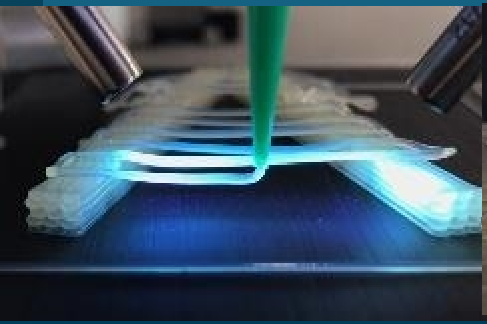
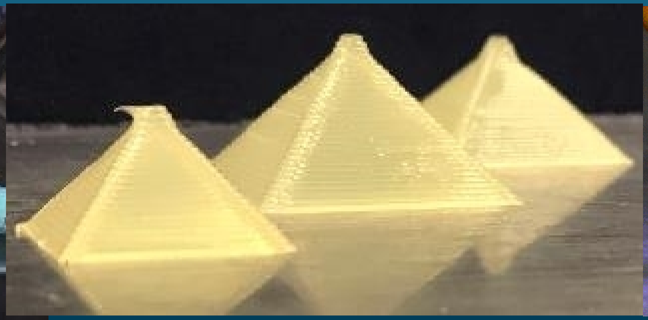
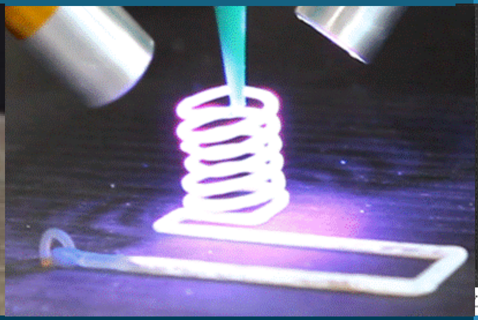
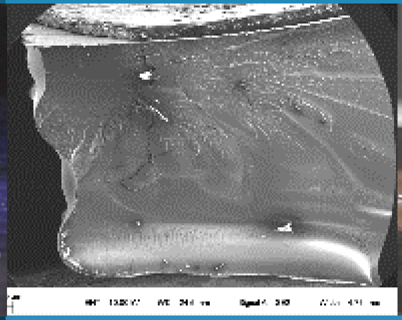
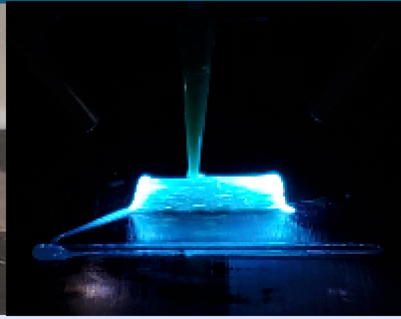
SAND2024-07866C

Sandia National Laboratories REMAT Team



New Approaches to Additive Manufacturing of Polymers with Ring-Opening Metathesis Polymerization

Leah N. Appelhans

Samuel C. Leguizamon[1], Devin J. Roach[1], Daniel R. Darby[1], Edgar B. Mejia[1,2], Andrew J. Greenlee[1,2], Luke McDougall[1], Adam W. Cook[1], Jeffrey S. Moore[2], Nancy R. Sottos[2], Yasmeen AlFaraj[3], Yuyan Wang[3], Jeremiah Johnson[3]

2 3 1

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Nick Monk

Victoria Rodriguez

SNL Undergraduate Interns

This work was supported as part of the Regenerative Energy-Efficient Manufacturing of Thermoset Polymeric Materials (REMAT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at the University of Illinois, Urbana-Champaign under award #DE-SC0023457 and at Sandia National Laboratories under contract DE-NA-0003525.

Acknowledgements

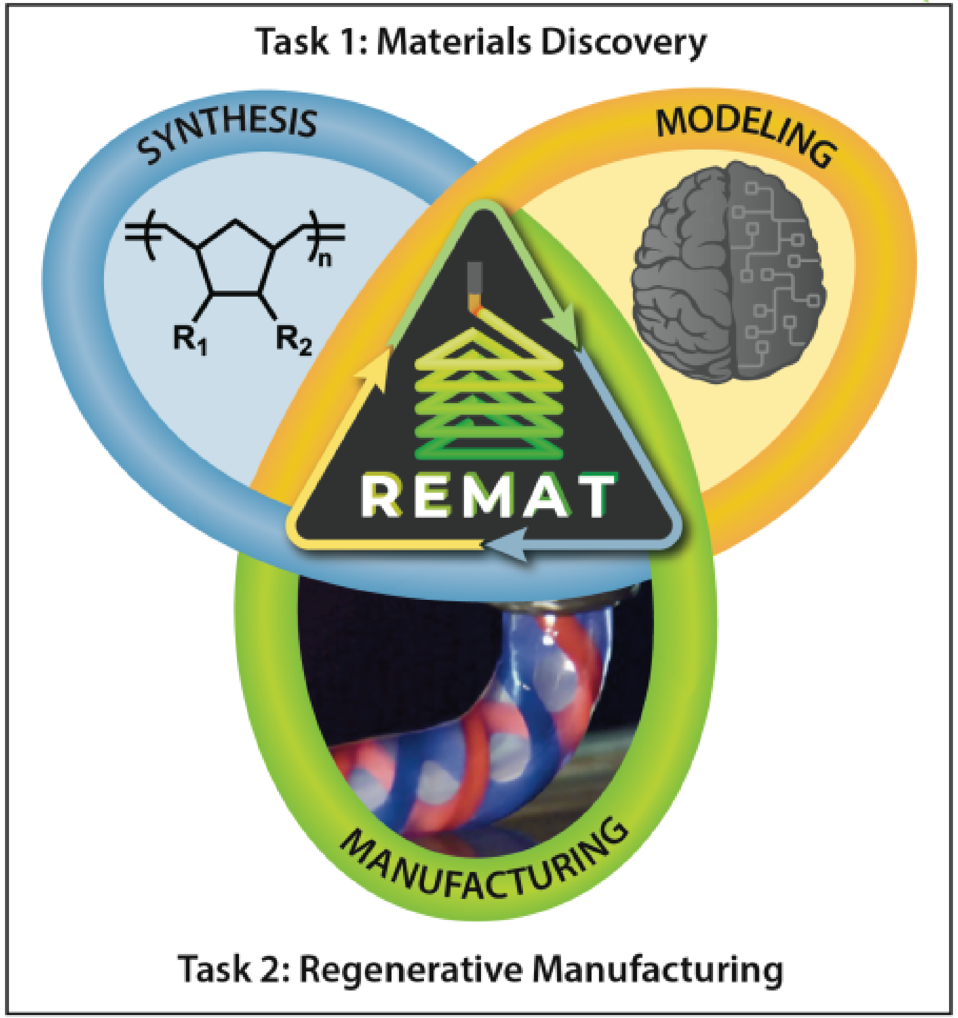
REMAT EFRC Team

Regenerative Energy-Efficient Manufacturing of Thermoset Polymeric Materials

Nancy Sottos (Director)

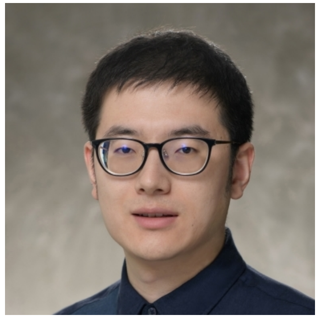
Jeffrey Moore (Deputy Director)

University of Illinois Urbana Champaign	**Jeff Baur, Randy Ewoldt, Philippe Geubelle, Sam Tawfick**
Harvard University	**Jennifer Lewis**
Massachusetts Institute of Technology	**Rafael Gomez-Bombarelli, Jeremiah Johnson**
Sandia National Laboratories	**Leah Appelhans, Adam Cook**
Stanford University	**Yan Xia**
University of Utah	**Matthew Sigman**



REMAT Team

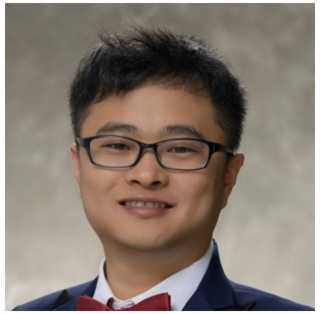

Dan Darby


Zhenchuang Xu


Andrew Greenlee


Edgar Mejia


Sam Knight


Qibang Liu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Lauren Chua


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Luke McDougall


Victoria Rodriguez


Leah Appelhans


Jeremiah Johnson


Rafael Gomez-Bombarelli


Philippe Geubelle


Jeffrey Moore


Nancy Sottos

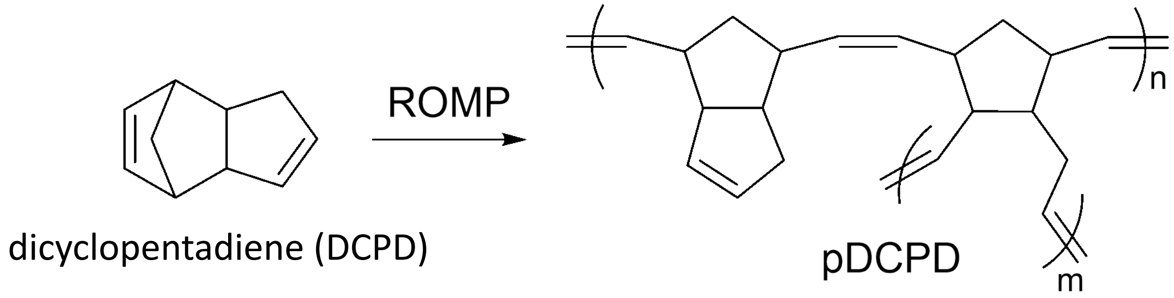

Adam Cook


Sam Leguizamon


Devin Roach

ROMP, FROMP, and PhotoROMP

ROMP: Ring Opening Metathesis Polymerization



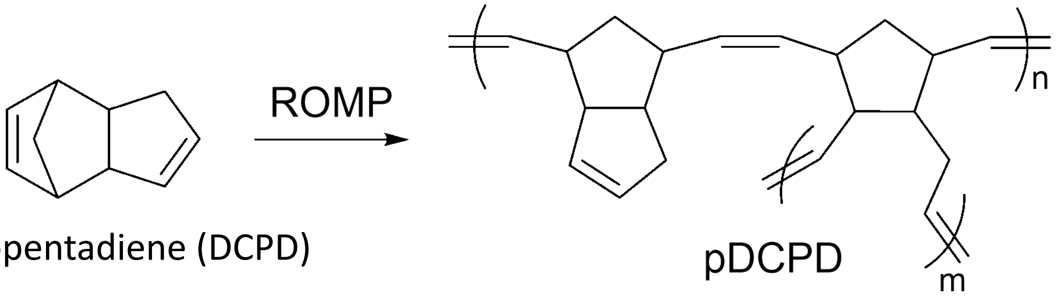
ROMP, FROMP, and PhotoROMP

PhotoROMP

R.A. Weitekamp, H.A. Atwater, R.H. Grubbs *J. Am. Chem. Soc.* **2013**, 135, 45, 16817-16820

O. Eivgi, R.S. Phatake, N.B. Nechmad, N.G. Lemcoff, *ACS Catal.* **2020**, 10, 2033−2038

ROMP: Ring Opening Metathesis Polymerization

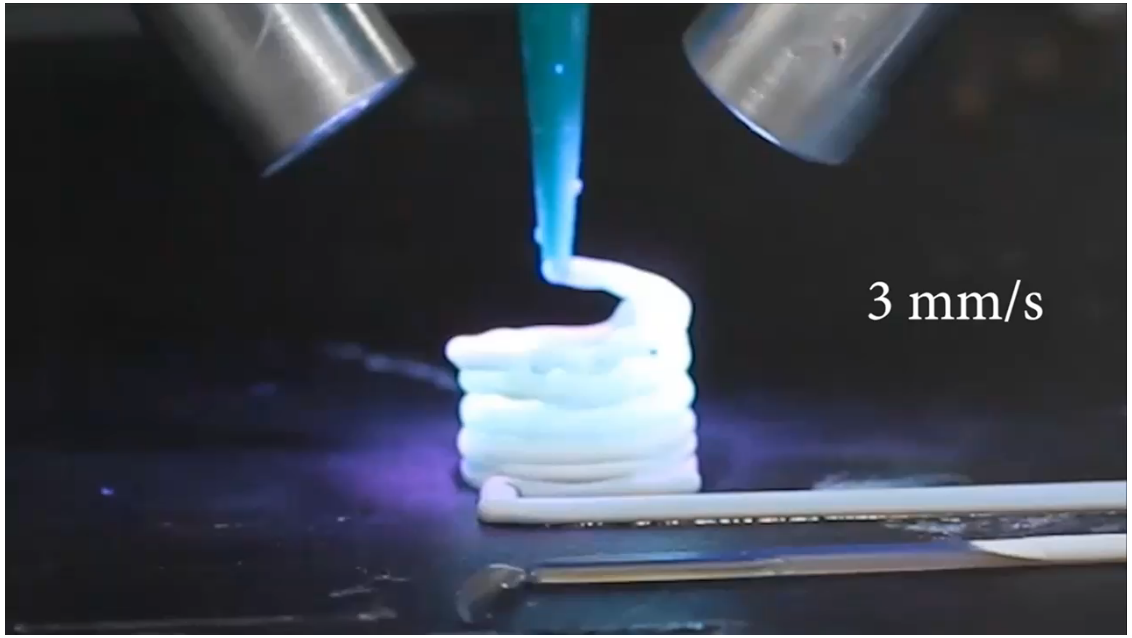


dicyclopentadiene (DCPD)

pDCPD

PhotoROMP: Photolatent polymerization utilizing ROMP

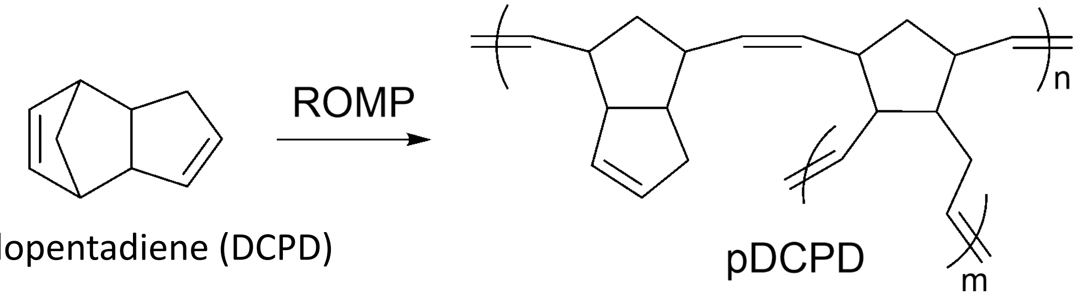
Printing with photoROMP



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

ROMP, FROMP, and PhotoROMP

ROMP: Ring Opening Metathesis Polymerization



PhotoROMP

R.A. Weitekamp, H.A. Atwater, R.H. Grubbs *J. Am. Chem. Soc.* **2013**, 135, 45, 16817-16820

O. Eivgi, R.S. Phatake, N.B. Nechmad, N.G. Lemcoff, *ACS Catal.* **2020**, 10, 2033−2038

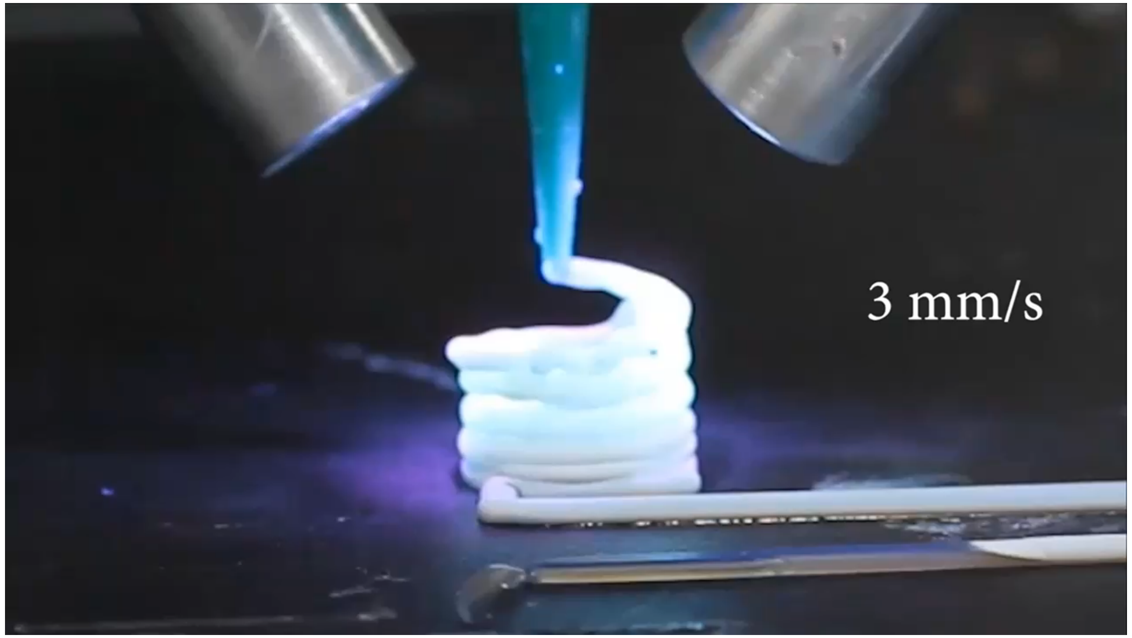
Frontal ROMP

Mariani, A., Fiori, S., Chekanov, Y. & Pojman, J. A. *Macromolecules* **2001**, 34, 6539-6541

