Connectivity reconfiguration for additive manufacturing

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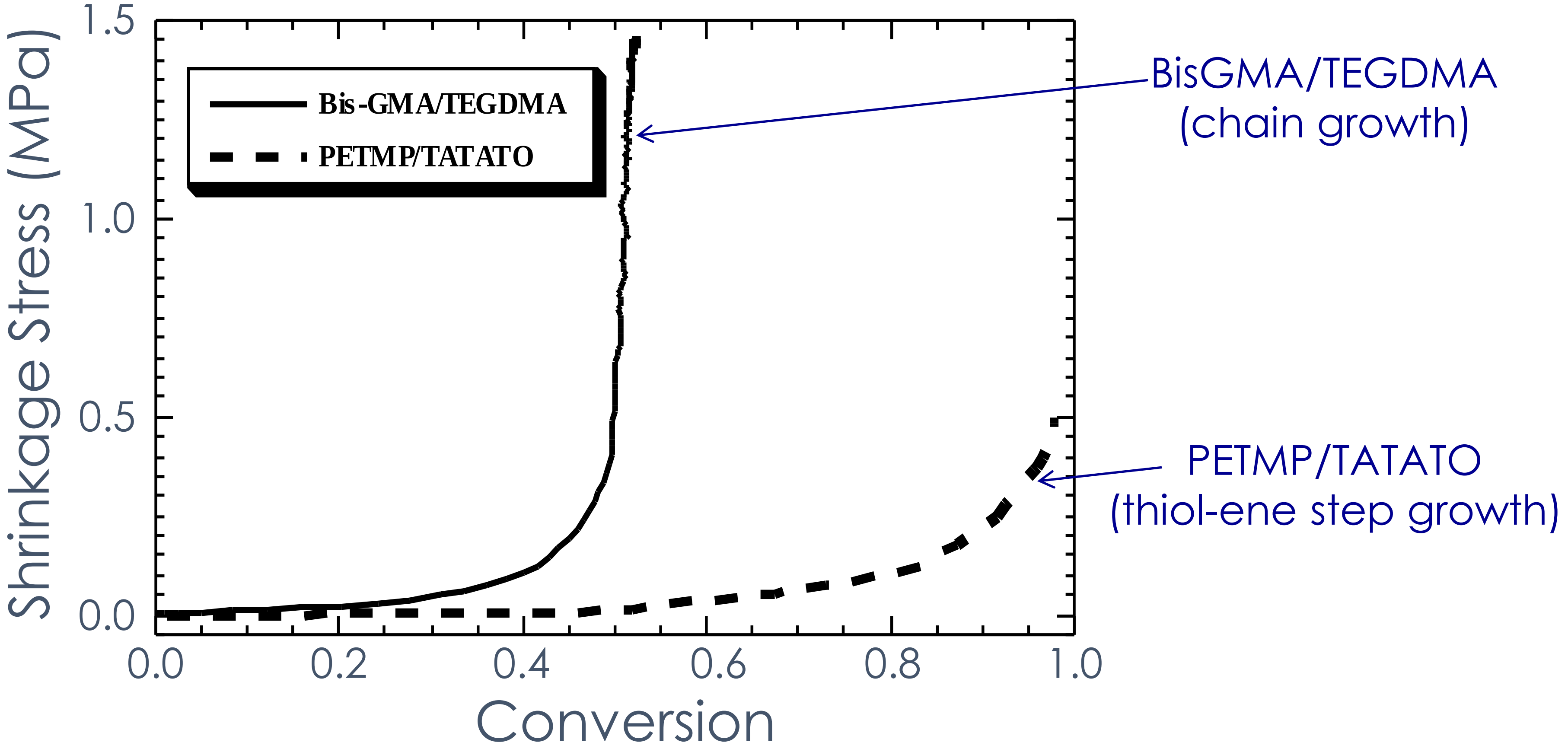
POLYMER DOJO

Photopolymerizations Generally Lead to Shrinkage Stress



Most thermosetting reactions/processes lead to stresses of various amounts

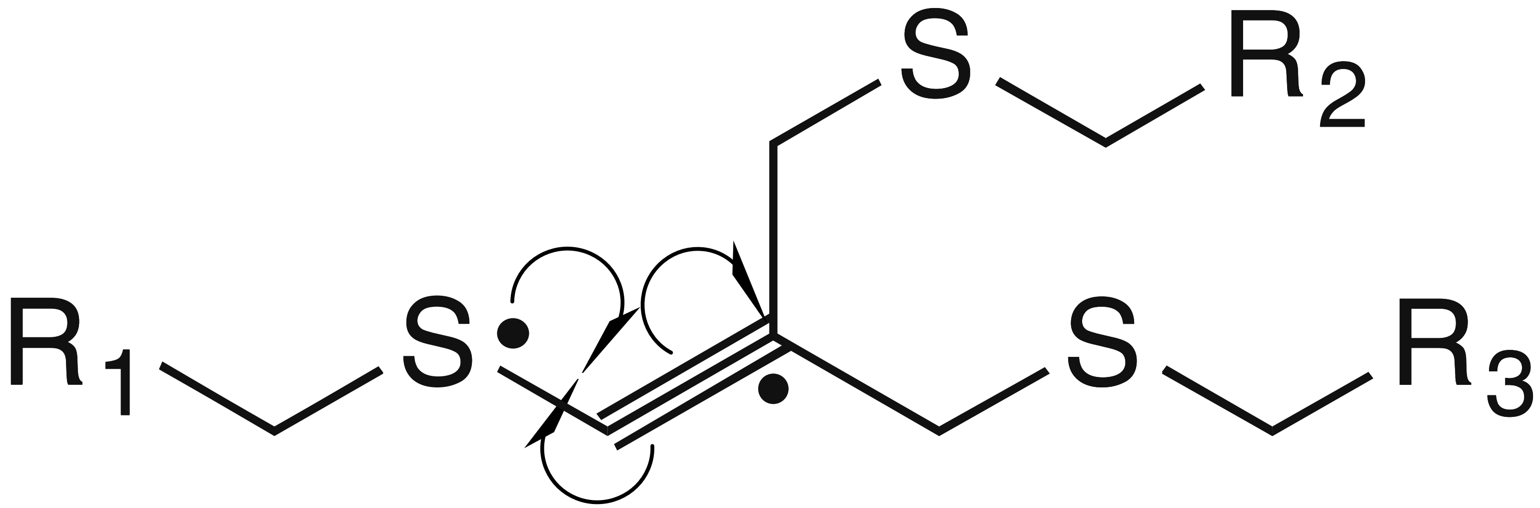
Solving Shrinkage Stress

- Shape/molecular structure of cross-linked polymers traditionally set, fixing in shrinkage stress
  - *Solution: Incorporate functional groups that reversibly cleave and reform in a controllable manner*

HOW?

- Select dynamic covalent backbone chemistry that rapidly and reversibly rearranges in the presence of active centers (radicals)
  - *Use light exposure to trigger the radical generation*

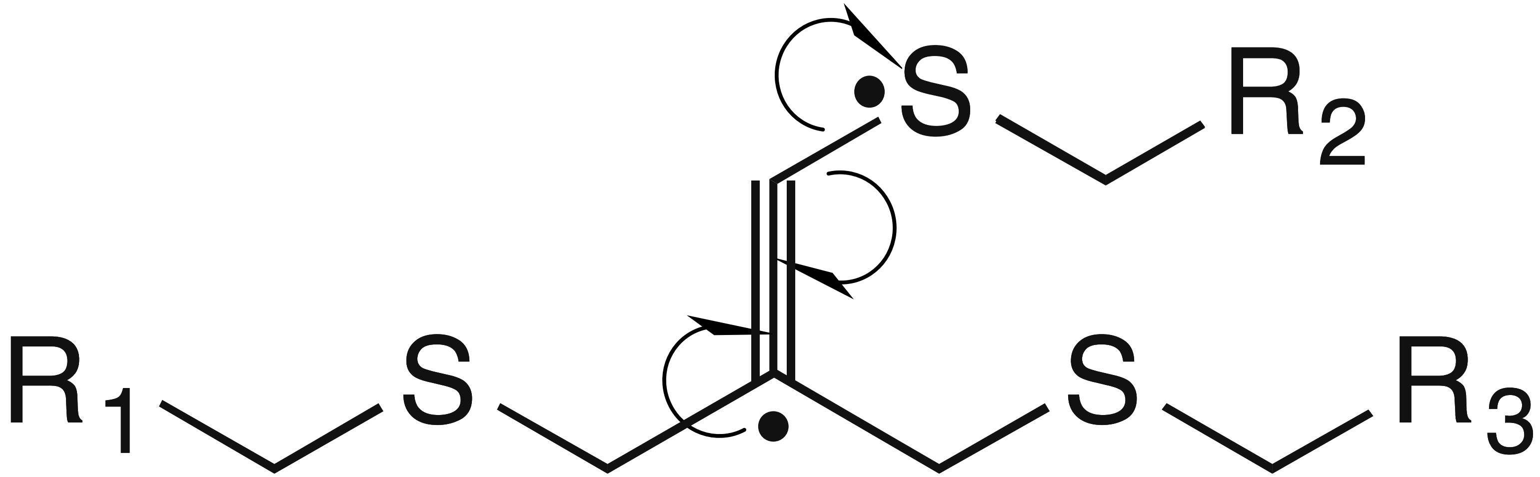
The Allyl Sulfide Functionality: Addition-Fragmentation Chain Transfer (AFCT)



New bond formation as a result of the radical reaction with the allyl sulfide

Cross-link or backbone linkage originally under stress

The Allyl Sulfide Functionality: Addition-Fragmentation Chain Transfer (AFCT)



Formation of a new “near-equilibrium” bond and reformation of the allyl sulfide

New bond formation as a result of the eradication reaction with the propagating radical

