Supporting Information to

Manipulation of Confined Polyelectrolyte Conformations Through Dielectric Mismatch

Trung Dac Nguyen[1] and Monica Olvera de la Cruz[1,2,*]
[1] Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208
[2] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208
Email: m-olvera@northwestern.edu

1. Supporting Movie

Movie S1: Four-fold conformation of the 100-mer polyelectrolyte with the counterions filled in the quarters. The cavity radius is $R = 6\sigma$. The surface charge density is $q_f\sigma^2/q = 0.2$. Trivalent counterion fraction is $\phi_m = 0.3$. The monomers are in cyan, monovalent counterions in orange, trivalent counterions in red, outer counterions in green; and small white spheres are interface beads. For clarity we only show the upper half of the interface particles (small white spheres) and outside counterions (green spheres) to better reveal the polyelectrolyte conformations and counterions inside the cavity.

2. Supporting Figures

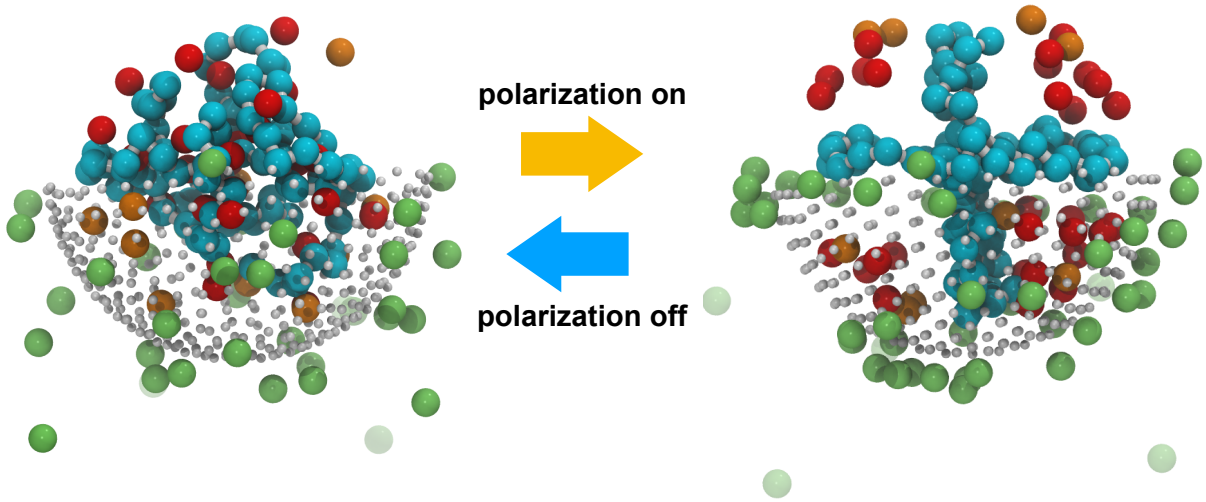

Figure S1: Reversible transformations between amorphous to four-fold morphologies when polarization effects are turned on and off. The cavity radius is $R = 6\sigma$ and trivalent counterion fraction $\phi_m = 0.3$. σ is the length scale of the exclude volume interaction between the monomers and the counterions (i.e. the Weeks–Chandler–Andersen potential). The monomers are in cyan, monovalent counterions in orange, trivalent counterions in red, outer counterions in green; and small white spheres are interface beads. Here and in the snapshots that follows, for clarity we only show the upper half of the interface particles (small white spheres) and outside counterions (green spheres) to better reveal the polyelectrolyte conformations and counterions inside the cavity.

