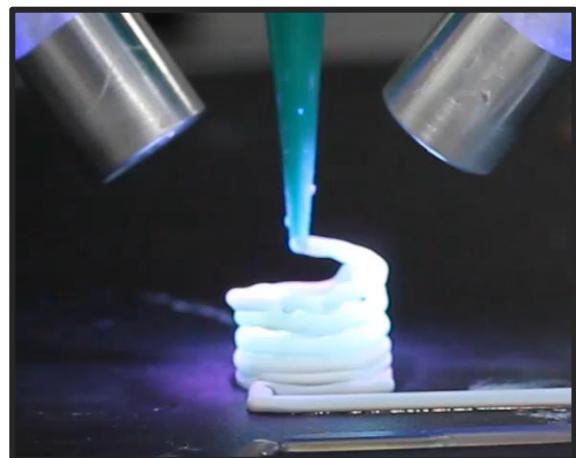
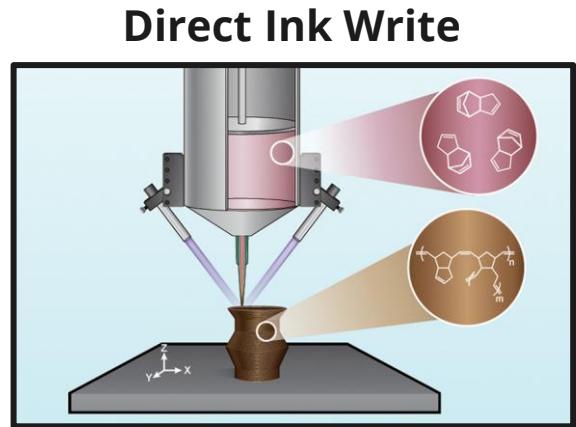
**THERMOSETS**

# ADDITIVE MANUFACTURING VIA PHOTOROMP

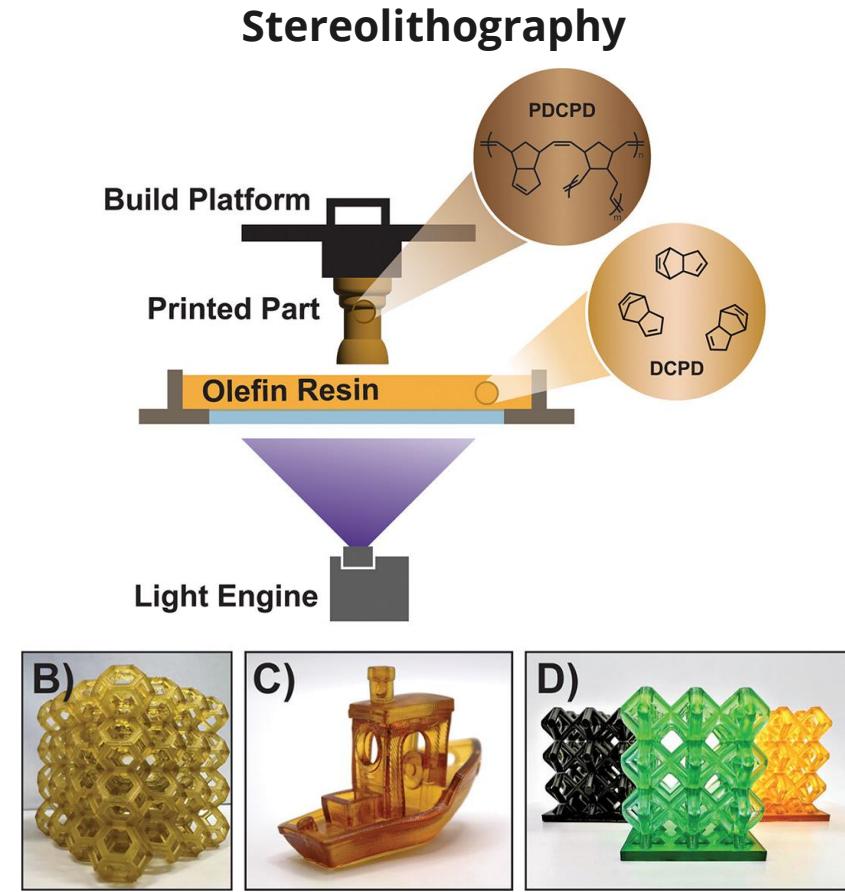
**photoROMP:** photoinitiated Ring-Opening Metathesis Polymerization

Photosensitizers make many Ru catalysts accessible

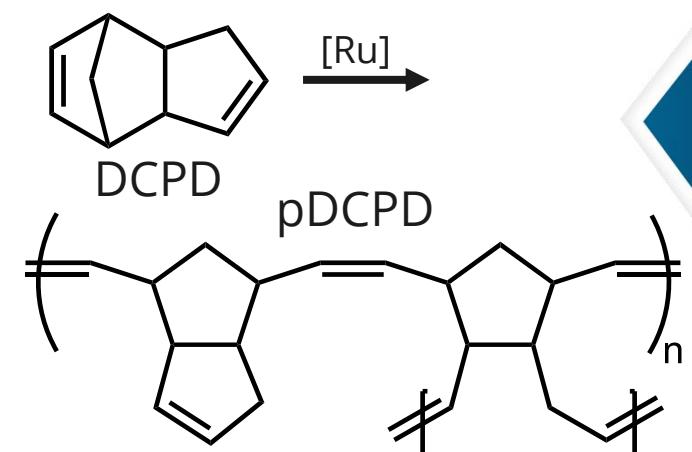
Additive manufacturing with **pDCPD:** poly(DiCycloPentaDiene)



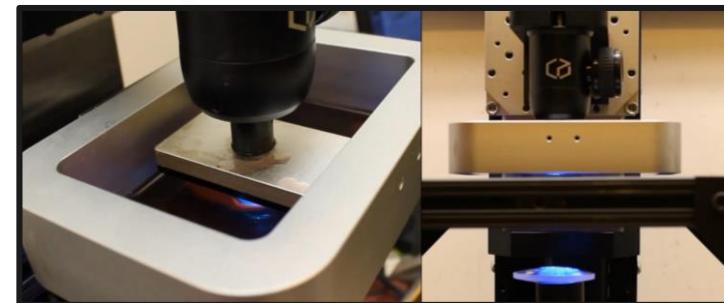
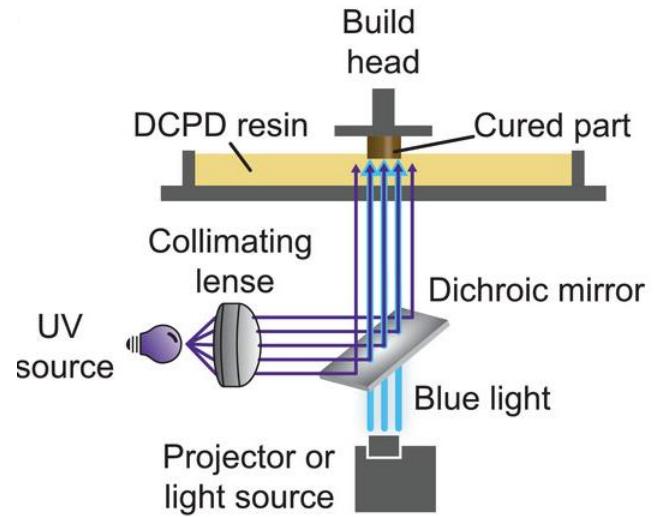
S. C. Leguizamon et al, *Chemistry of Materials*, 2021, 33.



A. J. Greenlee et al, *ACS Catalysis*, 2024, 14.

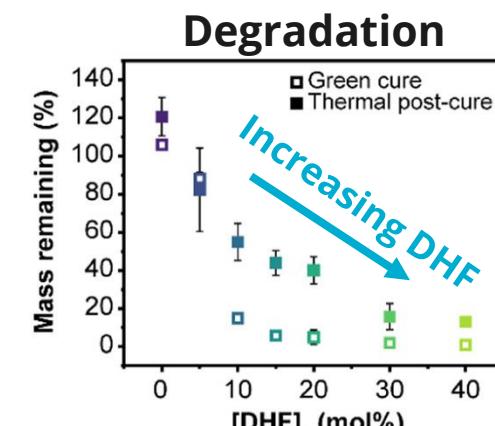
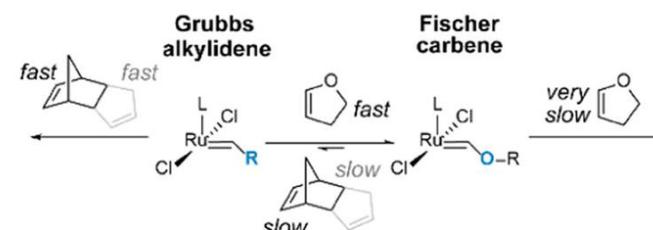
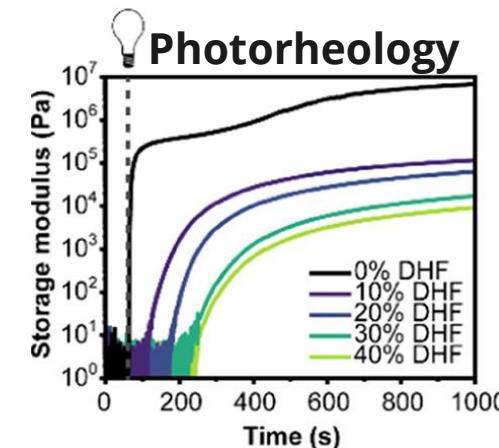
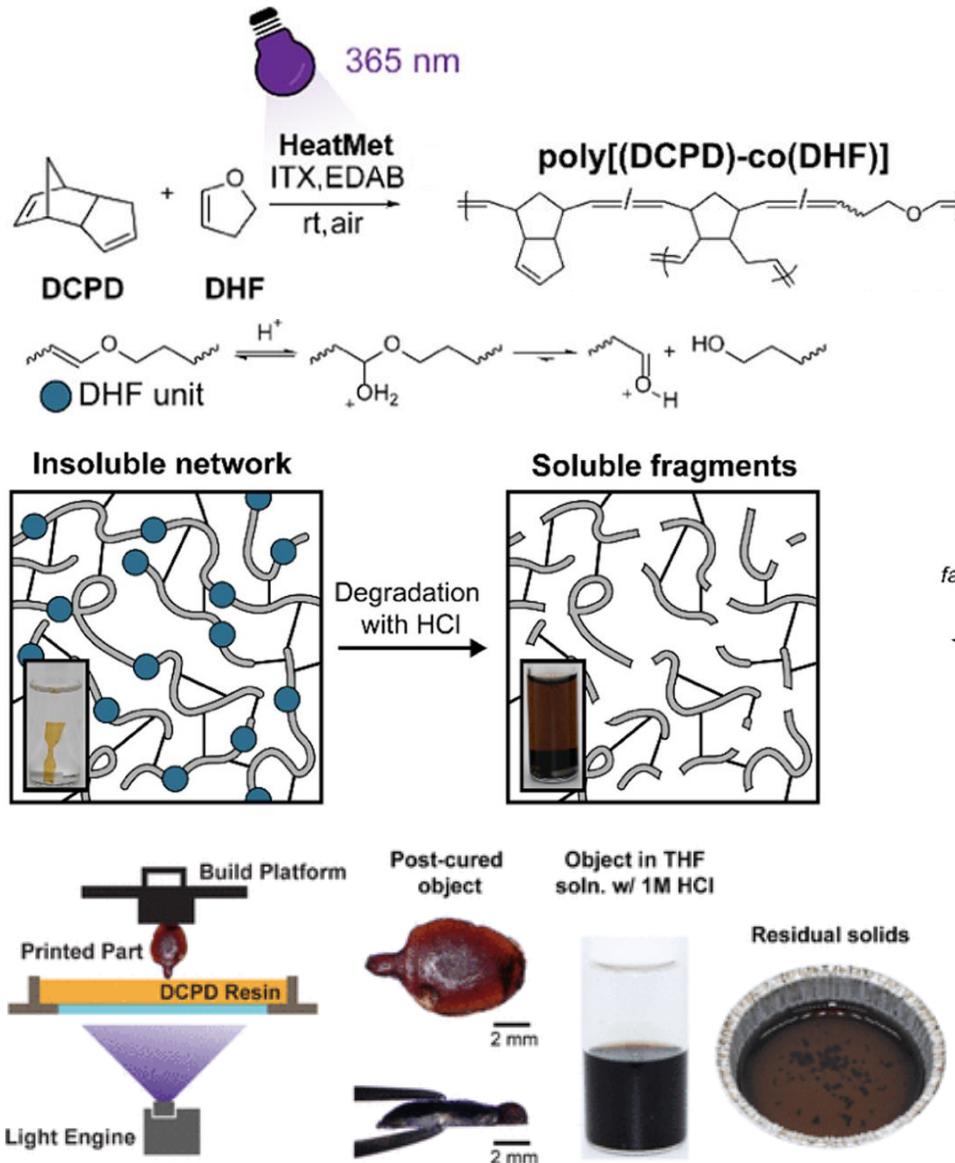


