

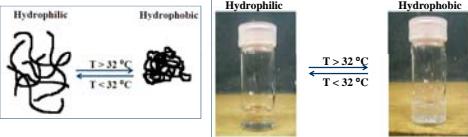
Cyclodextrin Assisted Assembly of Stimuli-Responsive Polymers in Aqueous Media

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Introduction

Temperature-Sensitive Polymers



pH-sensitive polymers

Acidic Groups (-COOH, -SO₃H)

Example: Polyacrylic acid

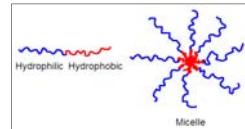
High pH	$\text{COOH} \rightarrow -\text{COO}^- + \text{H}^+$	Hydrophilic
Low pH	$-\text{COO}^- + \text{H}^+ \rightarrow \text{COOH}$	Hydrophobic

Basic Groups (-NH₃⁺)

Example: Chitosan

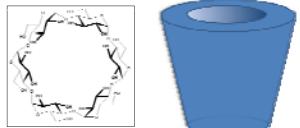
High pH	$-\text{NH}_3^+ \rightarrow -\text{NH}_2 + \text{H}^+$	Hydrophobic
Low pH	$-\text{NH}_2 + \text{H}^+ \rightarrow -\text{NH}_3^+$	Hydrophilic

Macromolecular Self-Assembly

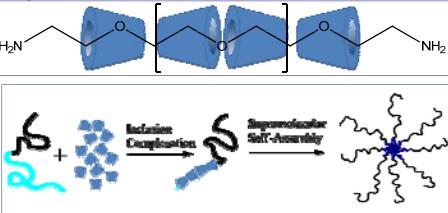


Cyclodextrin

α : 6 units
 β : 7 units
 γ : 8 units



Polymer Inclusion Complexes



References

- Huang, J.; Ren, L.-X.; Zhu, H.; Chen, Y.M. *Macromolecular Chemistry and Physics*. **2006**, *207*, 1764-1772.
 Dimitrov, I.; Trzebiak, B.; Müller, A. H. E.; Dworak, A.; Tsvetanov, C. B. *Progress in Polymer Science*. **2007**, *32*, 1275-1343.
 Liu, J. H.; Sondjai, H. R.; Tam, K. C. *Langmuir*. **2007**, *23*, 5106-5109.

Research Objectives

- Investigate the self-assembly of PEO-b-PNIPAM and PPO-b-PMAA
- Cyclodextrin Complexation
- Temperature Change
- pH Change

Instrumentation

Isothermal Titration Calorimetry



Measures the heat of binding as a titrant is added to a ligand

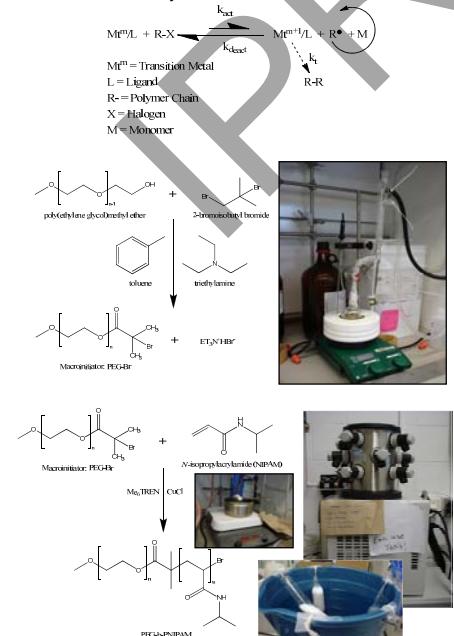
Static/Dynamic Light Scattering



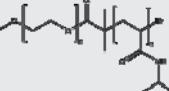
Measures the Hydrodynamic Radius (R_h) and Radius of Gyration (R_g) of particles in the system