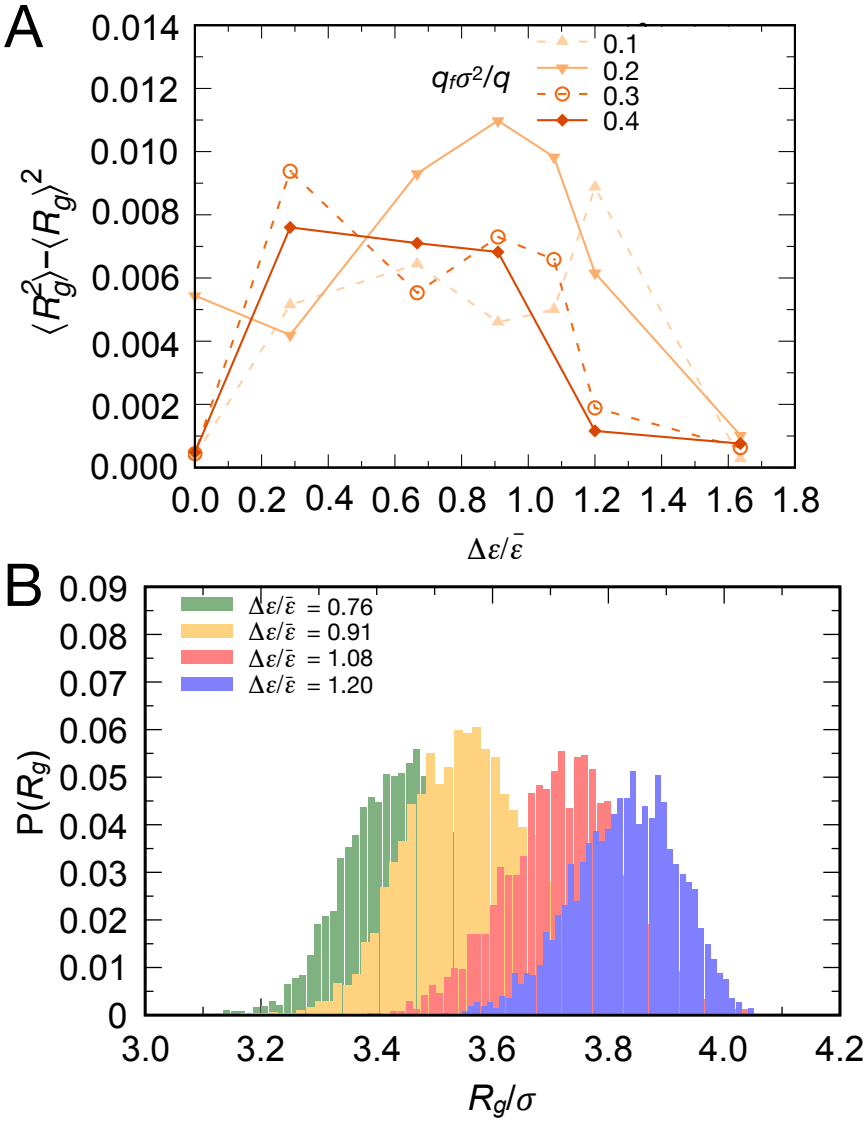

Figure S2: A) Fluctuations in the polyeletrolyte radius of gyration as a function of dilectric mismatch for different surface charge densities $q_f\sigma^2/q$, where q is the monomer charge, and σ is the distance unit of the exclude volume interaction between the monomers (i.e. the Weeks-Chandler-Andersen potential). B) Polyelectrolyte radius of gyration for different values of outside the relative permittivity ε_{out} and the corresponding dielectric mismatch $\Delta\varepsilon/\bar{\varepsilon}$ from unbiased simulations. The surface charge density is $q_f\sigma^2/q = 0.2$. The cavity radius is $R = 6\sigma$ and trivalent counterion fraction $\phi_m = 0.3$.