Robertson, I. D. *et al. Nature* **2018** 557, 223

PhotoROMP: Photolatent polymerization utilizing ROMP

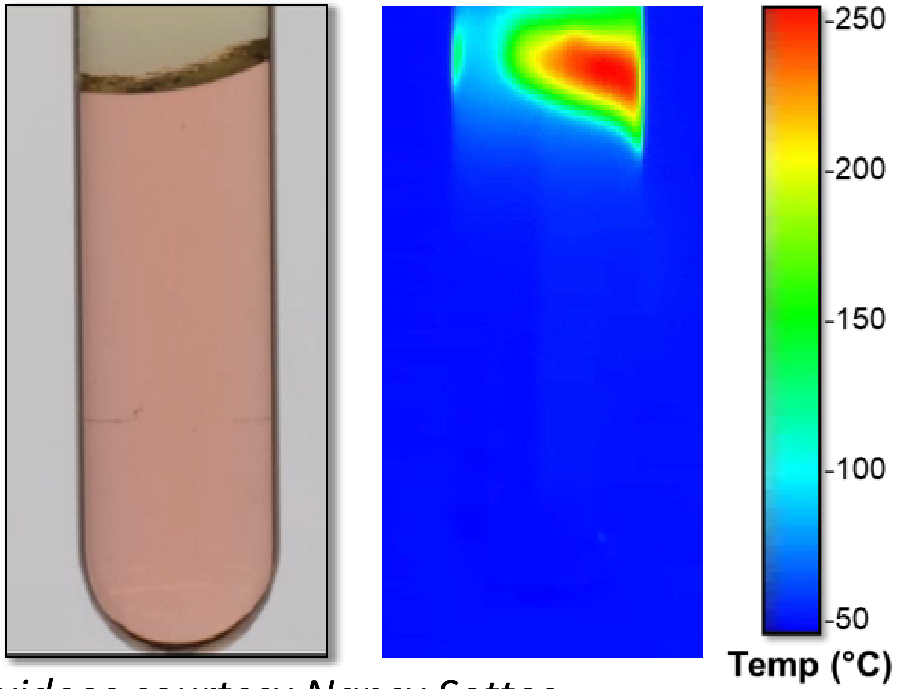
Printing with photoROMP



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

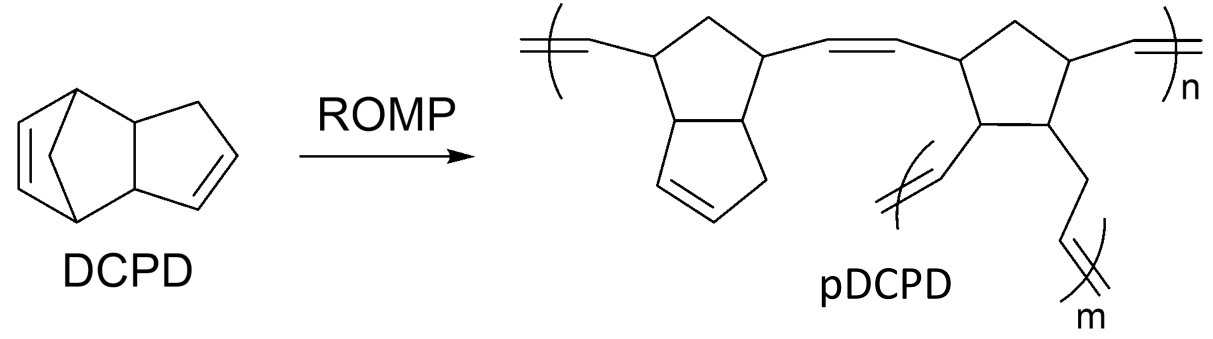
FROMP: Frontal ring-opening metathesis polymerization

FROMP of DCPD

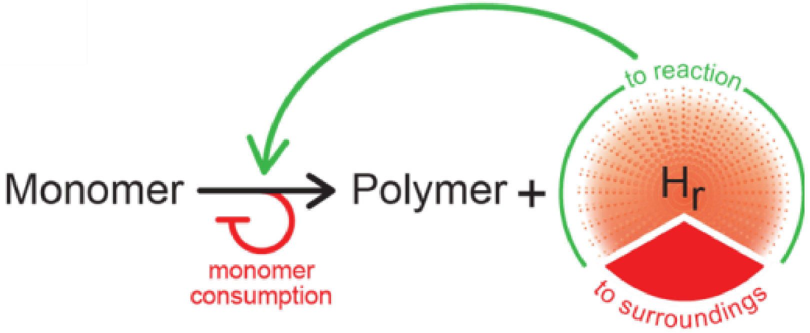


videos courtesy Nancy Sottos

Ring Opening Metathesis Polymerization and FROMP



Frontal polymerization: A reaction-thermal transport system



$$
\begin{cases}
\rho C_p \dfrac{\partial T}{\partial t} = \overset{\text{Transport}}{\boxed{\kappa \nabla^2 T}} + \overset{\text{Reaction}}{\boxed{\rho H_r \dfrac{\partial \alpha}{\partial t}}} \\
\dfrac{\partial \alpha}{\partial t} = A \exp\left(\dfrac{-E_A}{RT}\right) f(\alpha)
\end{cases}
$$

Important properties and variables:

H_r – heat of reaction
ρ – density
κ – thermal conductivity
C_p – specific heat
E_A – activation energy
α – degree of cure

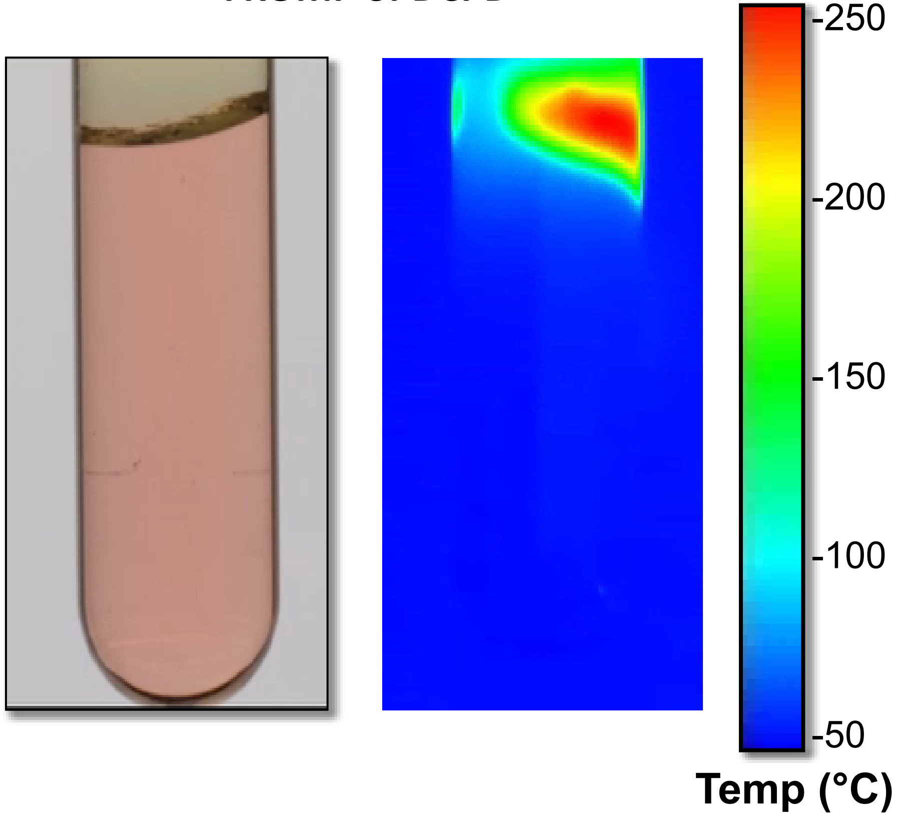
T_{max} – max temp
V_f – front velocity

Frontal ROMP

Mariani, A., Fiori, S., Chekanov, Y. & Pojman, J. A. *Macromolecules* **2001**, 34, 6539-6541