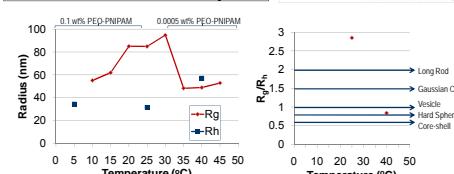
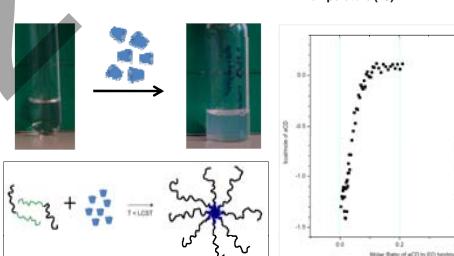
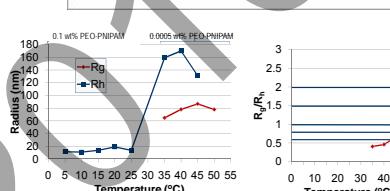
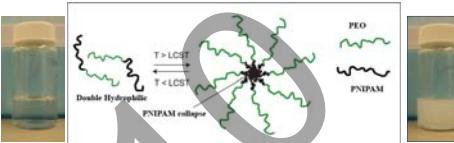
Polymer Synthesis

Atom Transfer Radical Polymerization

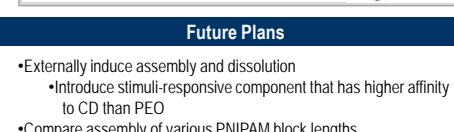
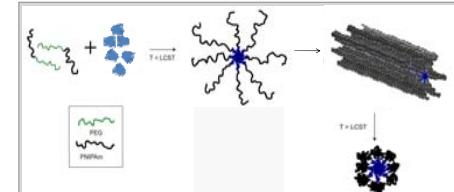


Project 1: PEO-b-PNIPAM (Cont.)

PEO	Complexes with α -CD	
PNIPAM	Temperature-Sensitive LCST $\sim 32^\circ\text{C}$	



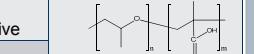
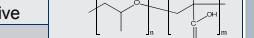
Summary



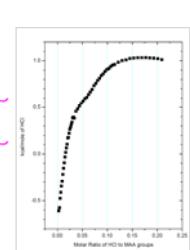
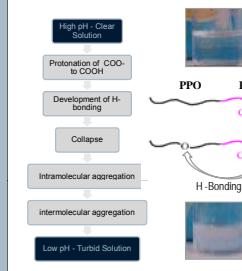
Future Plans

- Externally induce assembly and dissolution
- Introduce stimuli-responsive component that has higher affinity to CD than PEO
- Compare assembly of various PNIPAM block lengths

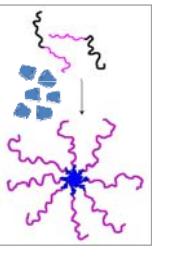
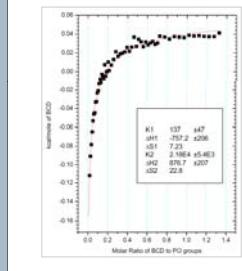
Project 2: PPO-b-PMAA

PPO	Complexes with β -CD	
PMAA	pH-Sensitive	

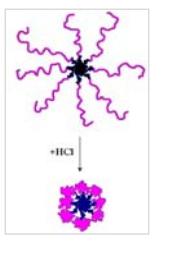
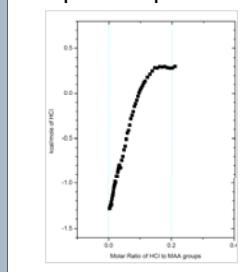
pH-Dependence



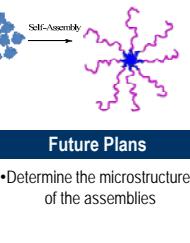
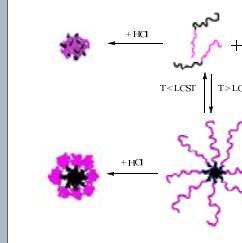
β -Cyclodextrin Dependence



Temperature Dependence



Summary



Future Plans

- Determine the microstructure of the assemblies