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

Jee Young Lee, Daniel J. Beltran, Arthi Jayaraman, and Darrin J. Pochan

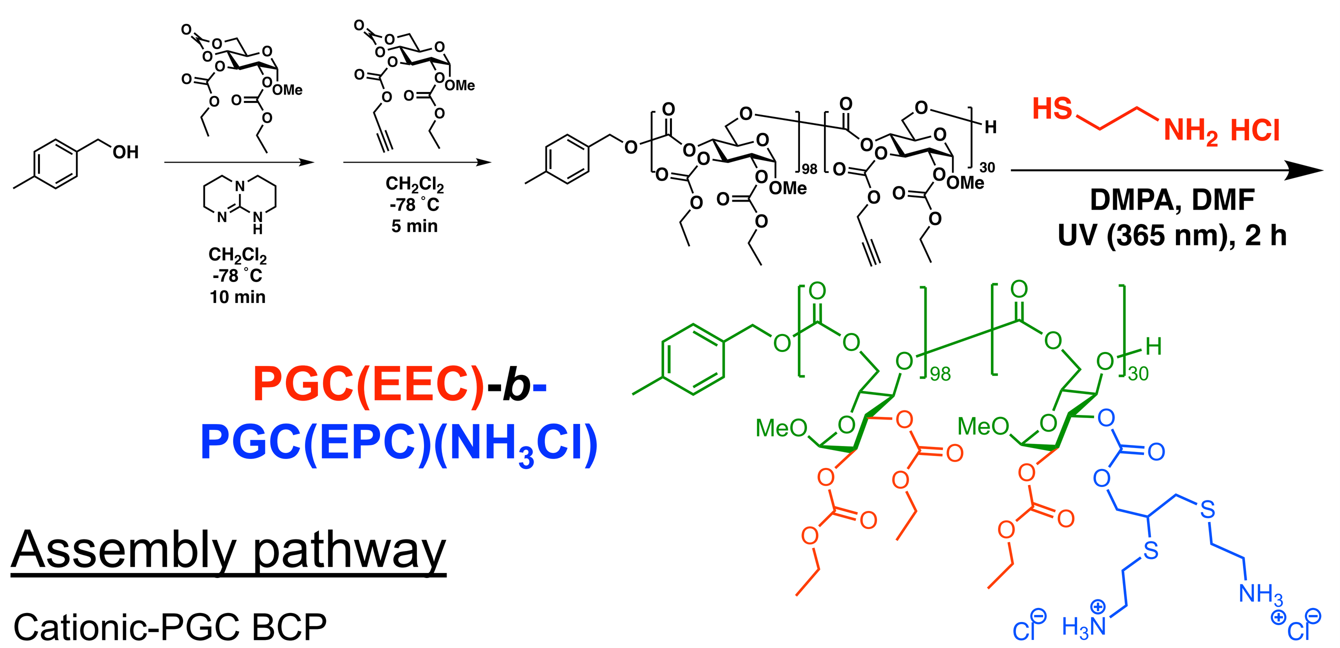
Department of Materials Science & Engineering and Chemical and Biomolecular Engineering

