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Sandia National Laboratories

Thermoset Polymerization Through Controlled Release of Metathesis Catalysts Encapsulated in Poly(phthalaldehyde)

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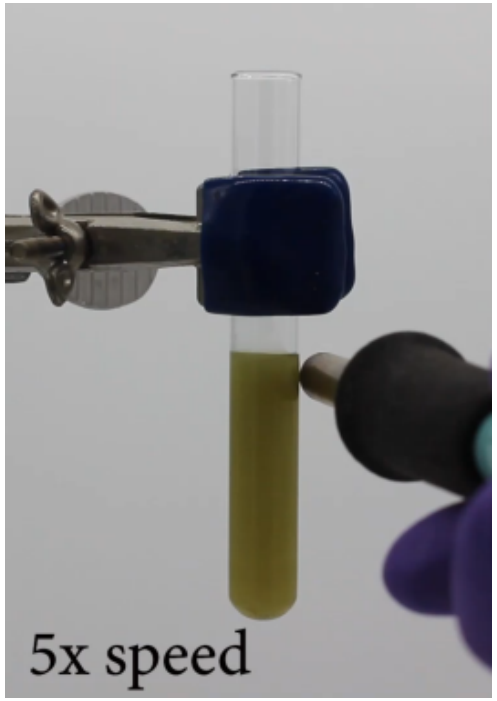
Frontal Polymerization (FP)

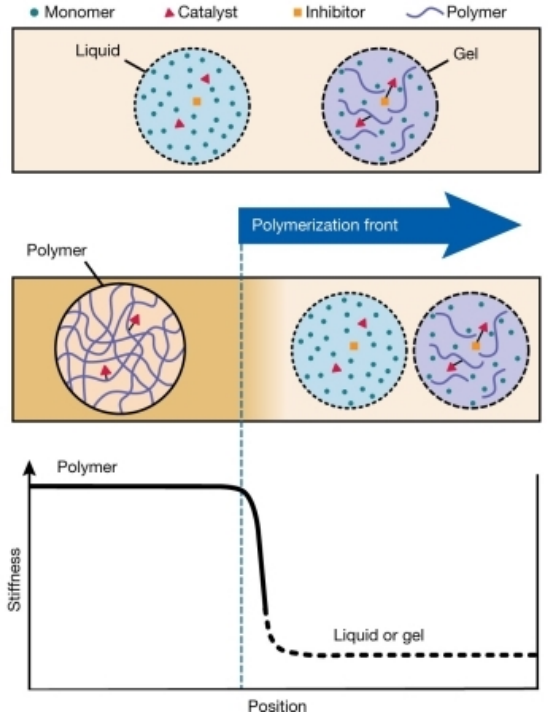
Rapid generation of polymeric materials that utilizes the intrinsic energy from heat of produced from an exothermic polymerization reaction