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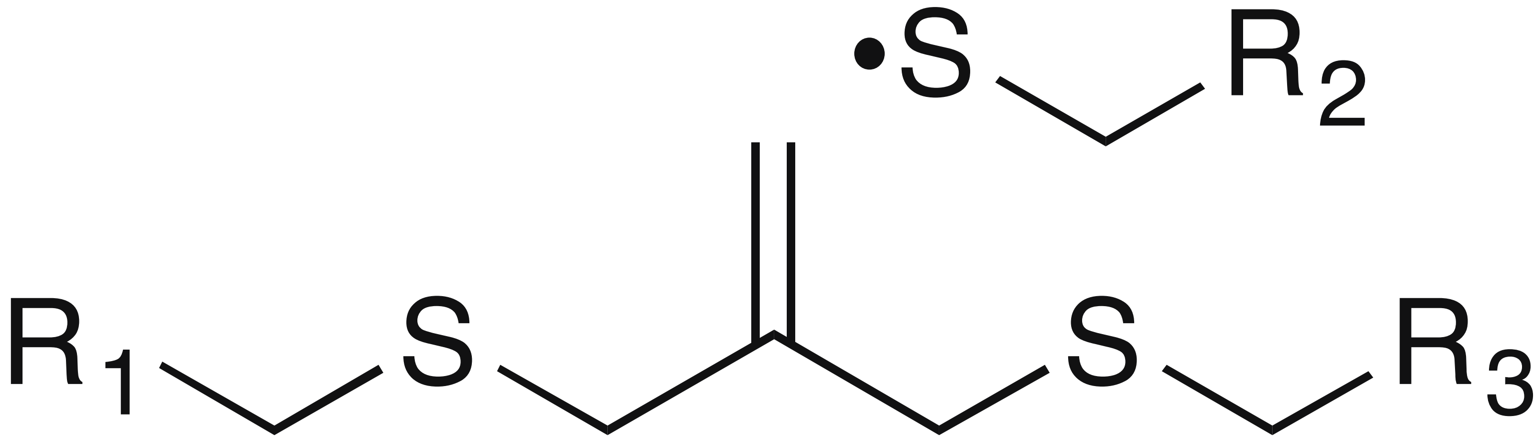
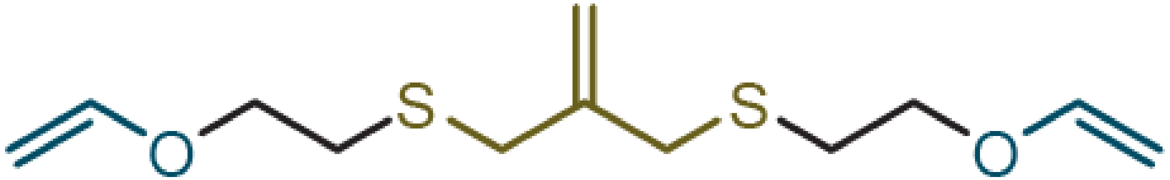
The Allyl Sulfide Functionality: Addition-Fragmentation Chain Transfer (AFCT)



Formation of a new "near-equilibrium" connection and reformation of the propagating radical

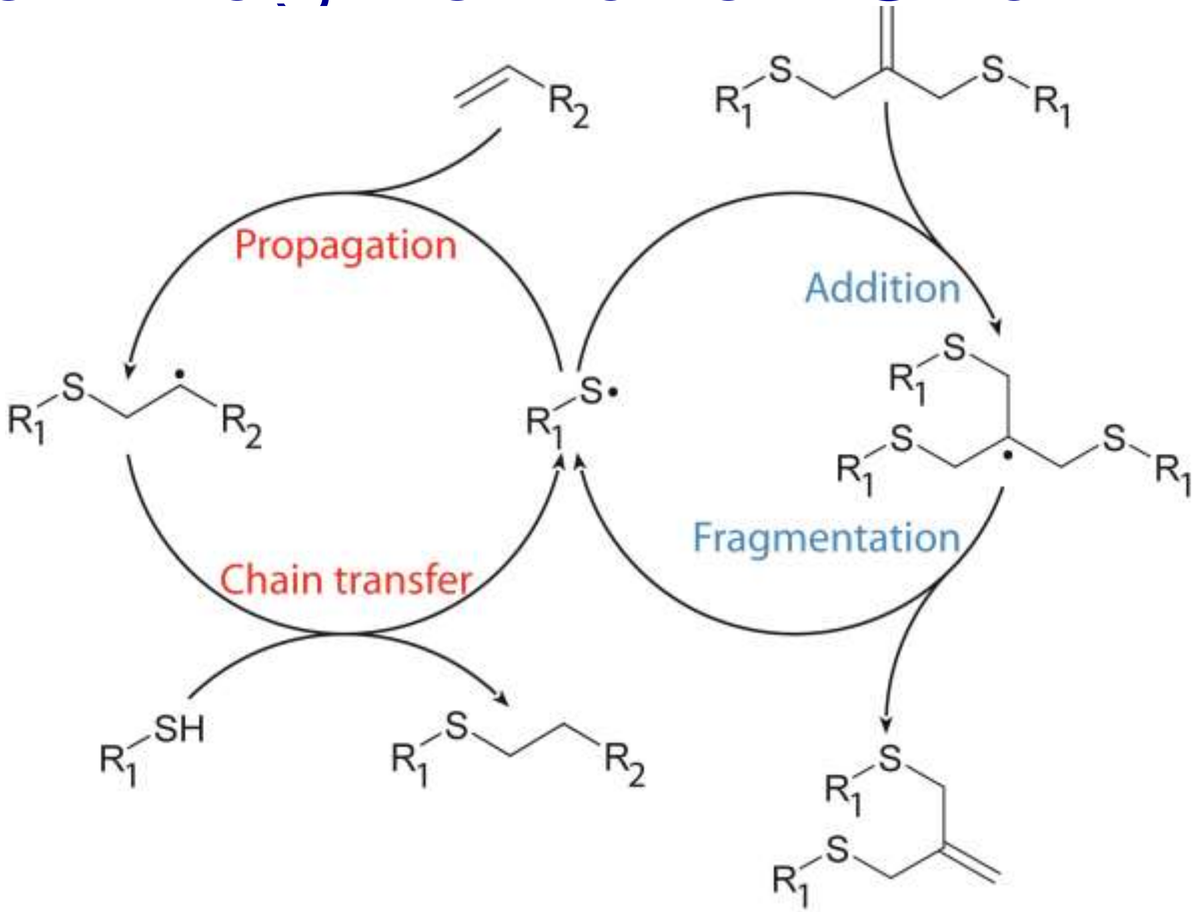
Hypothesis: Addition-fragmentation allows thiol-ene networks to find a lower energy state.

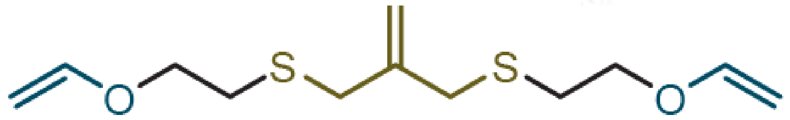
Reduction of stresses induced during photopolymerization?



2-Methylene-propane-1,3-di(thioethyl vinyl ether) (MDTVE)

Concurrent Thiol-Ene Polymerization/ Addition-Fragmentation Chain Transfer

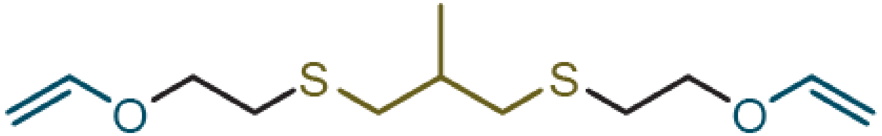




Incorporation of the Allyl Sulfide AFCT Functionality in a Thiol-Ene Network

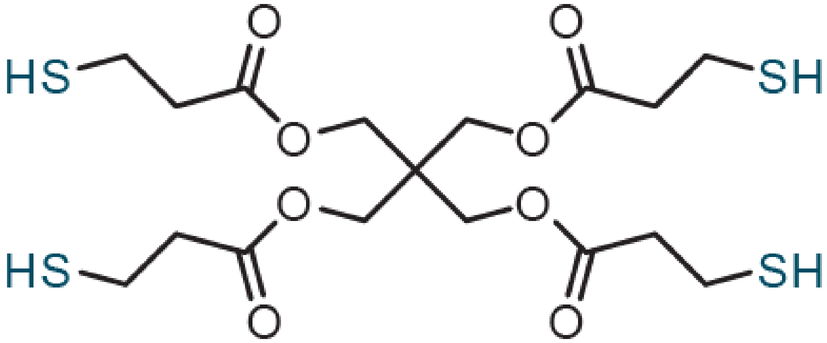
'Ene' monomer

2-Methylenepropane-1,3-di(thioethyl vinyl ether)
(MDTVE, "allyl sulfide")



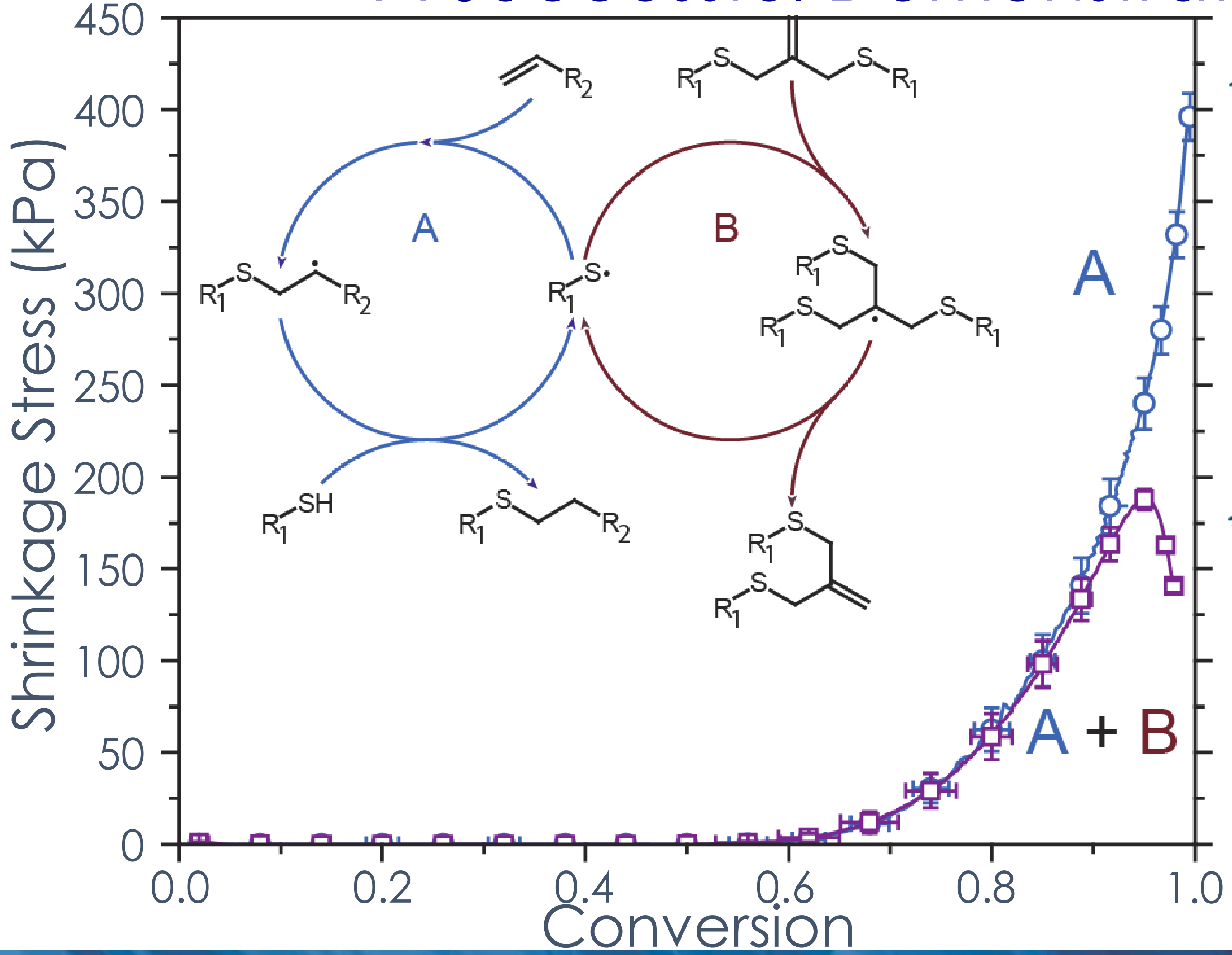
2-Methylpropane-1,3-di(thioethyl vinyl ether)
(MeDTVE, "propyl sulfide")

