

“Click” Polyelectrolytes for Rapid Exploration and Control of Complex Polymer Phase Behavior
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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 was 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

1. Developed post-polymerization functionalization approach for synthesis of compositionally-varied polyelectrolyte libraries
2. Prepared and characterized initial library of polymers with varying charge density and hydrophobicity, and demonstrated that charge density dominates the phase behavior and viscoelastic response when the interactions between hydrophobic groups are weak relative to the available thermal energy
3. Extended synthetic approach to allow incorporation of a wider range of hydrophobic comonomers, including aromatic comonomers, enabling in-depth investigation of the role of different types of chemical interactions between chains

Results and Discussion: As described in our last annual report, we successfully achieved our goal of developing a platform for rapid synthesis of polyelectrolyte libraries *via* post-polymerization functionalization of poly(N-acryloxy succinimide). As depicted in Fig. 1, we then used this approach to investigate a series of coacervates with different charge densities and hydrophobicities; the nonionic acrylamide units bore either no alkyl group (forming hydrophilic nonionic sites) or a butyl sidechain (forming hydrophobic nonionic sites). In a paper recently published in *Macromolecules*,¹ we showed that while the phase behavior and viscoelasticity of the materials depended strongly on the charge density of the polymers, they were mostly independent of the hydrophobicity of the nonionic unit. This result suggests that the strength of hydrophobic interactions is critical: because the strength of the attractive interaction between two hydrated butyl chains is small relative to the available thermal energy, they may not be strong enough to measurably affect the coacervate properties, and stronger interactions are likely necessary to tune the phase behavior and viscoelasticity of these materials.

To further investigate this conclusion, we have extended our synthetic approach to allow incorporation of a much wider range of hydrophobic sidechains, including alkyl chains up to 12 carbons long, and branched, cyclic, and aromatic sidechains, as shown in Fig. 2. We are now systematically exploring the tradeoffs between polymer solubility and coacervate properties as a function of charge density and hydrophobe size. Although this work is still in progress, we are particularly interested in understanding the role of aromatic interactions such as cation- π interactions; our

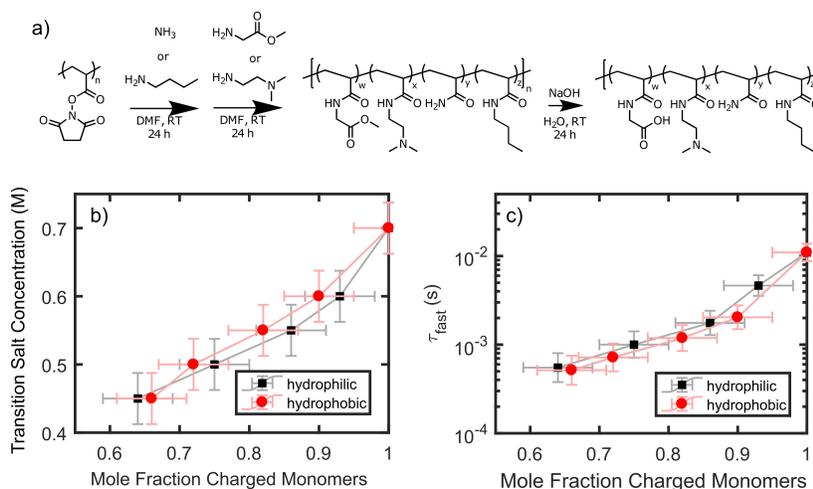


Figure 1. (a) Functionalization of poly(N-acryloxy succinimide) affords synthesis of compositionally-varied polyelectrolytes. With short alkyl sidechains, the phase behavior (b) and relaxation times (c) of the materials are similar between materials with hydrophobic or hydrophilic neutral comonomers.

preliminary results on commercially-available polymers suggest that these types of interactions may play a significant role, and the post-polymerization approach will allow us to investigate their role in a manner analogous to mutation experiments that have been used to investigate the role of cation- π and π - π stacking interactions in biological systems.

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 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.

We have begun to expand this technique to materials with both a wider range of hydrophobic alkyl chains and aromatic functional groups, building on preliminary experiments conducted on commercially-available polymers. Going forward, we will continue to leverage the flexibility of this synthetic platform to explore materials with more compositional complexity, and will keep pushing toward true “high-throughput screening” approaches to rapidly explore the available composition space.

Impact of Research on PI and Student Careers: Funding through the PRF Doctoral New Investigators program has supported one graduate student (full time) and two undergraduate researchers (summer). This results obtained with this funding formed the basis of the graduate student’s (and the lab’s) first paper, and we anticipate that a second manuscript on this work will be submitted in the next six months. Both undergraduate researchers supported by the award also made significant contributions, and will be included as co-authors on future papers from our group on this class of materials. One of these undergraduate researchers has graduated and taken a job in industry, where their PRF-supported research experience was considered a significant plus by the responsible hiring manager; the other undergraduate researcher plans to apply to graduate school this fall, and their PRF-funded research experience will provide significant evidence supporting their promise as a graduate student researcher. The PI additionally presented results from this work at the March 2019 meeting of the American Physical Society, and submitted a follow-on funding proposal to another agency in Summer of 2019.

Selected References

[1] Huang, J.; Morin, F. J.; Laaser, J. E. *Macromolecules* **2019**, *52*, 4957–4967.

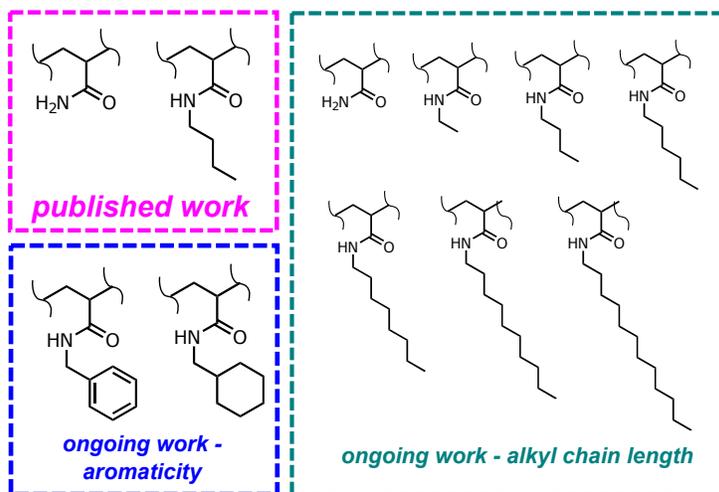


Figure 2. Hydrophobic sidechains being used in ongoing investigations of the roles of hydrophobicity and aromaticity in the phase behavior and viscoelasticity of polyelectrolyte complex coacervates.