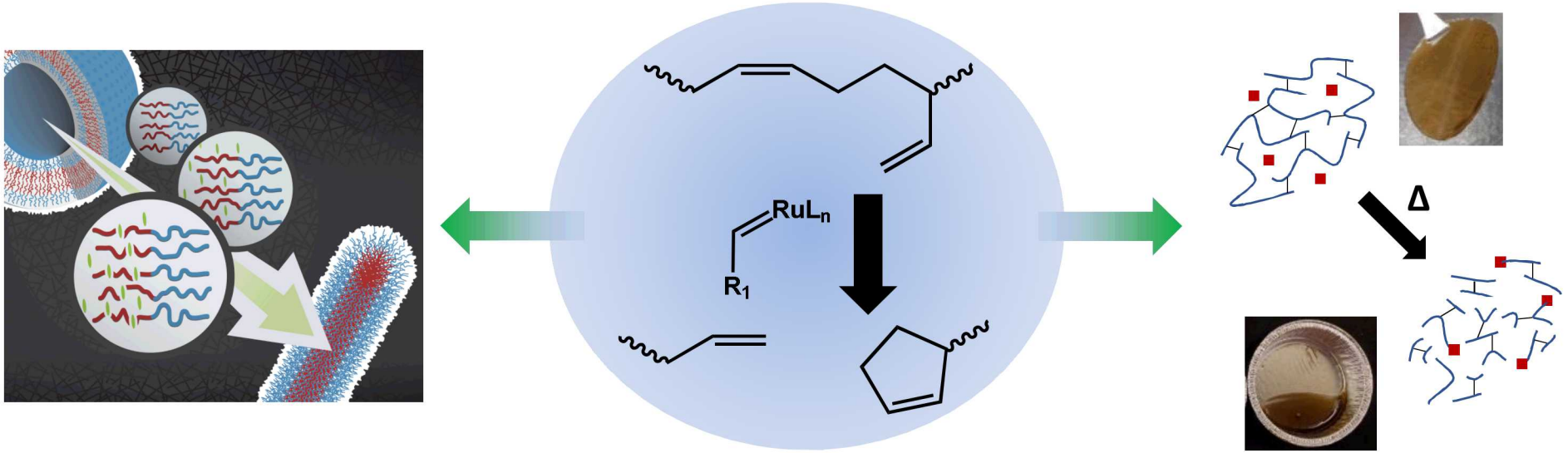
SAND2019-9800C



Exploiting Metathesis Depolymerization of Polybutadiene for Responsive Materials

Brad H. Jones

August 26, 2019

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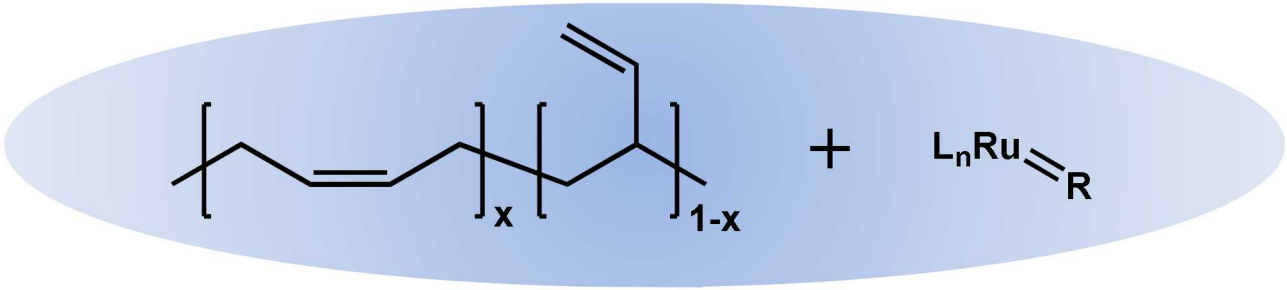
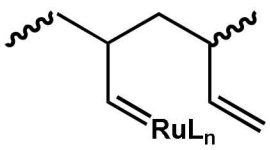
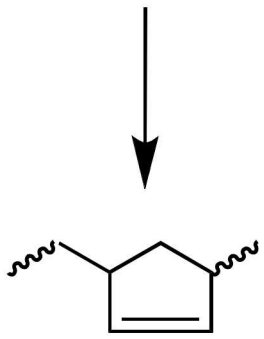
Alkene Metathesis of Polydienes

Polydienes are cyclized/cleaved by Ru carbenes via ring-closing metathesis

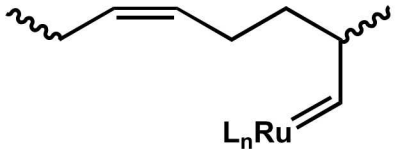


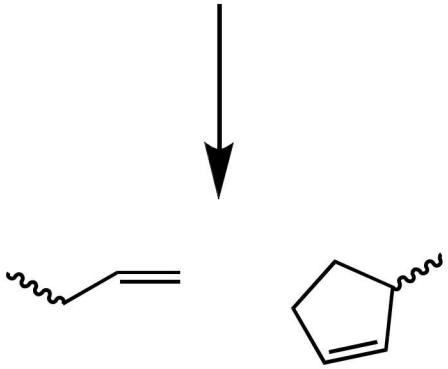
1,2/1,2 diads



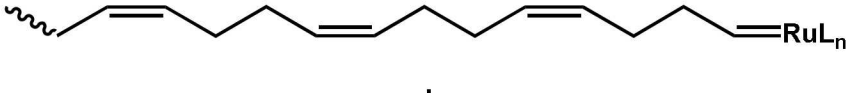


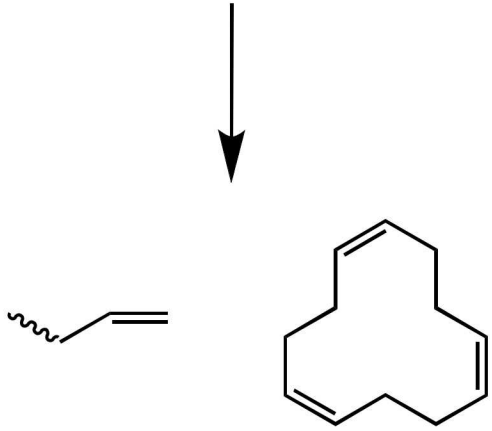
1,4/1,2 diads





chain backbiting



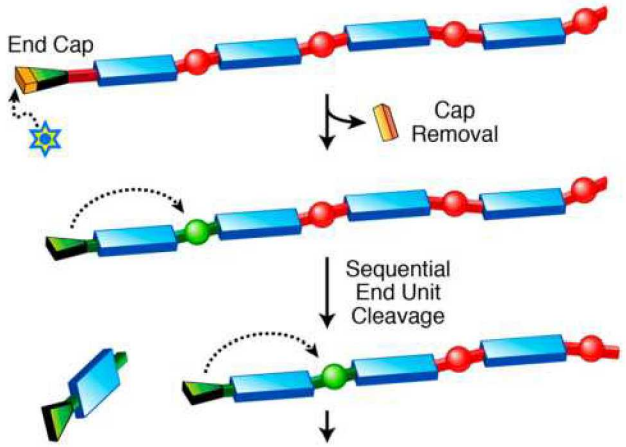


(1) Abendroth, H.; Canji, E. *Makromol. Chem.* **1975**, *176*, 775-779; **(2)** Coates, G. W.; Grubbs, R. H. *JACS* **1996**, *118*, 229-230; **(3)** Watson, M. D.; Wagener, K. D. *Macromolecules* **2000**, *33*, 1494-1496; **(4)** Dewaele, A.; *et al. Catal. Sci. Technol.* **2016**, *6*, 7708-7717.

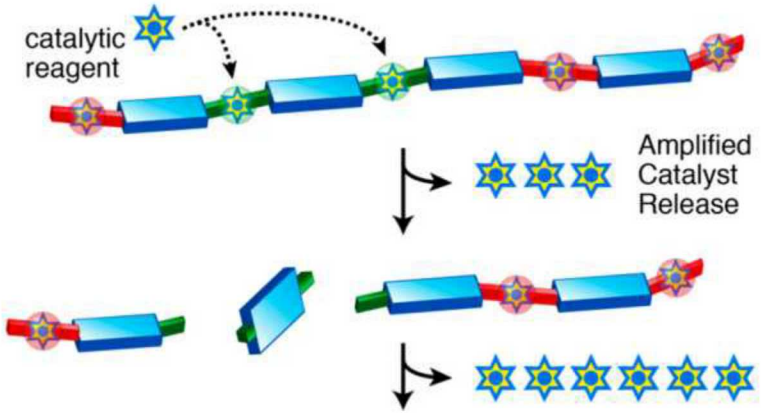
Depolymerizable Polymers

Many self-immolative and chain-shattering polymers have been developed

self-immolative

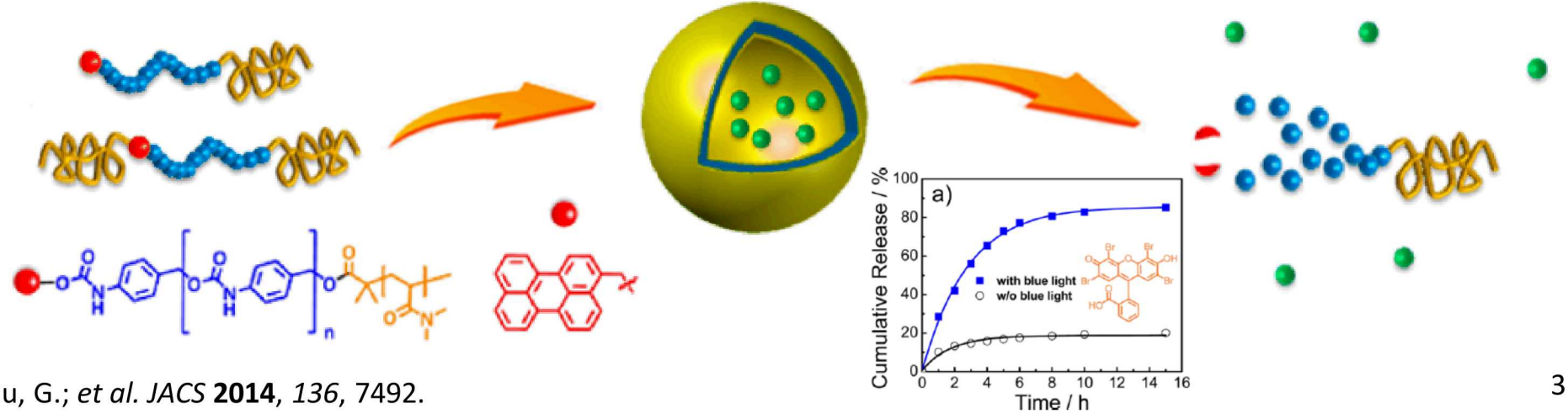


chain-shattering



Miller, K. A.; *et al. JACS* **2019**, *141*, 2838-2842.

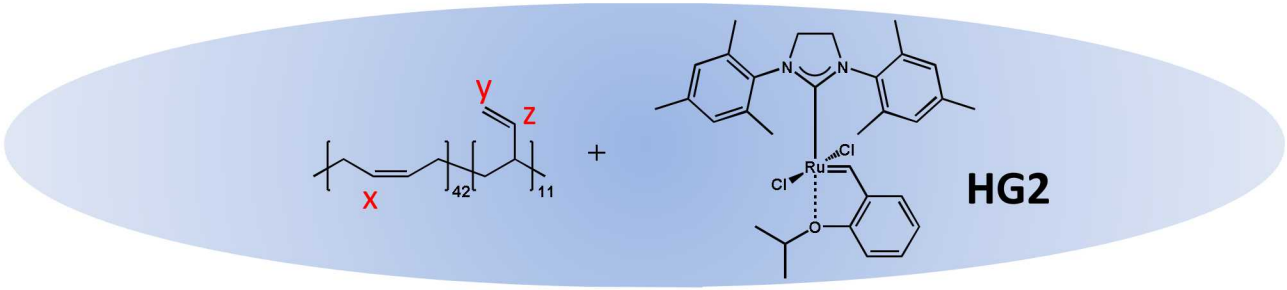
In block polymers, such principles have been used to trigger disassembly



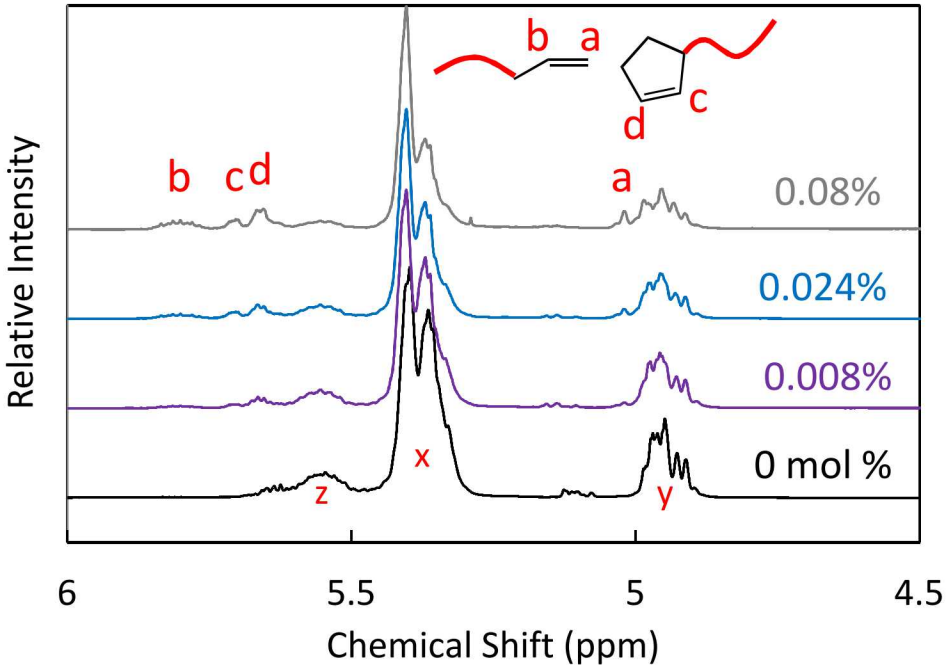
Liu, G.; *et al. JACS* **2014**, *136*, 7492.

