Supporting Information

**Total energy of the system.** In order to describe the internal energy leading to the formation of the complex, it was computed in the simulations. The energy is calculated as the sum of the kinetic $E_{\text{kin}}$, conservative $U_C$, spring harmonic $U_S$, and electrostatic $U_{\text{electr}}$ contributions,

$$E = E_{\text{kin}} + U_C + U_S + U_{\text{electr}},$$

(1)

where

$$E_{\text{kin}} = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2,$$

$$U_C = \frac{1}{2} \sum_i \sum_{j>i} a_{ij} R_c \left( 1 - \frac{r}{R_c} \right),$$

$$U_S = \sum_{(k,l)} K (r_{kl} - r_0)^2 / 2,$$

and $N_b$ is the number of bonds on the polyelectrolytes. The electrostatic energy between two Slater type charge distributions is [1, 2]

$$u_{ij}(r) = \frac{1}{4 \pi \epsilon_0 \epsilon_r} \frac{q_i q_j}{r} \left[ 1 - (1 + \beta r) e^{-2\beta r} \right].$$

(2)

Applying the Ewald technique to calculate the energy (and force) between pairs of charged particles, the electrostatic energy is given by

$$U_{\text{electr}} = \frac{1}{4 \pi \epsilon_0 \epsilon_r} \left[ \sum_i \sum_{j>i} q_i q_j \frac{\text{erfc}(\alpha r)}{r} \right] + \frac{2\pi}{V} \sum_{k \neq 0} Q(k) S(k) S(-k) - \frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2 - \sum_i \sum_{j>i} q_i q_j \left( 1 + \beta r e^{-2\beta r} \right).$$

(3)

The most relevant contribution during the formation of the complex is the electrostatic energy. In reduced units $U_{\text{electr}}^*$ is calculated as $U_{\text{electr}}^* = U_{\text{electr}} / k_B T_0$.

**Finite-size effects.** Additional DPD simulations of salt-free systems containing different number of particles were performed to evaluate finite-size effects on the conformation of the polyelectrolytes. We chose salt-free systems because they exhibited higher values of the radius of
gyration than systems with salt-added. We simulated states in different regions of $\delta$ values: $\delta = 10, 20, 35, 40$ and 60%.

Special attention was paid at $\delta = 10\%$ because at this condition the polycation exhibited a high value of $R_{ee}^* \approx 11$ in the box of length $L^* = 15$, as shown in Fig. 6 c). A set of new simulations were conducted at $\rho^* = 3$ and $T^* = 1$.

The starting configurations of the systems with number of particles $N = 17496, 24000$, and 81000, corresponding to cell lengths of $L^* = 18, 20$, and 30, respectively, were prepared with the polyelectrolytes in shrunken globular conformations, separated by at least $r^* = 10$ between centers of mass. The starting configuration of $N = 81000$ particles is shown in Fig. 1.

The energy of the systems was computed as the sum of the contributions previously described. These are shown as a function of the simulated steps in Fig. 2 for the the system with $L^* = 30$, starting from the initial configuration.

The inset shows the electrostatic energy and its decomposition in real, reciprocal, self, and tail contributions, corresponding to the four terms in Eq. 3. When the length of the simulation cell increases the electrostatic energy takes the same value within statistical error, as shown in Fig. 3, where the energy of the original system with $L^* = 15$ is also included. From these results it is shown that the electrostatic energy, which drives the formation of the complex between the two oppositely polyelectrolytes, is basically independent of the size of the simulation cell, or equivalently, of the number of particles in the system for canonical conditions.

The radius of gyration and end-to-end distance were calculated for low, intermediate and high values of $\delta$ considering different box sizes. The results are presented in Fig. 4. It was found that for $\delta < 35\%$ the size of the system strongly affects the radius of gyration and end-to-end
Figure 2: Time evolution of the internal energy of the system with $N = 81000$ and $L^* = 30$ decomposed in its different contributions, for $\delta = 10\%$, $T^* = 1$ and $\rho^* = 3$ in salt-free conditions. The inset shows the electrostatic part and its real, reciprocal, self, and tail contributions.

Figure 3: Time evolution of the electrostatic energy of the system with $\delta = 10\%$ for different box lengths, containing $N = 10125$, 17496, 24000, and 81000 particles.
distance of the large chain. However, these quantities remained the same in all the cases for the short chain.

For $\delta \geq 40\%$ the values of the radius of gyration and end-to-end distance of both polyelectrolytes show a smaller dependence on box size than those for low $\delta$.

![Graph showing radius of gyration and end-to-end distance](image)

Figure 4: Radius of gyration (upper panel) and end-to-end distance (lower panel) of the polyelectrolytes for different system sizes. Black and cyan symbols are results for the box of length $L^* = 15$. Open and filled squares are results for the cationic polyelectrolyte and open and filled circles for the anionic chain.

We observed that for $\delta = 10\%$ the short chain can displace along the large polyelectrolyte, whereas for $\delta$ values in $30 - 60\%$ range, the formation of a zipper structure or a conformation...
where the larger chain polymer rolls up over the shorter chain polymer, are noticeable. For \( \delta \geq 60 \), the formation of a compact structure is dominating.

The results obtained for finite size effects confirm the complex formation mechanism we studied. As the addition of salt in the system enhances the complex formation process, the effect of system size is important mainly for salt-free systems in the region of small \( \delta \).

References
