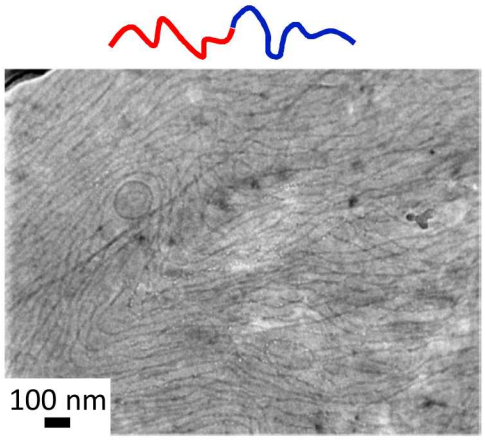
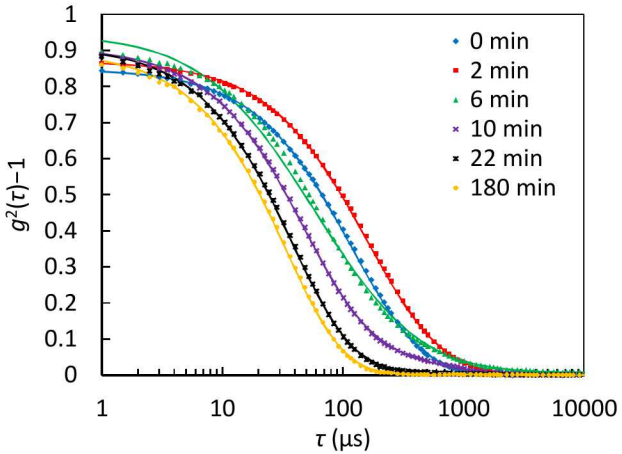
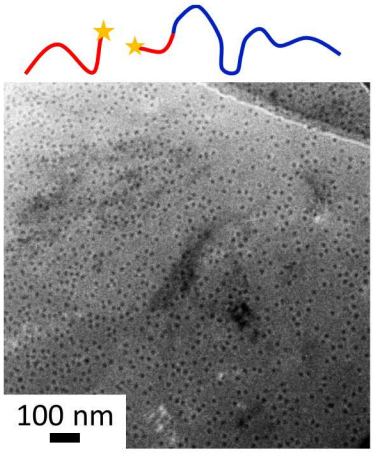
SAND2018-10544PE





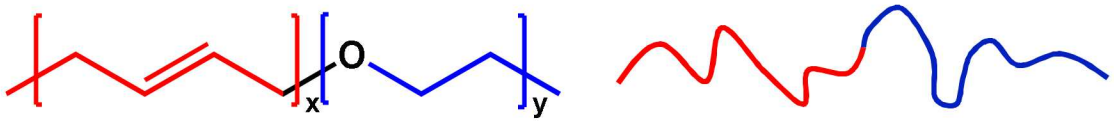


Dynamic Self-Assembly in Polybutadiene-Containing Block Copolymers induced by *In Situ* Metathesis

Jeremy Herman, Brad H. Jones, George D. Bachand, Sun Hae Ra Shin, Millicent A. Firestone, Walter F. Paxton

September 28th, 2018

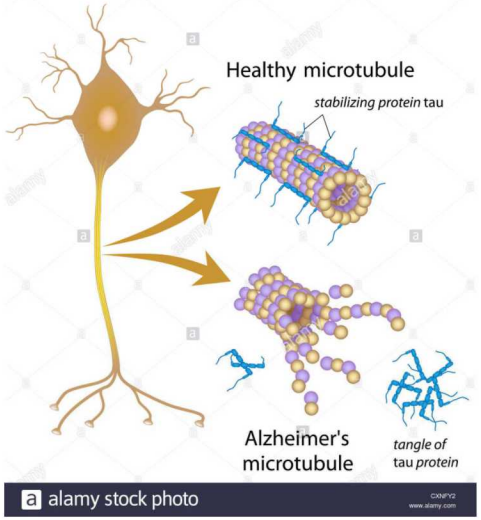
- Goal: To produce self-assembling block polymers that have been dispersed in different selected solvents and then to trigger morphological transitions on demand



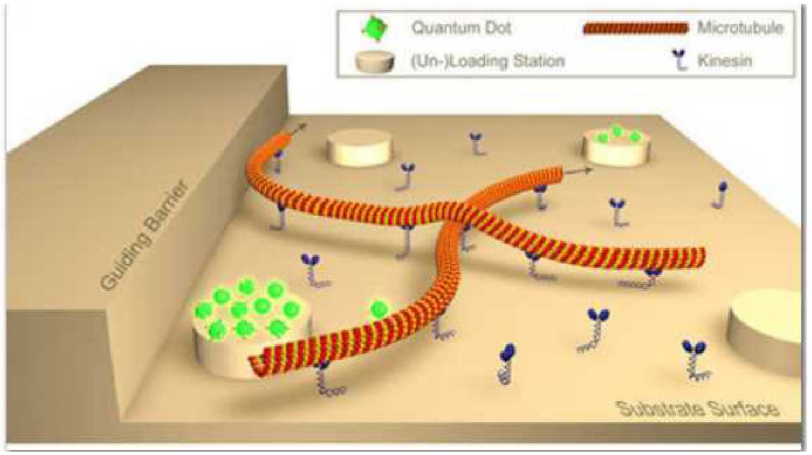
1,4 PB linked with PEO

- These polymers are comprised of Polybutadiene (PB) and Polyethylene Oxide (PEO)
- Applications: Biomimicry and nanotechnology
  - Ultimate goal is to create synthetic microtubules

Possible Alzheimer's Disease Treatment:



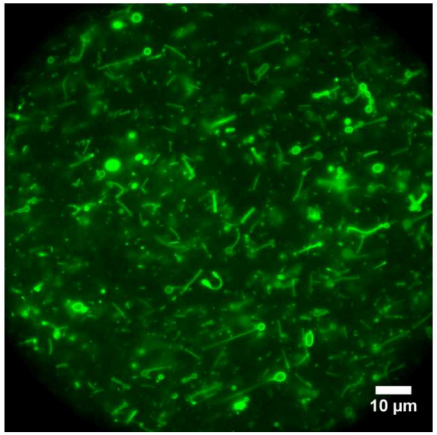
Nano Transport Technology:



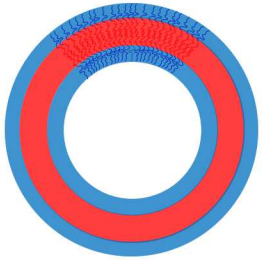
- These Block Polymers that have been dispersed in selective solvents form several different morphologies and the form that the aggregates take depends on the ratio of PB to PEO in the polymer

Vesicles

- Formed in water when the ratio of PB is greater than PEO



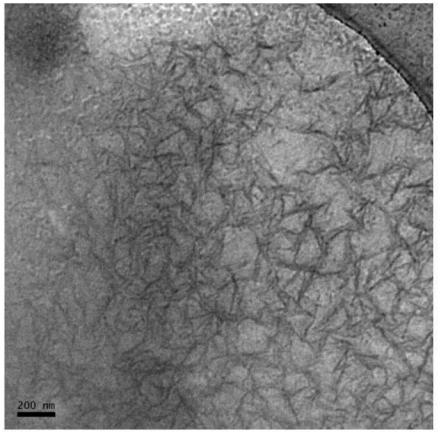
Fluorescent microscopy image of a vesicle forming polymer



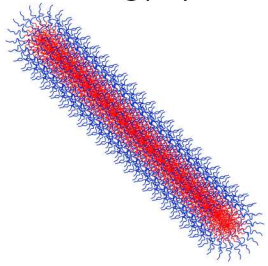
Drawing depicting the form of a vesicle

Cylinders

- Formed in water when the ratio of PB to PEO is equal



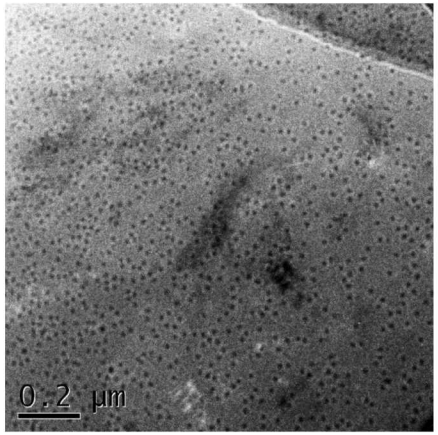
Cryo-TEM image of a cylinder forming polymer