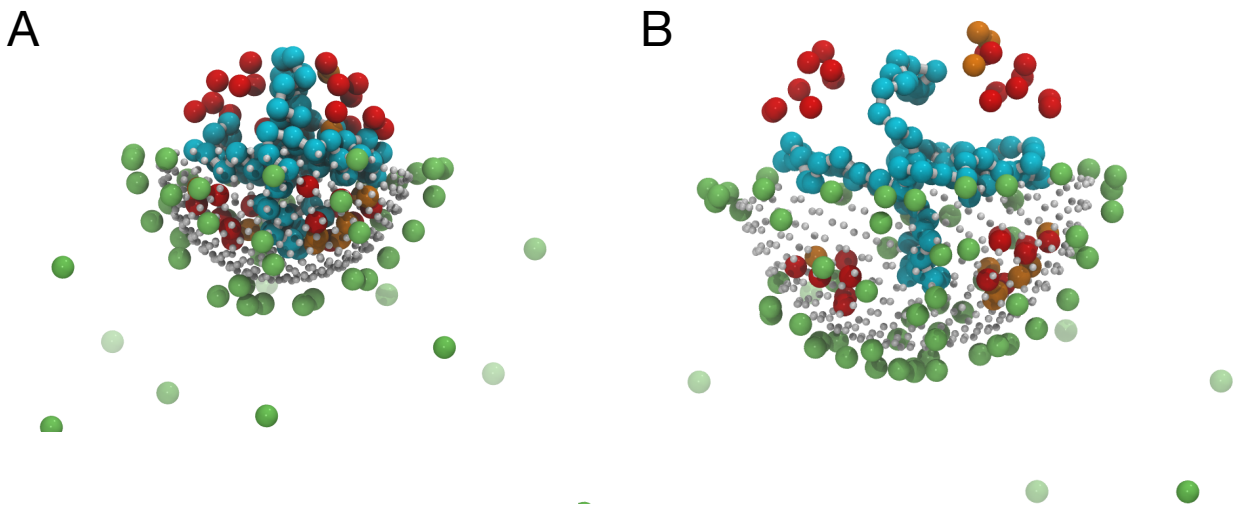

Figure S3: Representative snapshots of the equilibrium conformations of the polyelectrolyte for different cavity radii: A) $R = 5\sigma$ and B) $R = 7\sigma$. The surface charge density is $q_f\sigma^2/q = 0.2$. Trivalent counterion fraction is $\phi_m = 0.3$.

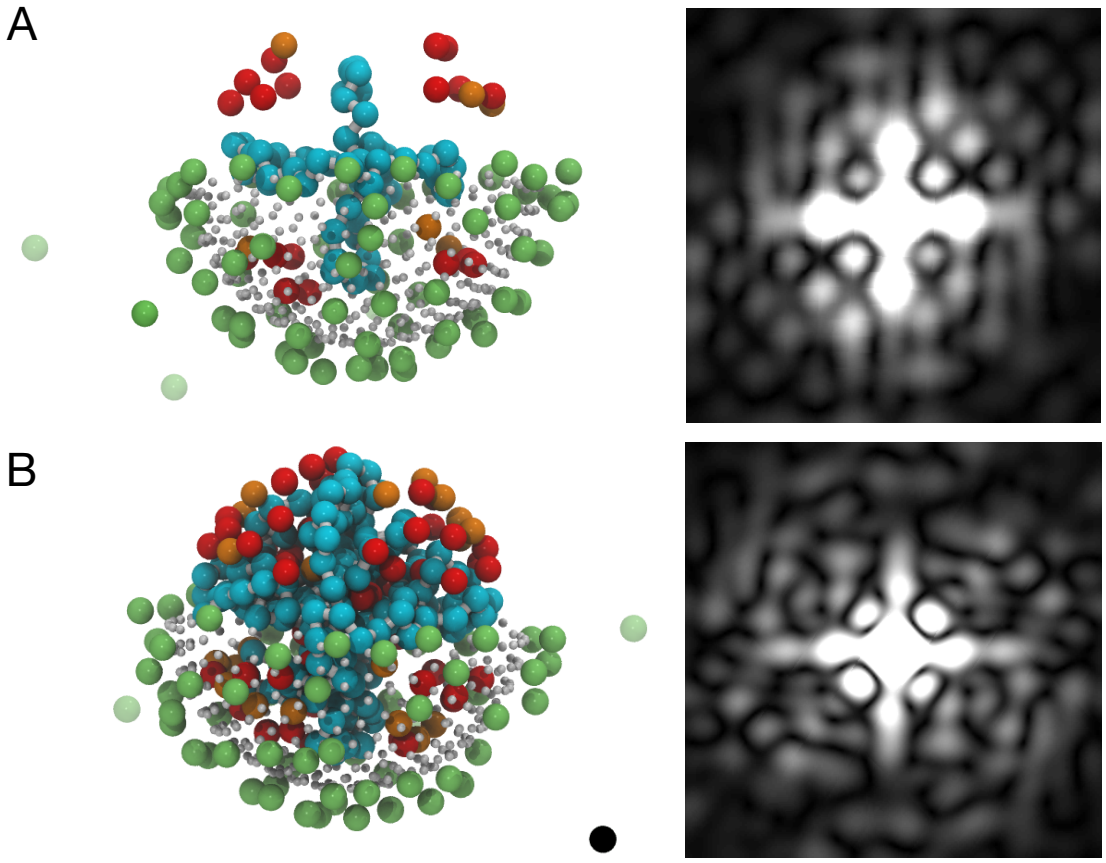

Figure S4: Representative snapshots of the equilibrium conformations of the polyelectrolyte for different chain lenghths: A) $N = 60$; B) $N = 200$. Insets are the diffraction pattern taken along the four-fold symmetry axis. The cavity radius is $R = 6\sigma$. Trivalent counterion fraction is $\phi_m = 0.3$.