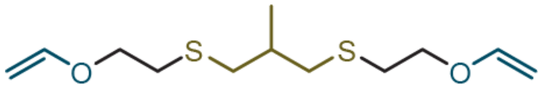
'Thiol' monomer

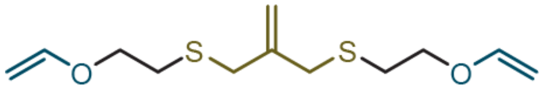


Pentaerythritol tetra(3-mercaptopropionate)
(PETMP)

Stress Relaxation During Photopolymerization: A Successful Demonstration

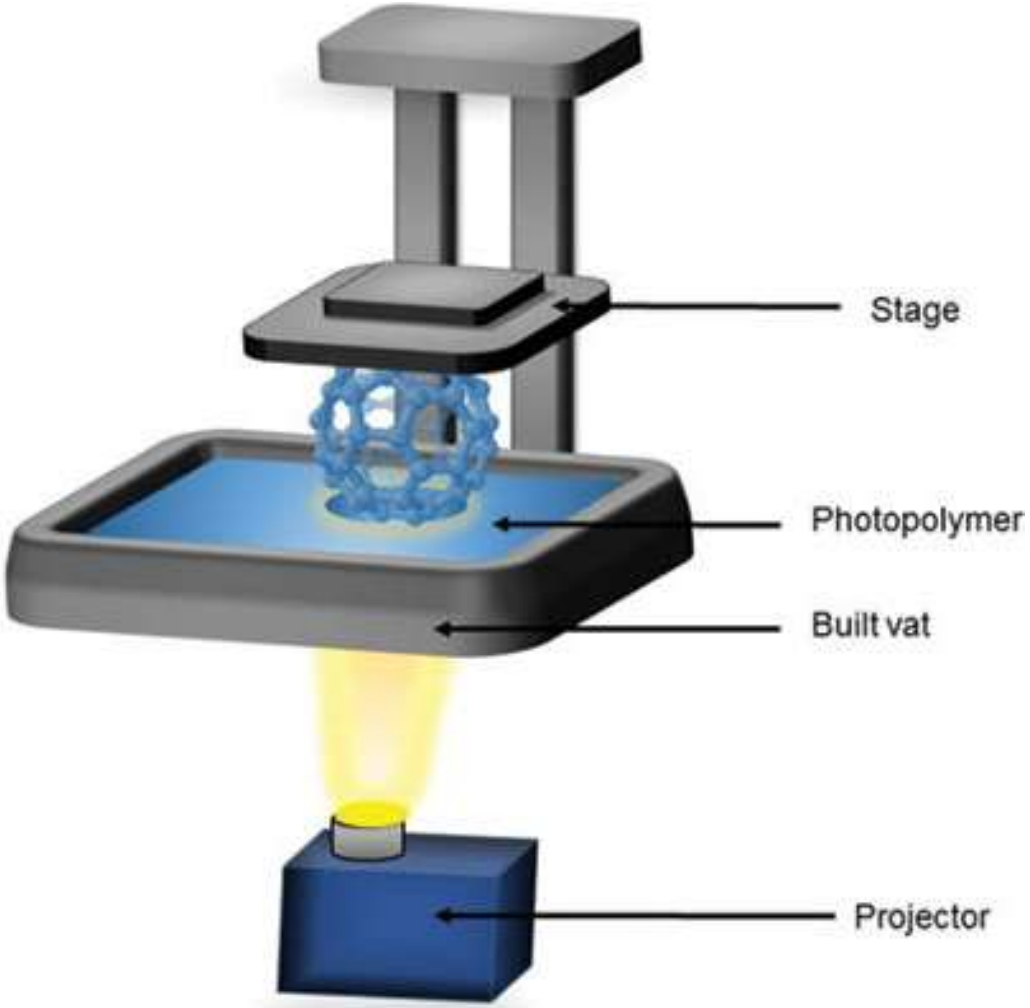






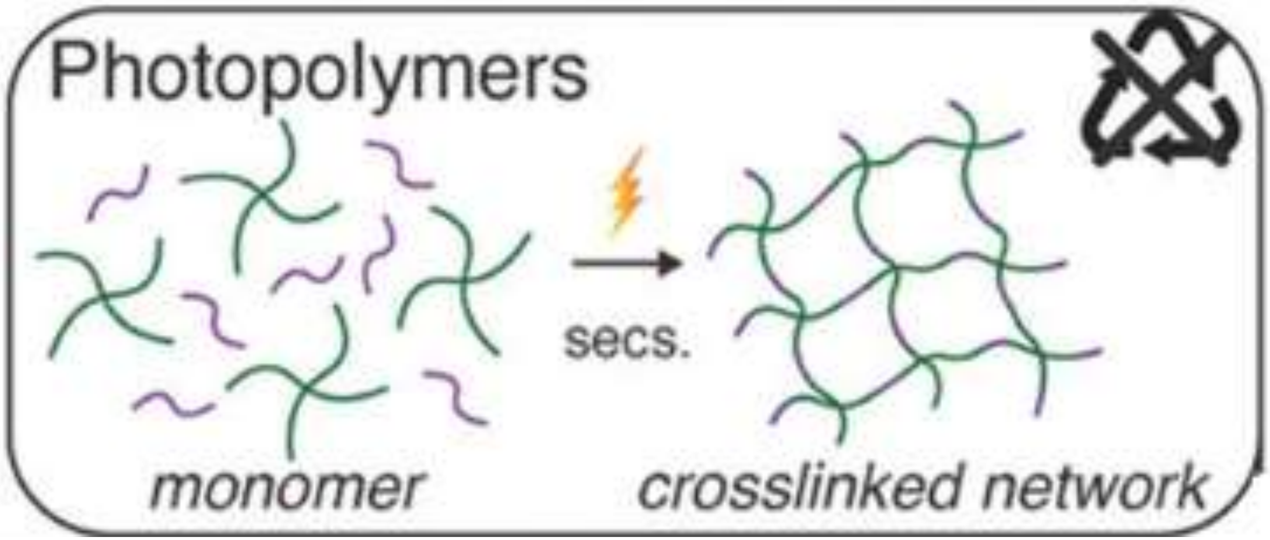
Irradiation: 365 nm, 0.8 wt% HCPK

Stereolithography (SLA)



Bottom-Up SLA

Photocurable thermosets

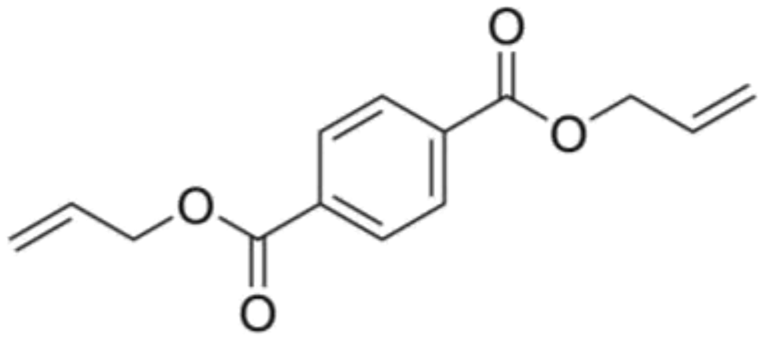


TMPTA (acrylate) ECC (epoxide)

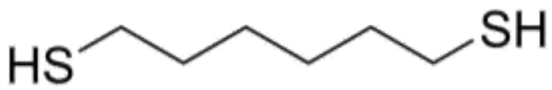
Thermoplastics in SLA

Unique challenges

- Photopolymerizable
- Rapid curing rate
- Solid-liquid phase separation



diallyl terephthalate
(DAT)