Molecular Weight Control

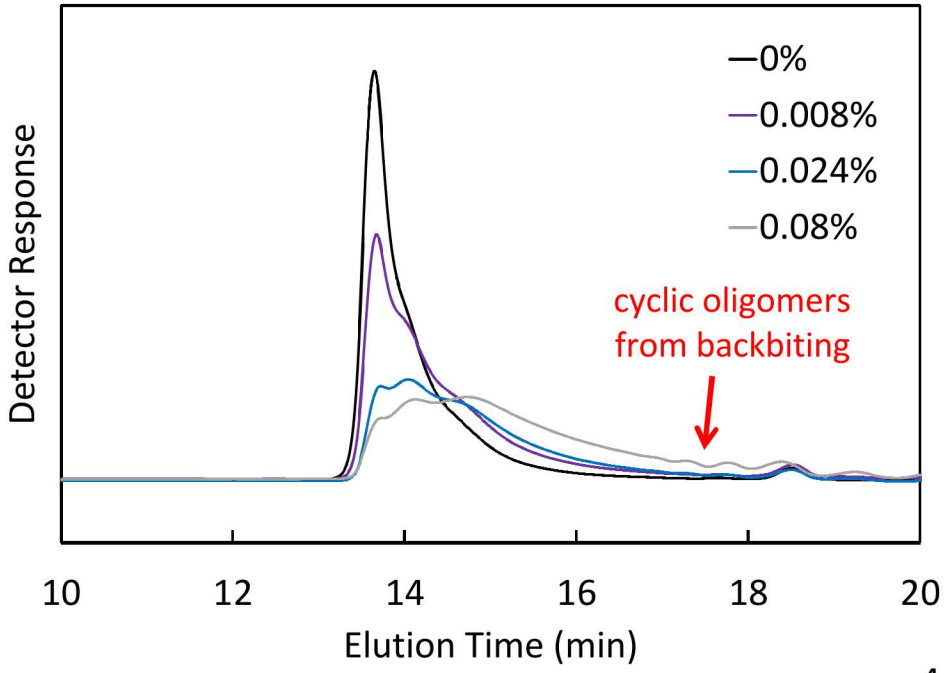
2nd gen Hoveyda-Grubbs catalyst gives rapid, controllable PB depolymerization



^{1}H nuclear magnetic resonance (NMR) spectra



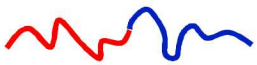
gel permeation chromatography (GPC) traces

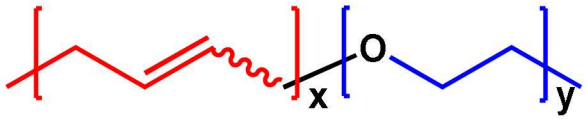


Can Metathesis Alter PB-Based Morphologies?

PB-PEO

$w_{PEO,i}$ = 0.49

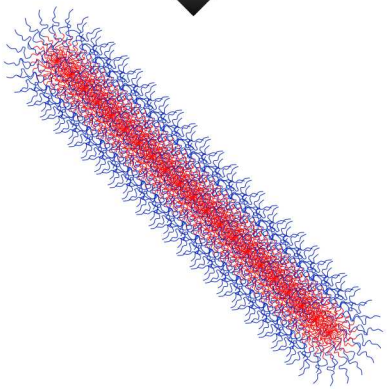


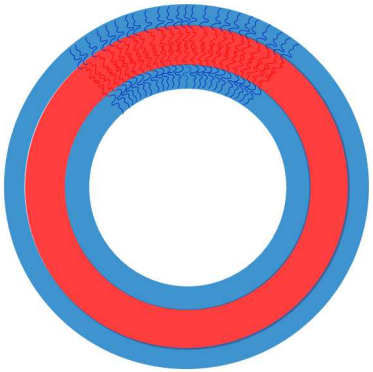


83% 1,4 units

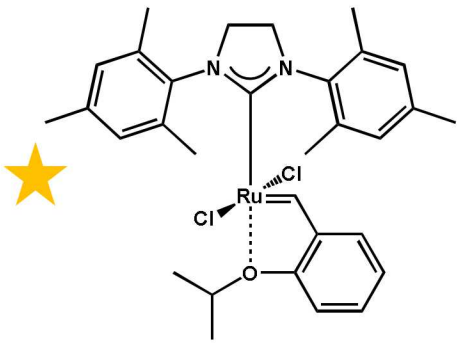
$w_{PEO,i}$ = 0.35

H_2O





H_2O



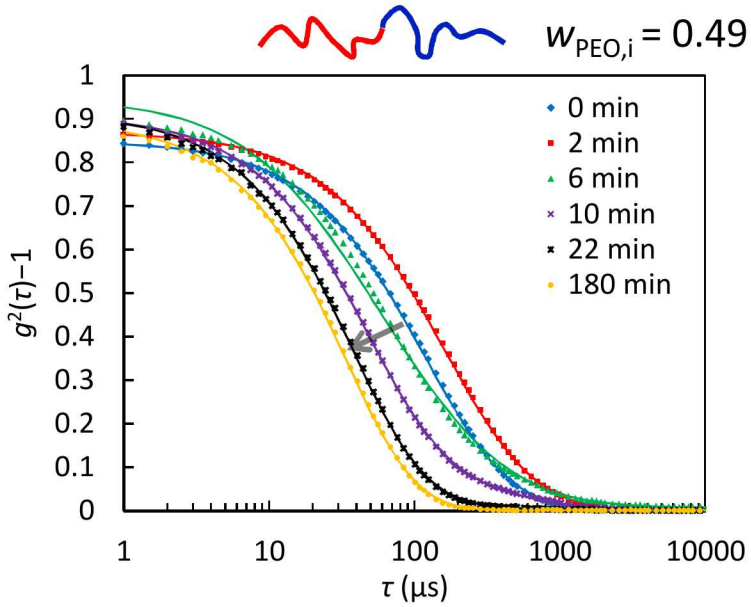
?

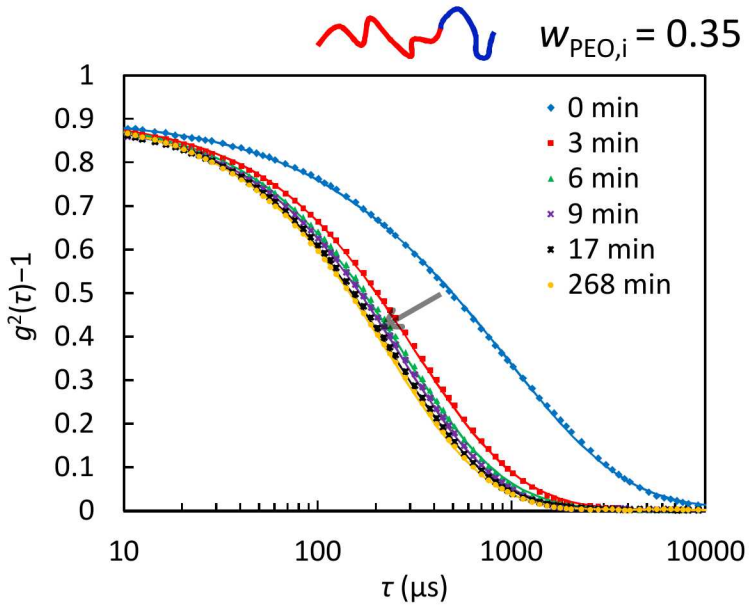
Jones, B. H.; *et al. Macromolecules* **2018**, *51*, 6543-6551.

Dynamic Light Scattering (DLS)

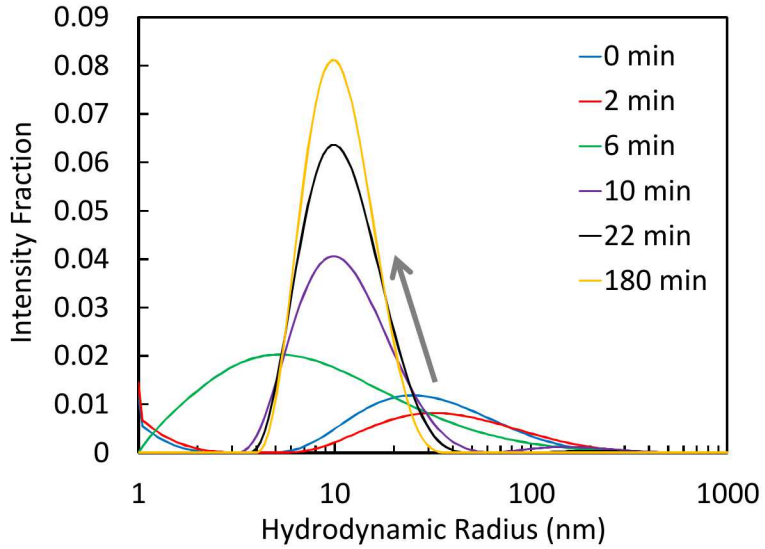
DLS data indicate a rapid decrease in hydrodynamic size upon catalyst exposure

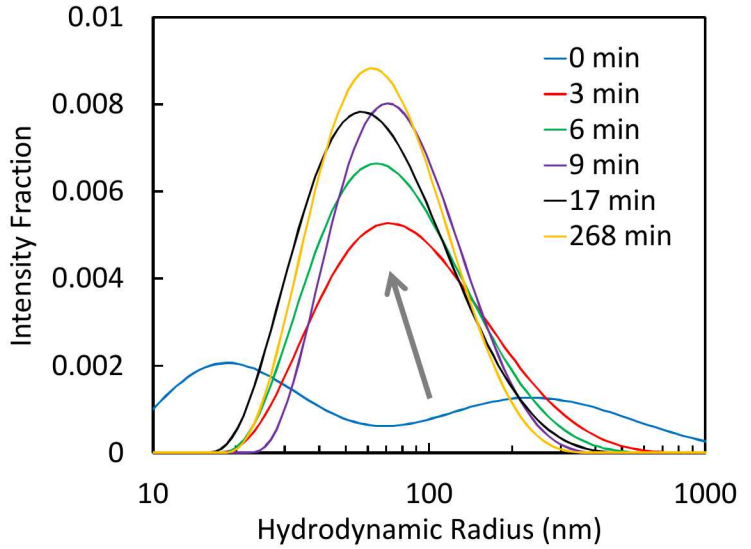
Autocorrelation functions





Size distributions (*via* CONTIN)