University of Delaware, Newark DE 19716

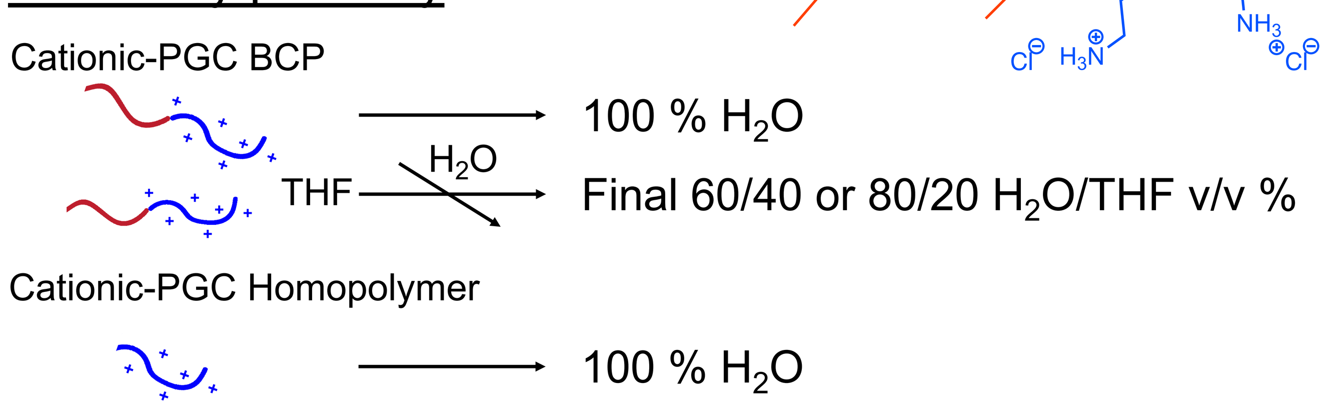
Abstract

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/H_2O 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 % H_2O forming spherical aggregates, also showed the uniqueness of PGC chain packing in the nanostructure where the ionic hydrophilic 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



Assembly pathway

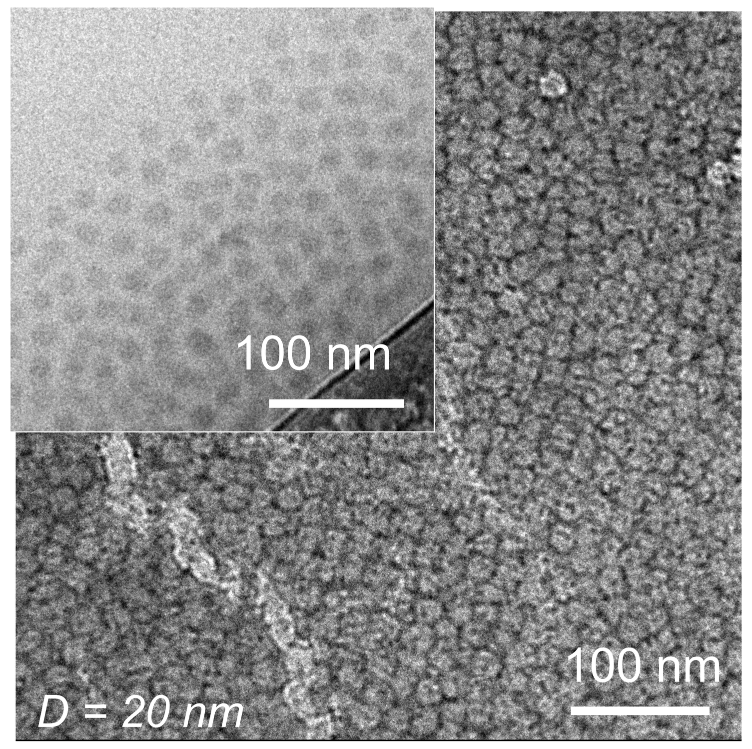


Acknowledgement

- This work is based upon work supported by the National Science Foundation under grant - DMREF 1629156, DMREF-1629094
- We acknowledge the Keck Center for Advanced Microscopy and Microanalysis.

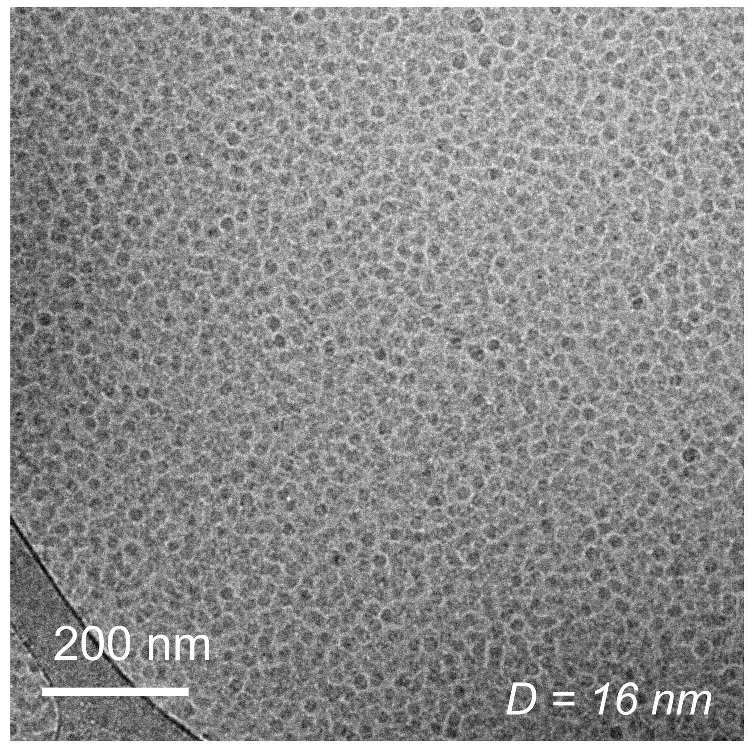
Glucose-based poly(D-glucose carbonate): Solution Assembly Behavior