Robertson, I. D. *et al. Nature* **2018** 557, 223

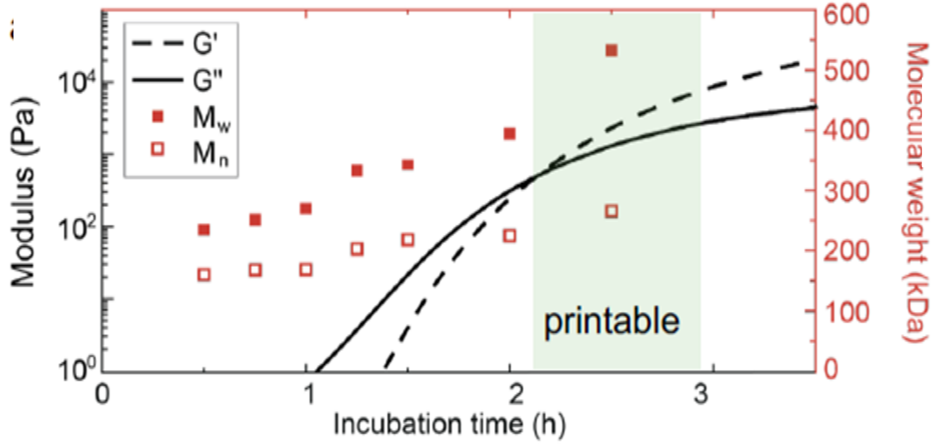
FROMP of DCPD



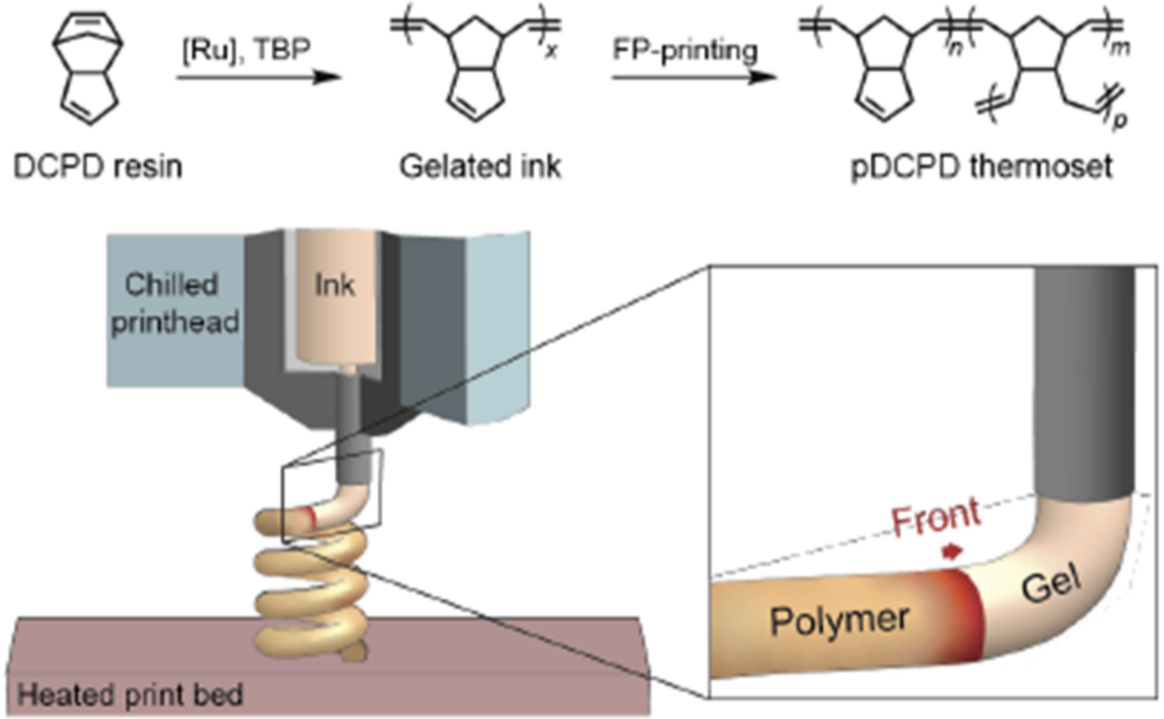
videos courtesy Nancy Sottos

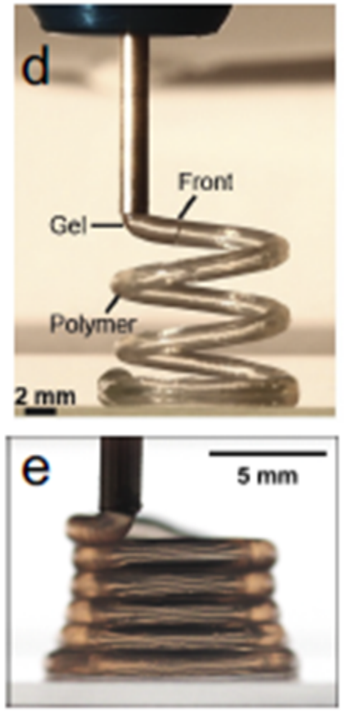
Printing with FROMP

Printing with FROMP

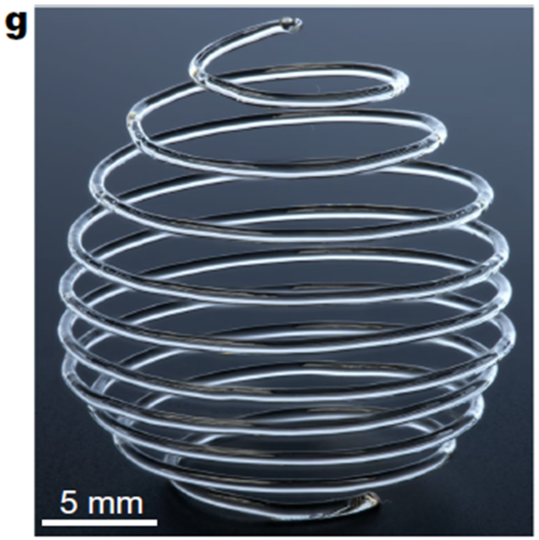


Aw, J. E. *et al. Advanced Materials Technologies*, **2022,** 202200230





Aw, J. E. *et al. Advanced Materials Technologies*, **2022,** 202200230

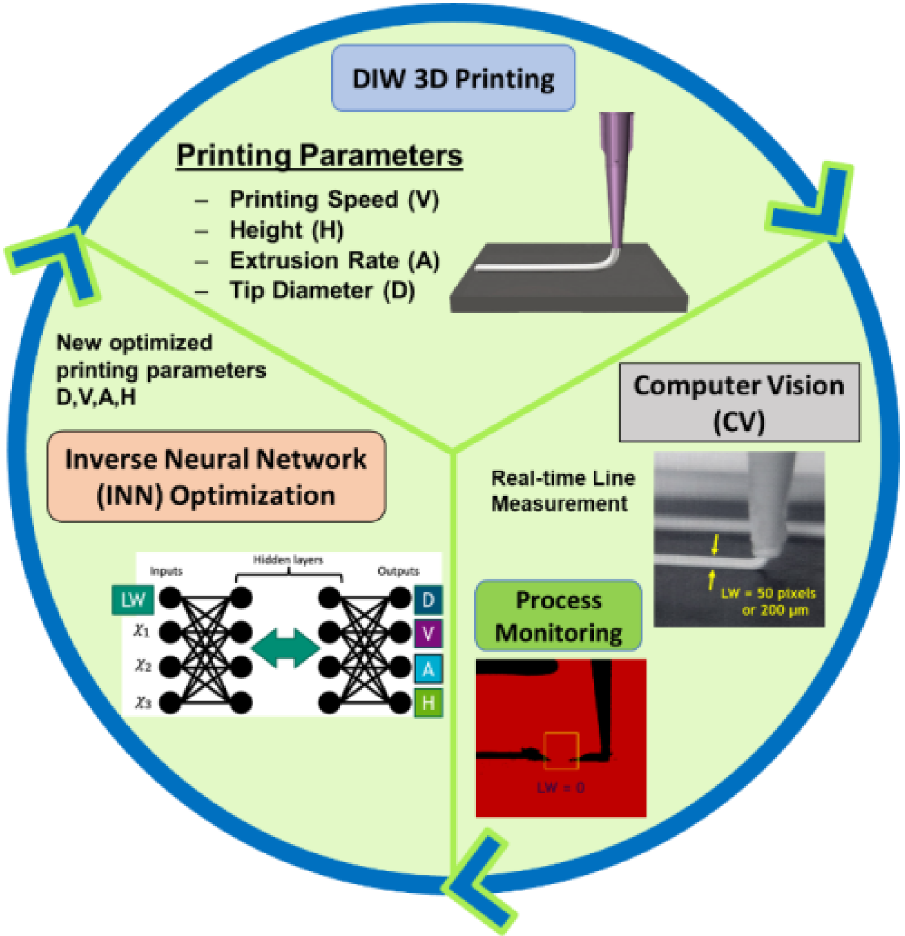


Robertson, I. D. *et al. Nature* **2018** 557, 223

Approaches to *in situ* Control

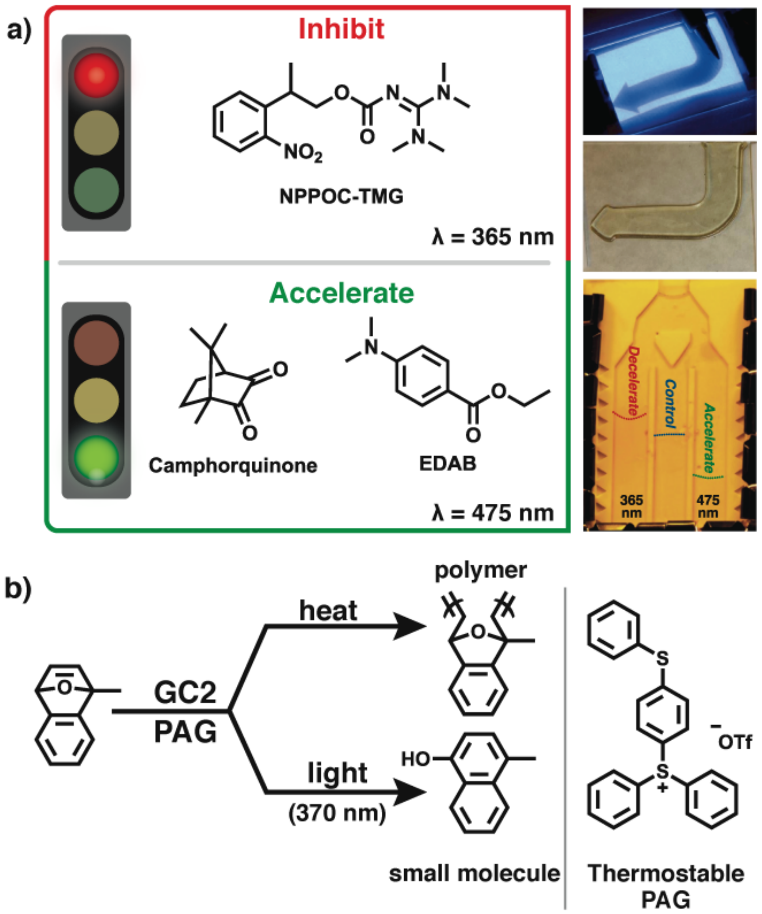
Closed Loop Process Control

Developing engineering approaches to facilitate printing with FROMP



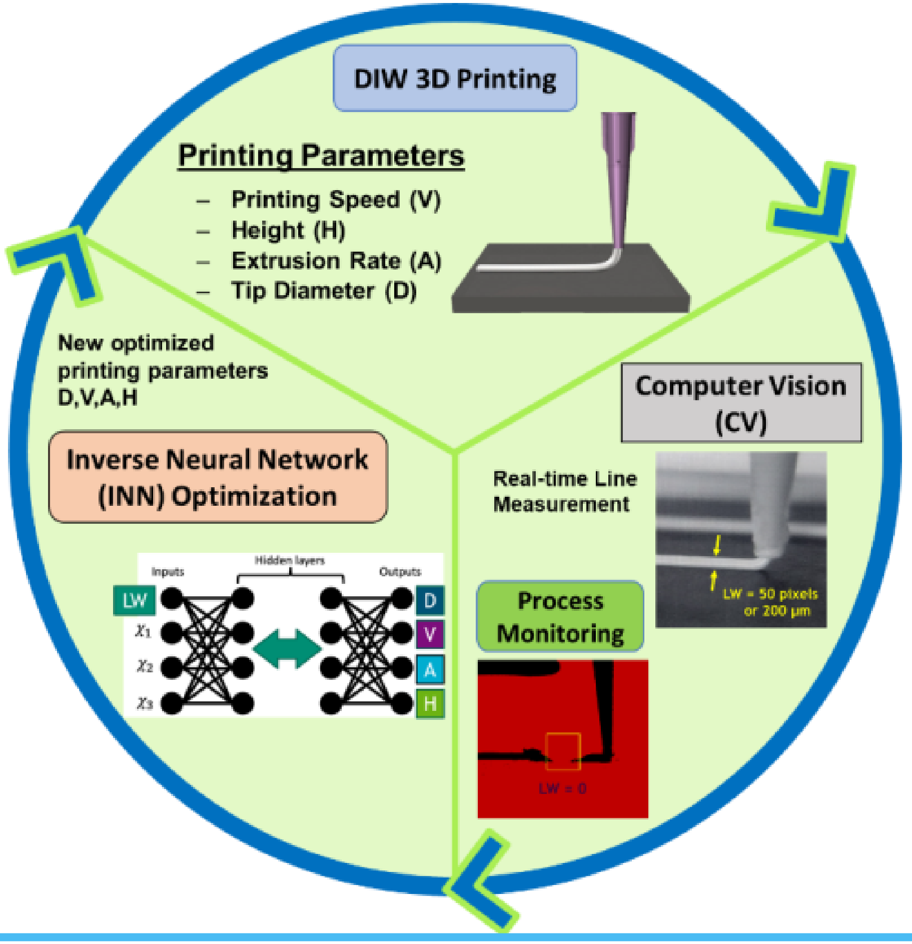
Photocontrol of FROMP

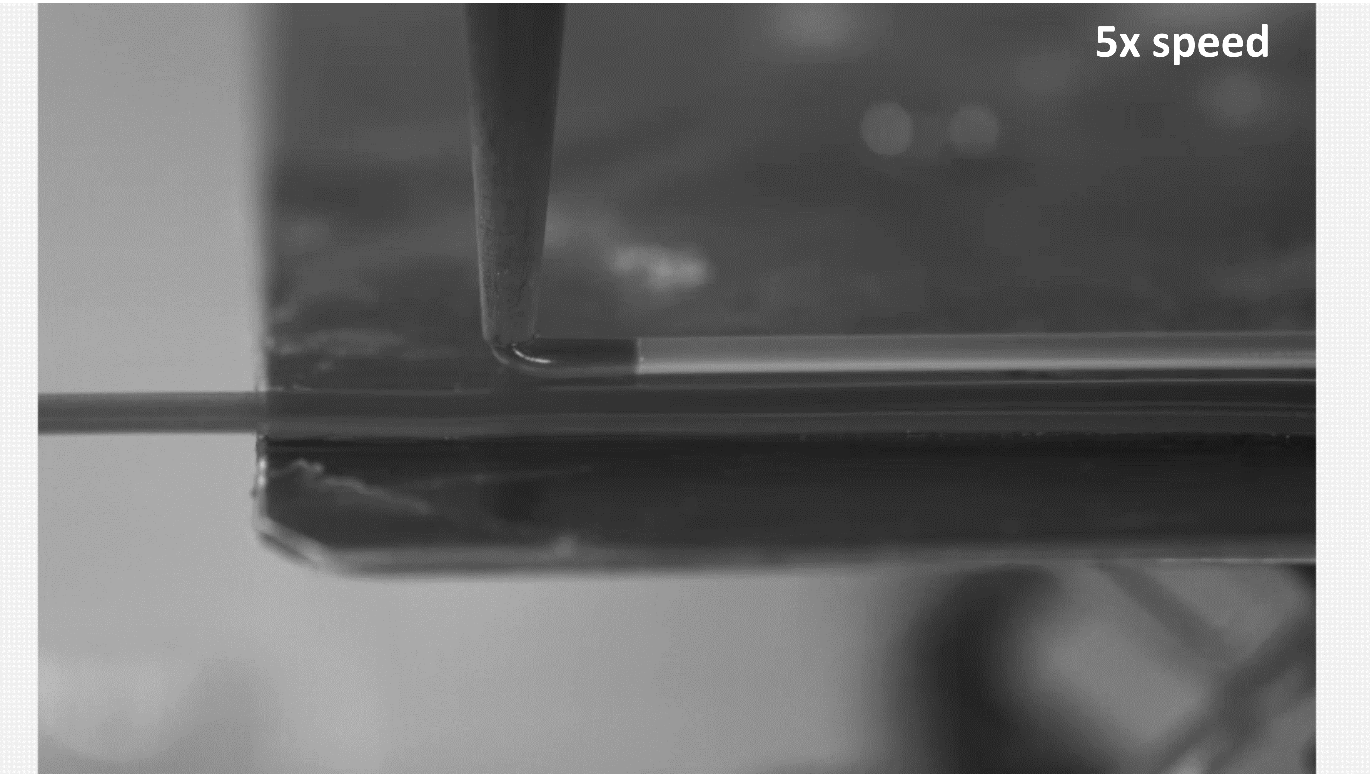
Can we use photochemistry for in situ control of front velocity and polymer composition?



In situ Closed Loop Feedback Control

Devin Roach, Edgar Mejia, Luke McDougall, Adam Cook

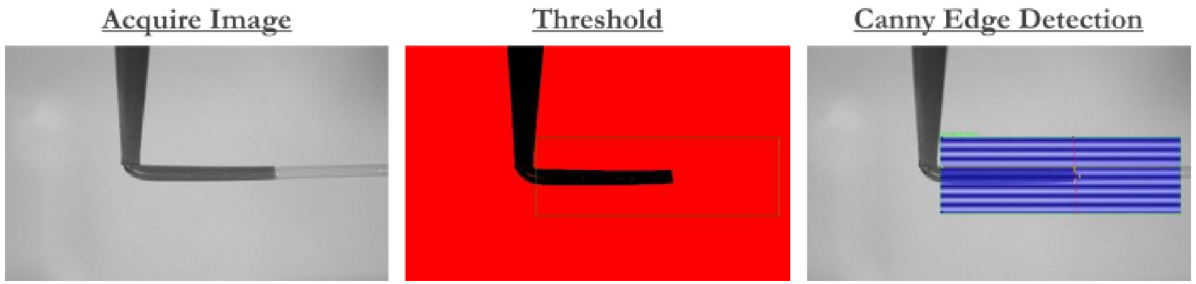


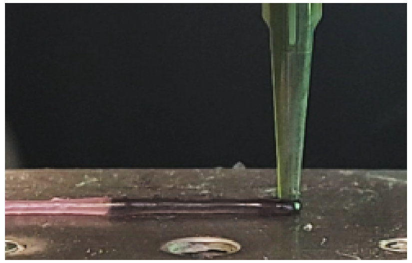


"Invertible Neural Networks for Real-Time Control of Extrusion Additive Manufacturing" D.J. Roach*, A. Rohskopf, W.D. Reinholtz, L.N. Appelhans, A.W. Cook* 2023, *Additive Manufacturing*

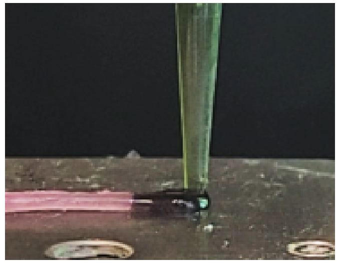
In situ Closed Loop Feedback Control

Real-time front rate measurement and in-situ print parameter optimization



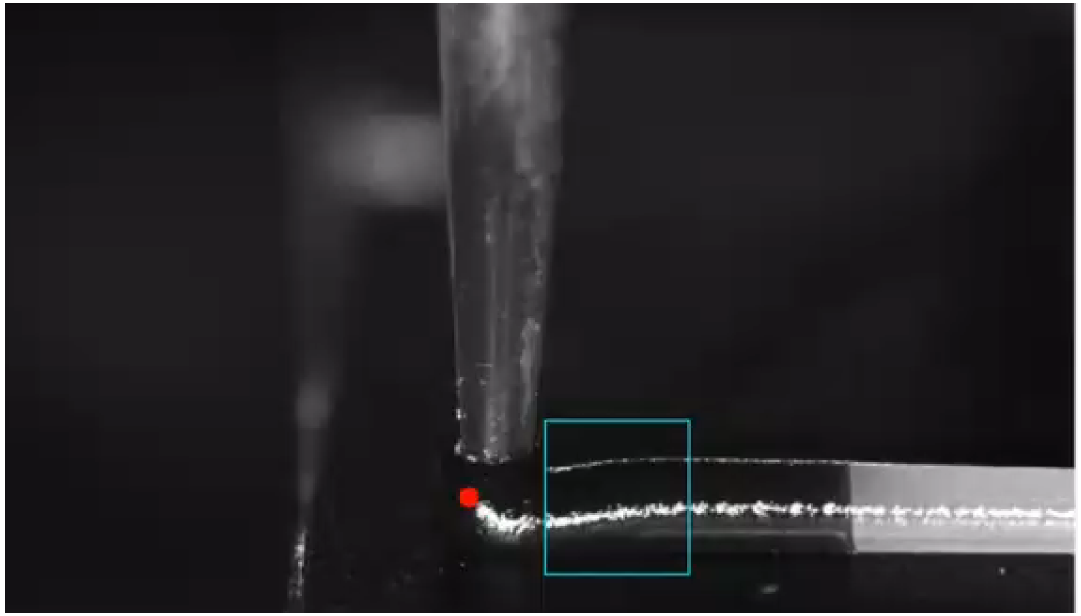


t = 5s



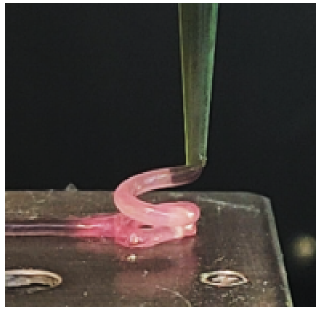
t = 30s

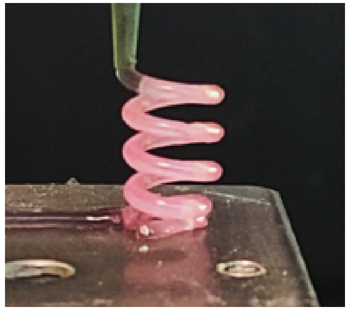
- Begin printing
- Measure tip-to-front distance
- Wait for front to “catch up”



DCPD:ENB [95:5] (10,000 Eq = 100ppm) – GC2 (1 Eq) – TBP (1 Eq) – Dye (0.5wt%)

Continue printing of object:

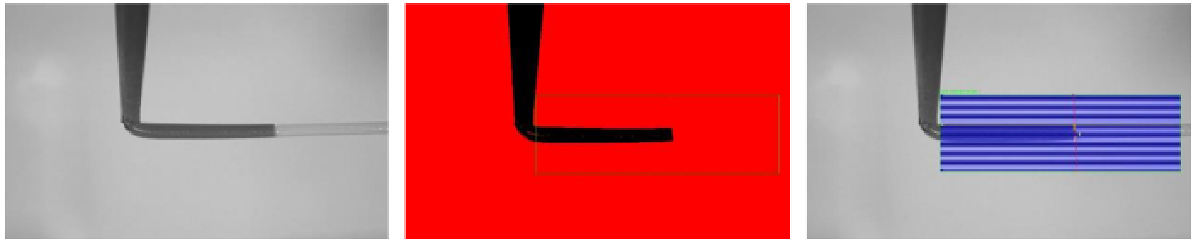


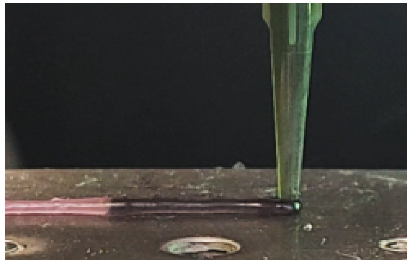


In situ Closed Loop Feedback Control

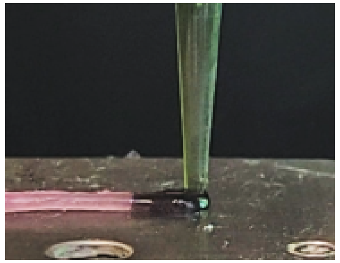
Real-time front rate measurement and in-situ print parameter optimization

Acquire Image | Threshold | Canny Edge Detection





t = 5s



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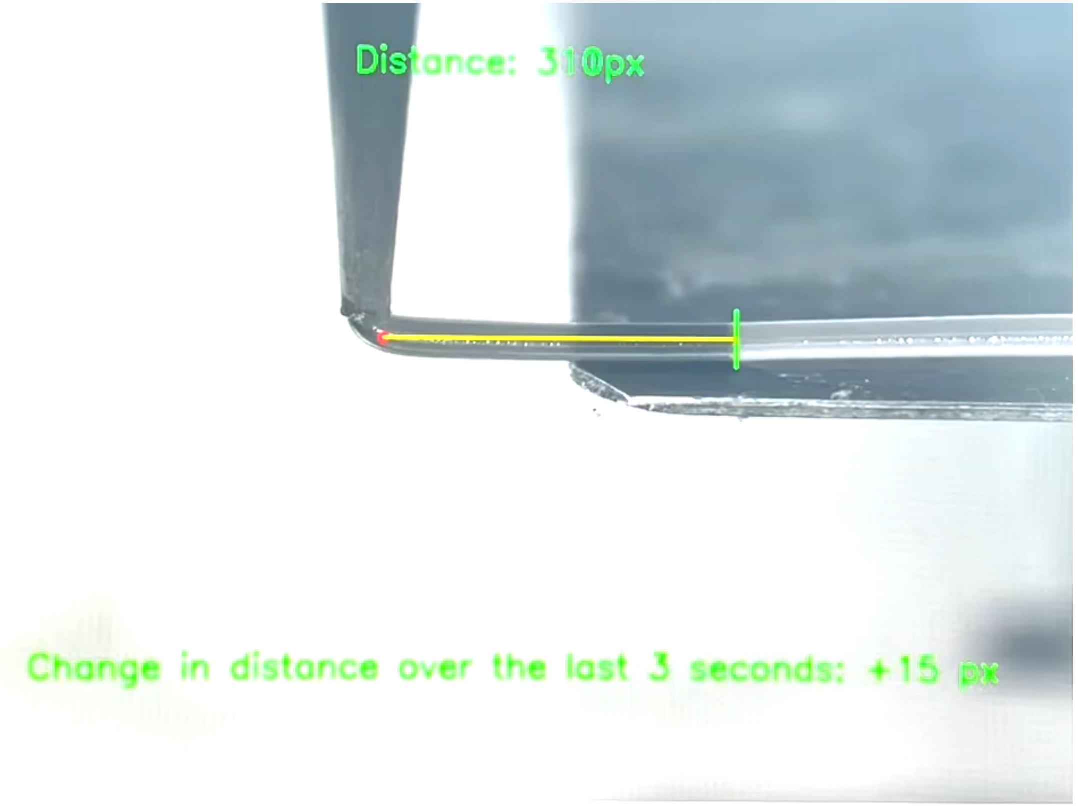
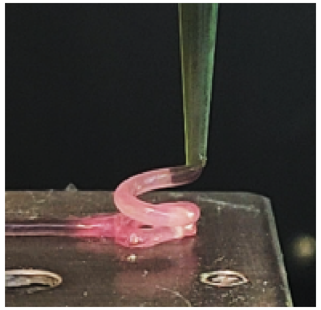
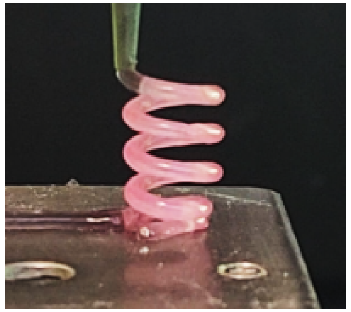


Continue printing of object:



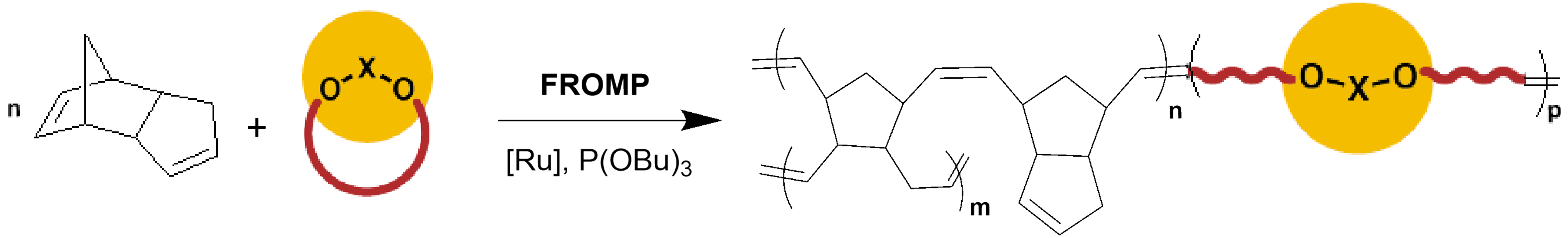


Integrating Degradable Comonomers

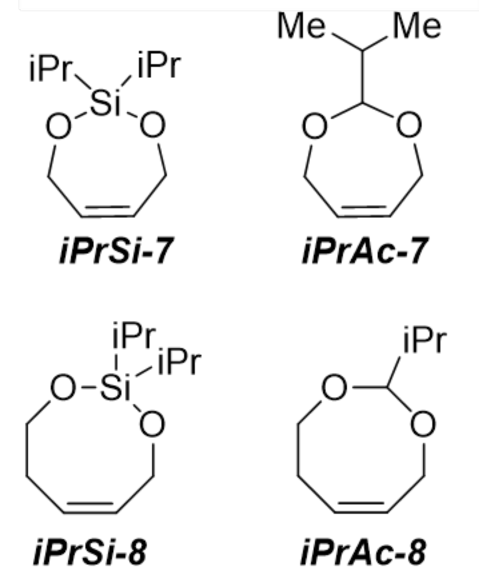
Jeremiah Johnson, Yasmeen Alfaraj, Yuyan Wang (MIT), Jeffrey Moore (UIUC)