1,6 – hexanedithiol

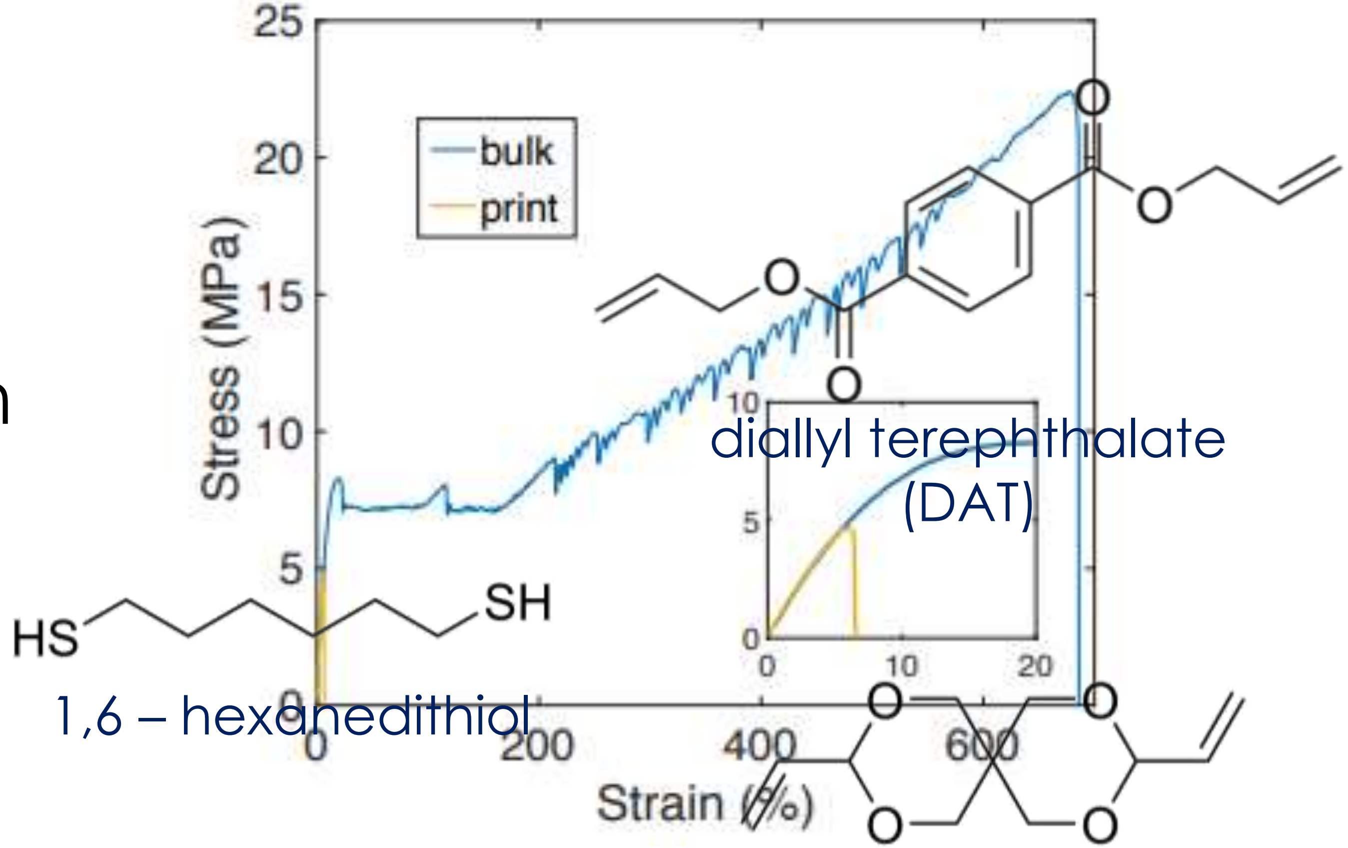
3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane
(DVTU)

Mater. Horiz. 2020, 7, 835
J. Appl. Polym. Sci. 2018, 135, 46259

Thermoplastics in SLA

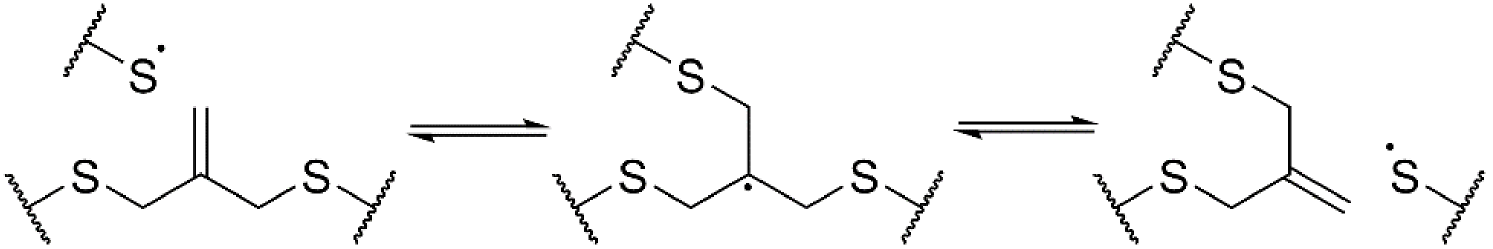
Unique <u>new</u> challenges

- Slow crystallization
- Poor interlayer adhesion



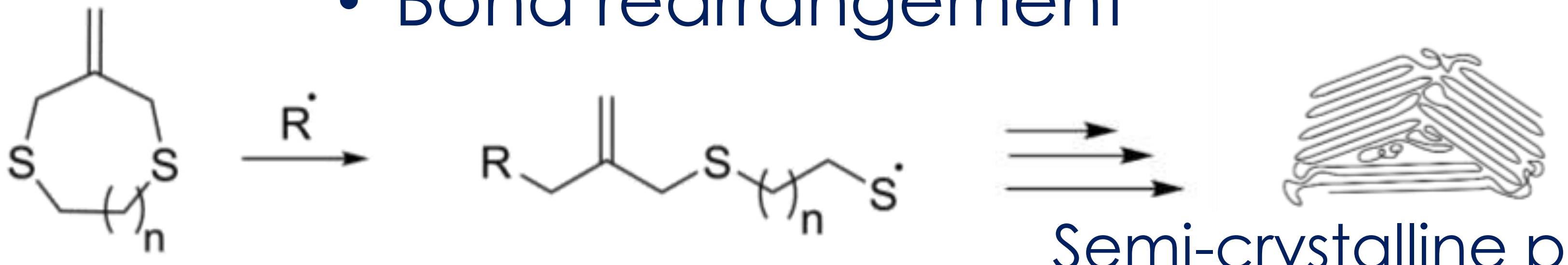
3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (DVTU)

Addressing Thermoplastic Limitations in SLA

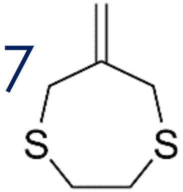


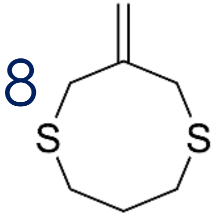
Addition-fragmentation chain transfer

- Stress relaxation
- Bond rearrangement



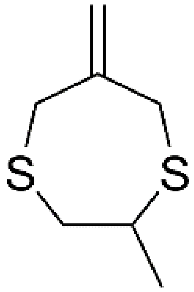
Semi-crystalline polymer

CAS7 

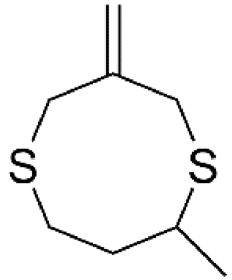
CAS8 

Macromol. 2010, 24, 10188
Macromol. 1996, 29, 22, 6983–6989

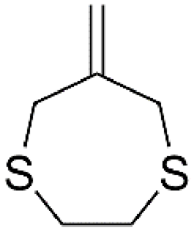
Photopolymerization Kinetics: DSC



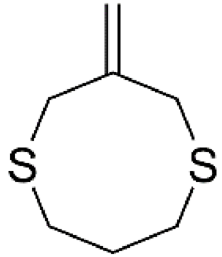
MDTE



MDTO



CAS7



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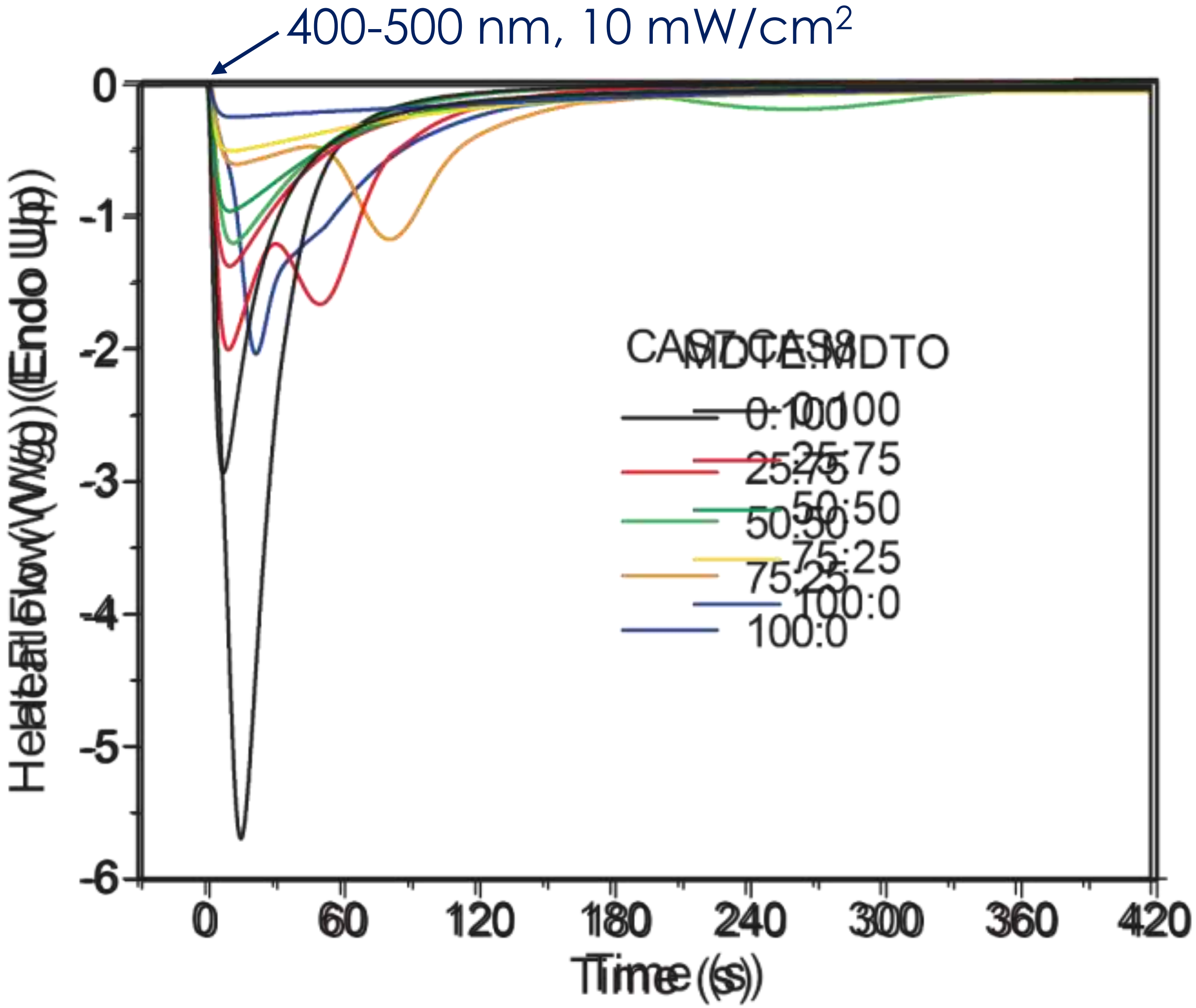
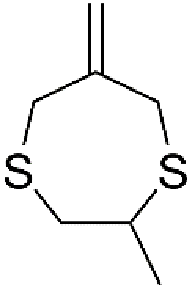