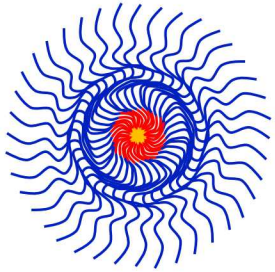
Drawing depicting the form of a cylindrical micelle

Spheres

- Formed in water when the ratio of PB is less than PEO

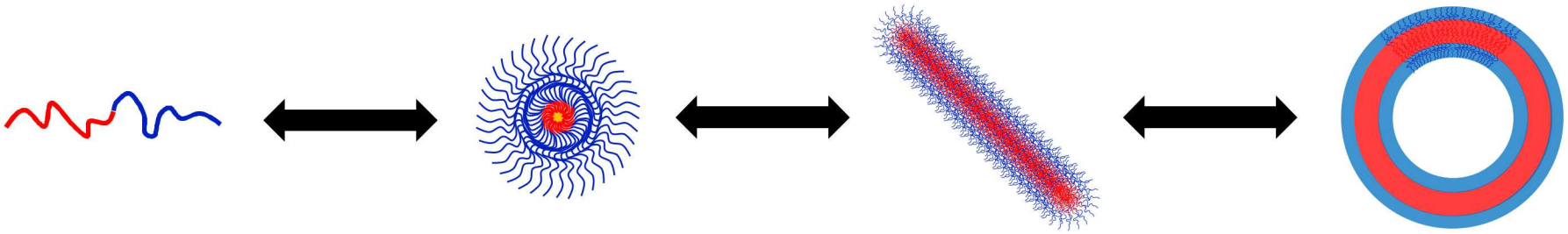


Cryo-TEM image of a spherical forming polymer



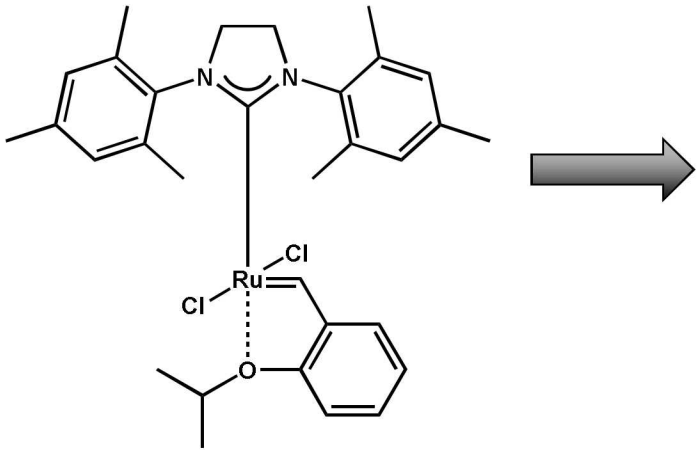
Drawing depicting the form of a spherical micelle

How do we trigger morphological transitions *in situ* and on demand?

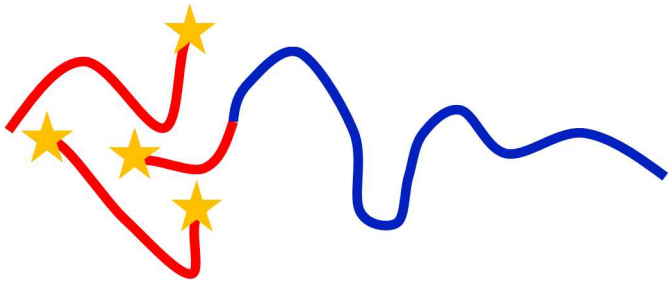


Answer: Introduce a Hoveyda-Grubbs catalyst (GC) to the already assembled aggregates

- This catalyst acts to depolymerize the PB block of the polymer through Olefin Metathesis



Chemical structure of catalyst

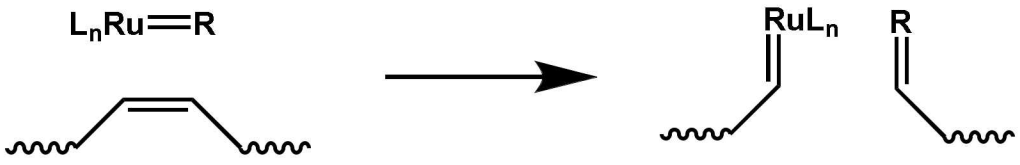


Visual representation of depolymerization of PB block of polymer

Metathesis of Polydienes

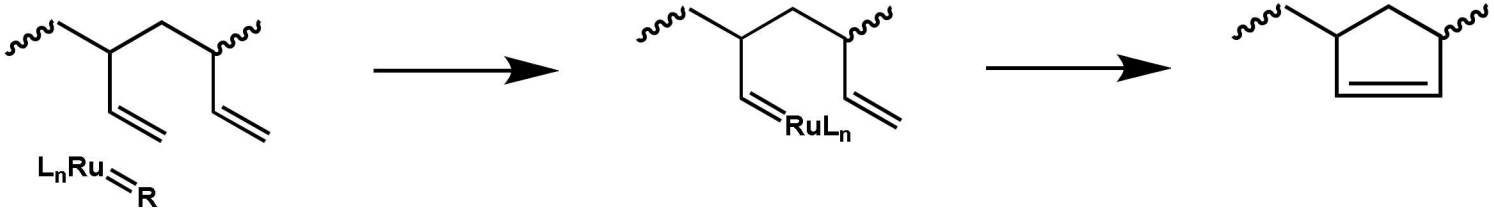
Olefin metathesis can be used to depolymerize or cyclize polydienes

pure 1,4-PB

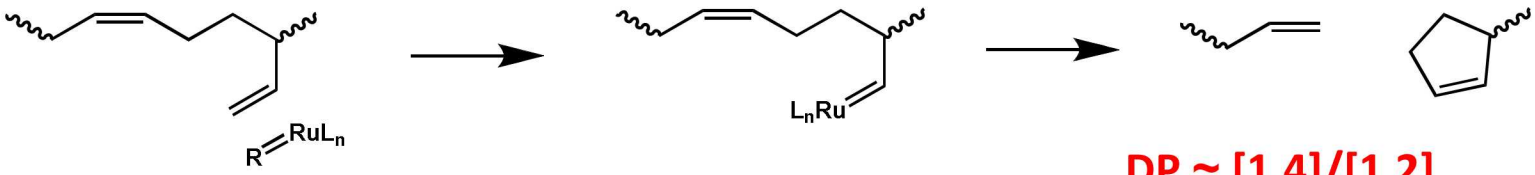


DP ~ [rep. units]/[cat.]

pure 1,2-PB



'real' 1,4-PB



DP ~ [1,4]/[1,2]

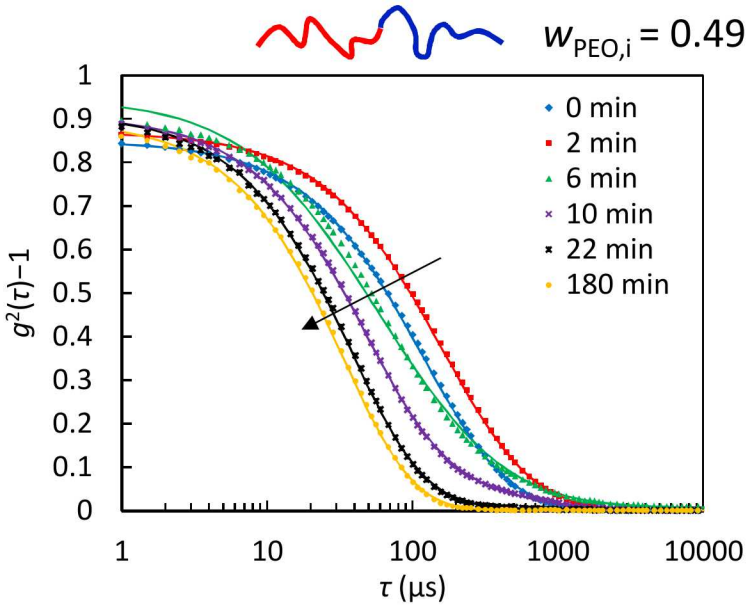
Coates, G. W.; Grubbs, R. H. *JACS* **1996**, *118*, 229-230