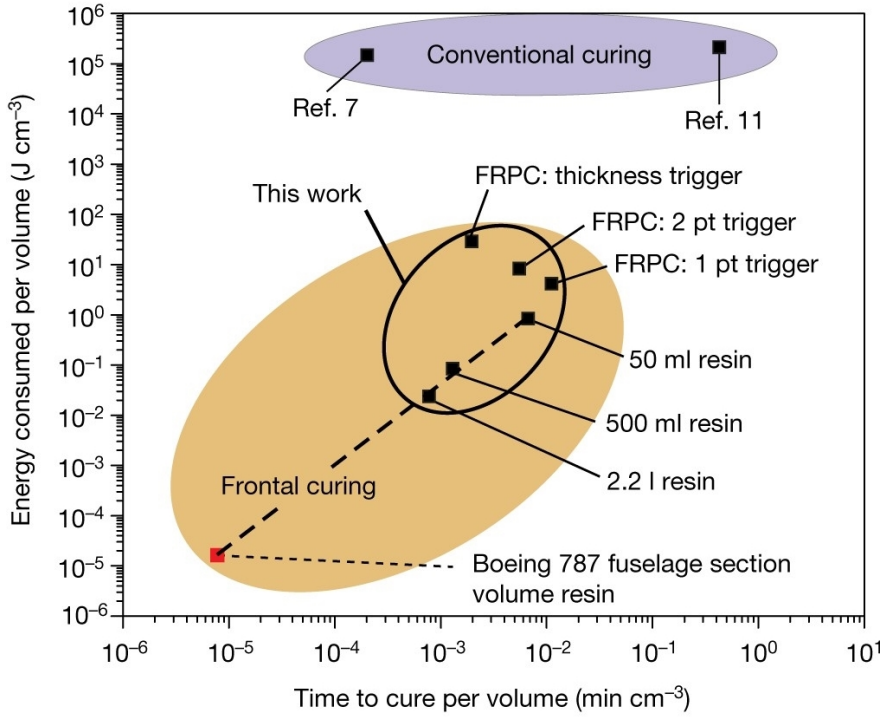
Reduces energy requirements

Reduces time to cure

Inexpensive equipment



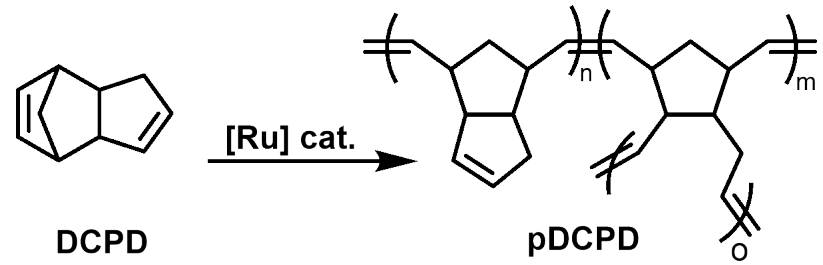




Davydovich, O. et al. *Macromolecules* **2023**, 56, *18*, 7543–7550

Robertson, I. D. et al. *Nature* **2018**, *557*, 223–227

Frontal Ring-Opening Metathesis Polymerization



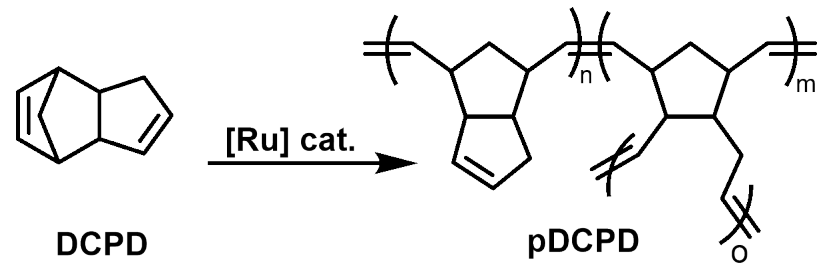
Strained Cyclic Olefins

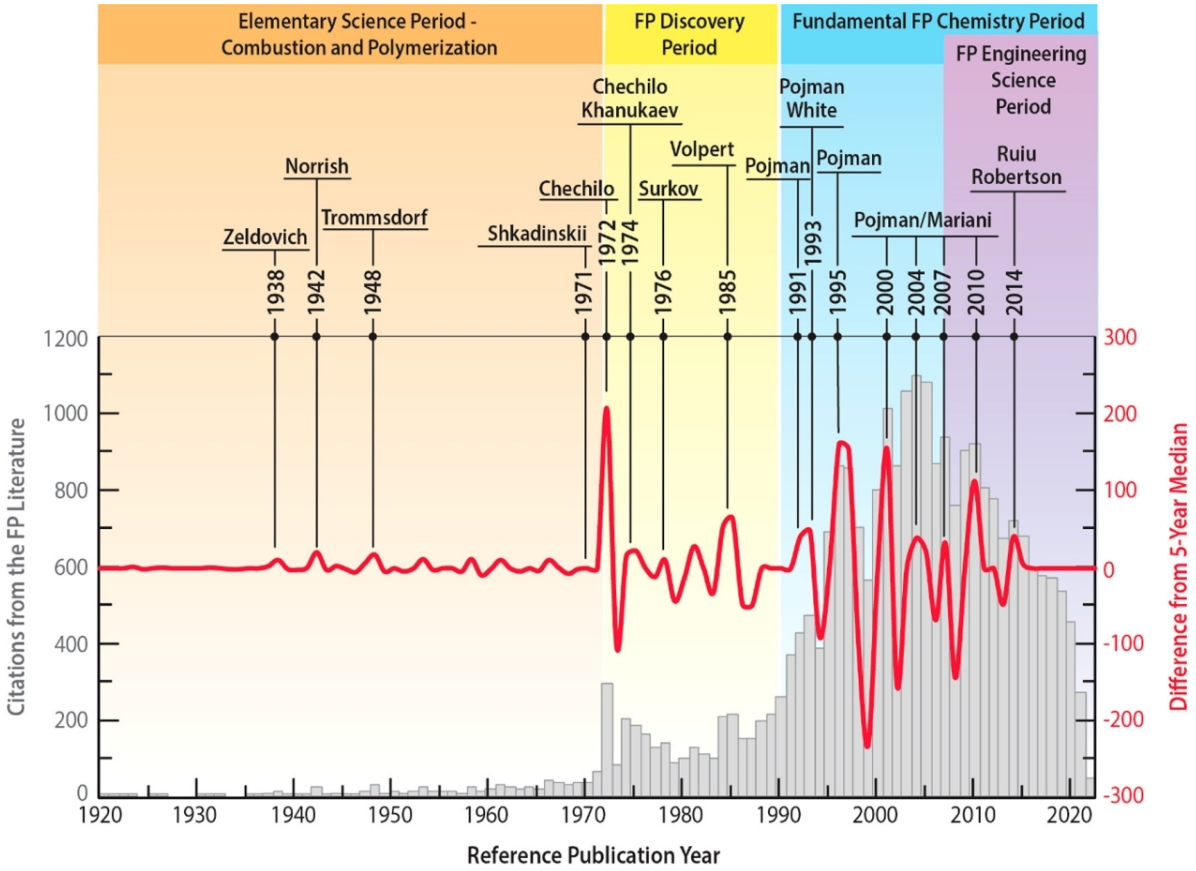
High Energy Density

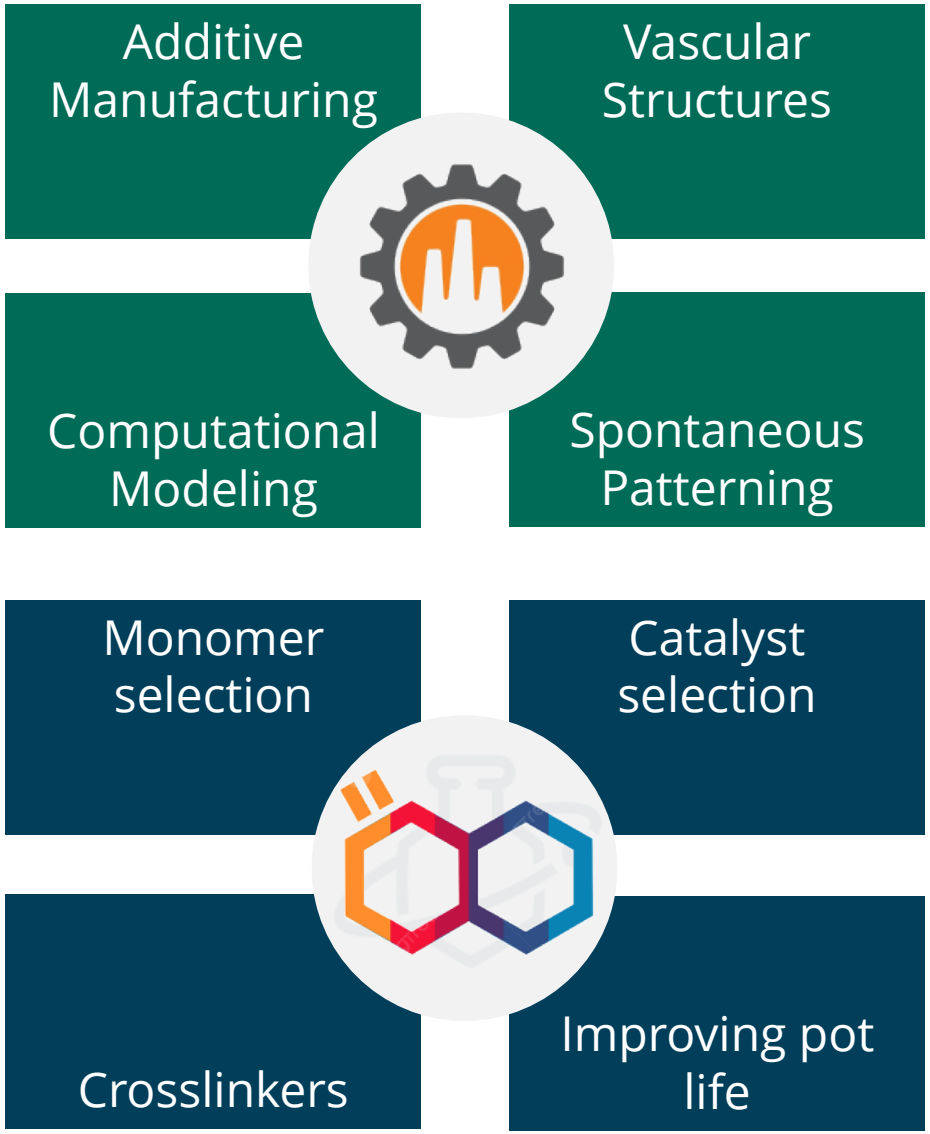
Fast Propagation Kinetics

Background Polymerization

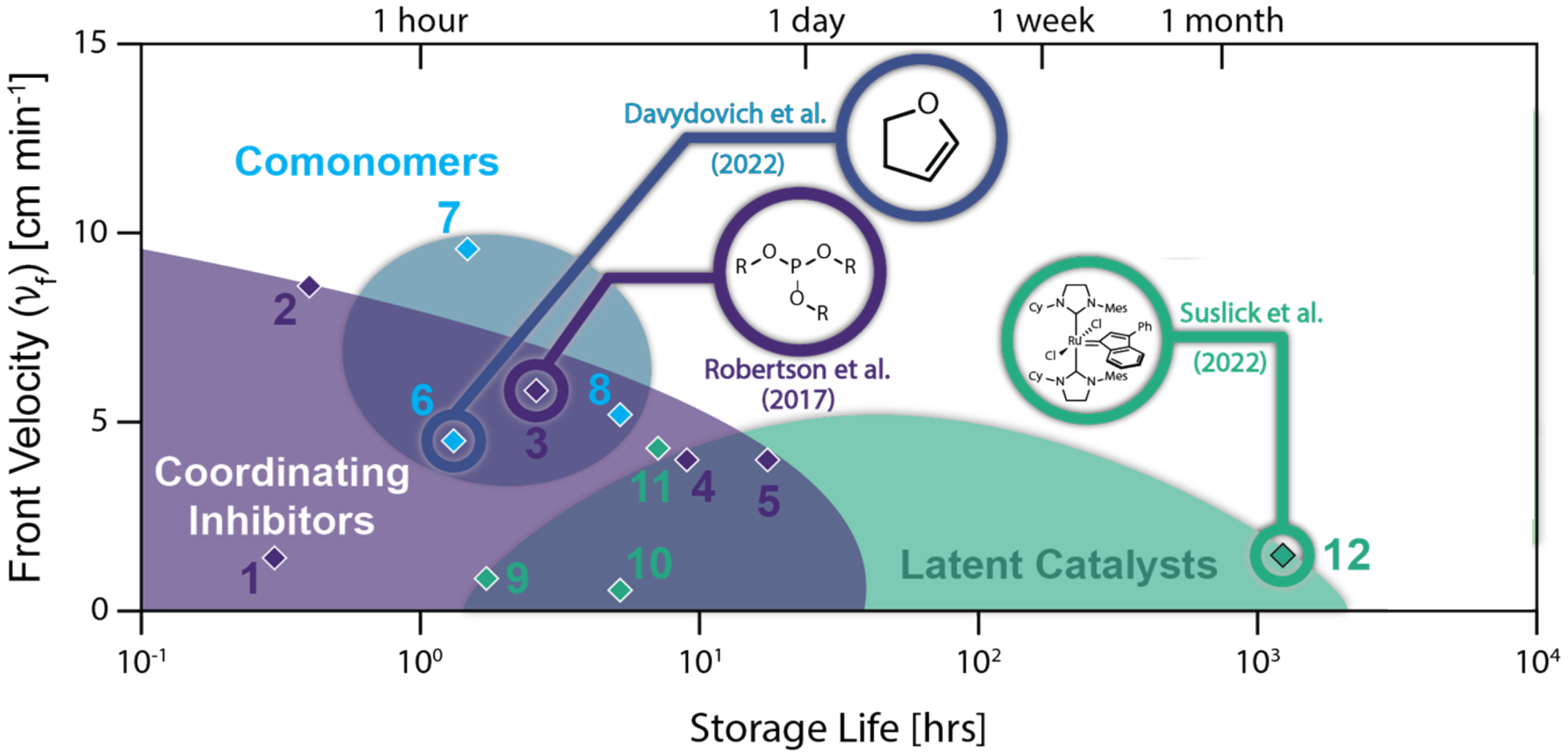
Frontal Ring-Opening Metathesis Polymerization







Frontal Polymerization Systems



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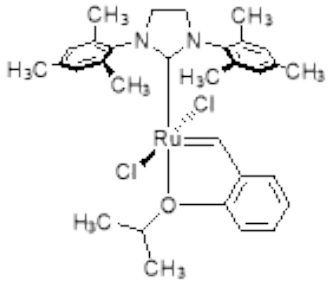
Frontal Polymerization using encapsulated catalysts

