Characterization of Poly(D-glucose carbonate) Block Copolymer Assemblies with cryoTEM, SANS, and CREASE

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Abstract
We characterize the solution assembly behavior of hydrophobic, semiflexible glucose based poly(D-glucose carbonate) (PGC) -based polymers. First, the fibril formation of PGC-based amphiphilic diblock copolymers (BCPs) using solvent mixtures shows a different assembly behavior compared to micelles constructed from coil-coil BCPS due to the significant stiffness and hydrophobicity of the PGC backbone chemistry. A THF/H2O solvent mixture was used to create a solvent quality gradient during which a hierarchical assembly pathway was observed with fibril precursor nanoparticles that linked together into fibrils. Second, the analysis of the same PGC BCP molecules assembled in 100 % H2O forming spherical aggregates, also showed the uniqueness of PGC chain packing in the nanostructure where the hydrophobic block of BCP is hypothesized to behave as a stiff, phase segregated amphiphilic polyelectrolyte due to the backbone chemistry. A separate investigation into the ionic PGC block equivalent homopolymers confirms uniform the particle formation in solution showing amphiphilic polyelectrolyte characters. Transmission electron microscopy, interpretation of the small-angle neutron scattering measurements fit with analytical models as well as genetic algorithm-based reverse engineering of structure confirmed these results. The results suggest that unconventional backbone chemistry-based molecules reveal unique effects of chain stiffness and hydrophobicity on block copolymer solution assembly when using glucose-based polycarbonates.

Chemistry/Methods

Glucose-based poly(D-glucose carbonate): Solution Assembly Behavior

1. PGC BCP
Spherical Aggregate Formation in H2O

2. PGC BCP
Hierarchical Assembly in Mixed THF/H2O

3. PGC Homopolymer
Aggregate Formation in H2O

2.1 Low water volume (40 v/v %)

2.2 High water volume (80 v/v %)

4. Structural Analysis using Scattering

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