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Sandia National Laboratories
Center 1800: Material, Physical and Chemical Sciences

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

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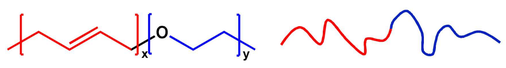
Background

Goal: To harness metathesis to control and manipulate the self-assembly of olefin-containing block polymers on demand



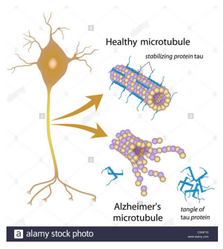
1,4 PB linked with PEO

- These polymers are comprised of Polybutadiene (PB) and Polyethylene Oxide (PEO)

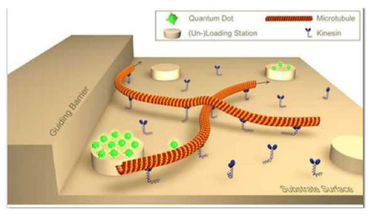
Applications: Biomimicry and Nanotechnology

- Ultimate goal is to create synthetic microtubules

Possible Alzheimer's Disease Treatment



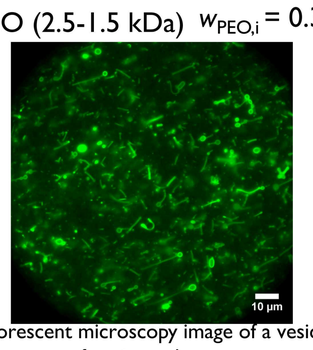
Nano Transport Technology:



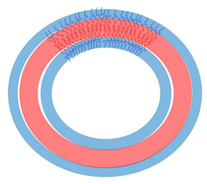
- Several different morphologies will occur when these polymers are dispersed and the form that these aggregates will take depends on the ratio of PB to PEO in the polymer

Vesicles

PB-PEO (2.5-1.5 kDa) $w_{PEO,i}$ = 0.35

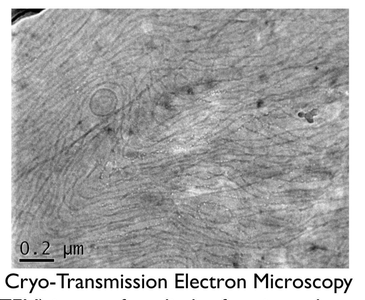


Fluorescent microscopy image of a vesicle forming polymer

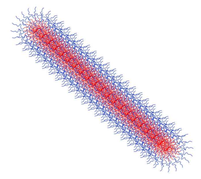


Cylinders

PB-PEO (2.0-2.0 kDa) $w_{PEO,i}$ = 0.49

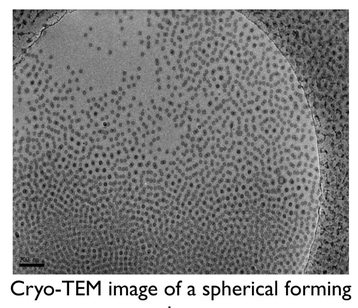


Cryo-Transmission Electron Microscopy (TEM) image of a cylinder forming polymer

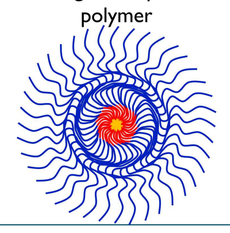


Spheres

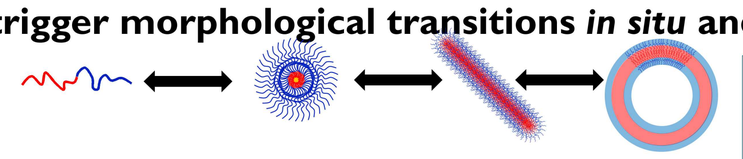
PB-PEO (4.8-5.8 kDa) $W_{PEO,I}$ = 0.55



Cryo-TEM image of a spherical forming polymer



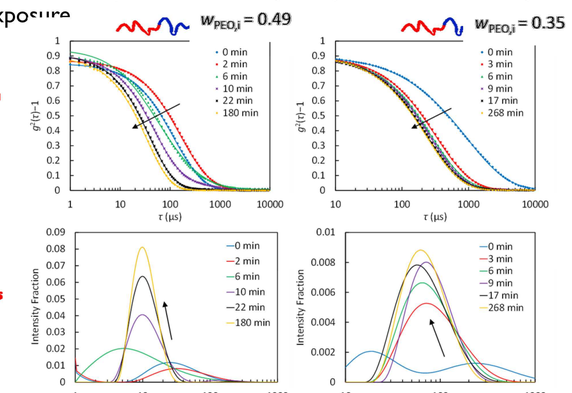
How do we trigger morphological transitions *in situ* and on demand?