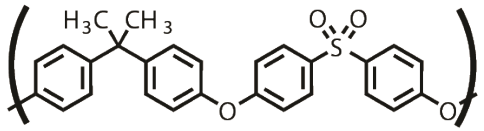
Microparticle Components

Pot life > 1 year

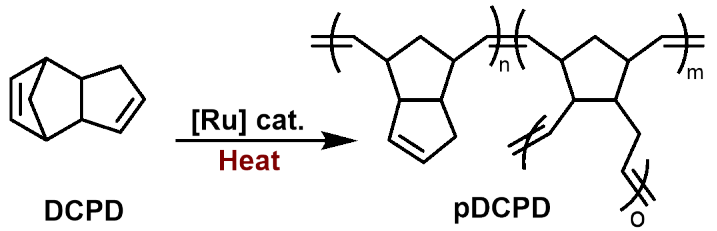
Frontal Polymerization

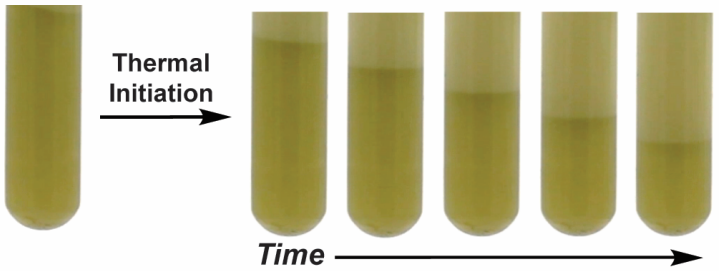


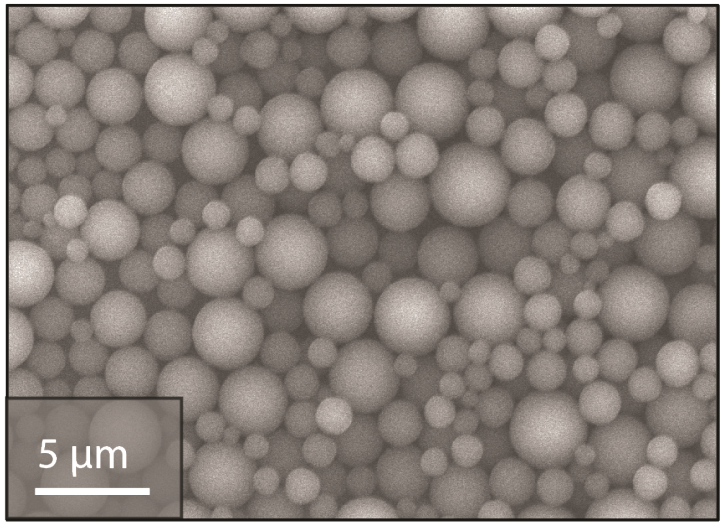
HG2

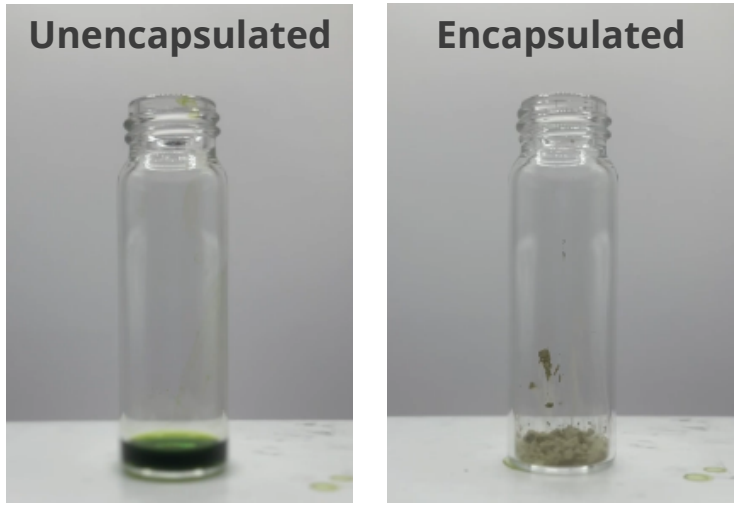


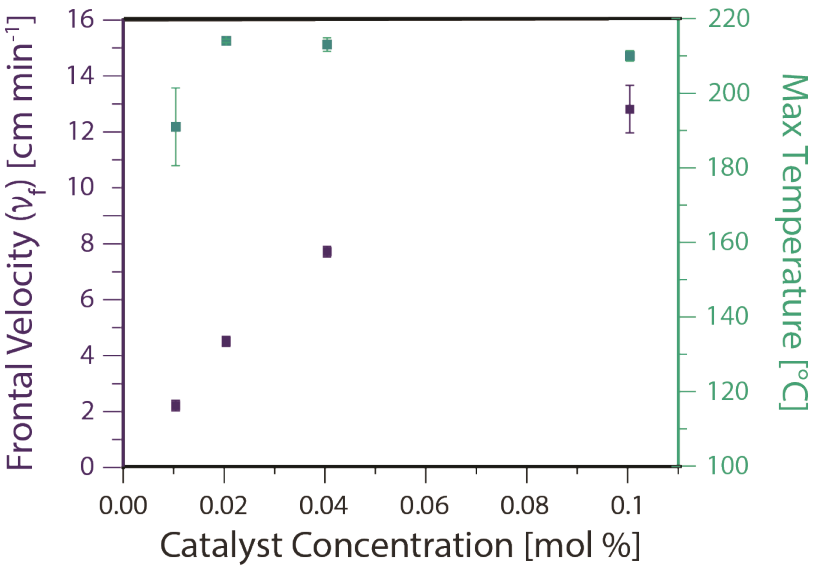
PSU





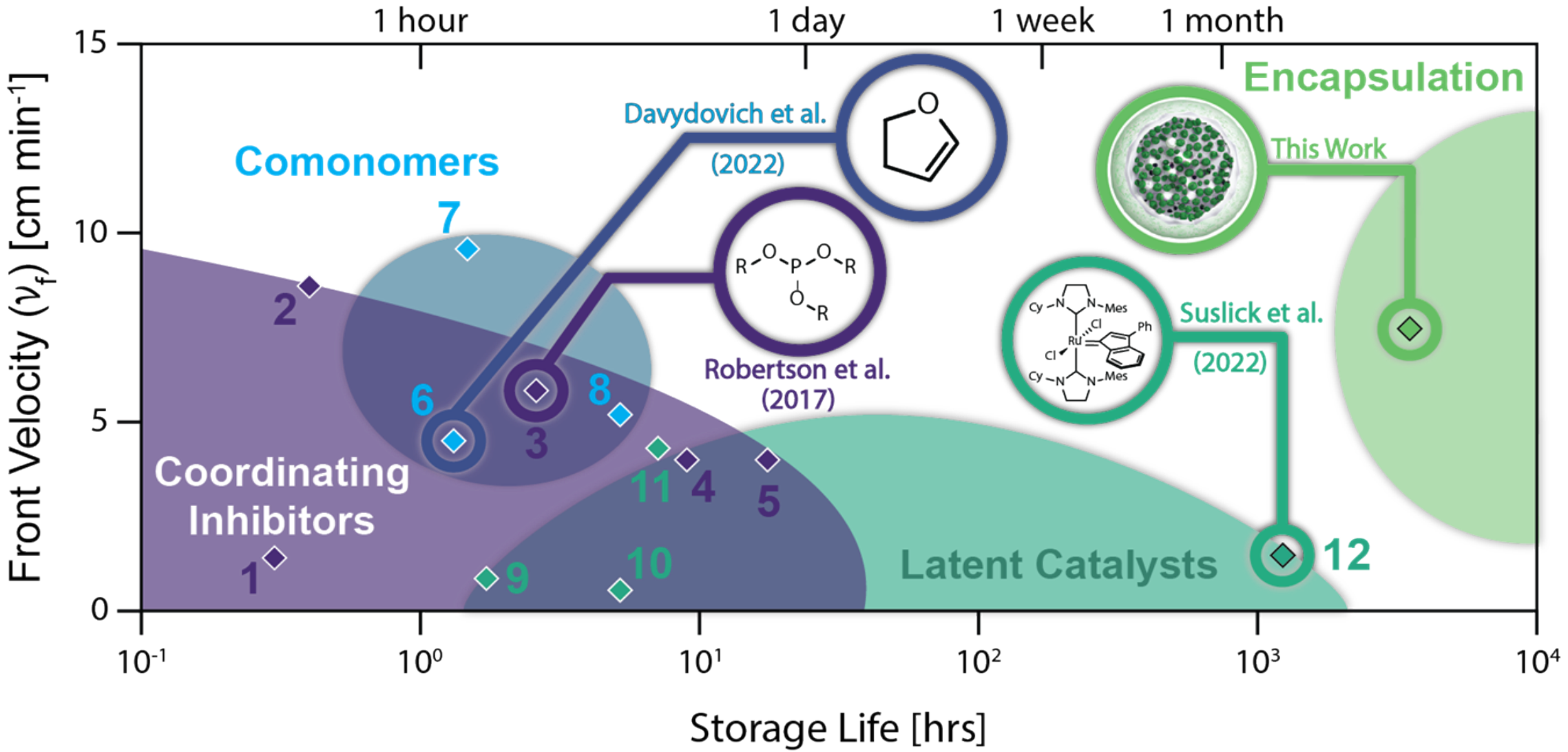






Davydovich, O. et al. *Macromolecules* **2023**, 56, *18*, 7543−7550

Frontal Polymerization Systems

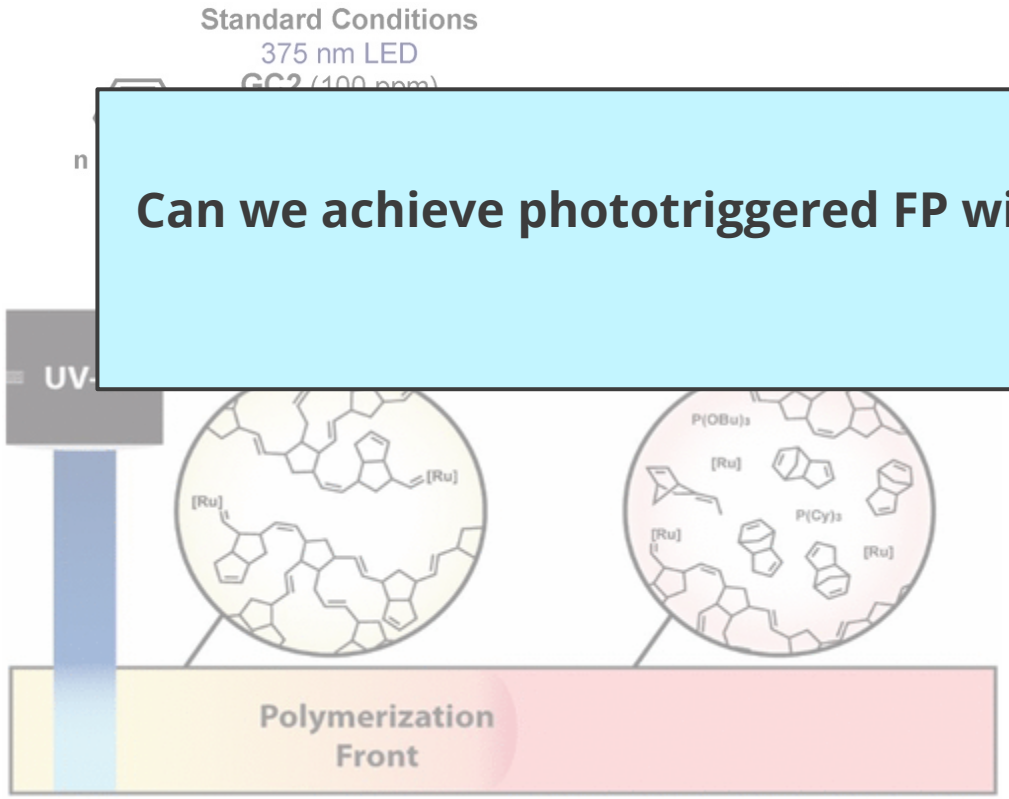


Davydovich, O. et al. *Macromolecules* **2023**, 56, *18*, 7543−7550

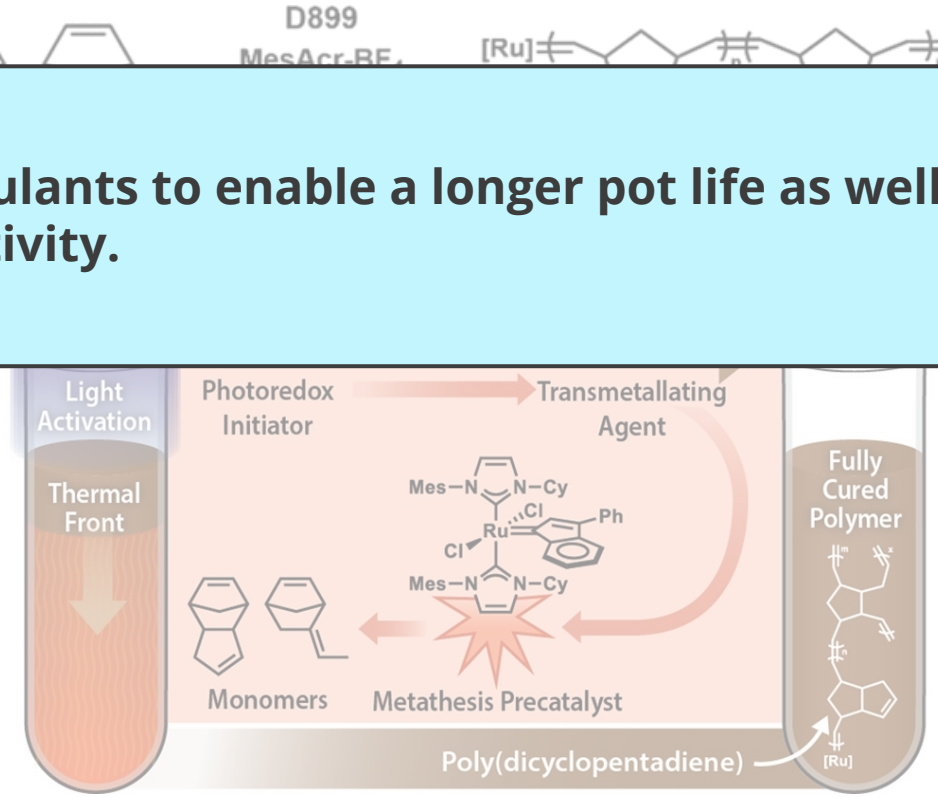
UV Triggered Frontal Polymerization

Demonstrated extensively via free-radical and cationic FP

Demonstrated UV initiated Grubbs activation for FP



Visible Light Activated FP



Can we achieve phototriggered FP with encapsulants to enable a longer pot life as well as high reactivity.

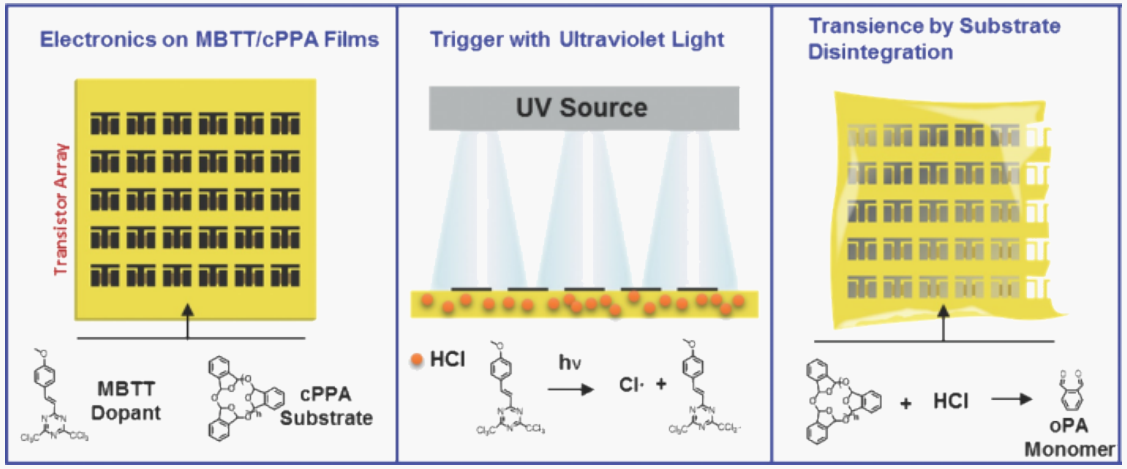
Katherine, S. J. et al ACS Macro Lett. **2020**, *9*, 11, 1563−1568.

Katherine, S. J. et al ACS Macro Lett. **2022**, *11*, 6, 780−784.

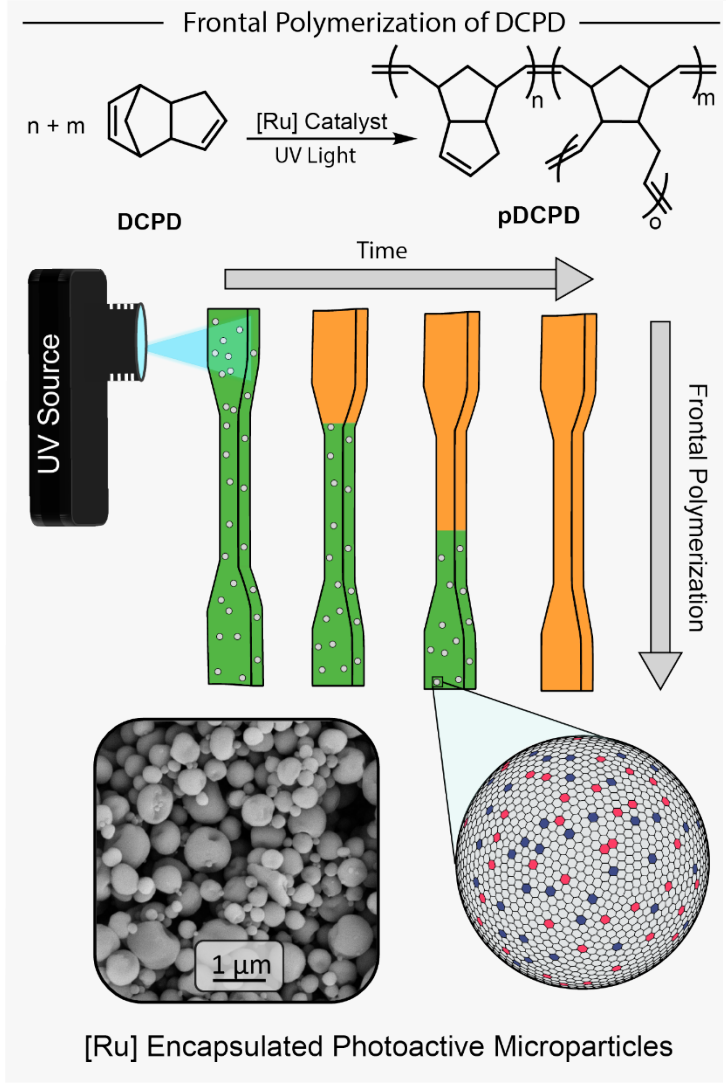
Manuscript Submitted

Photoactivation of encapsulant for Frontal Polymerization

1. Encapsulant readily depolymerizes via light
2. Encapsulant releases catalyst at elevated temperature
3. Rapid release of catalyst during frontal polymerization
4. Encapsulant insoluble in DCPD monomer solution
5. No reactivity between encapsulant and catalyst



Hernandez, H. L. et al. *Advanced Materials* **2014,** *26 (45),* 7637-7642.



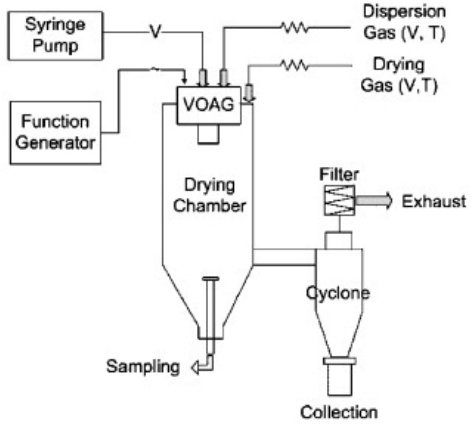
[Ru] Encapsulated Photoactive Microparticles

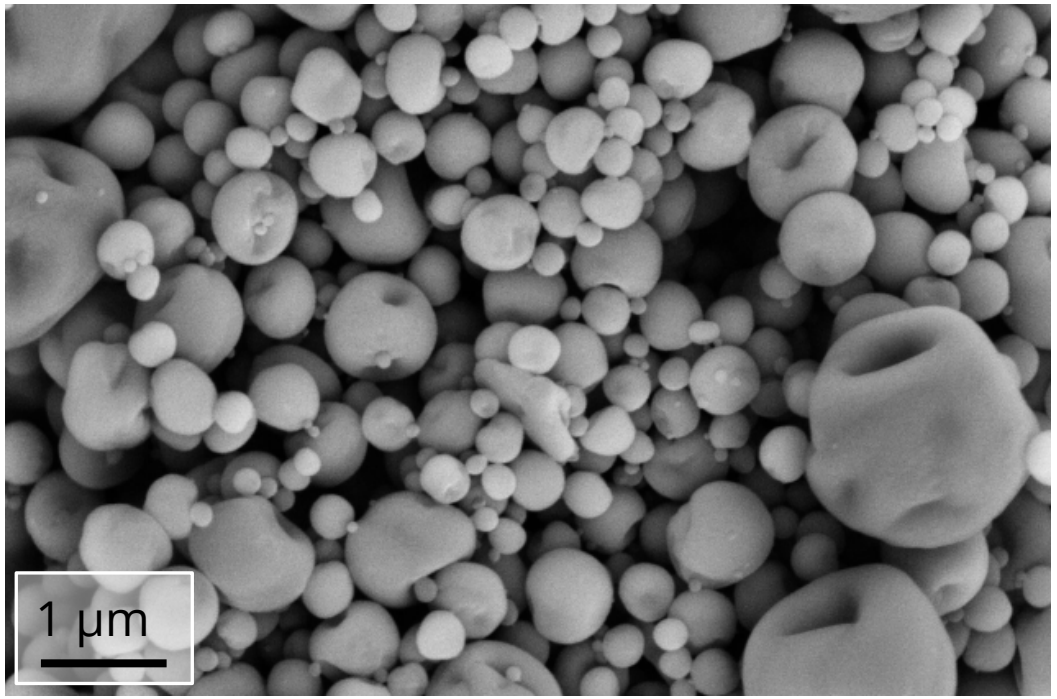
Particle Formation using Spray Drying

- Spray drying does not require emulsification
- Allows for versatility in particle formulation
- Continuous particle formation enables scalability
- No separation required