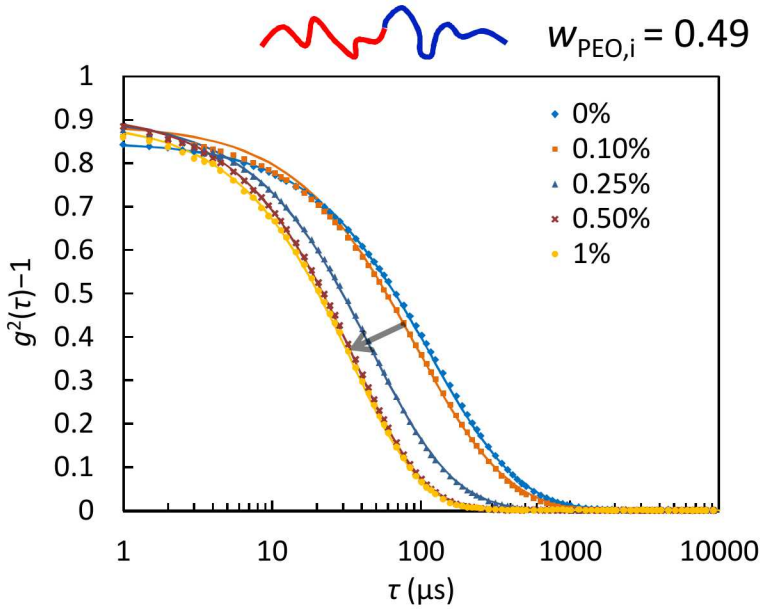


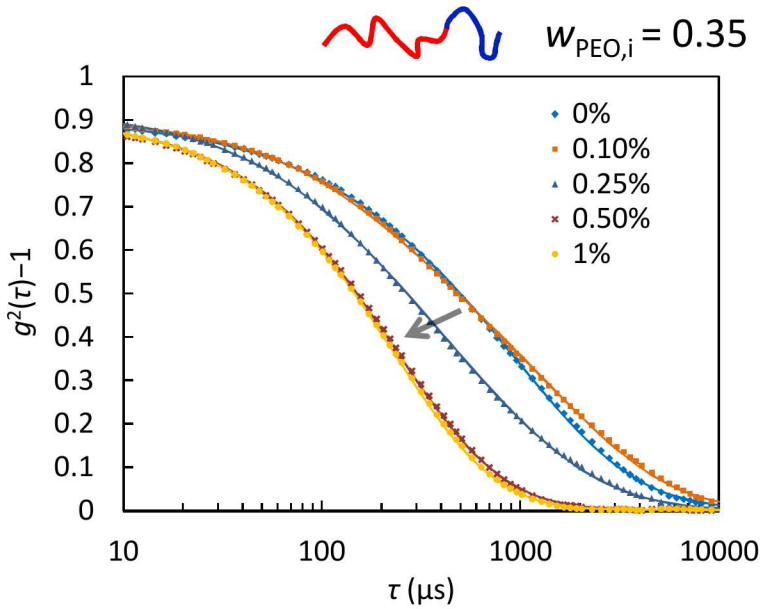


Dynamic Light Scattering (DLS)

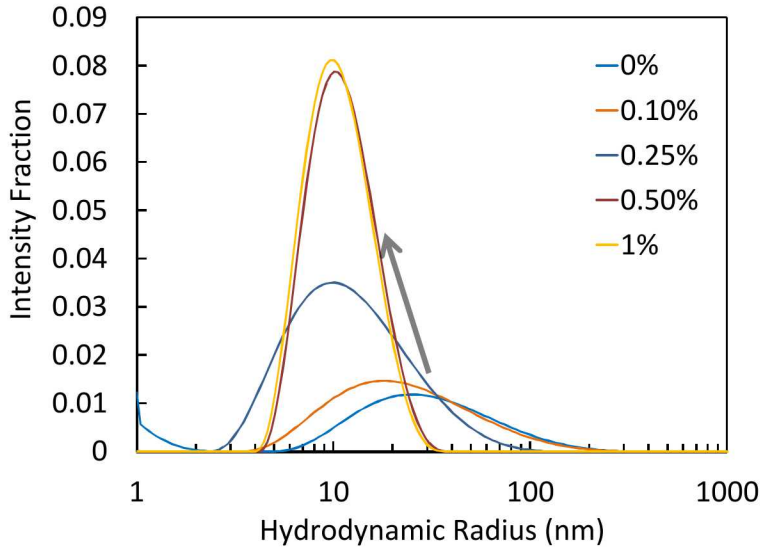
The final hydrodynamic size is dictated by the amount of catalyst added

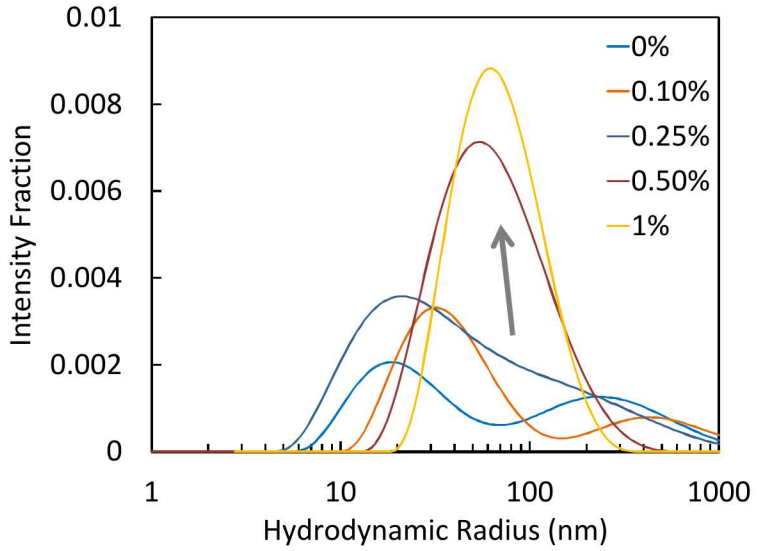
Autocorrelation functions





Size distributions (*via* CONTIN)

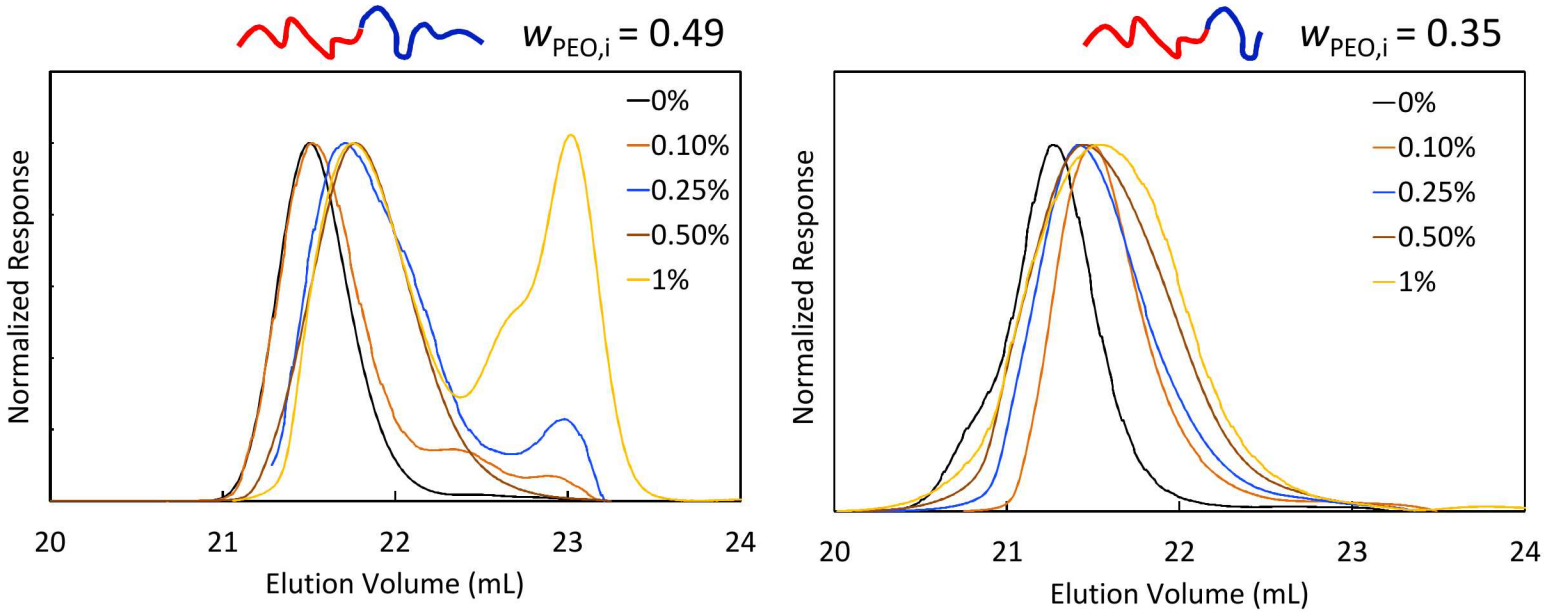




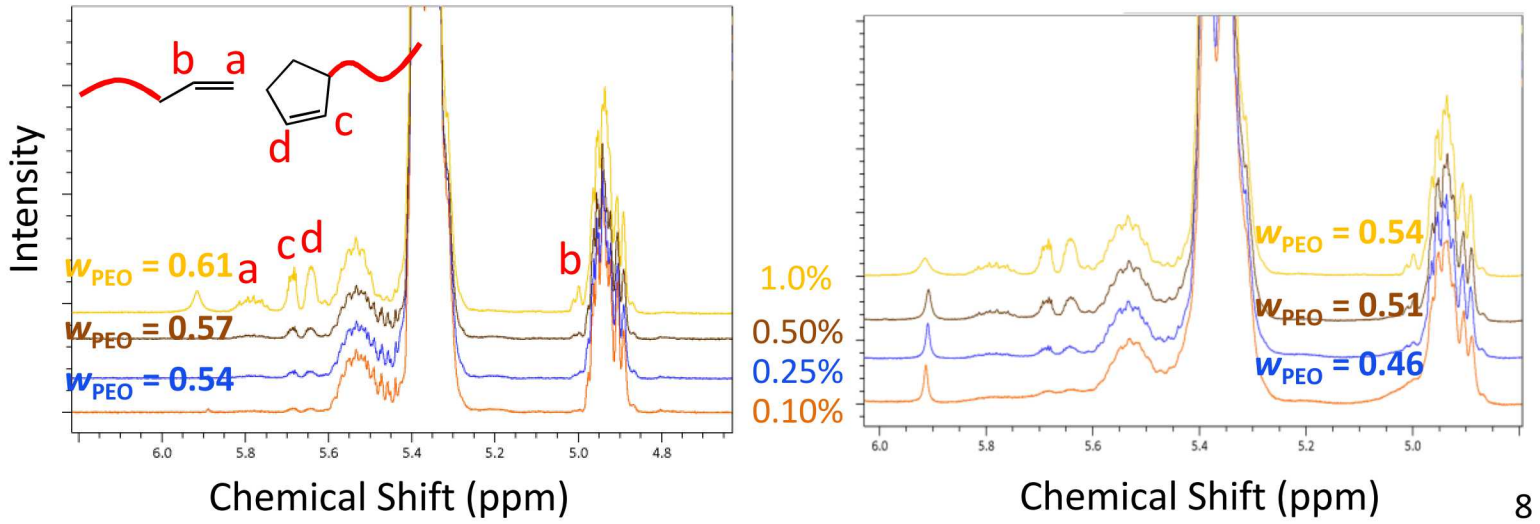
Evidence of Depolymerization

Analysis after freeze-drying indicates progressive depolymerization

GPC traces

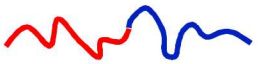


^{1}H NMR spectra



Morphological Transitions

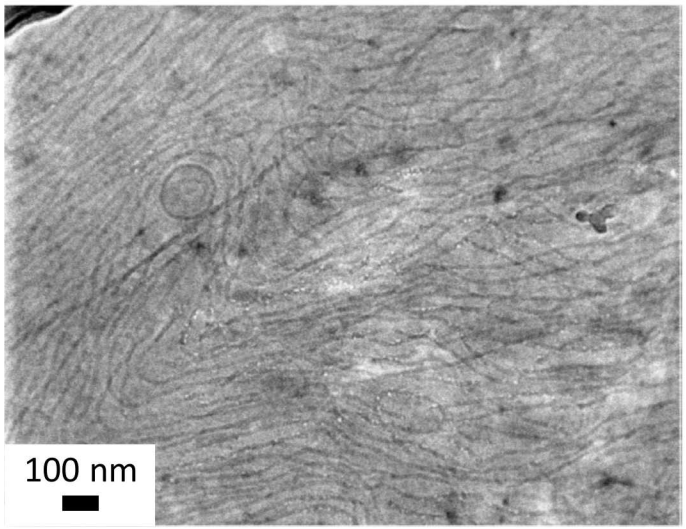
Cryo-TEM/FM suggests cylinder->sphere and vesicle->cylinder at 1% catalyst

