Resin Design for Spatial Control of Photopolymerization in Volumetric Additive Manufacturing (VAM)

Caitlyn Cook (cook92@llnl.gov)

LLNL: M. Shusteff, J. Oakdale, D. Porcincula, J. Schwartz, A. Kaczmarek, E. Fong, B. Moran, T. Weisgraber, K. Champley

UC Berkeley: H. Heidari, H.. Taylor

U Colorado, Boulder: A. Muralidharan, C. Rackson, B. McLeod

RadTech 2020
Orlando, Florida

Berkeley
UNIVERSITY OF CALIFORNIA

University of Colorado
Boulder

LLNL-PRES-805199

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Lawrence Livermore National Laboratory

What is Volumetric 3D Printing?

Complex 3D structures in a single step (without layering)

What is Volumetric 3D Printing?

- VAM = volumetric AM: the entire part is the unit operation

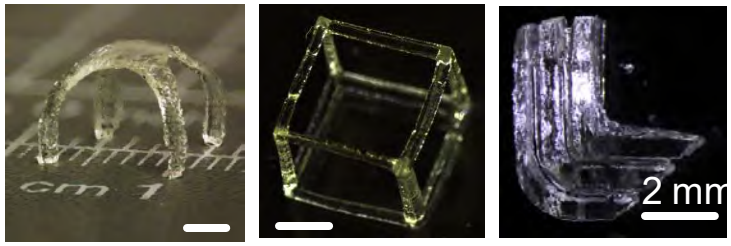
SCIENCE ADVANCES | RESEARCH ARTICLE

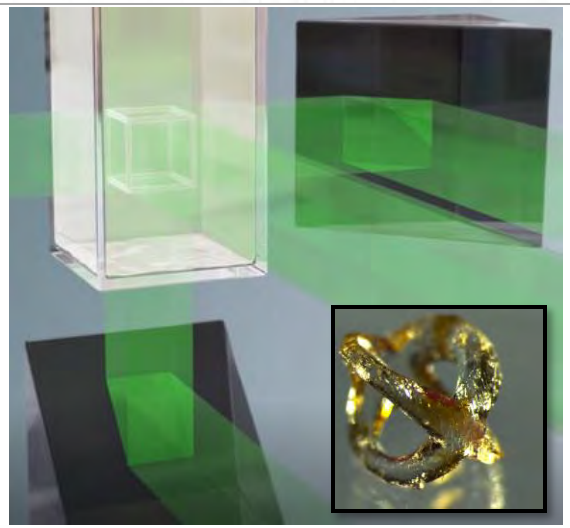
MATERIALS SCIENCE Shusteff *et al*, *Sci Advances* **3** (12) Dec **2017**.

One-step volumetric additive manufacturing of complex polymer structures

Maxim Shusteff,[1,2]* Allison E. M. Browar,[1,3] Brett E. Kelly,[1,4] Johannes Henriksson,[1,5] Todd H. Weisgraber,[1] Robert M. Panas,[1] Nicholas X. Fang,[6]* Christopher M. Spadaccini[1]*

1. First attempt: orthogonal overlapped illumination patterns
   - Simultaneous from multiple directions
   - Implemented using holographic image projection





2. CAL = computed axial lithography (a.k.a. tomographic VAM)
   - Sequential illumination from many angles inspired by CT imaging

3D PRINTING Kelly *et al*, *Science* **363** (6431), Jan **2019**, p.1075.

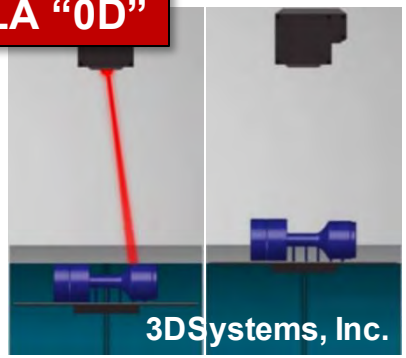
Volumetric additive manufacturing via tomographic reconstruction

Brett E. Kelly[1,2]*, Indrasen Bhattacharya[3]*, Hossein Heidari[1]*, Maxim Shusteff[2], Christopher M. Spadaccini[4], Hayden K. Taylor[1]†

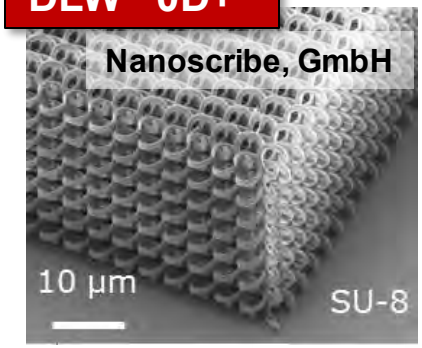
Why is Volumetric AM Necessary?

- Traditional AM approaches have required **serial repetition** of **low-dimensional** unit operations

SLA "0D"

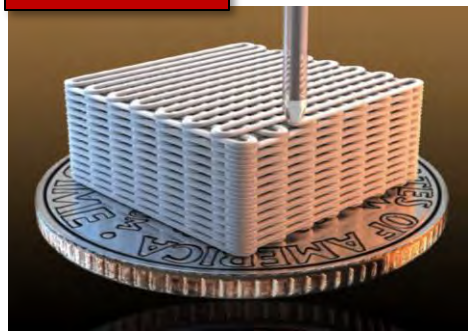


DLW "0D+"

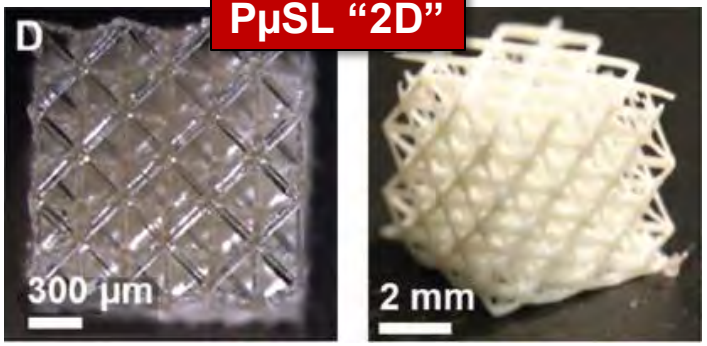


FFF/FDM "1D"

DIW "1D"



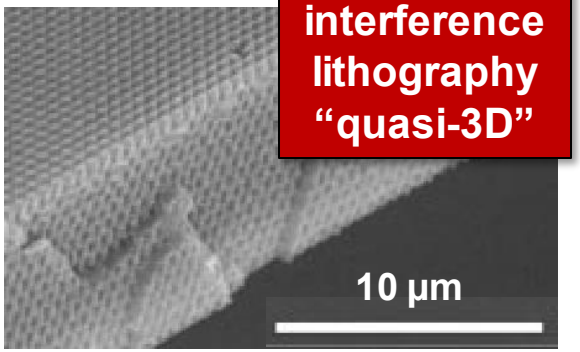
PµSL "2D"



Zheng *et al*, *Science* **344**:6190, 1373 (2014)

CLIP "2D+"

interference lithography "quasi-3D"



Campbell et al, *Nature* **404** 53-56, (2000)

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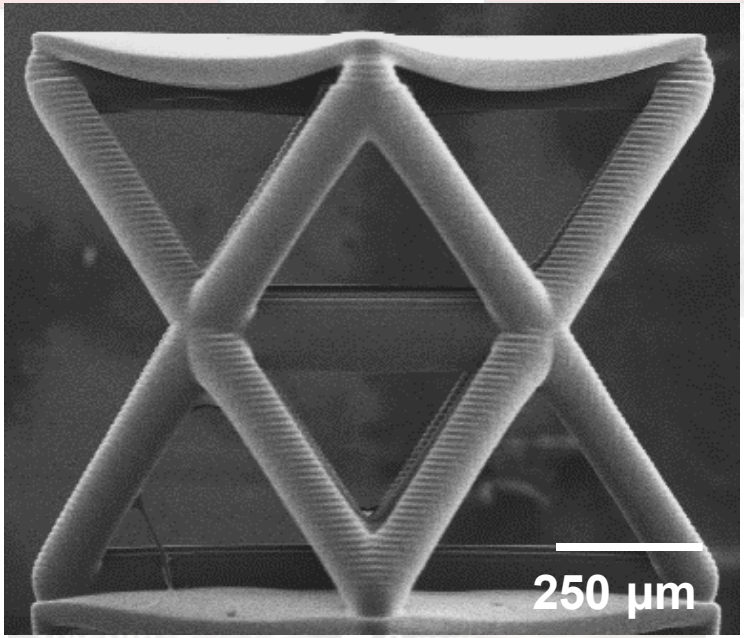
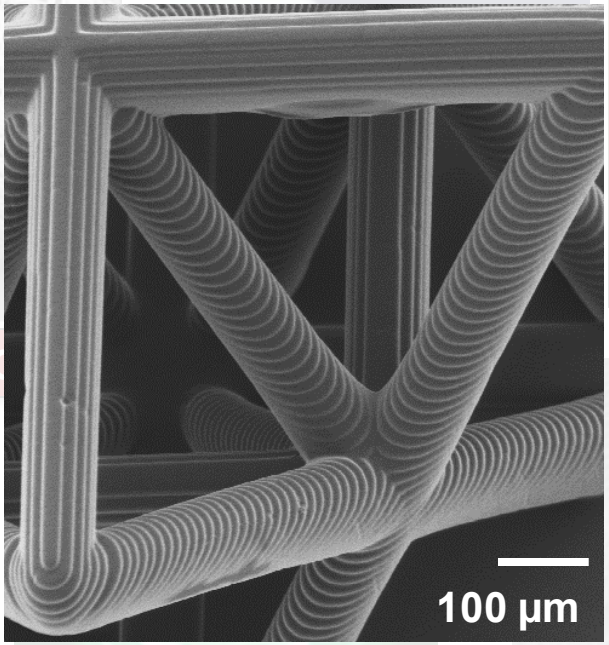
SLA "0D"

DLW "0D+"



FFF/FDM "1D"



DIW "1D"

- Speed
- Layering artifacts
- Geometric limitations

Zheng *et al*, *Science* **344**:6190, 1373 (2014)

Carbon, Inc.

Campbell et al, *Nature* **404** 53-56, (2000)

3D volume-at-once fabrication can open a completely new design space

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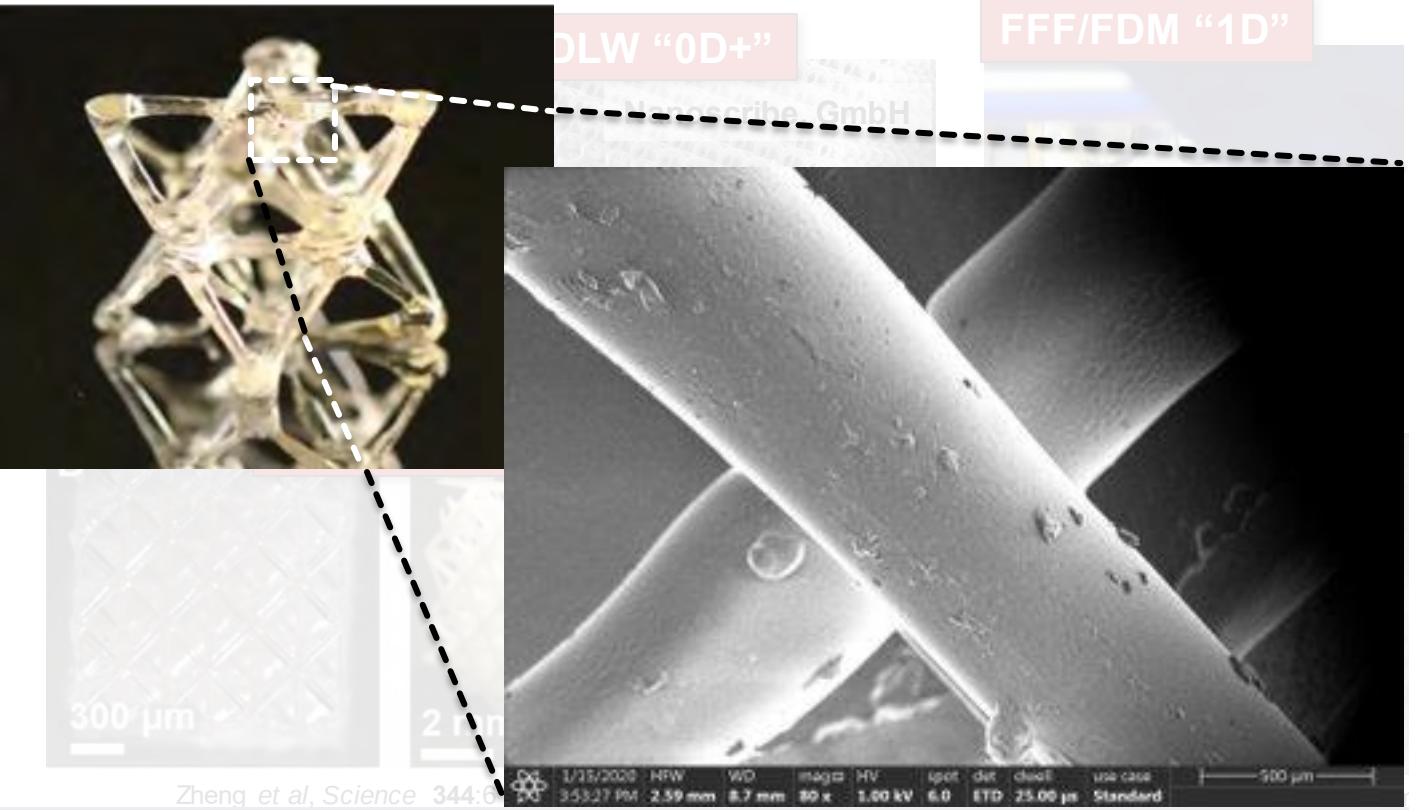


DLW "0D+"

FFF/FDM "1D"

DIW "1D"

- Speed
- Layering artifacts
- Geometric limitations

interference lithography "quasi-3D"

300 µm

2 mm

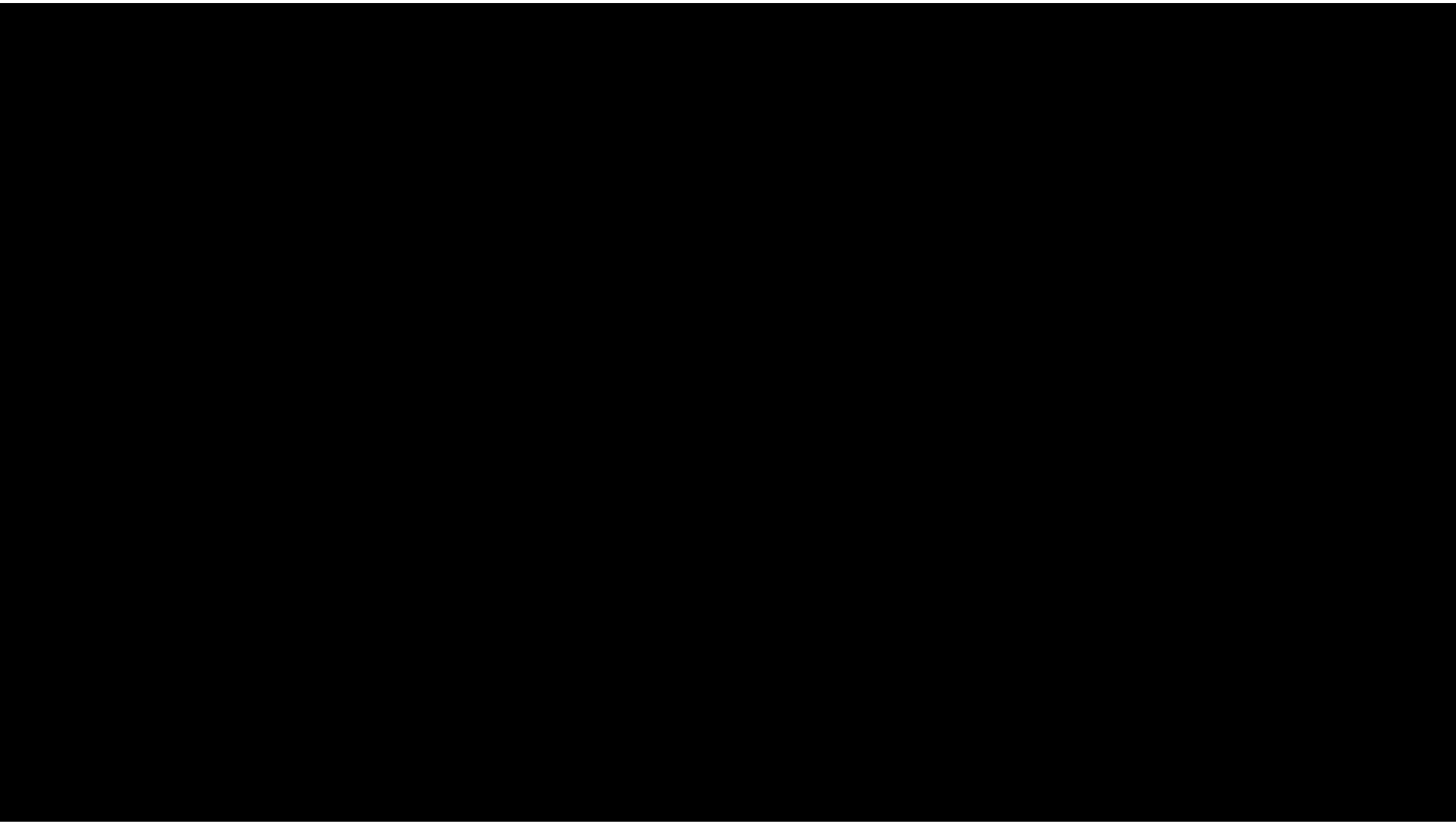
10 µm

Zheng *et al*, *Science* **344**:6

pbell et al, *Nature* **404** 53-56, (2000)

3D volume-at-once fabrication can open a completely new design space

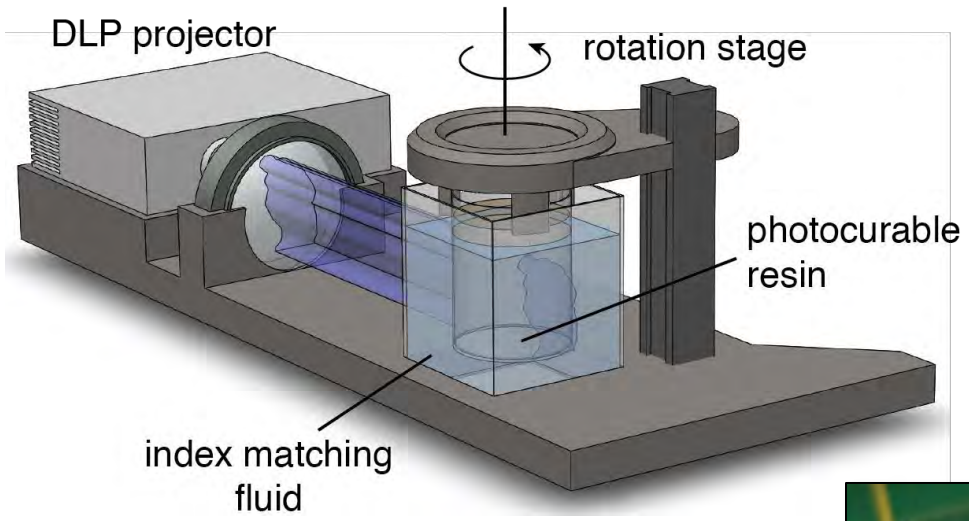
The CAL Process (Tomographic VAM)

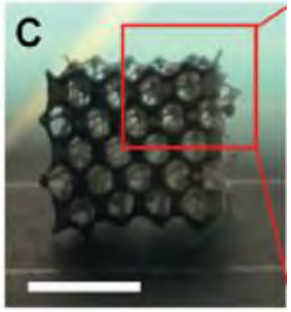


https://youtu.be/rS2P0n3_DBo

Tomographic Volumetric AM
(a.k.a. Computed Axial Lithography – CAL)

Berkeley
UNIVERSITY OF CALIFORNIA



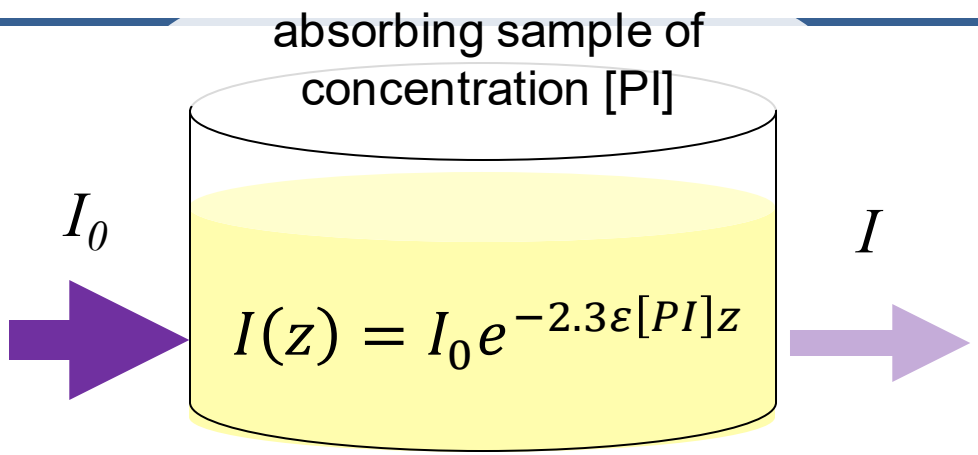


- High viscosity resin (~5000 cP)
- High transparency
- Thresholded non-linear response
- Modest power: ~10-100 mW/cm^2

CAL system is compact, low-cost, with new resin design requirements

Kelly *et al*, *Proc SFF Symposium*, **2017**, p. 938-950.
Kelly *et al*, *Science* **363**(6431), **2019,** p.1075-1079.

