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Fundamental Understanding of Anisotropic Ion Transport in Charged Block Copolymer Microdomains: Large-Scale Mesoscopic Simulations of Phase Diagrams, Ion Diffusion Pathways, and Electric-Field Effects

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Ionic conductivity in block copolyelectrolytes highly depends on the morphology of self-assembled microdomains at the molecular level. However, the influence of electrostatic interactions on morphology and ionic conductivity remains an obscure feature of this type of charged block copolymer (BCPs). Current theoretical understandings of phase diagrams of BCPs, whether obtained from mesoscopic dissipative particle dynamics (DPD) simulations[1-2] or self-consistent field theory (SCFT), haven't addressed the inherent difficulties of capturing the following elements simultaneously: (i) discretized local charge distributions and electrostatic interactions, (ii) quantifying the ionic transport process, and (iii) direct correlation between the ionic conductivity and the morphology anisotropy. Therefore, there are urgent needs to develop reliable computational tools to allow *de novo* design of charged BCP systems.

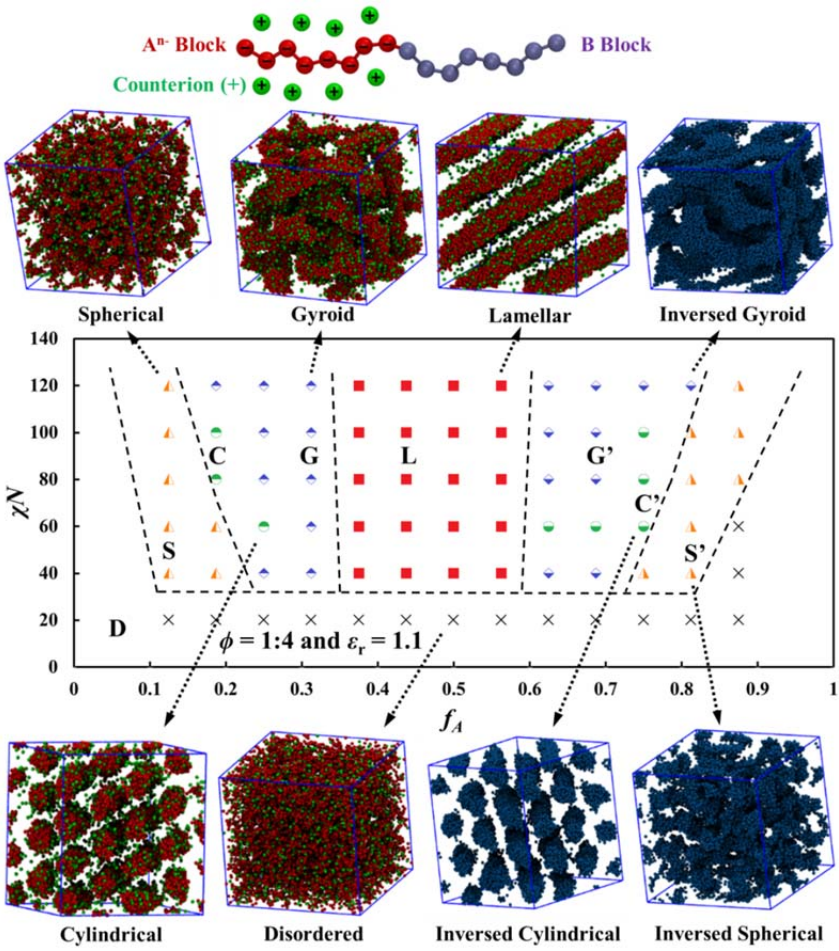

Figure 1: DPD-simulated phase diagram of A^{n-}B-type diblock copolyelectrolyte system with representative simulation snapshots. The dashed lines serve as a guide to the eye and map out the boundaries for major microphase transitions. The sketch of a single diblock copolyelectrolyte chain with counterions is shown on the top. For block-A-poor phases, only the A monomers (in red) and the counterions (in green) are shown in the snapshots, while for block-A-rich inverse phases, only the B monomers (in blue) are shown in the snapshots for clarity.

During Years 1 and 2 of this ACS-PRF project, we systematically predict the phase diagram and morphology of diblock copolyelectrolytes using a modified DPD simulation framework, considering both explicit electrostatic interactions and ion diffusion dynamics. **In Year 1**, various experimentally-controllable conditions are considered here, including block volume fraction, Flory-Huggins parameter, block charge fraction or ion concentration, and dielectric constant. Boundaries for microphase transitions are identified based on the computed structure factors, mimicking small-angle X-ray scattering patterns. The DPD-simulated phase diagram of a representative diblock copolyelectrolyte system under ϕ = 1:4 and ε_r = 1.1 is shown in **Fig. 1** with DPD simulation snapshots of the equilibrated microdomains. **In Year 2**, we develop a novel "diffusivity tensor" approach to predict the degree of anisotropy in ion diffusivity along the principal microdomain orientations, which leads to high-throughput mapping of phase-dependent ion transport properties. Inclusion of ions leads to a significant leftward and upward shift of the phase diagram due to ion-induced excluded volume, increased entropy of mixing, and reduced interfacial tension between dissimilar blocks. Interestingly, we