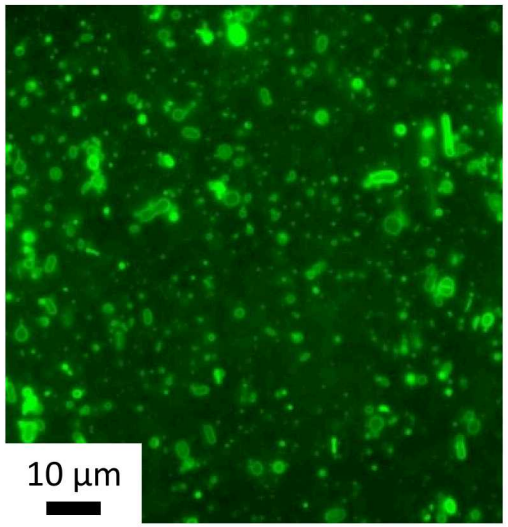


$w_{PEO,i}$ = 0.49

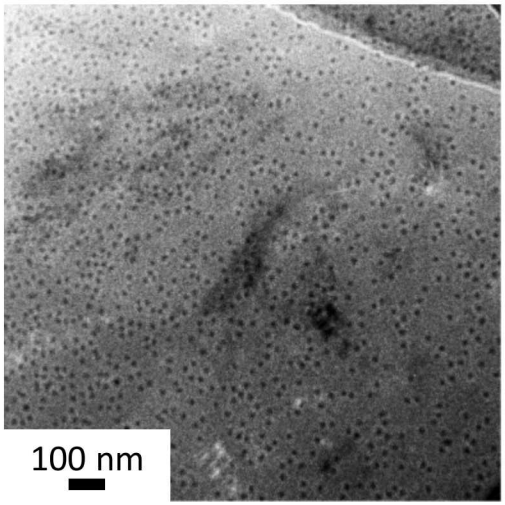
$w_{PEO,i}$ = 0.35

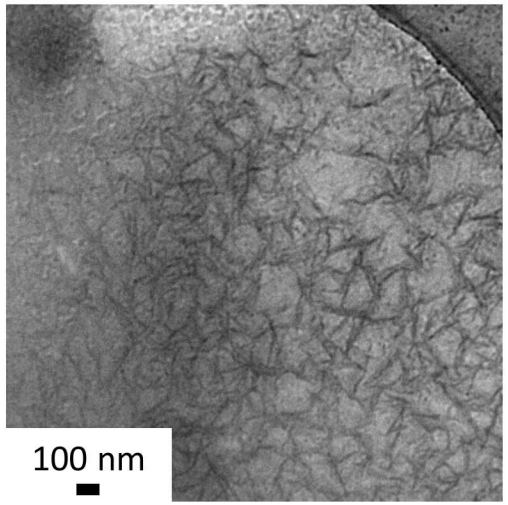
initial





final



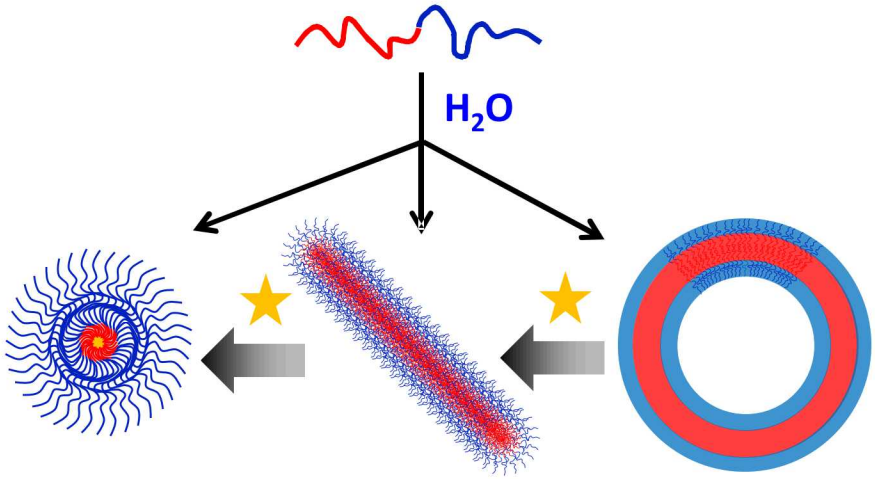


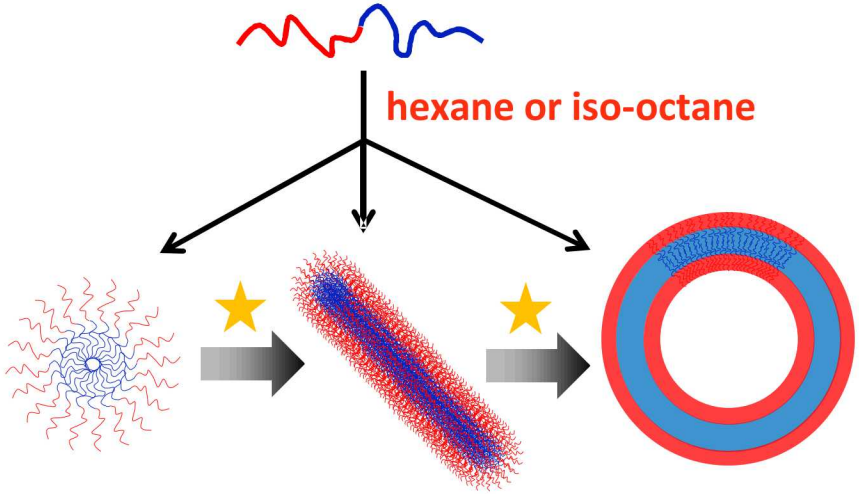
$w_{PEO,f}$ = 0.61

$w_{PEO,f}$ = 0.54

Assembly in Non-Polar Media

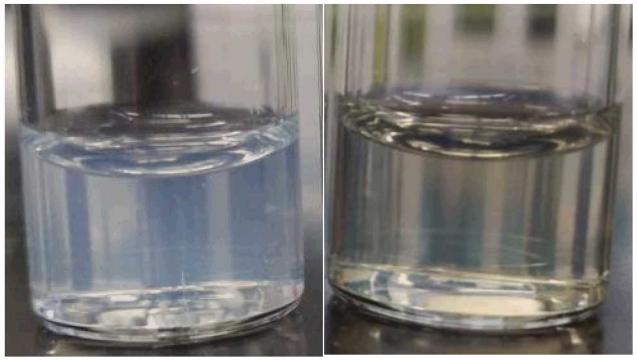
Initial DLS measurements suggest reverse effect possible with PB as corona