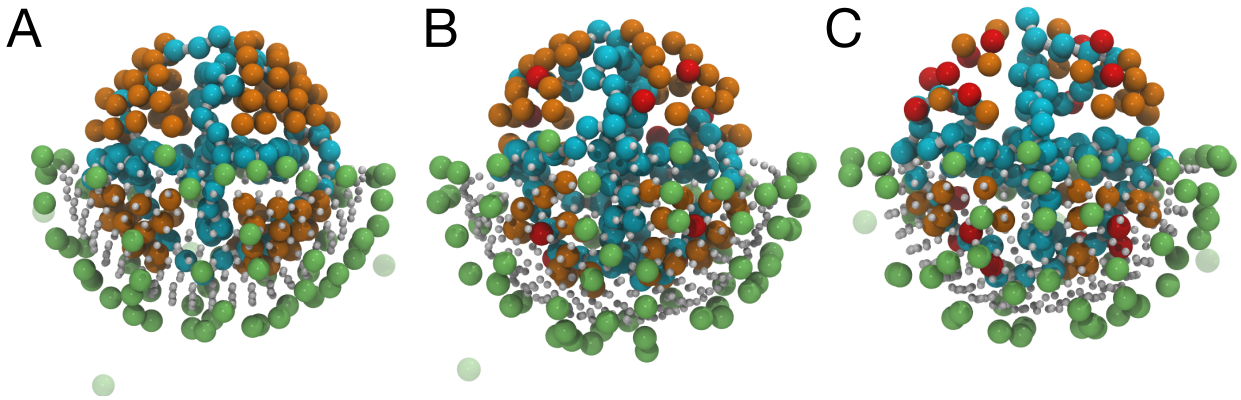

Figure S5: Representative snapshots of the conformations of the polyelectrolyte for different trivalent counterion fractions: A) $\phi_m = 0$; B) $\phi_m = 0.1$ and C) $\phi_m = 0.2$. The chain length is $N = 100$. The surface charge density is $q_f \sigma^2/q = 0.2$. The cavity radius is $R = 6\sigma$.

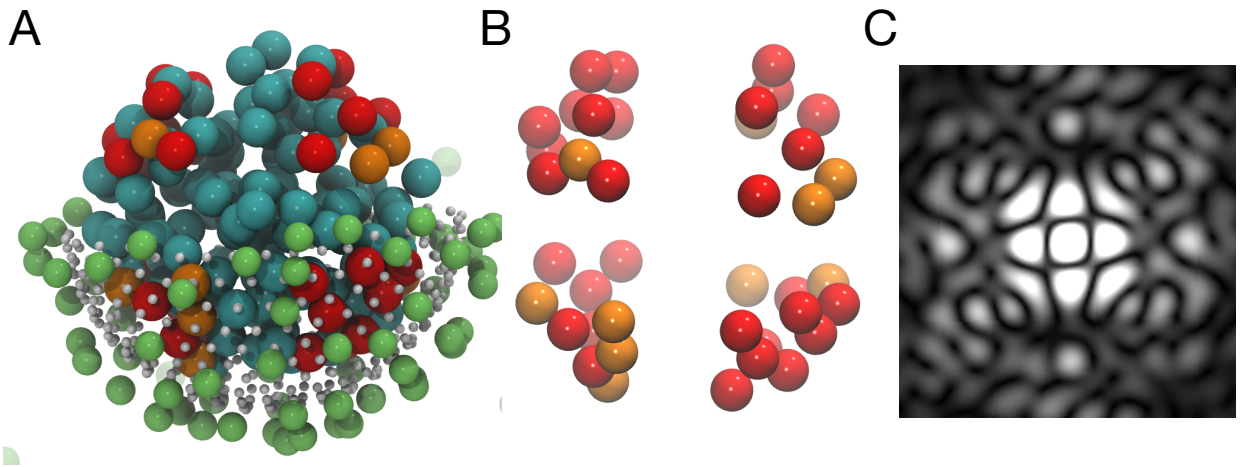

Figure S6: A) Representative equilibrated configuration of the monomers when all the bonds are removed. B) Only the counterions are visualized to show the simple cubic arrangement, as shown in the diffraction pattern in C). The dimensionless surface charge density is $q_f \sigma^2/q = 0.2$, and trivalent counterion fraction $\phi_m = 0.3$.