**Continuous AM via SWOMP**



J. C. Foster et al, *Advanced Science*, 2022, 9.

# DEGRADABLE PDCPD VIA PHOTOROMP

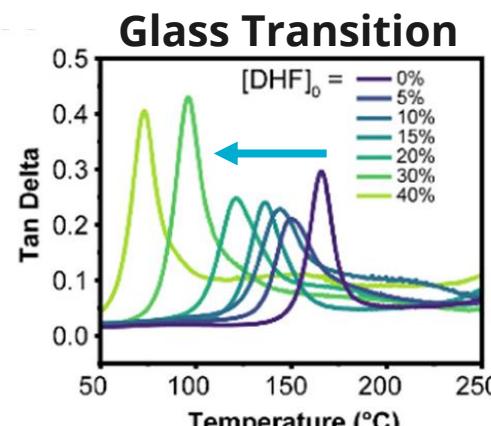


**Copolymerizing with DHF enables:**

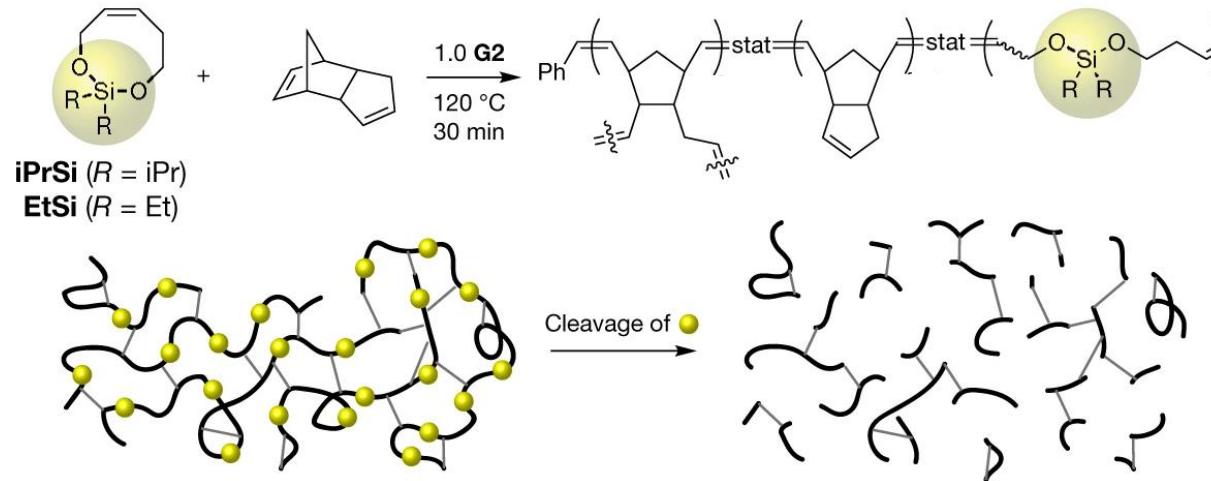
- ✓ Use of cheap, readily available comonomer
- ✓ Degradation of cleavable units

**Drawbacks of using DHF:**

- ⊖ Slow kinetics
- ⊖ Volatility - vat switching + post curing
- ⊖ High loading for better degradation



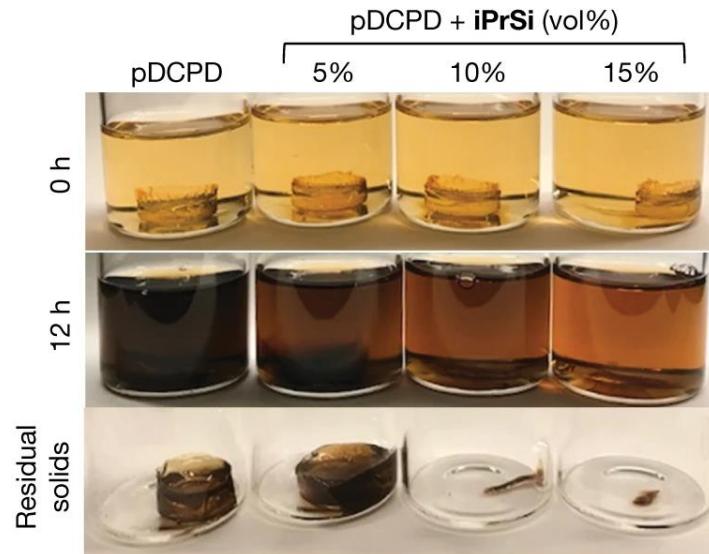
# SILYL ETHER MONOMERS FOR ROMP AND DECONSTRUCTION OF PDCPD



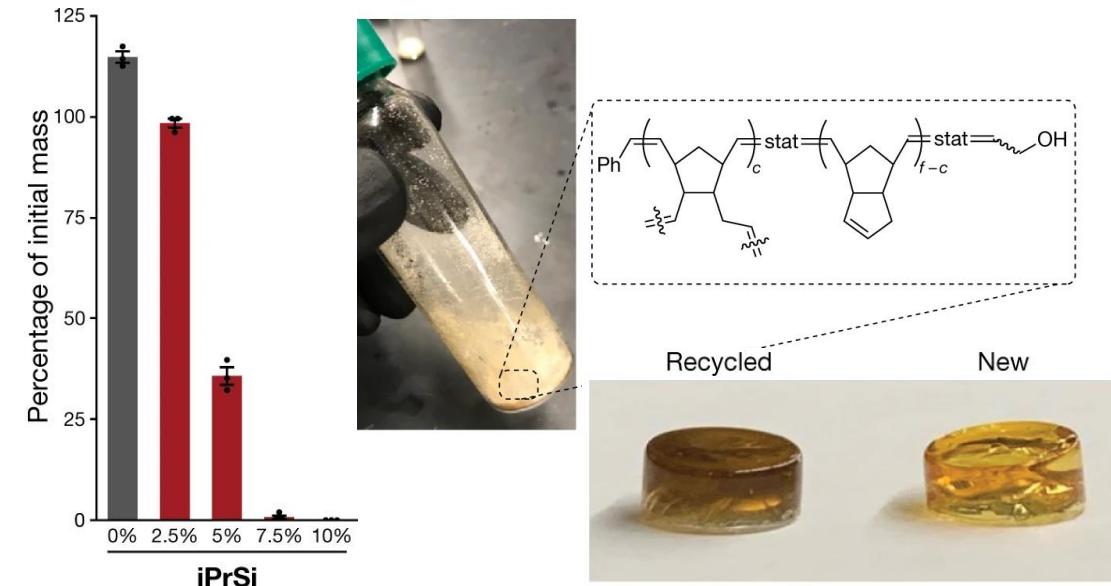
## Copolymerizing with iPrSi enables:

- ✓ Full deconstruction of thermosets
- ✓ Recovery of fragments that can undergo metathesis
- ✓ Recycling of fragments back into thermosets
- ✓ Maintenance of mechanical properties