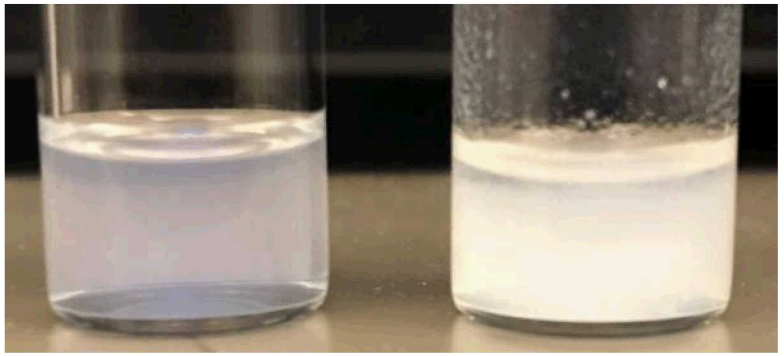
PB-PEO in H_2O, 1% catalyst

before after



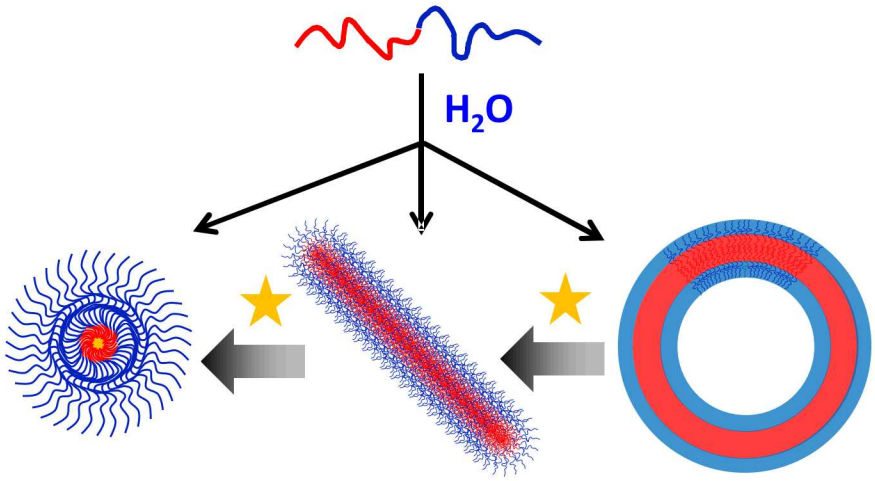
PB-PEO in hexane, 1% catalyst

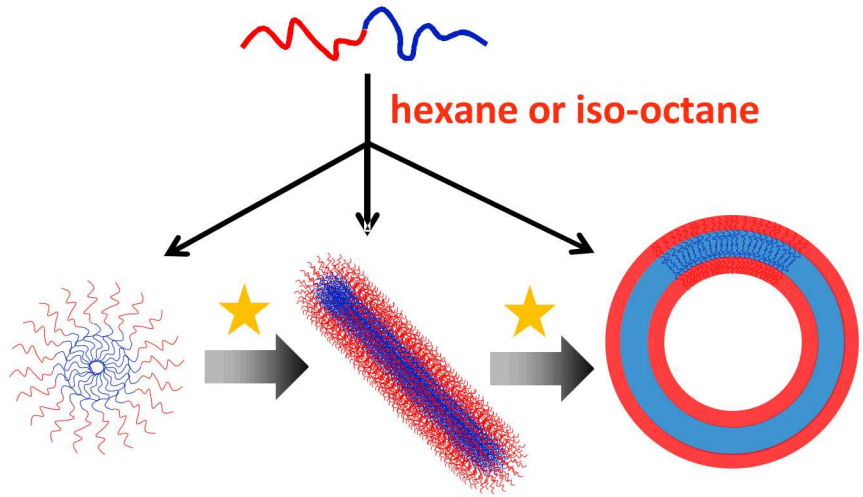
before after

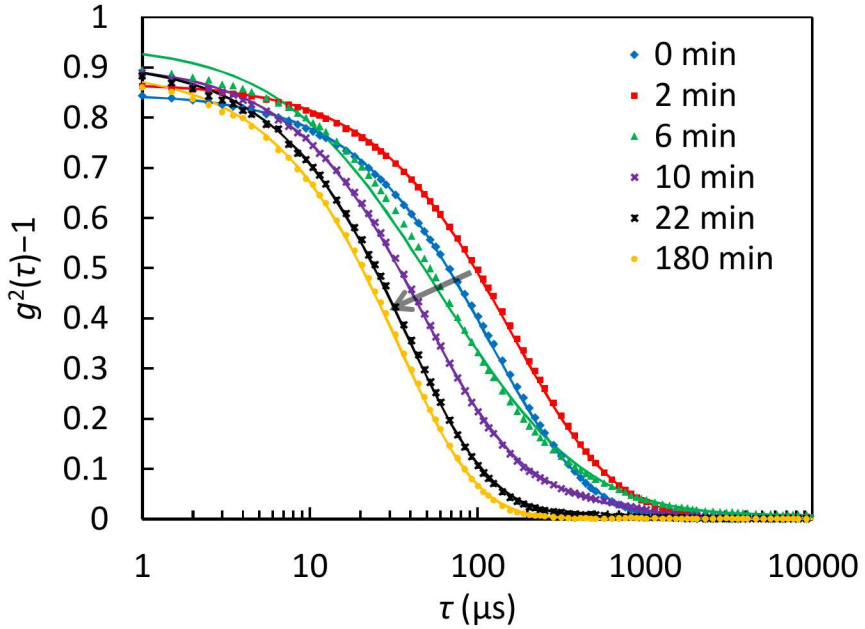


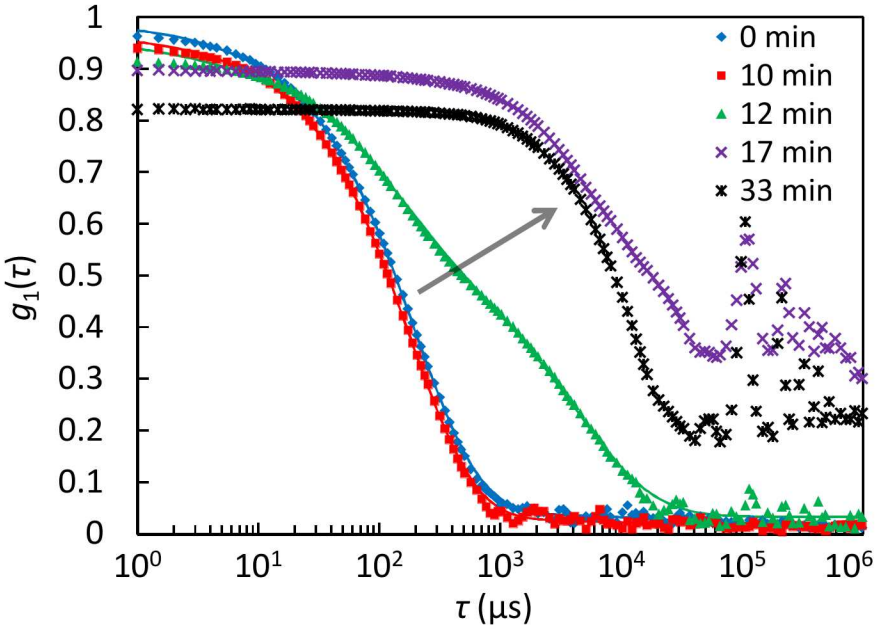
Assembly in Non-Polar Media

Initial DLS measurements suggest reverse effect possible with PB as corona



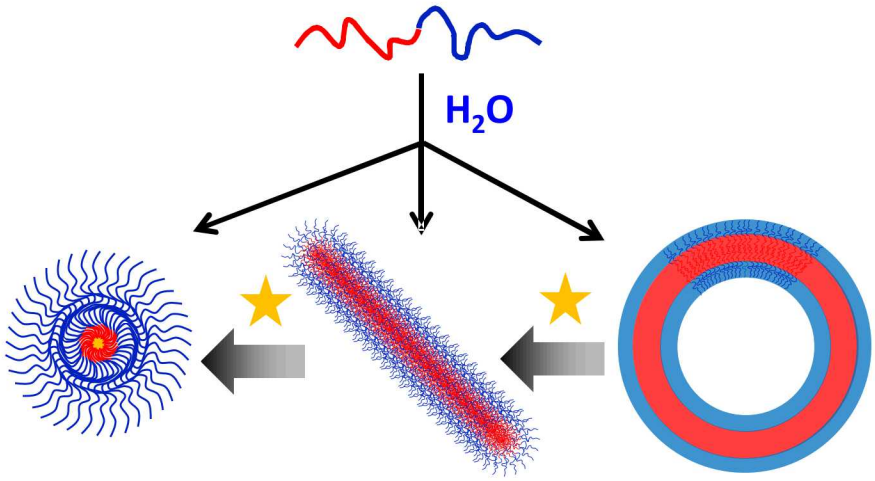


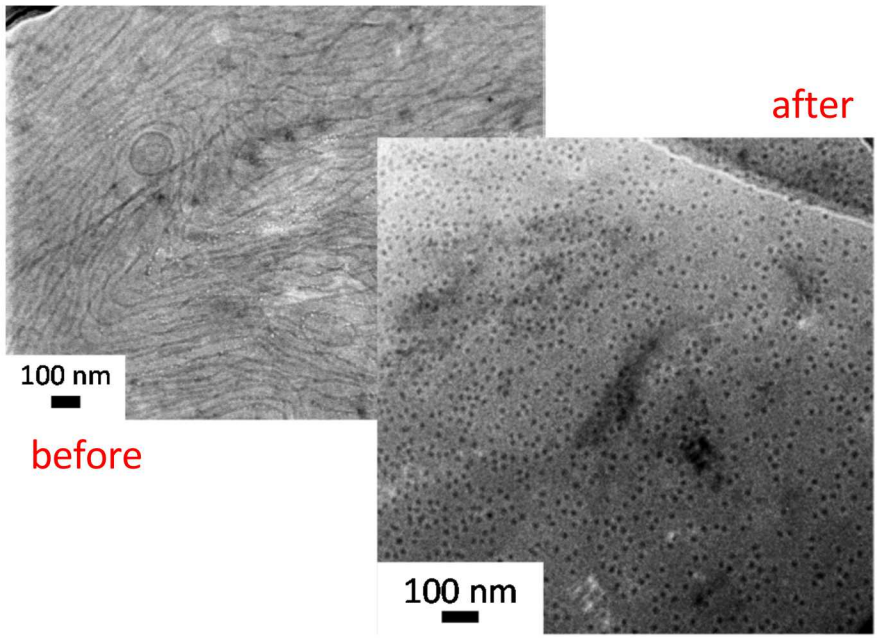


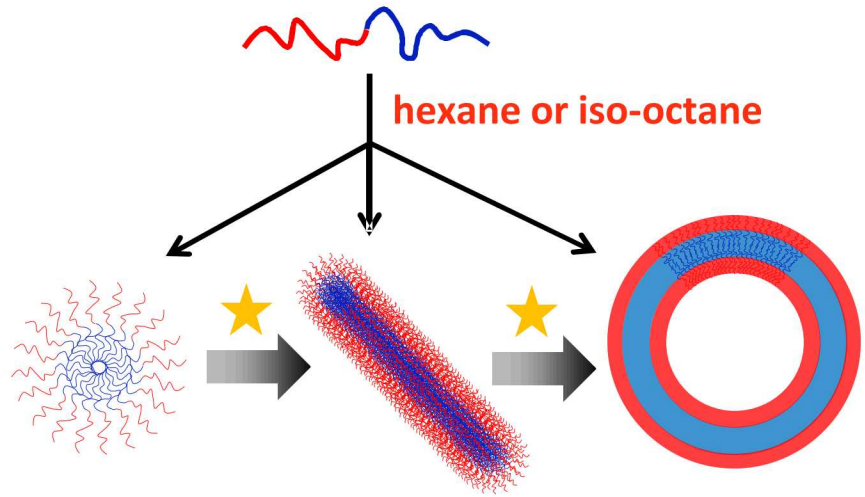


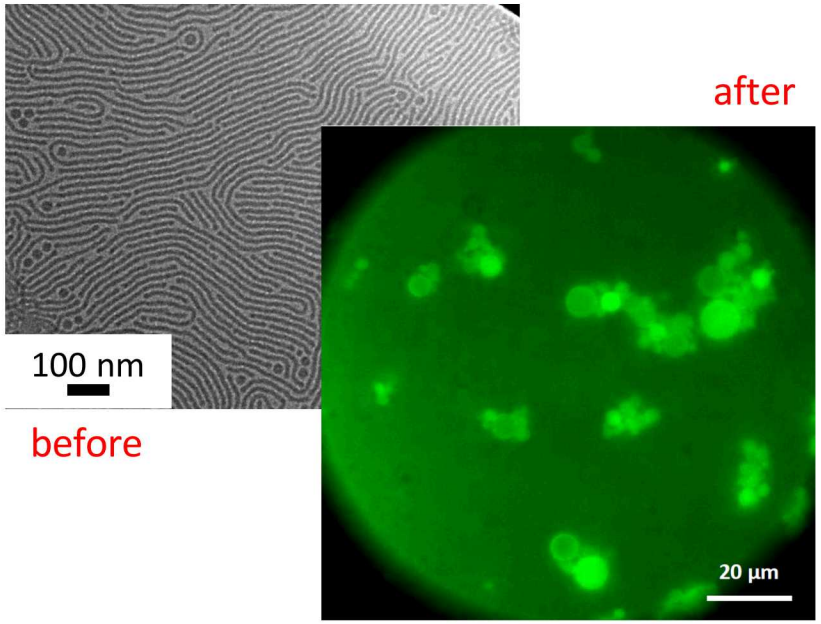
Assembly in Non-Polar Media

Initial DLS measurements suggest reverse effect possible with PB as corona





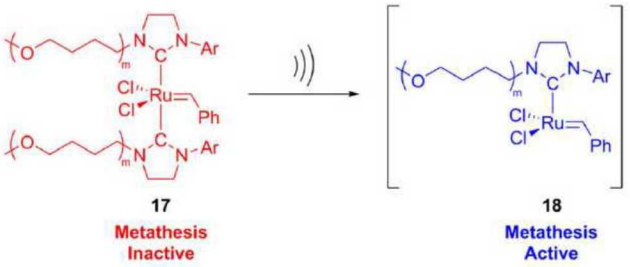




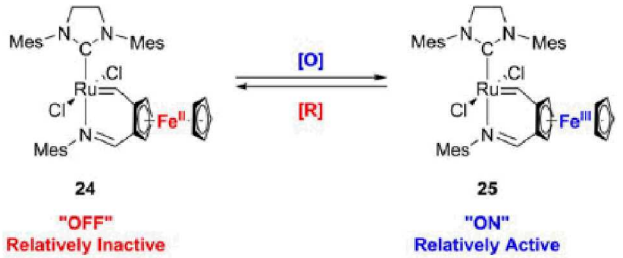
Latent Metathesis Catalysts

Latent, stimuli-responsive Ru carbenes represent a burgeoning field of study

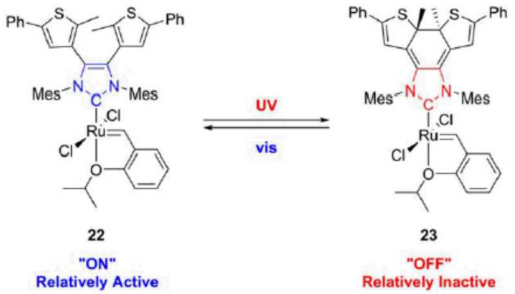
sonochemical activation



redox activation

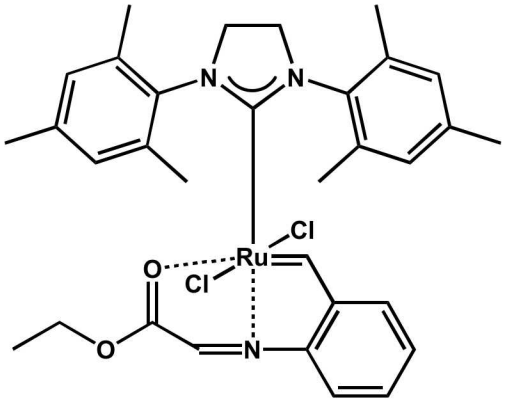


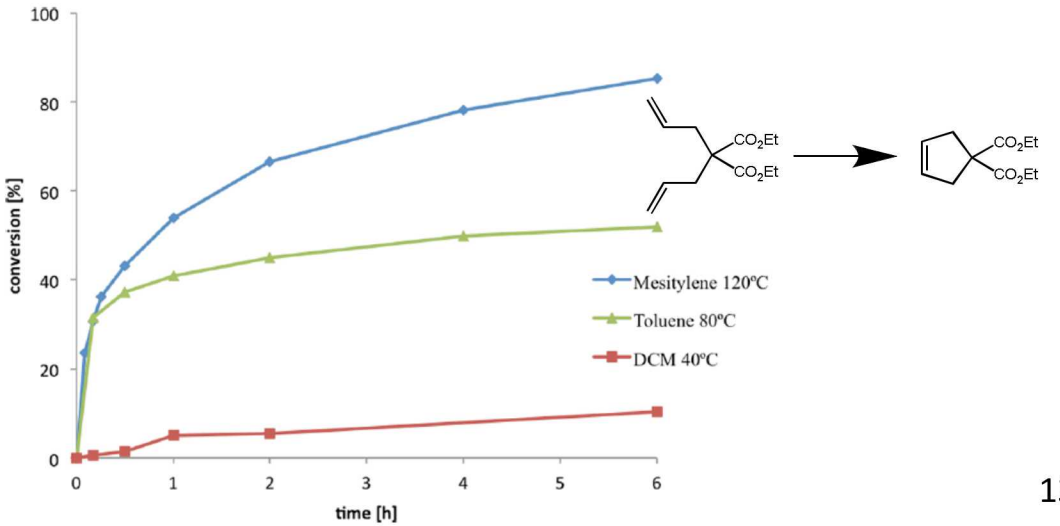
light activation



Teator, A. J.; Bielawski, C. W. *J. Polym. Sci. Polym. Chem.* **2017**, *55*, 2949-2960.

