

Polyelectrolyte Complexation in Non-Ideal Environments

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The phase behavior and viscoelastic properties of polyelectrolyte complexes (PECs) comprising oppositely charged polyelectrolytes (PEs) are dictated by the solution conditions (ionic strength, pH) and properties of the charged PEs (concentration, molecular weight, chemistry).¹⁻⁶ Typical studies on PECs have, however, been performed on model systems where the properties of the solution and polymers are well controlled. In contrast, *real* systems where PEs and PECs are employed involve exposure to non-ideal conditions, and little to no control can be exercised over the solution conditions and PE properties. The factors influencing PE complexation under these conditions remain to be probed.

In this presentation, we will describe our findings on the profound influence of divalent ions (e.g., Ca²⁺, Sr²⁺) on PEC properties. In charge-matched PE systems, the introduction of divalent ions will be demonstrated to reverse the phase composition and hinder chain relaxation.⁷ Preferential partitioning of divalent cations into the complex phase will be shown to stand in stark contrast to the depletion of monovalent ions (Na⁺) from the complexes. Concomitantly, electrostatic bridging of polyanion chains by divalent cations will result in hindered chain relaxation, manifesting as a non-monotonic evolution of the shear moduli of the complexes with increasing divalent salt concentrations. Relatedly, a failure of time-salt and time-ionic strength superposition approaches in presence of divalent ions will be discussed, underscoring the non-trivial influence of these ions on chain relaxation behavior. The consistency of these observations across polymer concentrations, as well as length-matched and mismatched PEC systems, will be presented.

In addition to variation in the nature and composition of the solution, non-idealities in PE composition and architecture are often encountered. The landscape of fundamental studies is still dominated by systems of strong polyelectrolytes with idealized symmetries, in length, architecture, charge density, and concentrations, making it difficult to translate results from the laboratory to industrial processing. These non-idealities will be addressed to mimic and represent realistic conditions under which PE complexation occurs. These non-idealities will be shown to influence the extent of complexation, salt resistance, phase composition, and viscoelastic behavior in PECs. Further, design guides for inducing complexation and altering the processability of these PE complexes will be discussed.

¹ S. Srivastava, *et al.*, *Advances in Chemical Physics*, **161**, 499 (2016).

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³ L. Li, *et al.*, *Macromolecules*, **51**, 2988 (2018).

⁴ L. Li, *et al.*, *Macromolecules*, **53**, 7835 (2020).

⁵ V.M.S. Syed, *et al.*, *ACS Macro Lett.*, **9**, 1067 (2020).

⁶ C.E. Sing, *et al.*, *Soft Matter*, **16**, 2885 (2020).

⁷ D. Iyer, *et al.*, *J. Polym. Sci.*, **59**, 2895 (2021).