Engineering Molecular Interactions Beyond Charge/Charge Interactions in Functional Polyelectrolyte Complexes

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Design Goals

Polyelectrolyte complexes: associative phase separation between oppositely-charged polymers in water

Competing non-covalent interactions drive association

PVBtMA

PSS

Results and Discussions

Morphology of Polyelectrolyte Complexes

Complexes undergo a solid to liquid transition as a function of salt

Polymers were synthesized with aqueous RAFT polymerization

Co-solvents can also tune the morphological phase transition of polyelectrolyte complexes

Water Content & Binodal Phase Diagram

NaBr (M)	Weight Percentage	NaBr (M)	Weight Percentage
0	91.8	2.5	64.2
0.5	84.3	3	62.0
1	78.1	3.5	60.6
1.5	76.8	4	59.0
2	73.4	4.5	58.6

Binodal phase diagram (hydrophilic polypeptides)

Li, L. et al. *Macromolecules* 2018, 51, 2988–2995.

Salt & Temperature Effects in Rheology

Salt Effects on Dynamics

Temperature Effects on Dynamics

Structural Evolution by SAXS & Cryo-TEM

Solid Complex (0-2M NaBr)

Liquid Coacervate (2.5-4M NaBr)

Particle Counting Analysis

SAXS and Cryo-TEM reveal a consistent mechanism that accounts for the rheological properties and phase behavior of PVBtMA/PSS complexes.

To the extent of our knowledge, this is one of the first experimental reports to capture and highlight **salt-stiffening behavior, water loss, phase behavior, nanoscale cluster formation, and a structural evolution spanning high salt content during solid-to-liquid phase transition in bulk PEC assemblies.**

The styrenic polyelectrolytes represent only one set of possible monomer families that can be constructed to further explore this wide parameter space. These findings advance our fundamental understanding on the physical behavior of polyelectrolyte complexes, specifically those formed by strongly interacting polyelectrolytes, and thus will bring new insights into the design and applicability of complex-based materials.

Summary, References, and Acknowledgements

References

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- Meng, S.; Ting, J. M.; Wu, H.; Tirrell, M. V. "Solid-to-Liquid Phase Transition in Polyelectrolyte Complexes" *In Preparation*.
- Meng, S. et al. "Effect of Mixed Solvents on Polyelectrolyte Complexes with Salt" *Colloid Polym. Sci.* **2020**, Accepted.

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