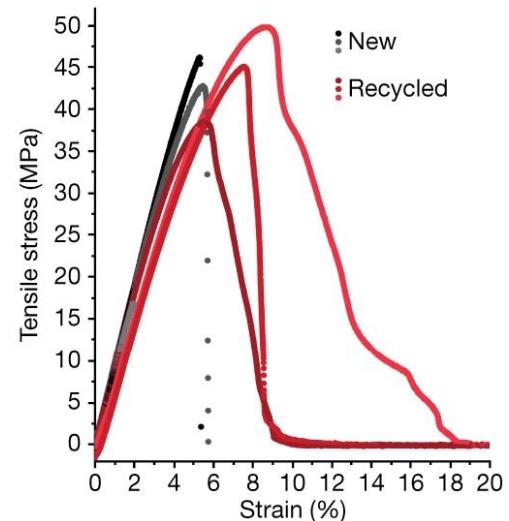
### Deconstruction



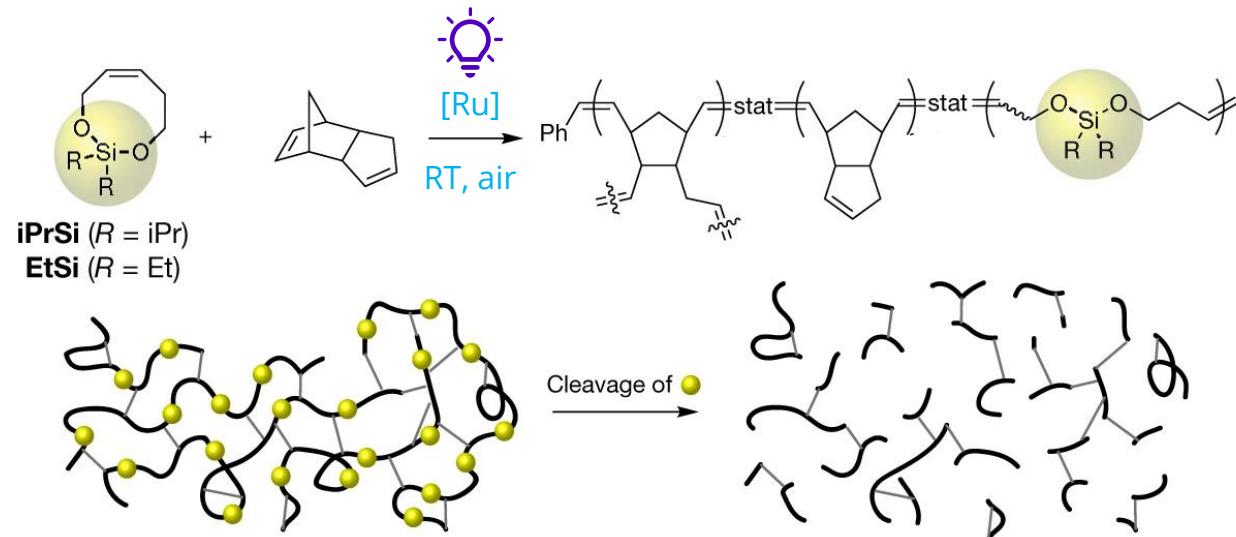
### Recyclable fragments



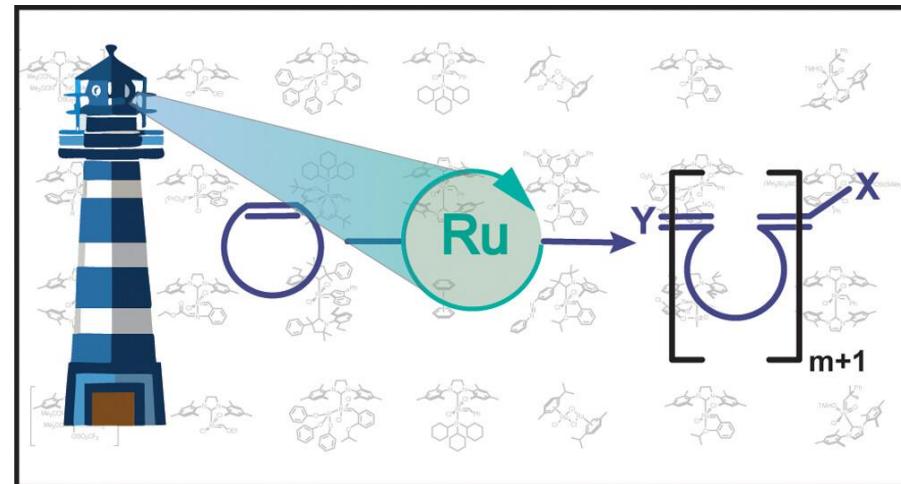
### Maintained mechanics



# EXPLORATION OF SILYL ETHER MONOMERS IN PHOTOROMP



- Amiability of Ru catalyst, photosensitizer, and coinitiator combinations to silyl ether inclusion
- Kinetics and ability to print via photoROMP
- Materials properties (mechanical, thermal)
- Deconstruction of networks
- Fragment recovery and recycling
- Ability to print over multiple generations of deconstruction



Investigate silyl ether monomers for photoROMP



Characterize materials properties

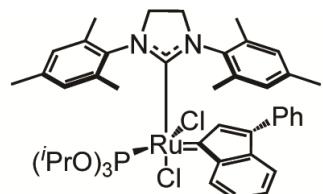


Deconstruct materials and recycle fragments



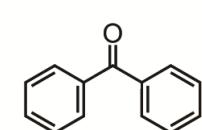
Print materials over multiple regenerations

# PHOTOROMP KINETICS AND PRINTING WITH SILYL ETHERS



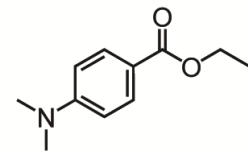
M220

0.04 mol%



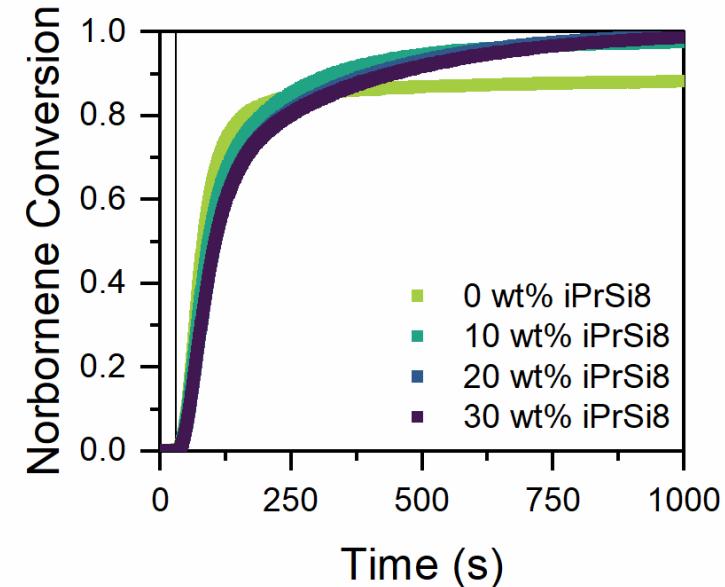
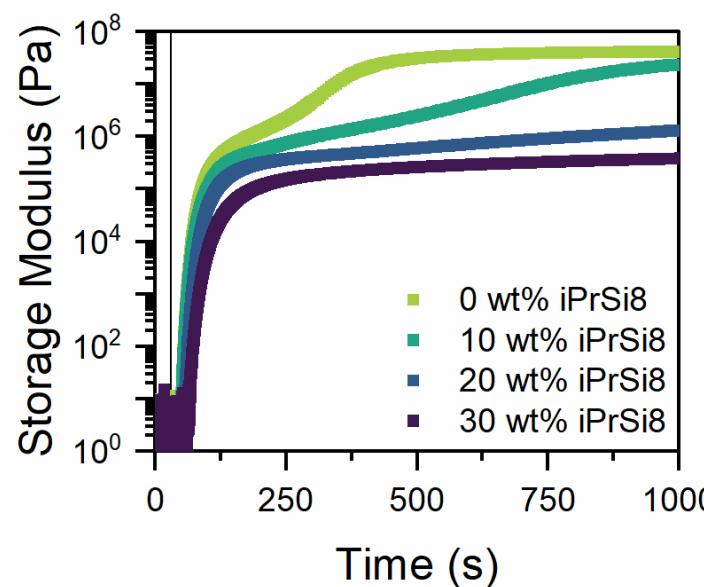
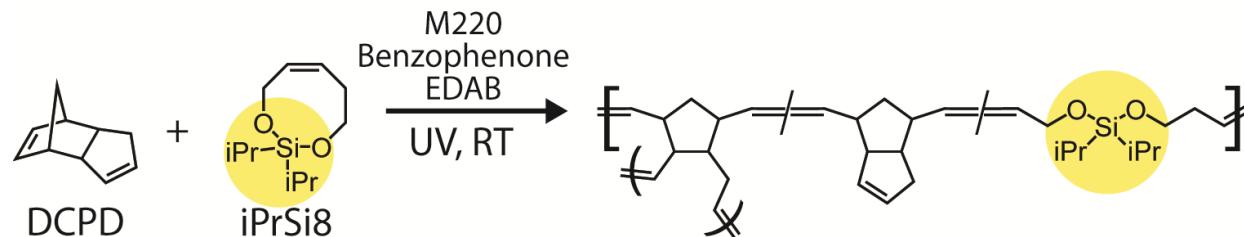
Benzophenone