- Morphology and size distribution difficult to control
- Requires optimization of parameters

  Flow rate, drying temperature, solvent, concentration





Vehring, R. et al *J. Aerosol Sci.* **2007,** 38, 7, 728-746

Manuscript Submitted

Particle Formation using Spray Drying

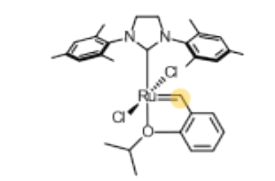
- Spray drying does not require emulsification
- Allows for versatility in particle formulation
- Continuous particle formation enables scalability
- No separation required

- Morphology and size distribution difficult to control
- Requires optimization of parameters
- High Encapsulation Efficiency
- Yield ranges from 50 - 80 %

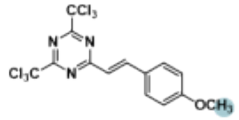
Particle Formulations

- 12 phr Hoveyda Grubbs 2nd Gen. Cat
- 88 phr Cyclic polyphthalaldehyde
- 0 - 10 phr MBTT

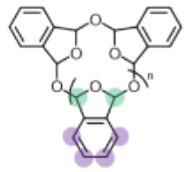
phr = parts per hundred rubber



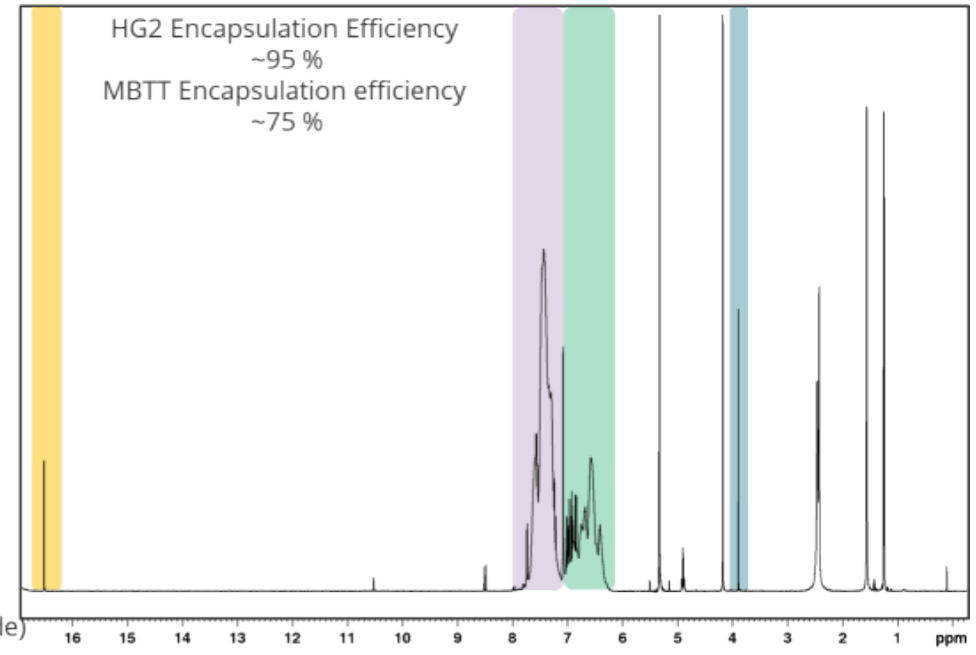
Hoveyda Grubbs
Second Generation



MBTT



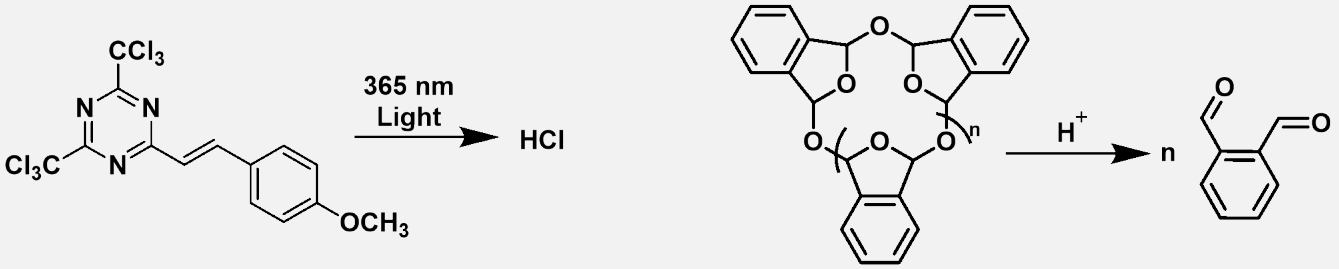
Cyclic Poly(phthalaldehyde)

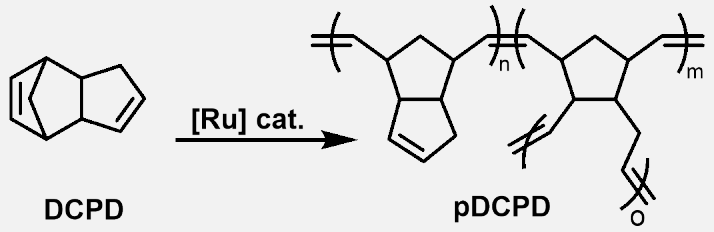


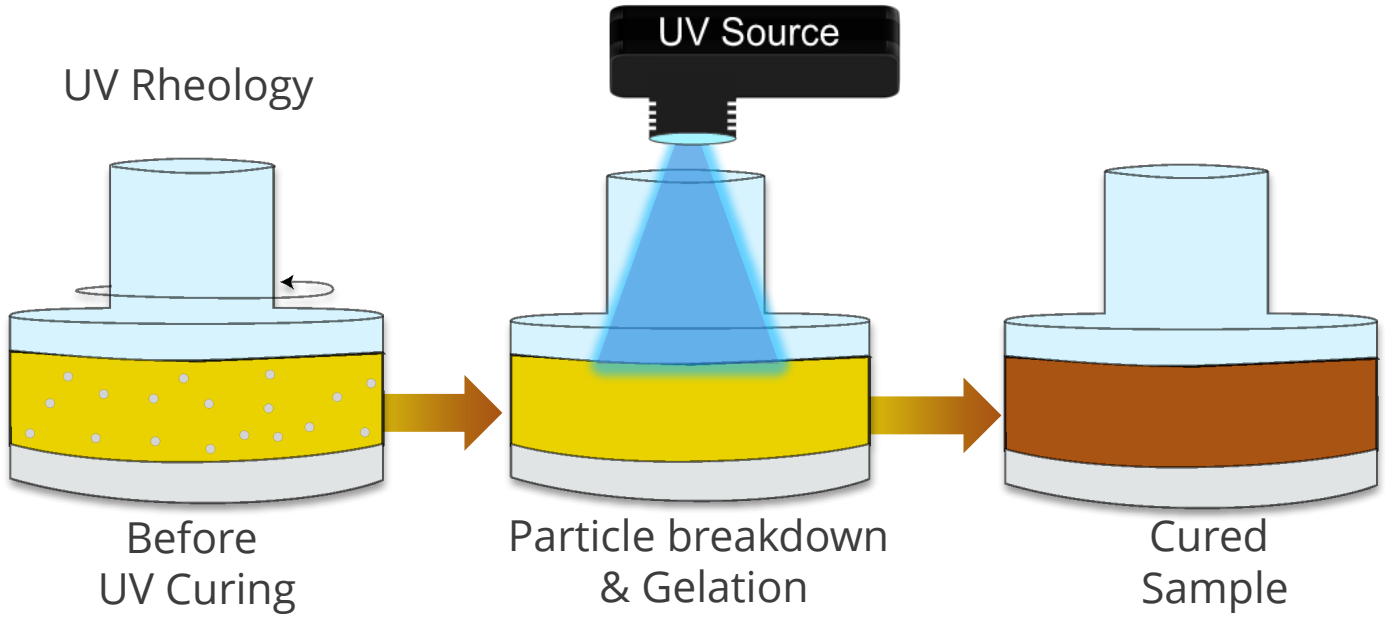
Manuscript Submitted

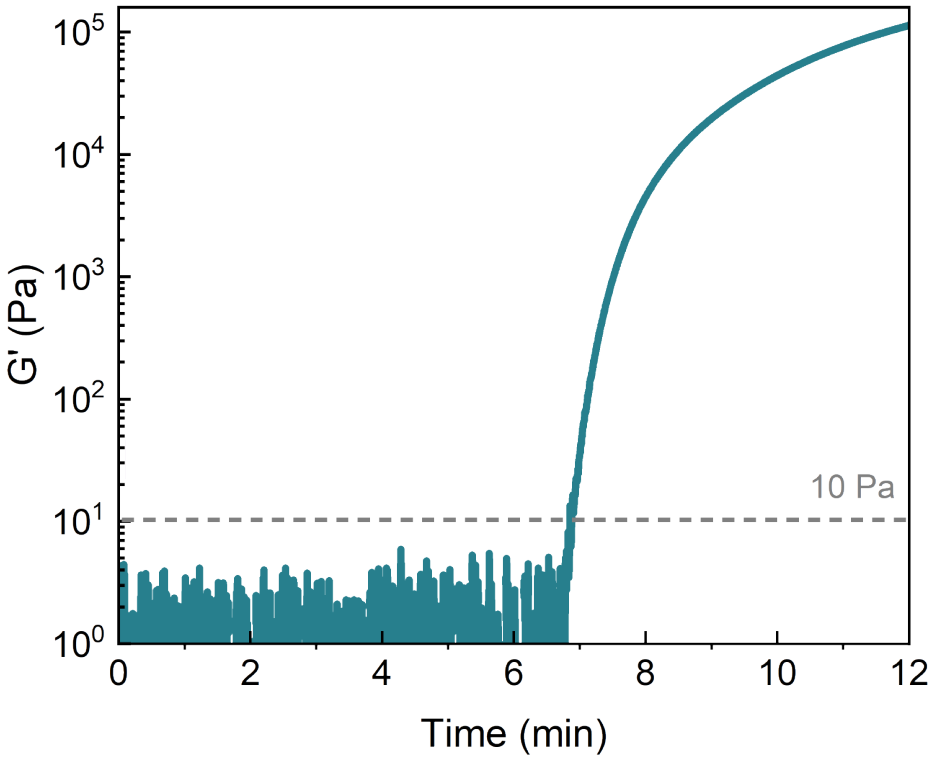
Characterizing photoinitiated ROMP of DCPD