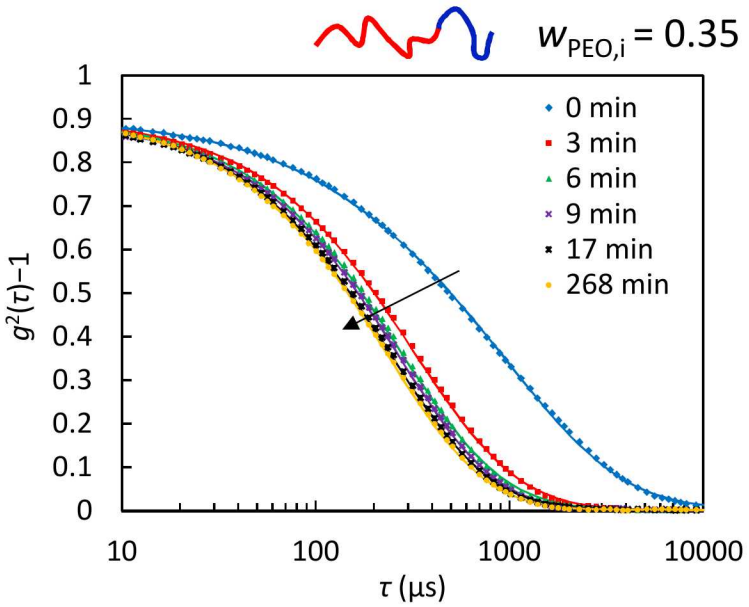
Watson, M. D.; Wagener, K. D. *Macromolecules* **2000**, *33*, 1494-1496.

Dynamic Light Scattering (DLS)

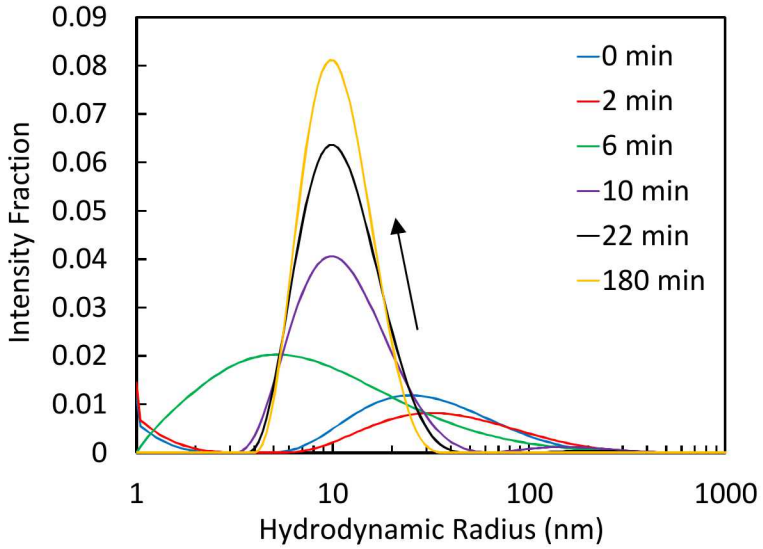
DLS data indicate a rapid decrease in hydrodynamic size upon catalyst exposure

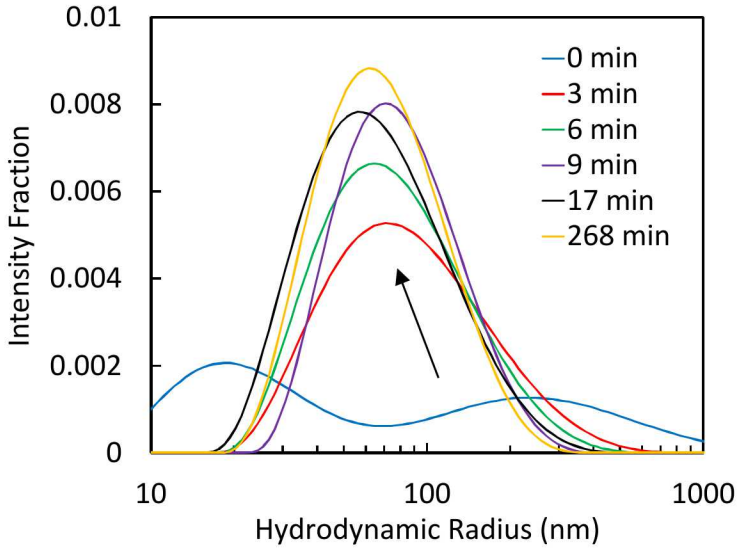
Autocorrelation functions





Size distributions (*via* CONTIN)

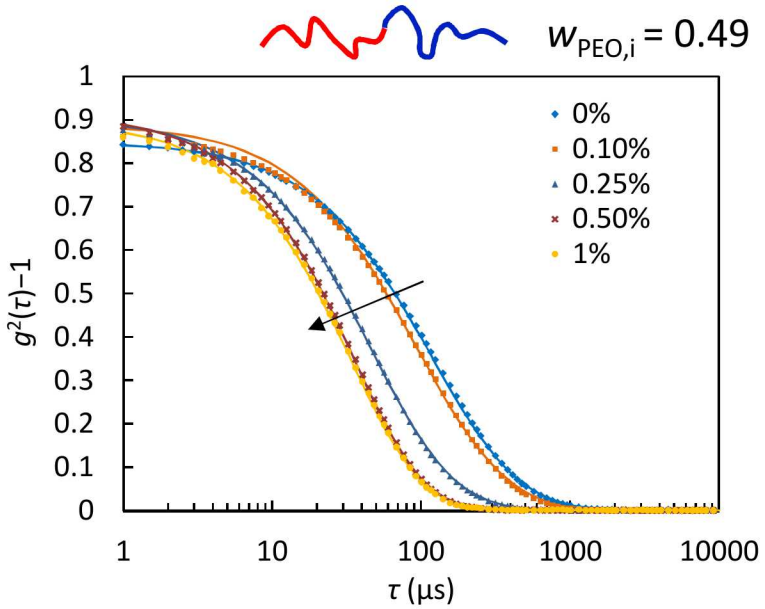


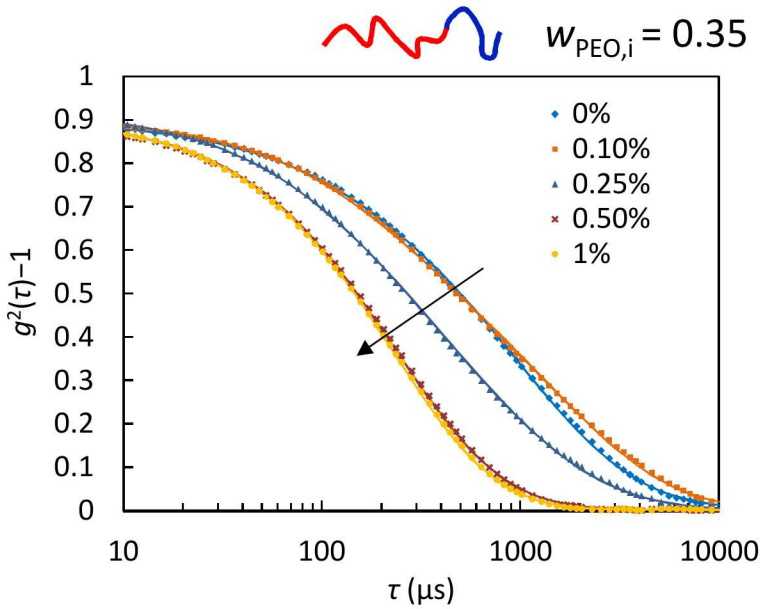


Dynamic Light Scattering (DLS)

