Chemical Engineering Dissertation Defense

Augmented Permittivity and Complex Self-Assembly in Zwitterionic Block Polymers

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Abstract

The properties of block polymers (BPs) are intricately coupled to the dynamic and rich nature of the nanostructured assemblies which result from the phase separation between blocks. The introduction of strong secondary forces, such as electrostatics and hydrogen bonding, into block polymers greatly influences their self-assembly behavior, and therefore affects their physical and electrochemical properties often in non-trivial ways. The recent surge of work expanding our understanding of complex spherical packing in block polymers (BPs) has unlocked new design space for the development of advanced soft materials. The continuous matrix phase which percolates throughout spherical morphologies is ideal for many applications involving transport of ions or other small molecules. Thus, determining the accessible parameter range of such morphologies is desirable. Bulk zwitterion-containing BPs hold great potential within the realm of electroactive materials while remaining relatively untapped. Architecturally and compositionally asymmetric diblock polymers were prepared with the majority block having zwitterions tethered to side chain termini at different ratios. Thermally reversible Frank-Kasper phases are observed in multiple samples. The kinetic influences are described by the temperature-dependent static permittivity. Polyzwitterions combine the attractive features of zwitterions with the mechanical support and processability of polymeric materials. Among these attractive features is a potential for superior permittivity which is limited by the propensity of zwitterions to pack into strongly associating structures. Complex BP self-assembly embodies a plethora of packing frustration opportunities for optimizing polyzwitterion permittivity. The capabilities of this novel approach are revealed here, where the permittivity of a polyzwitterionic block is enhanced to a level comparable to that of pure liquid zwitterions near room temperature ($\varepsilon \sim 250$), but with less than a third the zwitterion concentration. Furthermore, the augmented permittivity phenomenon was found to occur only at the block interface while non-interfacial zwitterions contribute very little, highlighting the potential for improvement by several fold. The mechanistic source of permittivity enhancement from a single zwitterion-tethered block polymer is deductively isolating through a series of thermal pathways and control experiments which reveal, validate, and negate contributions from the block interface, and supported by theoretical arguments.

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