FROMP

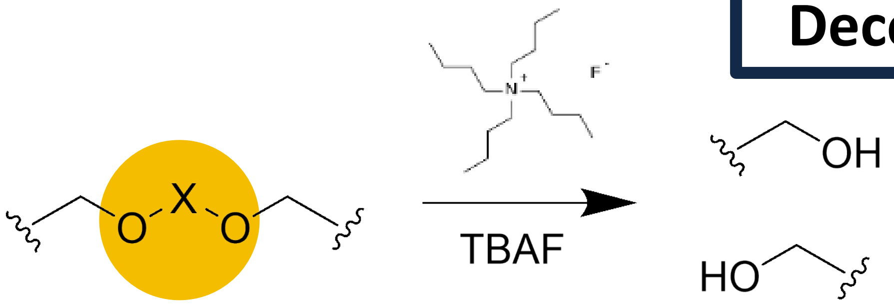
Cleavable co-monomer



Cleavable co-monomers



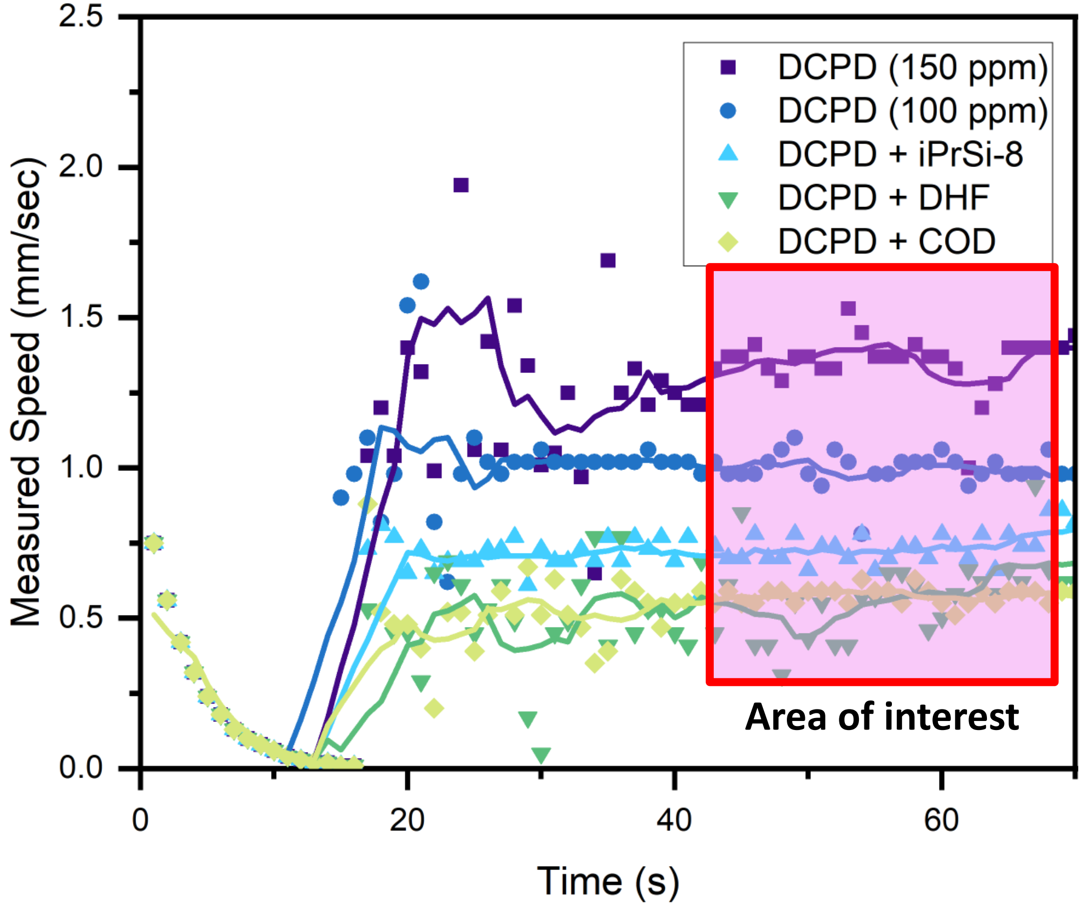
Deconstruction



Triggered deconstruction (either fluoride or acid), leaving handles for upcycling

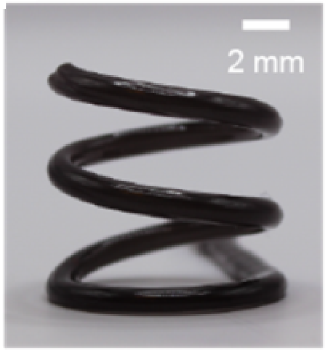
Lloyd, E., et al. ACS Appl. Eng. Mater., 1, 1, 477-485, **2022**

In Situ Monitoring with Degradable and Regenerated Resins

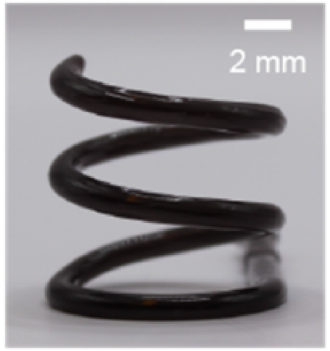


Formulation: Comonomer to DCPD [7.5 mol%] - GC2 (1 Eq) – TBP (1 Eq) – Dye (0.5 wt%).
DCPD + iPrSi-8 (150 ppm) / DCPD + DHF (150 ppm) / DCPD + COD (100 ppm)

1st Generation

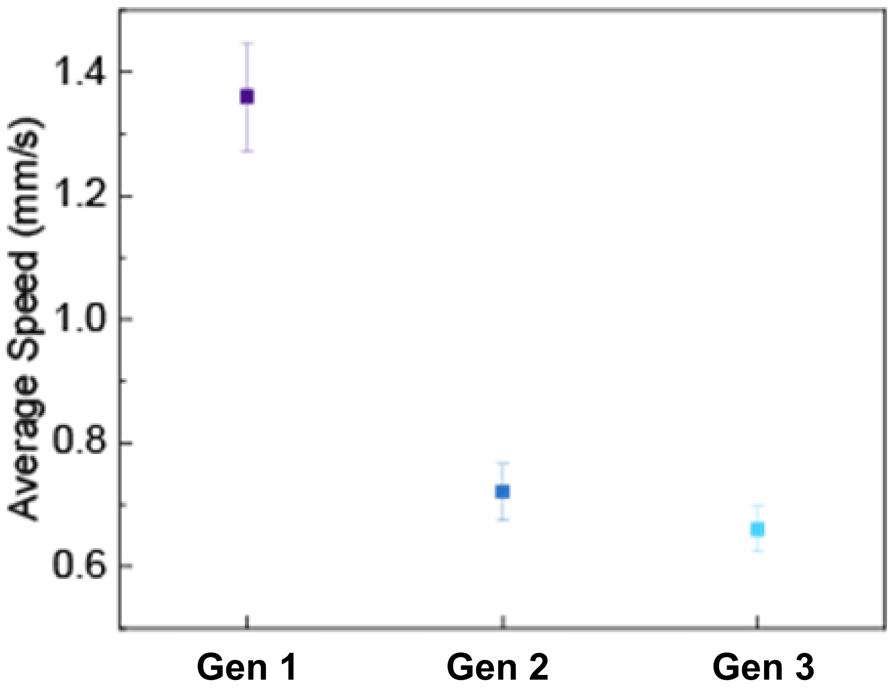


2nd Generation



3rd Generation

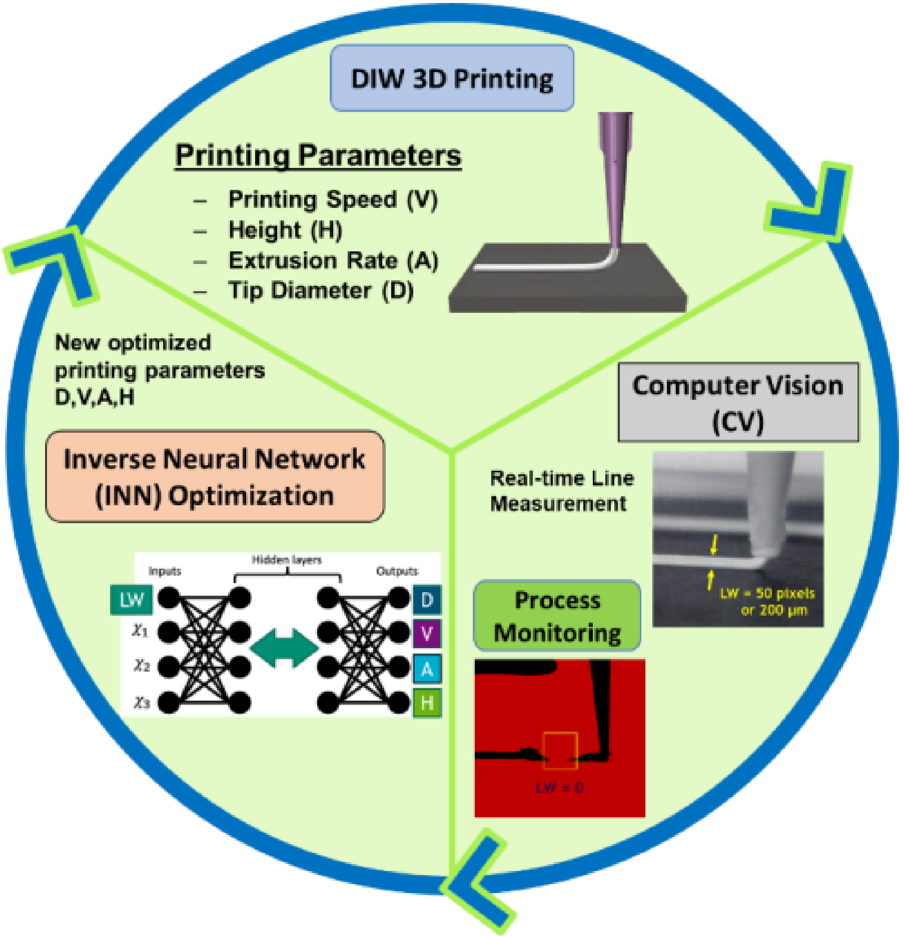
Average front speeds for three generations of resins with 20 wt% reclaimed oligomers.



Approaches to *in situ* Control

Closed Loop Process Control

Developing engineering approaches to facilitate printing with FROMP



Photocontrol of FROMP

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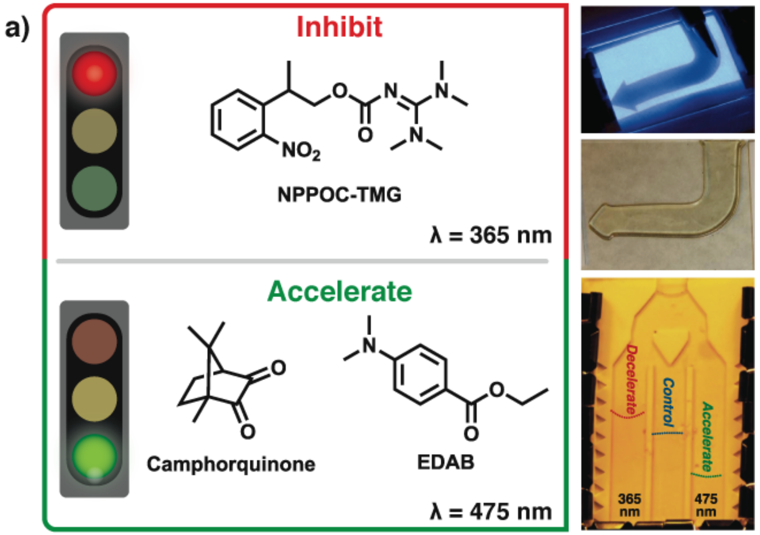
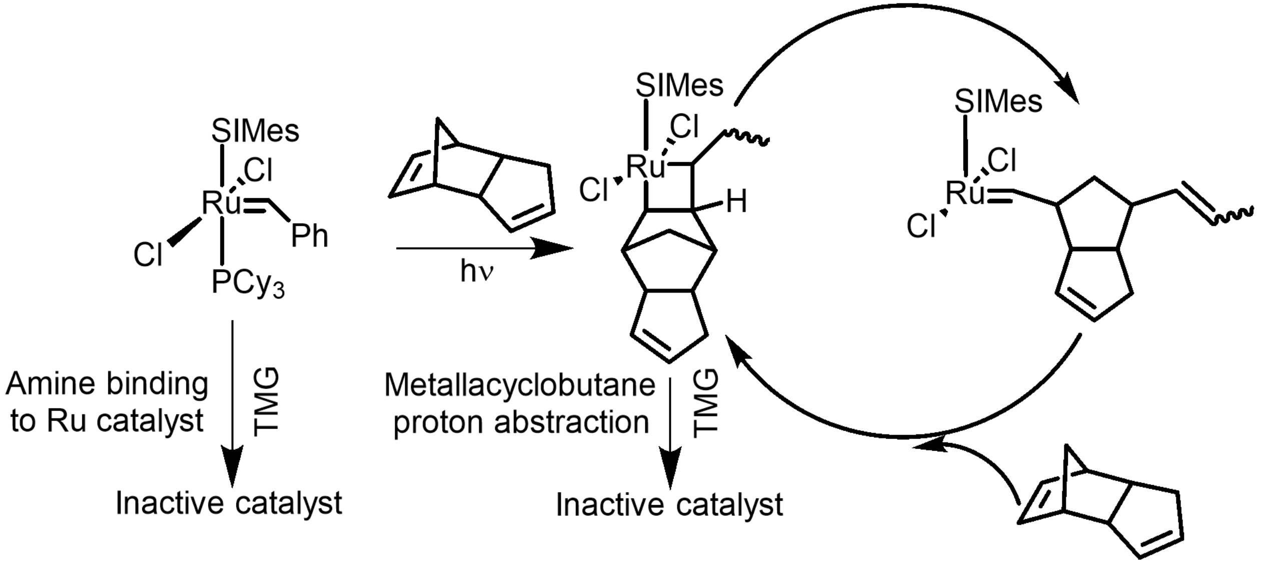


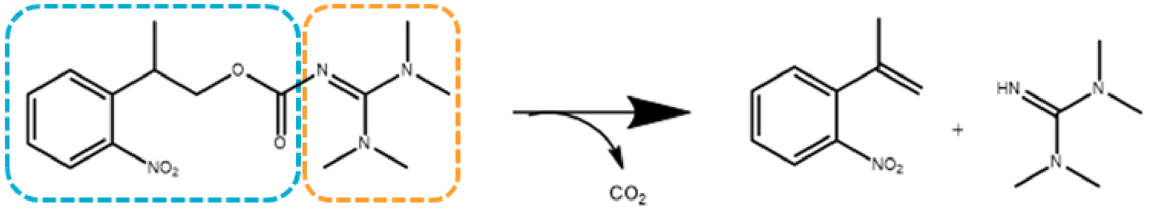
Approaches to FROMP Photocontrol

Catalyst-Based Photocontrol

Use photomasked additives that accelerate or decelerate FROMP through interaction with the catalysts



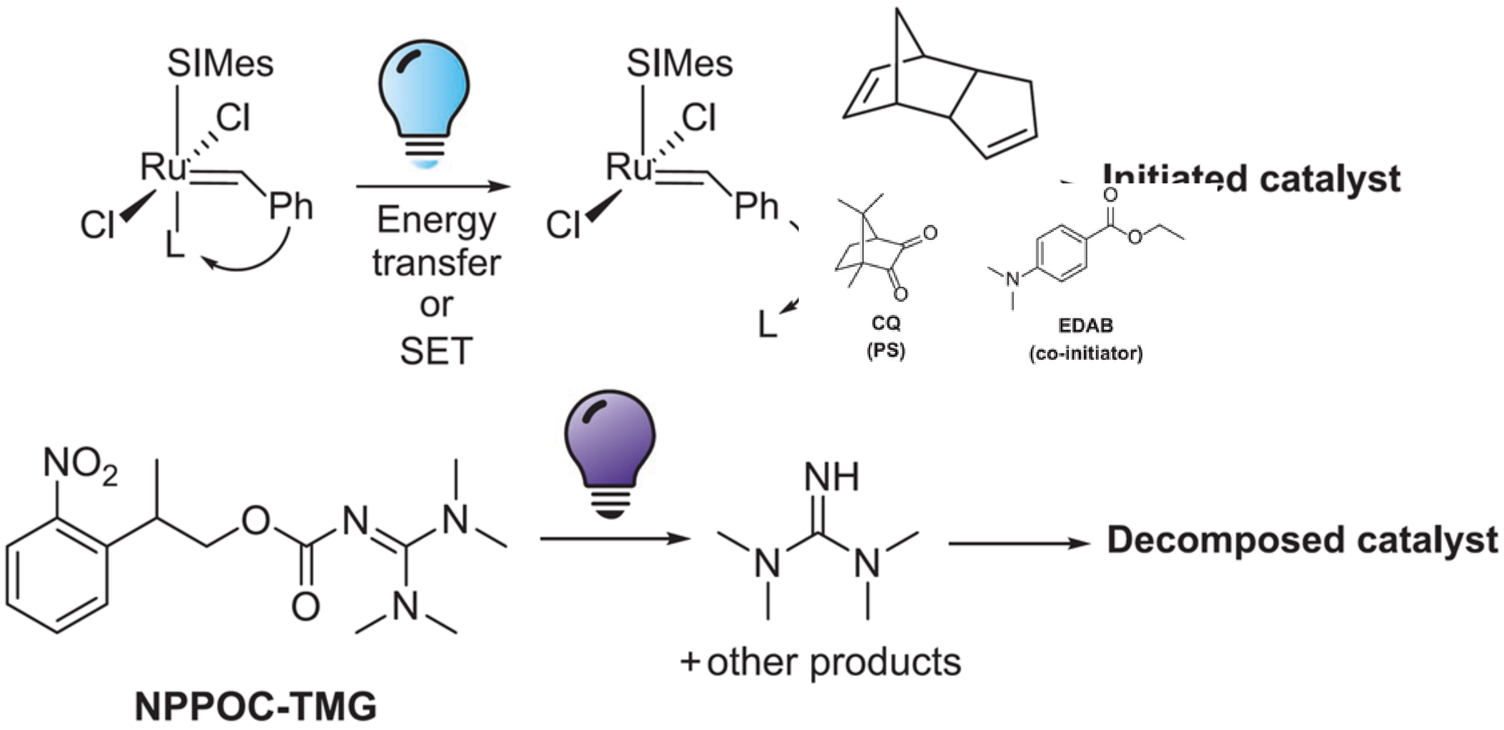
Photobase generator (PBG)