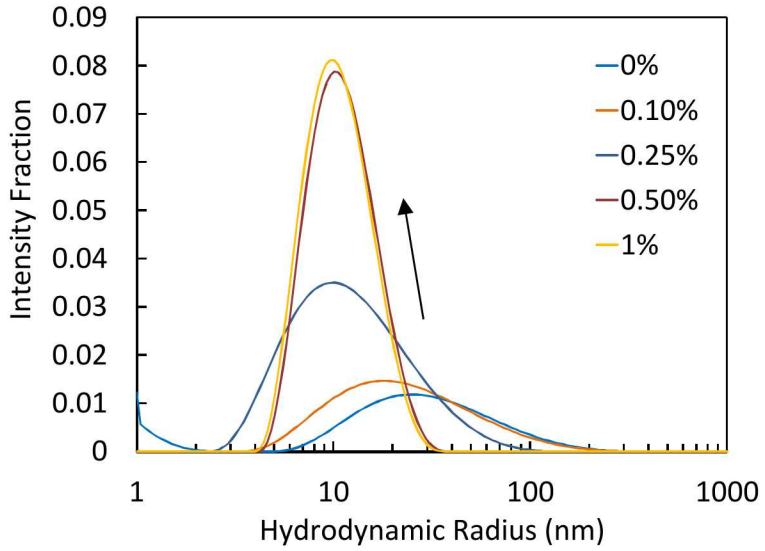
The final hydrodynamic size is dictated by the amount of catalyst added

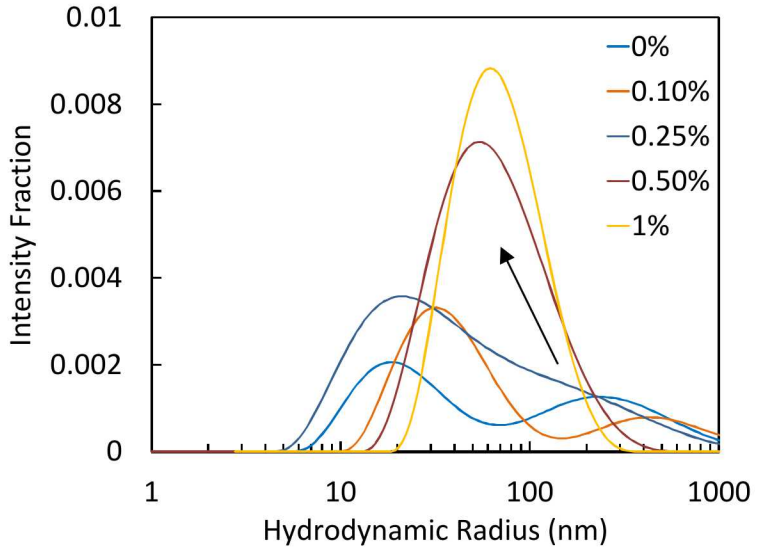
Autocorrelation functions





Size distributions (*via* CONTIN)

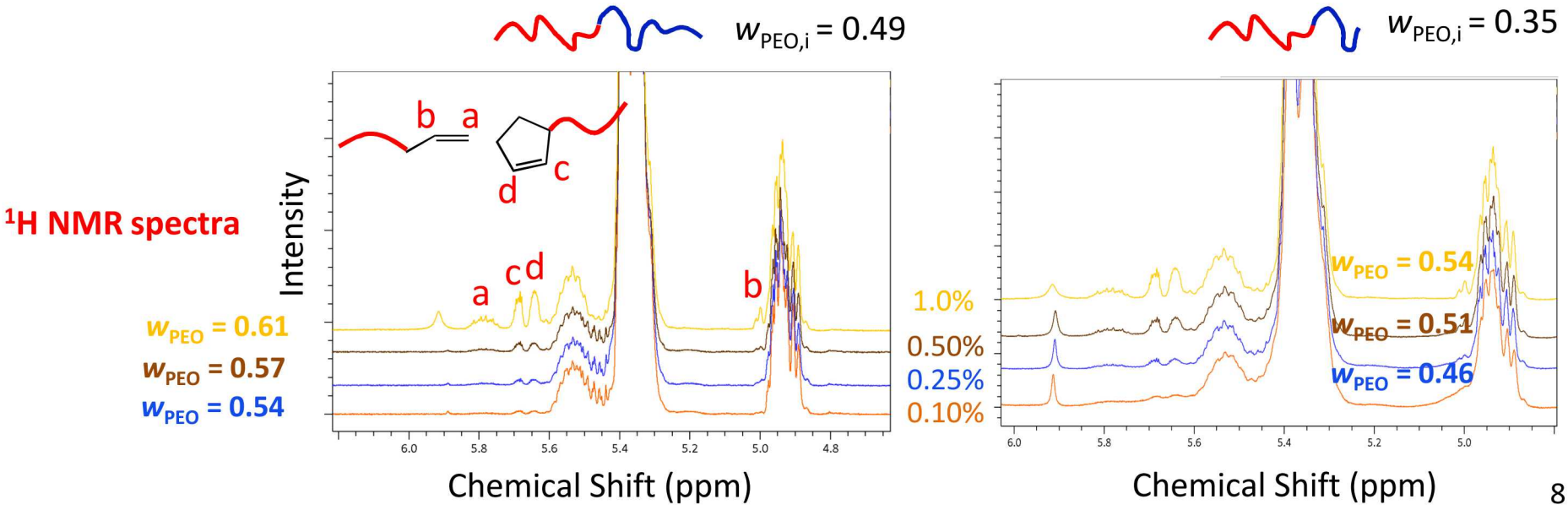




Evidence of Depolymerization

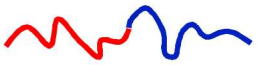
Analysis after freeze-drying indicates depolymerization by ring-closing metathesis

Technique utilized: Nuclear Magnetic Resonance Spectroscopy (NMR)



Morphological Transitions

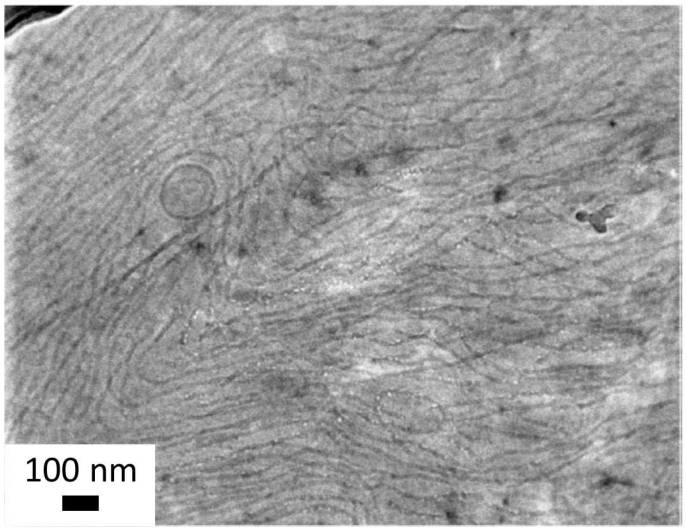
Cryo-TEM/OM suggests cylinder->sphere and vesicle->cylinder at 1% catalyst