Beer-Lambert Absorption

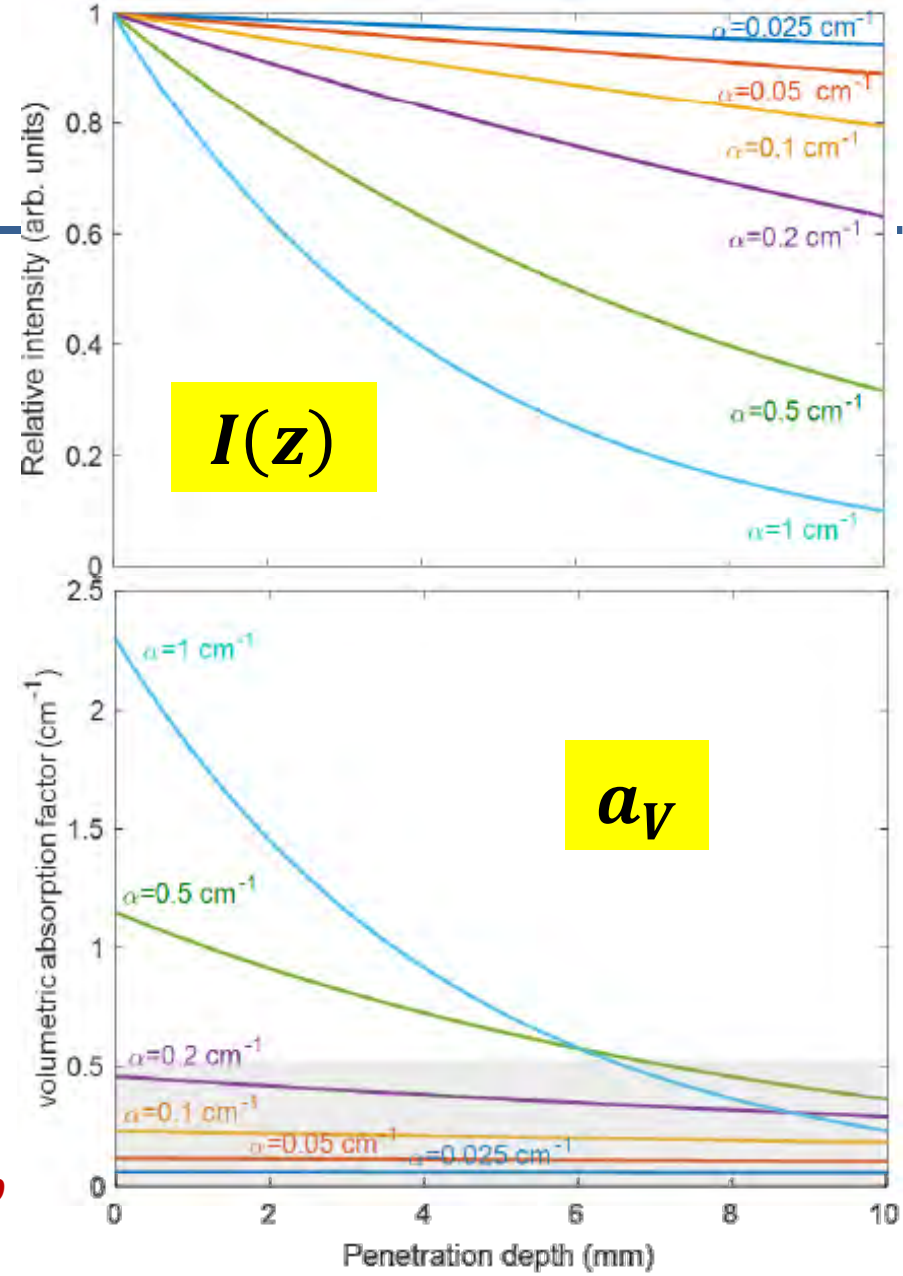


Depth coordinate z ⟶

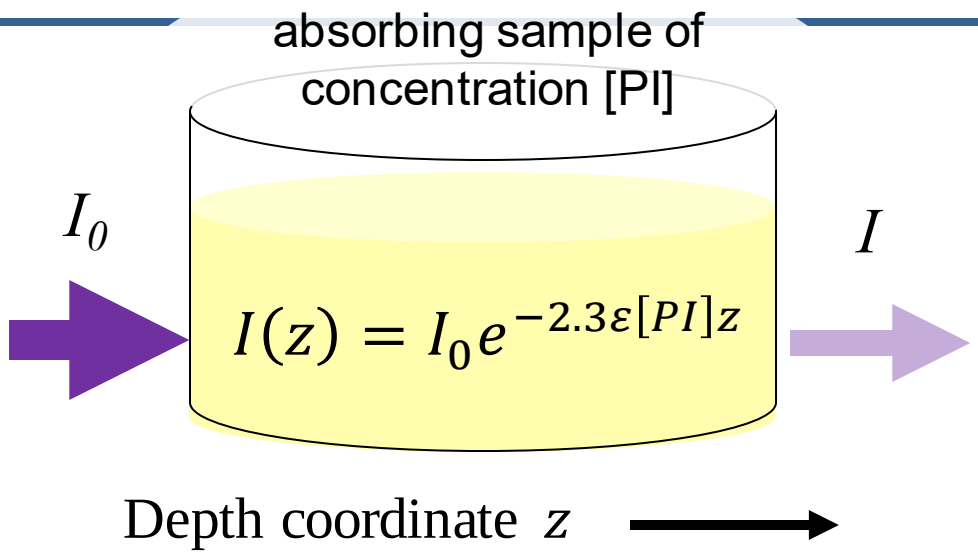
$$I(z) = I_0 e^{-\alpha z} \quad \left(= I_0 e^{-z/D_p} \right)$$

$$P_{abs}(z) = \left| \frac{dI(z)}{dz} \right| = I_0 \, \alpha e^{-\alpha z}$$

$$\boldsymbol{E_{VOL} = P_{abs}(z) t_{exp} = I_0 \underbrace{\alpha e^{-\alpha z}}_{a_V} t_{exp}}$$



Beer-Lambert Absorption



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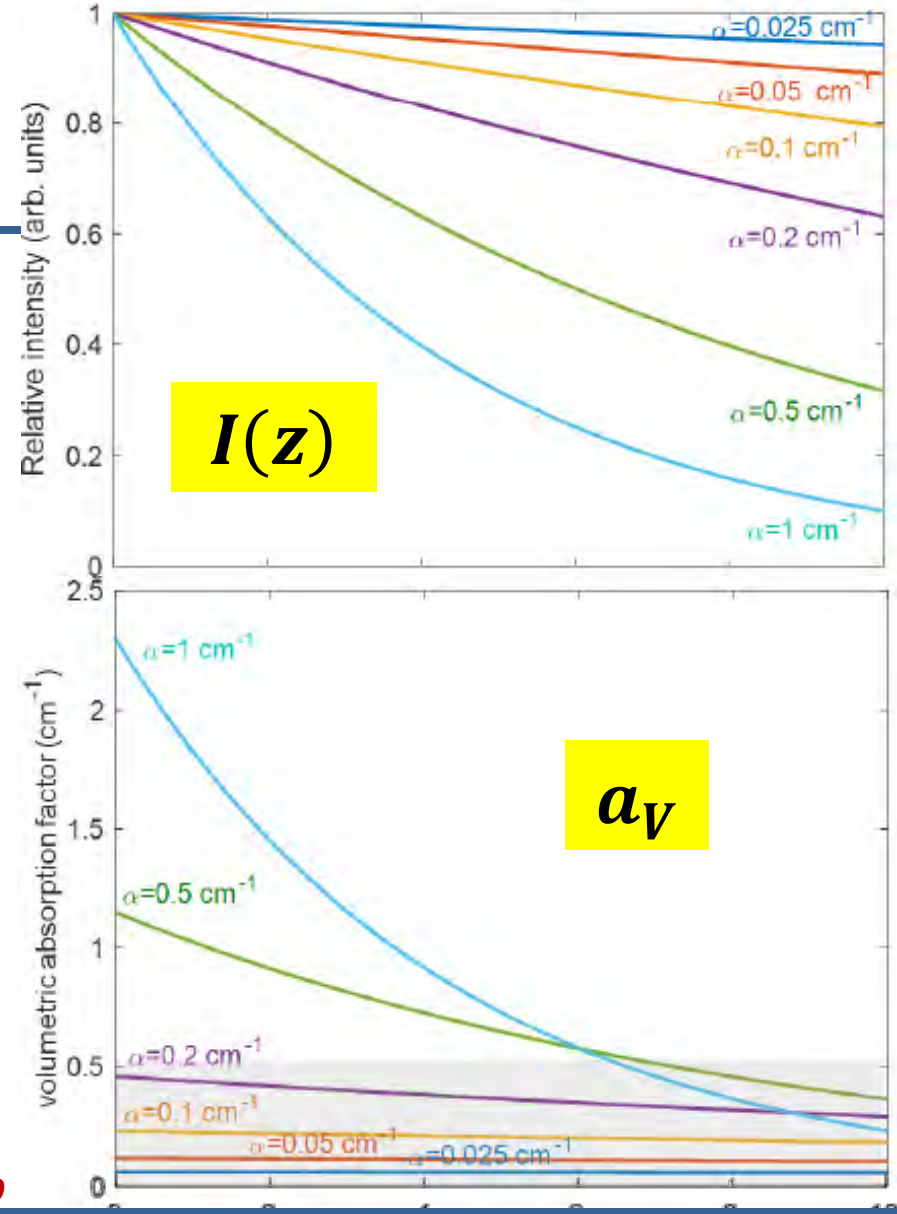
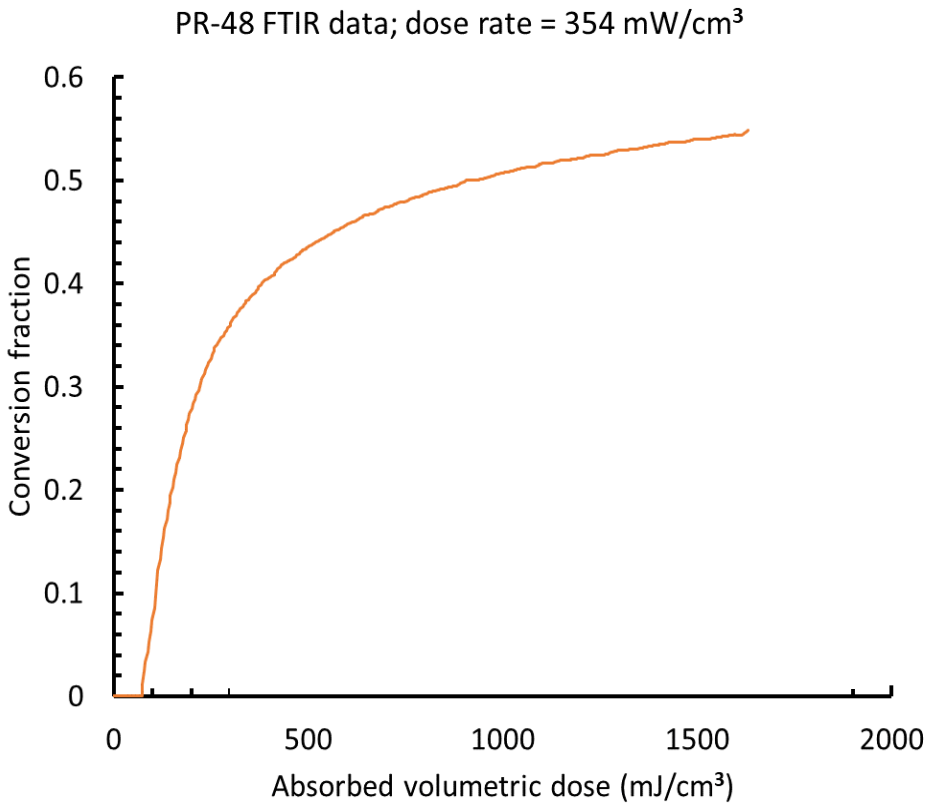


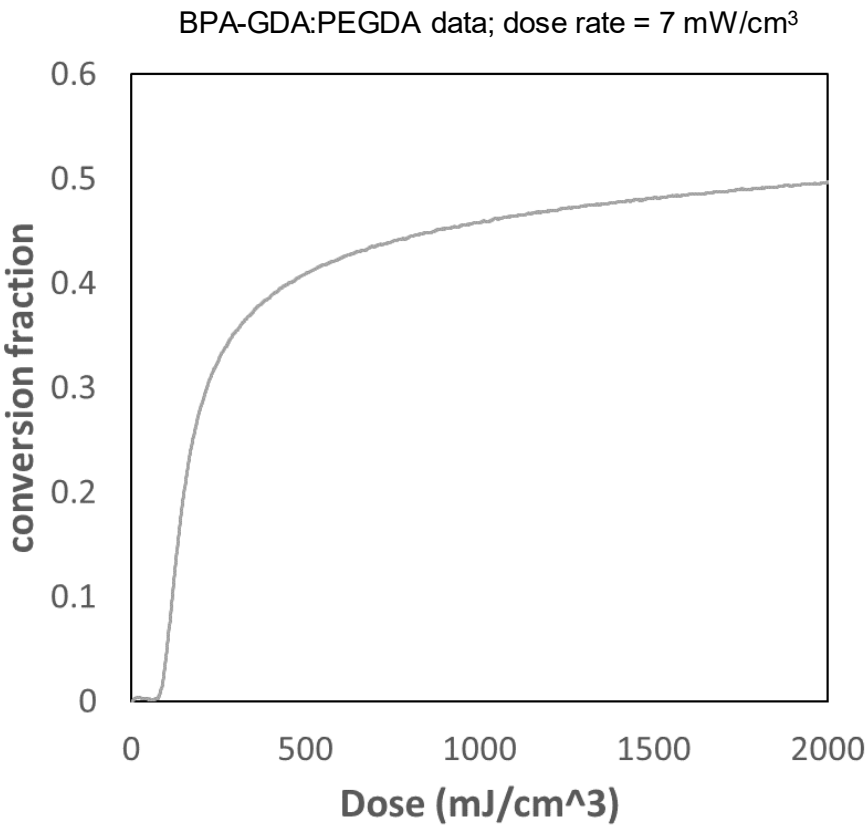
Dose (mJ cm^{-3}) is a more representative measure of energy absorbed

VAM dose rate compared to SLA

SLA resin



VAM resin



VAM dose rate compared to SLA

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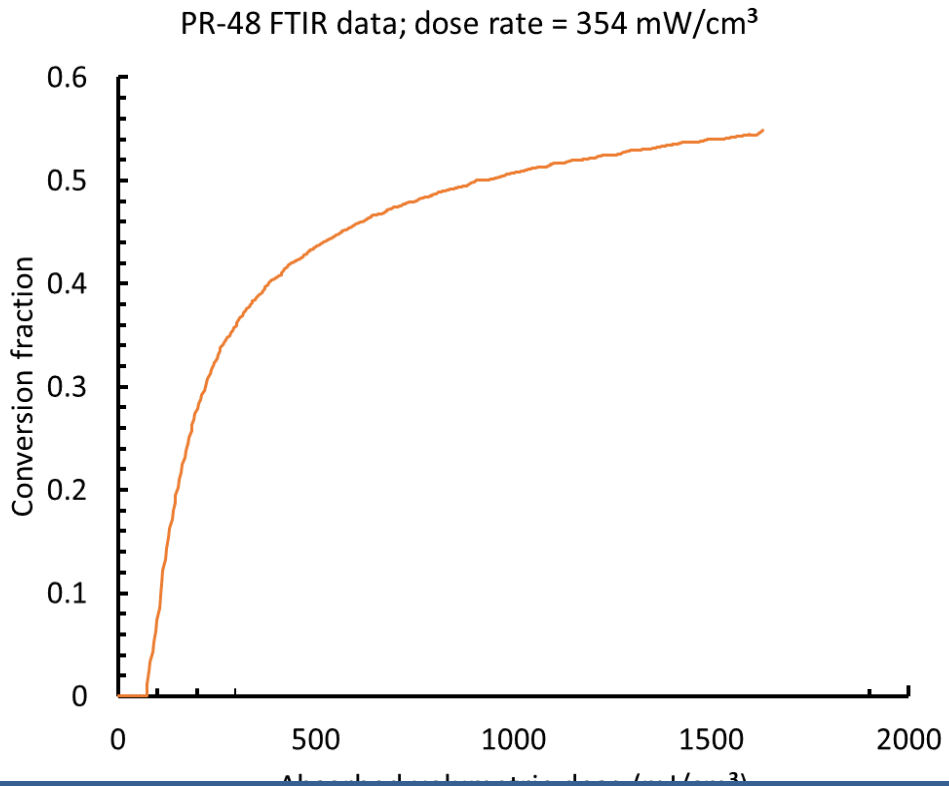
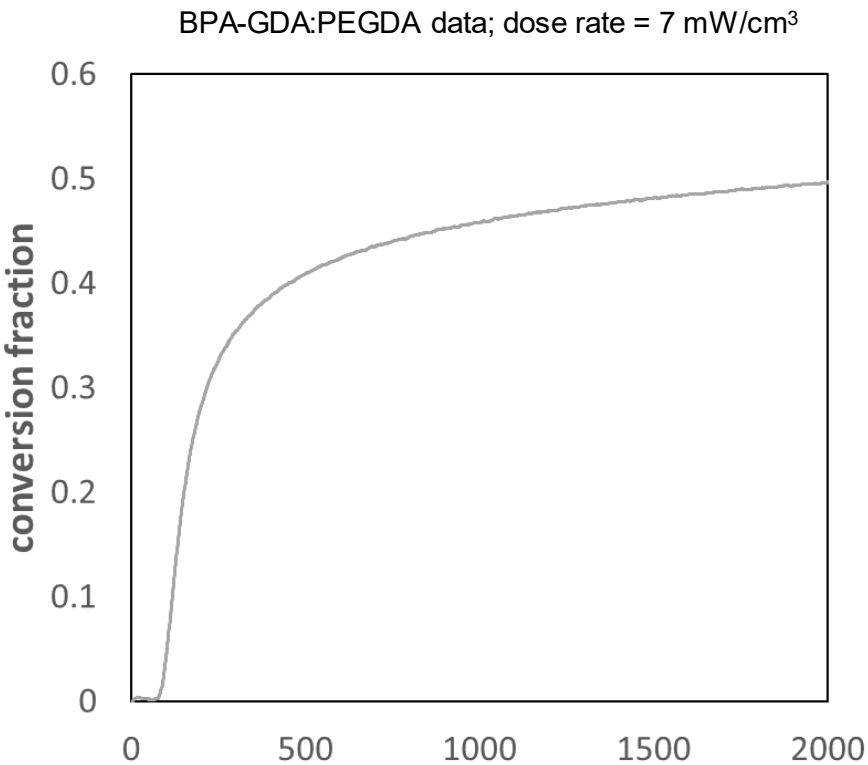