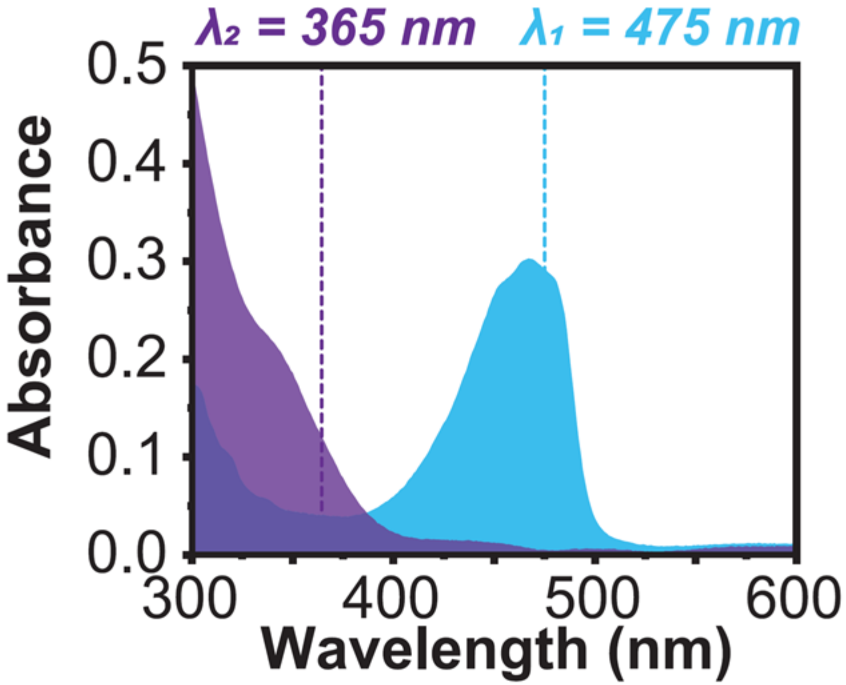


B.J. Ireland, B.T. Dobigny, D.E Fogg *ACS Catal.* **2015**, *5*, 8, 4690–4698

J.A.M. Lummiss, B.J. Ireland, J.M. Sommers, D.E. Fogg *ChemCatChem* **2014**, 6, 459 – 463

Catalyst-based Photocontrol: PhotoROMP Prior Work





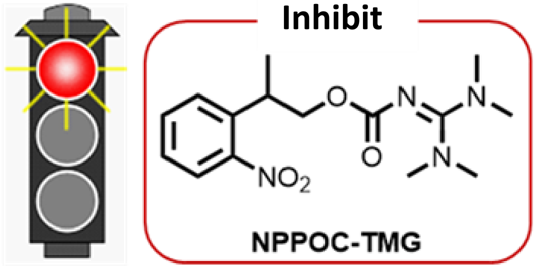
Leguizamon, S. C.*; Monk, N.T; Hochrein, M.T.; Zapien, E.M.; Yoon, A.; Foster, J.C.; Appelhans, L.N.* *Macromolecules*, **2022**, 55, 18, 8273
DOI: 10.1021/acs.macromol.2c01244

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,* 2200770
DOI: 10.1002/advs.202200770

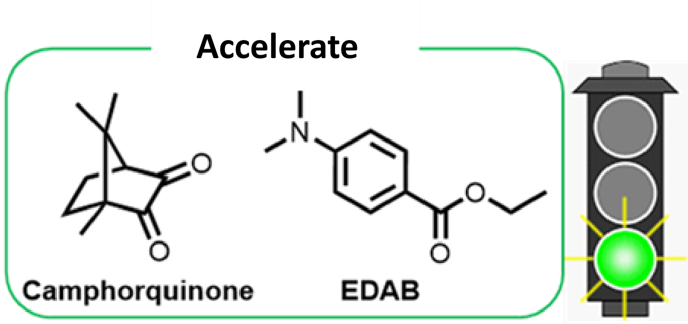
Catalyst-based Photocontrol: FROMP

Dan Darby, Sam Leguizamon (SNL), Andrew Greenlee, Jeffrey Moore (UIUC)

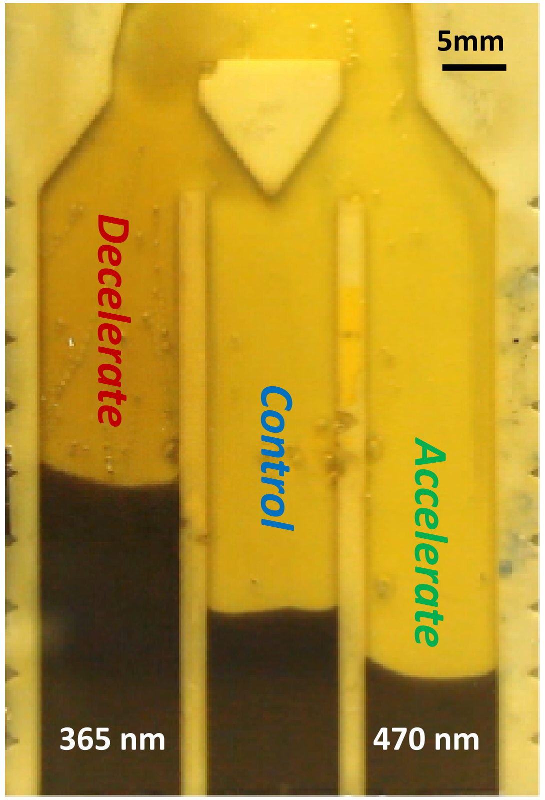
Orthogonal Catalyst-Based Photocontrol



λ = 365 nm

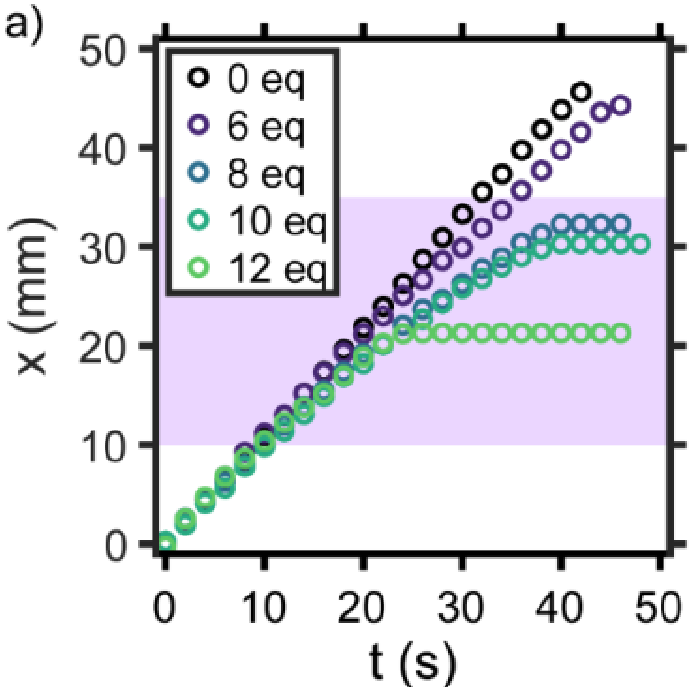


λ = 470 nm

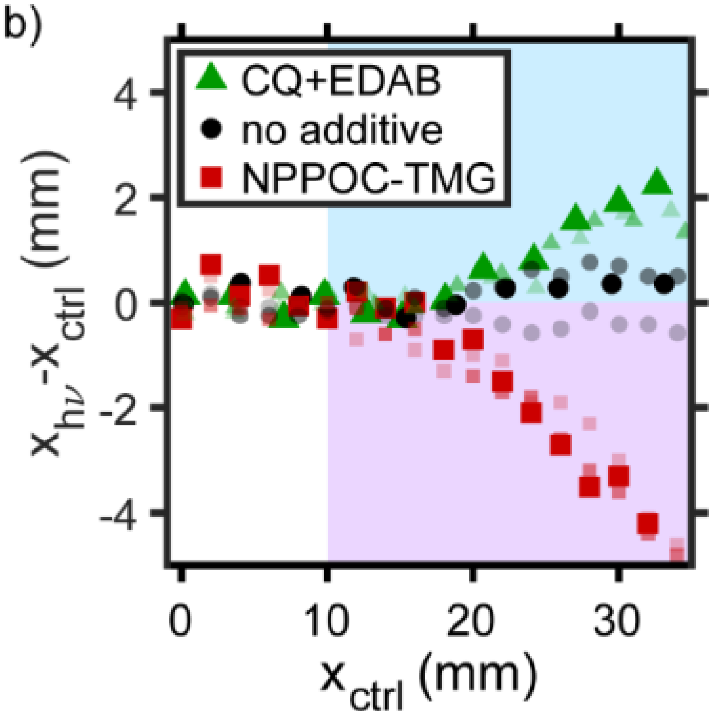


DCPD:ENB (95:5 wt), 150 ppm GC2/TBP
8 eq NPPOC-TMG, 0.5 wt% CQ 1 wt% EDAB
0.5 wt% thermochromic dye
365 nm, ~200 mW/cm^2 , 470 nm, ~250 mW/cm^2

Inhibit

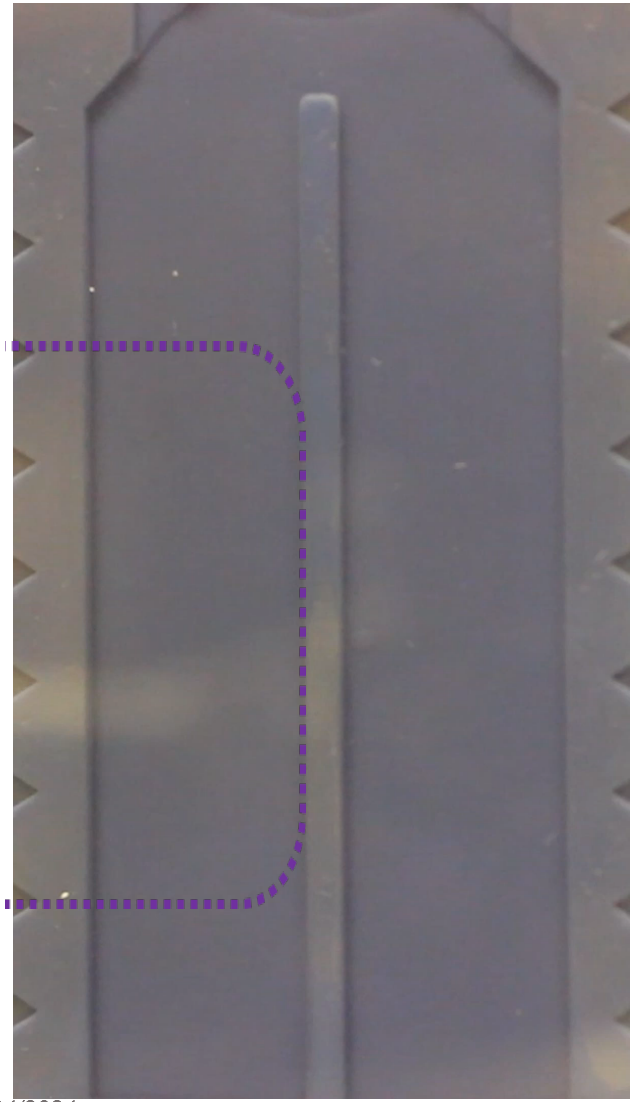


Accelerate



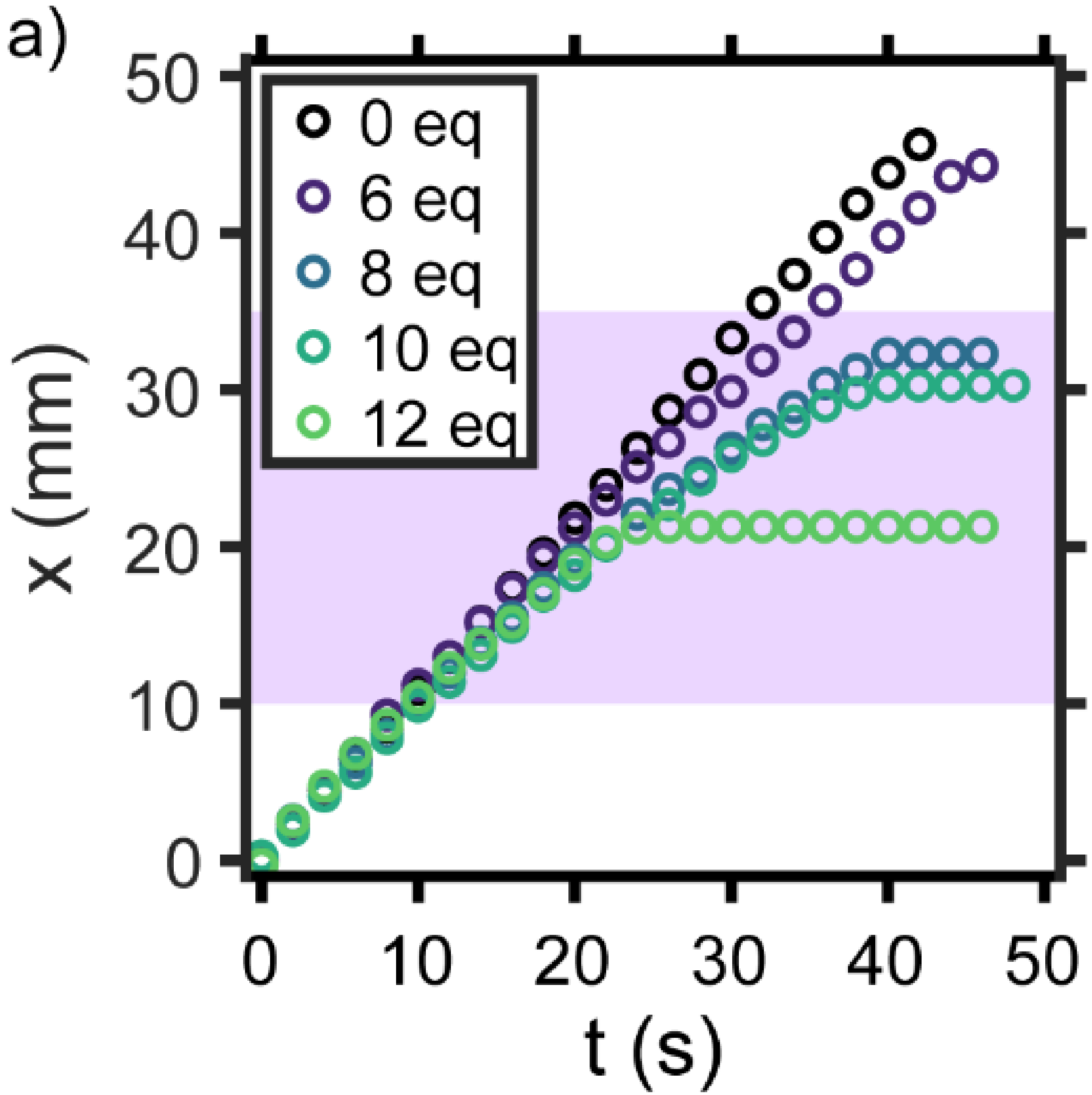
Catalyst-based Photocontrol

Photobase with *in situ* irradiation



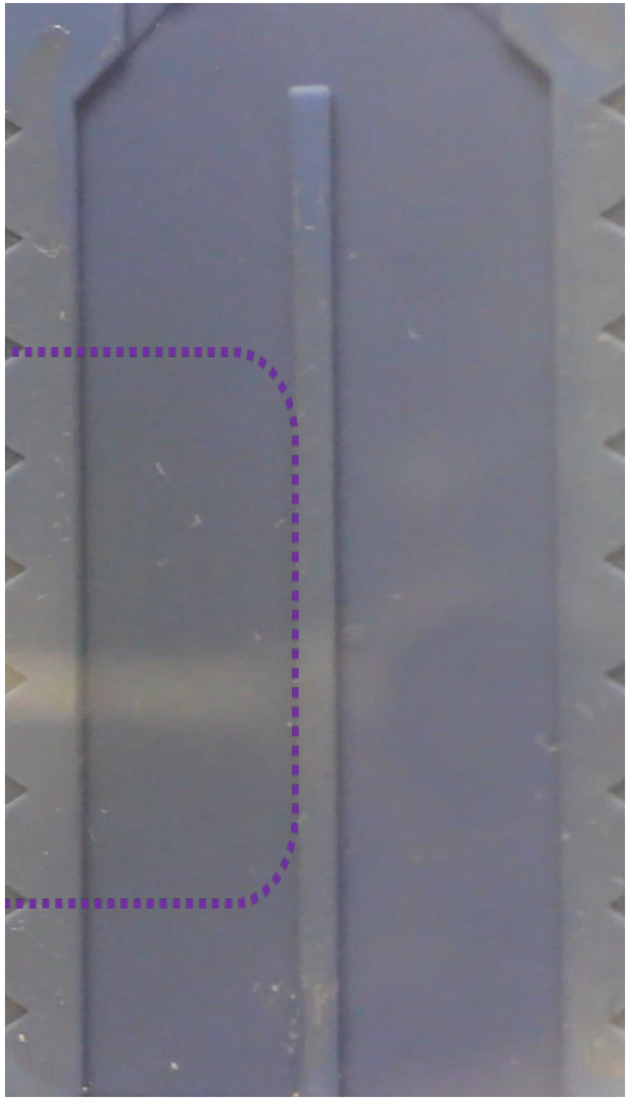
DCPD:ENB (95:5 wt)
10 equiv NPPOC-TMG:GC2
180 mW/cm^2, 365 nm
in situ irradiation
0.1 wt% thermochromic dye