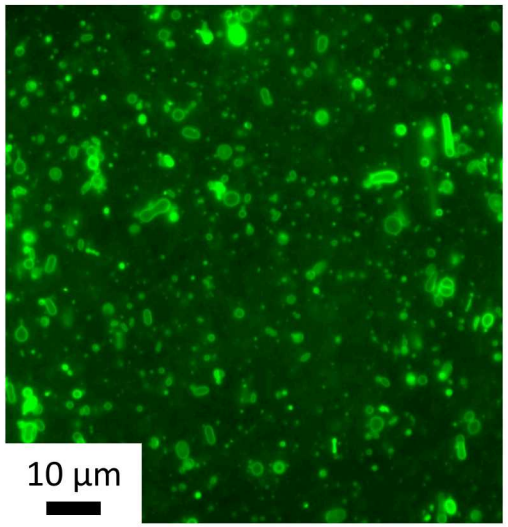


$w_{PEO,i}$ = 0.49

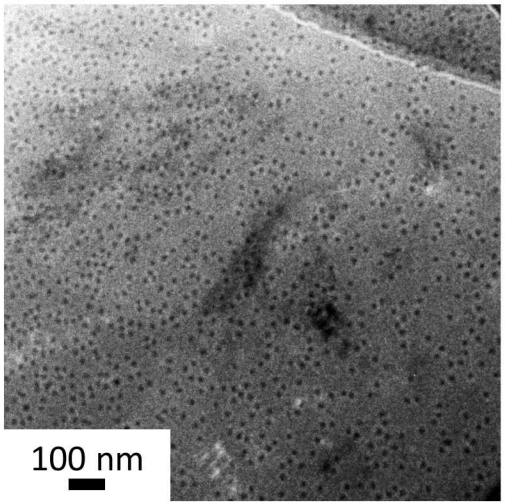
$w_{PEO,i}$ = 0.35

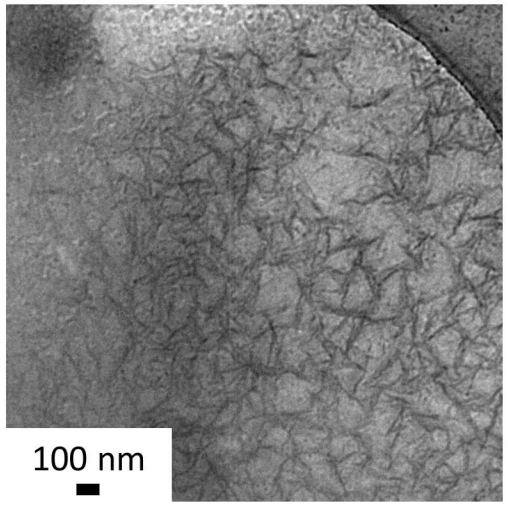
initial





final





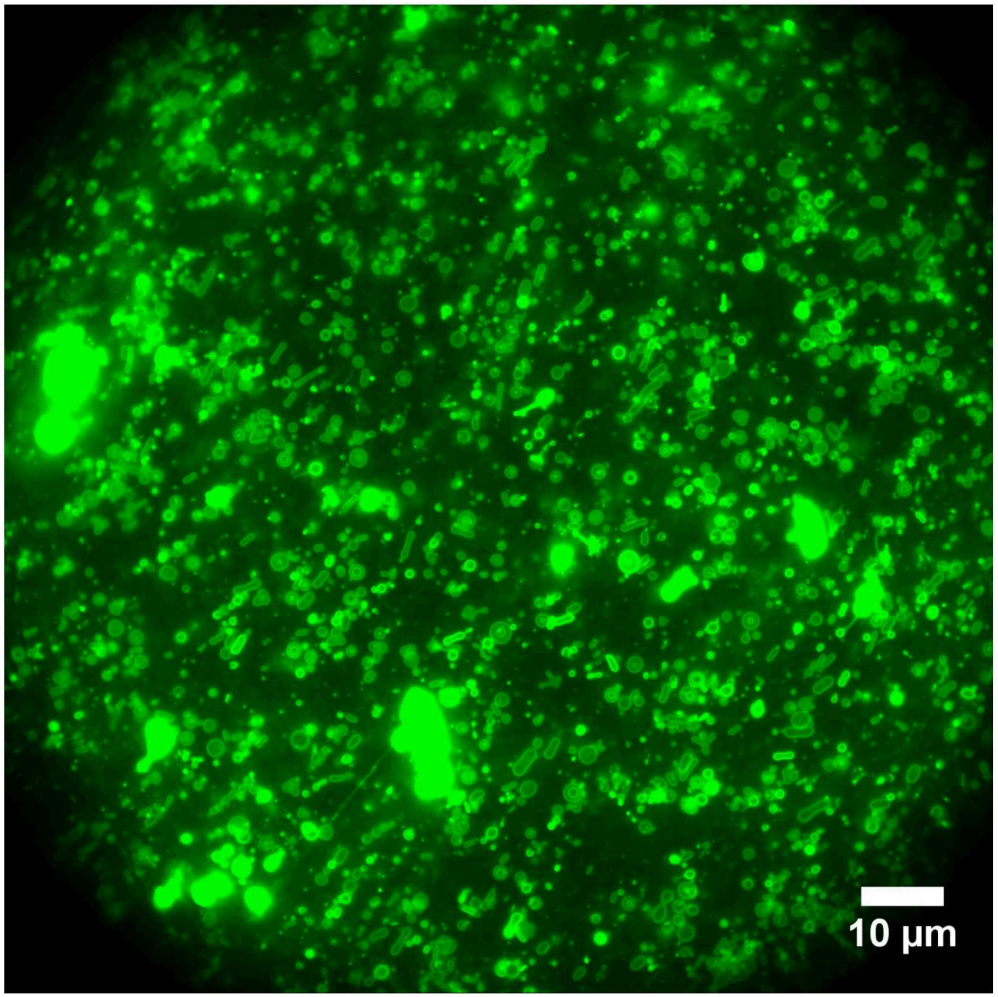
$w_{PEO,f}$ = 0.61

$w_{PEO,f}$ = 0.54

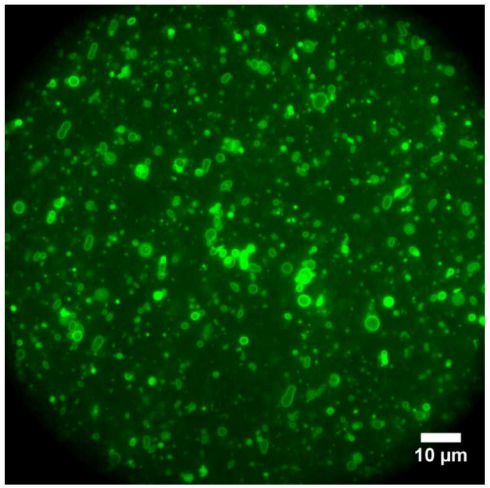
Morphological Transitions

OM time-lapse after injection of catalyst shows reduction in particle size

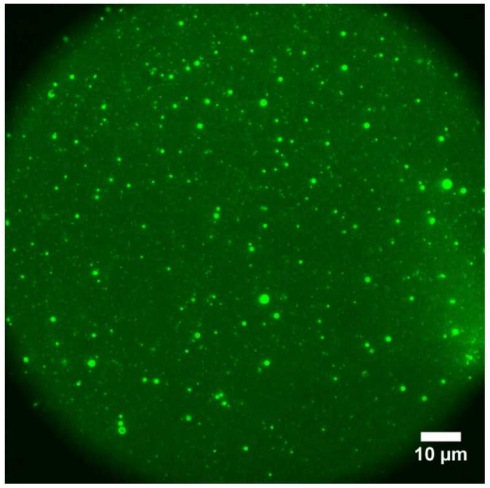
timelapse, each frame is 20 sec



before $w_{PEO,i} = 0.35$



