Supporting Information: Isotropic-to-Nematic Transition in Salt-Free Polyelectrolyte Coacervates from Coarse-Grained Simulations

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1 Spacial Distribution of Order Parameter for Salt-Free Coacervates Formed by Semiflexible PEs around Transition Bending Constant

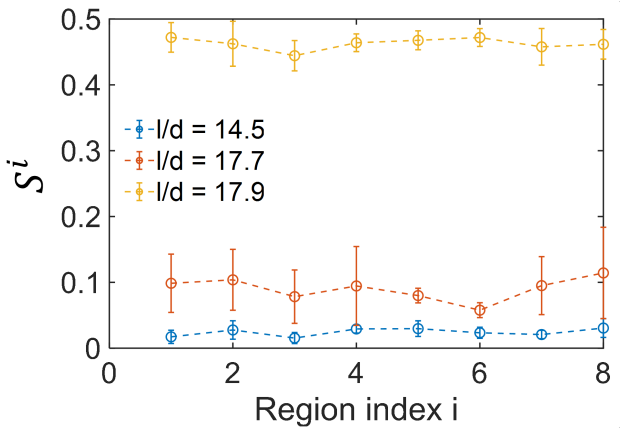

Figure S1: Order parameter S^i in each cubic sub-region of the simulation box as a function of region index i for salt-free coacervates at three bending constants. Blue: $l/d = 14.535$; Red: $l/d = 17.762$; Yellow: $l/d = 17.975$. Simulation parameters: $f_+ = f_- = 1.0, l_B/\sigma = 3$.

2 Isotropic-to-Nematic Transition in Salt-Free Coacervates Formed by Semiflexible PEs with Different Initial Configurations

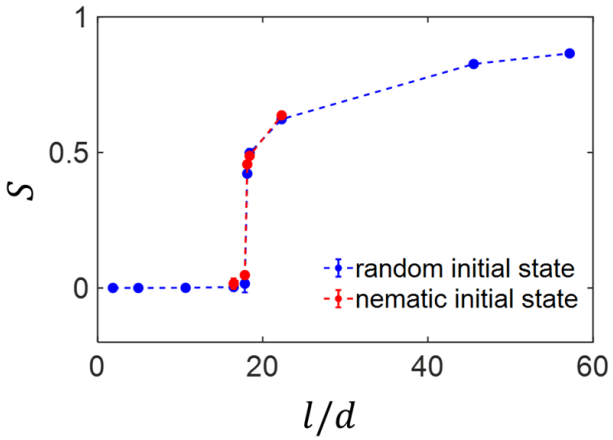

Figure S2: Order parameter S as a function of the chain stiffness l/d for salt-free coacervates with different initial configurations. The blue curve shows results for the random initial state (self-avoiding random walk) while the red curve shows results for the nematic initial state. Simulation parameters: $f_+ = f_- = 1.0, l_B/\sigma = 3$.

3 Coexistence of the Nematic and Isotropic Phases in Charged System with NVT Ensemble Simulation

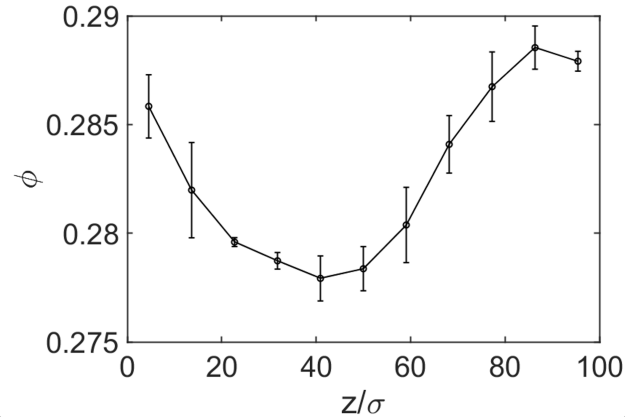

Figure S3: The average volume fraction ϕ as a function of z axis position for NVT ensemble of oppositely charged polymers. The average values are calculated by block averaging ϕ for each sub-region of the simulation box (evenly divided the box along z axis). To ensure equilibration, before calculating the average values, long simulation was performed until the profile of ϕ was stable as the simulation time further increased. Simulation parameters: $f_+ = f_- = 1.0, l_B/\sigma = 3$, chain length $N = 20$, number of Chains $n = 2880$, box size $(x/\sigma = y/\sigma = 40, z/\sigma = 100)$.

4 Isotropic-to-Nematic Transition for Neutral Semiflexible Polymer Solution with Different Initial Configurations

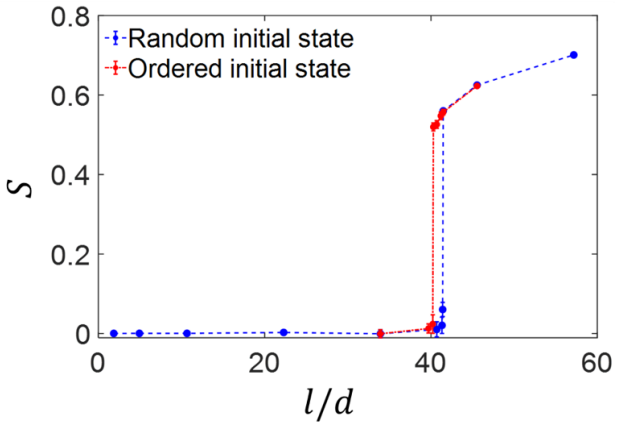

Figure S4: Order parameter S as a function of the chain stiffness l/d for neutral semiflexible polymer solution with different initial configurations. The density of each point is the same as the equilibrium density of salt-free coacervates with the same chain stiffness. The blue curve shows results for the random initial state (self-avoiding random walk) while the red curve shows results for the nematic initial state.

