

“Click” Polyelectrolytes for Rapid Exploration and Control of Complex Polymer Phase Behavior
Jennifer Laaser, University of Pittsburgh

Project Overview: Polyelectrolyte complexes and coacervates are a versatile class of materials, and precise control of their phase behavior and viscoelasticity are critical for enabling use in applications from separations membranes to drug delivery. Polymer composition is a powerful, but largely unexplored, design parameter for controlling the properties of these materials. In this project, our goal is to develop a comprehensive understanding of how polymer composition controls the phase behavior and physical properties of polyelectrolyte complexes by developing a **platform for rapid synthesis** of diverse polyelectrolyte and polyampholyte libraries, **characterizing their phase behavior and viscoelasticity** across a broad range of polymer compositions and solution conditions, and develop an **algorithmic approach** for designing materials with targeted viscoelastic properties.

Summary of Major Accomplishments to Date (September 2018):

1. Developed post-polymerization functionalization approach for synthesis of compositionally-varied polyelectrolyte libraries
2. Prepared initial library of polymers with varying charge density and hydrophobicity
3. Characterized phase windows and viscoelastic properties of complex coacervates formed from initial polymer library
4. Demonstrated that charge density is a significantly stronger determinant of phase behavior and viscoelasticity than comonomer hydrophobicity

Results and Discussion: Our first goal in this work was to develop a versatile platform for synthesis of diverse polyelectrolyte and polyampholyte libraries *via* post-polymerization functionalization of a single polymer backbone. As outlined in our original proposal, we chose poly(N-acryloxysuccinimide) (poly(NAS)) as our target polymer, because the activated esters in the sidchain can be easily substituted with primary amines to form polyacrylamides with useful sidechain functionality. Although our original intent was to convert the poly(NAS) to poly(allyl acrylamide) and then introduce composition variation through thiol-ene “click” reactions with a variety of functionalized thiols, we quickly realized that it is simpler to directly substitute the poly(NAS) with a variety of functionalized amines, as outlined in Fig. 1.

Using this approach, we successfully synthesized an initial polymer library of 18 polymers with charge densities ranging from 50 to 100%, using two different charged units (carboxylic acids and tertiary amines for the anionic and cationic moieties, respectively) and two neutral comonomers (butyl acrylamide and acrylamide) with significantly different hydrophobicities. We then formed complexes of the polymers with opposite charge but matched charge density and hydrophobicity, and characterized both their phase behavior, *via* turbidity measurements, and their viscoelastic properties, *via* small-amplitude oscillatory shear rheology. As illustrated in Fig. 2, polymers with similar charge densities had similar relaxation timescales, regardless of the comonomer hydrophobicity. This unexpected result suggests that charge density is one of the most important factors controlling the materials properties of complex coacervates.

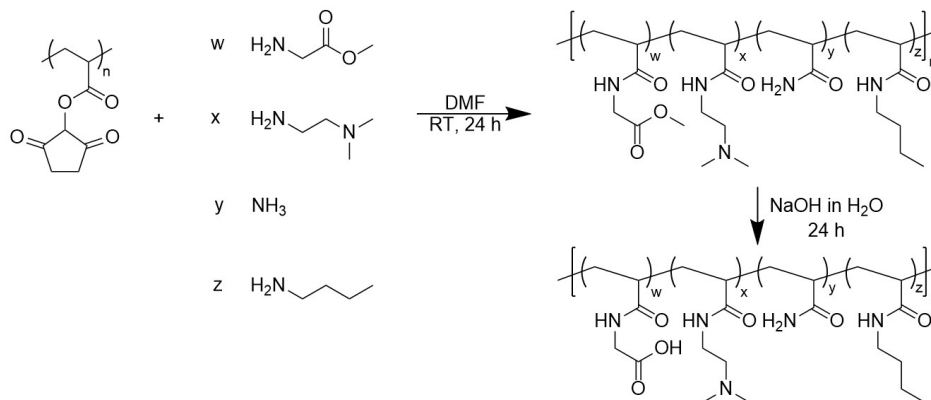


Figure 1. Compositionally-varied polyelectrolyte libraries are synthesized by post-polymerization functionalization of poly(N-acryloxysuccinimide) with mixtures of functionalized primary amines.

