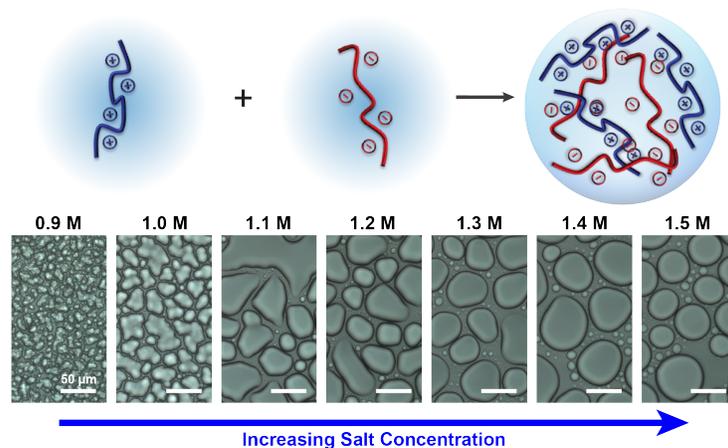


PRF#: 56281-DN17

Project Title: Designing the Liquid-to-Solid Transition in Polyelectrolyte Complexes

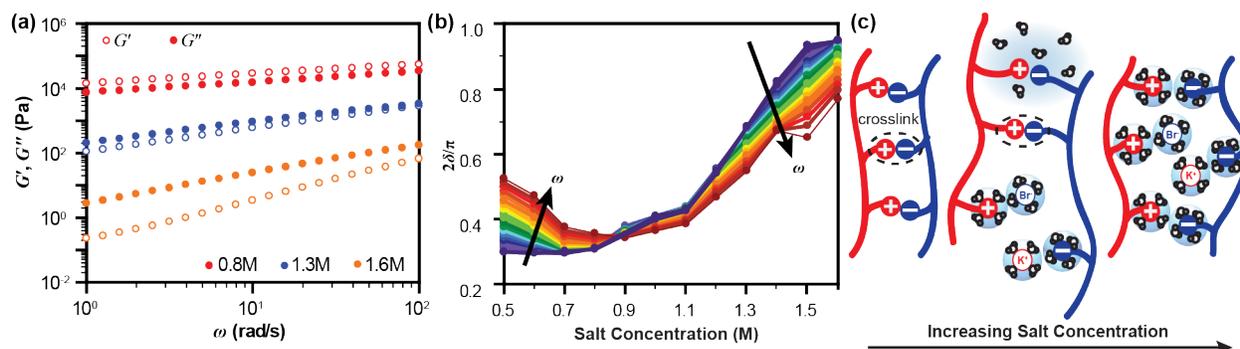
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The goal of this ACS PRF New Investigator award was to elucidate the nature of liquid-to-solid transitions that have been observed in polyelectrolyte complexes (PECs) such that these materials could be harnessed for a range of applications. Polyelectrolyte complexation refers generally to an associative phase separation that results from the electrostatic and entropic interactions between oppositely charged macro-ions in water, and can result in solid PECs or liquid complex coacervates. Previous work by Schlenoff and coworkers demonstrated the ability to use salt to plasticize solid PECs such that a continuous transition from a solid precipitate to a liquid coacervate could be observed (Figure 1).<sup>1</sup> These results indicated that the main difference between the two phases was largely the strength of the intermolecular interactions driving complexation and the extent to which salt and water were excluded from the final complex. Thus, while there is tremendous potential to harness this salt-driven phenomenon to enable processing and use of these materials, the exact nature of the transition was unknown.



**Figure 1.** Schematic depiction of PEC formation. Optical micrographs show the transition from solid, gel-like PECs to liquid complex coacervates as a function of increasing salt concentration.

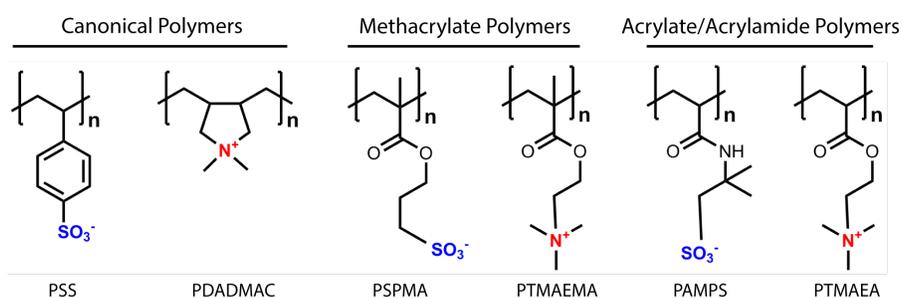
Our work utilized spectroscopic rheological analysis to clearly identify the nature of this salt-driven liquid-to-solid phase transition as physical gelation.<sup>2</sup> Year 1 experiments focused on the salt-driven liquid-to-solid transition in the canonical PEC system of poly(4-styrenesulfonic acid sodium salt) (PSS) and poly(diallyldimethyl ammonium chloride) (PDADMAC, Figure 3). We combined direct measurement of PEC phase behavior with a time-salt superposition analysis of the linear viscoelasticity of the materials. This superposition allowed for characterization of a much broader range of viscoelastic timescales than would otherwise be accessible in a typical rheometer. The resulting analysis of both liquid-like and solid-like samples highlighted a salt concentration at which the rheological behavior was frequency invariant – indicating gelation, where a network formed as a result of trapped electrostatic crosslinks that percolate the sample at a critical salt concentration to form a physical gel (Figure 2).



