DREXEL UNIVERSITY
Materials Science and Engineering
College of Engineering

PhD Thesis Defense

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Zoom link: https://drexel.zoom.us/j/83561599496

Structure and Properties of Advanced Polymeric Particles Templated by Miniemulsion Crystallization

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In this thesis, advanced polymeric micro/nanoparticles are fabricated utilizing a recently developed miniemulsion crystallization system in which polymer crystallization is carefully controlled in emulsion droplets to produce spherical, hollow single crystal-like polymer capsules termed "crystalsomes." This work is broken into two parts where the first focuses upon developing multicomponent/multicompartment crystalsomes by utilizing polymer blending or incorporation of inorganic nanoparticles at the curved droplet interface of the miniemulsion. The second focus is an analysis of various crystalsomes structure and properties as a function of curvature.

Within part one of this work, two new multicomponent crystalsome systems are fabricated. First, a polymer blend of two amphiphilic block co-polymers is utilized, where they serve as macromolecular surfactants to stabilize the emulsion. The hydrophilic blocks are identical, and the hydrophobic segment is amorphous for one polymer and crystalline for the other. The phase behavior between the hydrophobic blocks is controlled to produce a multicompartment crystalsome that can subsequently serve as a precursor to a porous, crystalline polymer capsule. Second, a multicomponent crystalsome is fabricated where Iron oxide (FeNP) nanoparticles are incorporated at the interface of the emulsion. The FeNPs produce a Pickering emulsion by pinning to the interface and forming a colloidosome structure. Subsequently, poly (l-lactic acid) (PLLA) homopolymer is crystallized at the colloidosome interface. It is shown that the introduction of FeNPs has a significant influence on crystalsome morphology. Curvature dictated crystal growth and the location of FeNPs within the structure is explored.

In part two of this work, two crystalsome properties are studied as a function of curvature. First, the PLLA homopolymer is utilized as a model system to study thermal behavior differences between the generally observed 2D planar PLLA single crystals and the 3D curved PLLA crystalsomes. A combination of Differential Scanning Calorimetry and *in situ* heating Wide-angle X-ray diffraction identify new melting phenomena in the crystalsomes that is attributed to the edgeless and self-confined nature of the crystal. Second, the optical properties of the newly developed semi-conducting poly (3-hexylthiophene) (P3HT) crystalsome are studied as a function of curvature. Electron microscopy, diffraction and thermal analysis confirm the formation of P3HT crystalsomes and a new 1D crystal growth behavior in nano-confined curved space is observed. The UV-Vis absorption behavior proves to be a sensitive probe of the crystalline order within the 3D crystals.