4:1 wt:wt M220



EDAB

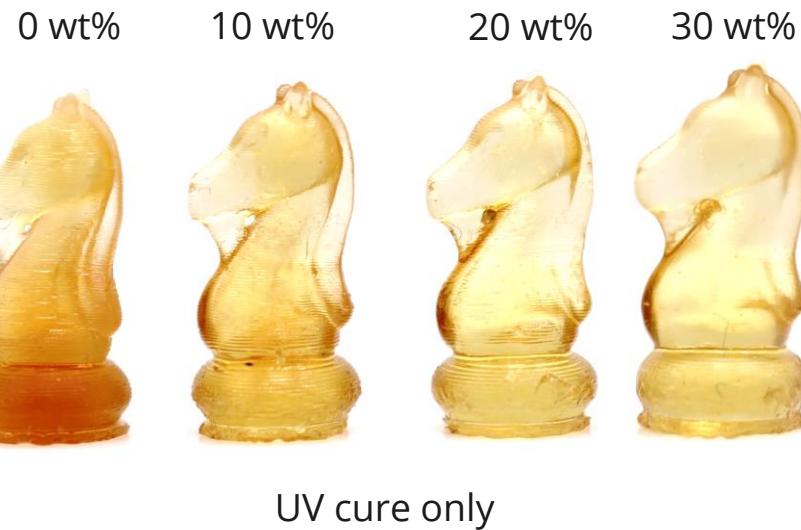
8:1 wt:wt M220



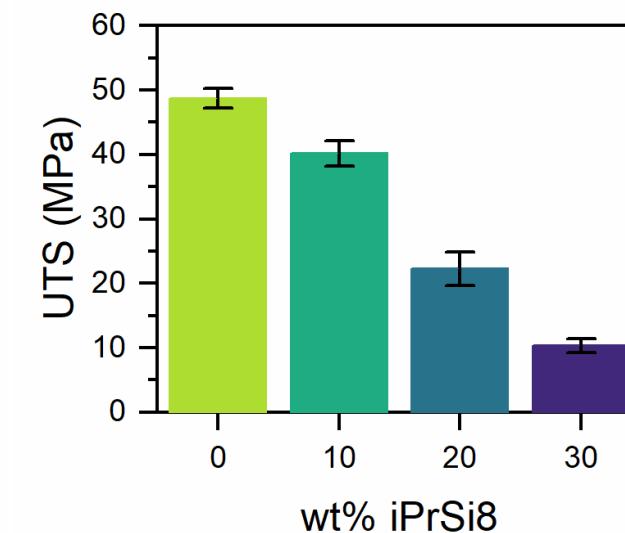
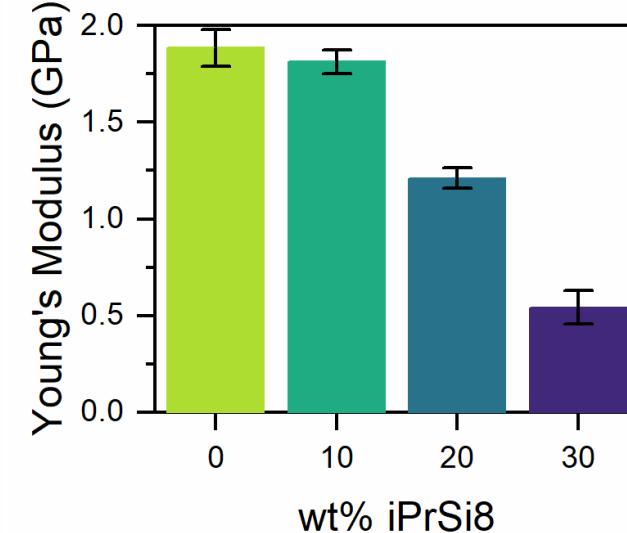
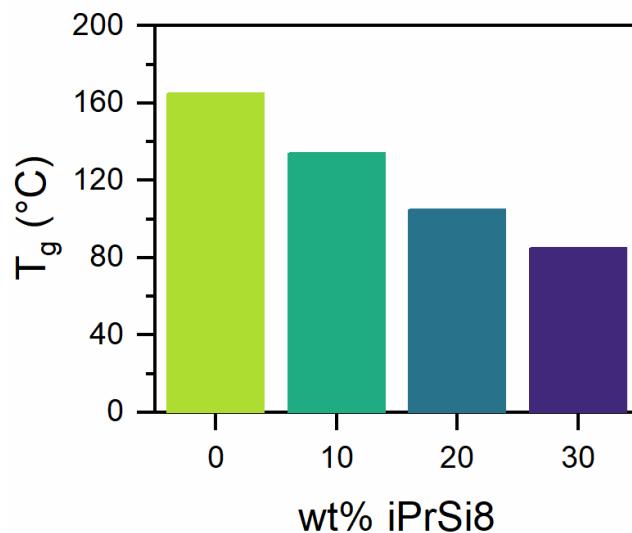
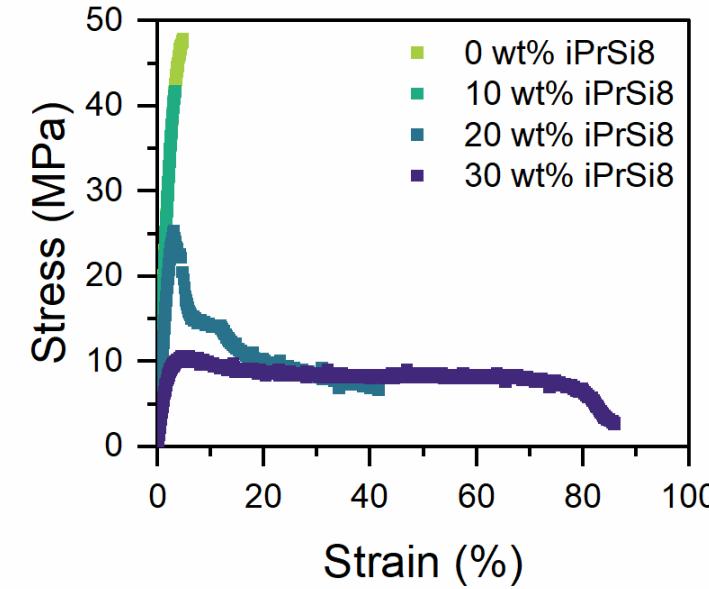
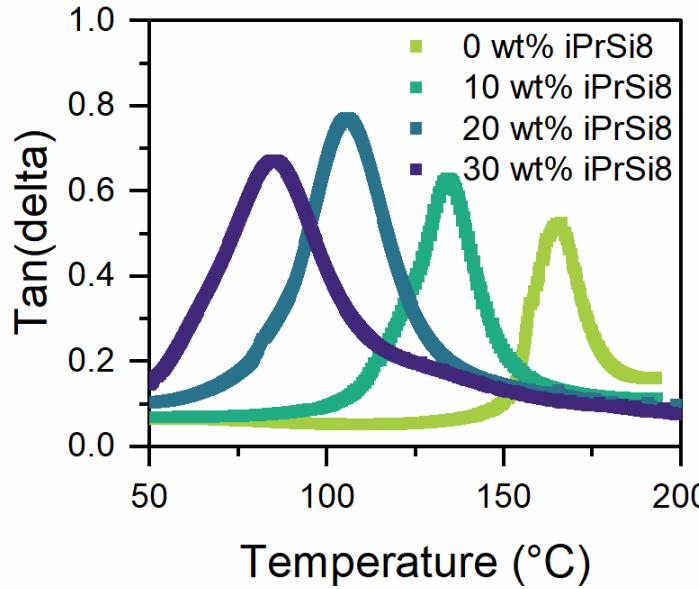
iPrSi8 comonomer enables:

- ✓ Fast kinetics
- ✓ Printing with VPP
- ✓ Relatively stable resin

## iPrSi Loading



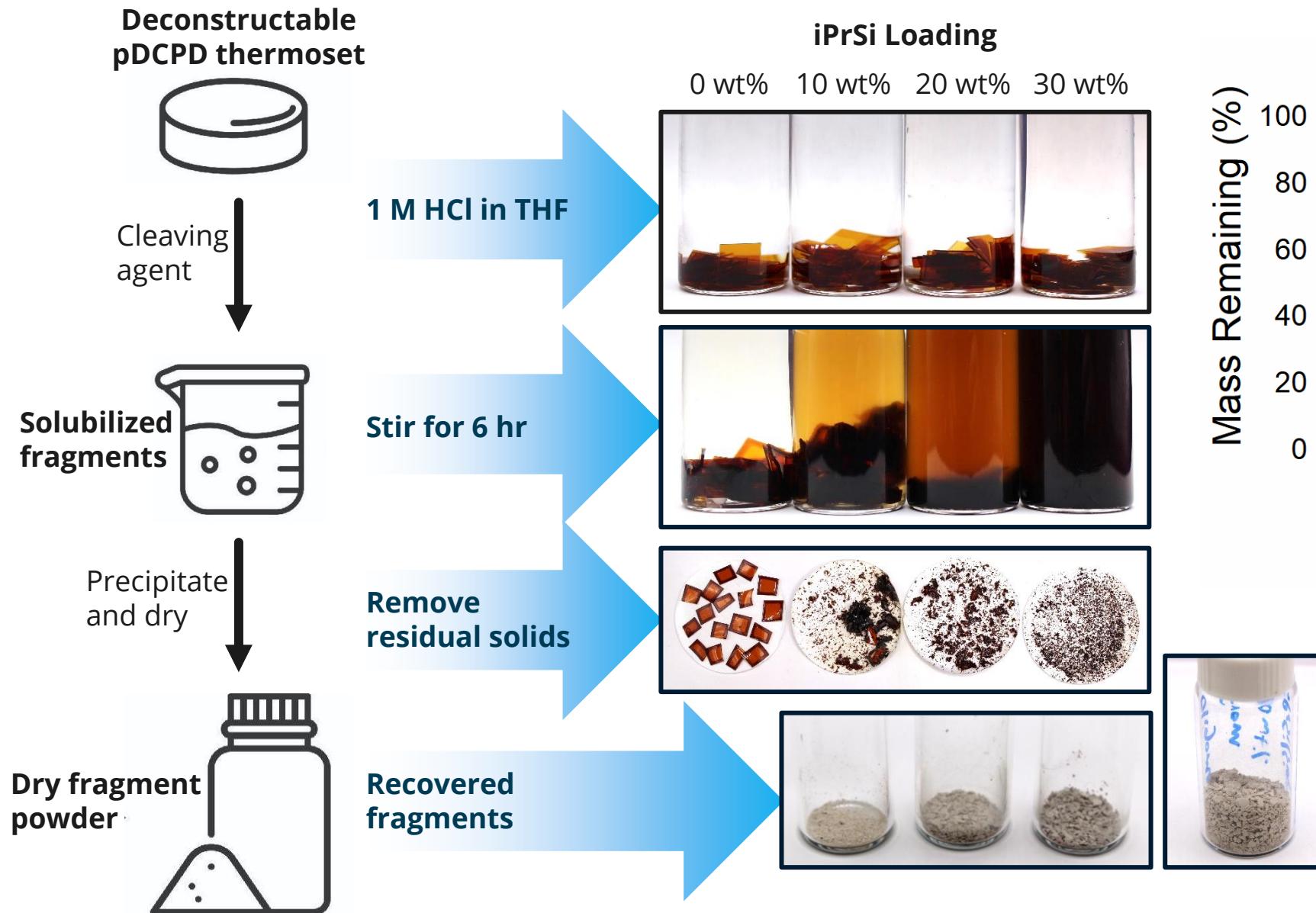
# MATERIALS PROPERTIES WITH SILYL ETHER INCLUSION