1. PGC BCP Spherical Aggregate Formation in H_2O



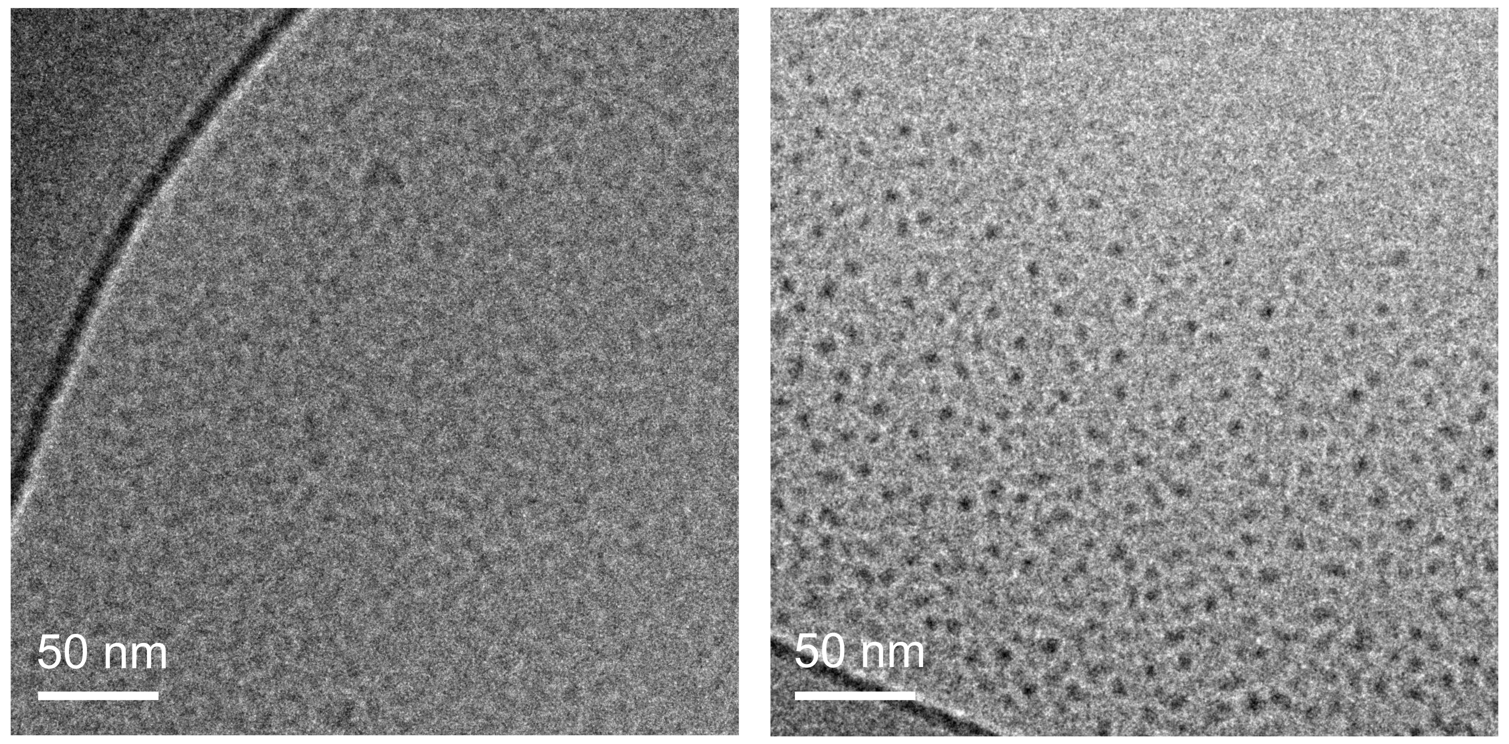
TEM images of 0.1 wt % cationic-modified PGC BCP show spherical aggregates in water. Inset: Cryo-TEM

