Ph.D. DISSERTATION DEFENSE

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Degree: Doctor of Philosophy
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Title: Electron-Beam Patterning Shape-Shifting Gel-based Micro-Helices and Micro-Ribbons

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ABSTRACT

Patterning surfaces with desirable structures and multifunctionalities and at nano- and micro-length scales is essential for engineering functional materials. This research explores advanced applications of electron-beam lithography (EBL), specifically focusing on two distinct aspects: the design of surface-tethered shape-morphing microgels and surface pattering with orthogonal functionalities. EBL offers high-resolution, mask-free patterning at nano-length scales by exposing polymeric precursors to energetic radiation. Firstly, diverse incident electron energies are employed for the fabrication of shape-morphing microgels from homopolymer films of poly (acrylic acid) (PAA). Patterning sub-micrometer thick films of PAA induces crosslinking reactions, creating gradients in crosslink density that result in nonhomogeneous swelling properties. Upon hydration, these gradients lead to bending and shearing deformations that transform 2D predesigned shapes to intricate 3D structures. Notably, micro-helices can be generated by patterning straight lines. The helical properties such as radius and chirality can be programmed by controlling the internal stresses from the asymmetric swelling via the incident electron doses and the intentional patterning of swelling asymmetries. Since PAA is a weak polyelectrolyte, increasing the pH from below to above the PAA pKa substantially increases the swelling stress to the point where plastic deformation happens. The helical pitch concurrently changes from minimal to non-minimal, a property associated with in-plane mechanical asymmetries. This new approach allows for creating microgels with non-trivial 3D geometries including rolls, rings, and more complex shapes. Secondly, the electron beam influences both the patterned structure and chemical functionalities. The investigation into the behavior of poly (ethylene glycol) (PEG) when end-functionalized with hydroxyls or biotins reveals dose-dependent thickness changes and additional chemical functionalities by radiation chemistry along the polymer main chain and biotin groups. These findings highlight the use of the non-traditional processing variables of electron-beam patterning to create shape-morphing microgels and the potential for precise control over the chemical functionalities embedded within the microgels.