3x speed
10 mm



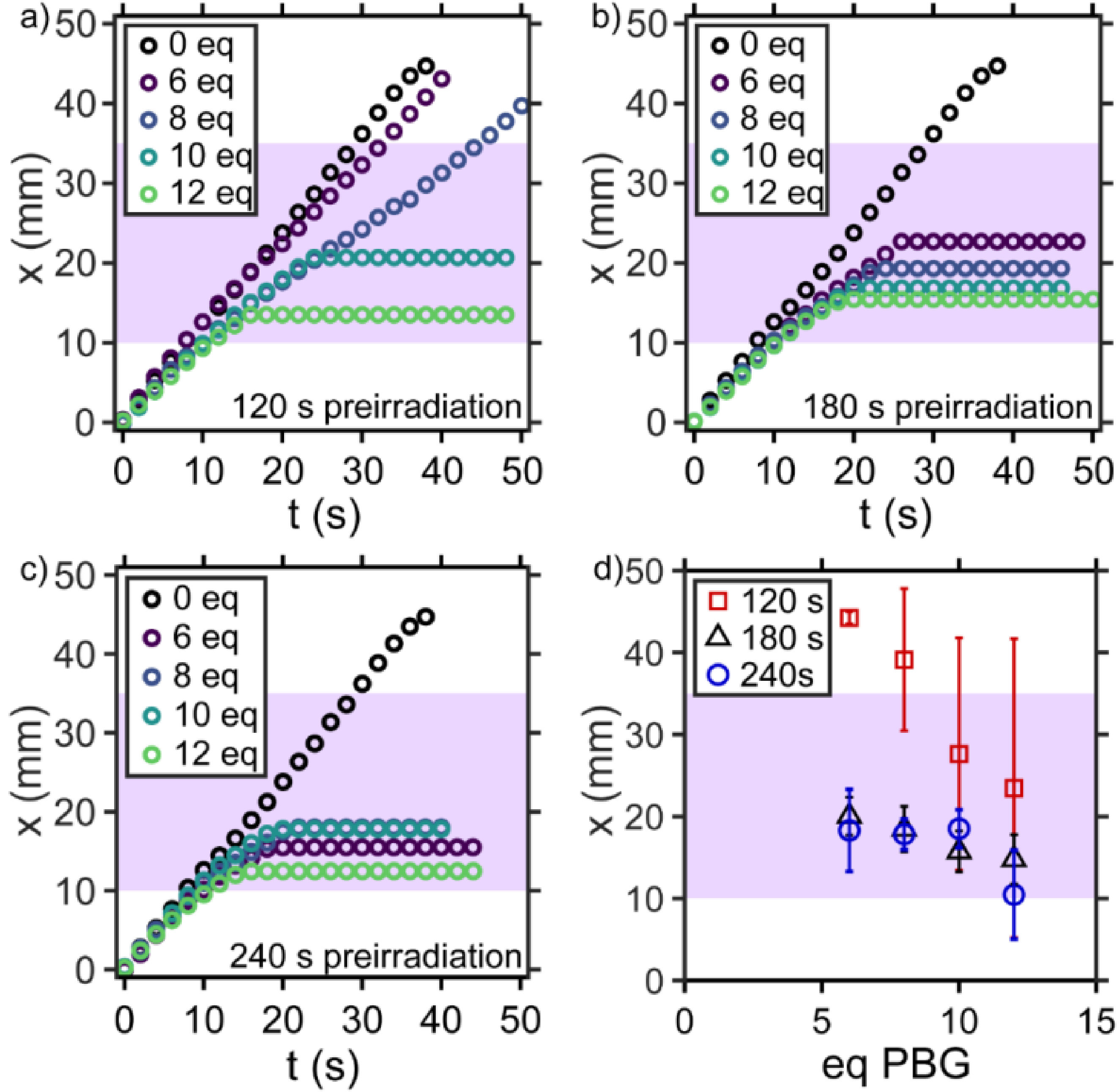
Catalyst-based Photocontrol

Photobase with pre-irradiation



DCPD:ENB (95:5 wt)
8 equiv NPPOC-TMG:GC2
30 mW/cm^2, 365 nm
180s pre-irradiation
0.1 wt% thermochromic dye

3x speed
10 mm

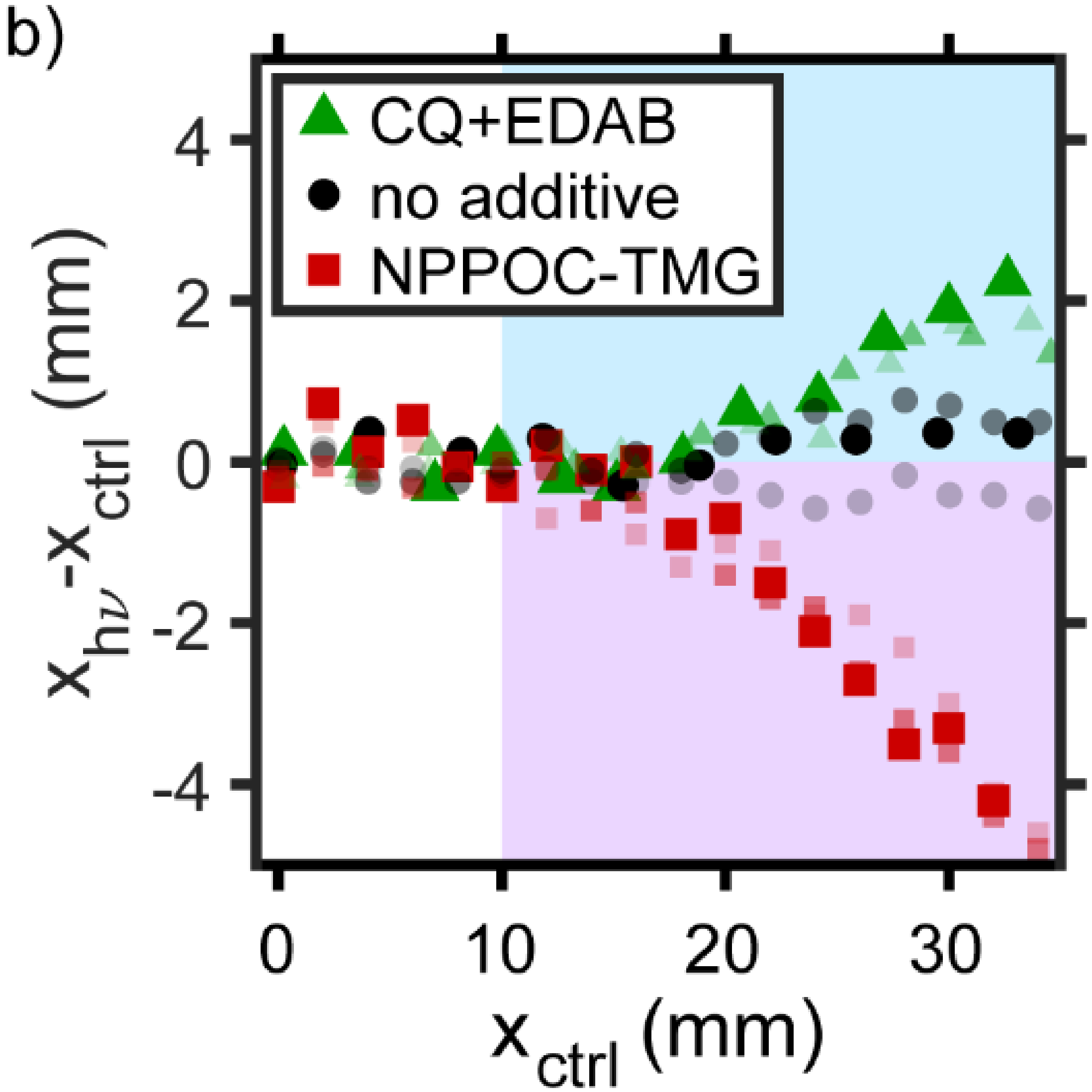


Catalyst-based Photocontrol

Photosensitizer with *in situ* irradiation

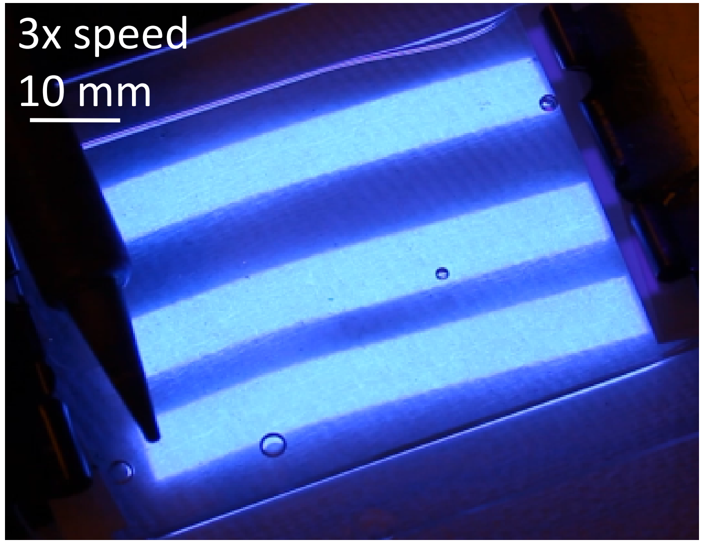
DCPD:ENB (95:5 wt)
8 equiv NPPOC-TMG:GC2
0.5 wt% CQ 1 wt% EDAB 200 mW/cm², 470 nm
in situ irradiation
0.1 wt% thermochromic dye

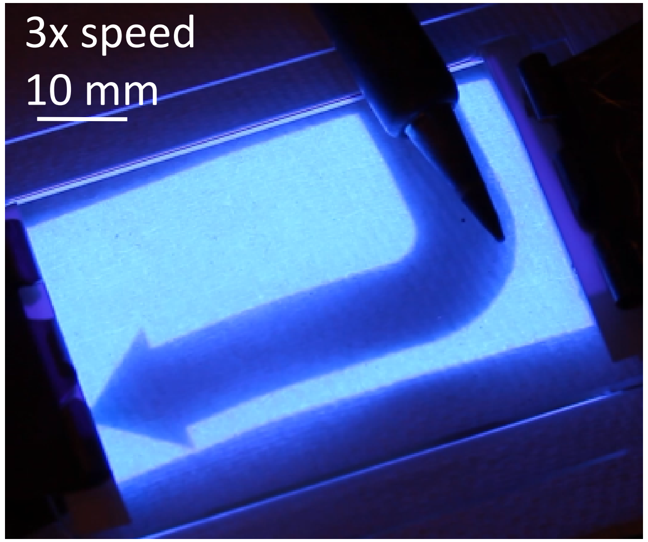
3x speed
10 mm



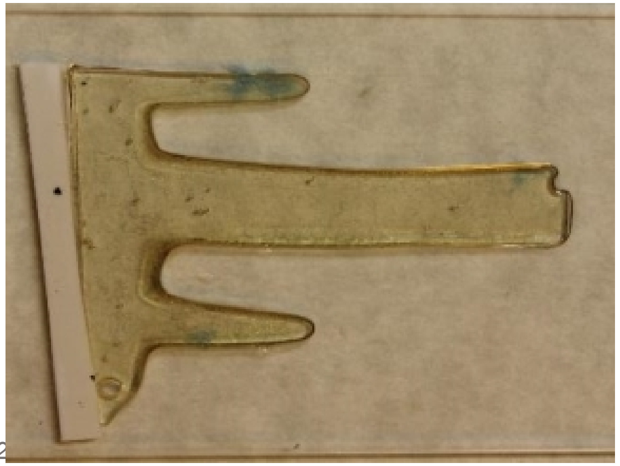
Catalyst-based Photocontrol

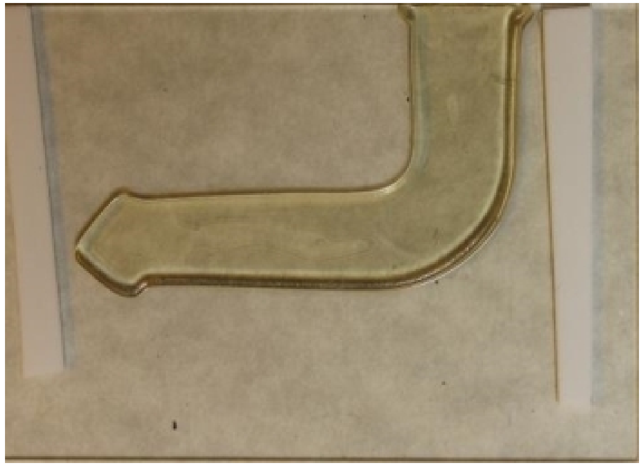
Patterning



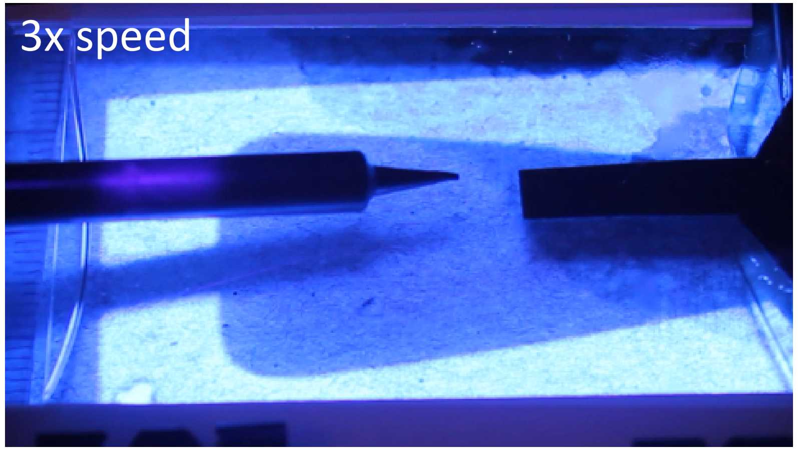


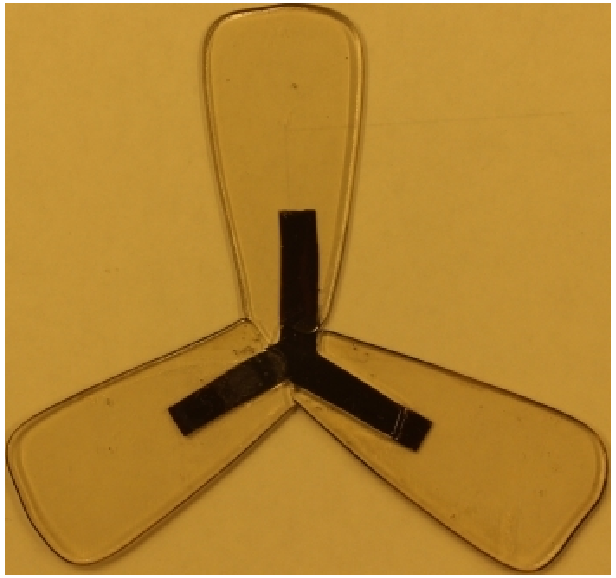
DCPD (10,000 eq.) / GC2 (1 eq.) / TBP (1 eq.) / NPPOC-TMG (8 eq.) w/ 3 min pre-irradiation at 30 mW cm^{-2}