HeatMet is a commercially available Ru carbene exhibiting thermal latency

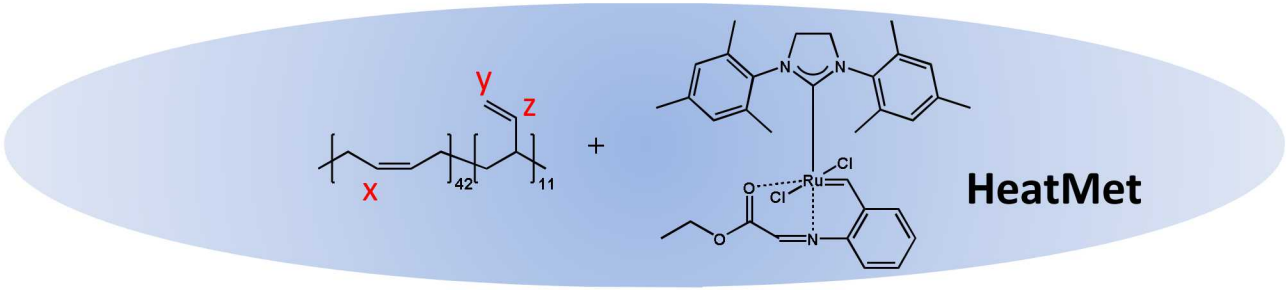




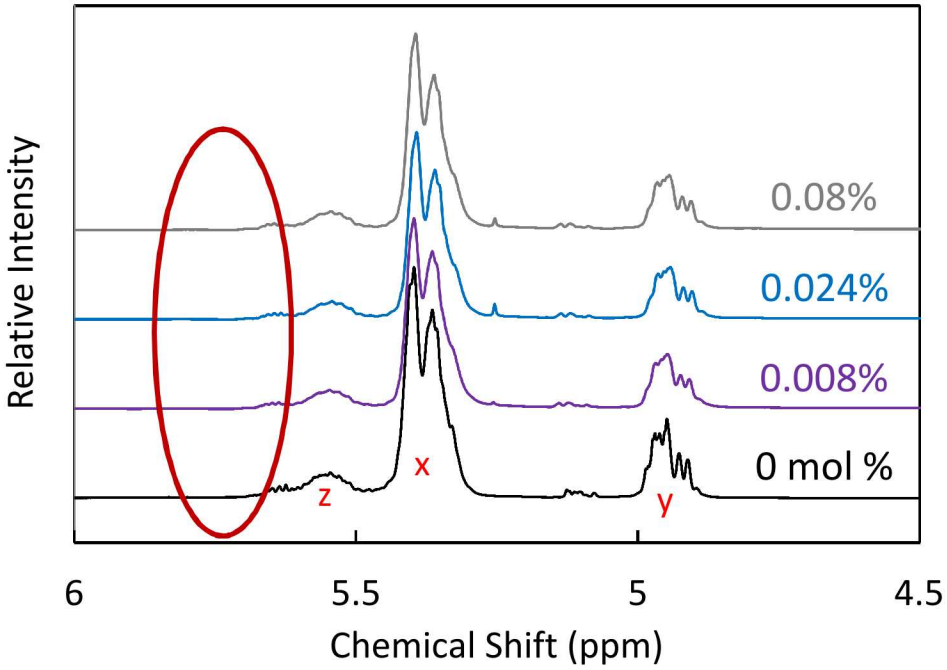
Czarnocki, S.; *et al. ACS Catal.* **2017**, *7*, 4115-4121.

Thermal Latency with HeatMet

HeatMet exhibits excellent stability towards PB under ambient conditions

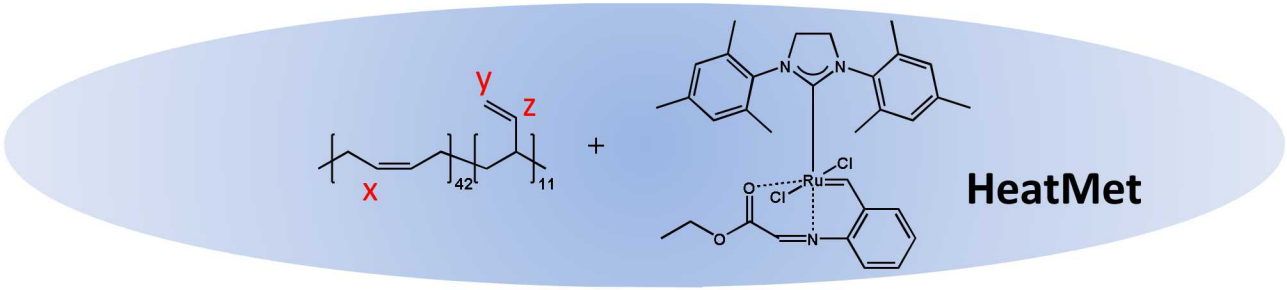


^{1}H NMR spectra after 3 days at 25 °C

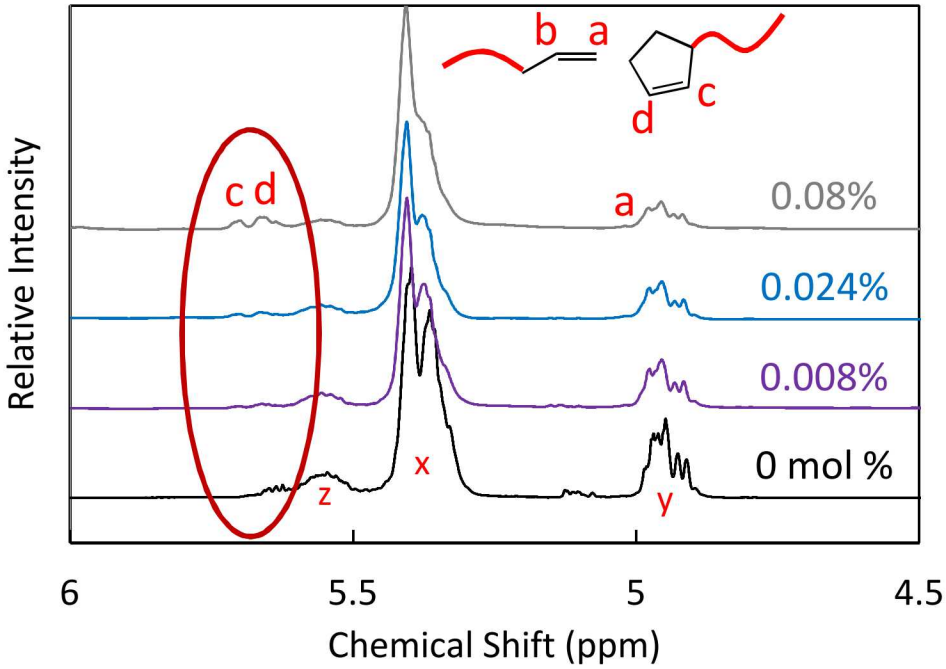


Thermal Latency with HeatMet

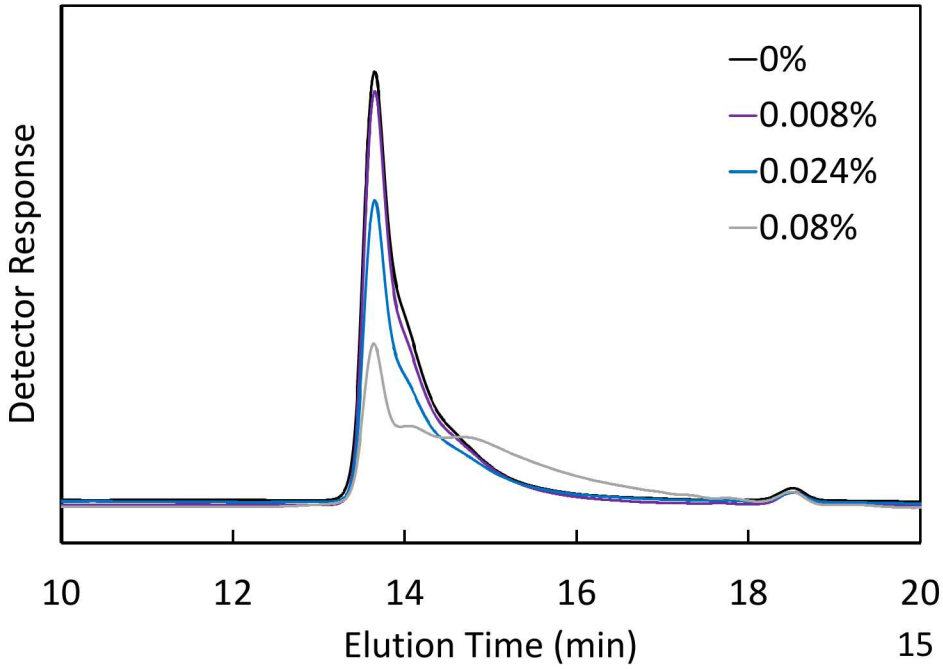
HeatMet exhibits excellent stability towards PB under ambient conditions



^{1}H NMR spectra after 1 hr at 100 °C

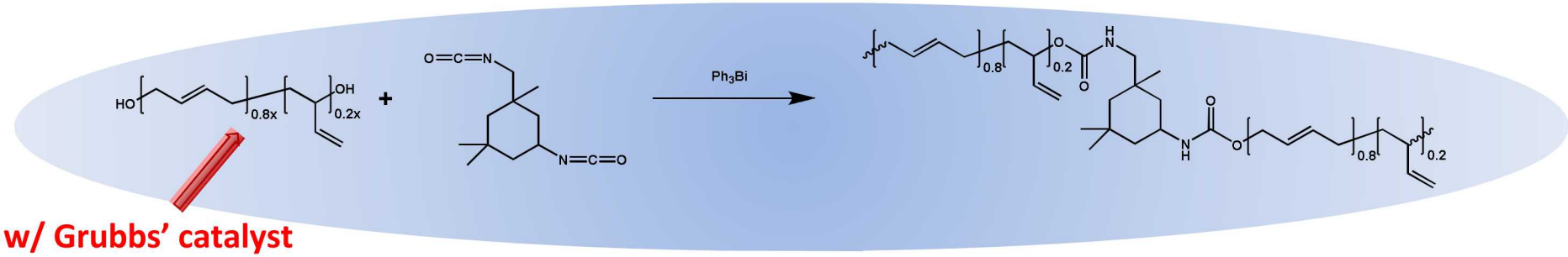


GPC traces after 1 hr at 100 °C

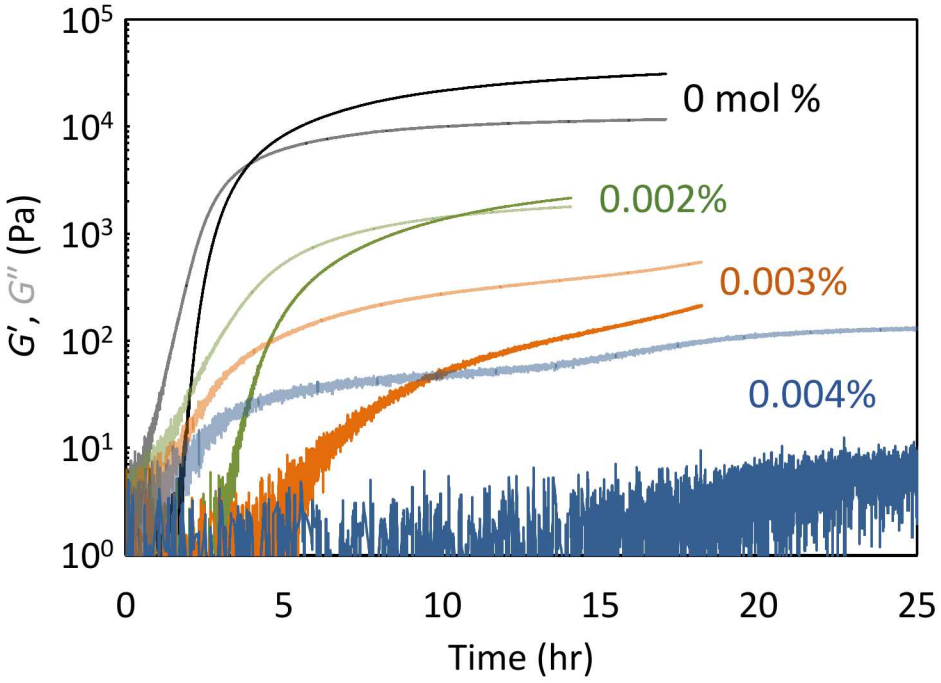


Depolymerization of a Thermally Cured Network

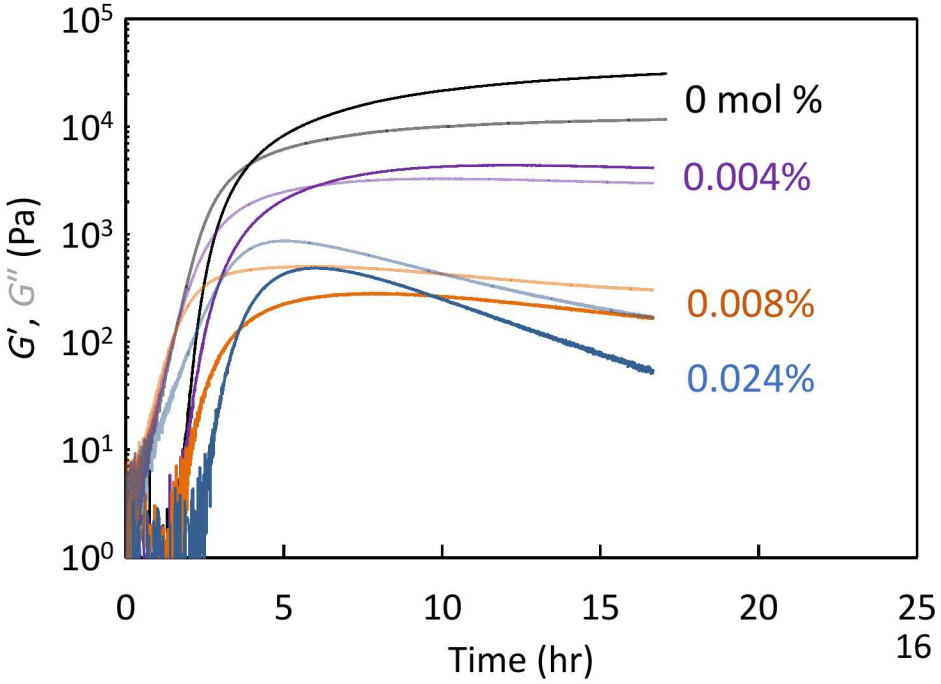
Classic urethane-linked PB networks exhibit orthogonal cure and depolymerization