5 Isotropic-to-Nematic Transition in Salt-Free Coacervates Formed by Semiflexible PEs with Different Charge Fractions of Polycations

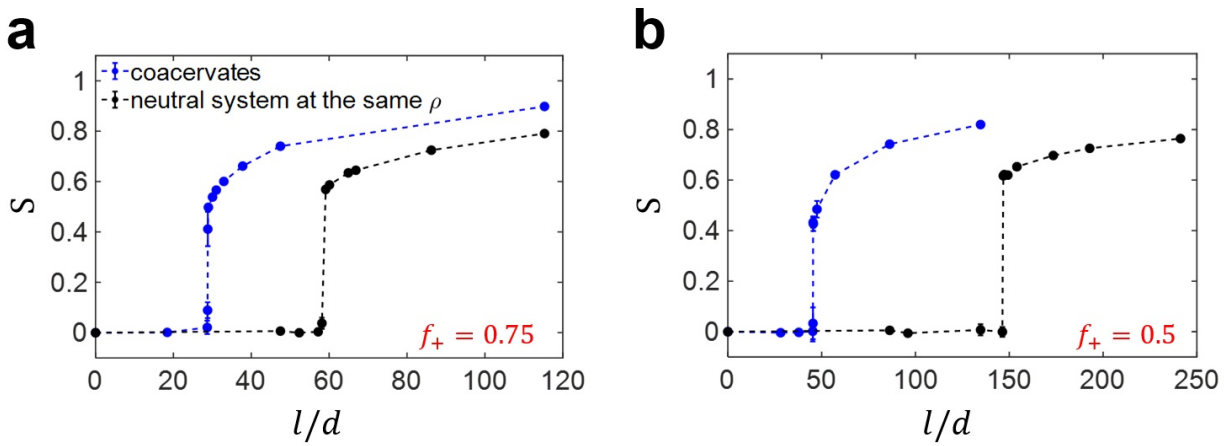

Figure S5: Dependence of order parameter S on chain stiffness l/d for coacervates and corresponding neutral system at same density with charge fraction of polycations in coacervates: a) $f_+ = 0.75$; b) $f_+ = 0.5$. Blue curves show results for coacervates while black curves show results for corresponding neutral systems. Simulation parameters: $f_- = 1.0, l_B/\sigma = 3$.

6 Nematic Order Parameter along the z-Axis of PEs within Salt-Free Coacervate Interfaced with the Supernatant Phases

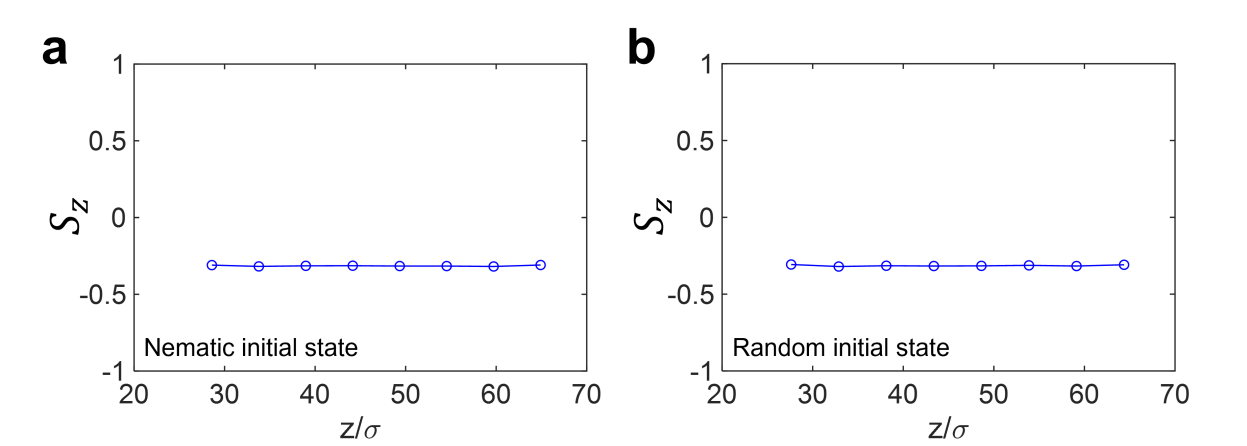

Figure S6: The nematic order parameter S_z characterizing the ordering along the z-axis, i.e., perpendicular to the coacervate-supernatant interface, as a function of sub-region center z position for two different initial states: a) nematic initial state (corresponding to Figure 8a); b) random initial state (corresponding to Figure 8b). The errors are within the symbols. Simulation parameters: $f_+ = f_- = 1.0, l_B/\sigma = 3$.