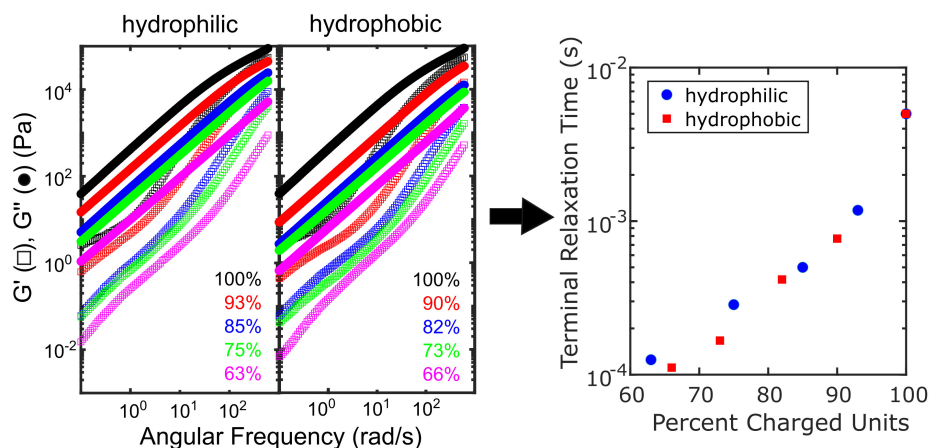


Figure 2. Rheological measurements on polyelectrolyte complexes with varied charge density and hydrophobicity demonstrate that charge density is a significantly stronger determinant of their viscoelasticity than is hydrophobicity.

To date, we have focused primarily on developing the chemistry for polyelectrolyte library synthesis through experiments on the model system described above. However, an important goal in our original proposal was the ability to rapidly and efficiently explore the vast compositional space available in these materials via high-throughput screening techniques. To this end, we have begun employing multiplexed characterization capabilities such as plate reader-based turbidity measurements for identification of the critical salt concentration. Going forward, an important challenge will be extending these high-throughput approaches to all steps of the synthesis and characterization process. In particular, the rheology measurements must currently be carried out sequentially on relatively large amounts of material, and are a significant bottleneck in the screening process. To this end, we are investigating alternative methods, such as light-scattering-based microrheology experiments, that may allow us to rapidly screen the materials' viscoelasticity on much smaller sample volumes. We anticipate that this approach will allow us to achieve our goal of rapidly exploring the available compositional space to identify polyelectrolyte complexes with precisely targeted materials properties.

Conclusions & Future Work: We have developed a versatile method for preparing compositionally-varied polyelectrolyte libraries using post-polymerization functionalization of poly(N-acryloxy succinimide). Using this platform, we have investigated an initial series of polyelectrolyte complexes with varied charge density and hydrophobicity, and have shown that charge density is an important determinant of the properties of these materials. Going forward, we will leverage the flexibility of this synthetic platform to explore materials with more compositional complexity, with a particular focus on employing high-throughput characterization techniques to rapidly explore the available composition space.

Impact of Research on PI and Student Careers: To date, funding through the PRF Doctoral New Investigators program has supported one graduate student (full time) and one undergraduate researcher (summer). This funding enabled the graduate student to obtain enough data to prepare for their third-year oral exam, which they will take in November 2018. This student is also drafting a paper on the work described in this report, which will be the student's first publication and the first publication of the PI's independent career. The PI additionally presented preliminary data from this work at the March 2018 meeting of the American Chemical Society, and is preparing a full funding proposal on this work for submission in the 2018-2019 academic year.