Dynamic shear moduli during cure at 70 °C, **w/ HG2**

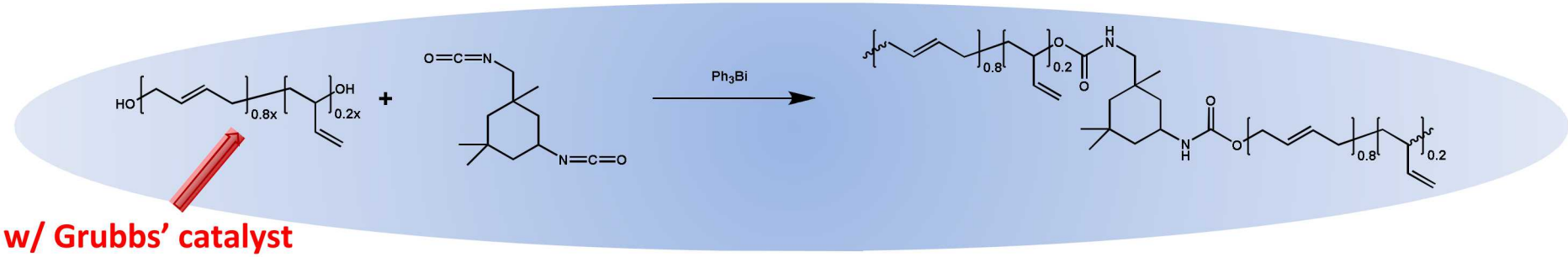


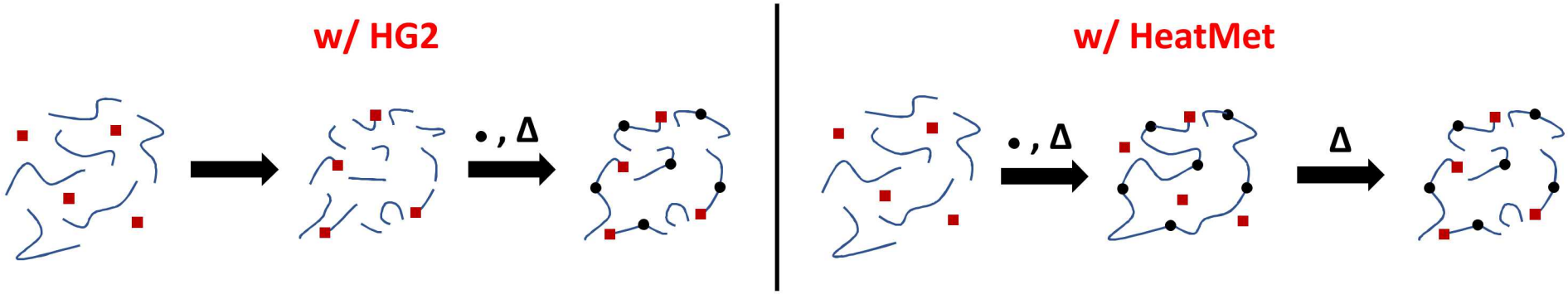
Dynamic shear moduli during cure at 70 °C, **w/ HeatMet**



Depolymerization of a Thermally Cured Network

Classic urethane-linked PB networks exhibit orthogonal cure and depolymerization





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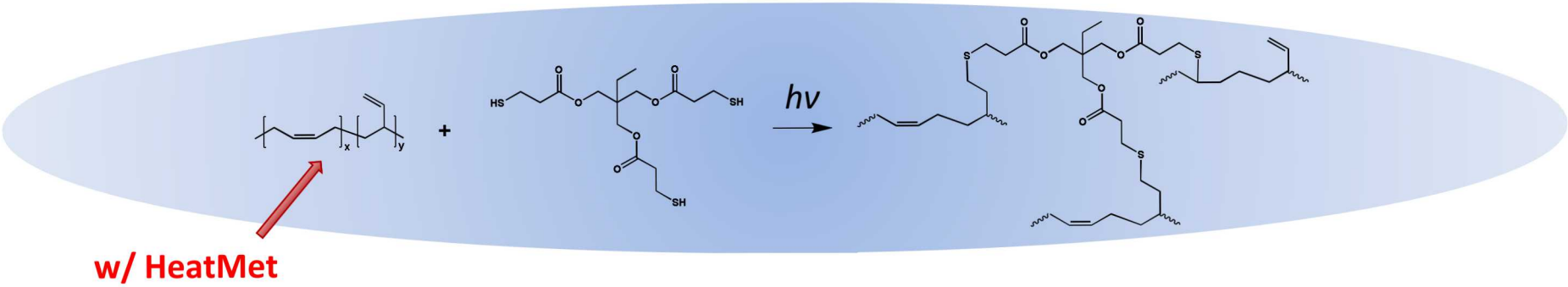
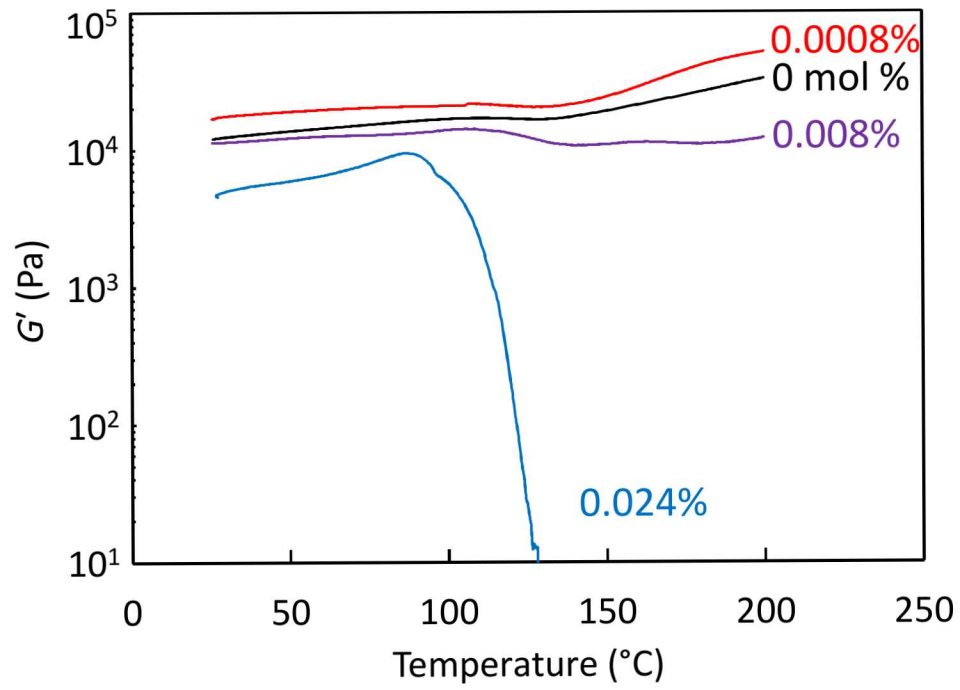
Depolymerization of a Photocured Network

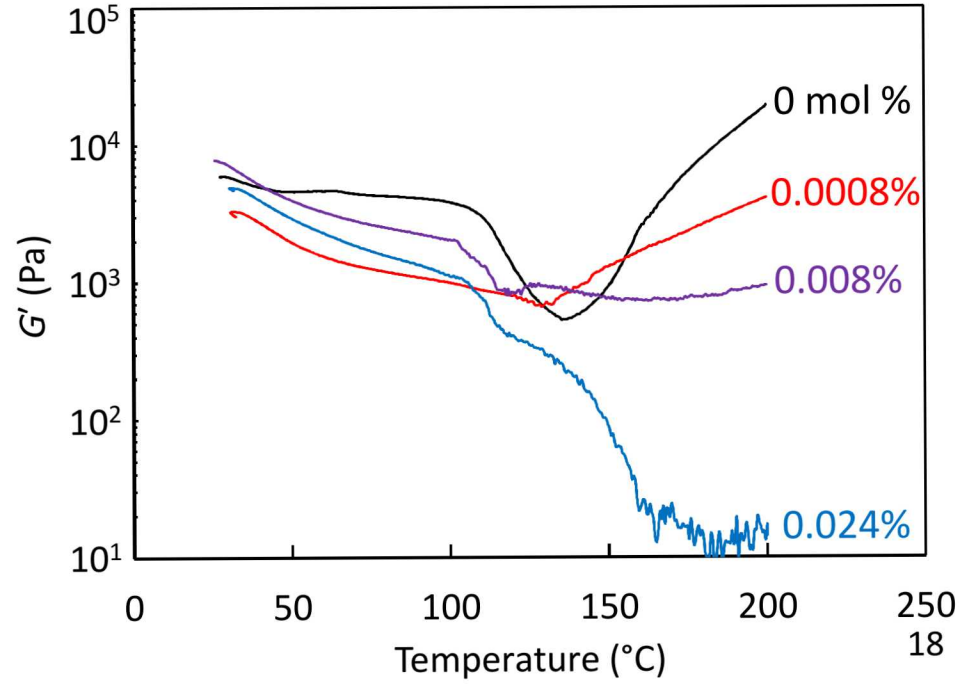
Cure and depolymerization can be fully decoupled in a photocured network