**As iPrSi8 loading increases...**

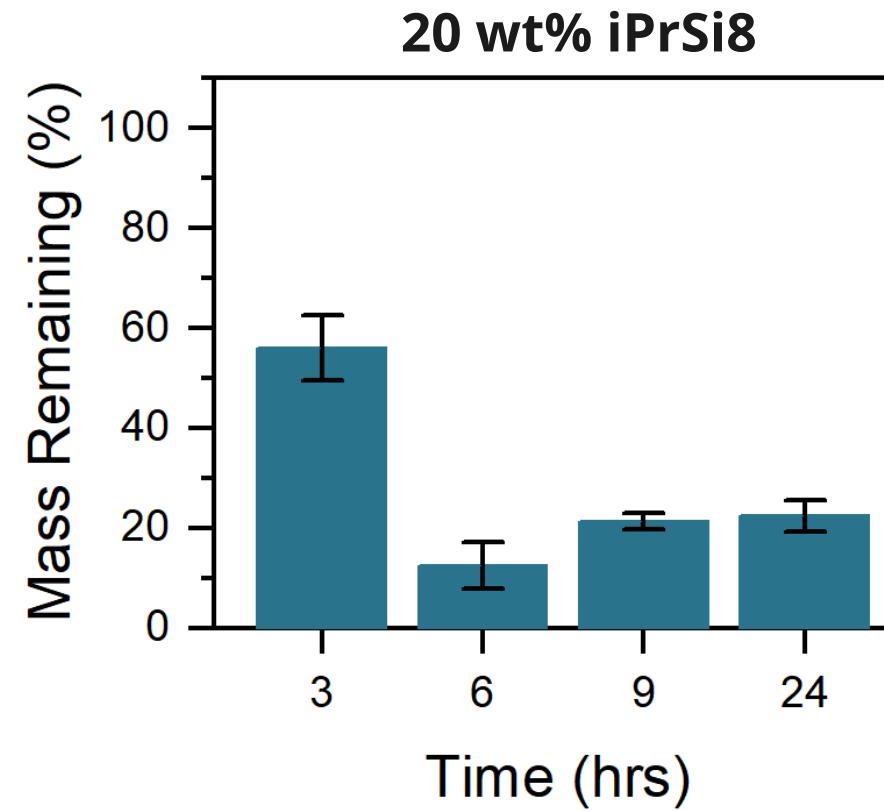
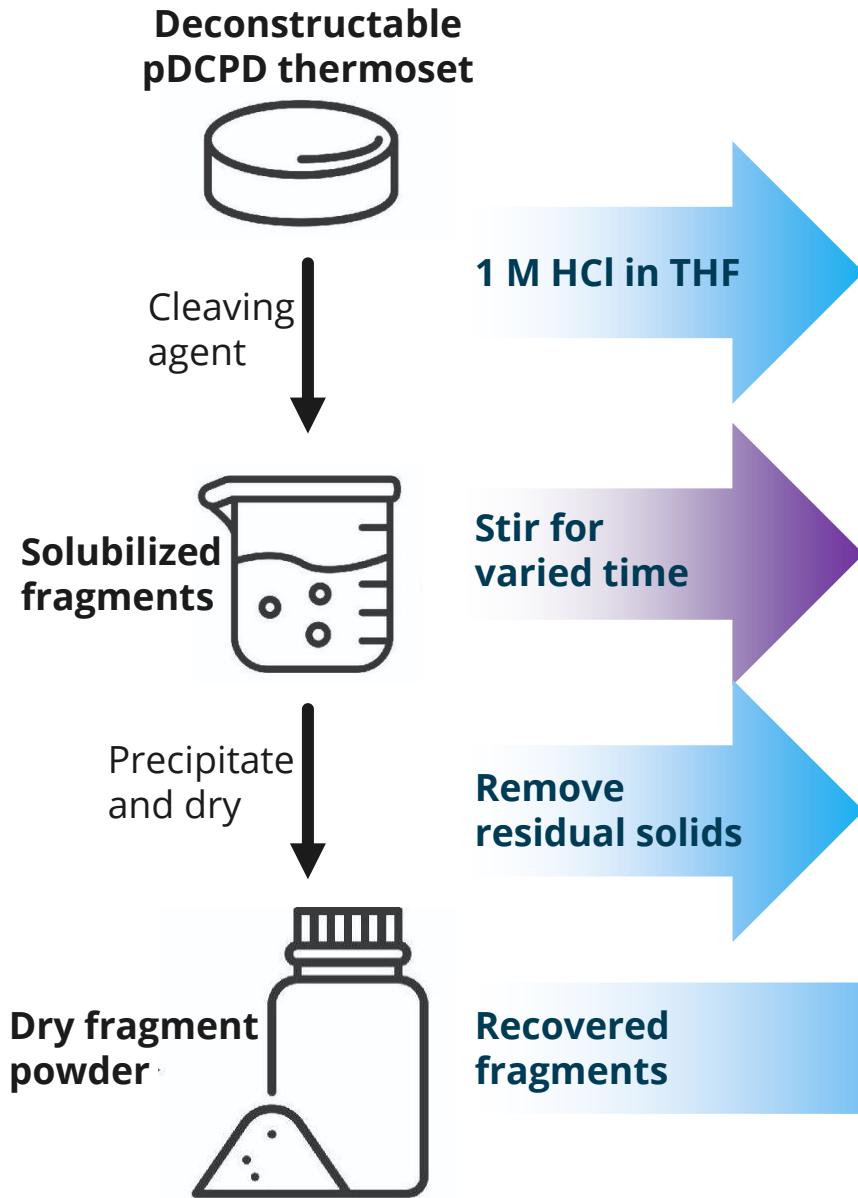
- Glass transition decreases
- Young's modulus decreases
- Tensile strength decreases

# DECONSTRUCTION OF THERMOSETS WITH SILYL ETHER



- Do not see full deconstruction of networks
- Increasing iPrSi8 beyond 20 wt% does not benefit degree of deconstruction

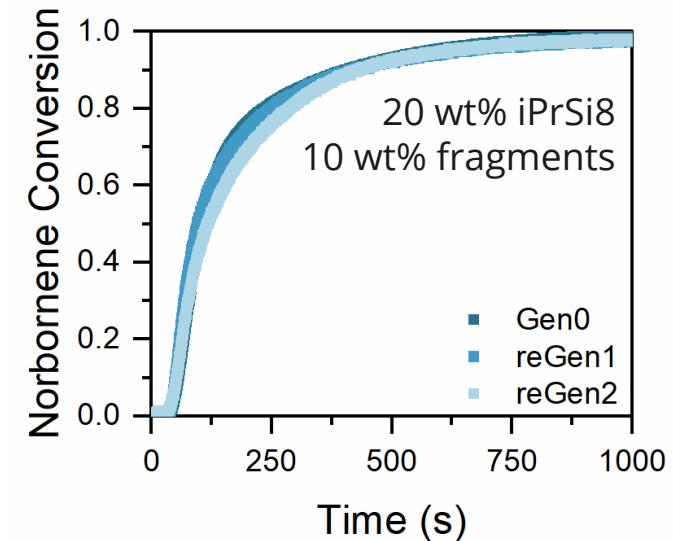
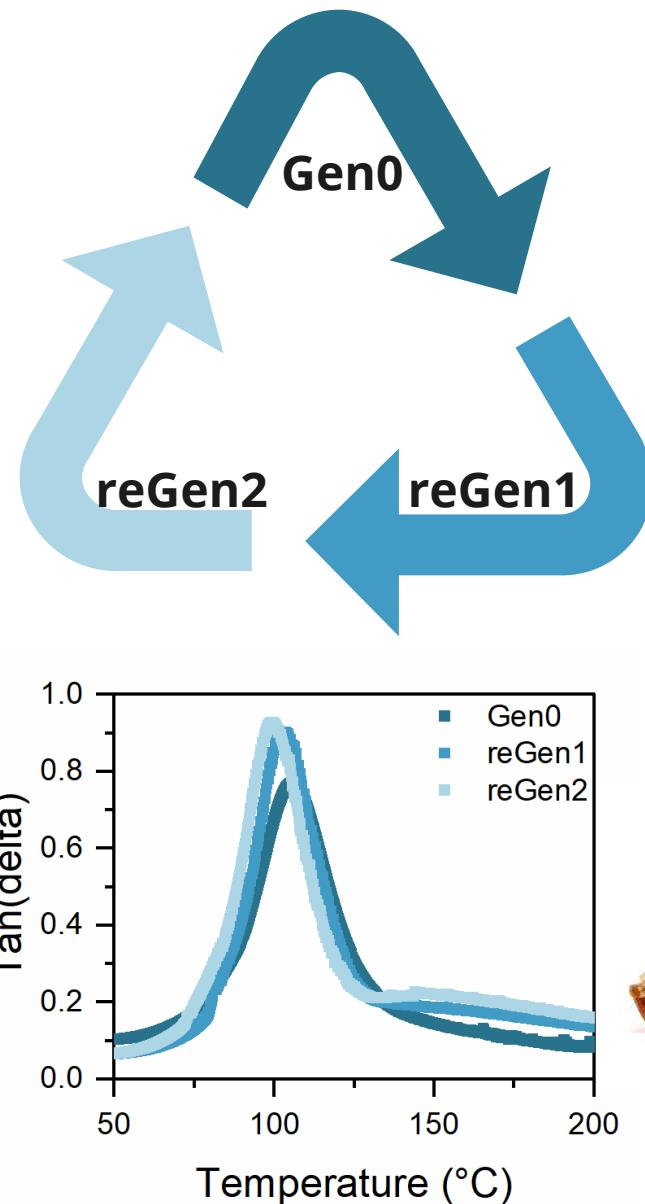
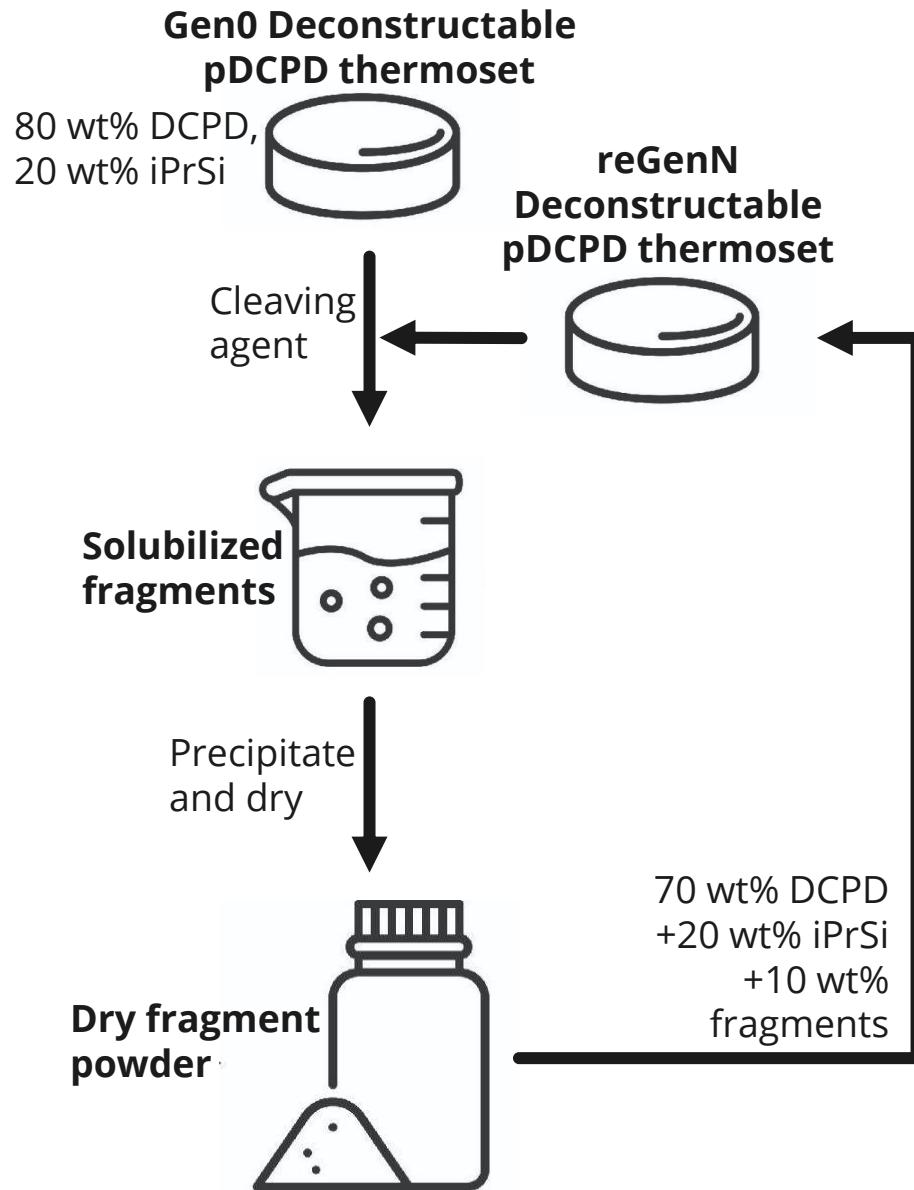
# DECONSTRUCTION OF THERMOSETS WITH SILYL ETHER



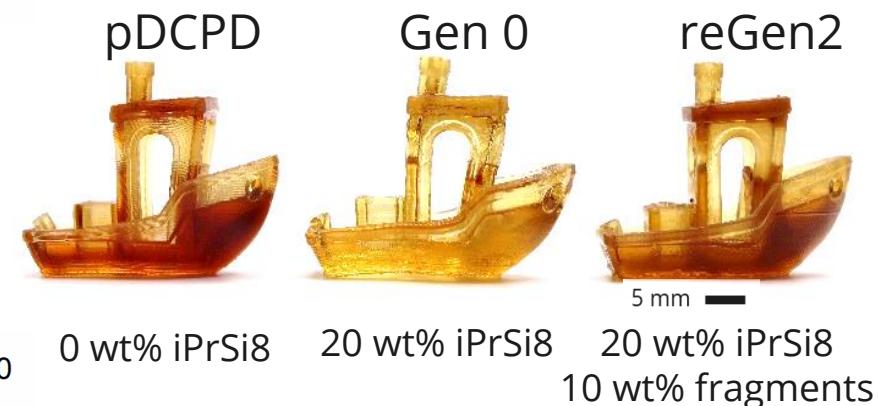
...but does the deconstruction time matter?