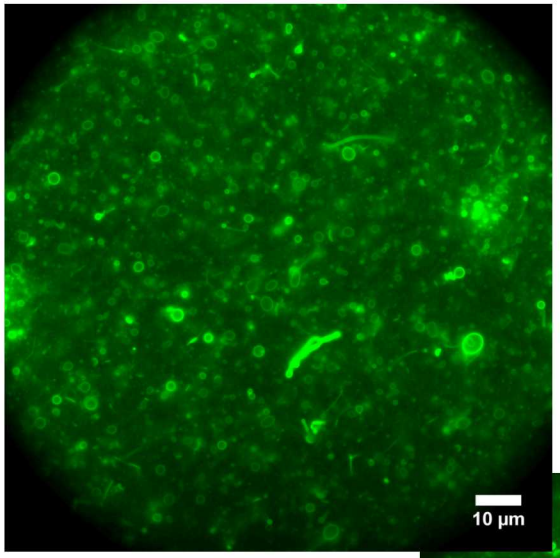
after $w_{PEO,f} = 0.54$



Effect of PB Composition

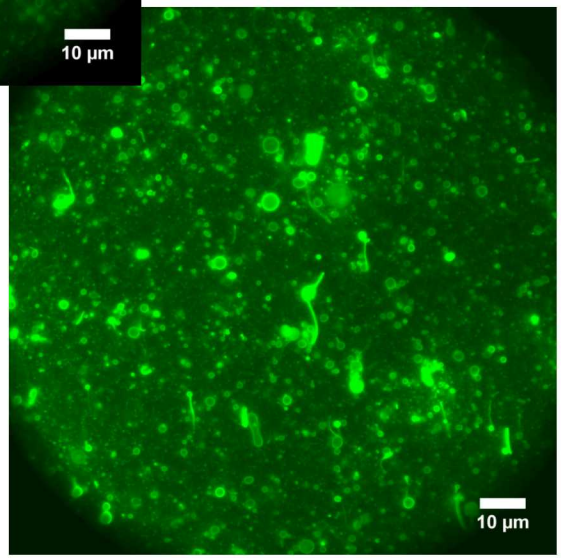
Morphological changes when using predominantly 1,2-PB are negligible

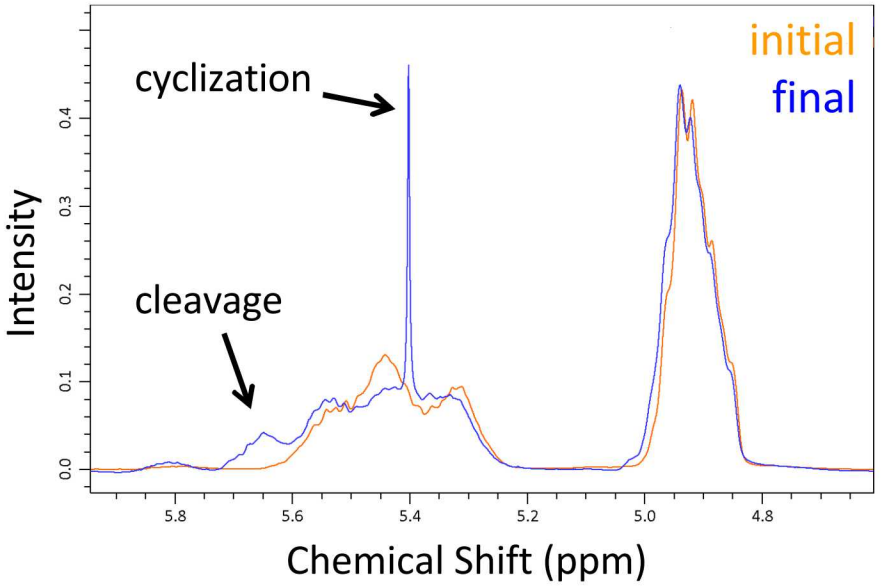
81% 1,2 units → $w_{PEO,i} = 0.34$

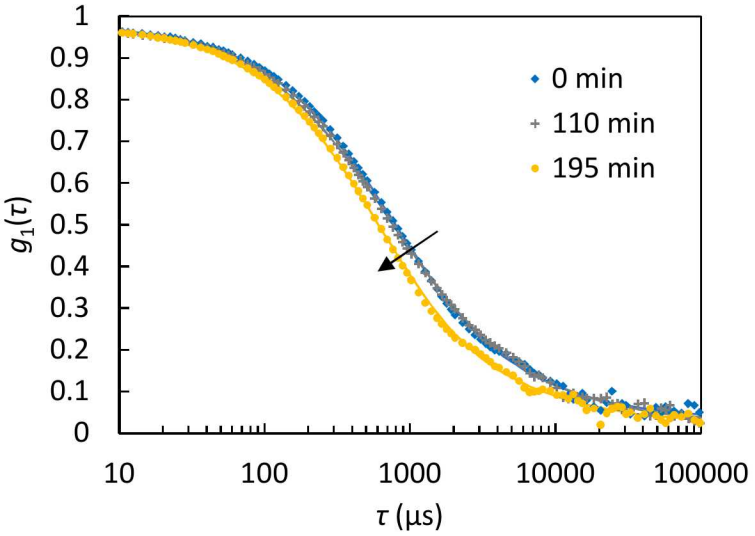


initial

final
(10% catalyst)





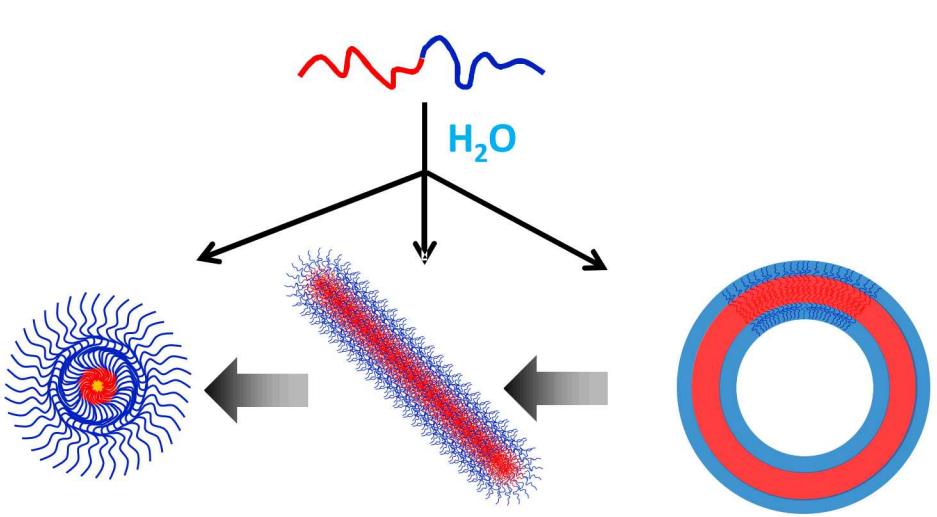


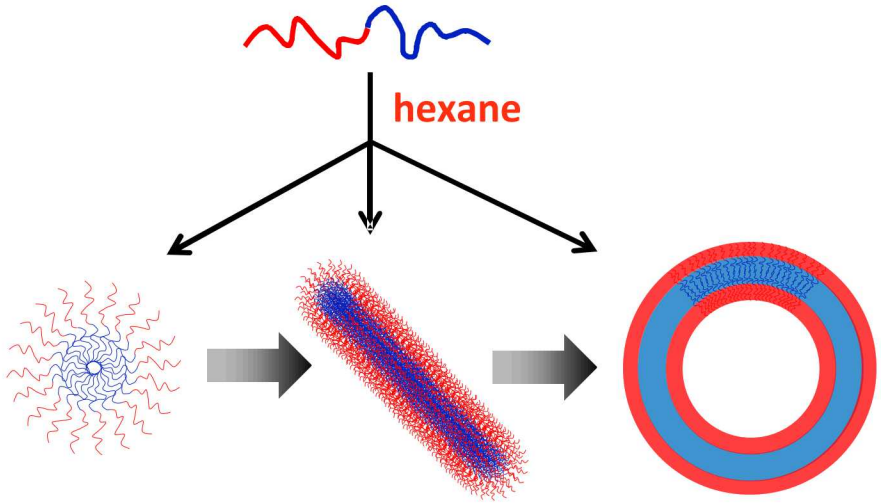
What happens when we change the media in which the polymers are dispersed?

