**Selective Midblock Modification of Thermoplastic Elastomers:  
Phase Behavior, Stimuli-Responsiveness and Unexpected Functionality**

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**ABSTRACT**

Block copolymers continue to capture the attention of the academic and industrial worlds due largely to their fascinating ability to spontaneously self-assemble into a wide variety of "soft" nanostructures that are ideally suited for a broad range of diverse nanotechnologies. The development of thermoplastic elastomers (TPEs), such as triblock copolymers with glassy endblocks and a rubbery midblock, also endows these materials with elastic network-forming characteristics, and selective solvation of the rubbery midblock results in thermoplastic elastomer gels (TPEGs) with remarkable mechanical properties for stimuli-responsive materials such as dielectric and shape-memory elastomers, which will be discussed. We also examine the rich phase behavior afforded by these materials and discuss the importance of the midblock bridging fraction. While most block copolymers are inherently nonpolar, targeted functionalization of block copolymers can permit these materials to be used in polar environments. Sulfonation of block copolymers, for example, yields materials that possess amphiphilic properties for new applications such as separation membranes and fuel cells.  Combination of TPEs with a sulfonated midblock produces a unique TPEG that is capable of forming a physical hydrogel. We have recently demonstrated that these materials are competitive candidates for electroactive media, selective membranes and soft photovoltaics. Unfortunately, the inherently high incompatibilities and glass transition temperatures of such block ionomers effectively prevent the use of thermal annealing, routinely employed to refine the morphologies of nonionic block copolymers. An alternative approach is therefore required to control morphological development in block ionomers. This presentation likewise explores the morphological characteristics of midblock-sulfonated block ionomers (SBIs) differing in their degree of sulfonation and cast from solvents varying in polarity, followed by solvent-vapor annealing (SVA). Electron microscopy and synchrotron scattering confirm that films deposited from different solvent systems form nonequilibrium morphologies due to solvent-templated self-assembly and drying. A series of SVA tests reveals that exposing cast films to the vapor of a polar solvent constitutes the most effective SVA protocol, yielding the equilibrium morphology anticipated from simulations. Discrete ion-rich microdomains are found to undergo a phase transformation and become continuous due to hydrothermal annealing, thereby causing the materials to become superabsorbent.