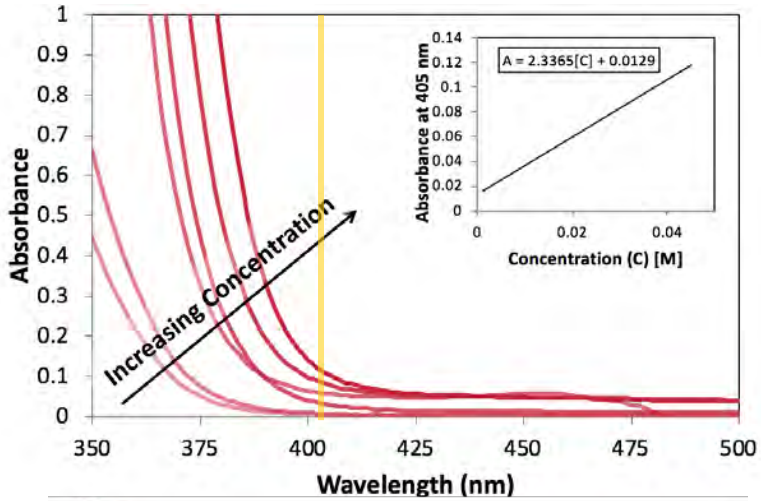
VAM resin



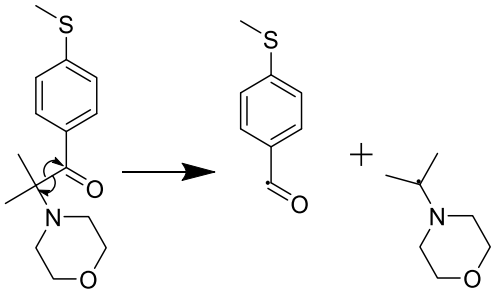
Lower dose rate (mJ cm^{-3}) required for VAM than SLA AM

High penetration depth in VAM resins

Type I

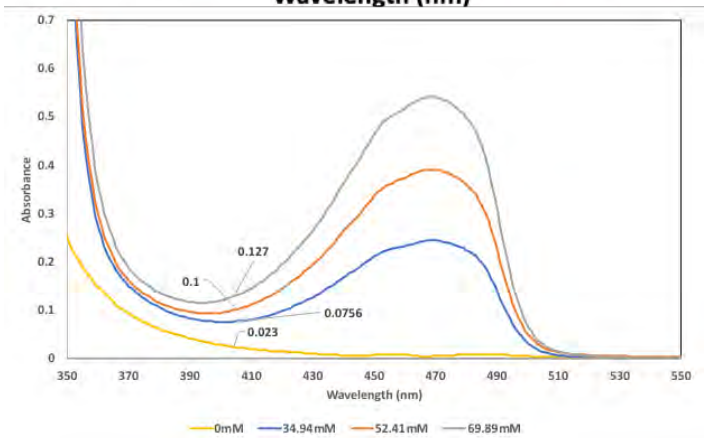


Irgacure 907

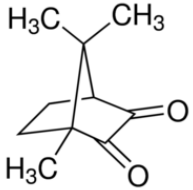


or

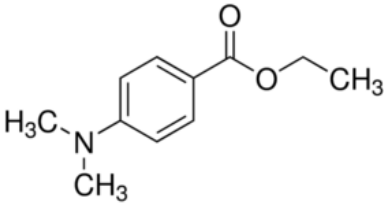
Type II



CQ-Camphorquinone

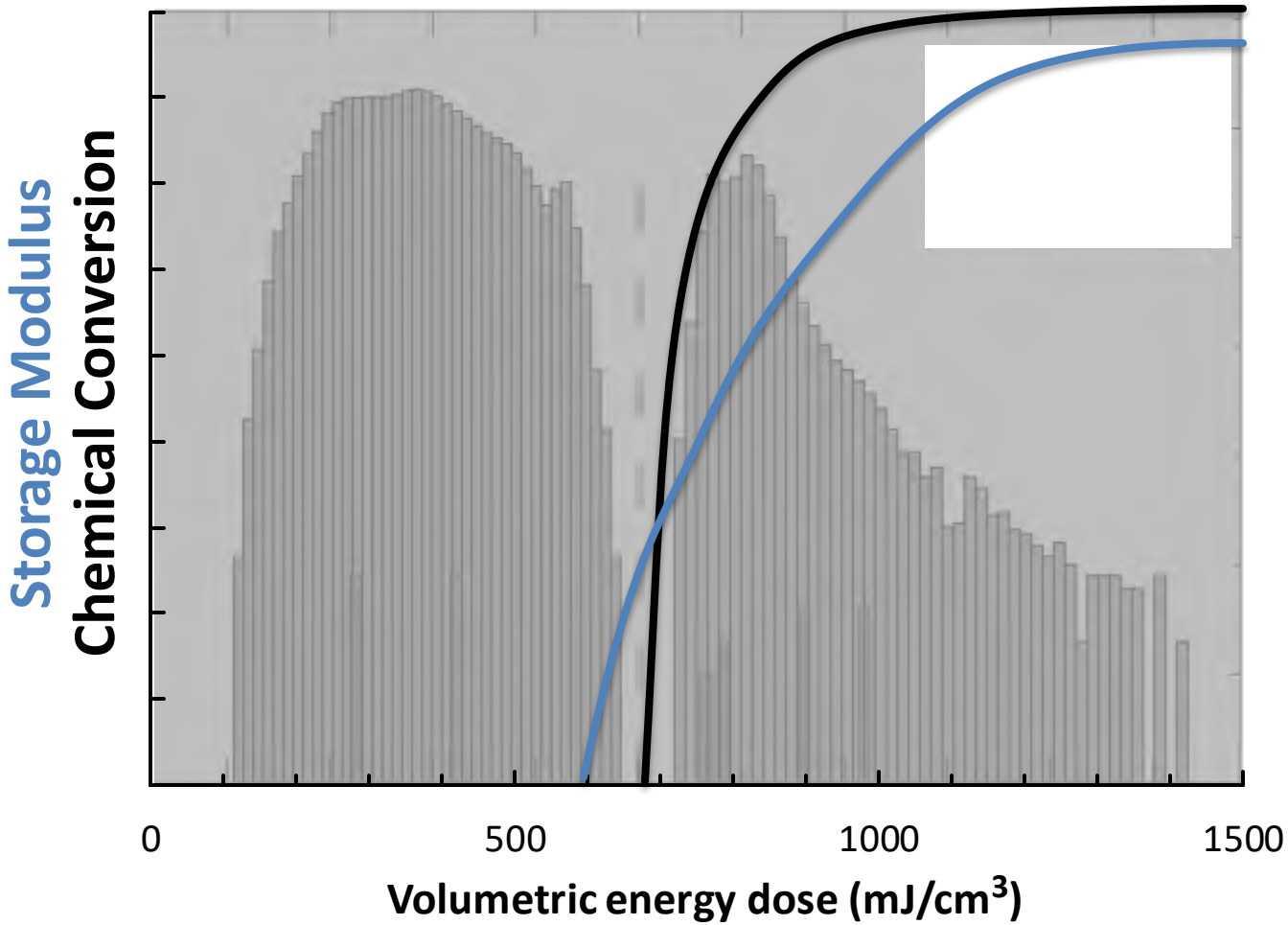


EDAB - ethyl-4-(dimethylamino)benzoate



Low absorbing photoinitiators at the projection wavelength is required

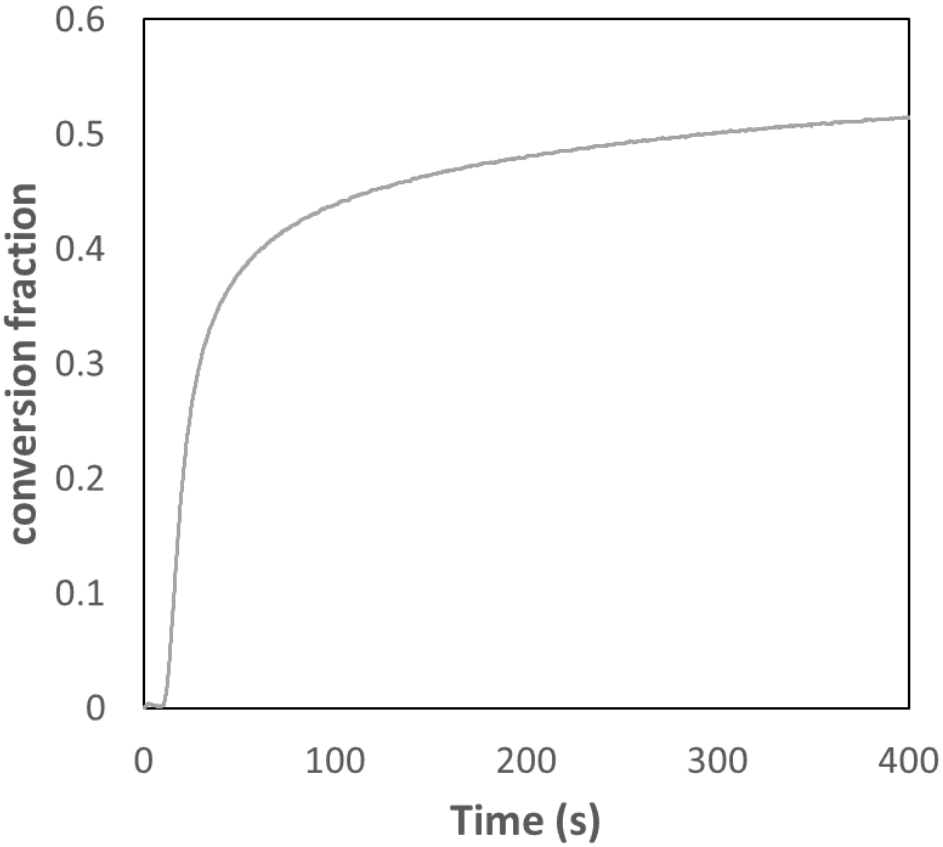
Dose Response of an Idealized Resin

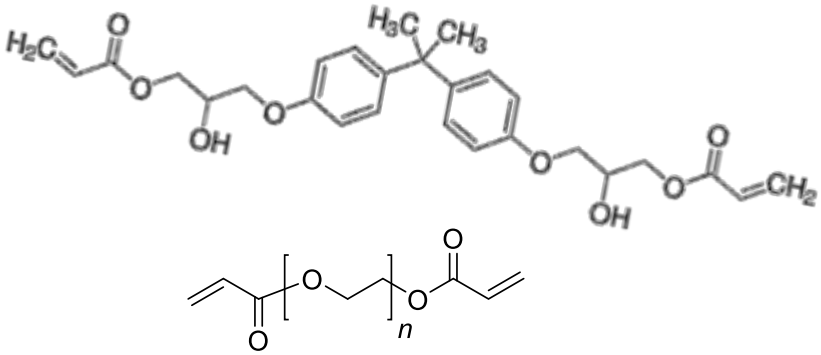


The volumetric energy dose (and the dose rate) are *the* critical parameters to control.

“Traditional” published VAM photopolymer

- Acrylated resin: 3:1 BPA-GDA:PEGDA-250 + CQ/EDAB





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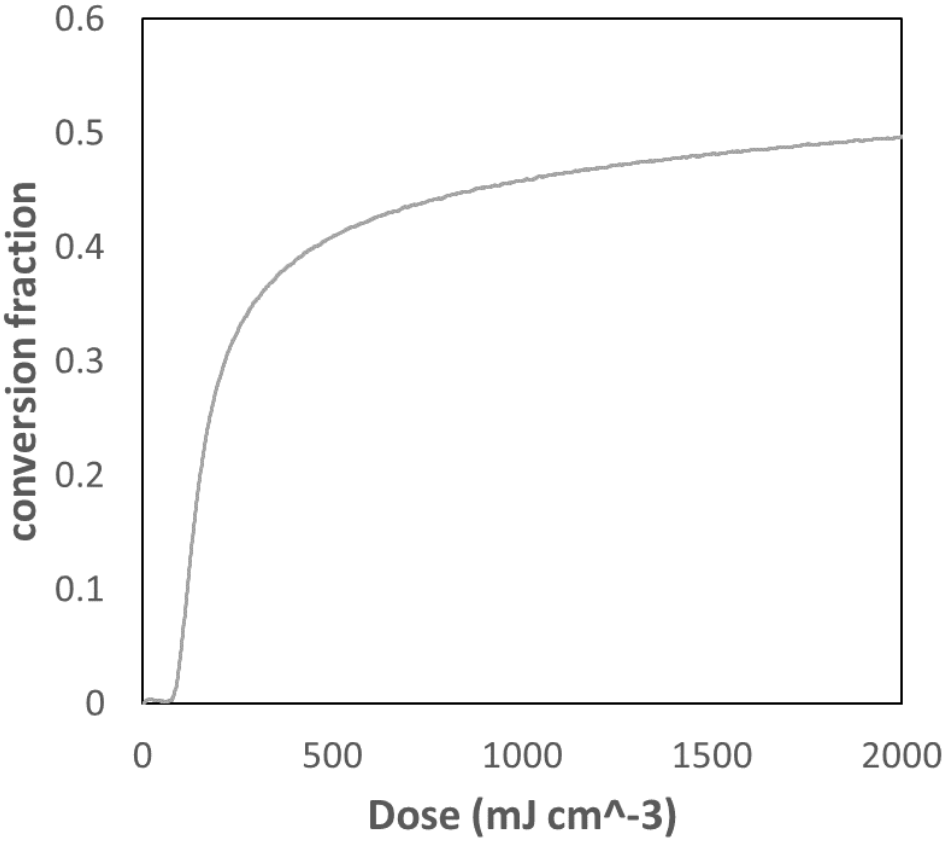

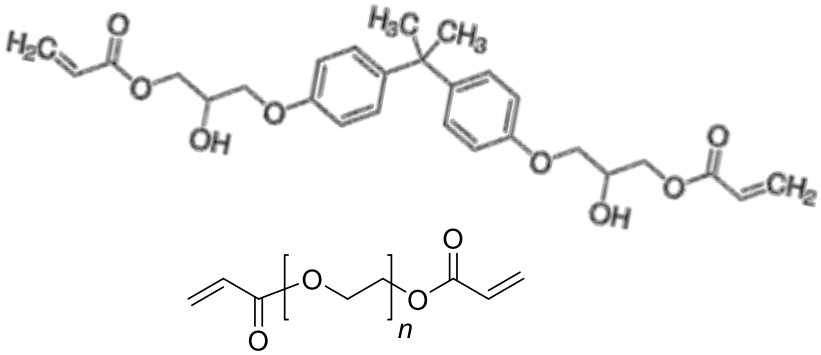

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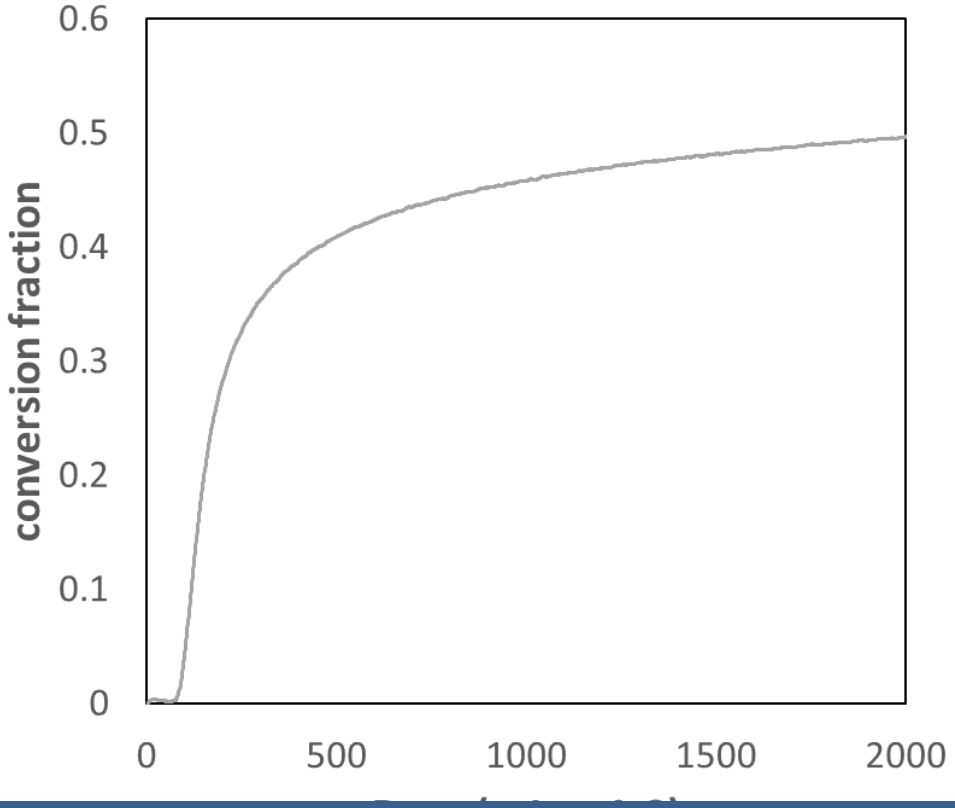
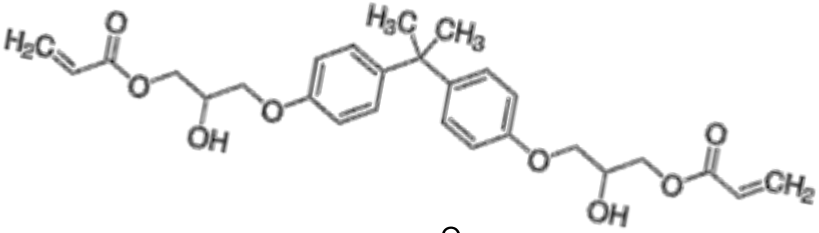
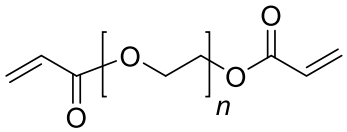
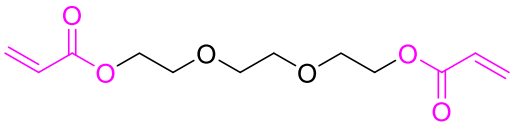




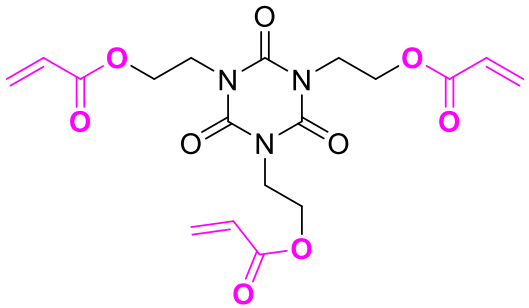


Can we increase mechanical properties from traditional acrylate photopolymers?