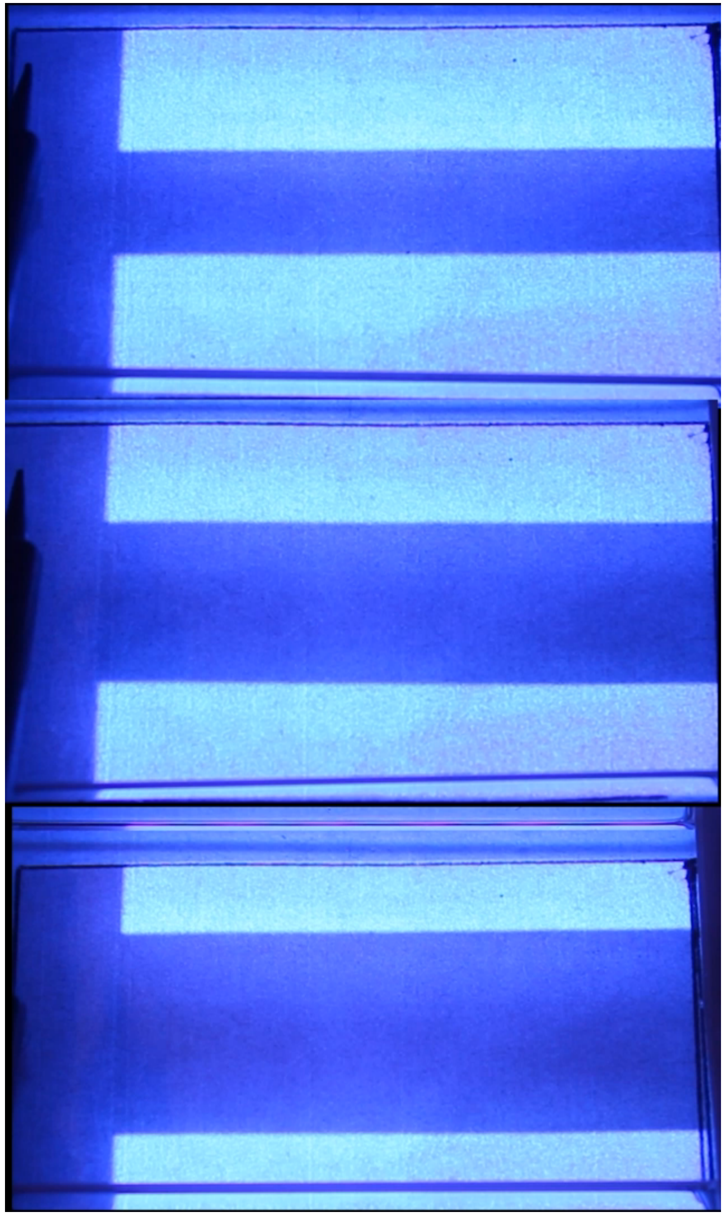
Embedded Objects

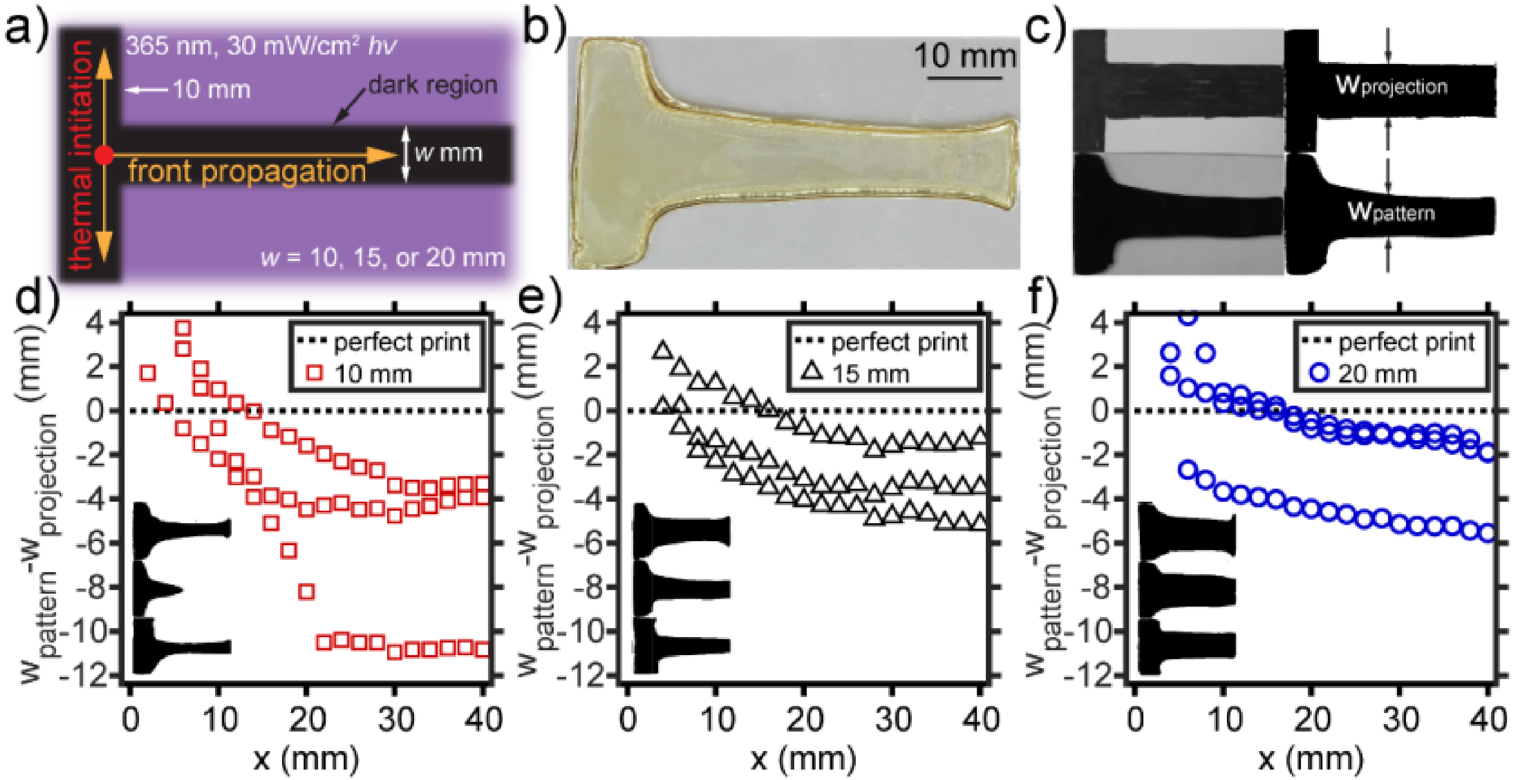




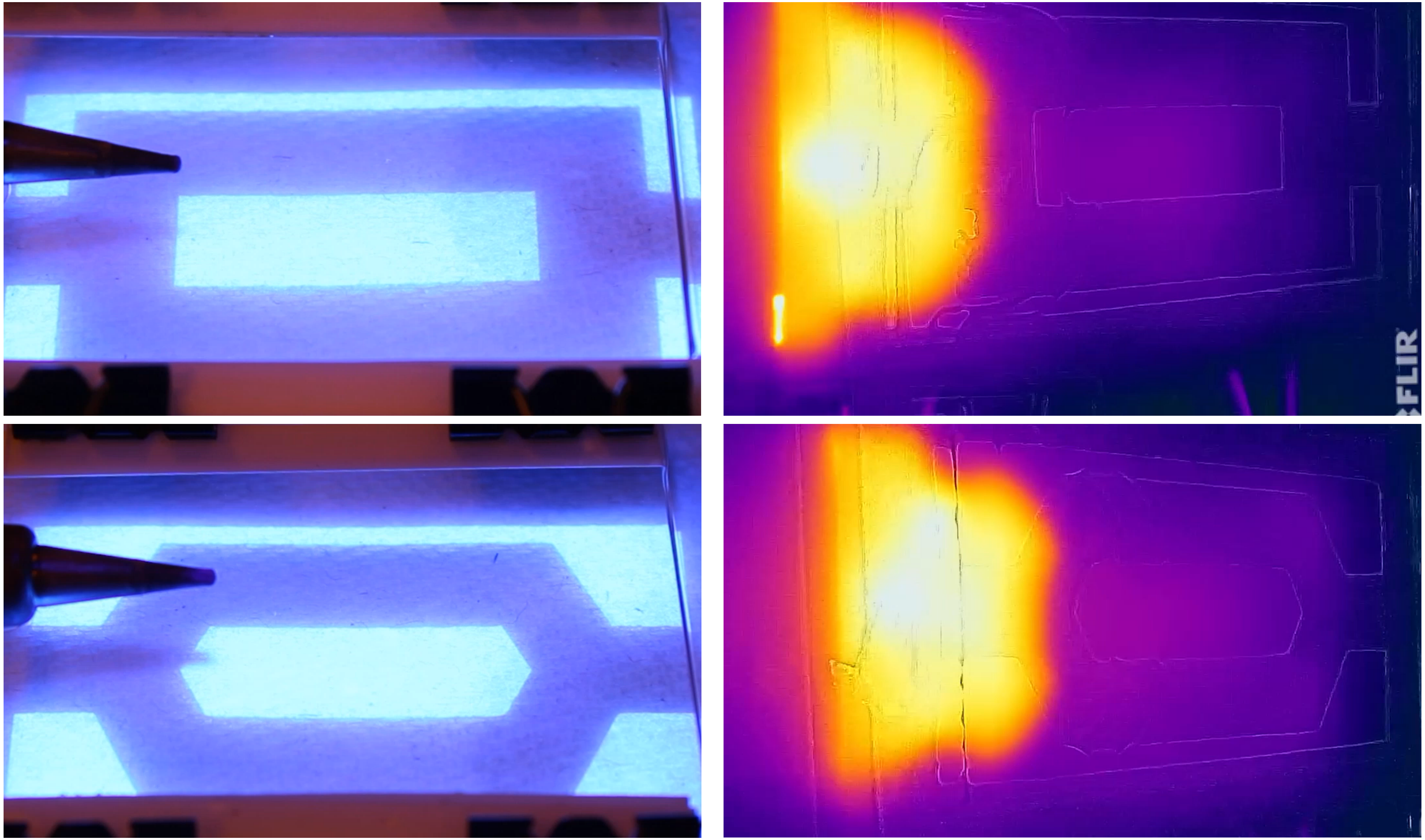
DCPD (10,000 eq.) / GC2 (1 eq.) / TBP (1 eq.) / NPPOC-TMG (8 eq.) w/3 min pre-irradiation at 30 mW cm^{-2}

Catalyst-based Photocontrol





Catalyst-based Photocontrol



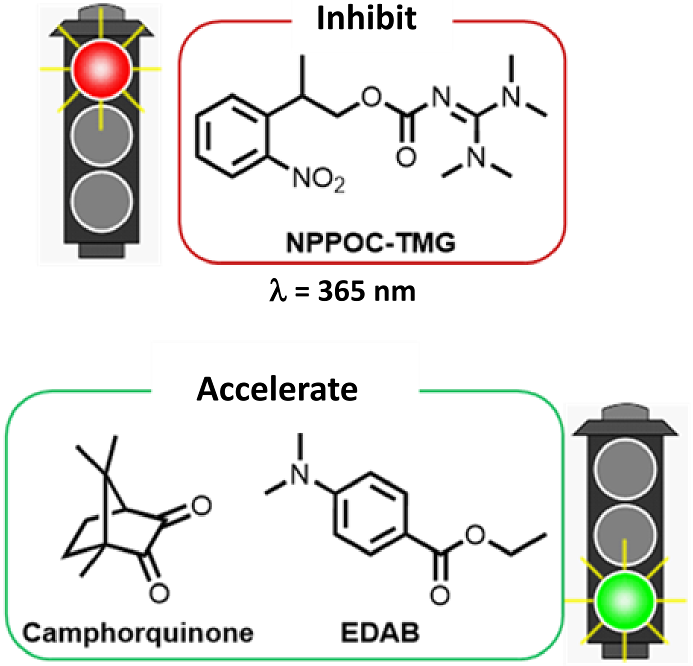
DCPD (10,000 eq.)
GC2 (1 eq.)/TBP (1 eq.)
NPPOC-TMG (8 eq.)
3 min pre-irradiation at 30 mW cm^{-2}

3x speed

Catalyst-based Photocontrol: FROMP

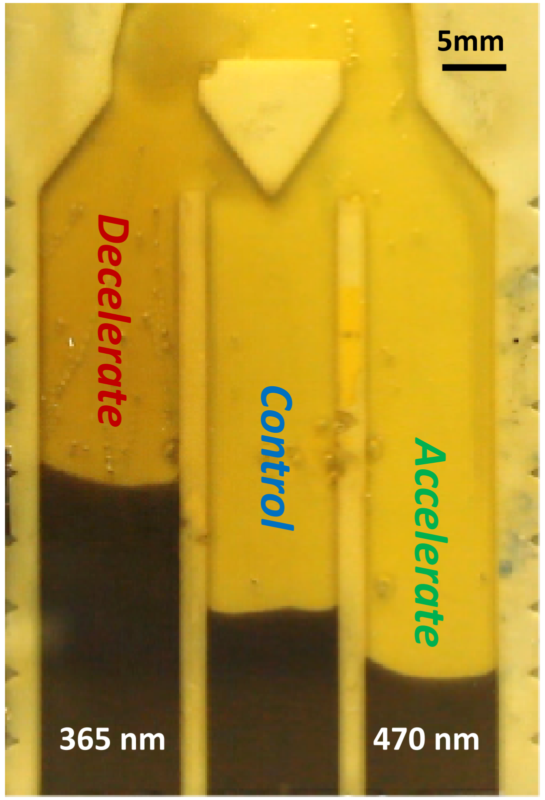
Dan Darby, Sam Leguizamon (SNL), Andrew Greenlee, Jeffrey Moore (UIUC)

Orthogonal Catalyst-Based Photocontrol



λ = 365 nm

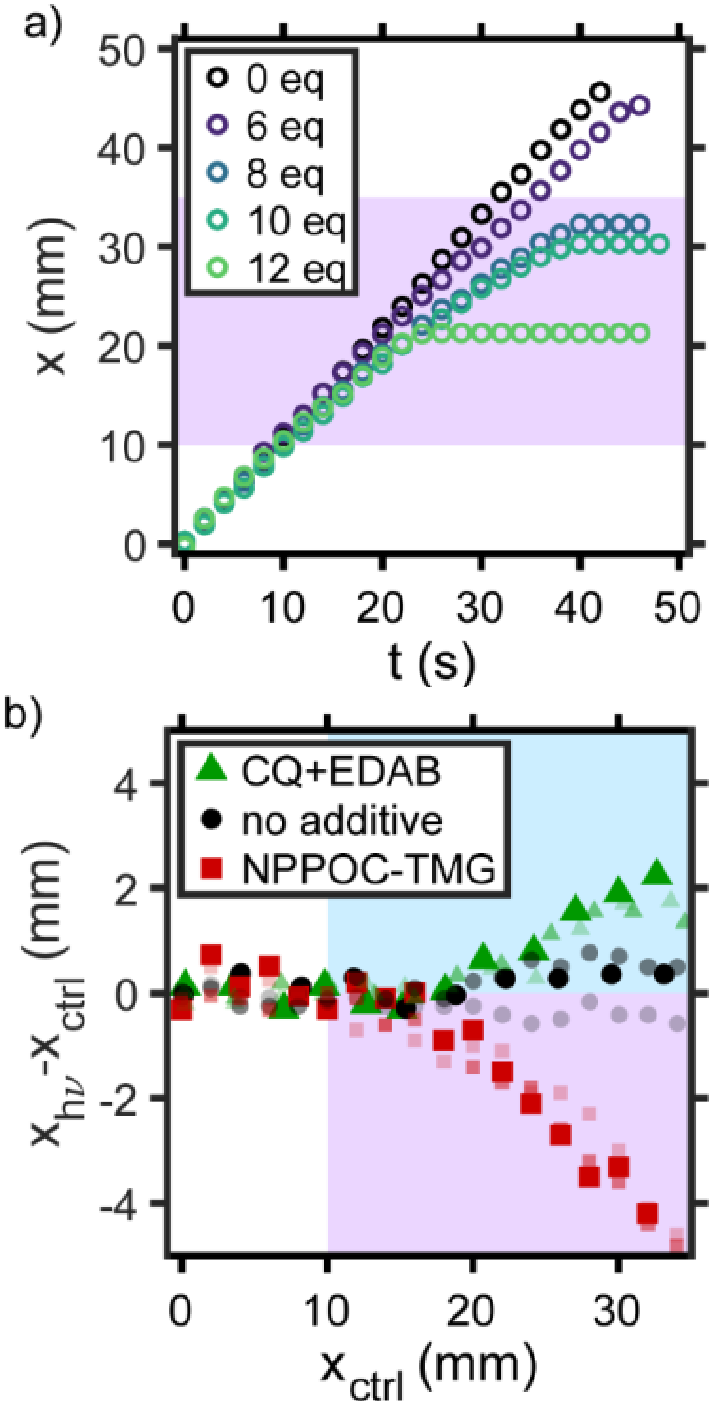
λ = 470 nm



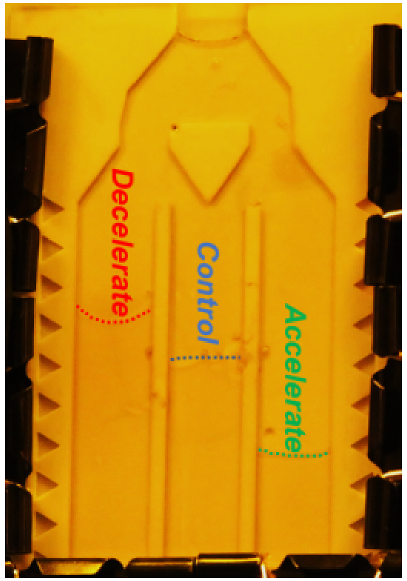
DCPD:ENB (95:5 wt), 150 ppm GC2/TBP
8 eq NPPOC-TMG, 0.5 wt% CQ 1 wt% EDAB
0.5 wt% thermochromic dye
365 nm, ~200 mW/cm^2, 470 nm, ~250 mW/cm^2

Inhibit

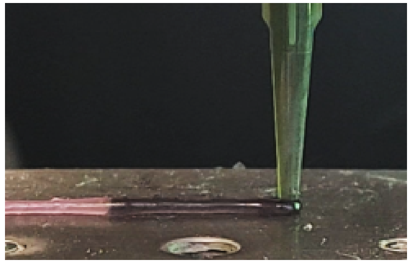
Accelerate

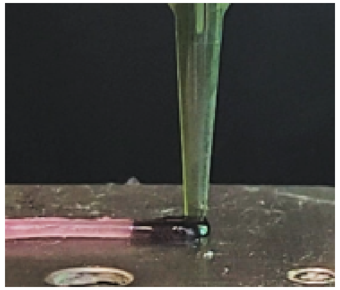


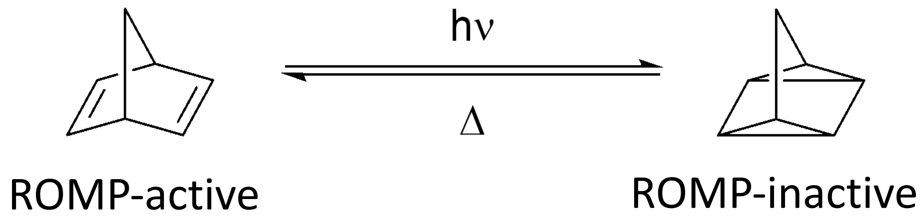
Next Steps

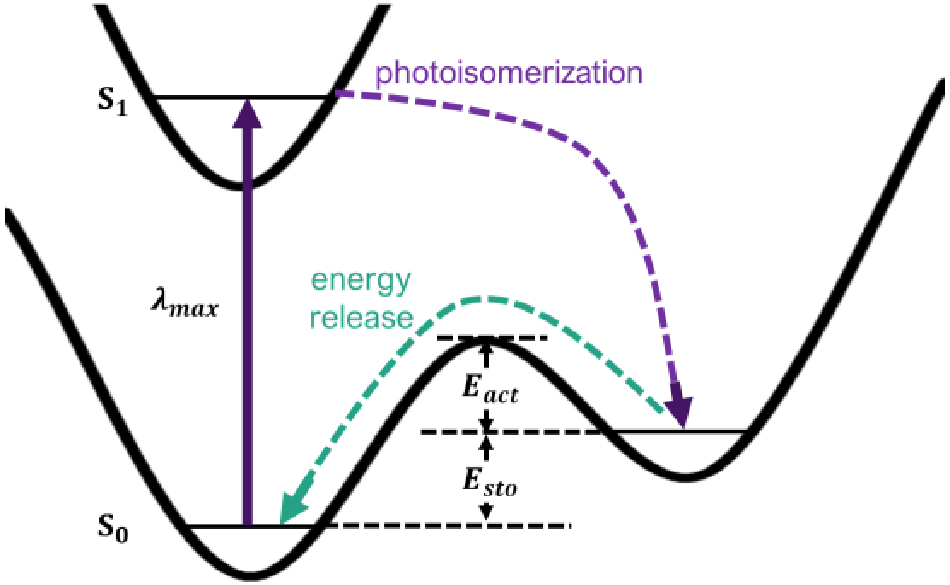


+









Integrated Photocontrol + Process Control

- Add automated photocontrol
- Add start/stop control
- Automate FROMP restart
- Improve "depth perception"

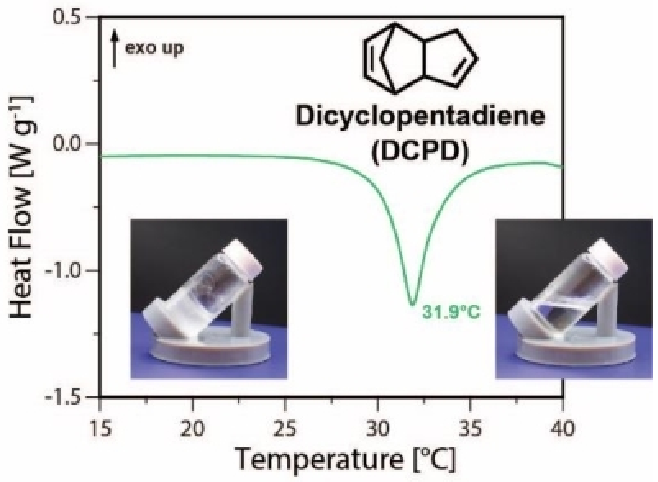
Monomer Based Photocontrol

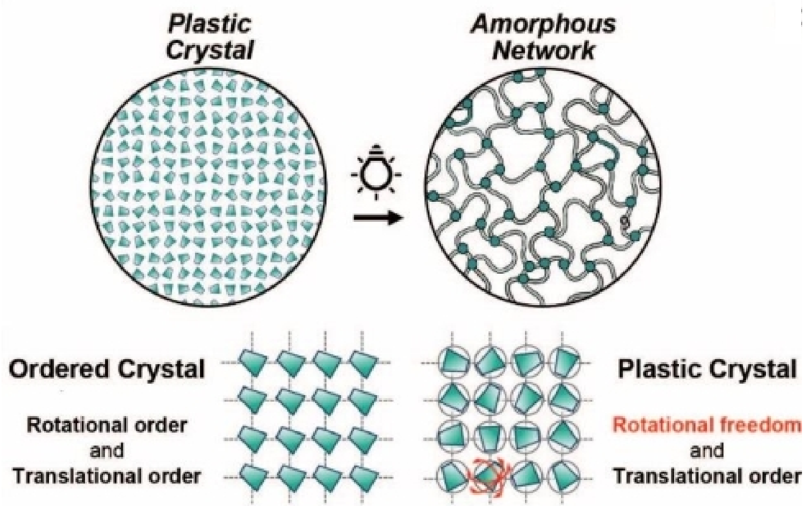
collaboration with Kasper Moth-Poulsen
Polytechnic University of Catalunya