Photoinduction time (PIT) defined as time to reach 10 Pa storage modulus









Manuscript Submitted

Photoinitiated ROMP of DCPD

Particles formulation tuned to control rate of photoinitiation

Successful Photoactivation

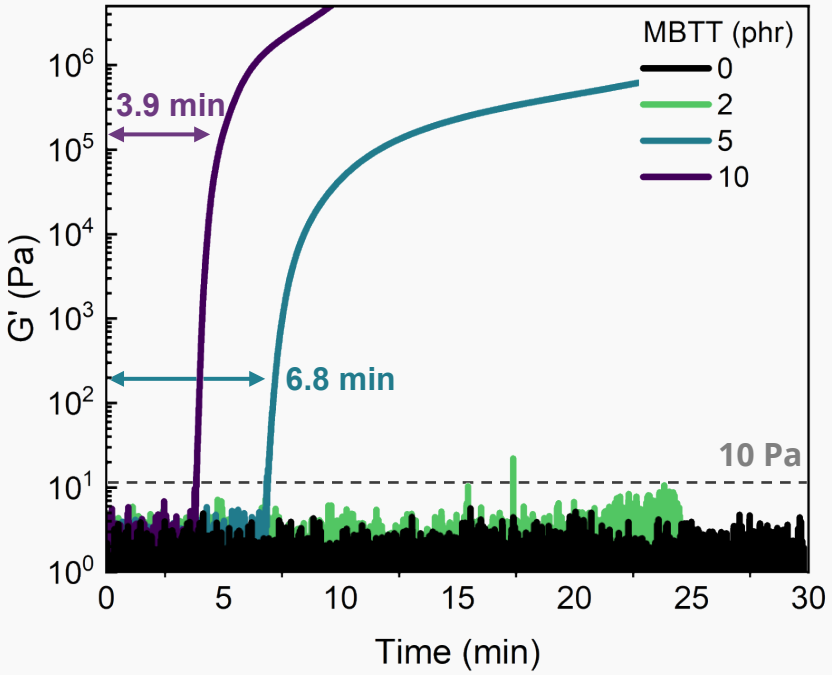
No background polymerization

Inefficient photoactivation

Requires 30x more MBTT

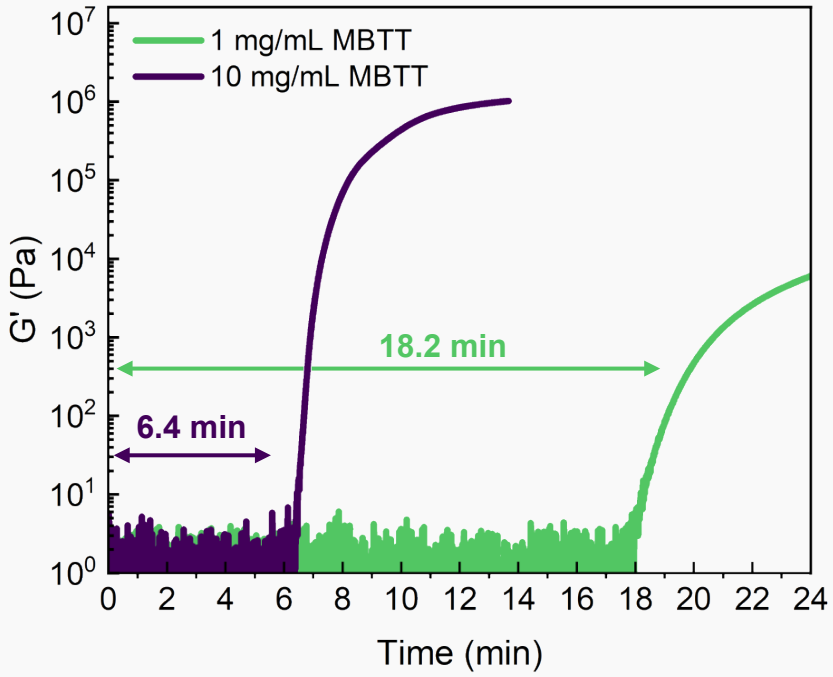
Particle loading decreases PIT

PAG Concentration



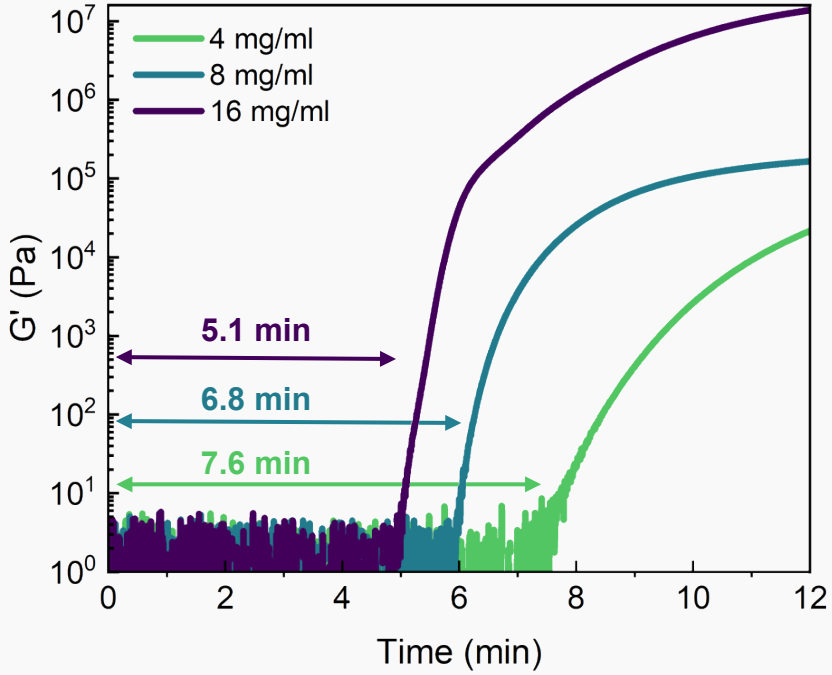
8 mg/ml (mg particles/ mL DCPD) | 25 °C | 27mW cm^{-2}

Ex-situ MBTT Incorporation



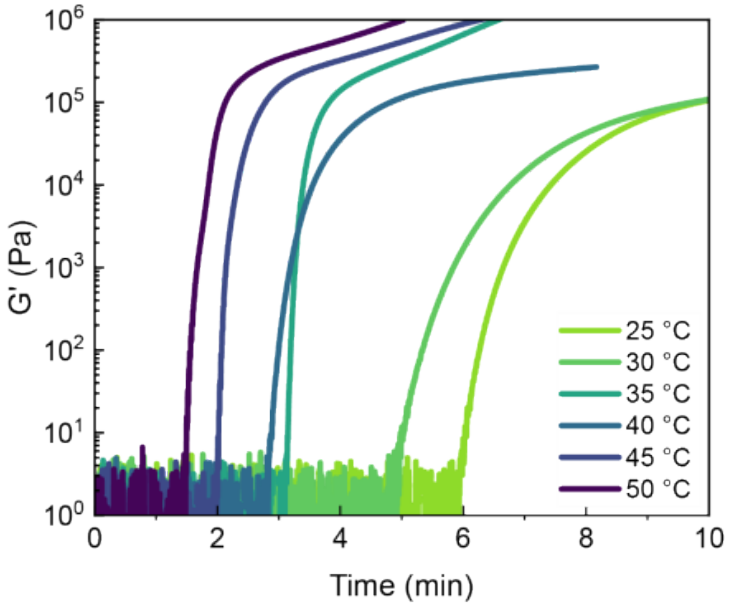
8mg/ml (mg particles (no MBTT) / mL DCPD)| 27 mW/cm^2

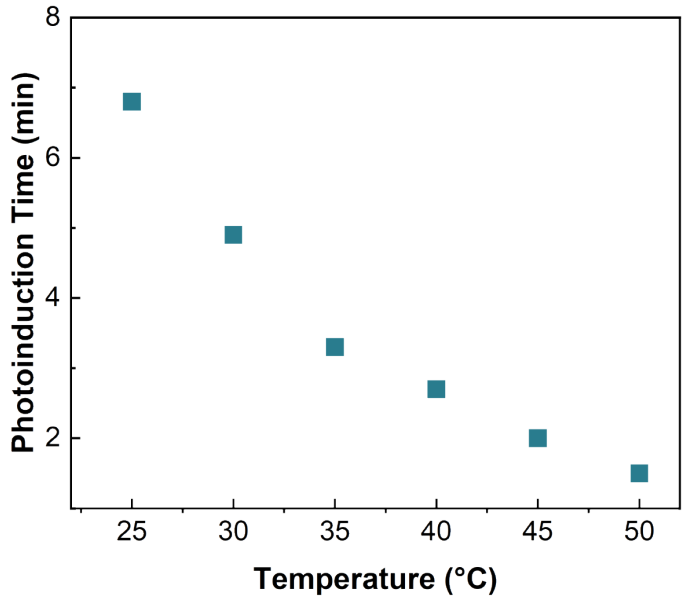
Particle Concentration



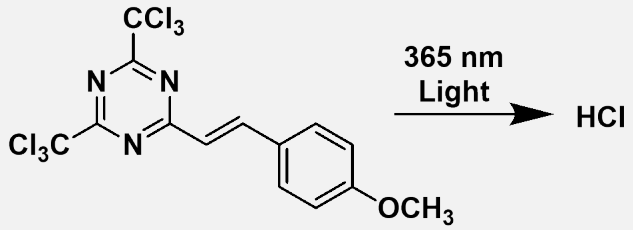
5 phr MBTT | 25 °C | 27 mW/cm^2

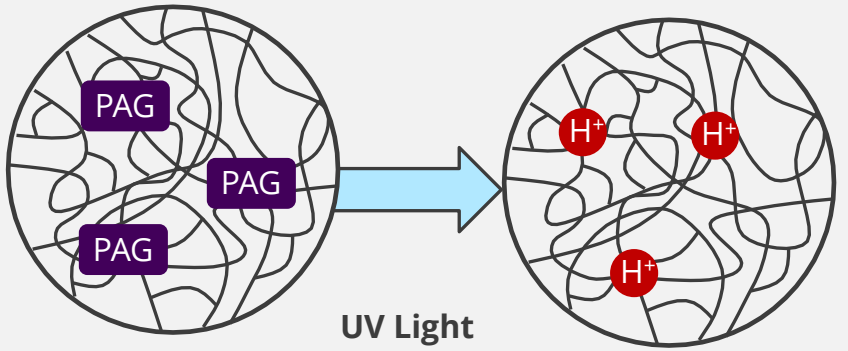
Temperature Significantly Reduces Photoinduction Time



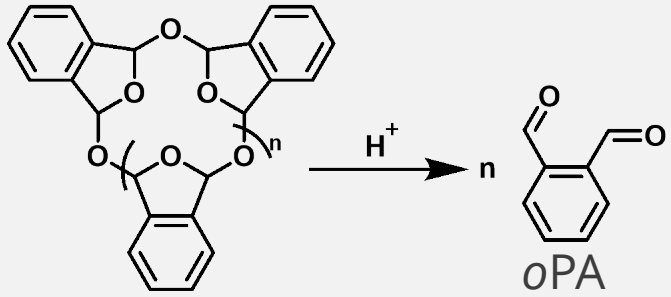


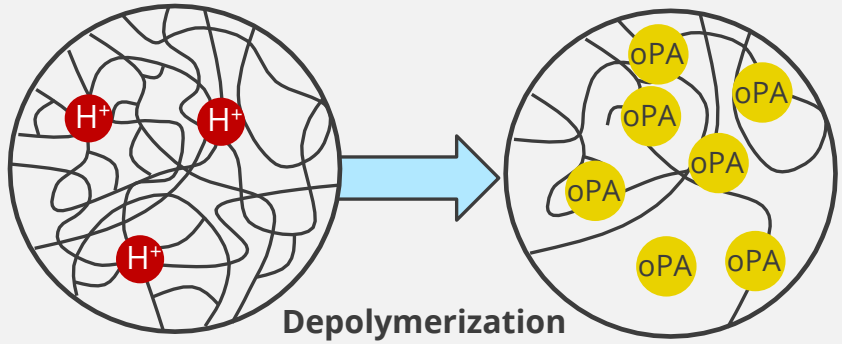
Acid Formation and Diffusion





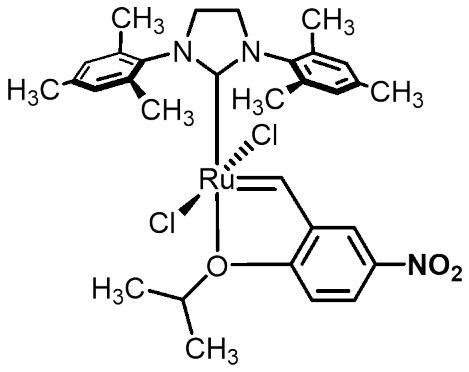
cPPA Depolymerization Rate



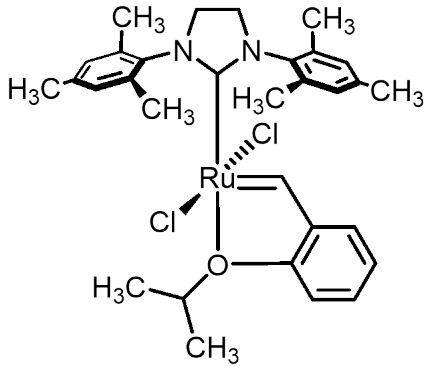


5 phr MBTT | 8mg/ml (mg particles/ mL DCPD)| 27 mW/cm²

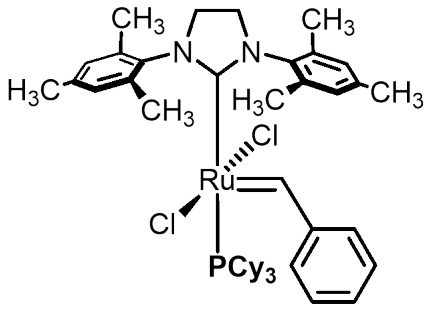
Temperature Significantly Reduces Photoinduction Time