0.5 wt% Irgacure 819, 405 nm @ 10 mW/cm^2

Photopolymerization Kinetics: Rheometry



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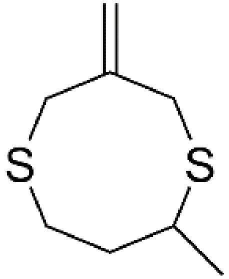

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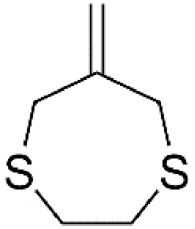

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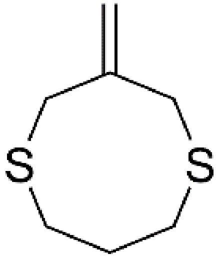

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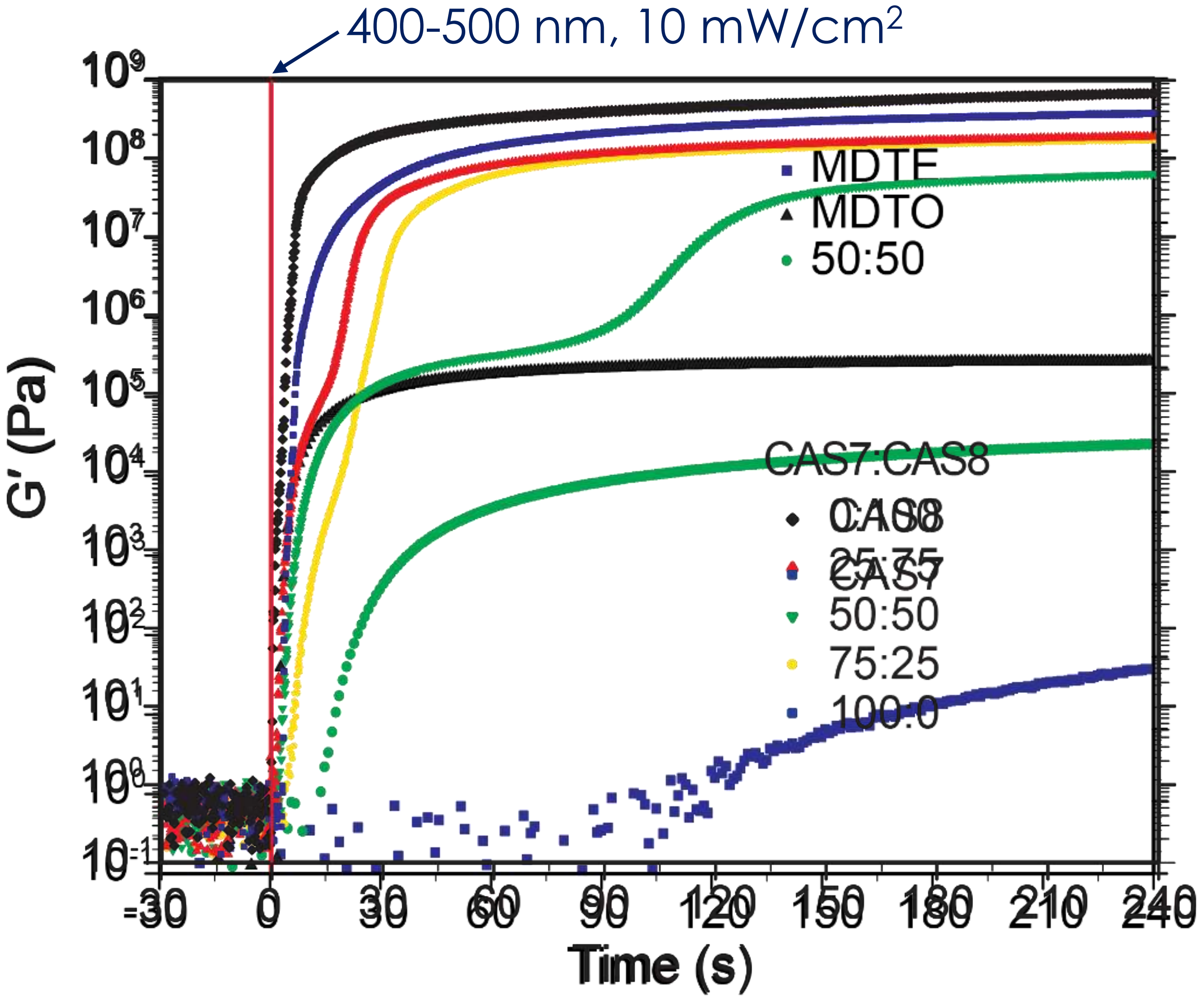
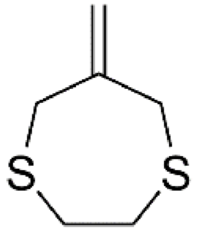


0.5 wt% Irgacure 819, 405 nm @ 10 mW/cm^2

Dark Crystallization



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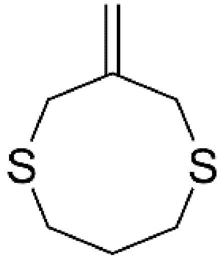
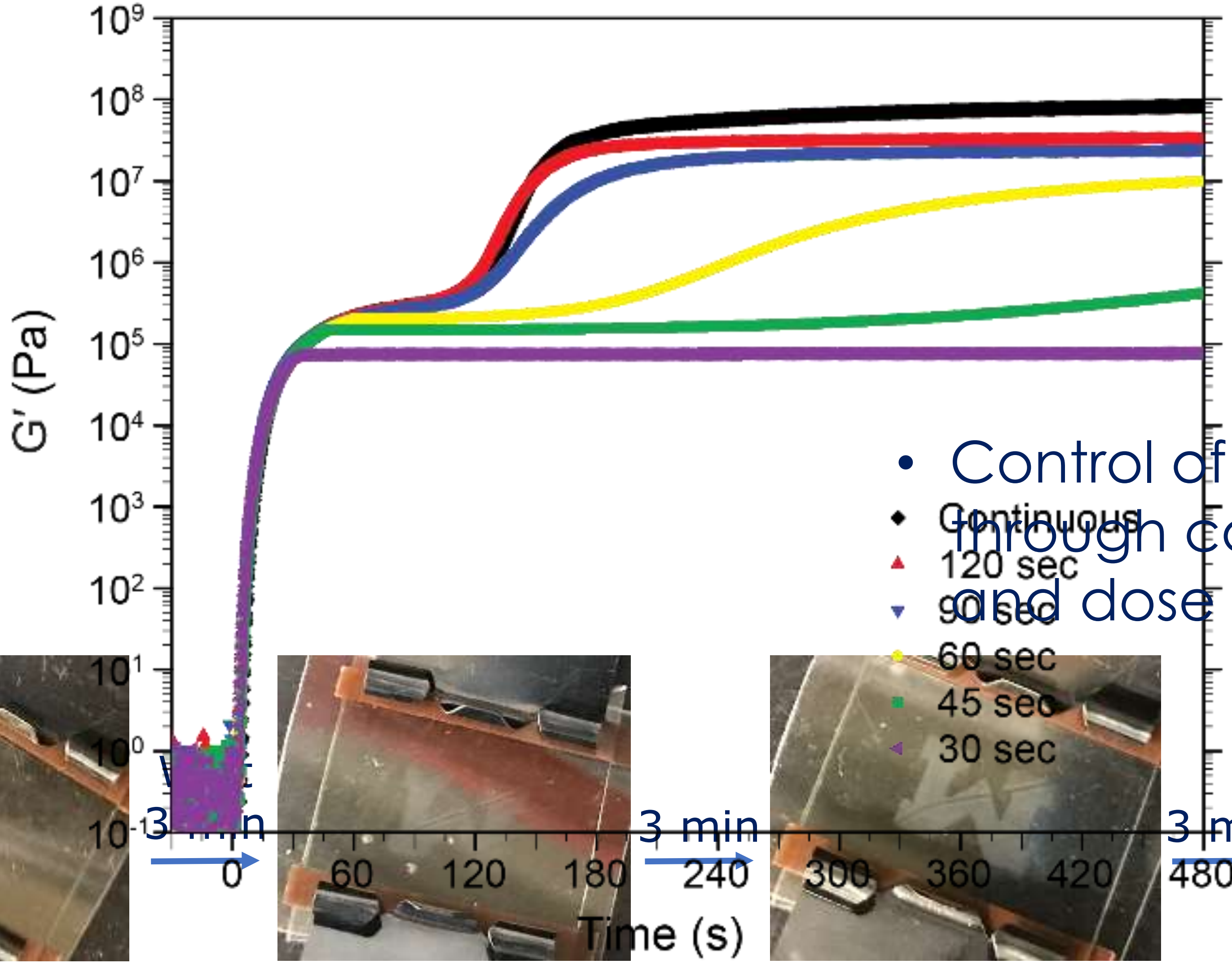
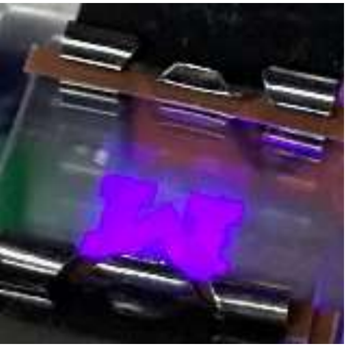