- Longer time does not benefit degree of deconstruction
- See slight increase in residual solid mass
- Visually appears to be a result of oxidation

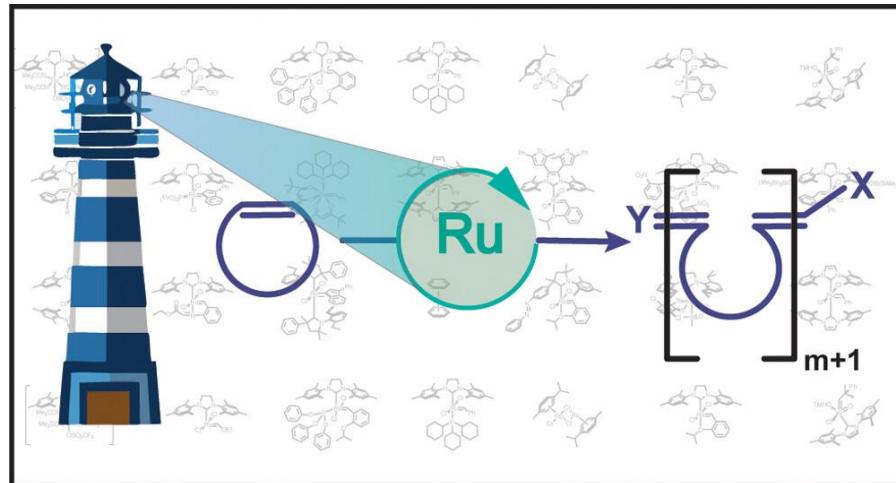
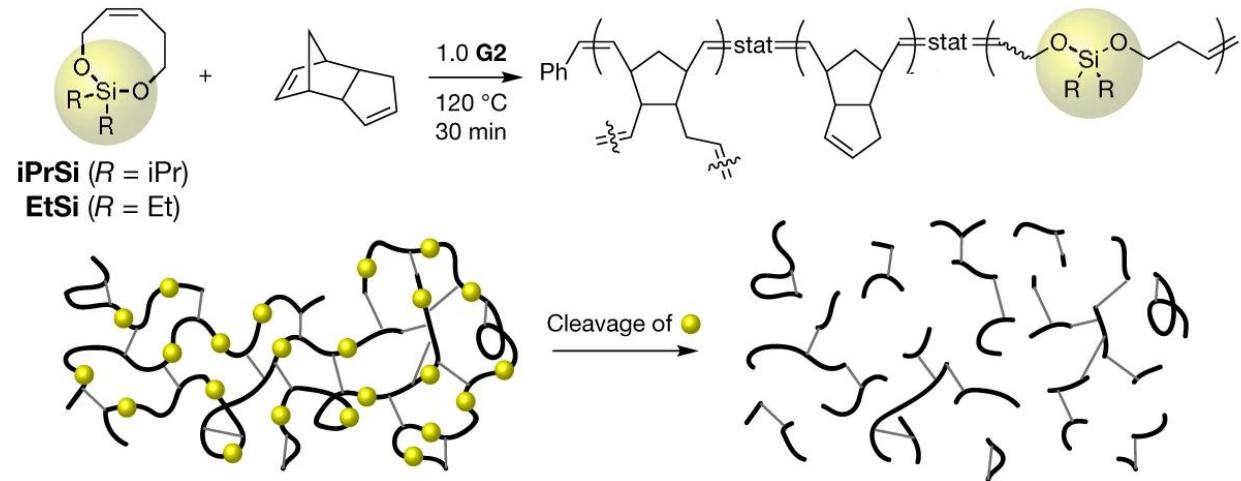
# REGENERATION AND PRINTING WITH RECOVERED FRAGMENTS



**Multigenerational recycling of deconstructed materials**



# CONCLUSIONS



Investigate silyl ether monomers for photoROMP



Characterize materials properties



Deconstruct materials and recycle fragments



Print materials over multiple regenerations



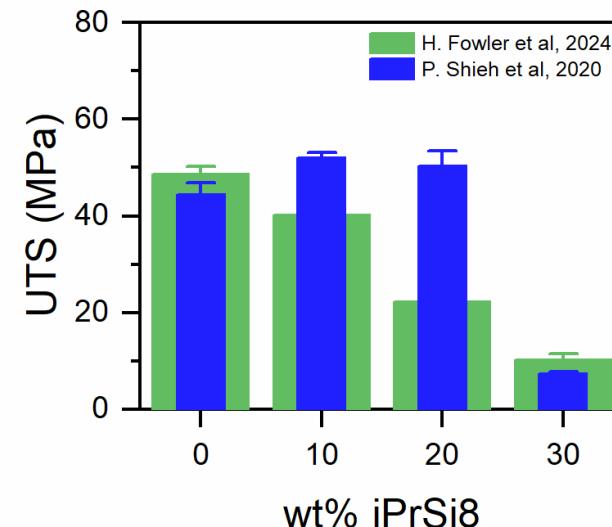
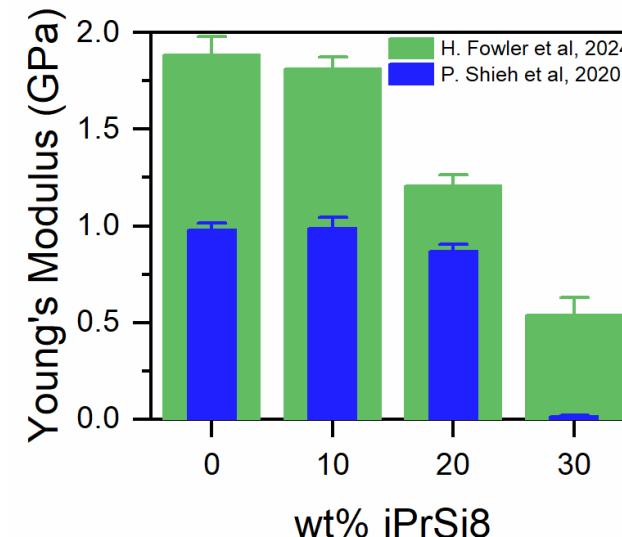
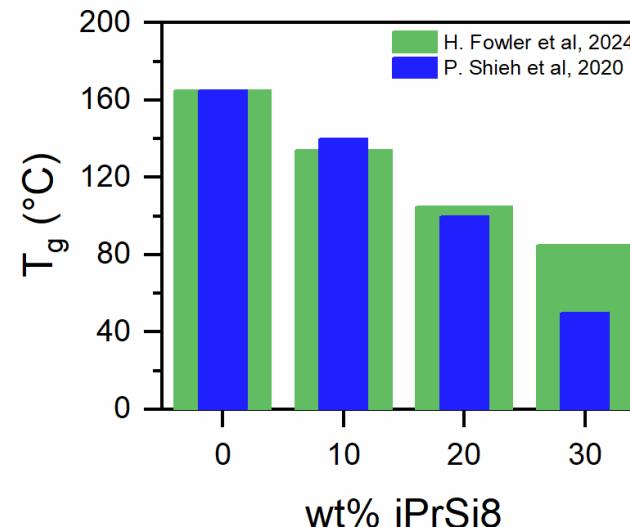
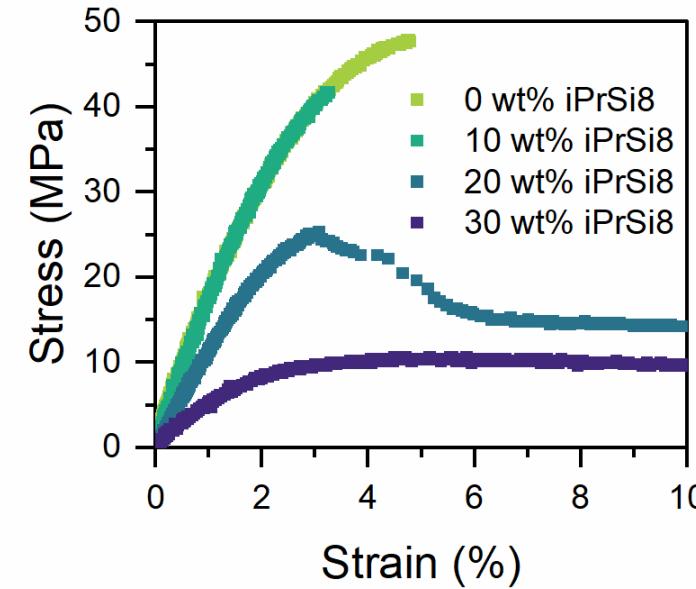
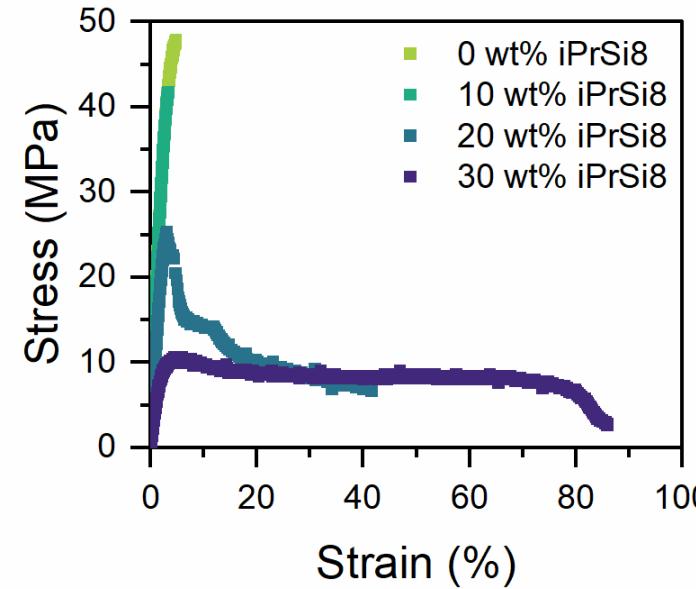
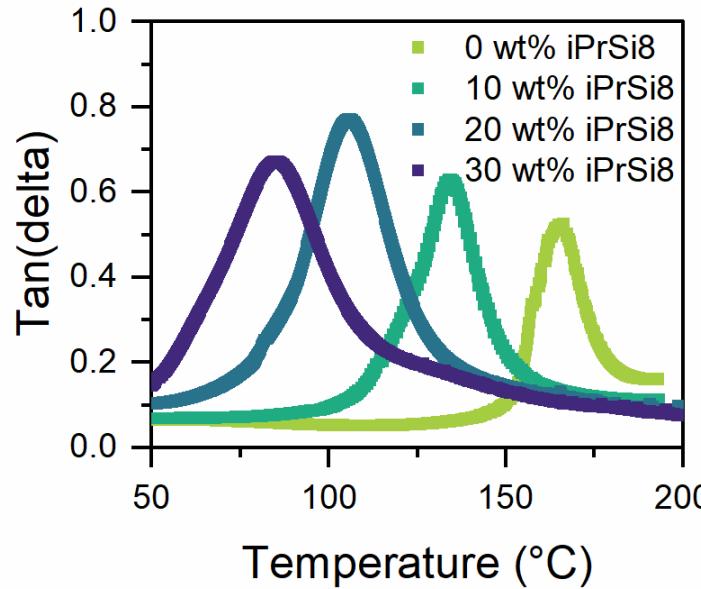
## Key takeaways