When we change the media from a polar solvent such as water to a non-polar solvent such as hexane:

- The structures that formed in water will be reversed in hexane
  - Vesicle forming polymers in water will be spherical forming in hexane
  - Sphere forming polymers in water will be vesicles in hexane
  - Cylinder forming polymers should stay relatively the same in either media

The way in which these polymers change with addition of GC is also expected to be reversed:

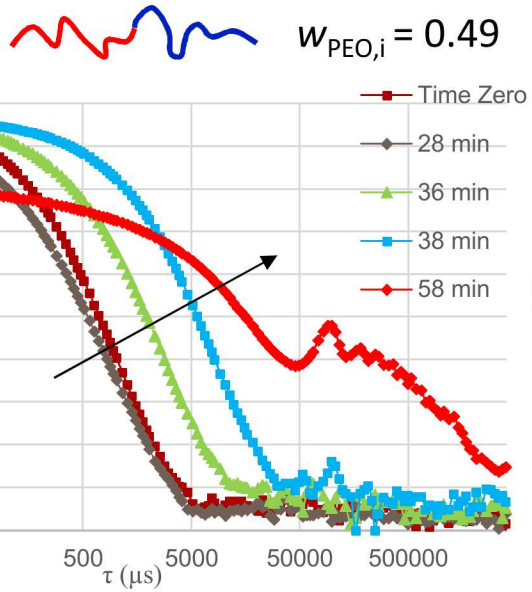


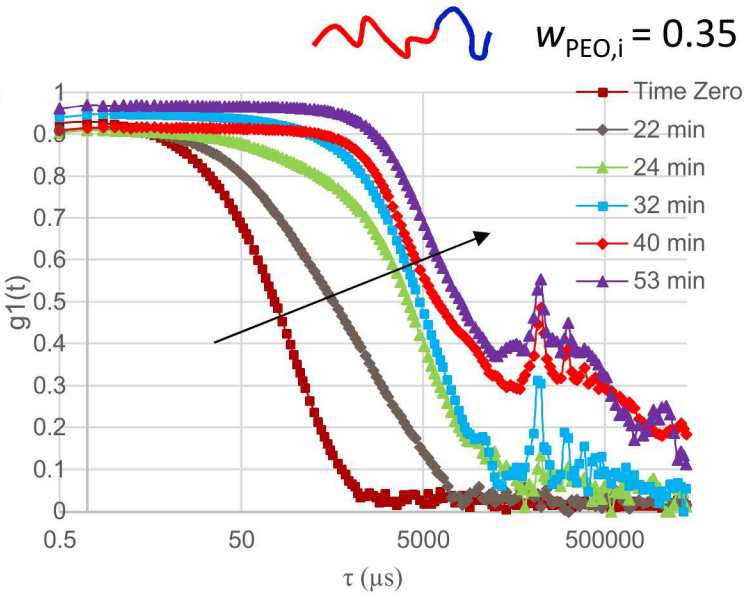


Dynamic Light Scattering (DLS)

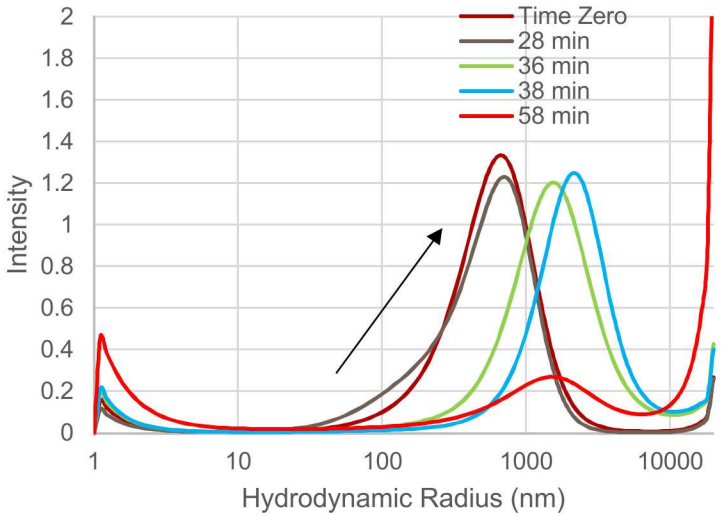
DLS data indicate a rapid increase in hydrodynamic size upon catalyst exposure

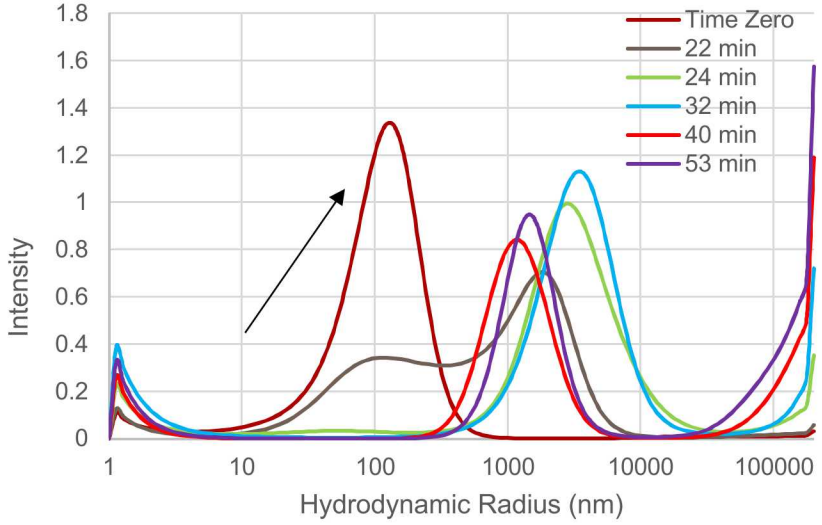
Autocorrelation functions





Size distributions (*via* CONTIN)





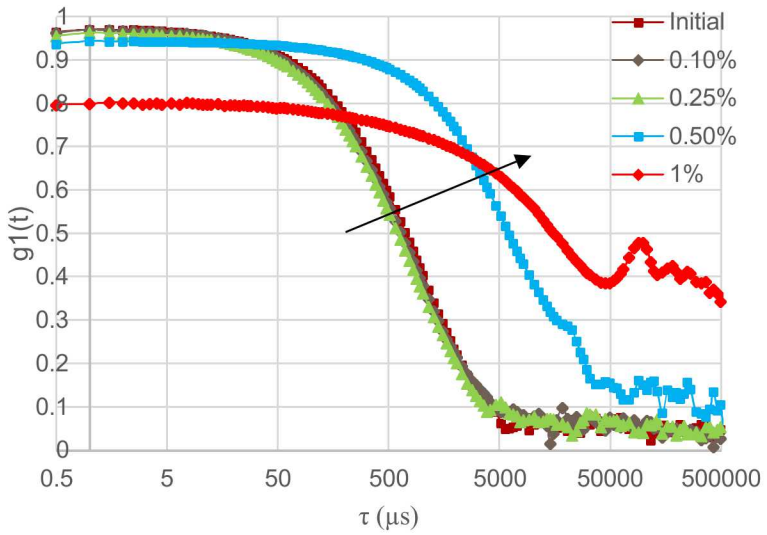
Dynamic Light Scattering (DLS)

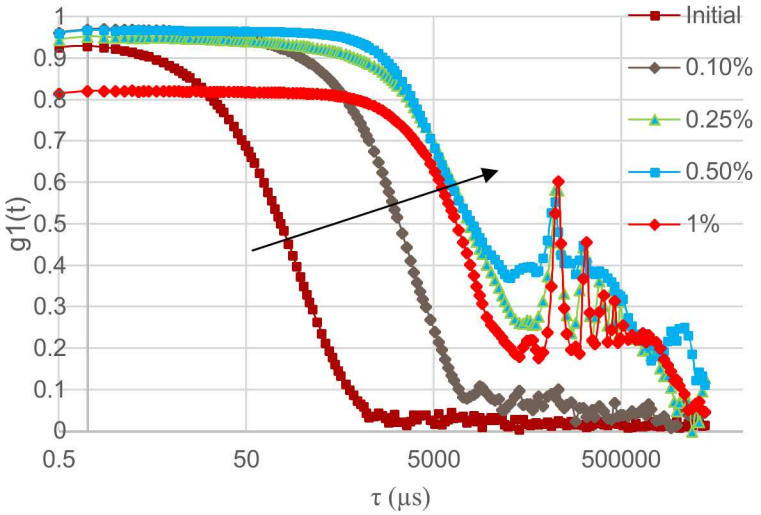
Once again we see that the final hydrodynamic size is dictated by the amount of catalyst added