2. PGC BCP Hierarchical Assembly in Mixed THF/H_2O



Cryo-TEM image of cationic-modified PGC BCP inverse aggregates in 100 % THF.:

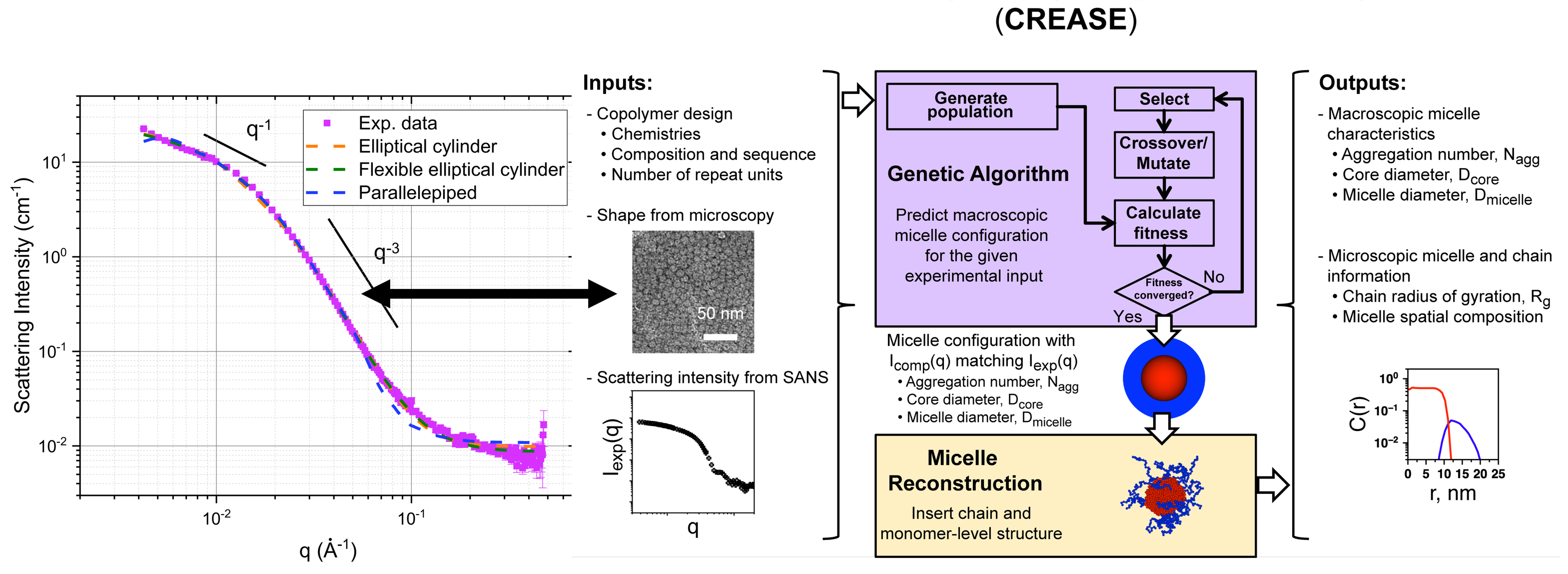
3. PGC Homopolymer Aggregate Formation in H_2O