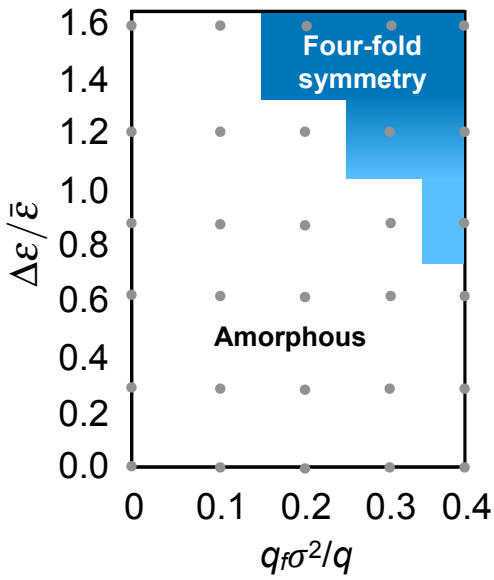

Figure S7: Phase diagram of equilibrium morphologies of the confined polyelectrolyte as function of the surface charge density ($q_f\sigma^2/q$) and dielectric mismatch ($\Delta\varepsilon/\bar{\varepsilon}$). Dots represent the state points where simulations are performed. The chain length is N = 100. The cavity radius is $R = 6\sigma$ and trivalent counterion fraction $\phi_m = 0.1$.

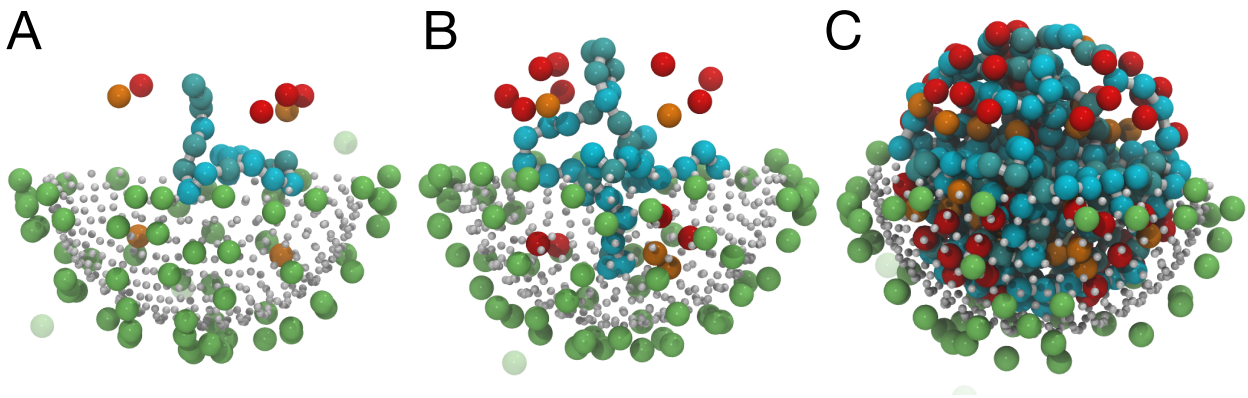

Figure S8: Representative snapshots of the conformations of the polyelectrolyte for extreme chain lengths: A) $N = 20$; B) $N = 40$ and C) $N = 250$. The cavity radius is $R = 6\sigma$. Trivalent counterion fraction is $\phi_m = 0.3$.