- Fast kinetics enable printing
- Easy deconstruction + fragment recovery
- Fragments can be recycled for multiple generations of printing



# SUPPLEMENTARY SLIDES

# COMPARISON OF PROPERTIES TO PREVIOUS WORK



# CURING CONSIDERATIONS

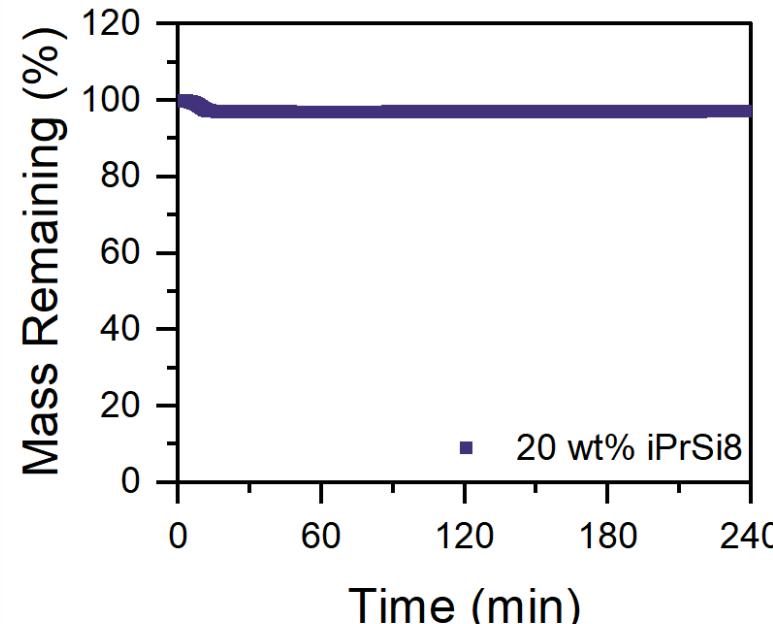
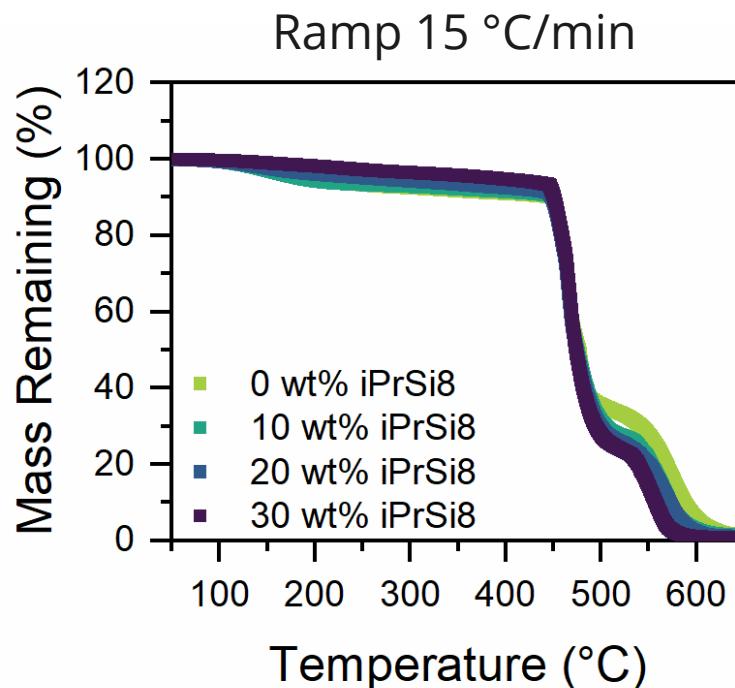


Curing process:

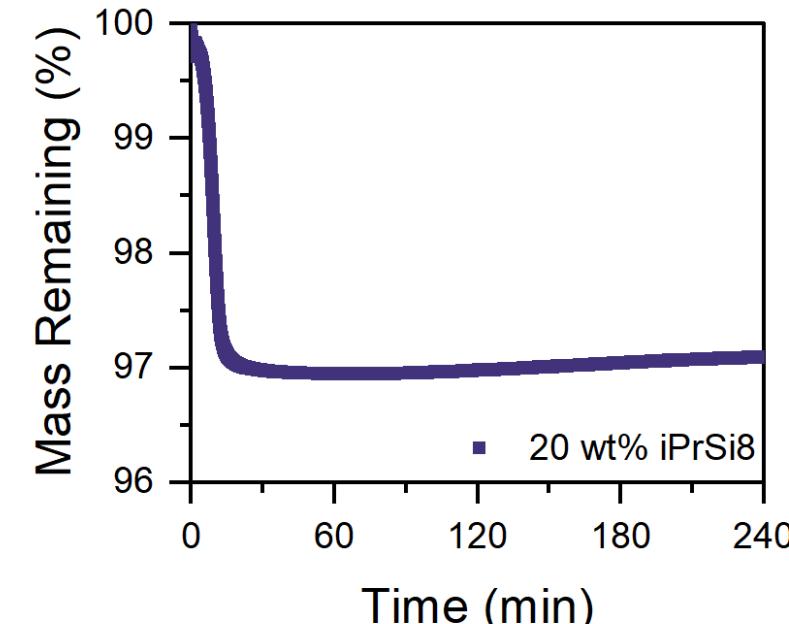
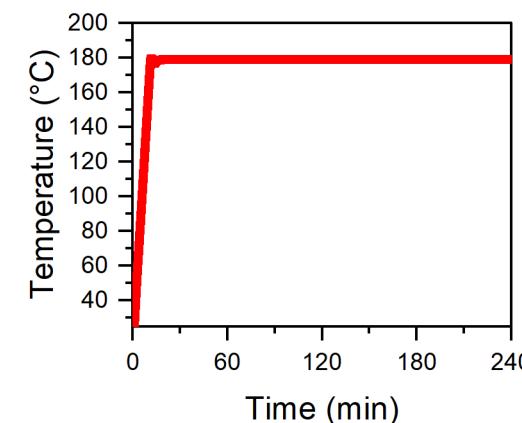
- Printing with UV light, high intensity ( $\sim 150 \text{ mW cm}^{-2}$ )
- 3 hr low intensity UV light ( $\sim 8 \text{ mW cm}^{-2}$ )
- 4 hr,  $180^\circ\text{C}$ , in air

TGA on UV exposed pDCPD

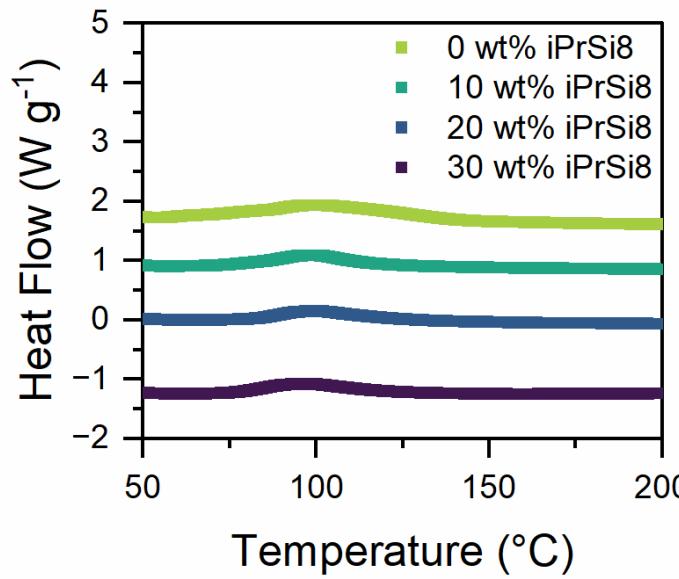
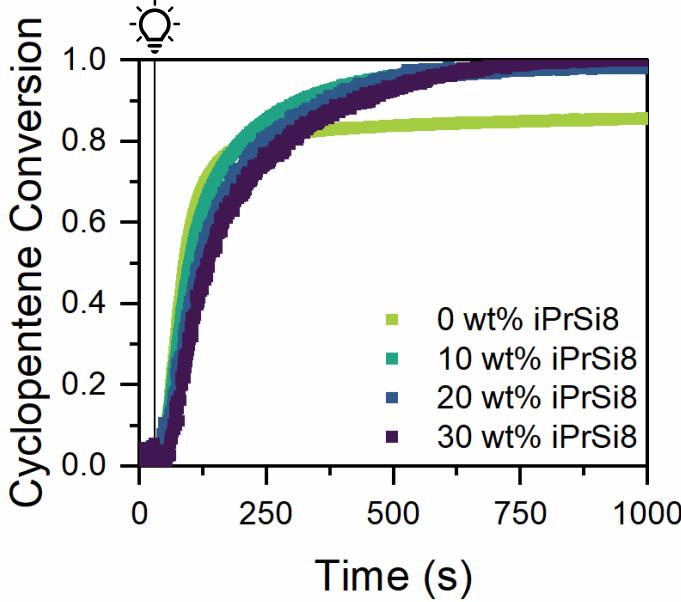
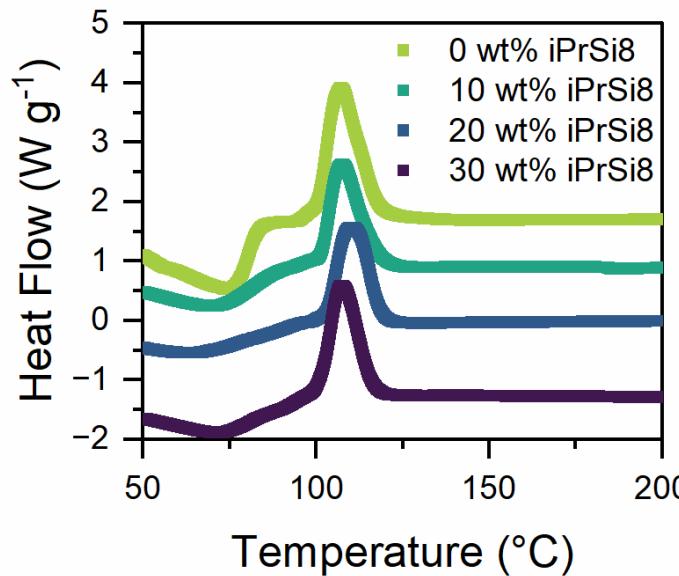
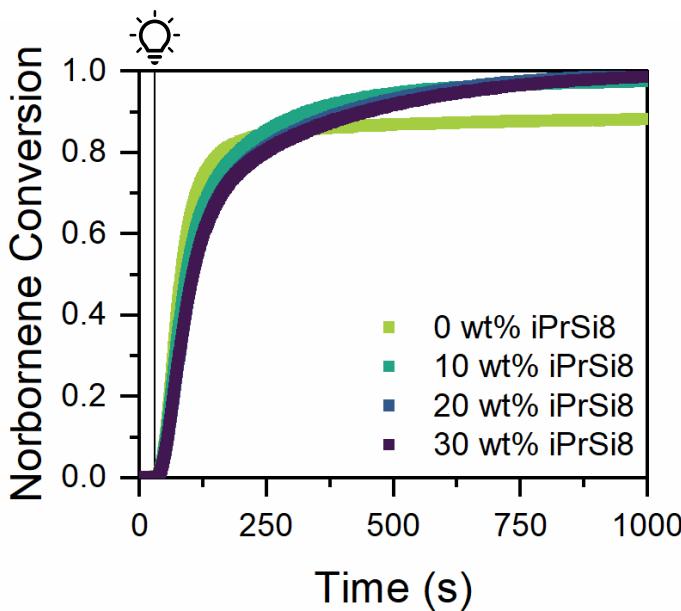
- Determine if degradation during thermal post cure occurs