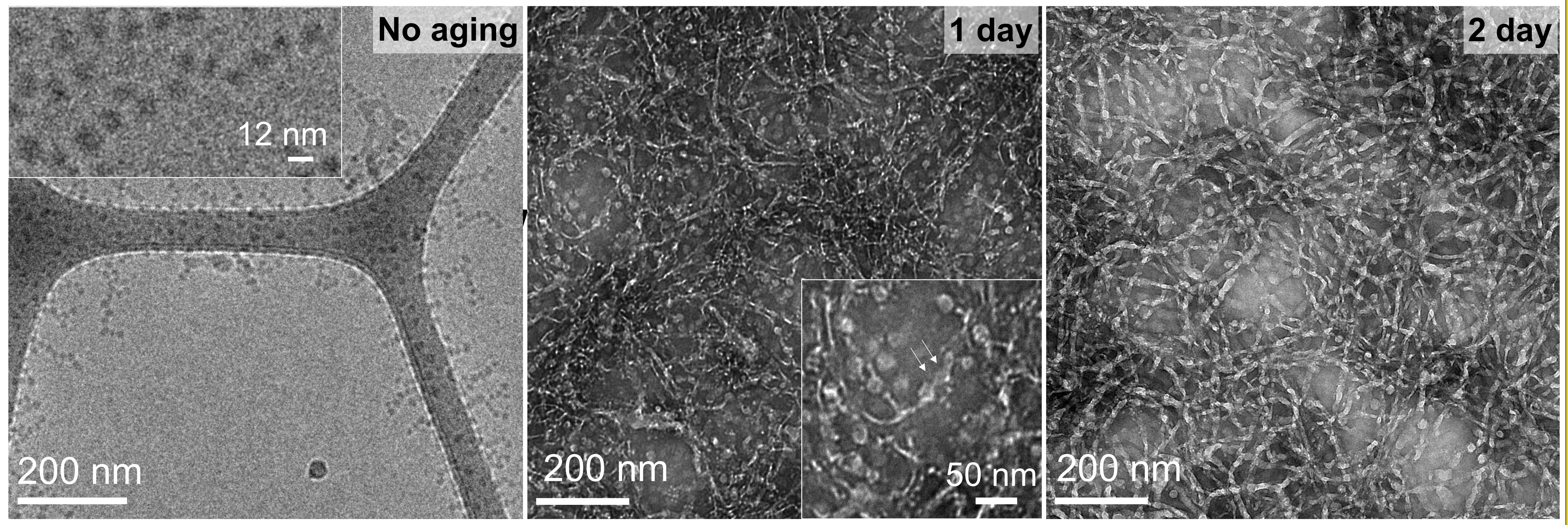
Cryo-TEM image (left) of cationic-modified PGC homopolymers in 100 % H_2O shows the aggregate formation in H_2O. Positive staining cryo-TEM (right) is provided to show better contrast. Ammonium Molybdate (16 wt %, pH adjusted) was used the positive staining.

4. Structural Analysis using Scattering

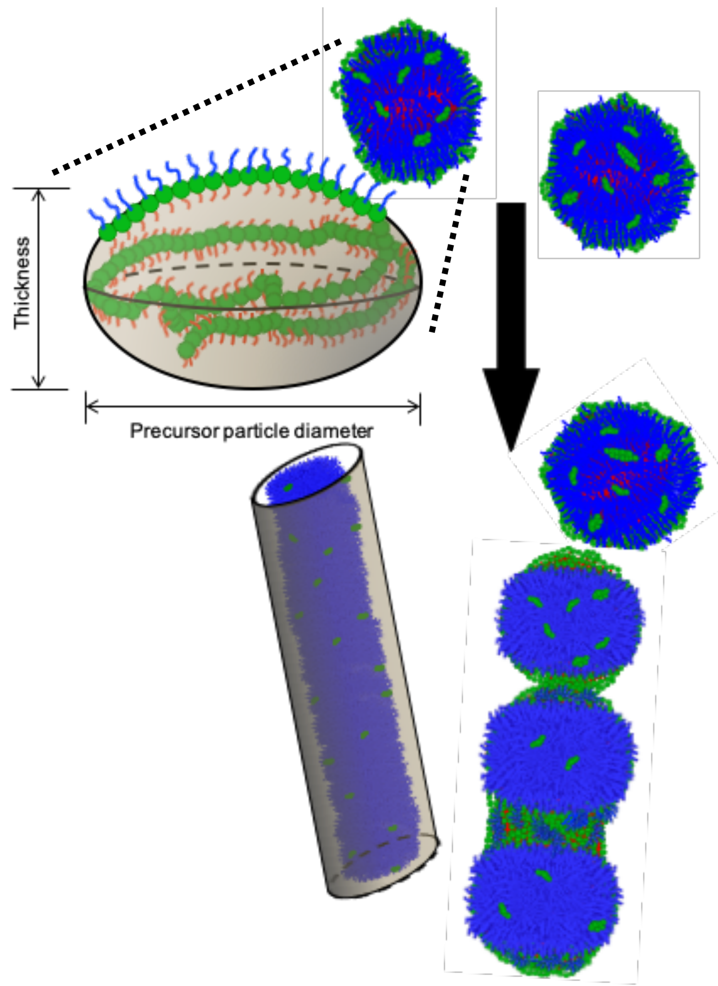
Computational Reverse-Engineering Analysis for Scattering Experiments (CREASE)