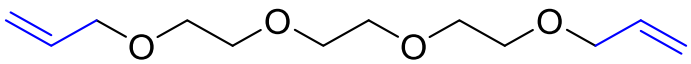
Expanding photopolymer chemistry to thiol-ene



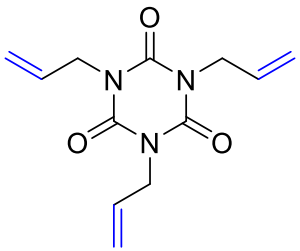
A: PEG Diacrylate



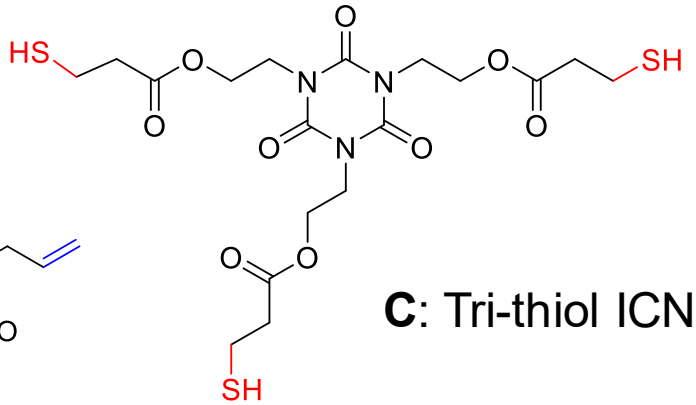
C: Tris[2-(acryloyloxy)ethyl] isocyanurate (TAEI)



A: Di-allyl "soft segment"



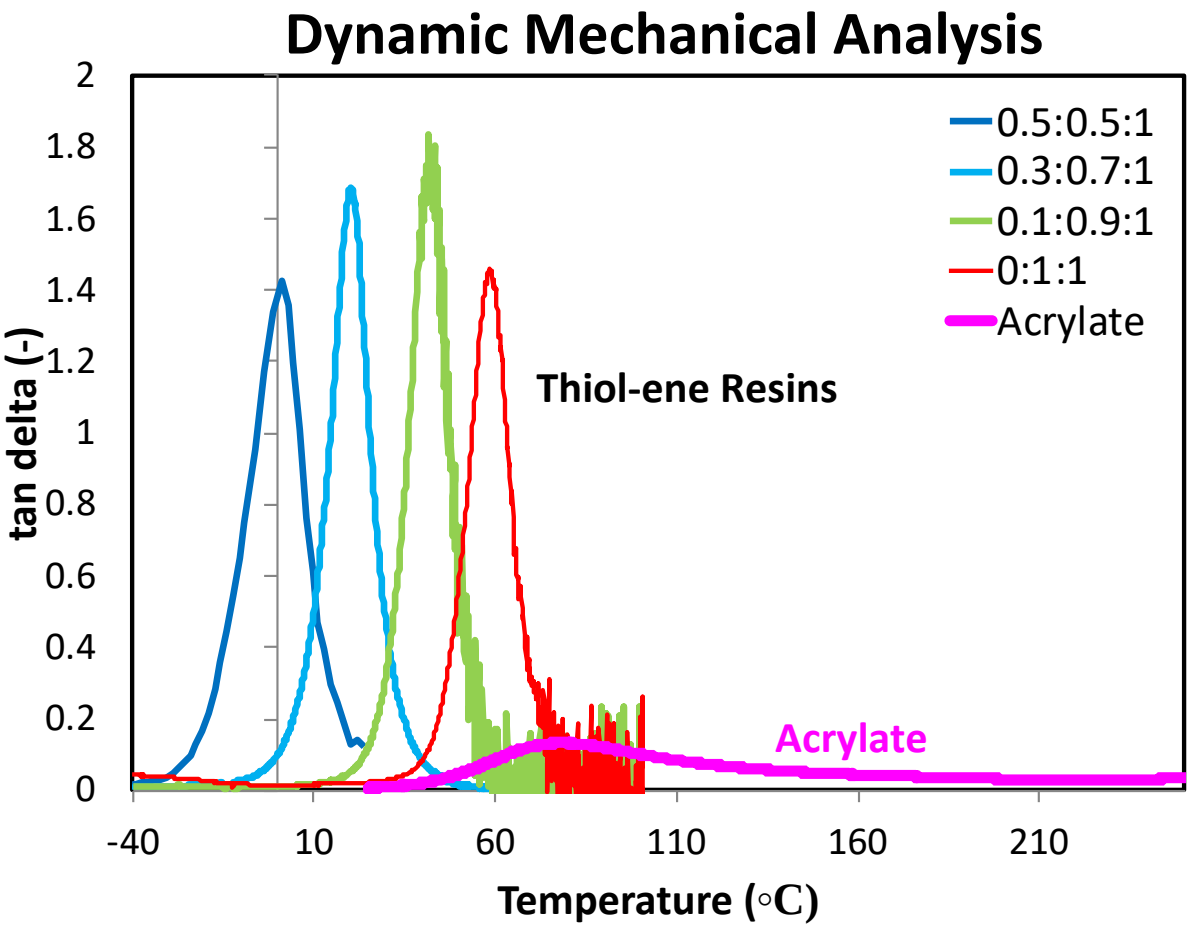
B: Tri-allyl ICN "rigid segment"



C: Tri-thiol ICN

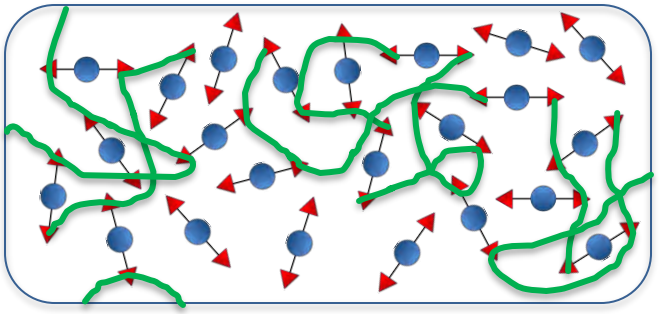
Comparing chain-growth vs step growth polymerizations to mechanical properties

Thiol-ene vs. acrylate network homogeneity



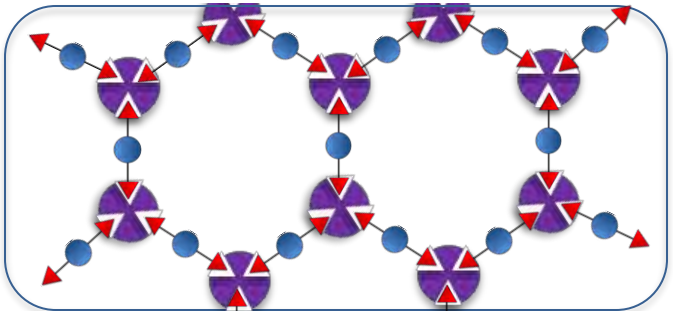
Acrylate

heterogeneous, microgel clusters

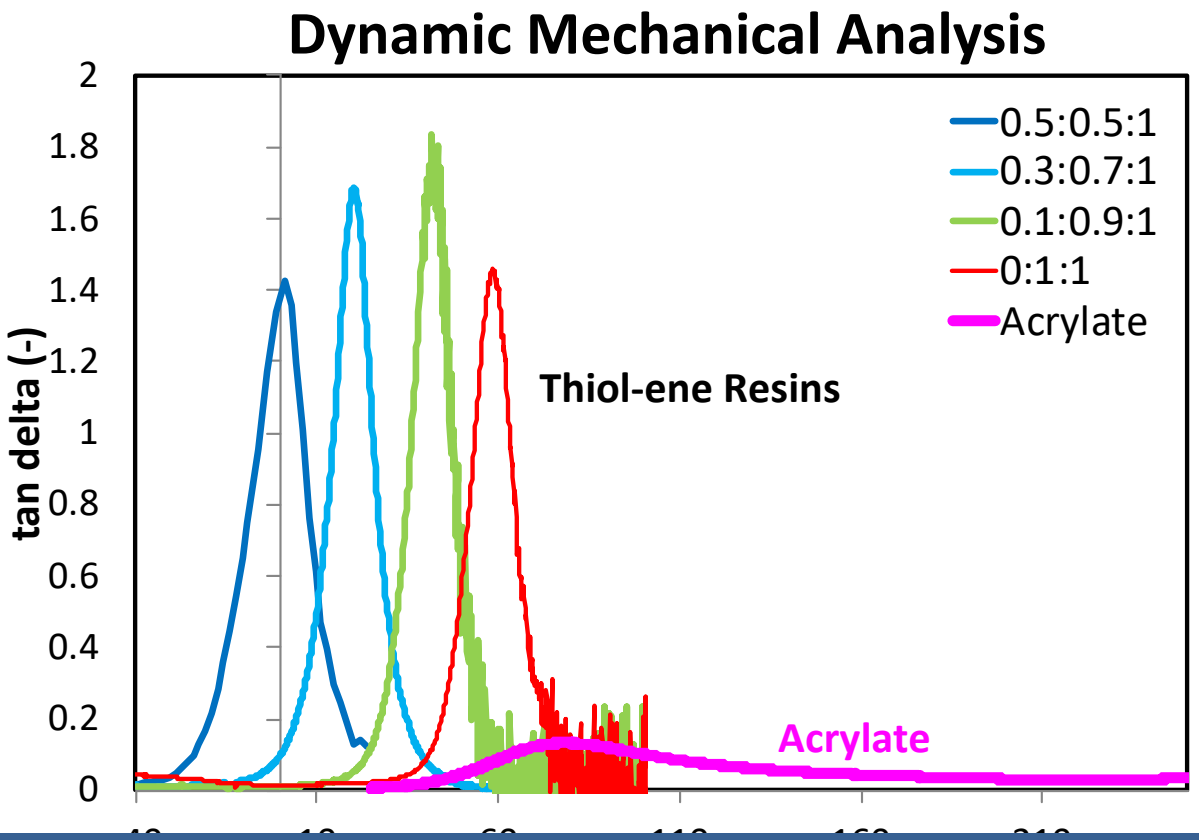


Thiol-ene

greater homogeneity



Thiol-ene vs. acrylate network homogeneity



Acrylate

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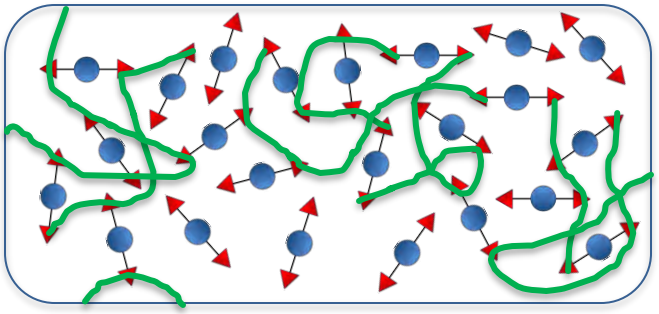
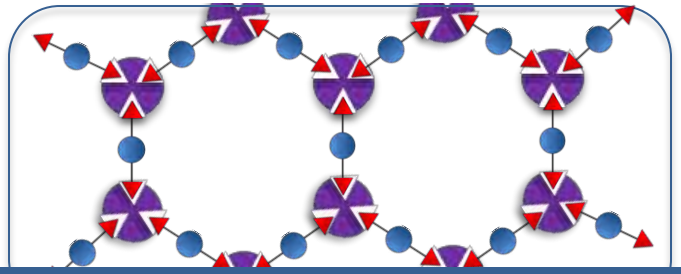


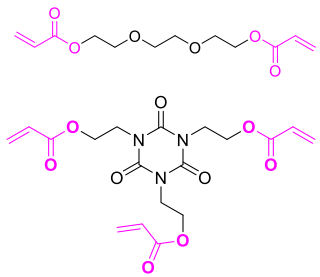
Thiol-ene

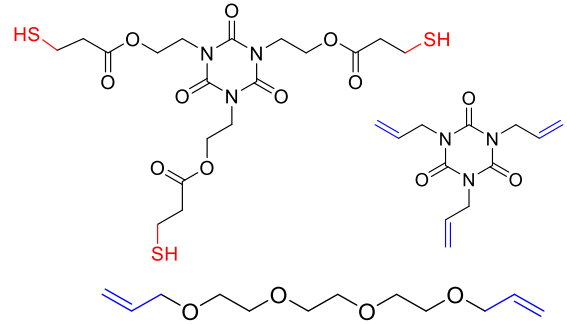
greater homogeneity

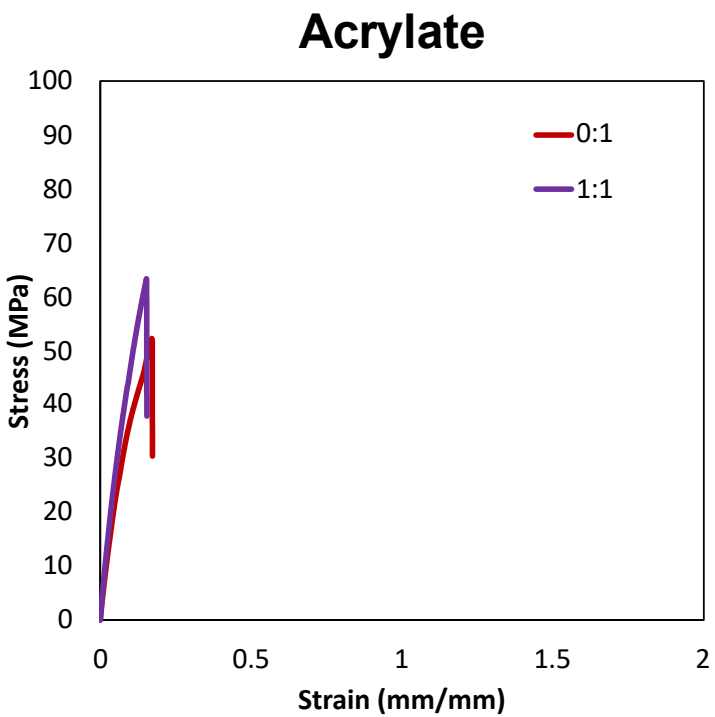


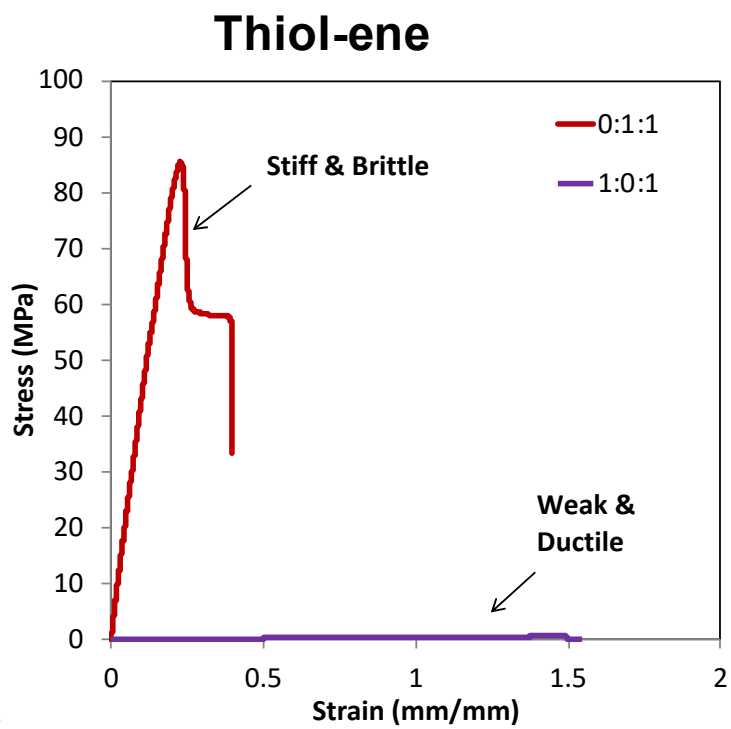
<u>Hypothesis</u>: Control of the network-level architecture through tuning of cure chemistry and cure rates will lead to more uniform tougher materials