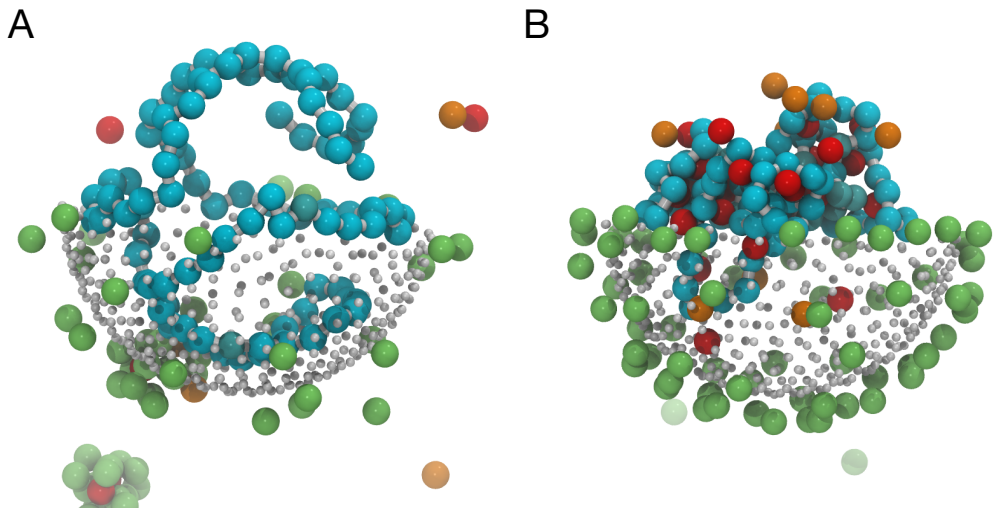

Figure S9: Four-fold symmetry conformations do not emerge A) when only the polyelectrolyte is confined inside the cavity while all the counterions are located outside; and when B) the relative permittivity inside the cavity is reduced to $\varepsilon_{in} = 10$, while $\varepsilon_{in} = 4$. The chain length is $N = 100$, the cavity radius is $R = 6\sigma$ and trivalent counterion fraction is $\phi_m = 0.3$.

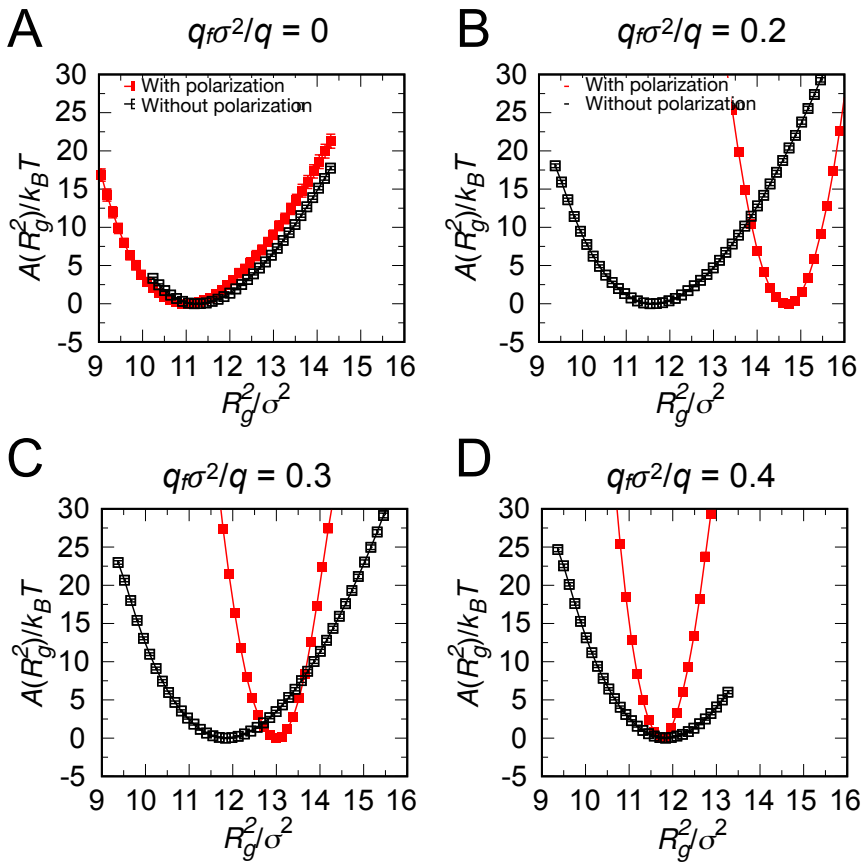

Figure S10: Free energy profiles of the polyelectrolyte (squared) radius of gyration for different dimensionless surface charge densities q_f. "With polarization" corresponds to $\varepsilon_{in} = 40$ and $\varepsilon_{out} = 4$; "Without polarization" corresponds to $\varepsilon_{in} = \varepsilon_{out} = 40$, or when polarization effects are excluded. Trivalent counterion fraction is $\phi_m = 0.3$. Error bars are the statistical errors obtained from bootstrapping analysis using WHAM.

