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KCl modulated D2O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films

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The modulation of thermoresponsive behavior of PNIPAM (or PNIPMAM) in aqueous solution has been widely studied by varying temperature, solvent composition, and salt concentration, which causes significant conformational changes between extended or collapsed chains via absorption or release of water. However, rare studies report on the salt effects on its block copolymer containing the zwitterionic poly(sulfobetaine)s (PSBs), especially in thin film geometry. In contrast, PSBs exhibit a UCST-type behavior in aqueous solution and are well-known as the closest structural analog to phospholipids and lipid membranes. To study the salt effect on D2O hydration and subsequent thermoresponsive behavior of PSBP-b-PNIPMAM thin films, we prepared thin films pre-loaded with KCl for the asymmetric DBC during film formation. The 'salting-in effect' of KCl on film composition and D2O distribution along with the film normal is studied by in situ spectral reflectance (SR) and time-of-flight neutron reflectivity (ToF-NR) in combination with isotope sensitivity, and the solvation-triggered phase transition upon D2O hydration and subsequent heating is probed in situ by Fourier transform infrared spectroscopy (FT-IR). Besides, the migration and/or aggregation of KCl domains inside the DBC thin films is also demonstrated by complementary methods, namely, X-ray reflectivity (XRR) and atomic force microscopy (AFM).

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