Thiol-ene Resin Provides Tunable Range of Mechanical Properties

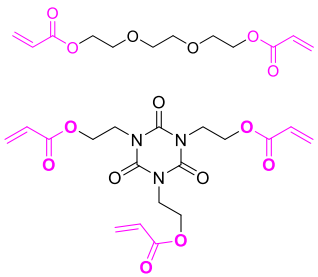


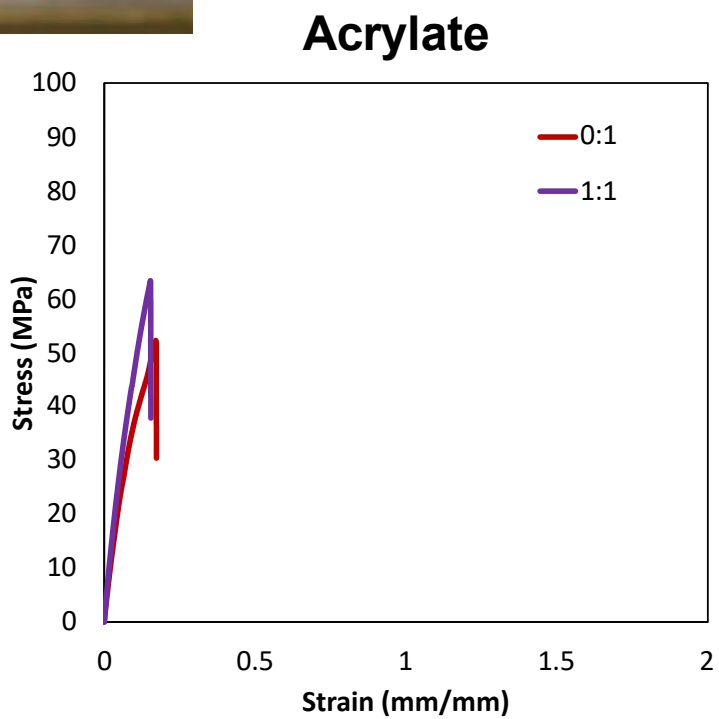


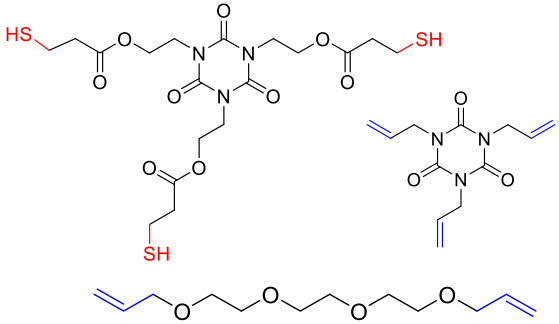


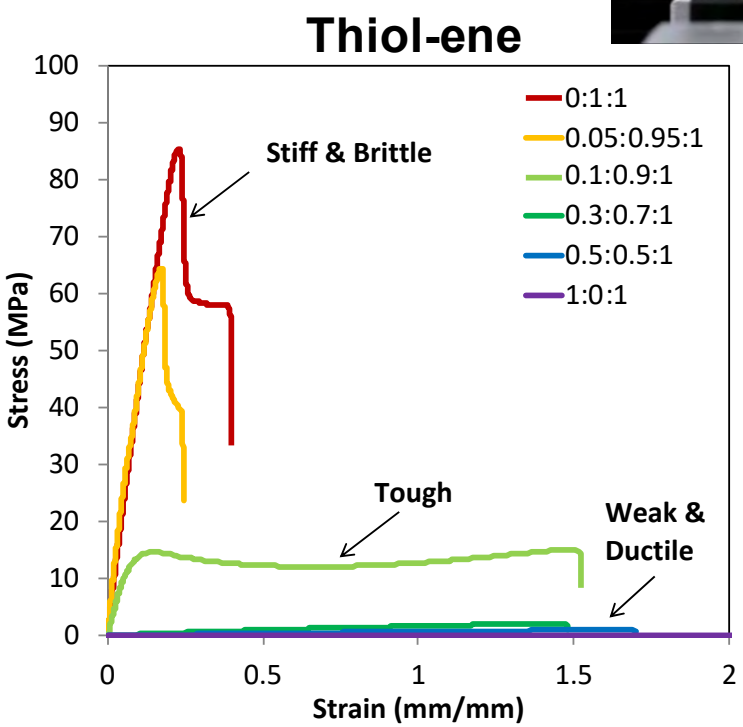


Thiol-ene Resin Provides Tunable Range of Mechanical Properties

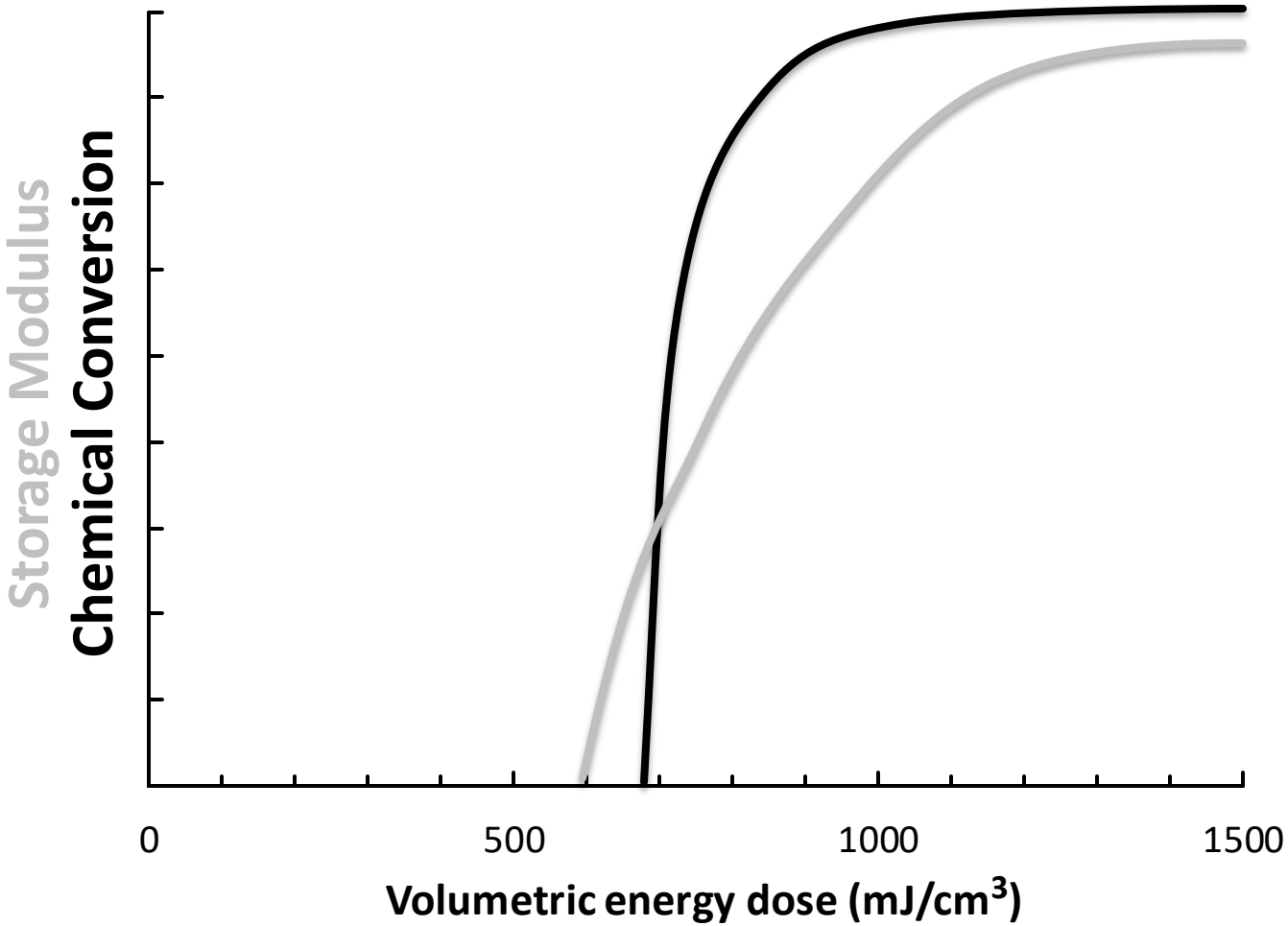






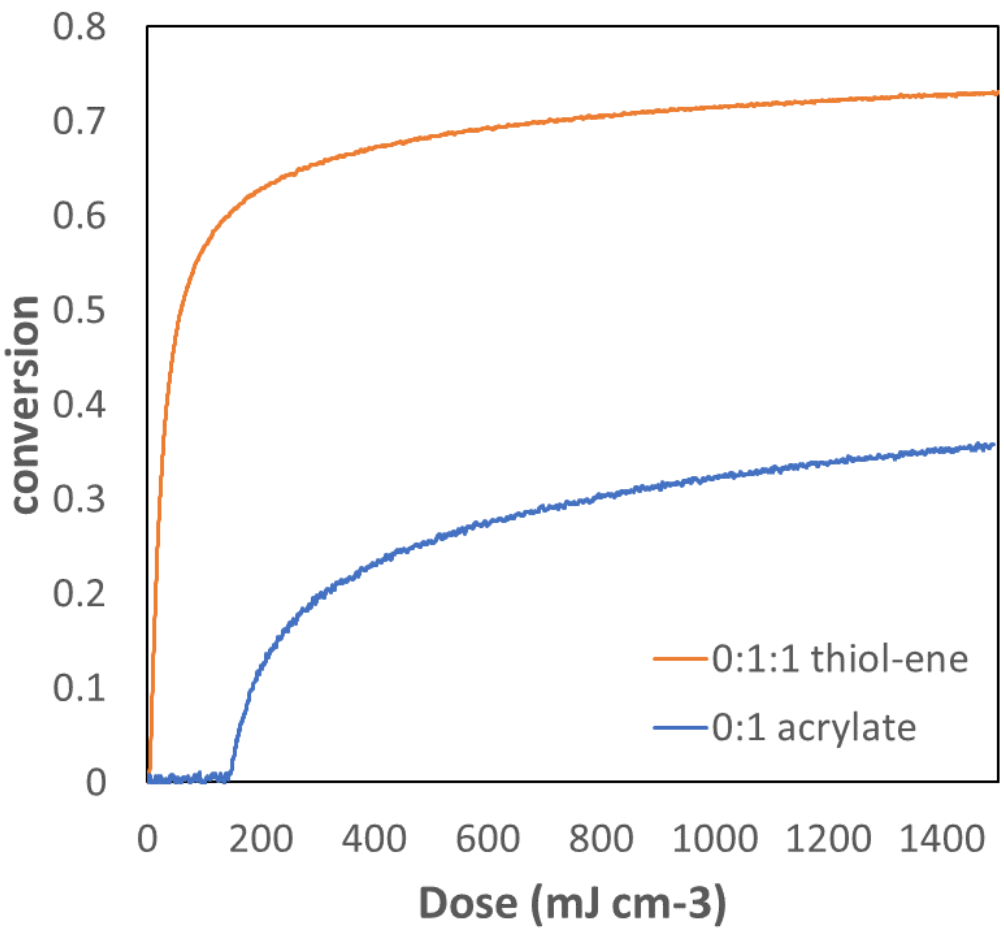


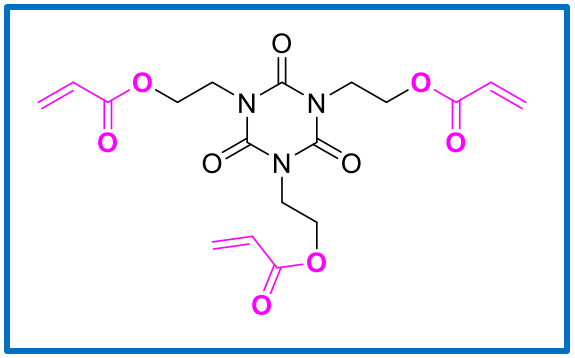
Dose Response of an Idealized Resin

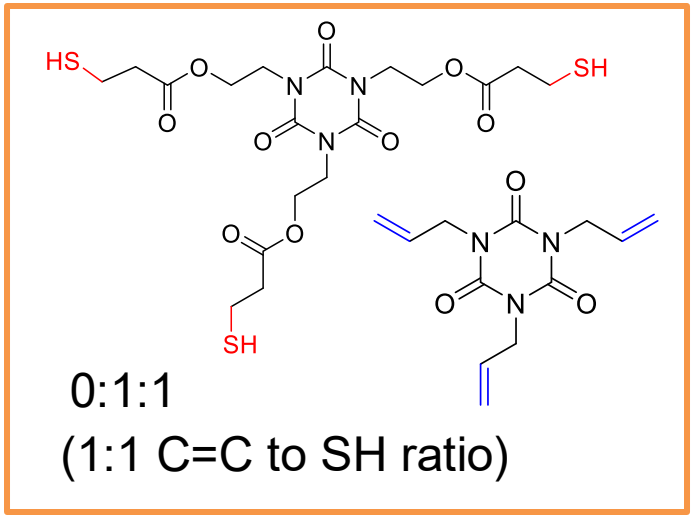


The volumetric energy dose (and the dose rate) are *the* critical parameters to control.

Thiol-ene resin vs. identical acrylated resin



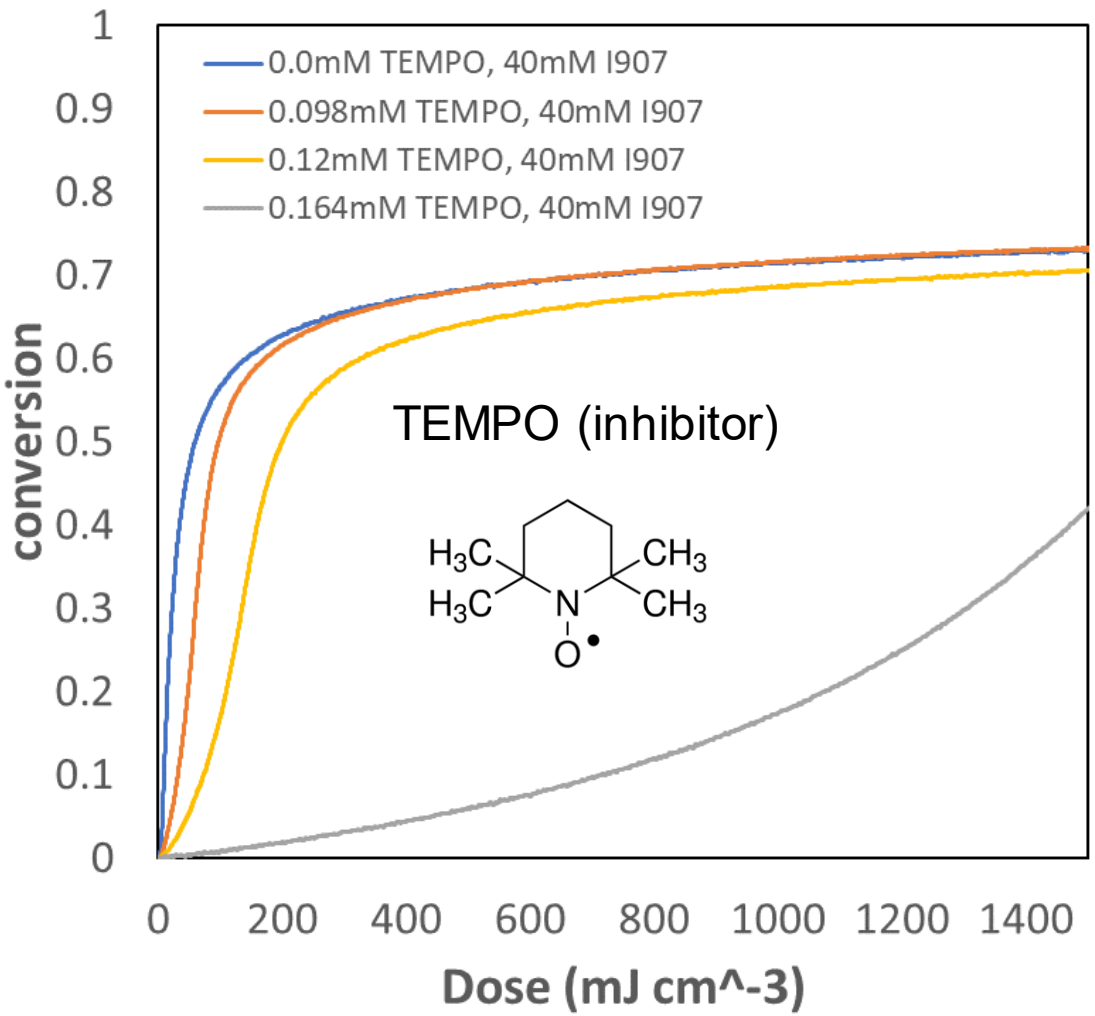




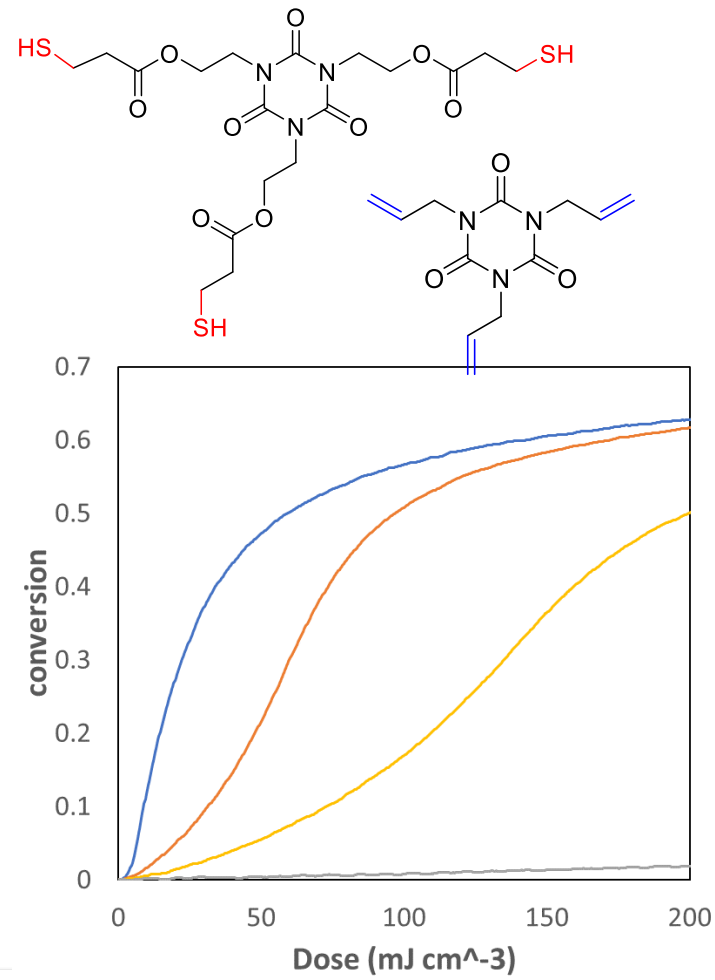
Thresholding required to use in thiol-ene without oxygen inhibition