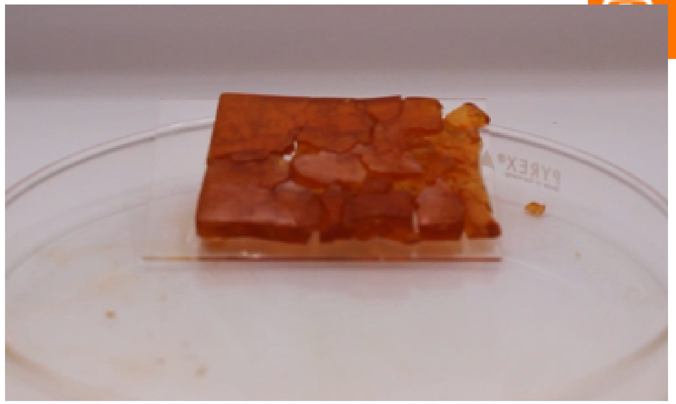
Solid-state PhotoROMP

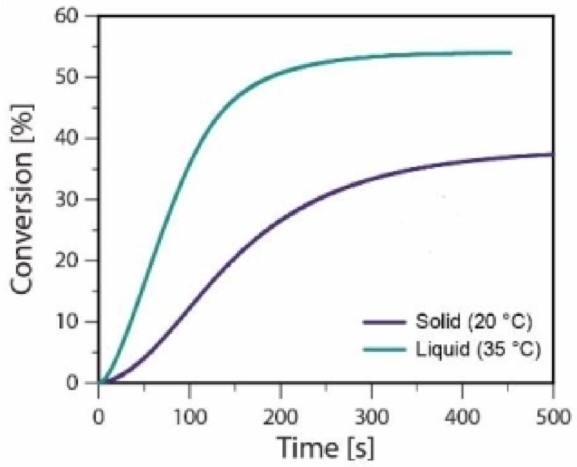
MSRF LDRD #23-0034: Sam Leguizamon and Matthew Hausladen

DCPD is not only a solid at RT, but ***a plastic crystal,*** allowing for photopolymerization in the solid-state

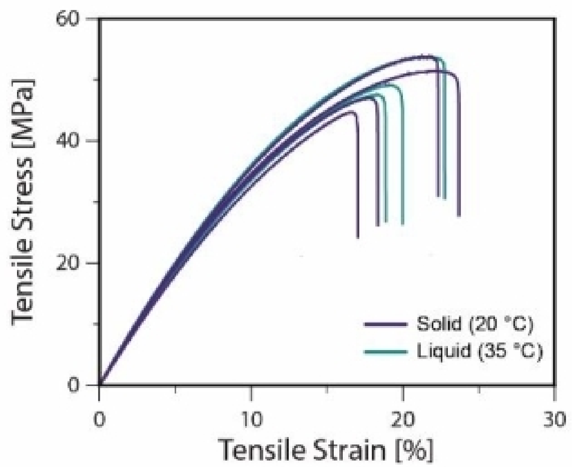


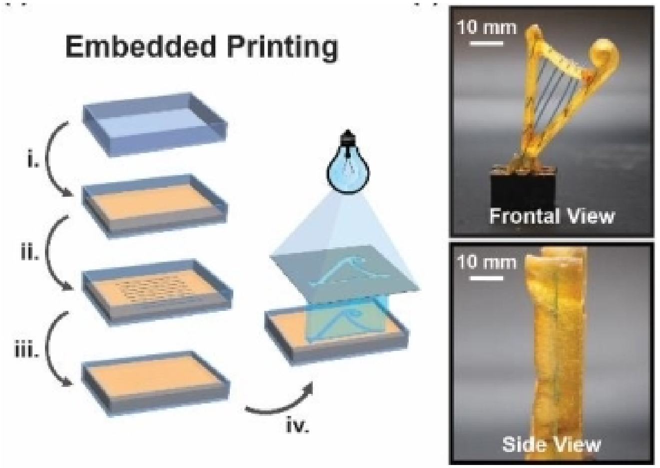






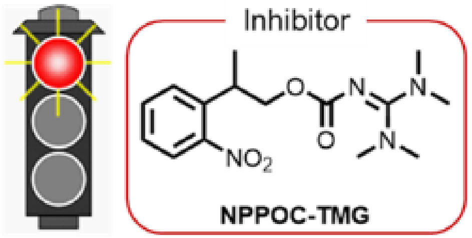
Appreciable conversion, even at reduced temperatures and no difference in mechanical properties after a thermal post-cure



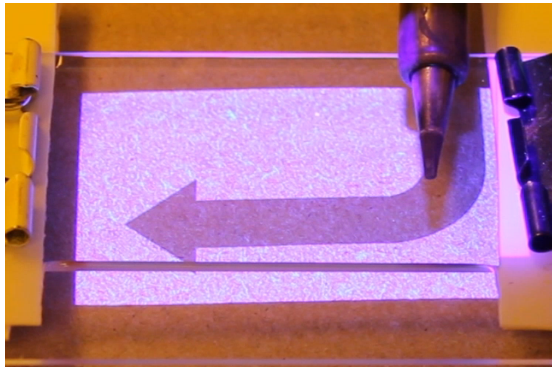


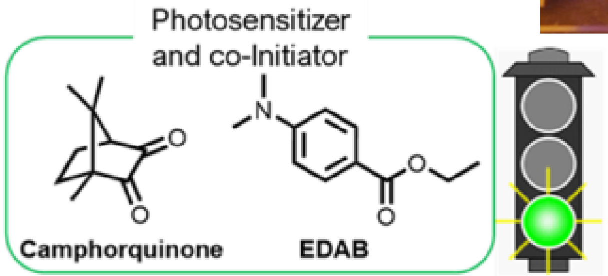
Summary

Catalyst Based Photocontrol of FROMP



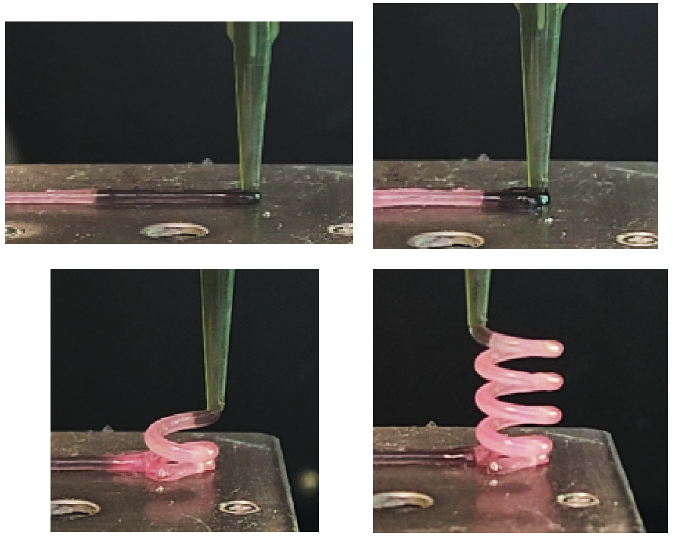
λ = 365 nm

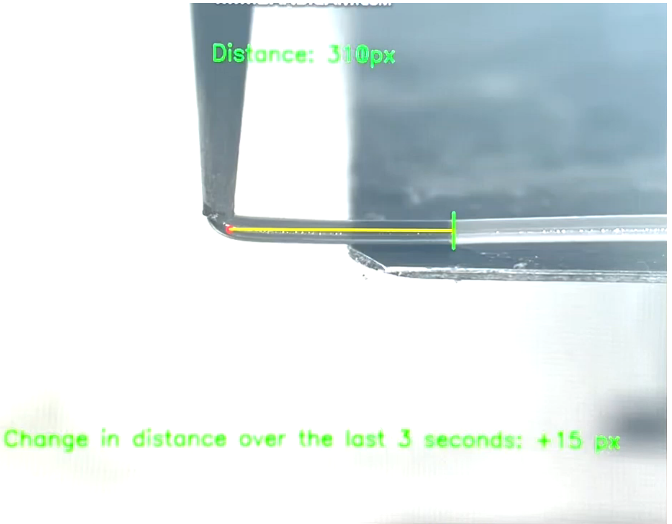




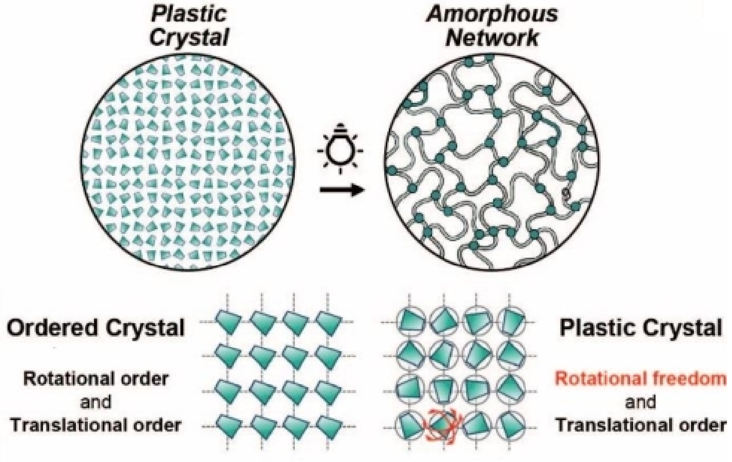
λ = 470 nm

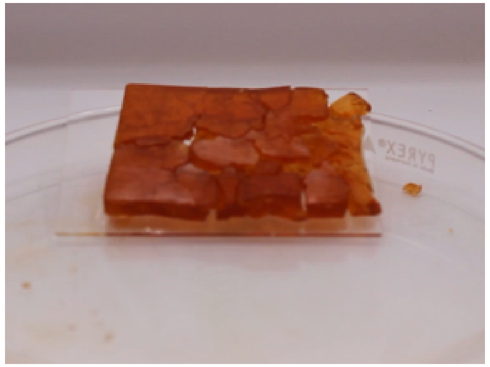
Closed Loop Autonomous Process Control

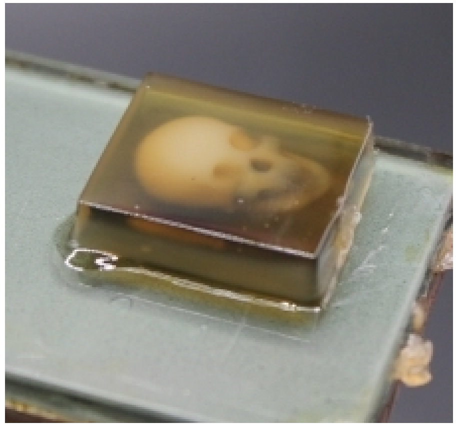




Solid State Printing with PhotoROMP

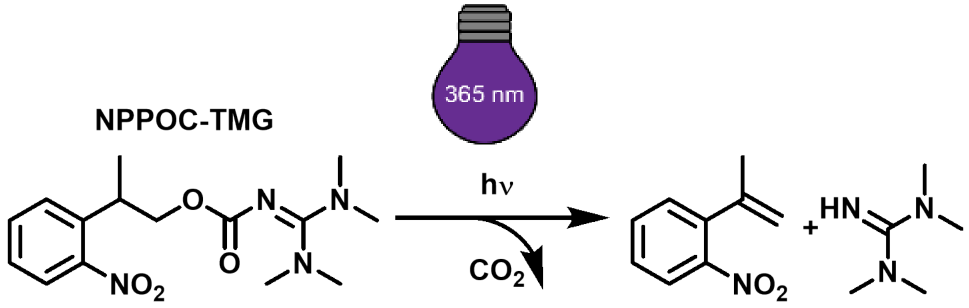






Supplementary Slides

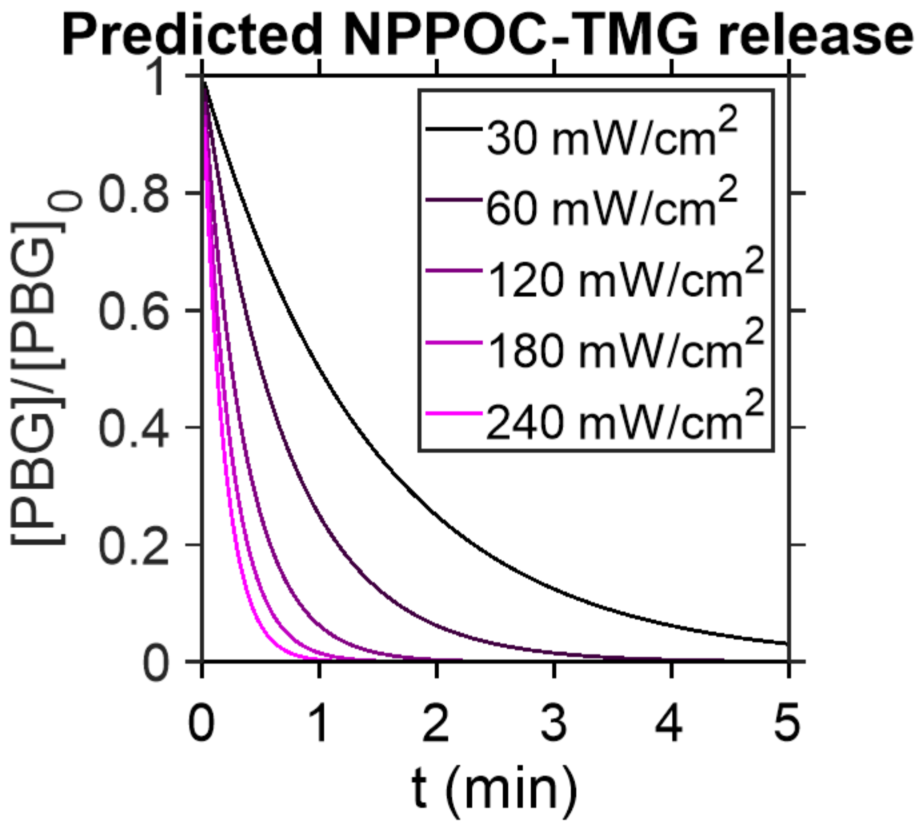
Catalyst-based Photocontrol



365 nm light liberates TMG
from NPPOC-TMG

$$-\frac{d[I]}{dt} = \frac{2.303\epsilon\phi[I]I_0\lambda}{N_{AV}hc}$$

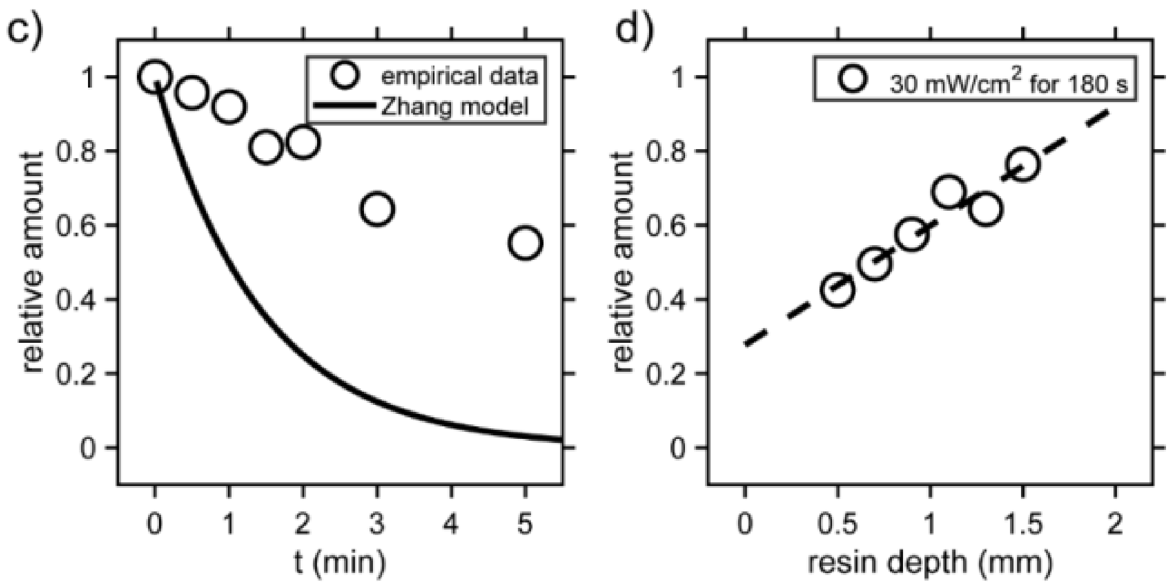
$[I]$ = concentration of PBG
t = time
I_0 = light intensity
λ = wavelength of light
$\epsilon\phi$ = photolytic efficiency



Zhang, X.; Xi, W.; Gao, G.; Wang, X.; Stansbury, J. W.;
Bowman, C. N. ACS Macro Lett 2018, 7 (7), 852-857

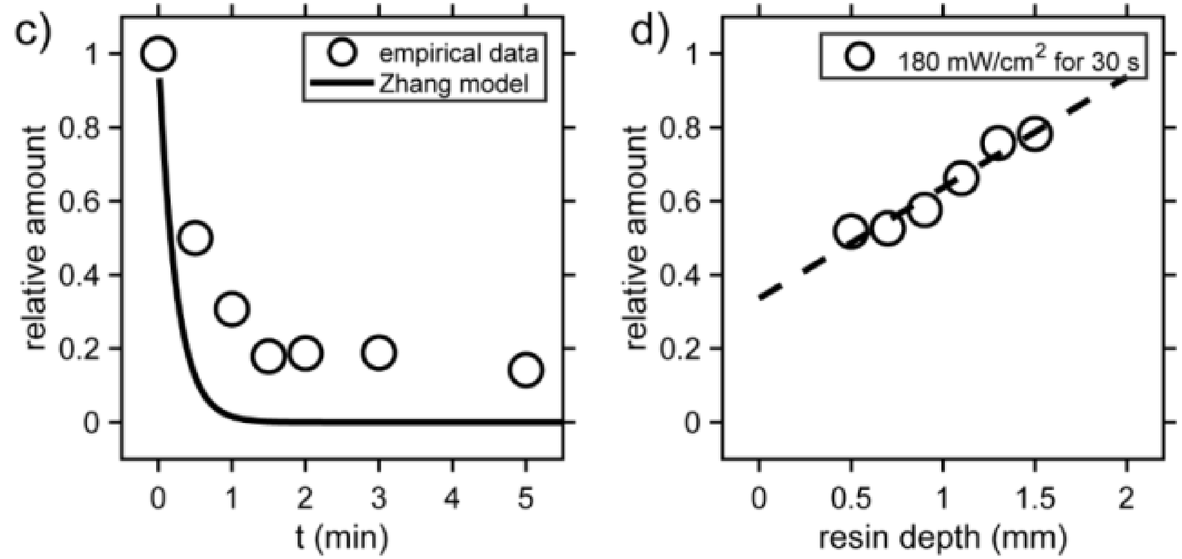
Catalyst-based Photocontrol

365 nm, 30 mW/cm^2, c) 1.3 mm thick



DCPD:ENB (95:5 wt), NO GC2/TBP,
100:1 mol/mol DCPD:NPPOC-TMG
365 nm, 30 mW/cm^2

365 nm, 180 mW/cm^2, c) 0.5 mm thick



DCPD:ENB (95:5 wt), NO GC2/TBP,
100:1 mol/mol DCPD:NPPOC-TMG
365 nm, 180 mW/cm^2

Catalyst-based Photocontrol