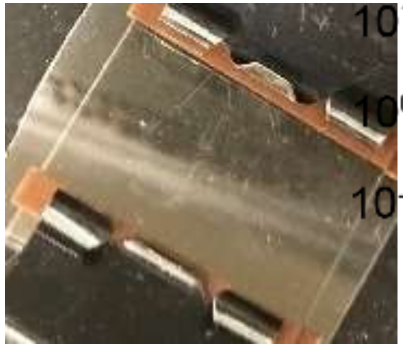
CAS8

50:50 CAS7:CAS8



- Control of crystallization through composition and dose of irradiation

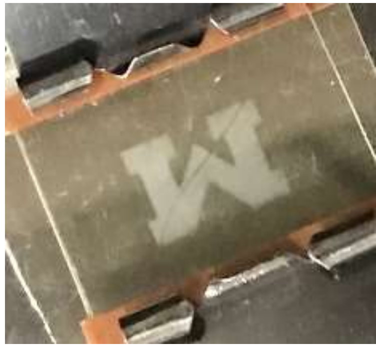




3 min

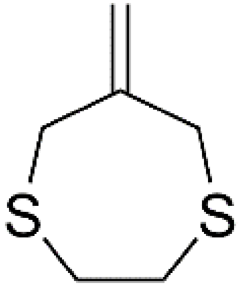
3 min

3 min

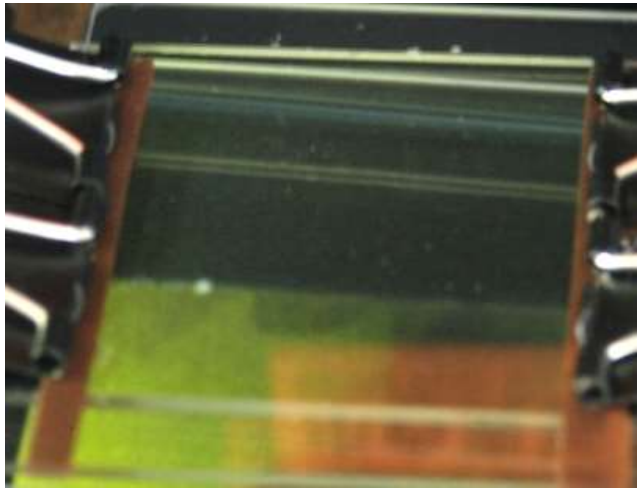


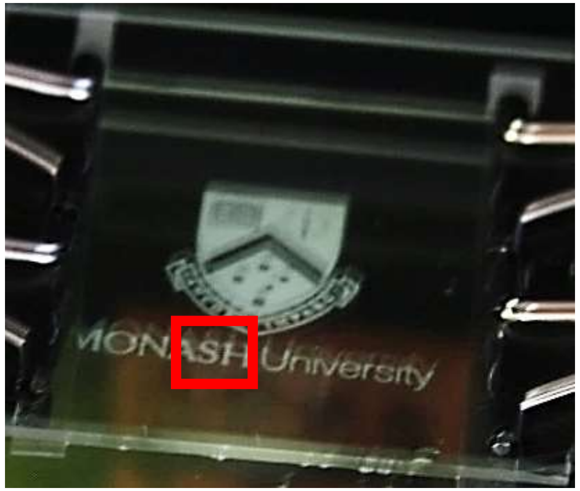
0.5 wt% Irgacure 819, 405 nm @ 10 mW/cm^2

Crystallization Photopatterning

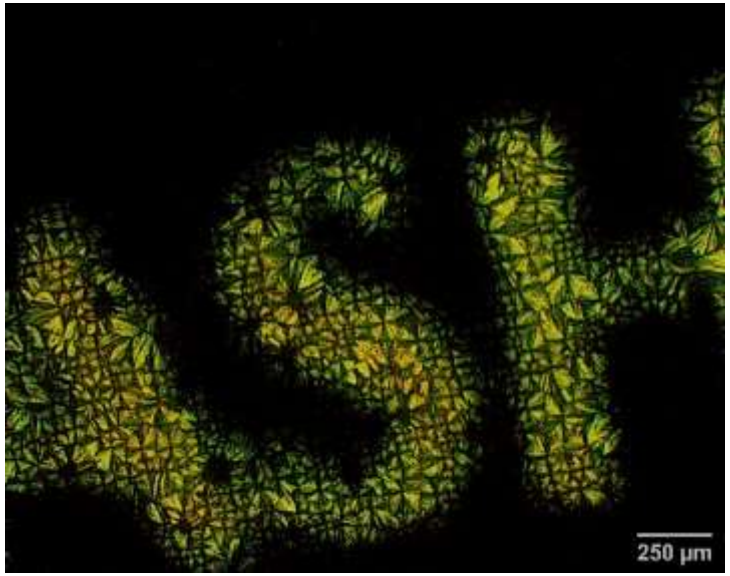


CAS7





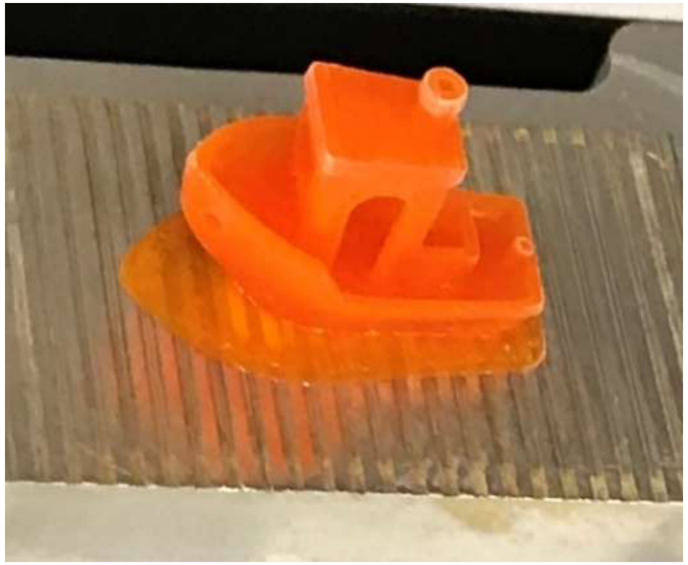
- Crystallization confinement enables layerwise photopatterning



0.5 wt% Irgacure 819, 405 nm @ 10 mW/cm^2

Stereolithographic Printing

CAS8



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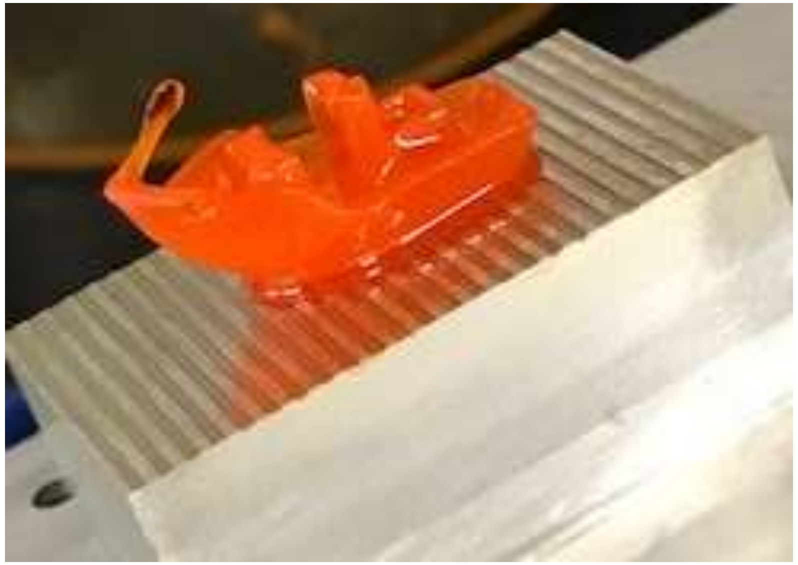
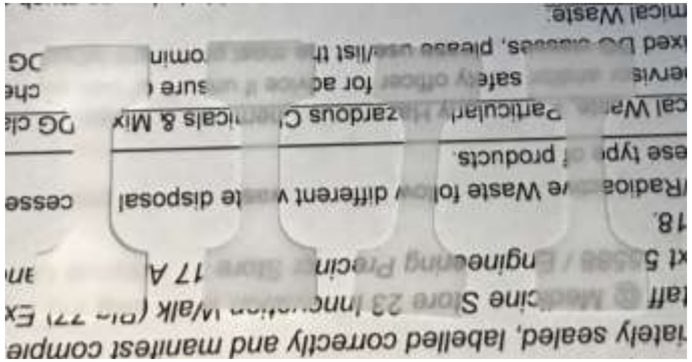