Tuning thiol-ene resin response

Varying TEMPO inhibitor concentration

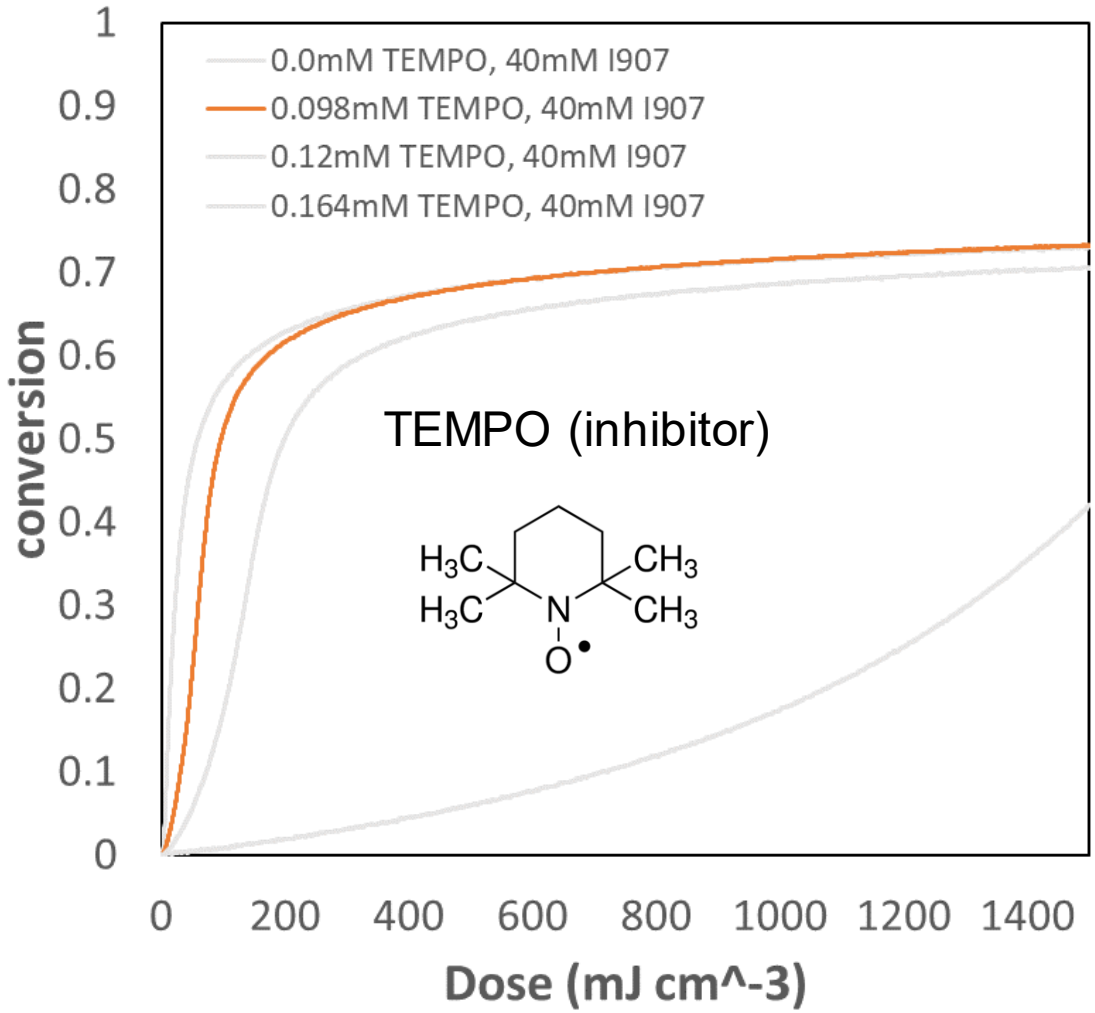


(1:1 C=C to SH ratio)

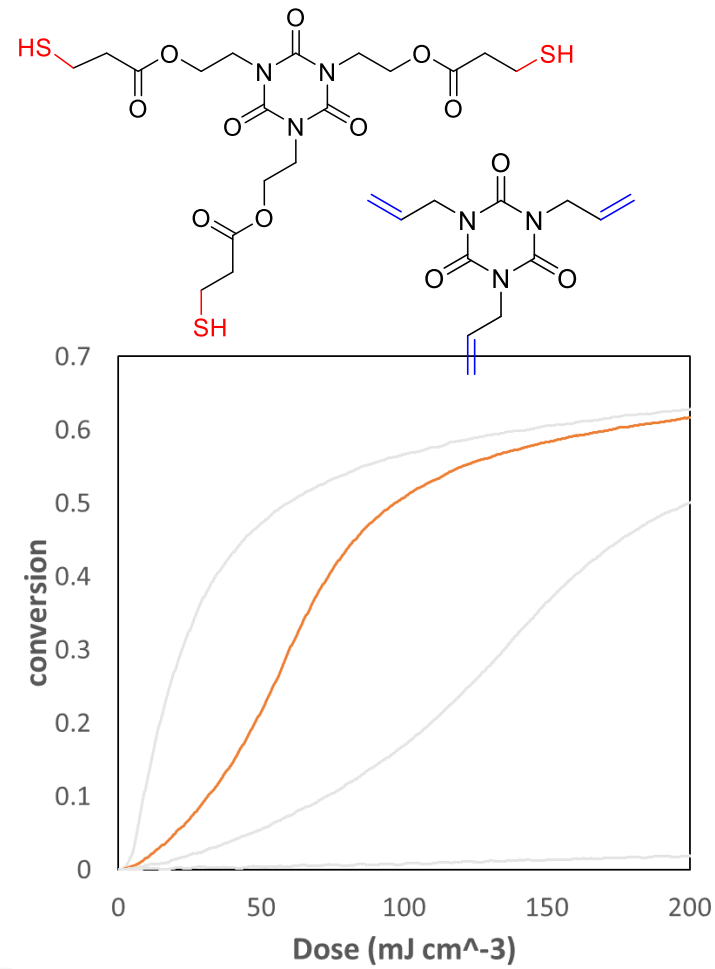


Tuning thiol-ene resin response

Varying TEMPO inhibitor concentration

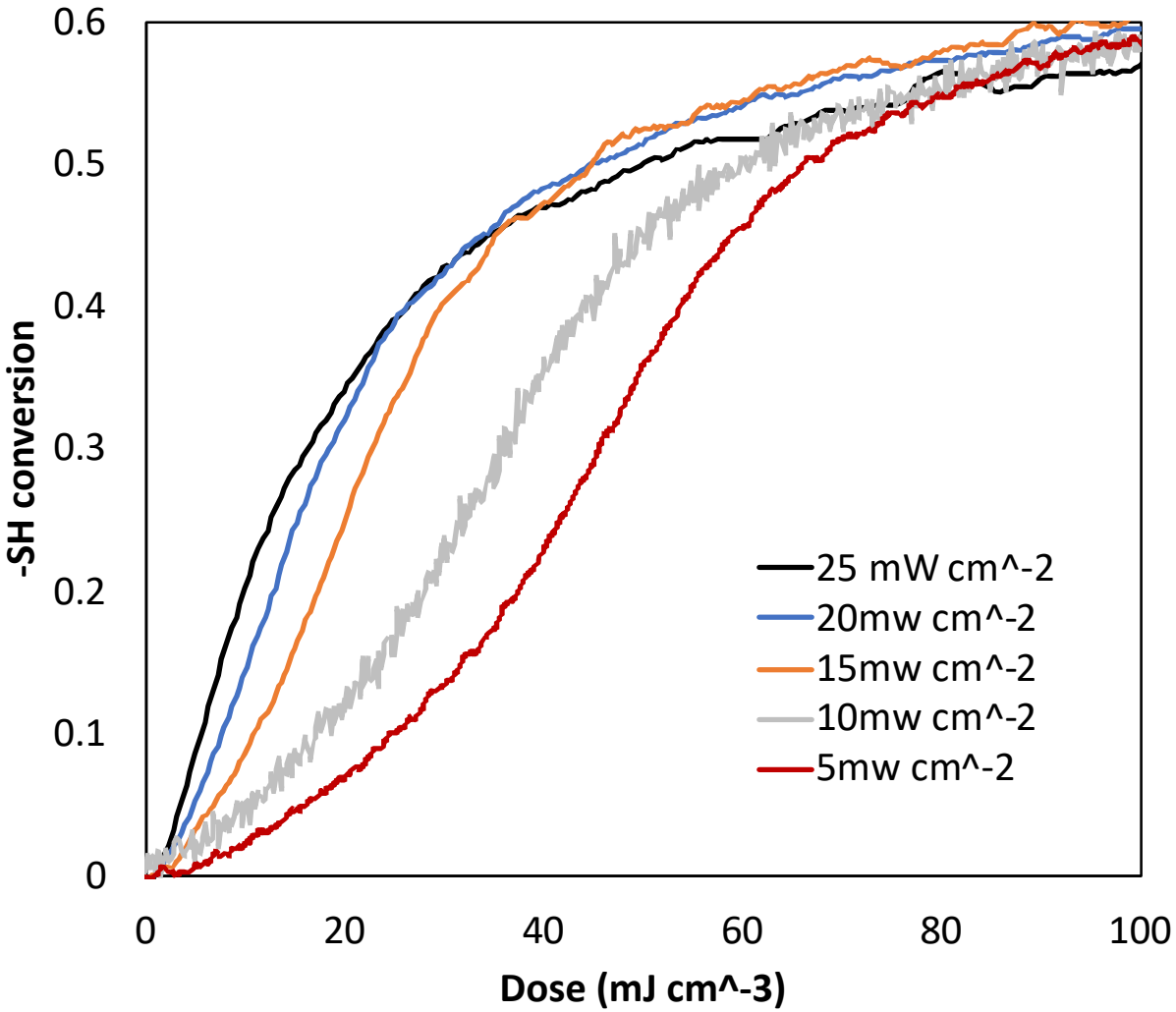


(1:1 C=C to SH ratio)

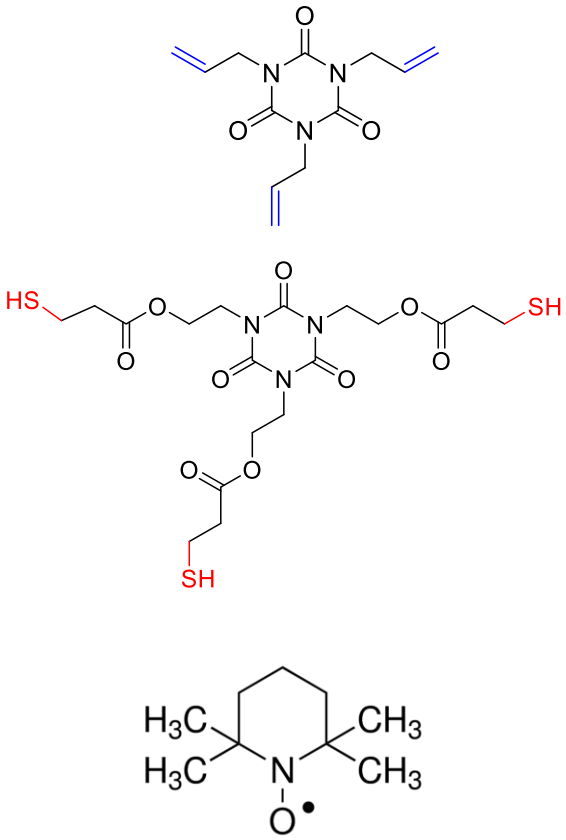


Tuning thiol-ene resin response

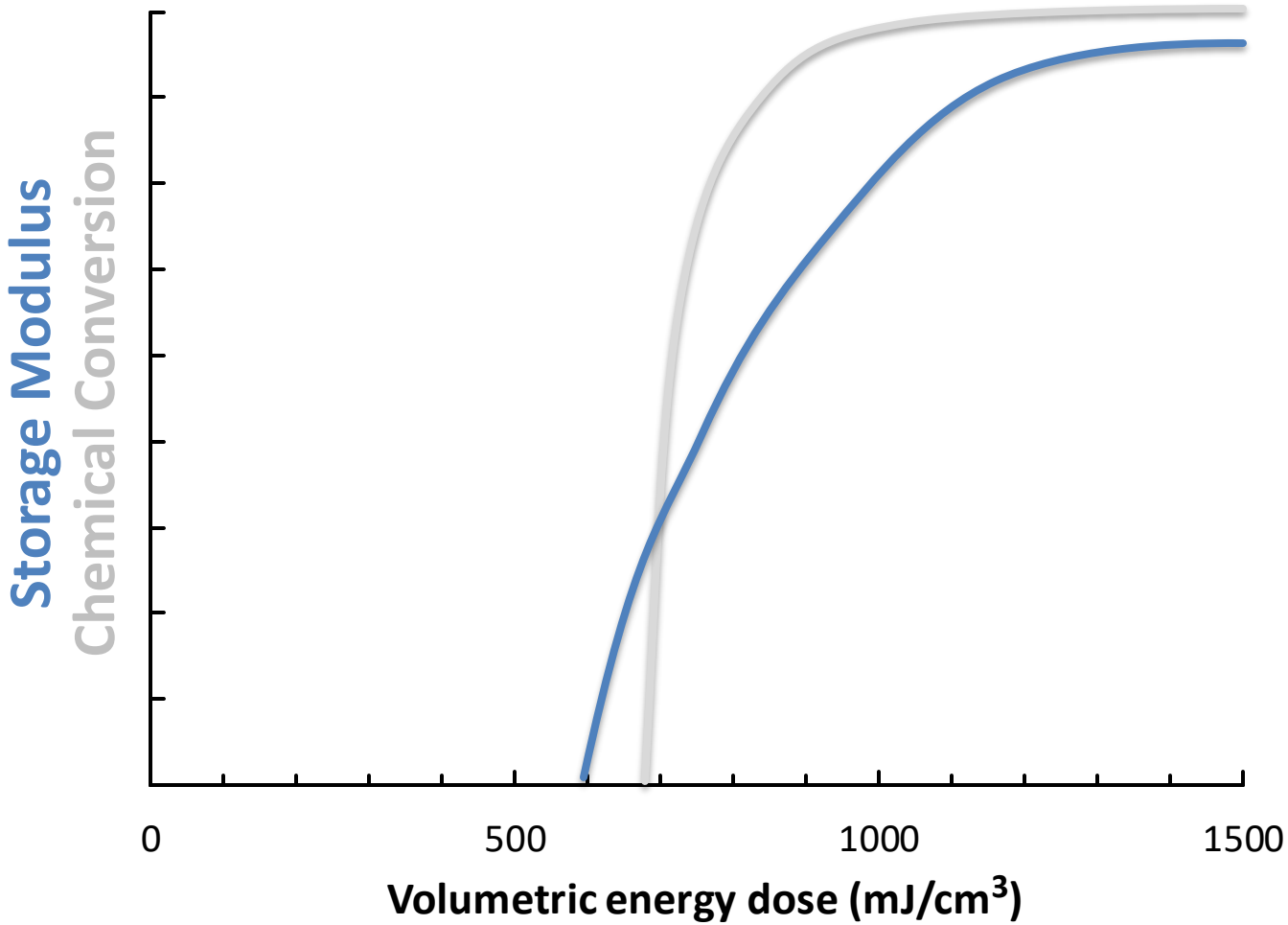
Varying light intensity across 405nm projector working range



(1:1 C=C to SH ratio)



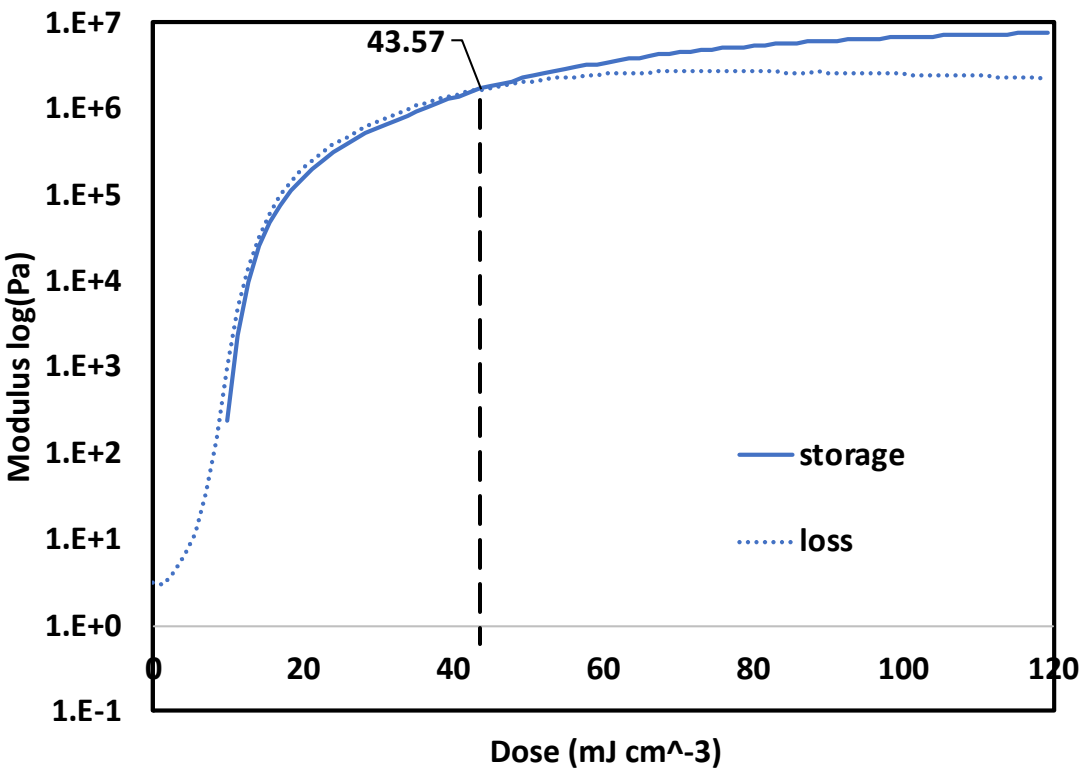
Dose Response of an Idealized Resin

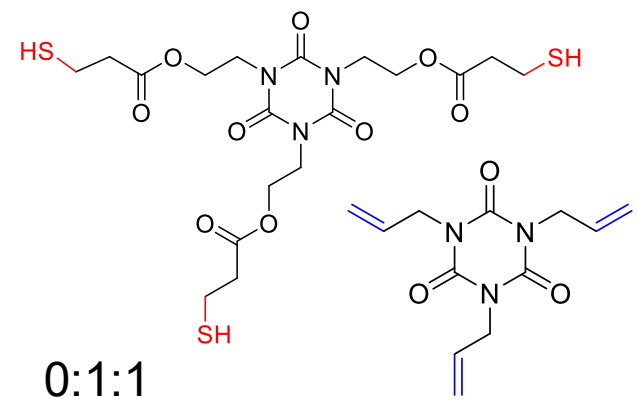


The volumetric energy dose (and the dose rate) are *the* critical parameters to control.

