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Thermodynamics of salt-doped polymers

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There is much current interest in salt-doped polymers as materials for energy applications. For example, a promising system for rechargeable battery applications consists of diblock copolymers of an ion-dissolving block, such as polyethylene oxide (PEO) and a nonconducting block such as polystyrene. Experimentally, it has been shown that the addition of lithium salts significantly alters the order-order and order-disorder transition (ODT) temperatures. In particular, the ODT temperature can increase substantially upon adding even a small amount of lithium salt, and the domain spacing in the ordered phases also increases significantly. Both changes are found to depend on the anion type. In this talk, I describe a simple theory for explaining these phenomena. A key effect is the solvation energy of the anions by the polymers, which we approximate using the Born solvation model. The difference in the Born energy between different polymers provides a driving force towards phase separation. By studying the shift in the mean-field spinodal of the disordered phase, we can identify an effective χ parameter, with a systematic dependence on the anion radius, in agreement with available experimental data. Furthermore, by studying the behavior of the domain spacing with salt concentration, we clarify the relationship between different definitions of the effective χ parameter. We propose that the effective χ parameter determined from the structure factor of the disordered phase is a more robust measure of the change in miscibility between the two blocks. Finally, we demonstrate that salt doping induces a strongly first-order transition from the disordered phase to the lamellar phase, with different salt concentrations in the two phases.