discover that the inverse topology gyroid and cylindrical phases are ideal candidates for solid-state electrolytes in metal-ion batteries. These inverse phases exhibit an optimal combination of high ion conductivity, well-percolated diffusion pathways, and mechanical robustness. Finally, we find that higher dielectric constants can lead to higher ion diffusivity by reducing electrostatic cohesions between the charged block and counterions to facilitate ion diffusion across block microdomain interfaces. **This work significantly expands the design space for emerging block copolyelectrolytes and motivates future efforts to explore inverse phases to avoid engineering hurdles of aligning microdomains or removing grain boundaries.** These research outcomes lead to a paper published in the leading polymer journal, ***Macromolecules***, 2018, 51(12), 4471–4483.[3]

Specifically, we take advantage of the explicit-ion DPD model to investigate the dynamic anisotropic ion diffusivities within the microdomains as a function of the diverse morphologies of diblock copolyelectrolytes (see **Fig. 2a-c** for the anisotropic lamellar L phase, the perfectly isotropic disordered D phase, and the fairly isotropic inverse cylindrical C' phase). The computed principal diffusivities quantify the contribution from each characteristic microdomain orientation. For example, for the anisotropic L phase, the principal ion diffusivities are $D_{\perp} < D_{\parallel}$ (see **Fig. 2d** for the ellipsoid-shaped 3D contour plot showing orientational anisotropy), which are normal and parallel to the lamellar microdomains, respectively. As expected, the principal ion diffusivities for the isotropic D phase are almost identical to each other (see **Fig. 2e** for the corresponding spherical 3D contour plot showing orientational isotropy).

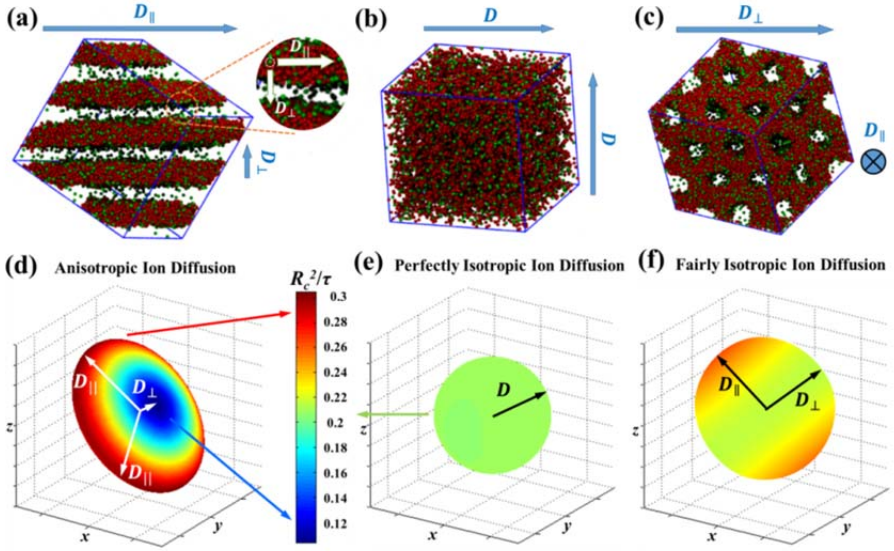

Figure 2: DPD simulation snapshots showing the morphologies of the (a) anisotropic L, (b) perfectly isotropic D, and (c) fairly isotropic C' phases of diblock copolyelectrolytes, which result in (d) anisotropic, (e) perfectly isotropic, and (f) fairly isotropic ion diffusivity contour plots computed using the ion diffusivity tensor **D**.

Impact on Career Development of PI and Graduate Students

This ACS-PRF award enables the PI and the two graduate students to **attend the MRS Fall Meeting & Exhibit in Boston**. The students gained valuable experience when presenting the research. They also get to know the broader research community and expand their academic vision. All these experience would help them in the future for search academic and industrial R&D positions. This ACS-PRF award will help **produce two PhDs** when the students defend their theses in summer 2019. In addition, the computational methodology developed using this award has enabled the PI to explore new research directions on ion diffusion in hybrid organic-inorganic perovskites, a promising photovoltaic material. The PI was able to secure a **three-year NSF grant** (CBET #1708968) based on knowledges learned from the ACS-PRF project.

References

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2. Gavrilov, A. A.; Kudryavtsev, Y. V.; Chertovich, A. V., Phase diagrams of block copolymer melts by dissipative particle dynamics simulations. *J. Chem. Phys.* **2013,** *139* (22), 224901.
3. Zhai, C.; Zhou, H.; Gao, T.; Zhao, L.; Lin, S., Electrostatically Tuned Microdomain Morphology and Phase-Dependent Ion Transport Anisotropy in Single-Ion Conducting Block Copolyelectrolytes. *Macromolecules* **2018,** *51* (12), 4471-4483.