25:75 CAS7:CAS8

Bulk Mechanical Properties



Increasing CAS8 content

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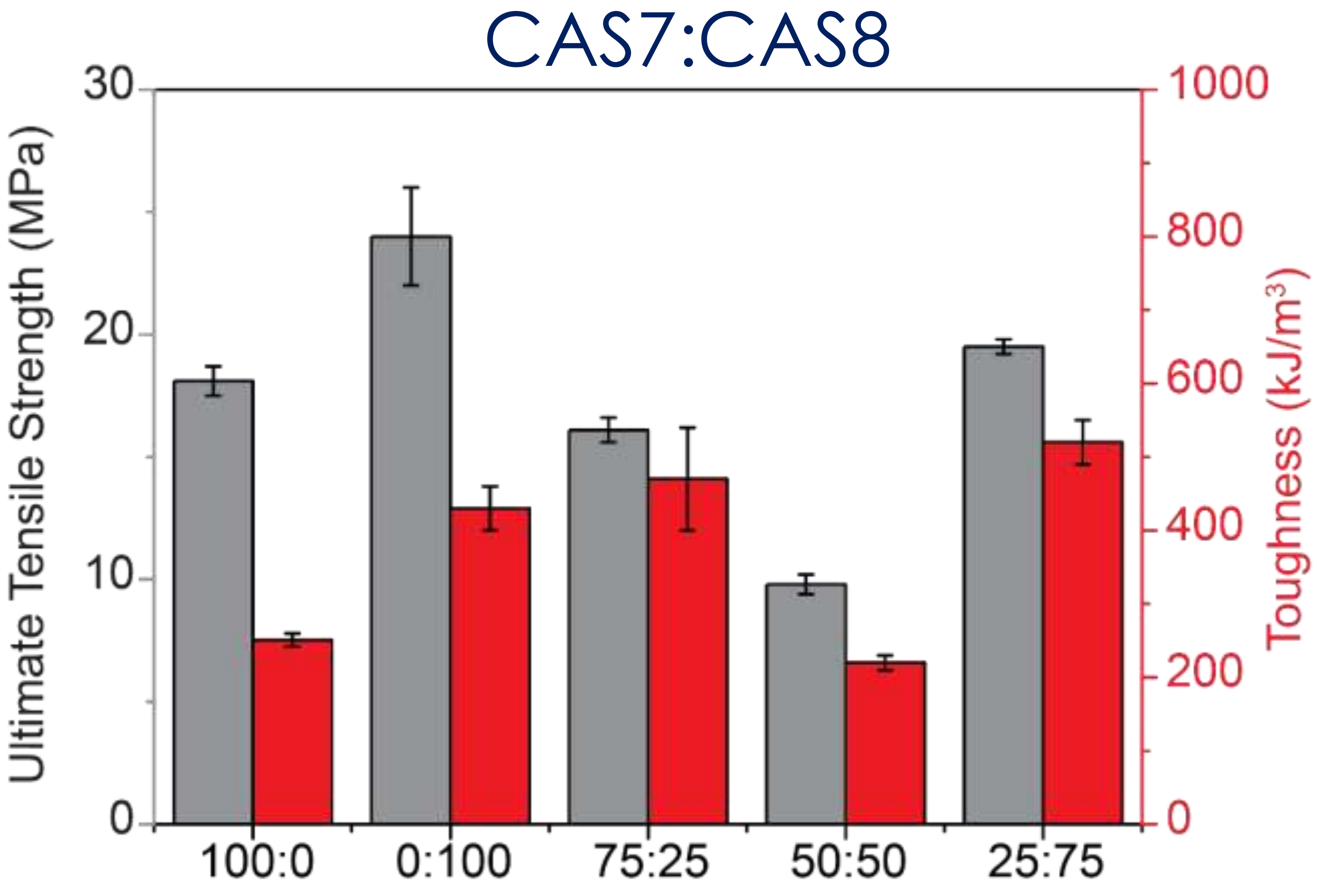
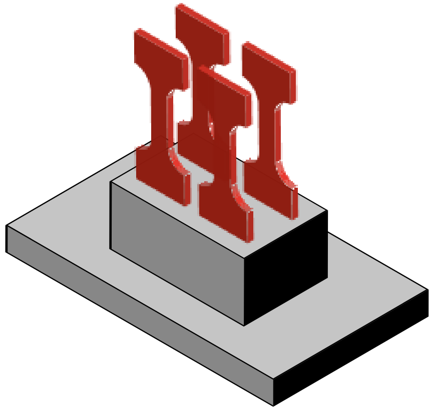
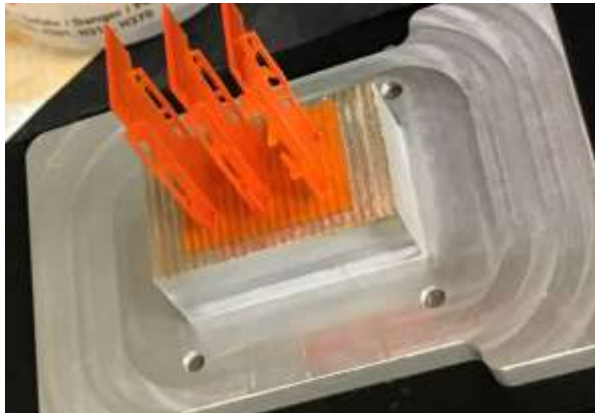
Increasing CAS7 content

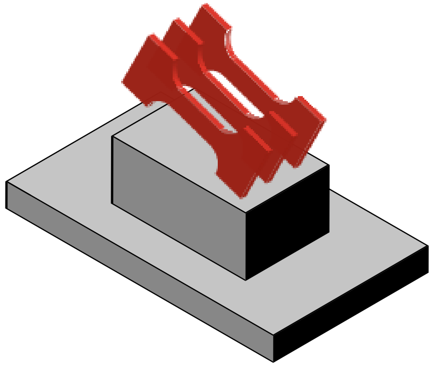


Printed Mechanical Properties



Printed 90°





Printed 45°

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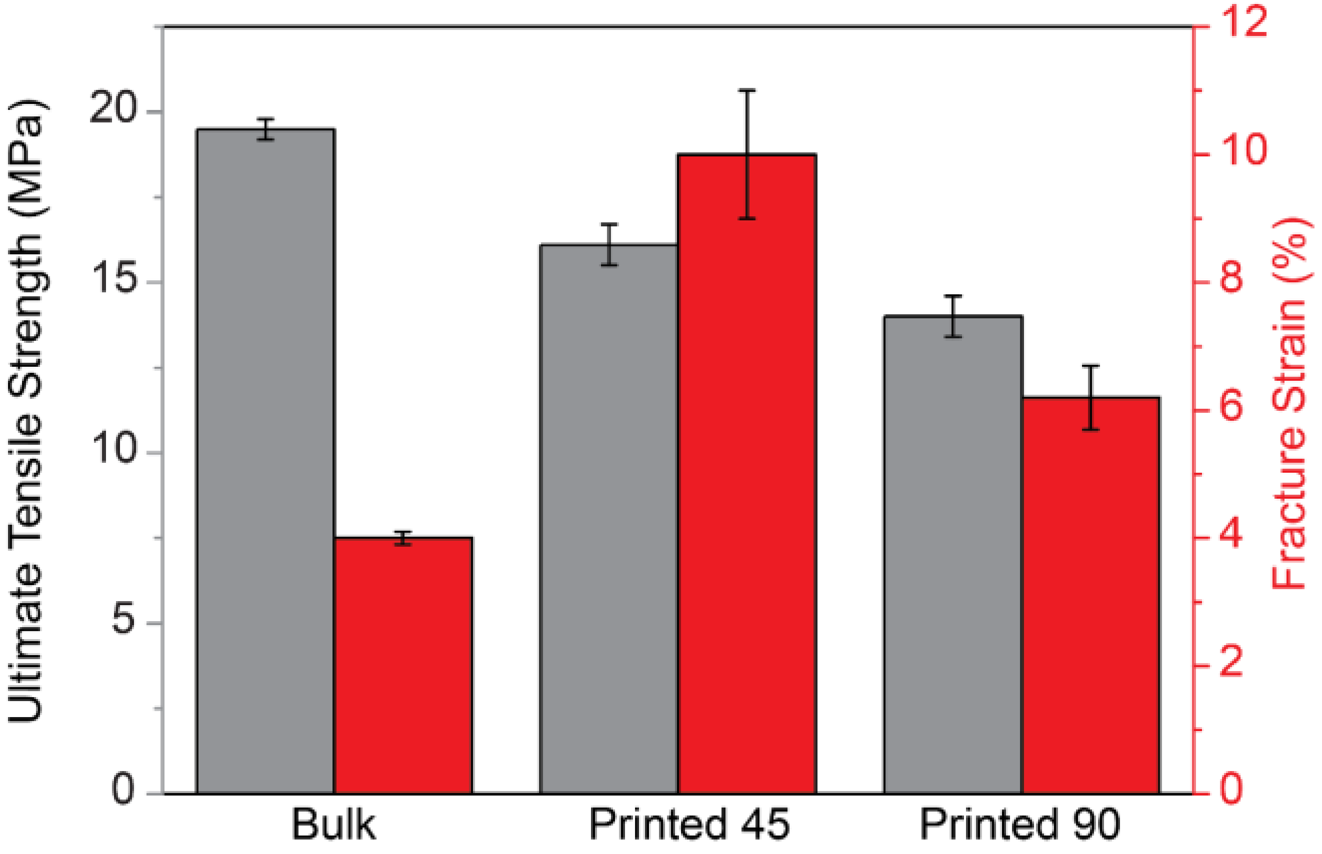
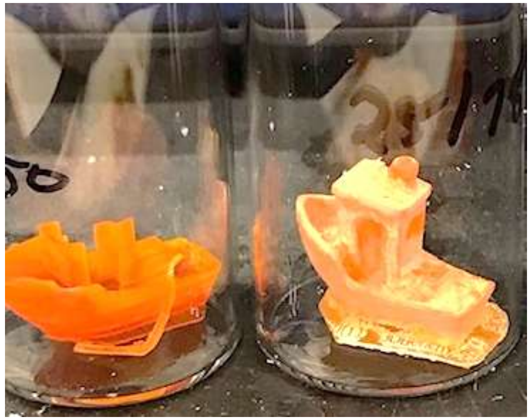
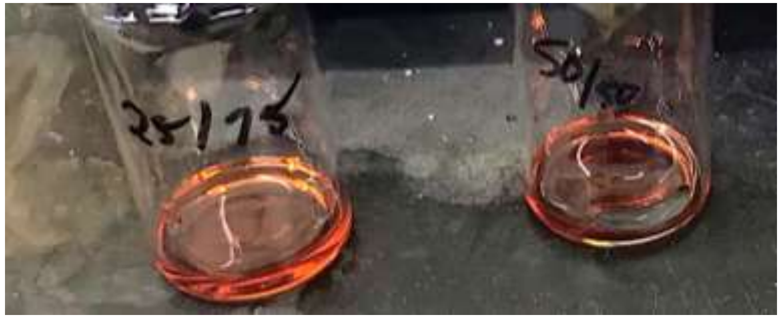


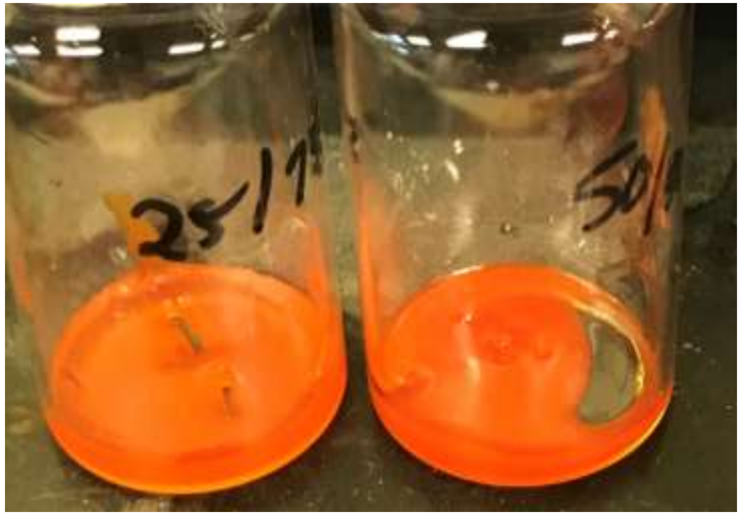
Thermoplastic Melting





Heating

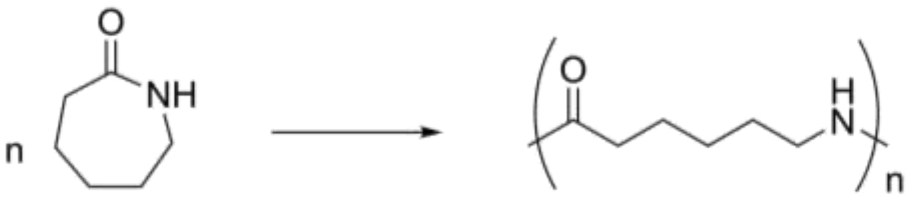
Cooling

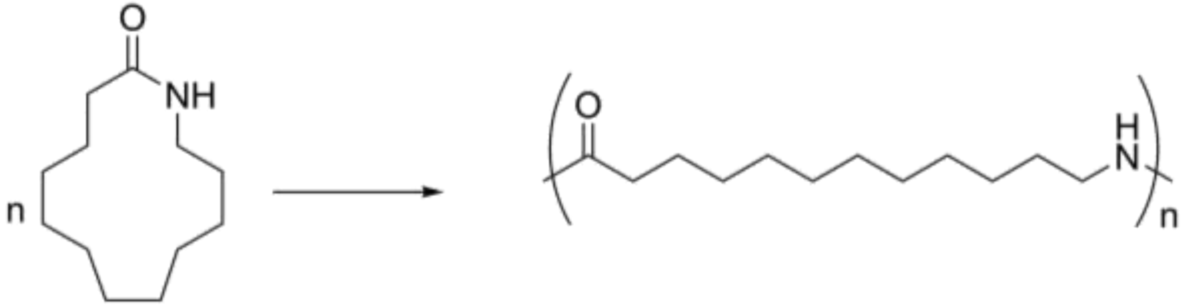


Ring-Opening Copolymers

Anionic ring-opening copolymerization of ε-caprolactam (CL) with ω-laurolactam (LL)