Nitro-Grela

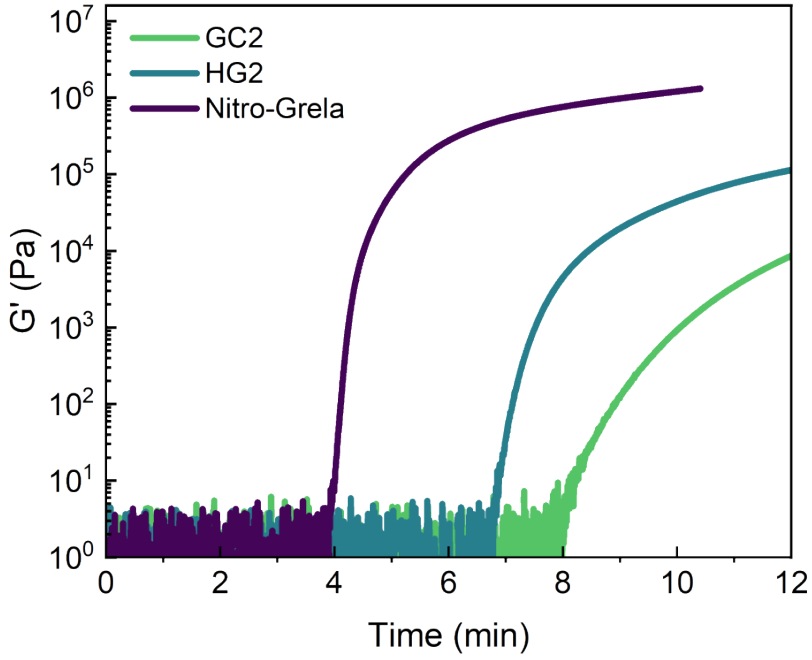


HG2



GC2

- Particle formation successful for various catalysts
- Versatility of spray drying method
- Effect of catalyst on photoinduction time
- Nitro-grela shows increased rate of photoinitiation



Catalyst	PIT (min)
GC2	8.2
HG2	6.8
Nitro-Grela	4.0

All catalysts added at 12 wt % loading

PIT_n= PIT normalized by MW

5 phr MBTT | 8mg/ml (mg particles/ mL DCPD)| 27 mW/cm²

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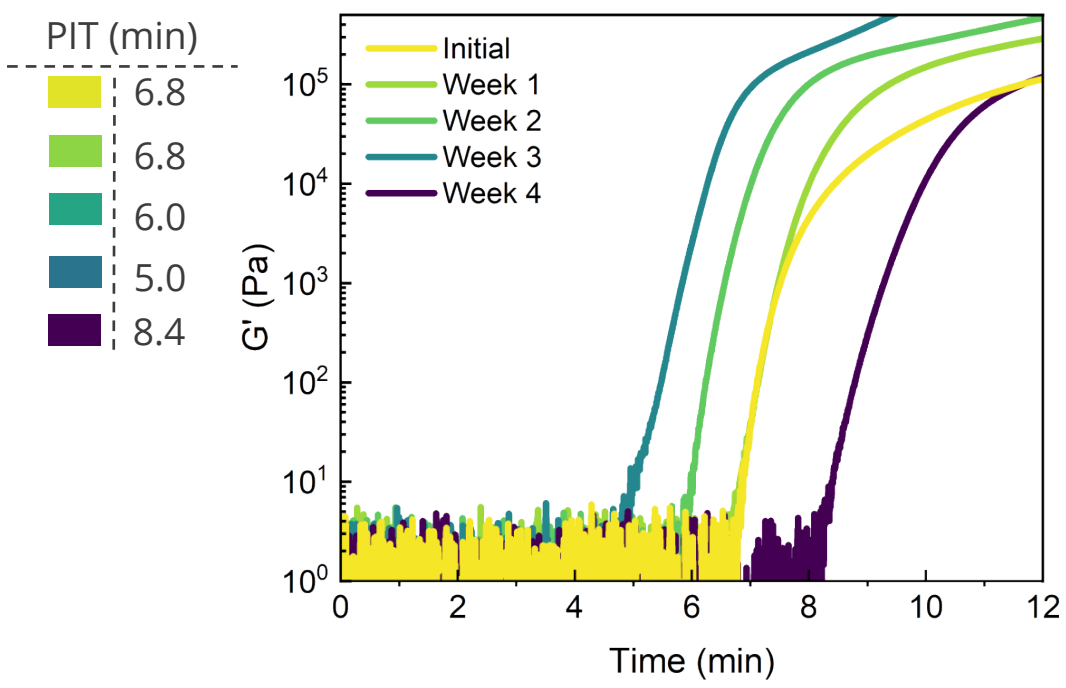
Photoactive Microparticle Stability in DCPD

Particles were stored in monomer solutions at room temperature in the absence of light over the course of one month

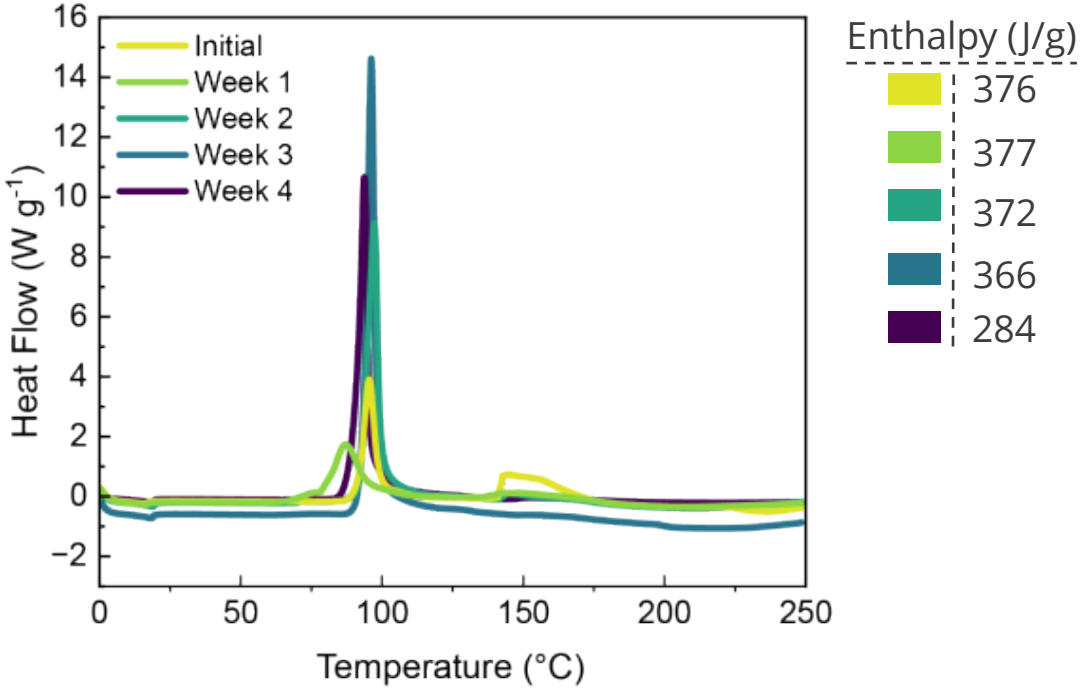
Decreasing photoinitiation times until the fourth week

- Background depolymerization of encapsulant
- Increased homogeneity and aggregate breakdown

After four weeks, localized gelation occurs due to released HG2



5 wt % PAG | 8 mg/ml (mg particles/ mL DCPD) 25 °C | 27mW cm^{-2}



5 wt % PAG | 8 mg/ml (mg particles/ mL DCPD) | 5 °C/min

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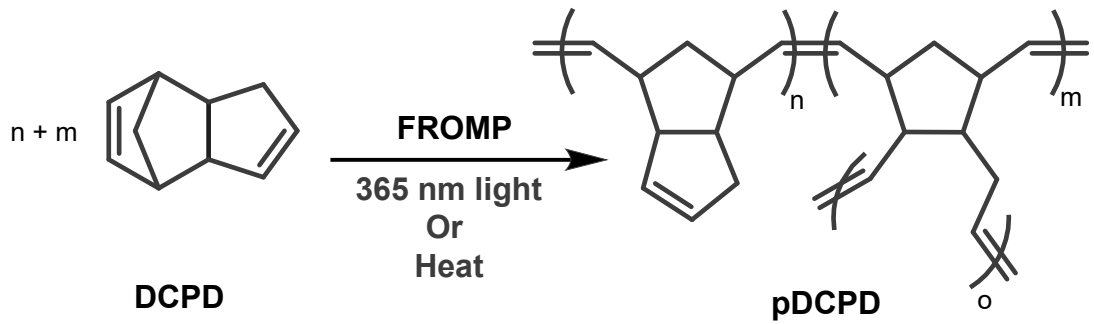
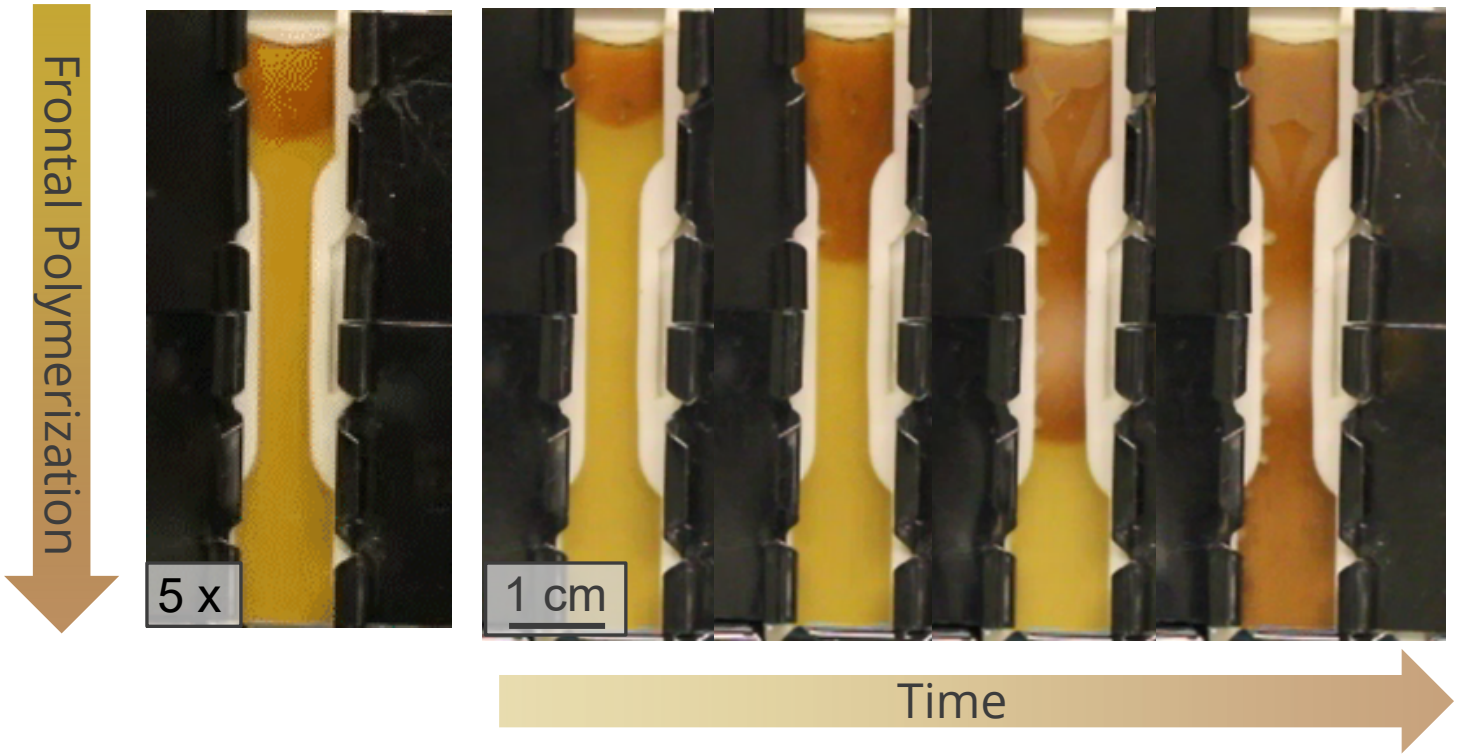
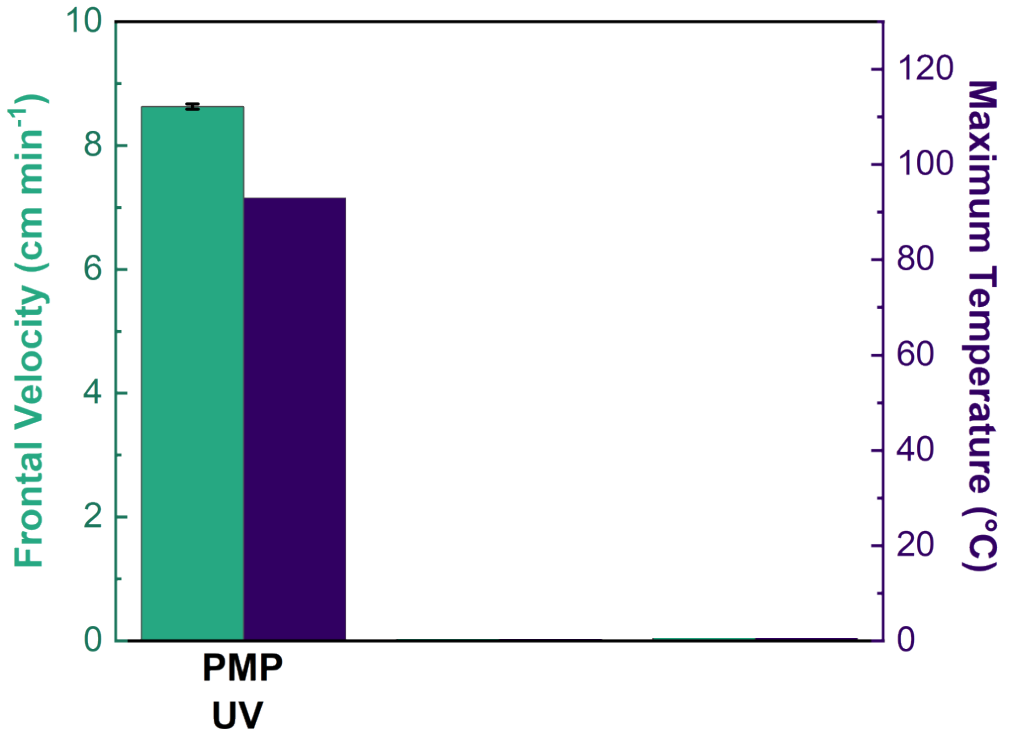
Photoinitiated Frontal Polymerization