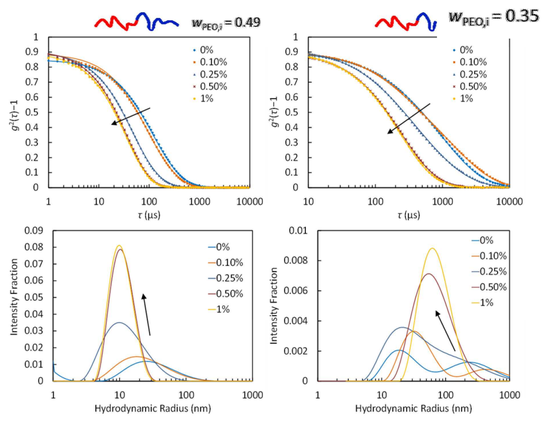
Aqueous Self-Assembly

Dynamic Light Scattering (DLS)

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

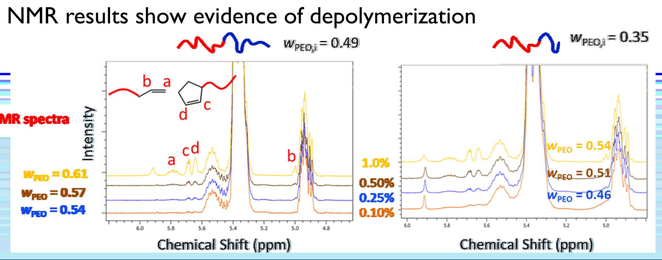


- The final hydrodynamic size is dictated by the amount of catalyst added



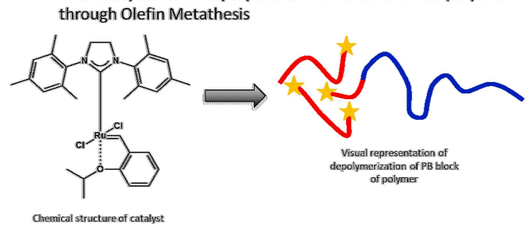
Nuclear Magnetic Resonance Spectroscopy (NMR)

- NMR results show evidence of depolymerization



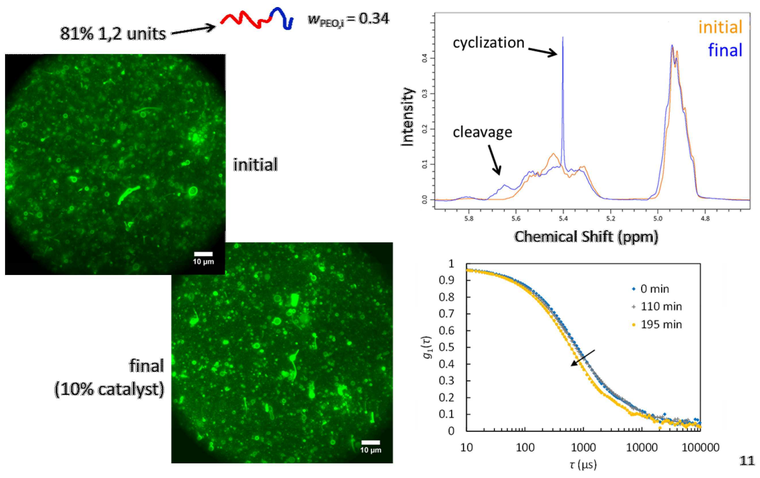
Answer: Introduce a Hoveyda-Grubbs catalyst (GC) to the already assembled aggregates