Oscillatory shear rheology of thiol-ene

10mW/cm^2
10mM I907
0.098mM TEMPO
Absorbance ~0.009 cm^{-1}; $a_V \approx 0.045$ cm^{-1}

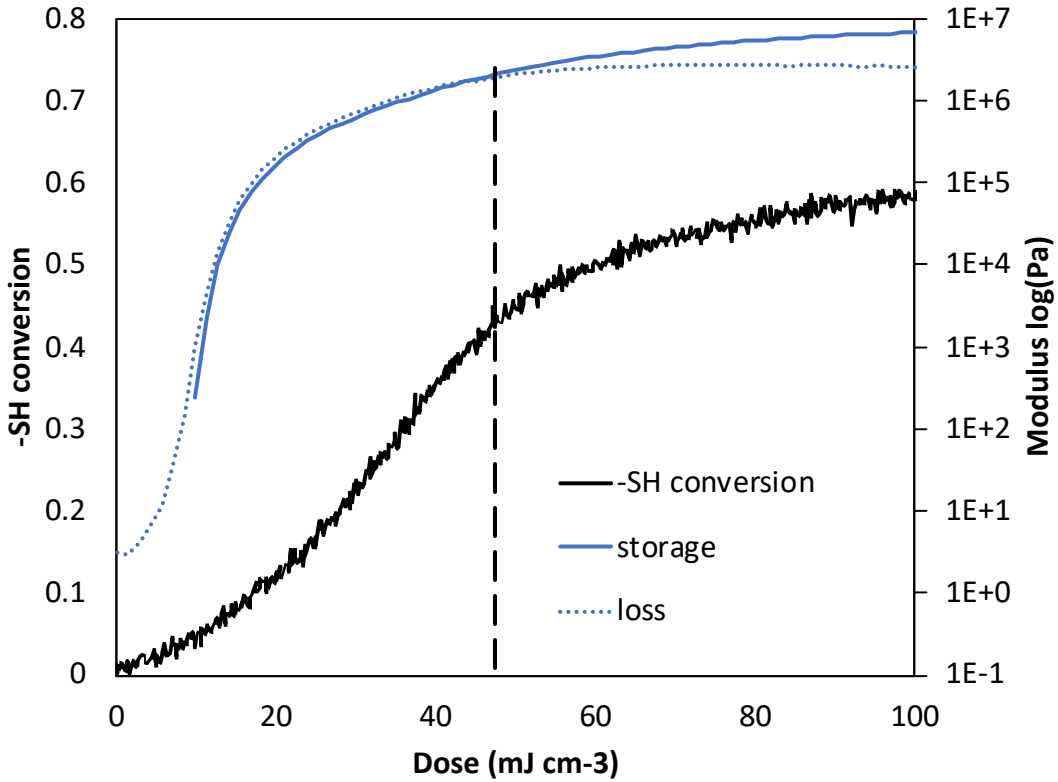


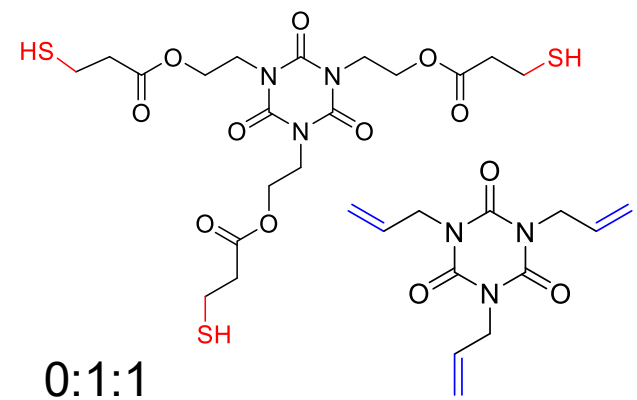


- Gelation point defined where storage modulus exceeds loss modulus

Gelation dose vs conversion dose

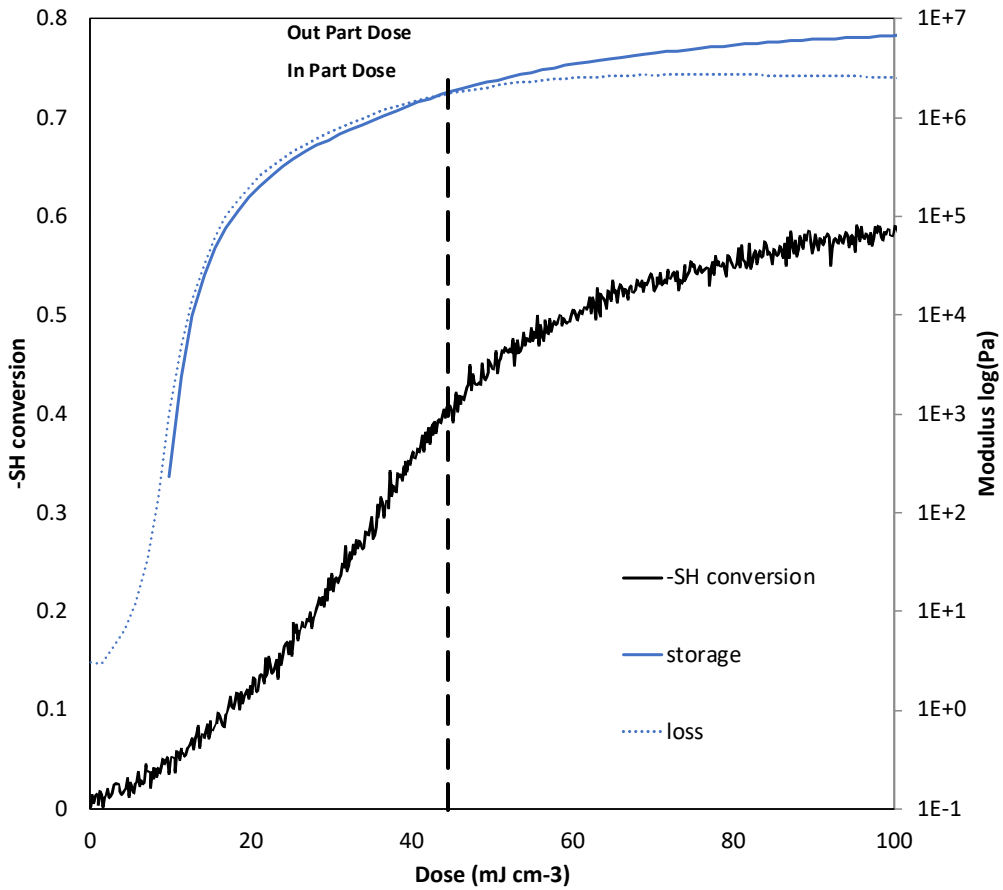
10mW/cm^2
10mM I907
0.098mM TEMPO
Absorbance ~0.009 cm^{-1}; $a_V \approx 0.045$ cm^{-1}

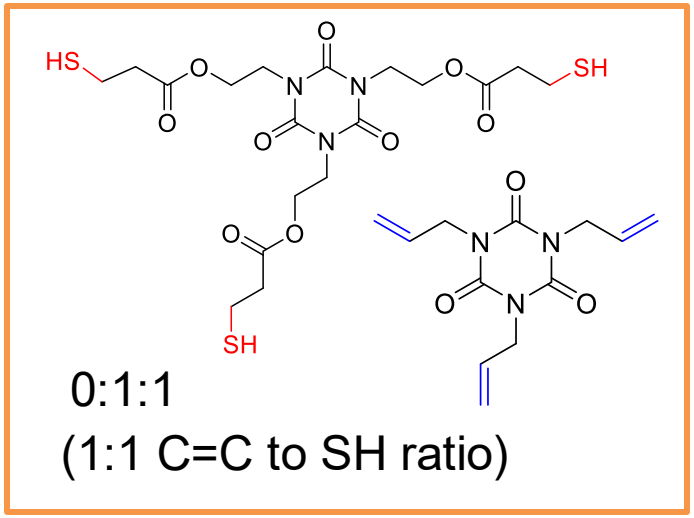




0:1:1
(1:1 C=C to SH ratio)

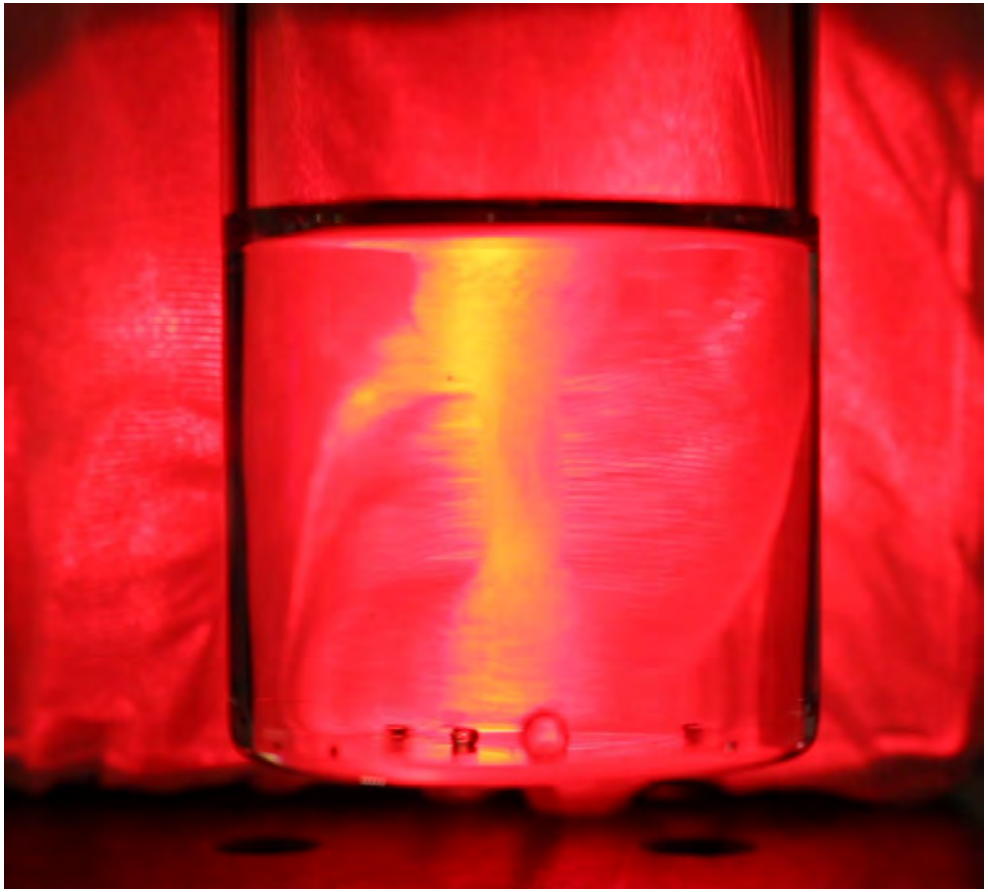
Dose Response of a Thiol-ene Resin

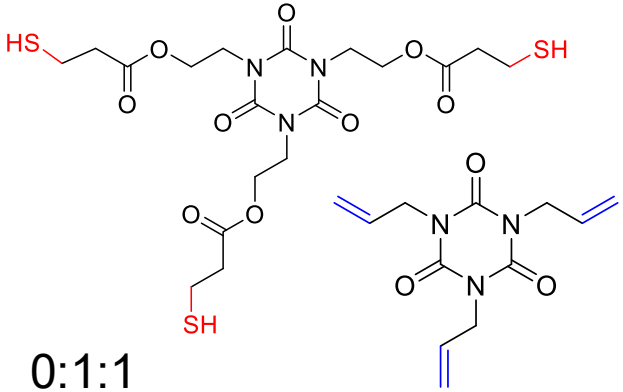




Dose mapping along with material characterization enables accurate print predictions

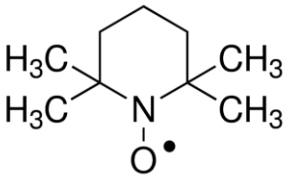
VAM print tensile properties match that of bulk



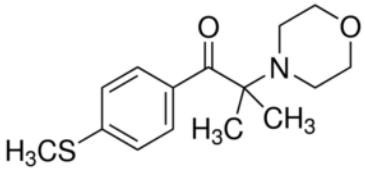


0:1:1
(1:1 C=C to SH ratio)

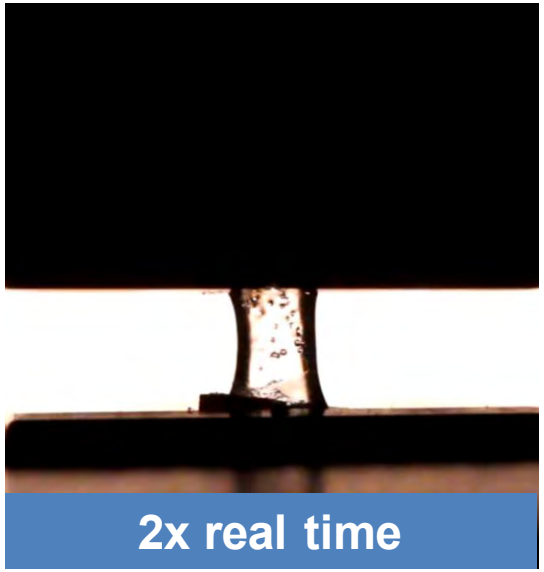
TEMPO (inhibitor)

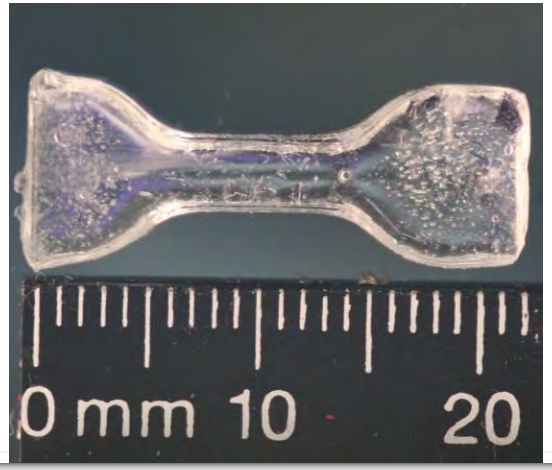


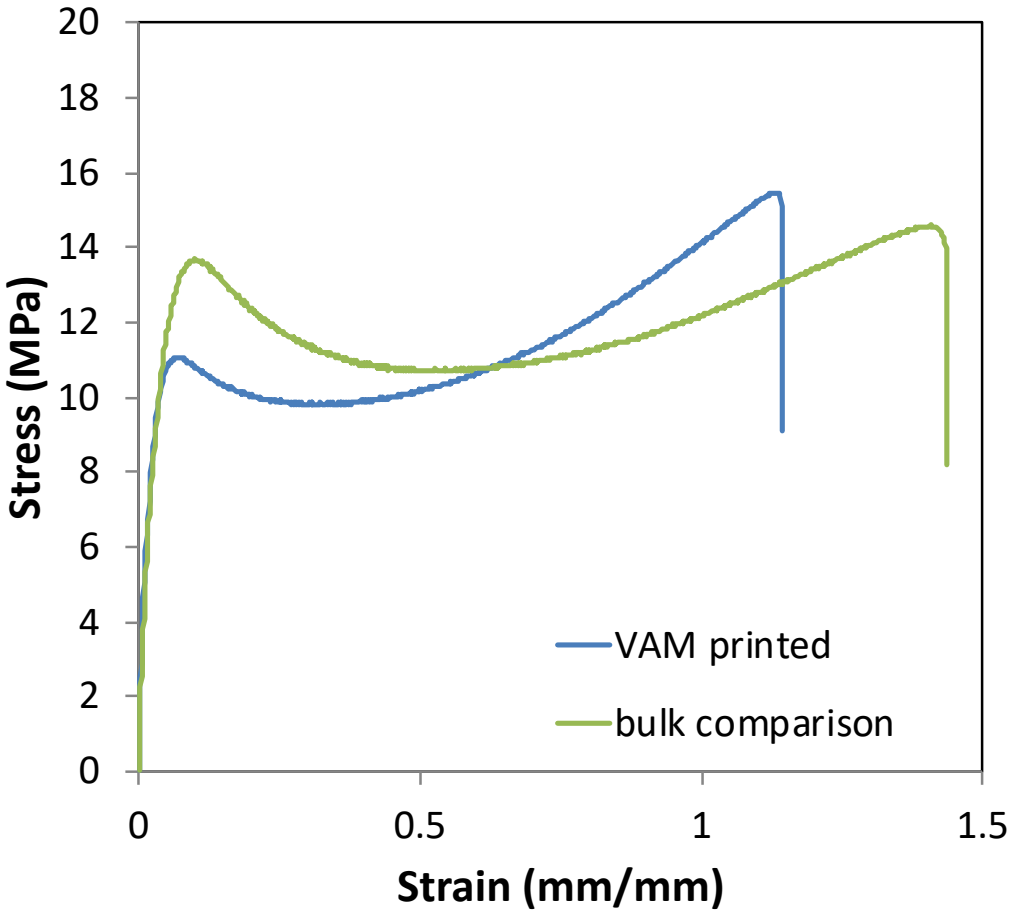
I907 (PI)



VAM print tensile properties match that of bulk





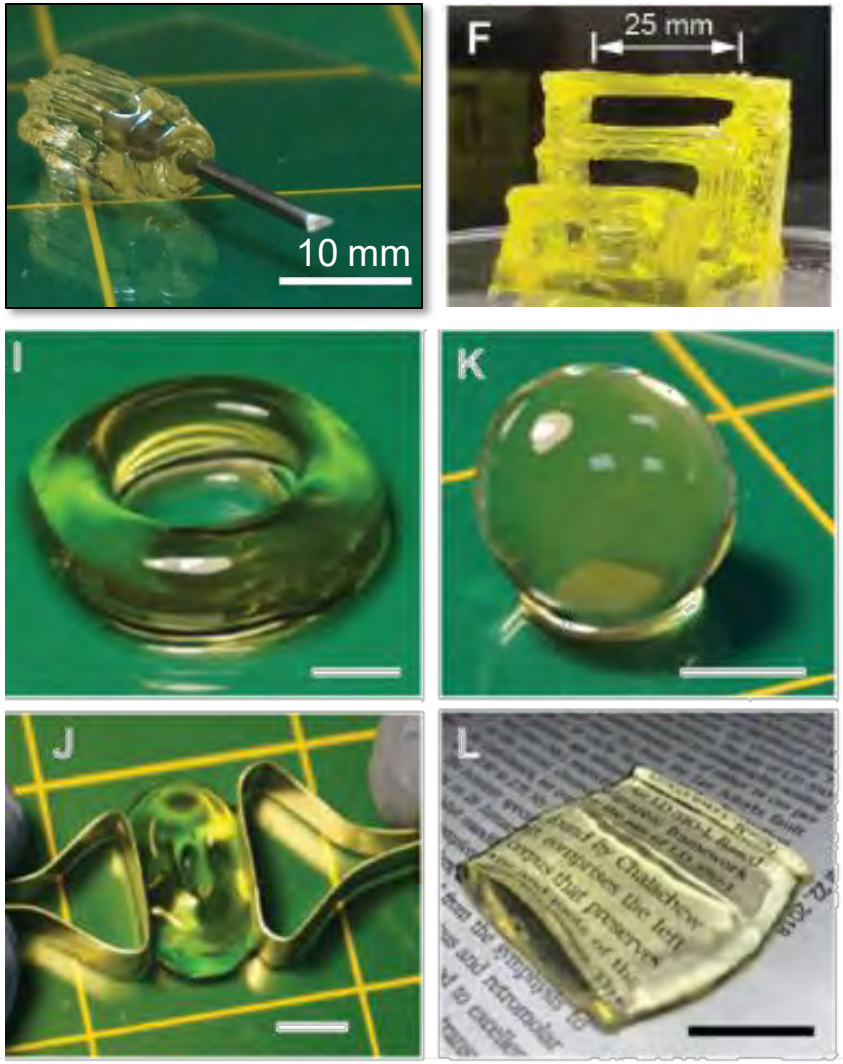


*bulk curing conditions matched that of VAM

We Expect Volumetric AM To Impact a Breadth of Application Areas

Berkeley
UNIVERSITY OF CALIFORNIA

- No geometric limitations? So far…
- Very soft materials (e.g. hydrogels), smooth surfaces, unsupported spans
- Pathway toward better 3D-printed engineering polymers
- Over-printing for multi-material parts



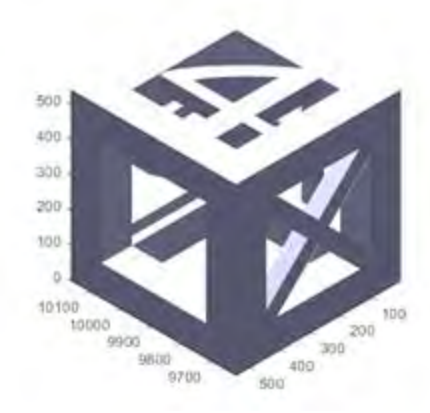
Kelly *et al*, *Science* **363**(6431), **2019,** p.1075-1079.
DOI: 10.1126/science.aau7114

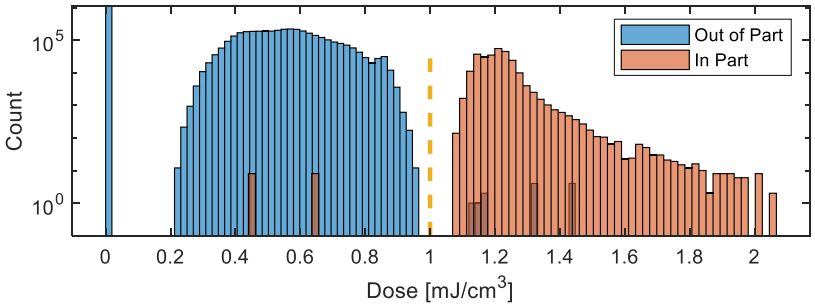
Outlook and Future Work

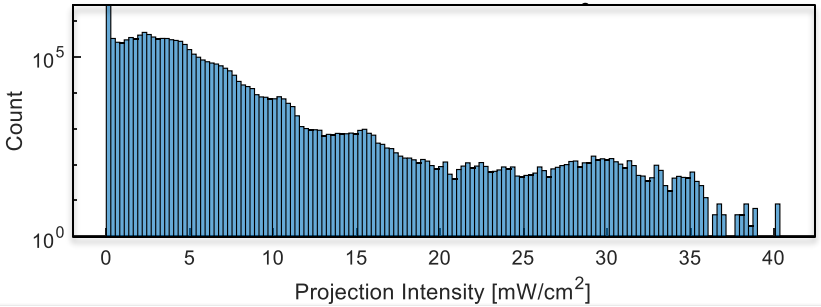
- Computational simulations
  - Multiscale modeling pipeline - from molecular to continuum scales (with ***R. Faller group at UC Davis***)
- Additional formulations
  - Hydrogels for bioprinting applications
  - Dual-cure networks
  - Epoxide systems; urethanes, silicones
- Other approaches to threshold behavior?