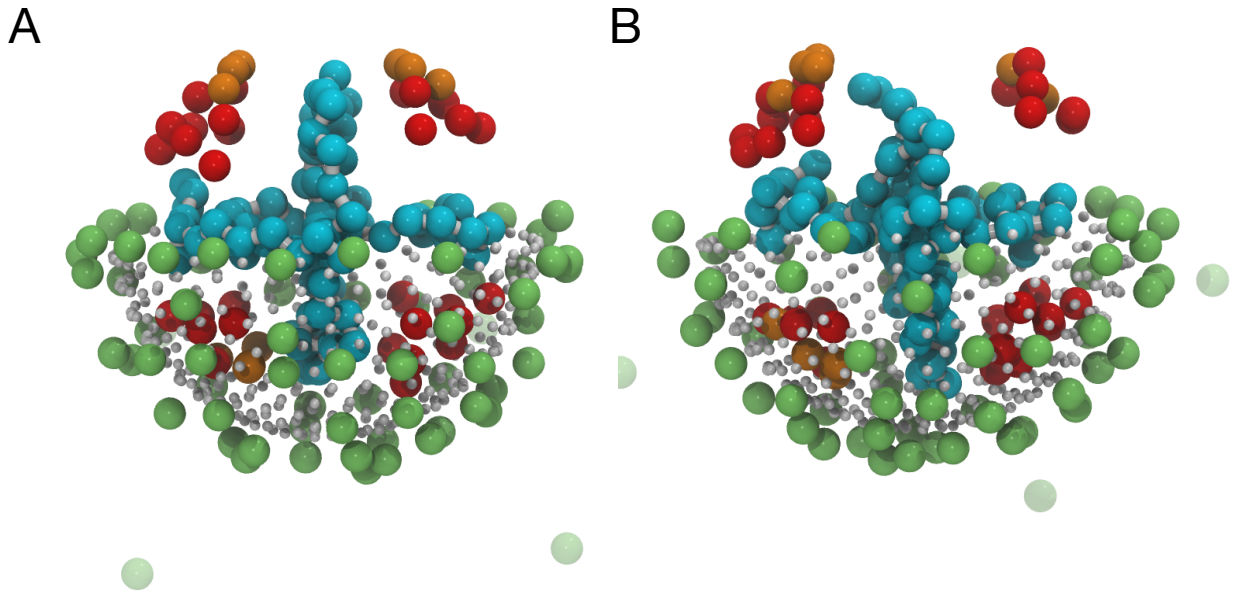

Figure S11: Representative snapshots of the equilibrium conformations of the polyelectrolyte for different dimensionless surface charge densities: A) $q_f\sigma^2/q = 0.3$; B) $q_f\sigma^2/q = 0.4$, where q is the monomer charge and σ is the distance unit of the exclude volume interaction between the monomers (i.e. the Weeks-Chandler-Andersen potential). Trivalent counterion fraction is $\phi_m = 0.3$.

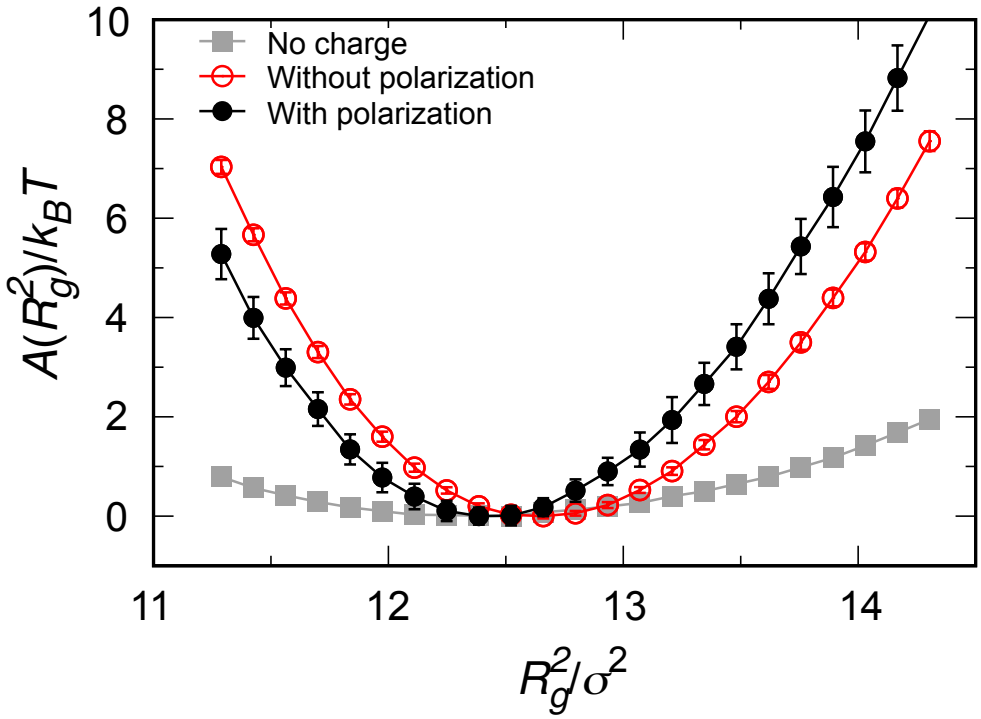

Figure S12: Representative equilibrated configuration of the monomers when the cavity surface is charge neutral $q_f = 0$. Error bars are the statistical errors obtained from bootstrapping analysis using WHAM. Trivalent counterion fraction is $\phi_m = 0.1$.

