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Structural Transformation and Morphology of Dipeptide Supramolecular Assemblies by Liquid-phase TEM

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The development of supramolecular chemistry provides an excellent framework for the design and fabrication of advanced materials from molecular assemblies. The supramolecular materials emerge through the self-assembly of monomeric building blocks, bound together in organized structures by non-covalent interactions. The ability to observe the dynamics and organization of these building blocks in liquids at the nanoscale is vital to our understanding of material formation in solution phase. Liquid-cell electron microscopy (LCTEM) has shown potential to analyze these materials in liquids with unprecedented spatial and temporal resolution. LCTEM imaging of these materials is challenging because they are largely comprised of low-atomic number elements that produce little contrast and are sensitive towards electron beam induced radiation damage. Here we report the first observation of nucleation, self-assembly, and structural transformation of dipeptide supramolecular assemblies by LCTEM.

The diphenylalanine structural motif and its derivatives are among the most widely studied peptide building blocks that allow the formation of ordered polymer-like assemblies at the nanoscale. These class of molecular species also exhibits polymorphism that is influenced by solution conditions such as pH, temperature, solvent composition and concentration. We tuned the reaction condition by flow-in reactant monomers into 2 separate inlets of the holder and made to mix immediately prior to the SiN_x window allowing the beginning of the reaction to be captured. We captured the self-assembly by recording static images of 1 min pulse to limit electron beam exposure for extended time scales. Such stroboscopic imaging reveals the formation of micelles by rapid condensation immediately when the reactants mix. Further flow of reactants leads to the formation of fiber-like morphologies. During this dynamic process, the coalescence of micelles was not observed suggesting fiber-like assemblies were formed by Ostwald ripening process, where the thermodynamic stability of fibrillar phase is greater than micellular phase.

We demonstrate for the first time that dynamics and self-assembly of highly beam sensitive low contrast materials like peptides can be imaged and recorded in solvated phase before the beam induced artifacts and damage occurs. This study also reveals that LCTEM can be applied to study the self-assembly of wide range beam-sensitive soft materials and biological materials.

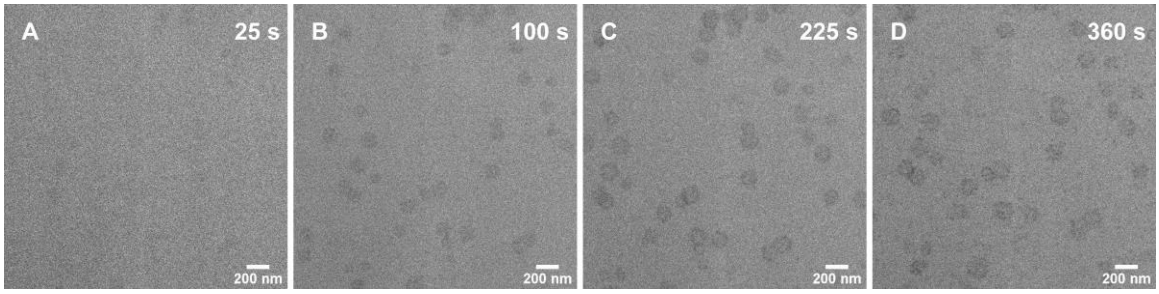

Figure 1. LCTEM snapshots of formation of dipeptide supramolecular assemblies.

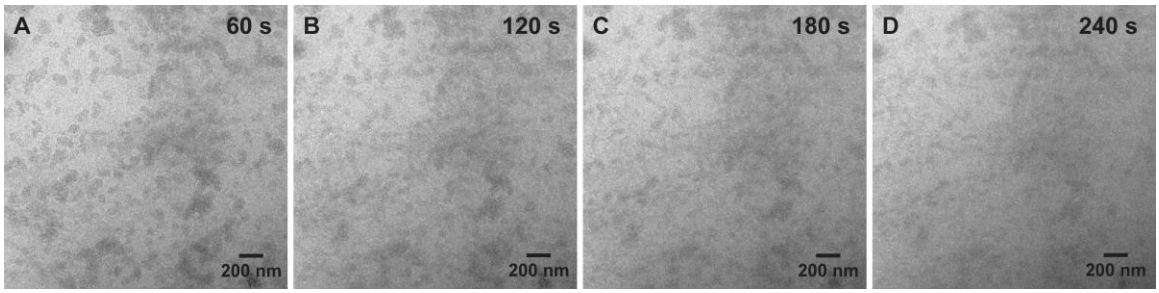

Figure 2. LCTEM snapshots of transformation of initially formed micellular phase to fibrillar phase.

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