Supplementary Material for
Charge Asymmetry Suppresses Coarsening Dynamics in Polyelectrolyte Complex Coacervation

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A. Other simulation details

As per convention in DPD, the reduced number density is set to $\rho = 3.0$. The characteristic time scale is given by $\tau = \sqrt{mr_c^2/k_{\mathrm{B}}T}$. The integration time step is set to $\delta t = 0.05\tau$. To prepare 125 pairs in large systems for studying coarsening dynamics, we first equilibrate one pair with a given λ in a $12r_c \times 12r_c \times 12r_c$ simulation box for $10^2\tau$, we then duplicate the small system 5 times in each direction to make the 125-pair systems in a $60r_c \times 60r_c \times 60r_c$ box. The positions and orientations of the polyion pairs become randomized on the order of $\sim 10\tau$, which is much shorter than the onset of coarsening ($> 100\tau$). The total simulation time is $5 \times 10^4\tau \sim 10^5\tau$. All the simulations are performed using the LAMMPS [1] platform.

B. PMF calculation between two polyion pairs

We use the adaptive bias force (ABF) algorithm [2, 3] implemented in LAMMPS [4] to calculate the PMF between two polyion pairs in a simulation box of $24r_c \times 12r_c \times 12r_c$. The center of mass distance r in the PMF calculation ranges from $0r_c$ to $15r_c$. The distance range is divided into consecutive windows of $0r_c \sim 1r_c$, $1r_c \sim 3r_c$, $3r_c \sim 6r_c$, $6r_c \sim 10r_c$ and $10r_c \sim 15r_c$ to improve the efficiency of the PMF calculations [3]. Each window is further divided into bins with equal width $0.1r_c$. The PMF in all windows reaches convergence before $5 \times 10^5\tau$.

C. Stability of a single droplet

To test the stability of a single droplet under charge asymmetry condition, we start our simulations with a single large, well-mixed droplet, and then turn on electrostatic interaction with a given charge asymmetry. Figure S1 shows that under good solvent condition ($\Delta a = 0$), droplets with $\lambda = 0.78, 0.82$ split into multiple clusters after we turn on electrostatics, indicating the equilibrium state at these asymmetry conditions should consist of multiple net-charged clusters. For $\lambda = 0.86$, the droplet stays stable during our simulation. However, this state

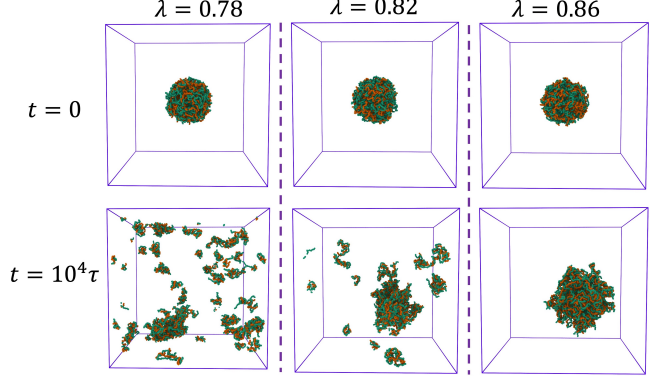might still be a metastable state as the multi-cluster state

FIG. S1. Simulations starting a single well-mixed droplet at = $0.78, 0.82, 0.86$, then turn on the electrostatics at good solvent condition.

could have lower free energy but might require high activation energy to split from a single droplet state.

D. Polarization between two charge-balanced droplets

To study the polarization as two charge-balanced pairs approach each other, we calculate the electric dipole moment of each pair given by $\vec{P}_\alpha = \sum_i q_{\alpha,i}\vec{r}_{\alpha,i}$, where $q_{\alpha,i}$ is the charge on monomer i and $r_{\alpha,i}$ is its vector position, and the sum is over all monomers in pair α ($\alpha = 1, 2$). The total dipole of the system is then $\vec{P} = \vec{P}_1 + \vec{P}_2$. $P_{||}$ is the projection of the total dipole moment onto the center-of-mass vector between the two pairs. Since by symmetry, $\langle P_{||}\rangle = 0$, we characterize the polarization by the second moment, $\langle P_{||}^2\rangle$.

In Fig. S1, we show $\langle P_{||}^2\rangle$ for three values of $\Delta a = 0, 10$, and 25. Polarization is stronger in systems with smaller Δa, with higher peak and wider range. Poorer solvent condition (larger Δa) results in weaker polarization, due to the compactness of the droplets.
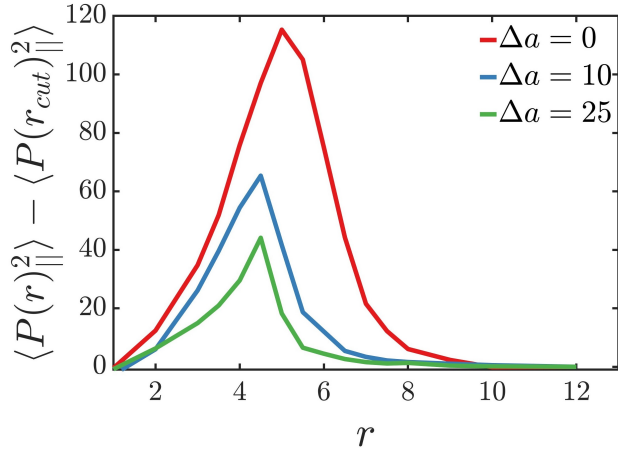
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FIG. S2. Fluctuation of the longitudinal component of the polarization $\langle P_{||}^2 \rangle$ as a function of the center-of-mass distance between the two polyion pairs under different solvent conditions. $r_{cut} = 12r_c$.

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