- Photoinitiation requires higher UV intensity
- Fast frontal velocities
- Thermal initiation shows minimal changes
- Comparable to control samples (**GC2**/TBP)



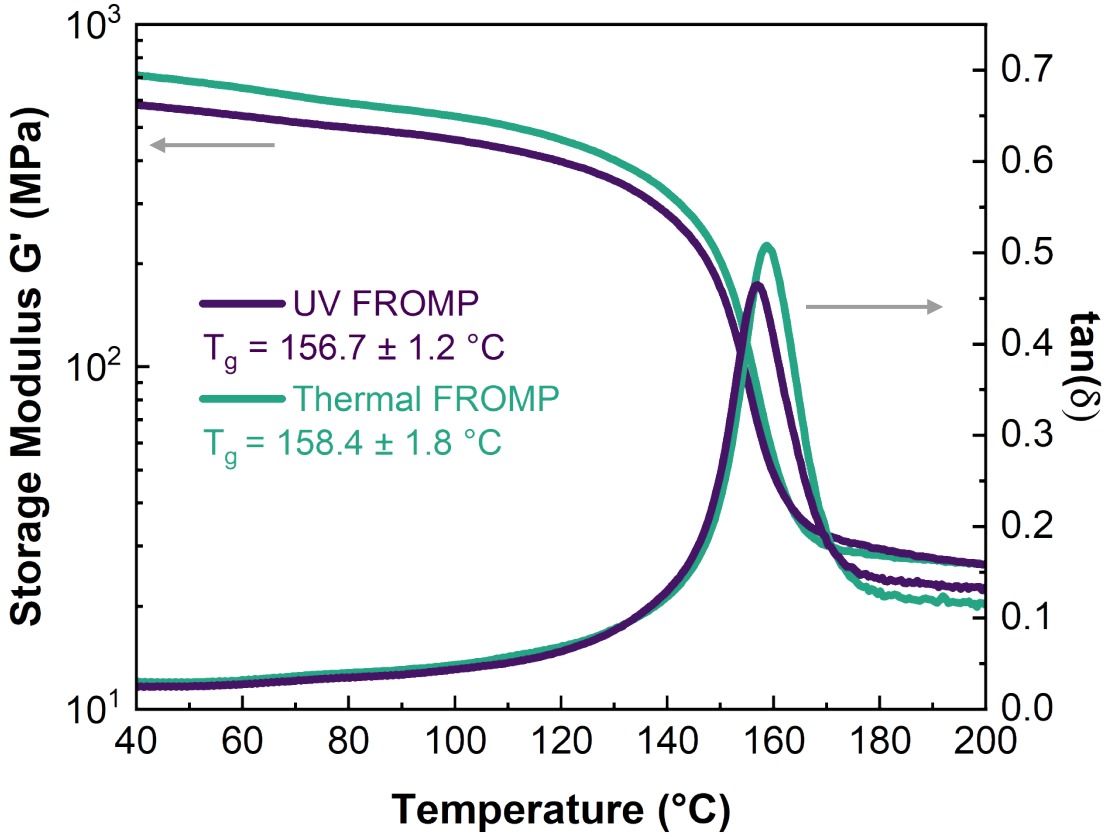


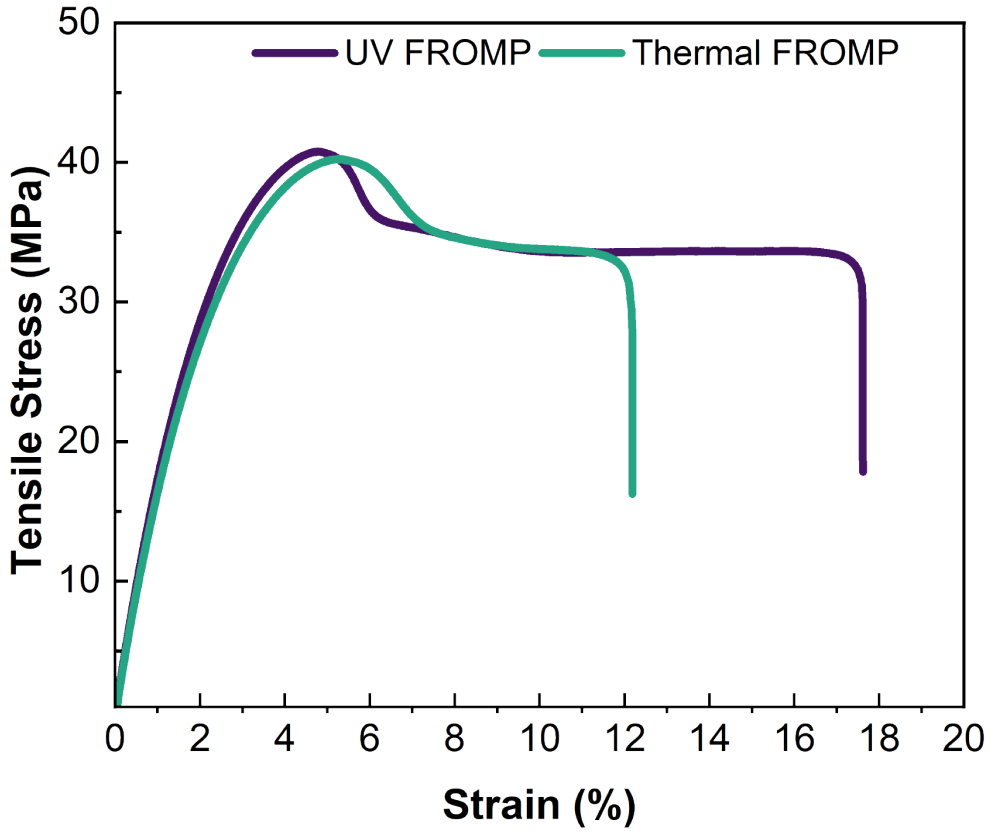
16 mg/ml (mg particles/ mL DCPD) | 25 °C | 330 mW cm^{-2}

Thermomechanical Properties of pDCPD materials

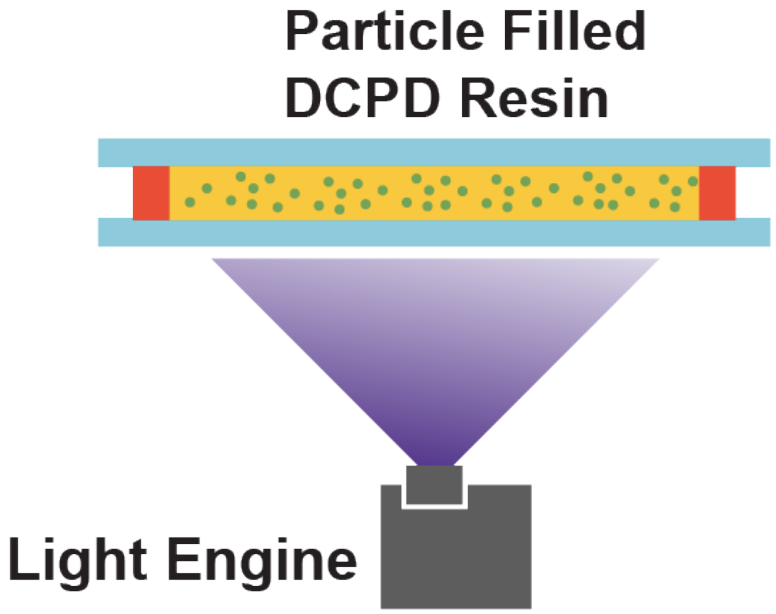
Minimal Changes between UV or thermally initiated Samples

Initiation Method	Degree of Cure	Young's Modulus	Tensile Strength
UV	0.92	39 ± 1	1.9 ± 0.1
Thermal	0.92	40 ± 1	1.8 ± 0.1

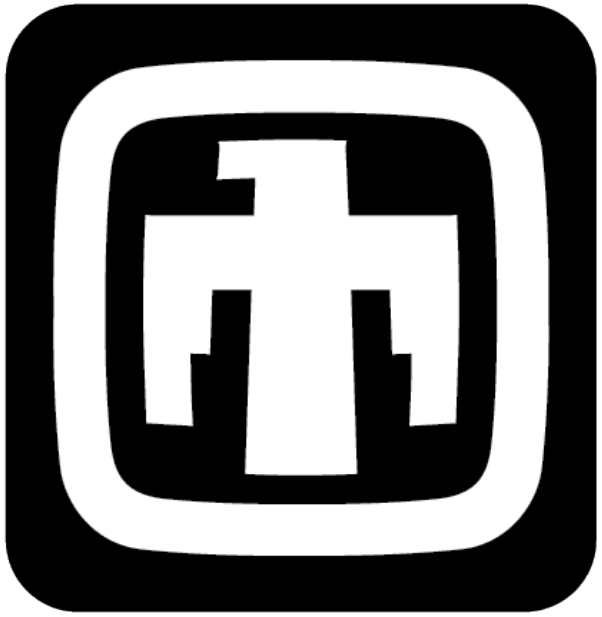




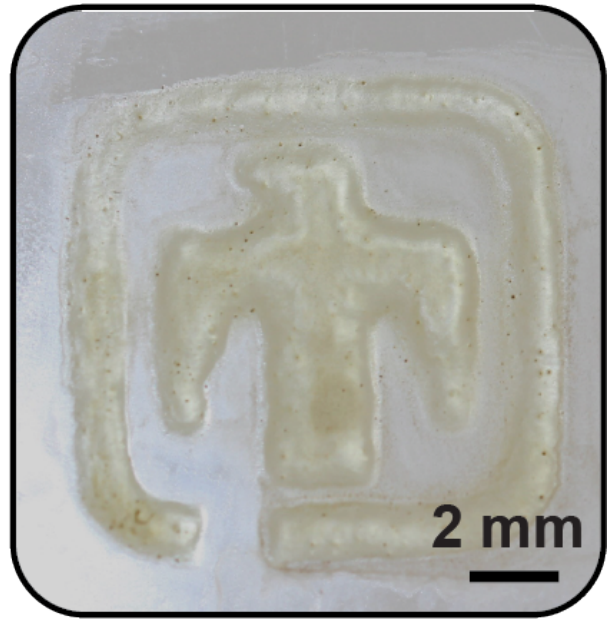
Vat polymerization using photoactivate microparticles