Storage modulus of cured **1,4-PB** upon heating

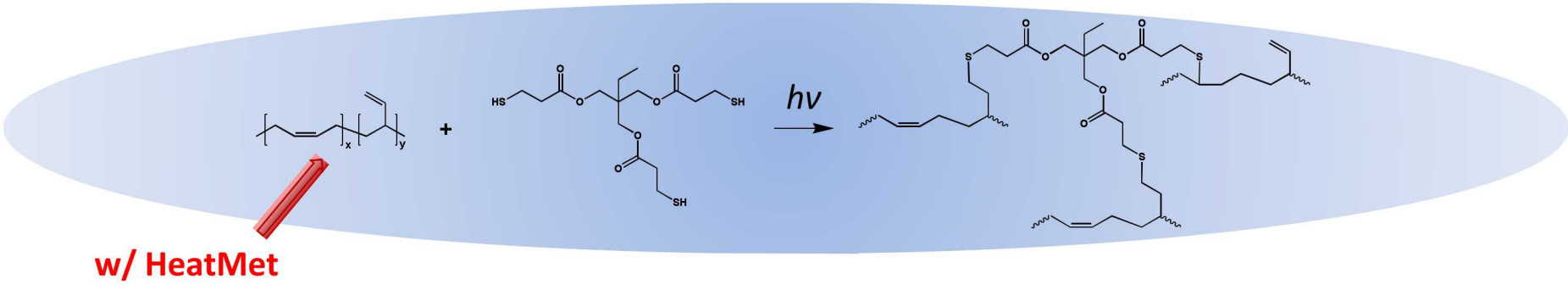


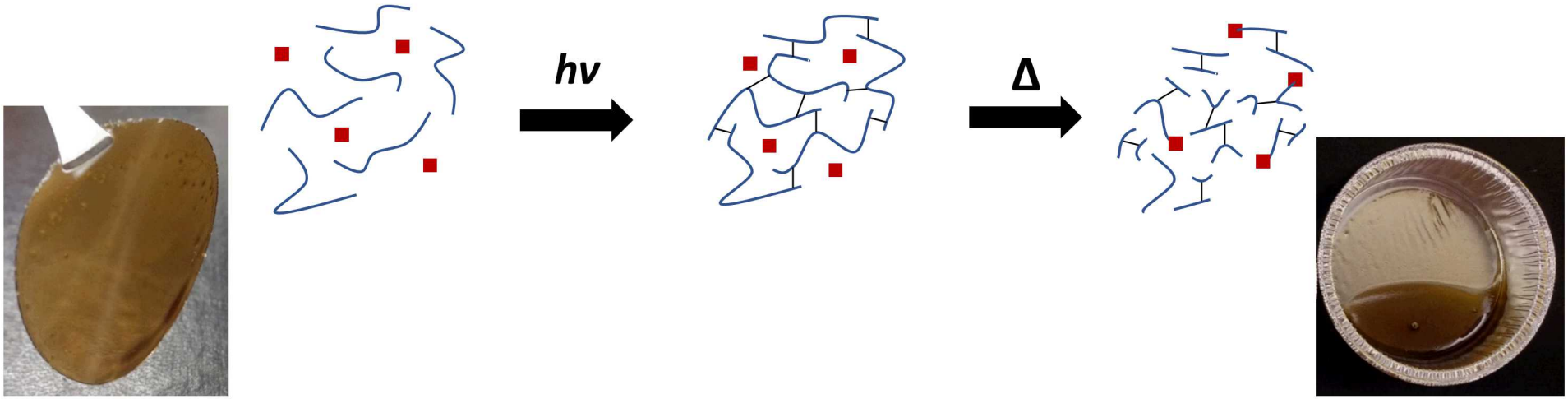
Storage modulus of cured **1,2-PB** upon heating



Depolymerization of a Photocured Network

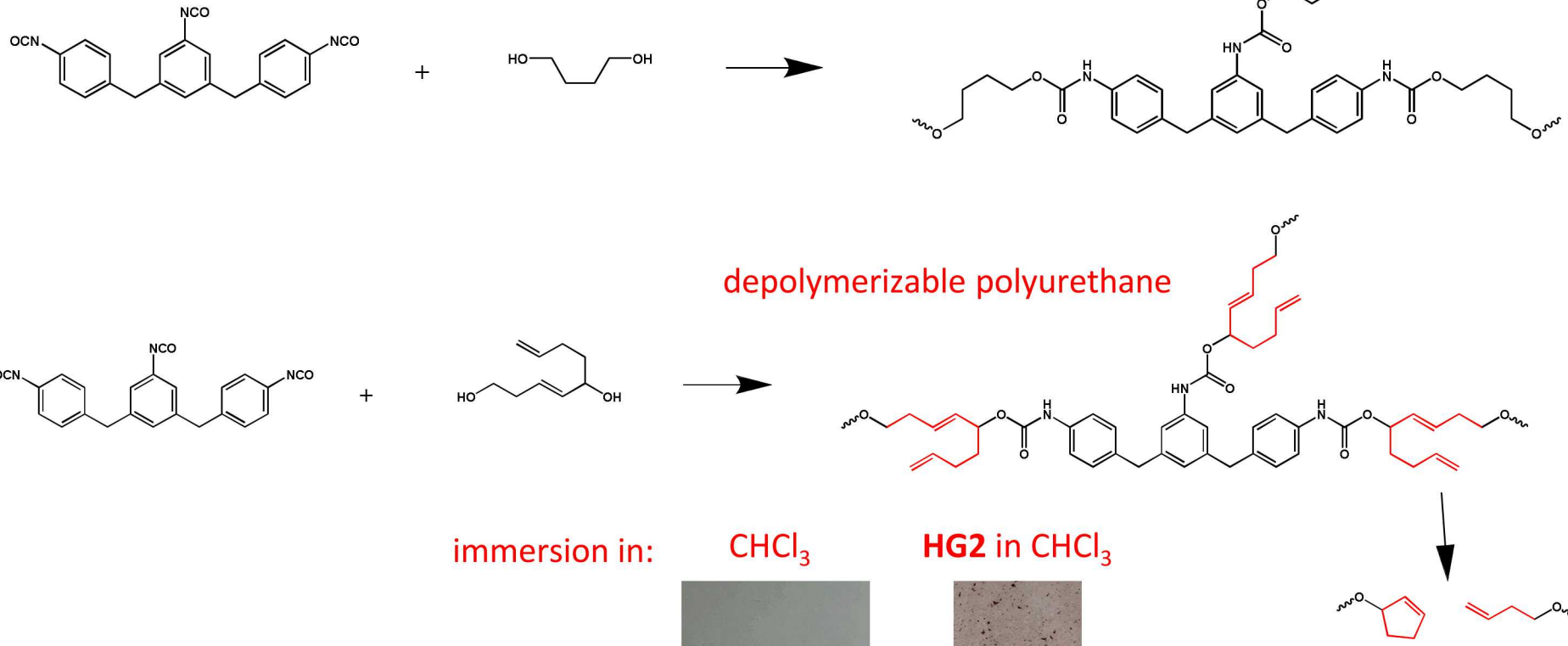
Cure and depolymerization can be fully decoupled in a photocured network





New Directions: Novel Depolymerizable Polymers

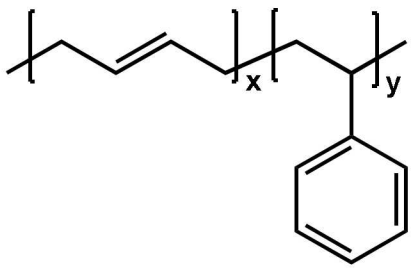
Custom monomers with ring-closing moieties offer new routes to depolymerization



depolymerizable PU foam after immersion in $CHCl_3$ vs. **HG2** in $CHCl_3$

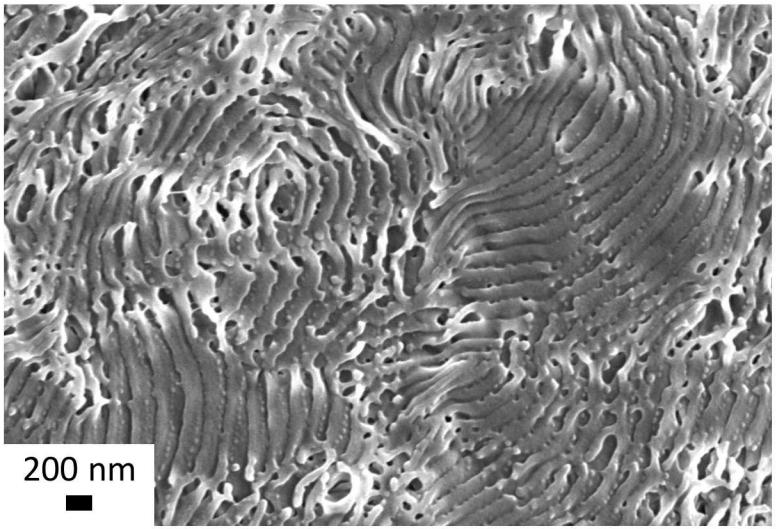
New Directions: Control Over Bulk Self-Assembly

Latent catalysts may offer stimuli-induced control over bulk block polymer morphology

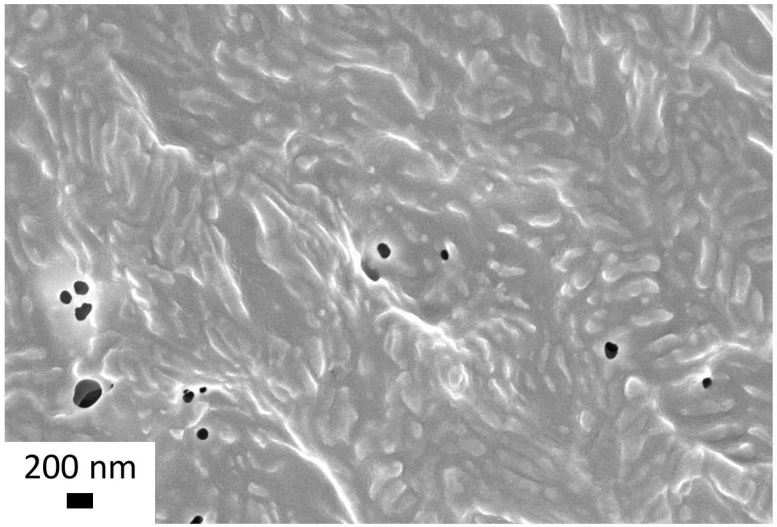


$w_{PS,i} = 0.47$

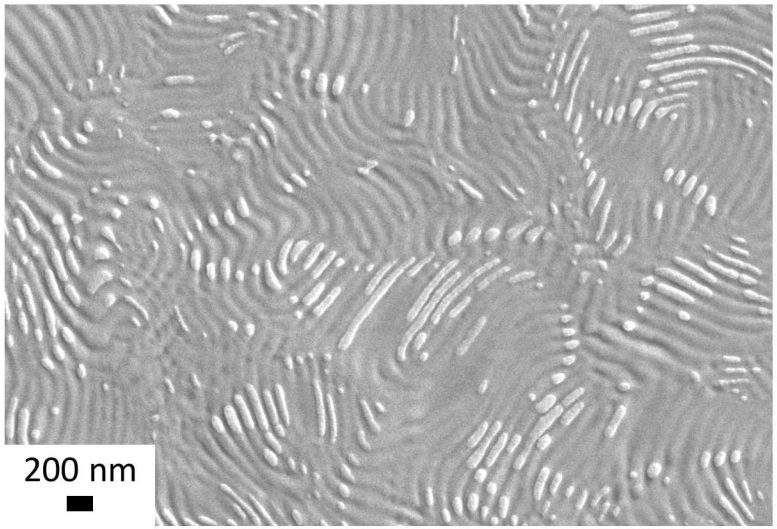
rapid film casting



thermal anneal, no HeatMet

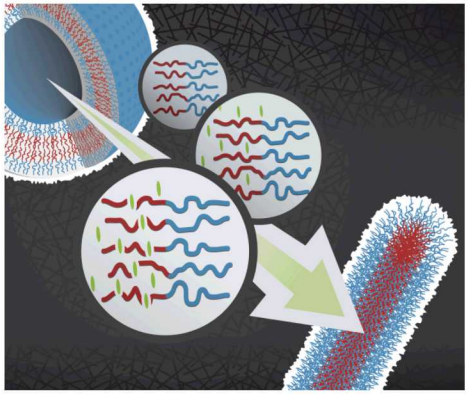


thermal anneal, with HeatMet



Secondary electron SEM images, contrast results from selective etching of PB domains

Conclusions and Acknowledgements



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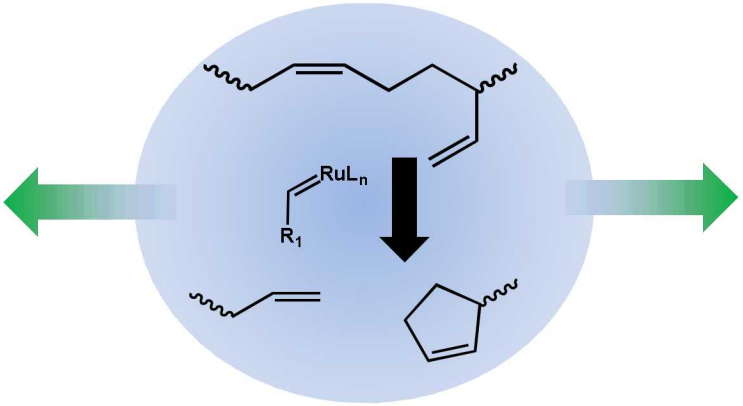

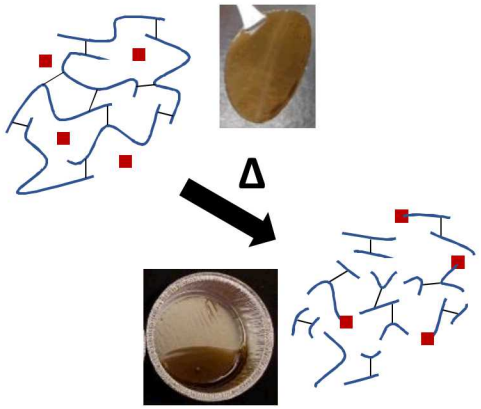

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