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Interaction and Anomalous Diffusion of Polyelectrolytes in Polyzwitterionic Complexes. KEHUA LIN, BENXIN JING, YINGXI ZHU, Wayne State Univ — Oppositely charged polyelectrolytes can associate in aqueous solution form distinct condensed phase such as liquid-like coacervates and solid/gel-like complexes. While a great deal is known about their phase behaviors, the interaction and structural dynamics of polyelectrolyte complexes remain unclear. Use zwitterionic polymer, poly (sulfobetaine methacrylate) (PSBMA), we compare its interaction and complex formation with polycation, poly(2-vinylpyridine) (P2VP) and polyanion, poly(styrene sulfonate) (PSS) in aqueous solution. We observe the formation of biphasic PSBMA-P2VP coacervates at low salt, in sharp contrast to the formation of PSBMA-PSS gel at the same solution condition, given that PSBMA is net negatively charged in the salted solution. To examine the interplay between polyelectrolyte interaction and structural dynamic of polyelectrolyte complexes, we investigate the self-diffusion of single P2VP and PSS in PSBMA-based complexes by fluorescence correlation spectroscopy and fluorescence recovery after photobleaching. Fickian diffusion behavior is observed with PSS in PSBMA-PSS gel. However, fast and slow diffusion modes are observed in the dense PSBMA-P2VP coacervate after the removal of supernatant, suggesting inhomogeous structure of dense coacervates. Fickian diffusion of P2VP in PSBMA-P2VP coacervates could be recovered at high salt. A simple model is proposed to describe the impact of competing electrostatic and entropic forces on the dynamic heterogeneity in macroscopically homogenous polyzwitterionic complexes.

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