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



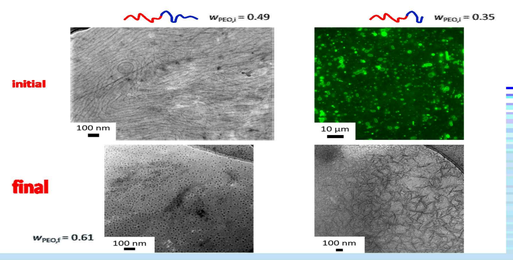
Effect of PB Composition:

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



Morphological Transitions

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



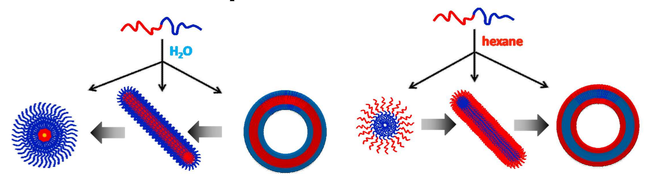
Alkane Self-Assembly

What happens when we change the solvent 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:

- PB and PEO now form the corona and the core of the self-assembled structure, respectively
- As opposed to water dispersed polymers, in hexane as the relative fraction of PEO in the polymer increases the equilibrium structures will favor those of decreasing interfacial curvature

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



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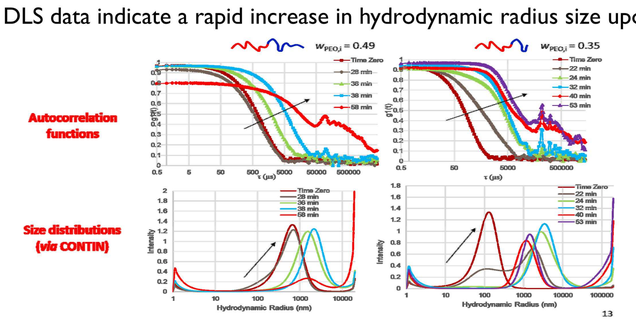
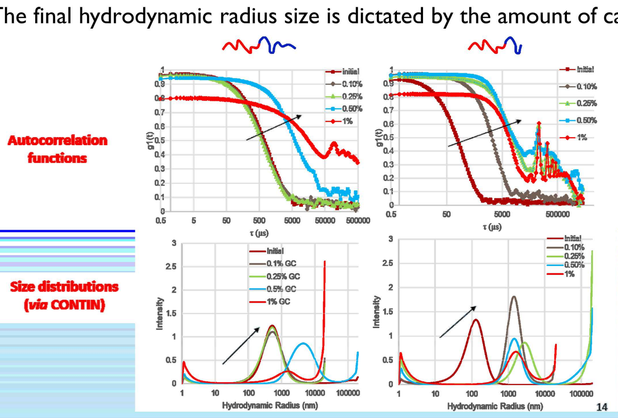
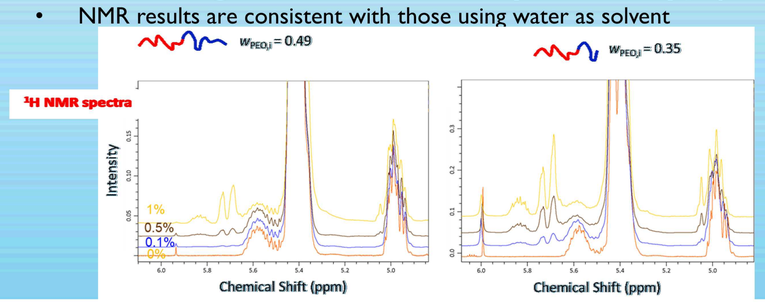


- The final hydrodynamic radius size is dictated by the amount of catalyst added



Nuclear Magnetic Resonance Spectroscopy (NMR)

- NMR results are consistent with those using water as solvent



Conclusions

- Metathesis depolymerization within PB-based micelles leads to rapid changes in morphology
- Apparent cylinder to sphere and vesicle to cylinder transitions observed in water in exemplary cases
- The depolymerization of PB enriches the block polymer in PEO and this enrichment drives the formation of larger structures in alkanes
- Catalyst loading and PB composition are key factors in determining final state

Future Work

- Complete morphological characterization and construct phase diagrams using microscopy and DLS
- Investigate the effect of catalyst stability and activity on morphology and dynamics
- Explore depolymerizable and polymerizable, or otherwise metathesis-active species in this general approach

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National Nuclear Security Administration

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