Photomask



Resulting Materials

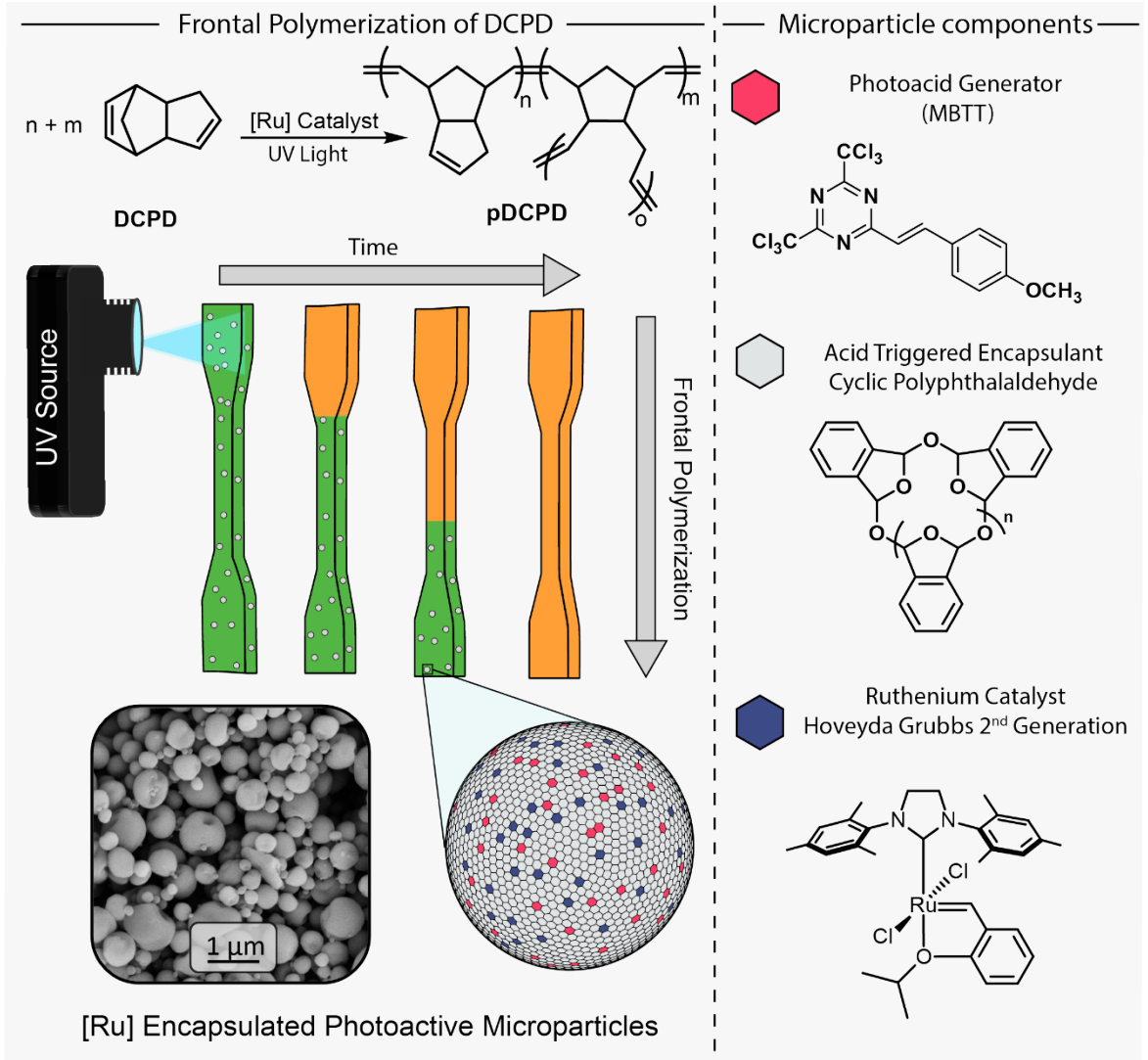


365 nm Light | 50 mW/cm² | 3 min

Summary

- Spray drying provides versatility in particles
- Particles stable in DCPD monomer solutions
- Allow for versatility in photoinitiation
- Successful frontal polymerization

Time



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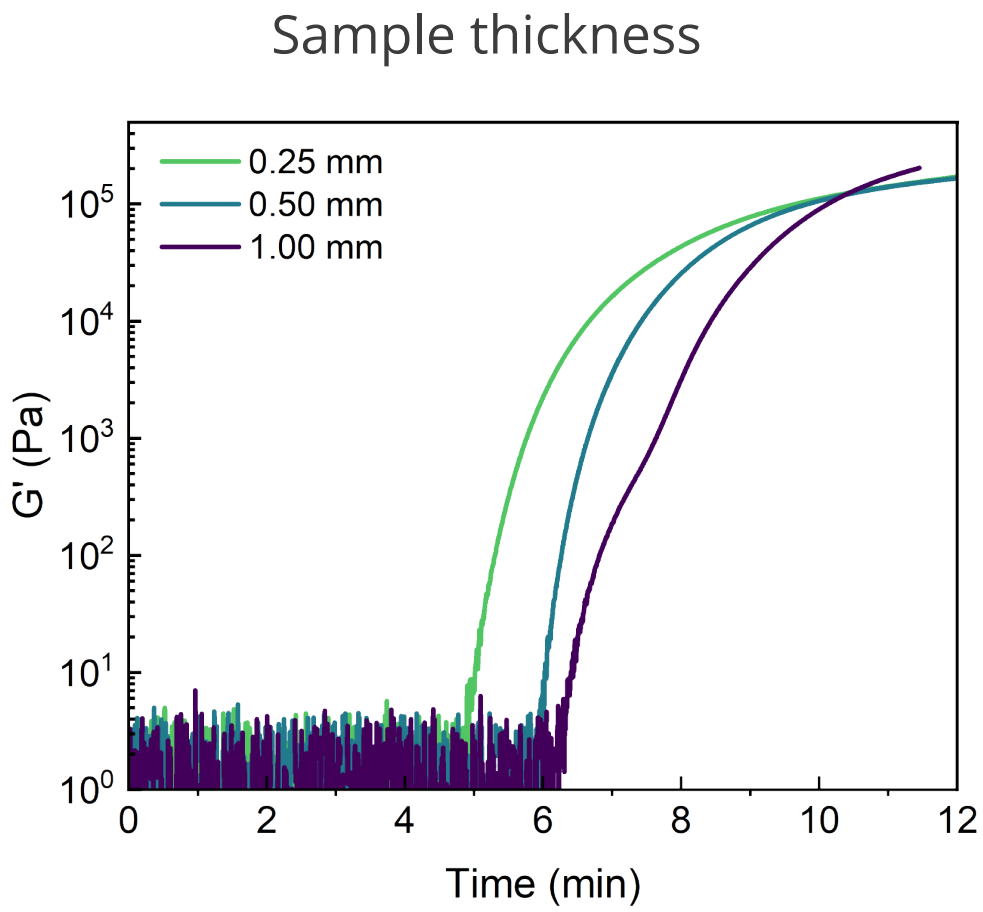
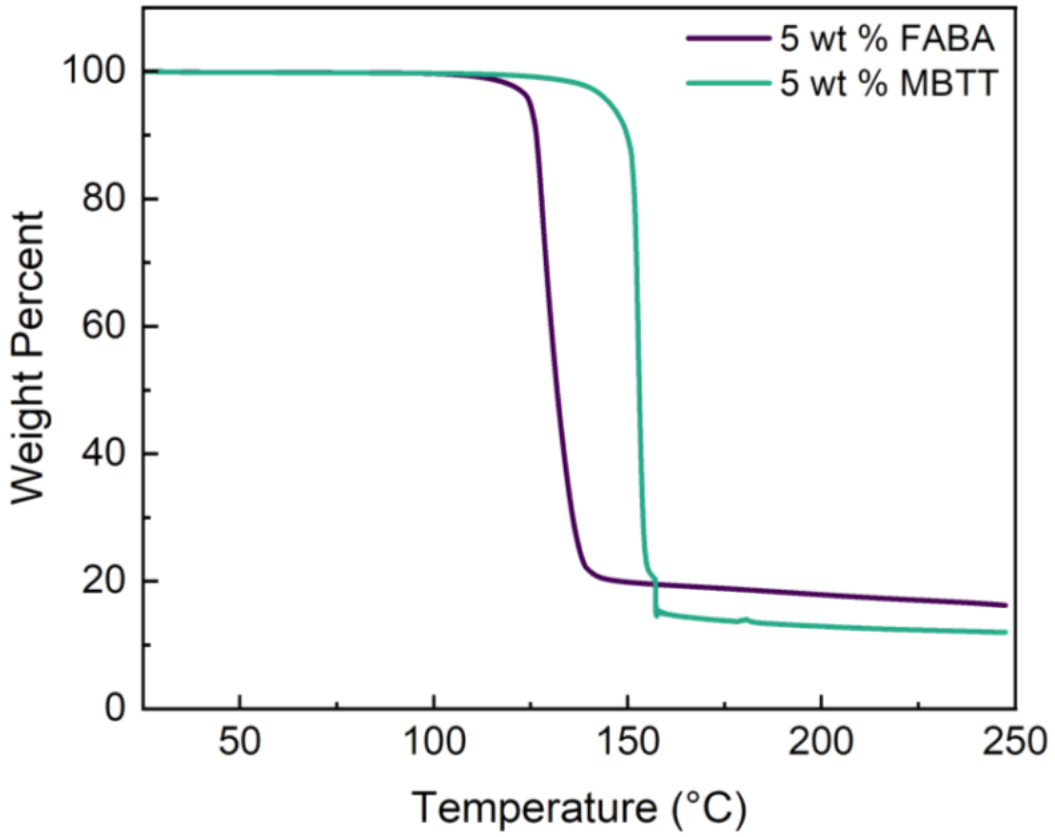
DOE EFRC Award # DE-SC0023457

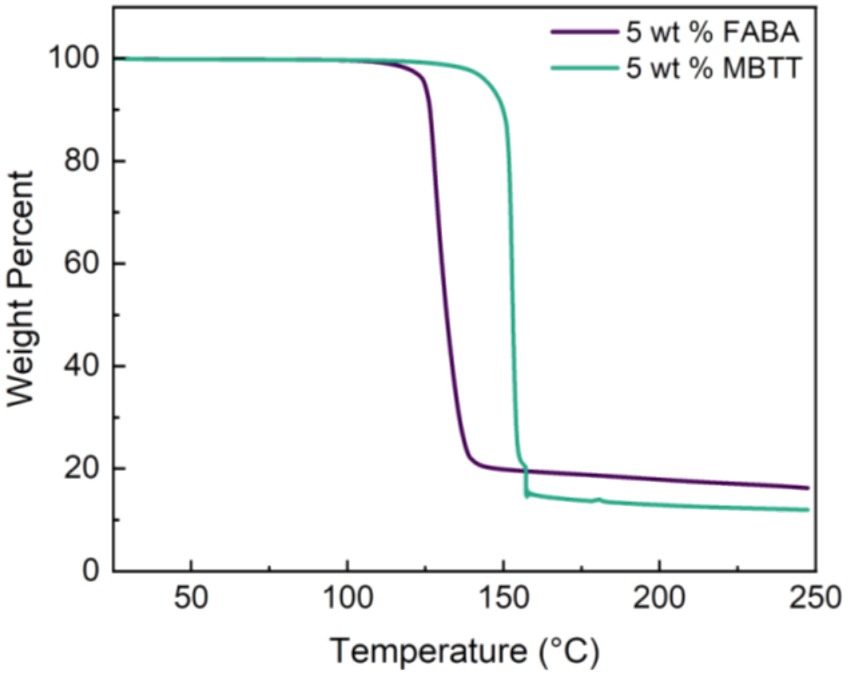
Sample thickness variation

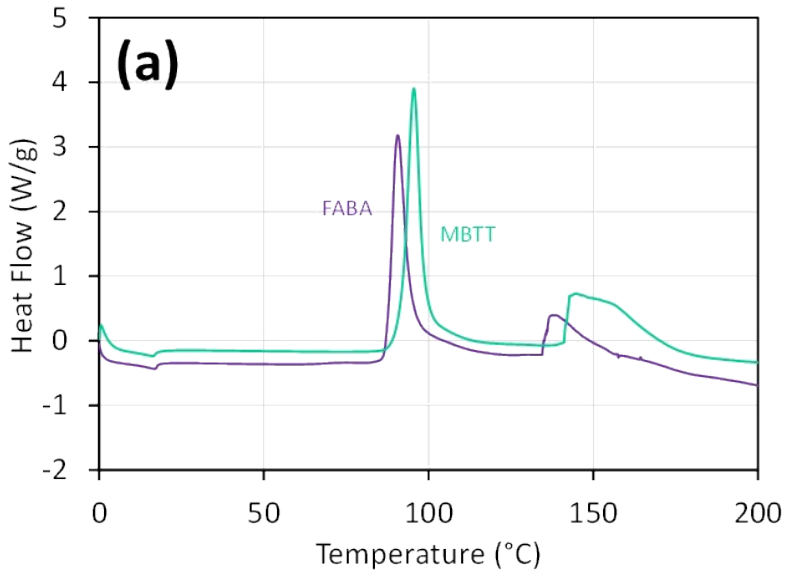


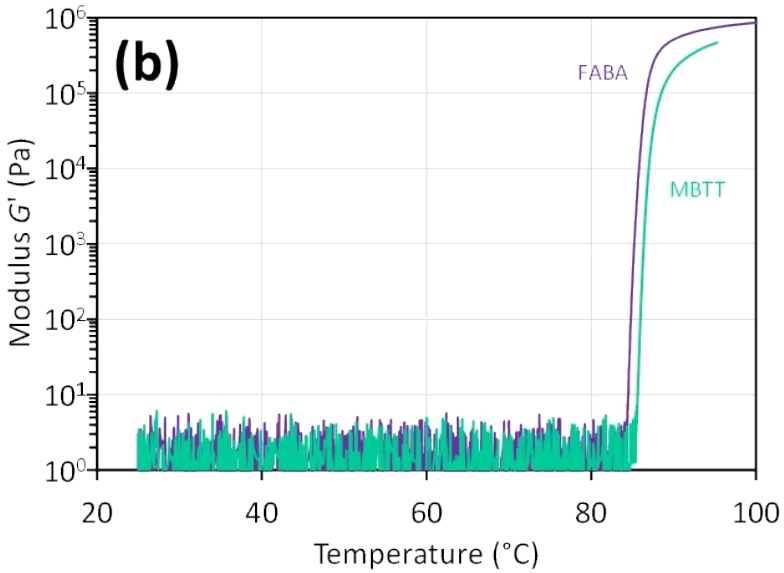
8 mg/ml (mg particles/ mL DCPD) | 25 °C | 27mW cm^{-2}

Thermogravimetric Analysis




5 wt % FABA
5 wt % MBTT
Weight Percent
Temperature (°C)


(a)
FABA
MBTT
Heat Flow (W/g)
Temperature (°C)


(b)
FABA
MBTT
Modulus G' (Pa)
Temperature (°C)