## Solvent Templating and Solvent-Vapor Annealing of Charged Thermoplastic Elastomers

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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. 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. Controlled use of solvency during dissolution and casting yields nonequilibrium materials with templated morphologies. 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 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, as well as unexpected in-plane ordering.

Dr. Richard J. Spontak is an Alumni Distinguished Professor of Chemical & Biomolecular Engineering and Materials Science & Engineering at North Carolina State University in Raleigh, NC. He received his B.S. degree in Chemical Engineering from the Pennsylvania State University in 1983 and was later awarded the Ph.D. degree in Chemical Engineering from the University of California at Berkeley in 1988. He then pursued postdoctoral research in Materials Science & Metallurgy at the University of Cambridge (U.K.) and Condensed Matter Physics at the Institute for Energy Technology (Norway). In 1992, he



accepted a faculty position at North Carolina State University. Since that time, Spontak has published over 275 research papers. His primary research interests relate to the phase behavior and morphology/property development of nanostructured polymers, polymer nanocomposites, electron microscopy, and stimuli-responsive media. He resides in Raleigh with his wife Josie and his two children, Danielle and Joshua.