**Figure 2.** (a) Frequency sweep data for PSS/PDADMAC samples showing the elastic ( $G'$ ) and viscous moduli ( $G''$ ) as a function of frequency ( $\omega$ ) for different salt concentrations. (b) The

normalized phase angle ( $2\delta/\pi$ ), as a function of salt concentration, showing frequency invariant behavior at 0.85 M KBr. (c) Schematic depiction of the salt-induced gelation observed in polyelectrolyte complexes. Decreasing salt, and thus water concentration results in the formation of trapped ion pair interactions that can ultimately percolate the sample and lead to gelation.

Subsequent efforts in Year 2 focused on understanding the effect of polymer chain length and hydrophobicity on PEC phase behavior and the resulting material properties. We expanded these studies beyond the canonical system of PSS/PDADMAC to systems of methacrylate (synthesized in collaboration with Prof. Todd Emrick's lab at the University of Massachusetts Amherst) and acrylate/acrylamide polymers (courtesy of Prof. Brent Sumerlin's lab at the University of Florida) where the structure of the polycation and polyanion was more closely matched (Figure 3). These two systems allowed for a direct comparison of the effect of a relatively small change in the polymer backbone chemistry. While the small difference of a methyl group in the polymer backbone might not be expected to have a large effect on the phase behavior or rheological properties of subsequent materials, a comparison of coacervates formed from equal length methacrylate polymers and similar acrylate/acrylamide polymers showed striking differences. Coacervates formed from acrylate/acrylamide polymers were much more sensitive to the amount of salt present in the system, and had significantly lower polymer concentration (~60% lower) than the equivalent methacrylate system, resulting in much softer and more liquid-like coacervates. Furthermore, analysis of the shift factors from a time-salt superposition analysis indicated a significantly lower activation energy barrier to chain rearrangement for the acrylate/acrylamide system. We hypothesize that the differences observed between these two polymer systems is a consequence of the increased flexibility of the acrylate/acrylamide backbone which decreased local connectivity, or number of consecutive pair-wise ionic interactions between two polymer chains.



**Figure 3.** The chemical structures of the canonical system of PSS/PDADMAC, a pair of matched methacrylate polyelectrolytes, and a pair of similar acrylate/acrylamide polyelectrolytes.

In the future we will continue to explore the effects of different polymer chemistries, testing both homopolymer and random copolymer systems. We also look to connect these kinds of fundamental studies with applications-based research where we look to harness changes in salt concentration to facilitate the processing and subsequent solidification of PEC materials, such as solid films and electrospun fibers.

#### Impact on Students and Career:

This ACS-PRF DNI grant was the first external research grant that was awarded to my lab. The support was instrumental in launching our foundational studies of how polymer chemistry affects the rheology and phase behavior of complex coacervate materials. This work enabled us to identify the nature of the salt-driven liquid-to-solid transition in PEC materials, and communicate a strategy for unambiguous characterization of these kinds of effects to the broader field. Furthermore, this research served as the basis for a NSF grant looking into how the rheology of coacervates affected the potential for preparing fibers via electrospinning.

This award has supported the PhD research of one of the first graduate students to join my lab. Her research has led to two publications to date, with at least three more manuscripts in preparation, as well as numerous presentations at the AIChE Annual Meeting, the ACS National Meetings, and the March Meeting for the APS, etc.

#### References:

- (1) Wang, Q.; Schlenoff, J. B. The Polyelectrolyte Complex/Coacervate Continuum. *Macromolecules* **2014**, *47* (9), 3108–3116.
- (2) Liu, Y.; Monami, B.; Winter, H. H.; Perry, S. L. Rheological Characterization of Liquid-to-Solid Transitions in Bulk Polyelectrolyte Complexes. *Soft Matter* **2017**, *13*, 7332–7340.