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Ions in block copolymers: Effects on thermodynamics, structural changes and electric field induced alignment.

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Block copolymers with added ions which selectively dissolve in one block are of interest as nanostructured polymeric ion conductors. In the microphase separated state such a system offers the possibility to simultaneously optimize different properties which would normally exclude each other. One block, being in the solid state, can give mechanical strength while the other block, typically in the liquid state, could be designed to achieve good ion transport. Oriented structures are especially interesting. We present two sets of experiments dealing with fundamental ion induced effects in block copolymers. It is generally observed that the addition of salt to a block copolymer leads to a strong increase of the order-disorder transition temperature and an increased domain spacing, i.e. conformational changes of the polymers. Based on a detailed analysis of small angle scattering data of two different copolymers (PS-b-PEO, PS-b-PVP) close to the order-disorder transition three contributions to the structural changes can be distinguished: an increased incompatibility between the different monomers, the additional volume of the added salt, and chain stretching due to coordination between polymer and salt. At the phase transition, i.e. at constant incompatibility χN, for low concentrations the increase in domain size is quantitatively explained by the volume of the added salt, at higher concentrations in addition chain stretching sets in. Structural and thermodynamic effects are considerably stronger in PEO than in P2VP. In a second experiment we study the effects of electric field induced interfacial polarization caused by the added salt. Impedance spectroscopy combined with orientation experiments at high fields enable a quantitative analysis of ionic polarization and a direct demonstration of its aligning effect on the interfaces. Field induced orientation effects are much stronger if the ionic charges come into play in comparison to much weaker dielectric effects. We present a physical model accounting for the differences.