Hold at 180 C for 4 hours



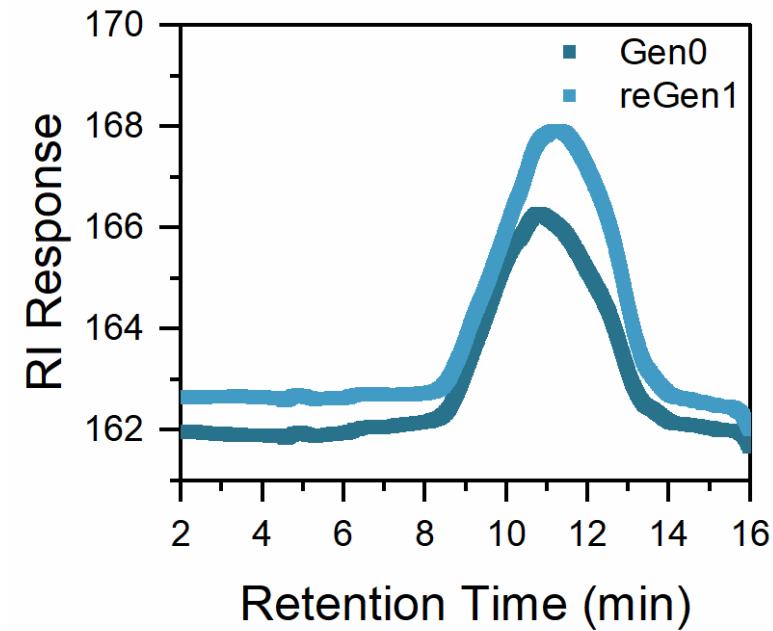
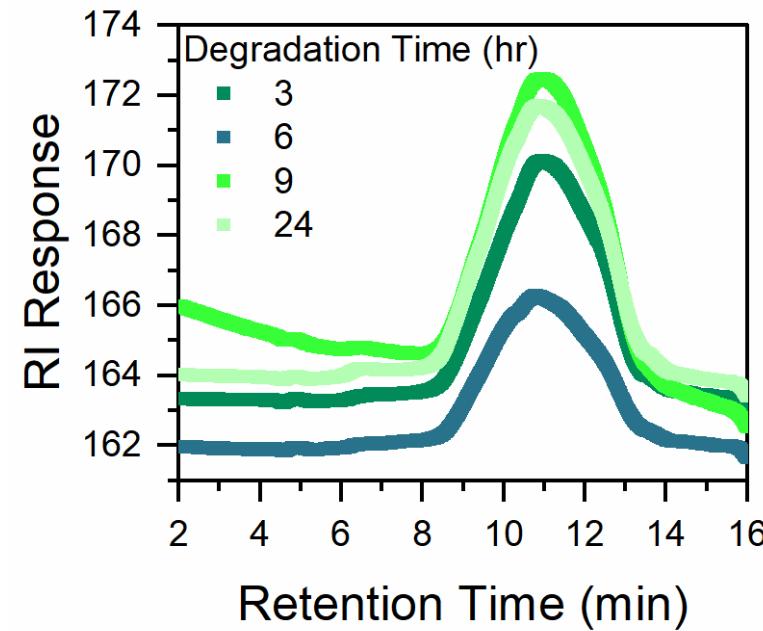
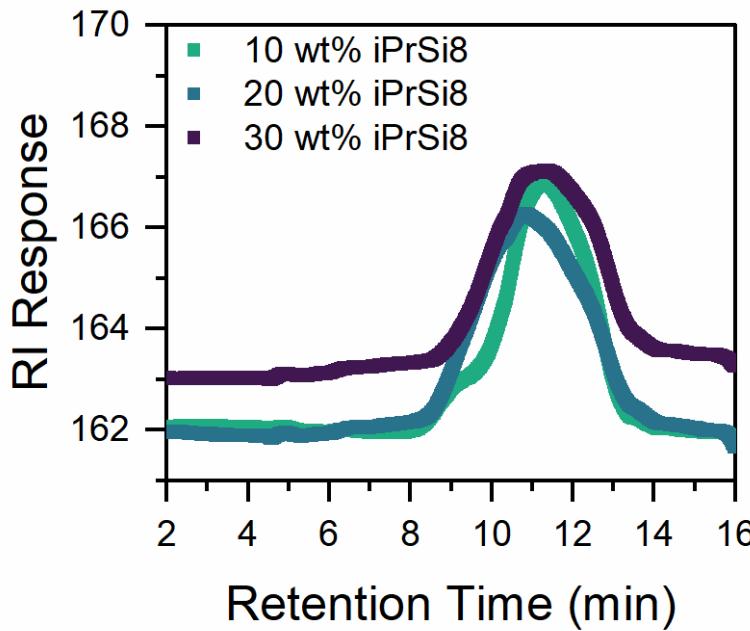
# CONVERSION OF UV CURED NETWORKS



iPrSi8 (wt%)	Resin Exotherm ( $\text{J g}^{-1}$ )	UV Exotherm ( $\text{J g}^{-1}$ )
0	292.6	65.6
10	187.1	33.5
20	166.7	28.1
30	169.1	27.3

- Real-time IR kinetic characterization indicates full conversion of norbornene, cyclopentene with inclusion of iPrSi8
- Residual exotherm decreases with iPrSi8 inclusion

# PRELIMINARY FRAGMENT SIZE CHARACTERIZATION

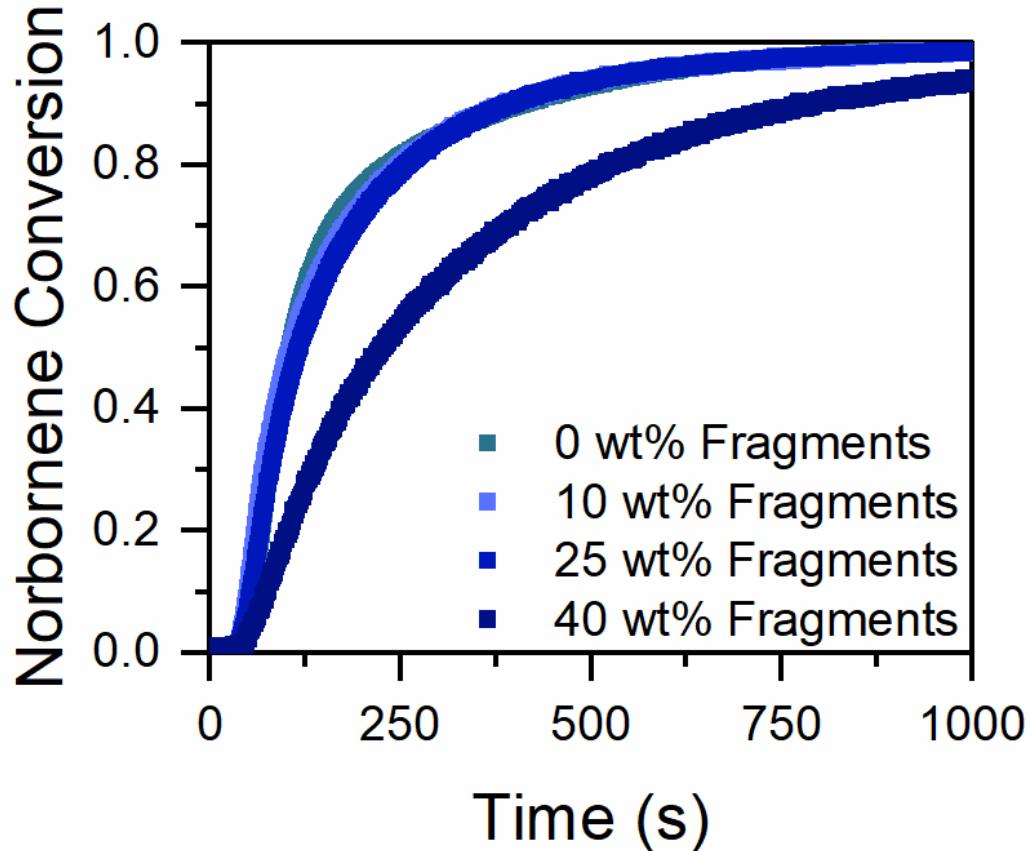


Wt% iPrSi	Mn (kDa)	PDI
10	4.96	2.38
20	5.65	2.45
30	4.59	1.95

Time (hr)	Mn (kDa)	PDI
3	5.40	2.32
6	5.65	2.45
9	5.52	2.29
24	5.48	2.53

- No noticeable trend yet, contrary to previous work
- Could be result of experimental conditions

# FRAGMENT LOADING EXPLORATION



- Increasing fragment loading eventually results in poor kinetics
- Could be due to hydroxyl group content (ends of fragment chains) slowing down kinetics
- Also appears to result in loss of mechanical properties (qualitatively)