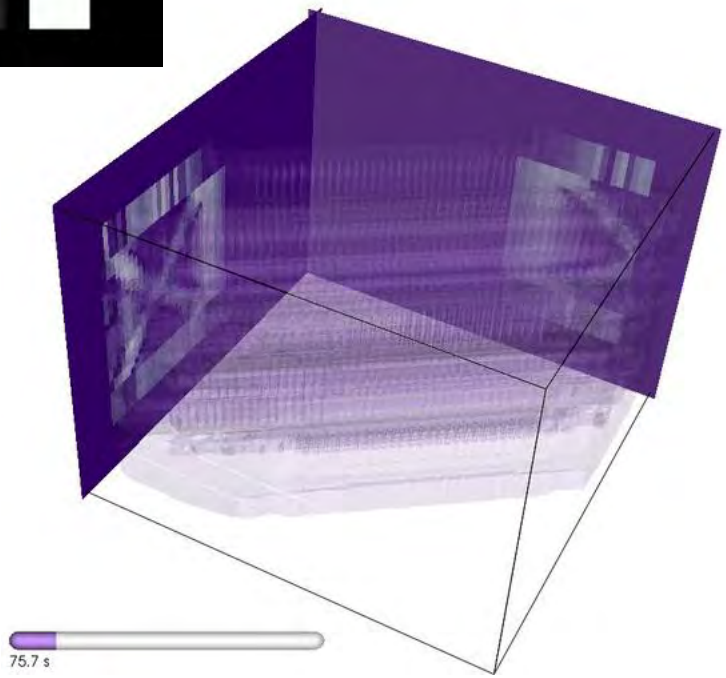
Lawrence Livermore
National Laboratory

Estimating 3D Dose Distribution *via* CT Algorithms



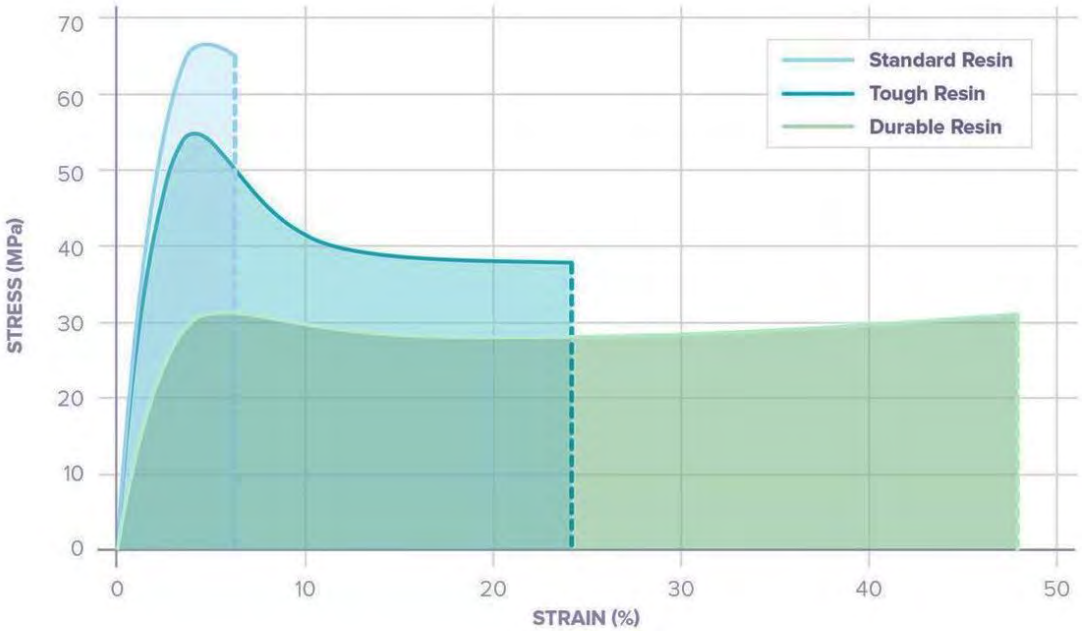




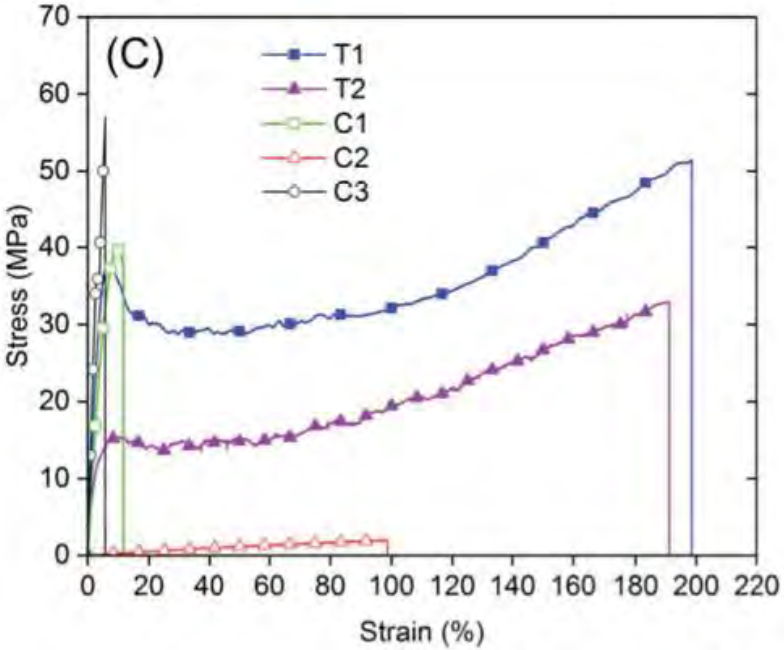


Comparison resins

FormLabs engineering resins



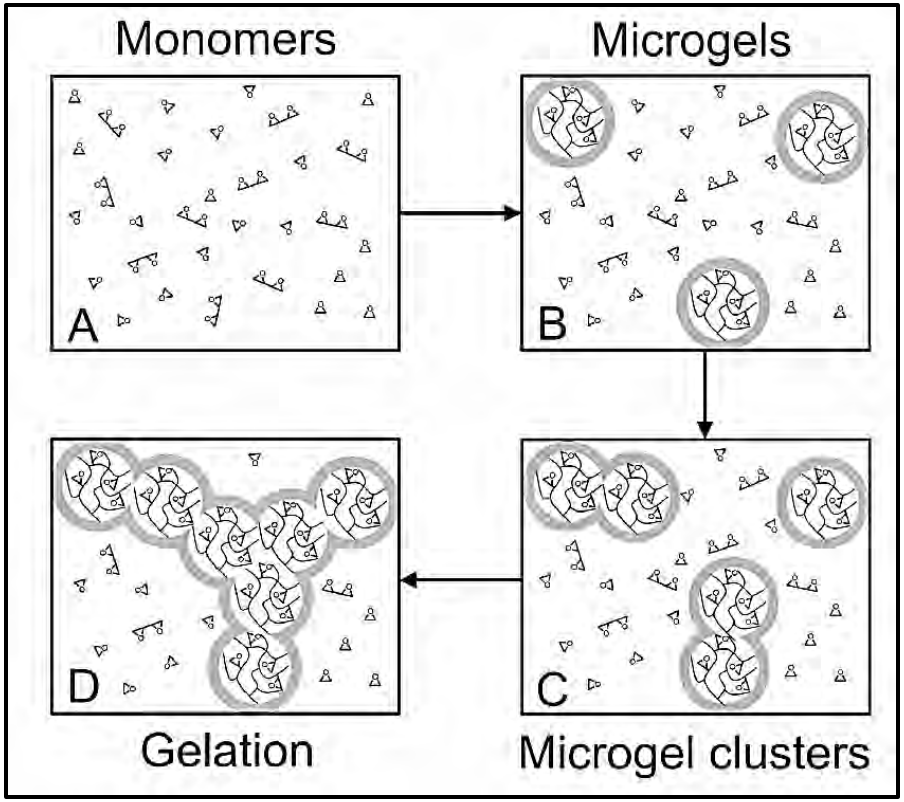
Tough triazole resins



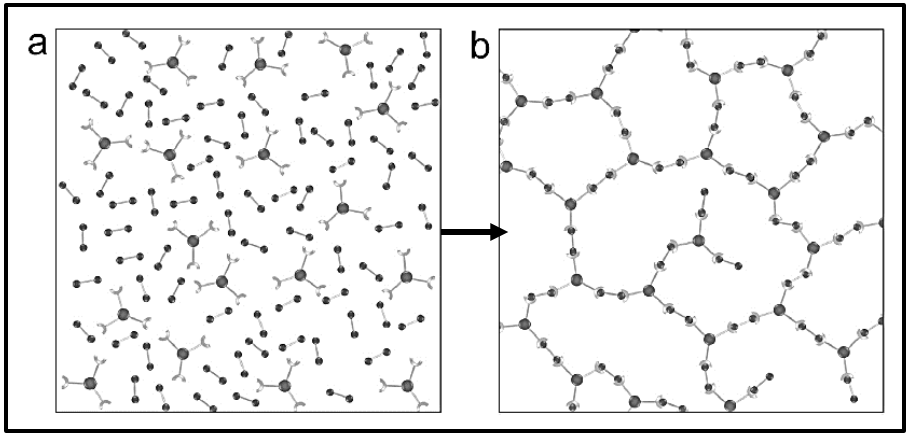
Song *et al*, *Adv Func Mater*, **2018**, *28,* 1801095.
(C. Bowman group, U. Colorado)
DOI: 10.1002/adfm.201801095

Step-Growth and Chain-Growth

Chain-Growth = Acrylates, Epoxies



Step-Growth = Thiol-ene

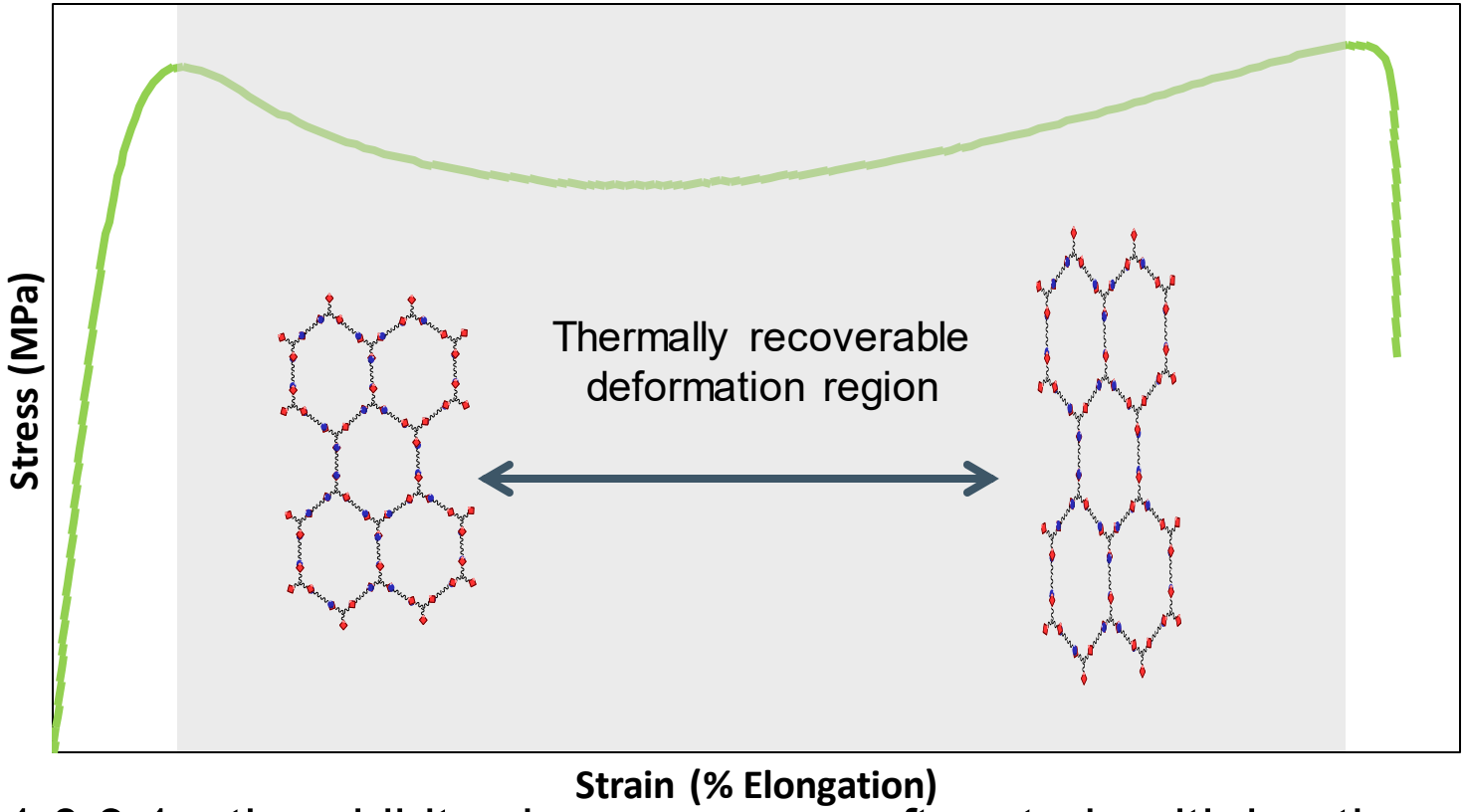


Figures from Vidil *et al*, *Progress in Polymer Sciences* 62, **2016**, 126-179

<u>Hypothesis</u>: Control of the network-level architecture through tuning of cure chemistry and cure rates will lead to more uniform tougher materials

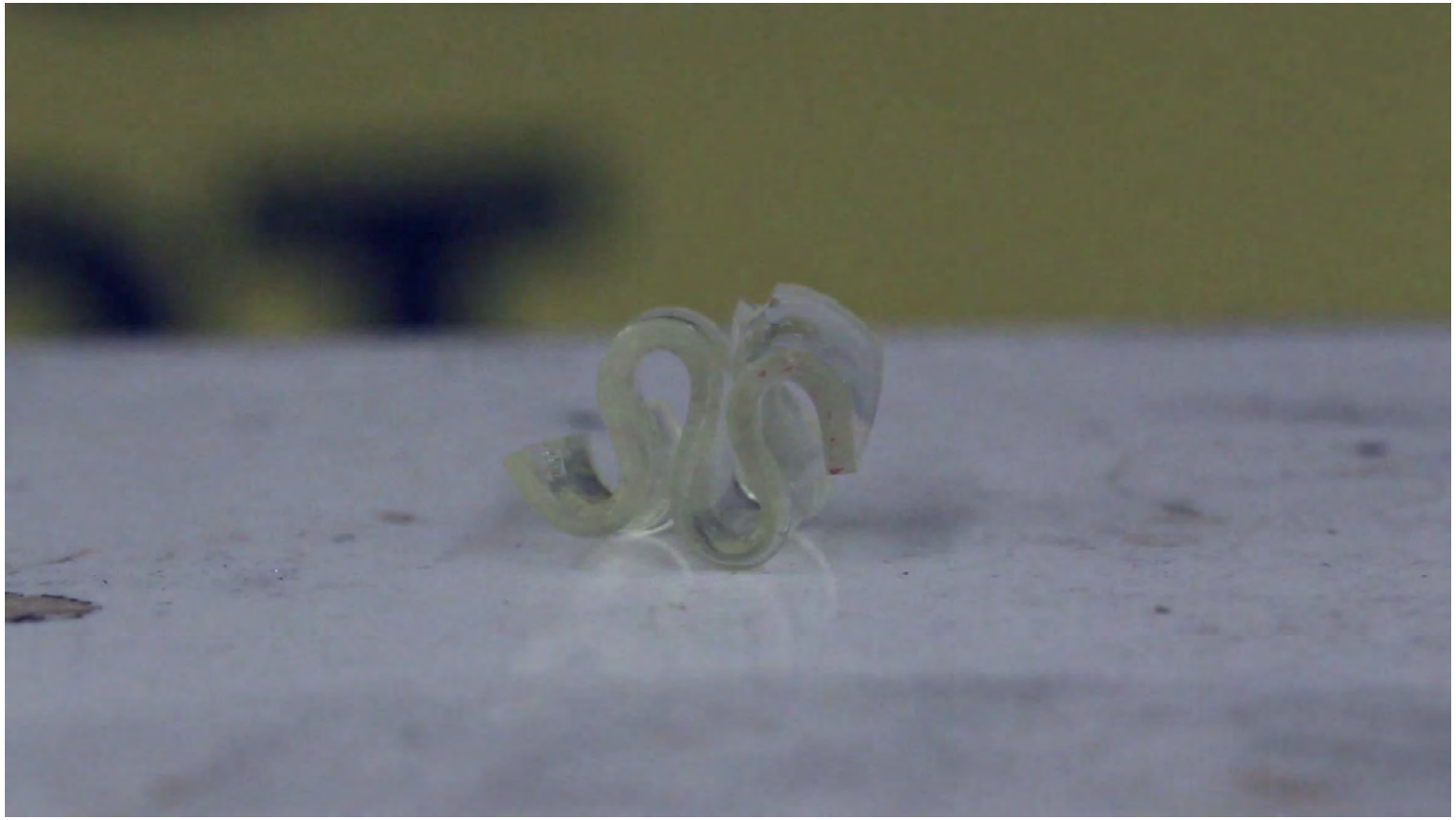
Thiol-ene Thermoplastic-like Shape Recovery

Thermoplastic Properties of 0.1:0.9:1 Thiol-ene



- 0.1:0.9:1 ratio exhibits shape recovery after strain with heating
- Heat relaxes chains in sample to original orientation and dimensions

Thiol-ene Thermoplastic-like Shape Recovery



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