$w_{PEO,i} = 0.49$

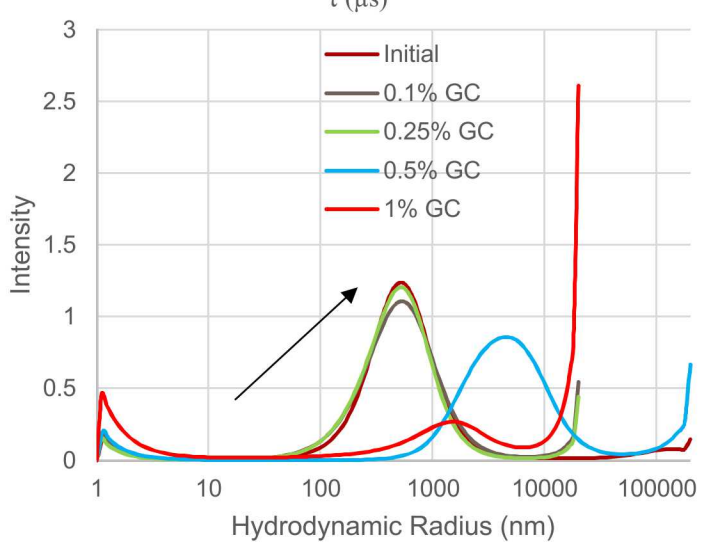
$w_{PEO,i} = 0.35$

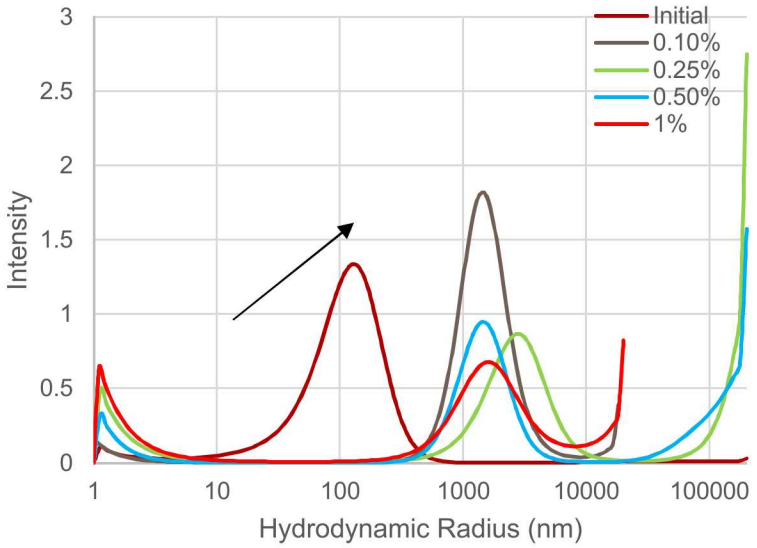
Autocorrelation functions





Size distributions (*via* CONTIN)

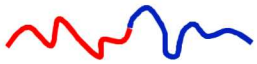




Evidence of Depolymerization

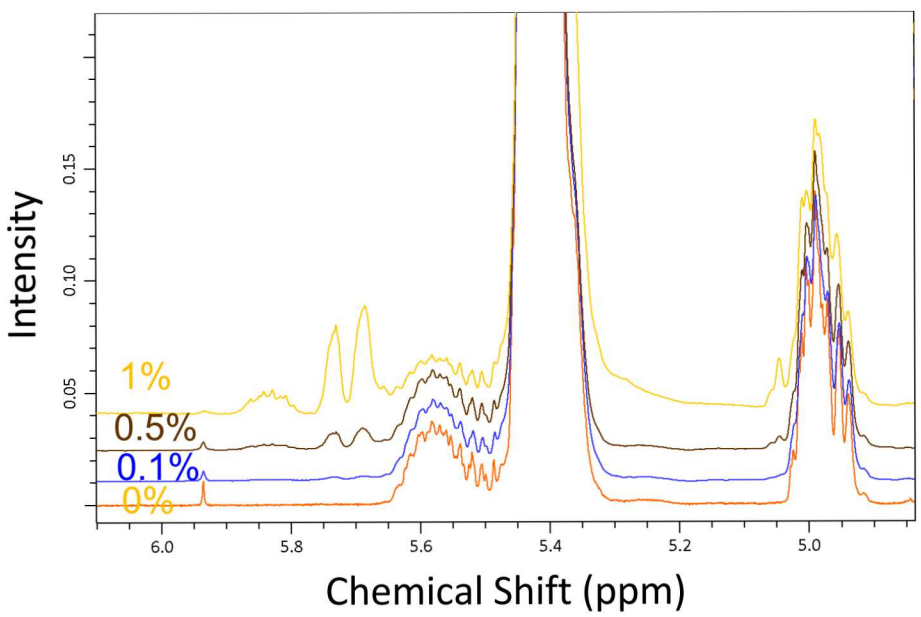
NMR results are consistent with those using water as solvent

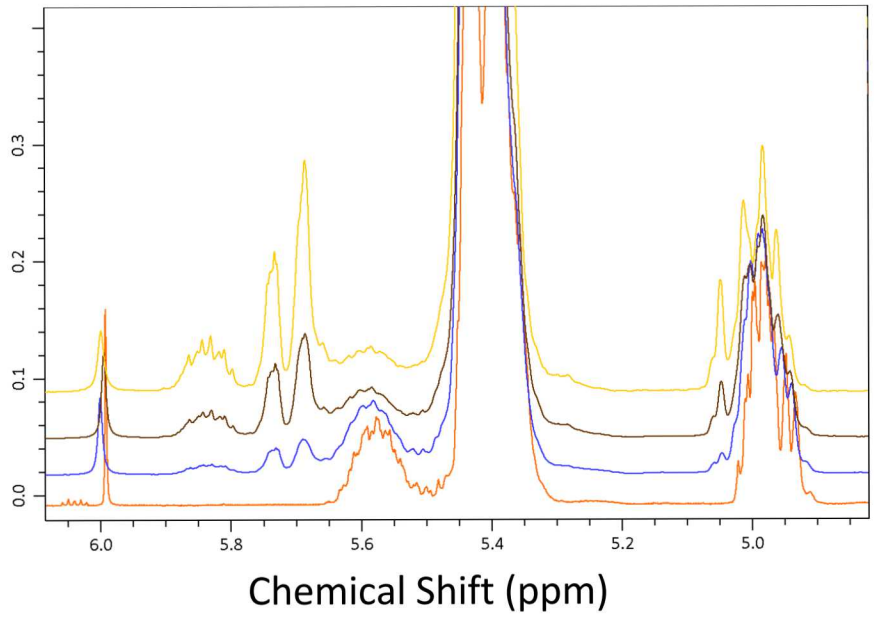
^{1}H NMR spectra



$w_{PEO,i}$ = 0.49

$w_{PEO,i}$ = 0.35





Conclusions

- **Metathesis depolymerization within PB-based micelles leads to rapid changes in morphology**
- **Apparent cylinder->sphere and vesicle->cylinder transitions observed in exemplary cases**
- **Apparent sphere->cylinder and cylinder->vesicle transitions also observed in non-polar media**
- **Catalyst loading and PB composition are key factors in determining final state**

Future Work

- **Attempting to visualize changes in non-polar media with same techniques used for polymers in water (Cryo-TEM/OM)**
- **Conducting these experiments in a glovebox instead of in open air**
- **This project has just begun so there are several more things to do!**

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Questions?