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Controlling the Morphological and Property Development in Charged Thermoplastic Elastomers for Emerging Applications

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ABSTRACT: Block copolymers possessing hard and soft segments and thus behaving as thermoplastic elastomers (TPEs) can be chemically functionalized for new and exciting technologies through either physical or chemical means. In the latter case, linear multiblock TPEs possessing a charged midblock avoids compromising network formation and stability in the presence of a polar liquid and affords advantageous properties for a growing number of contemporary applications such as desalination membranes, fuel cells, electroactive media, and photovoltaic devices. Unfortunately, their inherently high incompatibilities and glass transition temperatures effectively prevent the use of thermal annealing, routinely employed to refine the morphologies of their nonionic analogs. An alternative approach is therefore required to promote morphological equilibration in charged TPEs. This work explores the morphological characteristics of midblock-sulfonated pentablock ionomers cast from solution followed by solvent-vapor annealing (SVA). Transmission electron microscopy and microtomography (TEM and TEMT) confirm that films deposited from different solvent systems form nonequilibrium morphologies due to solvent-templated self-assembly and drying. A series of SVA tests performed on bulk films with solvents varying in polarity reveals that exposing as-cast films to a relatively nonselective vapor yields a highly oriented equilibrium morphology, as measured by small-angle X-ray scattering (SAXS) and predicted by simulations. When cast from a mixed polar/nonpolar solvent, the ionomer self-assembles into spherical ionic microdomains that are loosely connected. Upon exposure to liquid water, nanoscale channels irreversibly develop between the microdomains due to swelling and form a continuous, but irregular, mesoscale network. We use TEMT and real-time SAXS to follow and quantify this transformation, and show that the resultant morphology provides a highly effective diffusive pathway. We have also encountered an unexpected hydrothermal transition that promotes elevated swellability, thereby producing superabsorbent physical hydrogels.

BIOGRAPHY: Dr. Richard J. Spontak received his B.S. and Ph.D. degrees in Chemical Engineering from Penn State University and UC Berkeley, respectively. He pursued post-doctoral research at Cambridge University (U.K.) and the Institute for Energy Technology (Norway) before joining Procter & Gamble in 1990. He later accepted a faculty position at North Carolina State University, where he is currently an alumni distinguished professor and director of the Macromolecular Materials & Morphology Group. He has published over 280 scholarly papers relating to the phase behavior and morphology/property development of polymer nanostructures/nanocomposites, electron microscopy, and stimuli-responsive media. In recognition of his research, he has received the 2006 ACS (PMSE Division) Cooperative Research Award in Polymer Science & Engineering, the 2007 German Society for Electron Microscopy Ernst Ruska Prize, the 2008 ACS (Rubber Division) Chemistry of Thermoplastic Elastomers Award, the 2011 IOM3 Colwyn Medal, the 2012 NTNU Lars Onsager Medal, and the 2015 SPE International Award. An elected APS, IOM3 and RSC fellow, he is a member of the Norwegian Academy of Technological Sciences. He resides in Raleigh and enjoys spending time with his wife and two children.

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