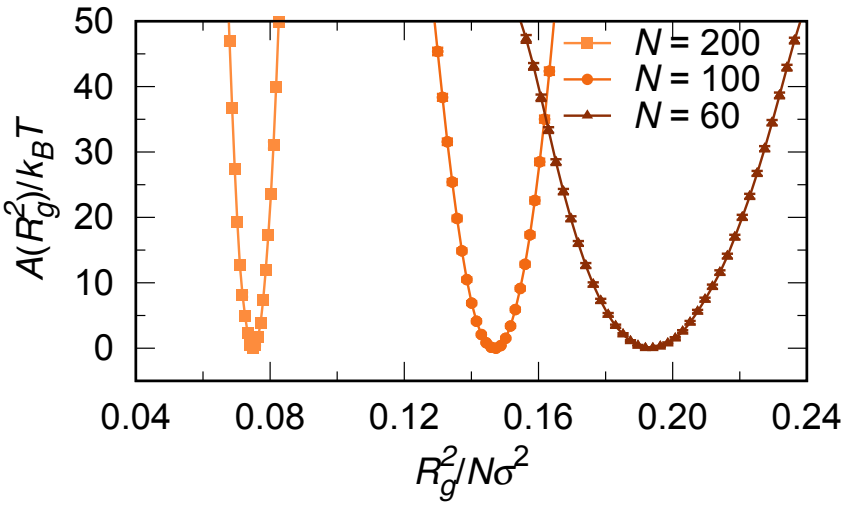

Figure S13: Free energy profiles of the polyelectrolyte (squared) radius of gyration for different chain lengths N for the same cavity radius $R = 6\sigma$. Trivalent counterion fraction is $\phi_m = 0.3$.

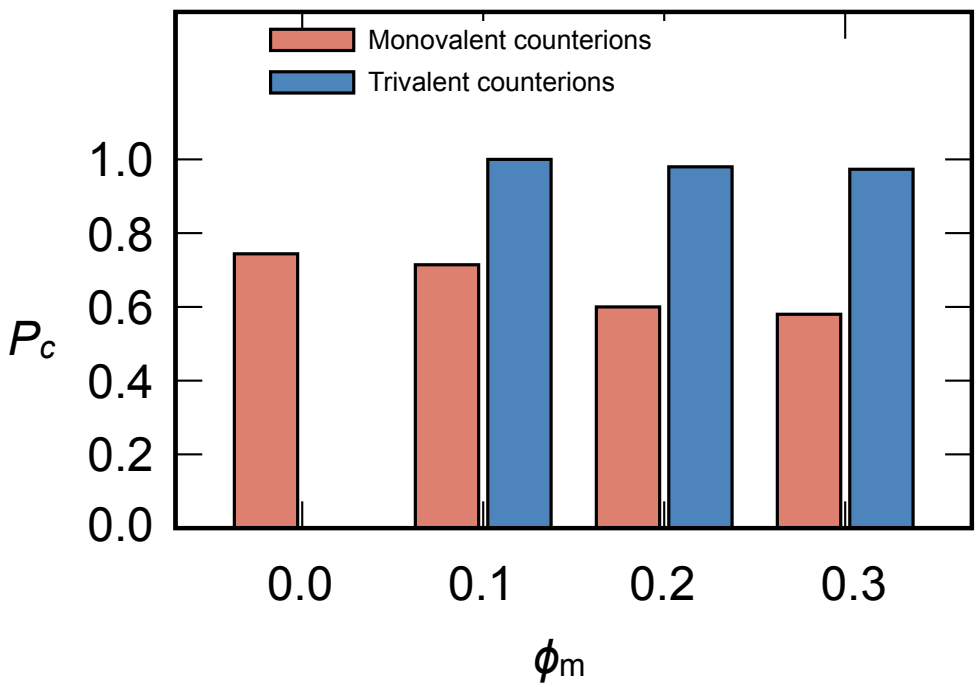

Figure S14: Probability of observing condensed counterions as a function of trivalent counterion fraction, ϕ_m. A counterion is considered condensed if it is within a cutoff distance of 1.2σ from a monomer of the polyelectrolyte. The cavity radius is $R = 6\sigma$. The cavity surface is charge neutral $q_f = 0$.