- More flexible chains
- Lower crystallinity

CL


LL


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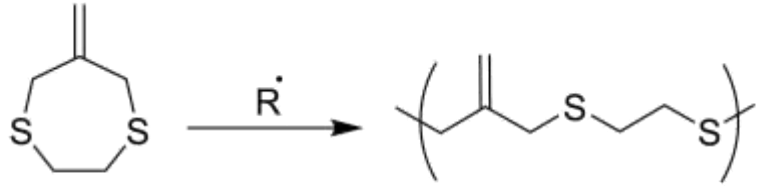

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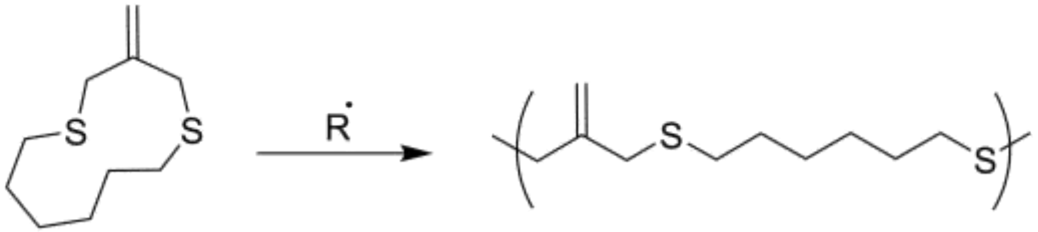

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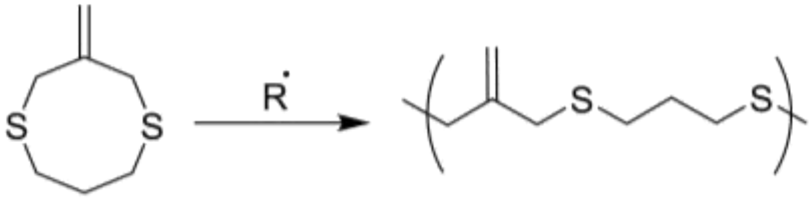

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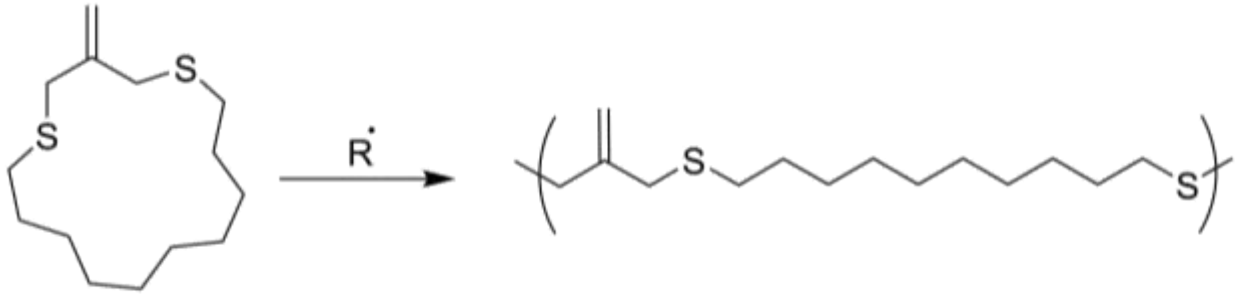
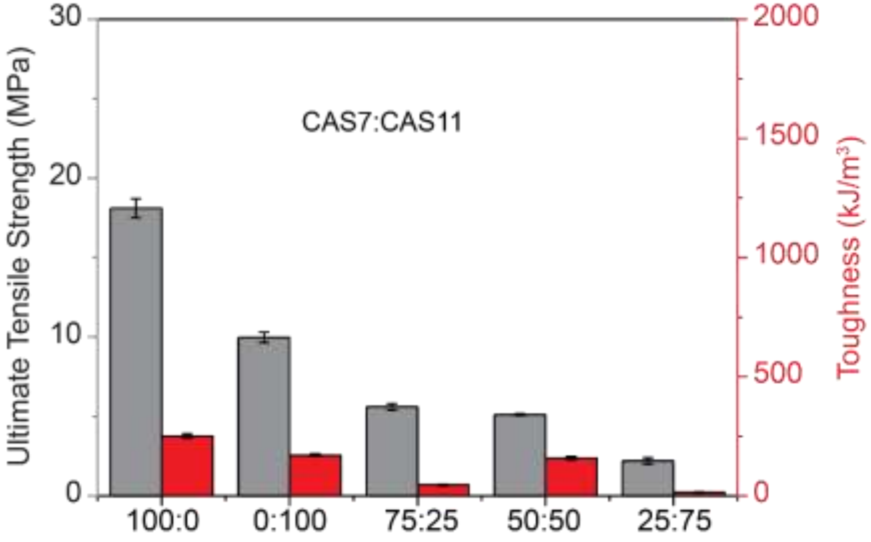
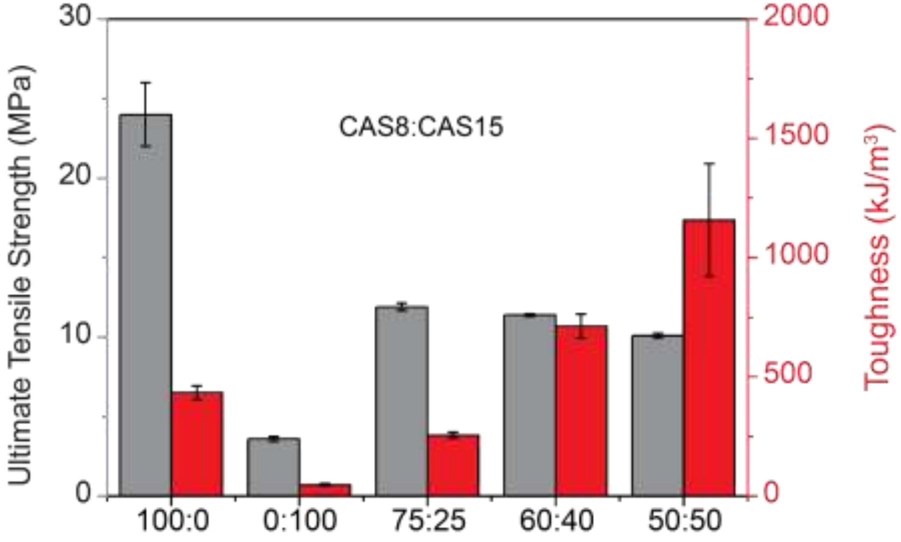
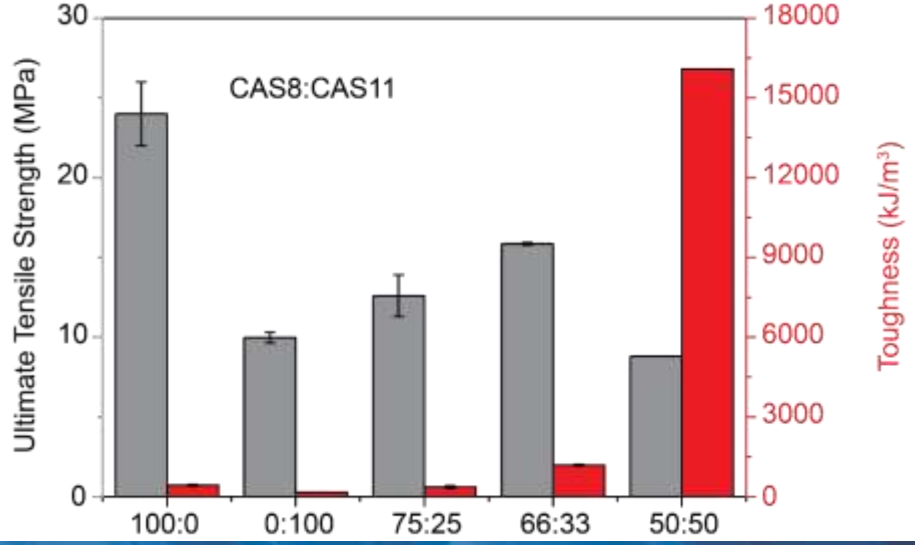
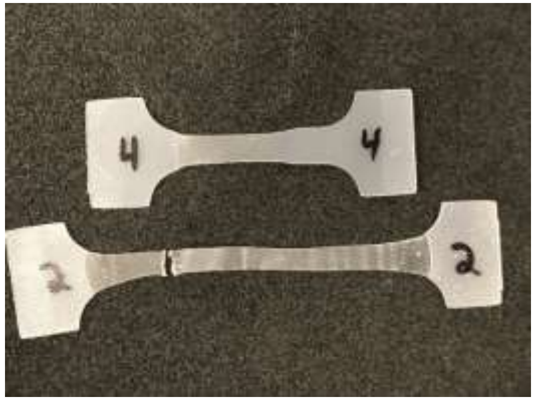


Mechanical Properties









50:50 CAS8:CAS11

Acknowledgements

<u>Scott Polymer Dojo</u>

Alex Commisso

Dr. Gopal Sama

- veski Innovation Fellowship
- ARC Future Fellowship
- ARC Discovery Project DP210100901

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POLYMER DOJO

MONASH University