

Multicompartment Micelles from Miktoarm Star Block Terpolymers

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Multicompartment Micelles

Vesicle Diblock copolymer

Multicompartment micelle Multiblock copolymer

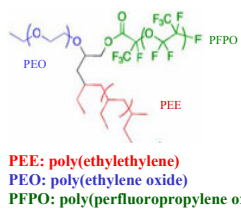
Prokaryotic cell
➢ A single lipid bilayer
➢ Simple, versatile

Eukaryotic cell
➢ Multiple functional units
➢ Complex, large

Laschewsky, A. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 274.

Miktoarm Star Block Terpolymer

Material Design



μ -EOF Multicompartment Micelles in Water

+ H₂O

PEO chain length increase

- Three-fold philicity to oil, super critical CO₂, and water;
- Immiscibility between PEE and PFPO;
- Suppress the formation of core-shell-corona structure.

Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98;
Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2004**, *37*, 8933;
Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Langmuir* **2006**, *22*, 9409.

High-ordered Micellar Structures for Advanced Drug Delivery

Hamburger Micelle from μ -EOF Star Terpolymer

PEE: Pyrene
PFPO: NFH

- Prototype of simultaneous storage of two payloads with prescribed stoichiometric ratio;
- Two types of domains plus two interfaces provide the opportunity of simultaneous double-delivery;
- Independent solubilization efficiencies.

Vesicle from μ -EOF Star Terpolymer

- Controlled distribution of recognition elements on the outer surface;
- Tunable permeation characteristics to multiple encapsulated agents;
- Inclusion of incompatible agents within laterally segregated compartments of the membrane.

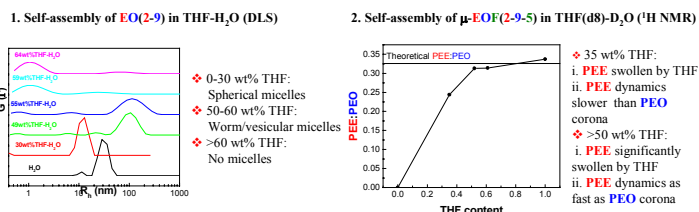
Lodge, T. P.; Rasdal, A.; Li, Z.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 17608;
Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Nano Lett.* **2006**, *6*, 1245.

Project One: Multicompartment Micelles in Solvent Mixture

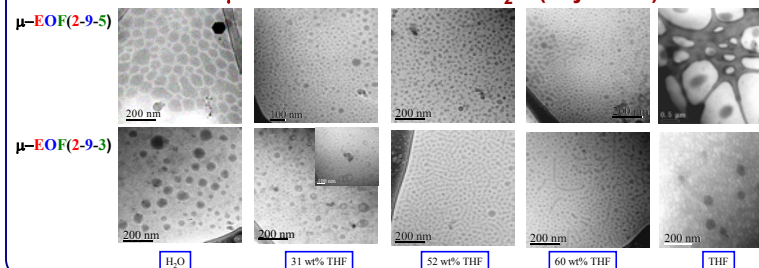
THF selective for PEE and PEO, poor for PFPO

- The transition of PEE block from the core to the corona induces the evolution of multicompartment micelles to mixed corona micelles.
- The transition and the swelling of PEE block change the micelle morphology, e.g., from vesicles to worms.

Multicompartment Micelles to Mixed Corona Micelles



μ -EOF Micelles in THF-H₂O (CryoTEM)



Summary One

- This type of evolution could be useful for sequential drug delivery, as any payload in the PEE block will be released first as it undergoes the transition.

Liu, C.; Hillmyer, M. A.; Lodge, T. P. *Langmuir* **2008**, *24*, 12001.

Synthesis and Characterization of μ -SODA

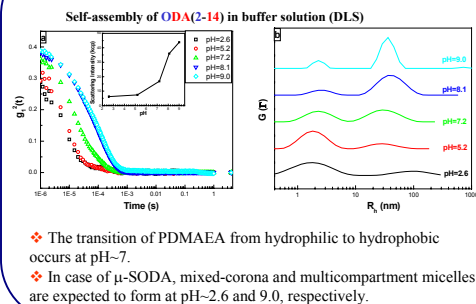
1. Synthetic route: Two living anionic polymerizations + one RAFT polymerization

2. Molecular characterizations:

SEC

¹H NMR

pH-response of PDMAEA Block



Summary Two

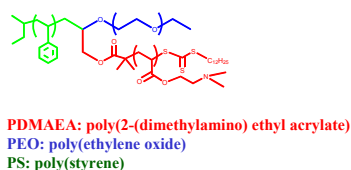
- The introduction of PDMAEA into miktoarm star framework does induce the evolution from multicompartment micelles to mixed corona micelles via pH change.
- It will be of interest to compare the present results with similar pH-responsive linear block terpolymers.

Liu, C.; Hillmyer, M. A.; Lodge, T. P. *Langmuir* **2009**, *25*, DOI: 10.1021/la800845u.

Project Two: pH-response Multicompartment Micelles

It is desirable to achieve the above evolution in a more biocompatible way, e.g., pH or temperature change.

Material Design



- PS: hydrophobic, PEO: hydrophilic;
- PDMAEA: hydrophilic at low pH and hydrophobic at high pH;
- PDMAEA immiscible with PS.

μ -SODA Micelles in Buffer Solutions (CryoTEM)