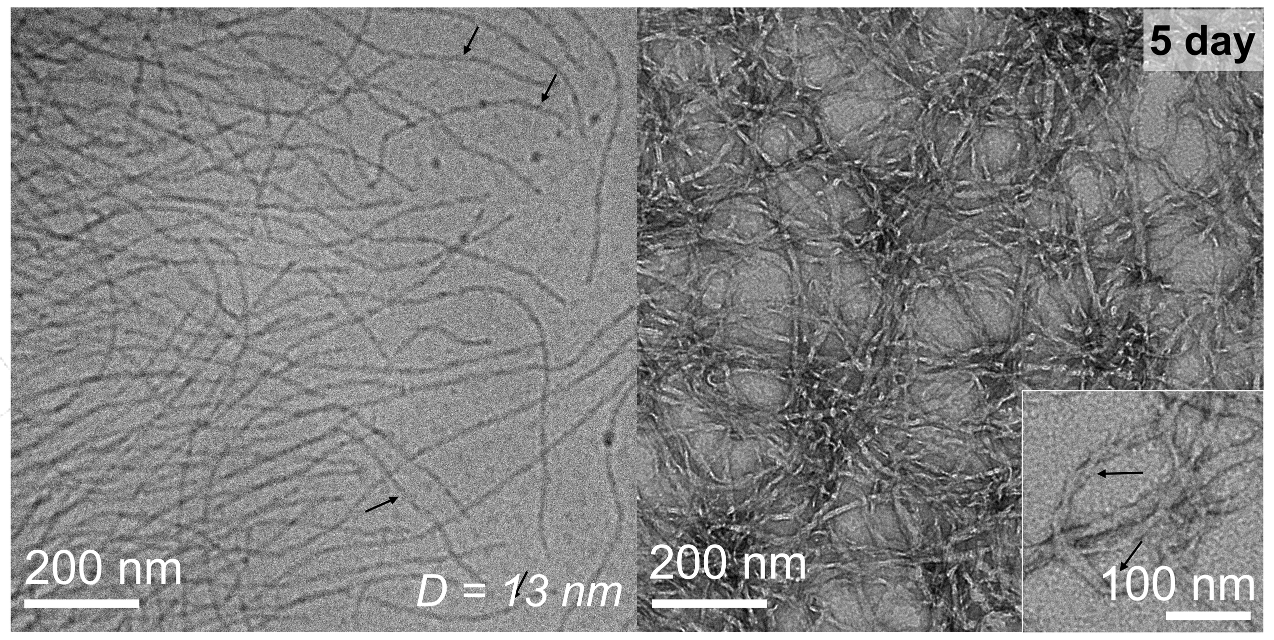


2.1 Low water volume (40 v/v %)



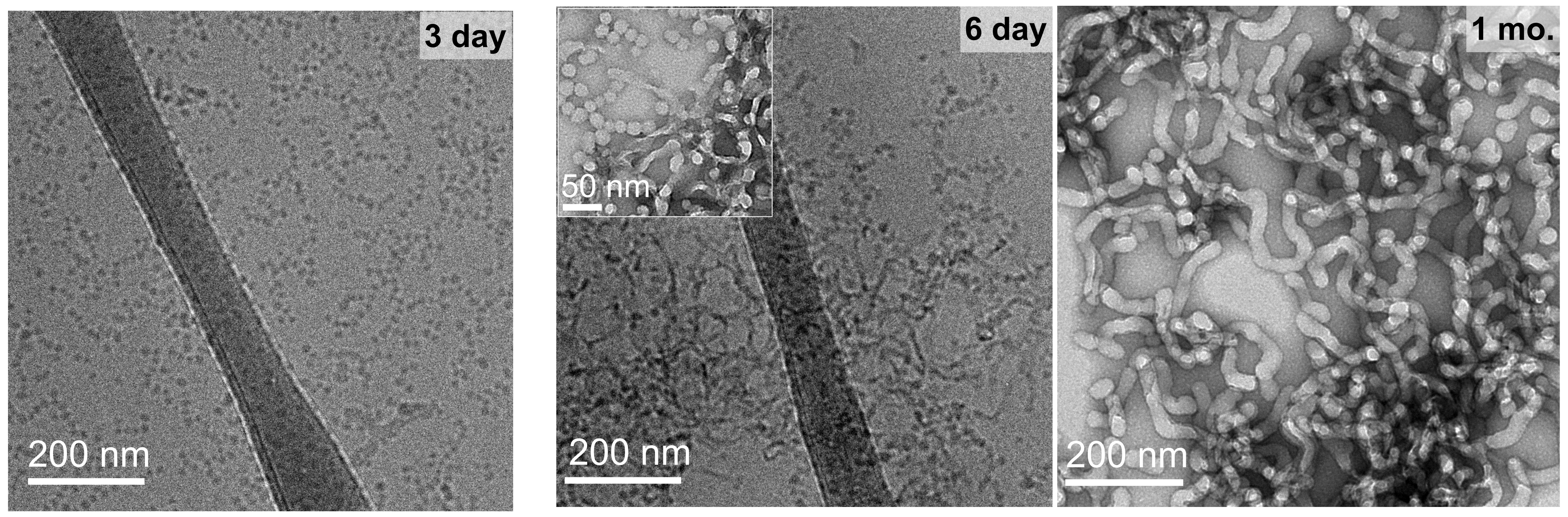
Cryo-TEM image of early assembly stage (no aging) is shown on the far left where individual precursors of 10-14 nm diameters are formed. With 1 day of aging, a regular TEM image of the intermediate stage shows mixed precursors and loosely formed fibril structures with irregular surfaces. The inset in shows a high magnification image of an early stage fibril with troughs showing fusion-like growth. With longer aging, the precursors disappear and more mature regular fibrils form (2 day). All regular TEM images are negatively stained for better contrast.





Cryogenic-TEM image (left) shows mature fibril structures with arrows showing twist regions with different density contrast along the fibril. A negatively stained TEM image (right) is provided to show more detailed characteristics such as folds and twists (inset) that are hard to observe from cryo-TEM due to a low contrast from solvent swollen nanostructures.

2.2 High water volume (80 v/v %)



Cryo-TEM image of early assembly stage (3 day aging) is shown on the far left where individual precursors of 10-14 nm diameters are formed. With 6 days of aging, a cryo-TEM image of the intermediate stage shows mixed precursors and loosely formed fibril network structures. 1 month of aging leads to fully mature networksAll regular TEM images are negatively stained for better contrast.

1. D. J. Beltran-Villegas, M. G. Wessels, J. Y. Lee, Y. Song, K. L. Wooley, D. J. Pochan, A. Jayaraman. Computational Reverse-Engineering Analysis for Scattering Experiments on Amphiphilic Block Polymer Solutions. *J. of Am. Chem. Soc.* **2019** *141* (37) 14916-14930
2. J. Y. Lee, Y. Song, M. G. Wessels, A. Jayaraman, K. L. Wooley, D. J. Pochan. Hierarchical Self-assembly of Amphiphilic poly(D-glucose carbonate) Block Copolymers in Solution. *Submitted*

August 3rd 2020