Supporting Information: Complex Coacervation of Statistical Polyelectrolytes: Role of Monomer Sequences and Formation of Inhomogeneous Coacervates

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1 Comparison of statistical properties of monomer sequence generated from simulation with theoretical prediction

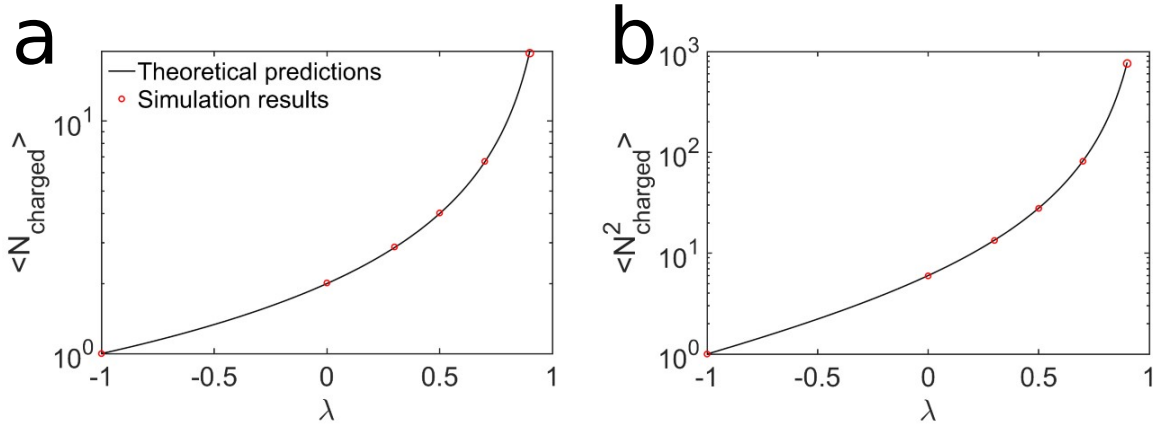

Figure S1: Semi-log plot of average charged block length $\langle N_{charged} \rangle$ and average squared charged block length $\left\langle N^2_{charged} \right\rangle$ as a function of λ for charge density $f = 0.5$. Black solid lines are theoretical prediction: $N_{charged} = \frac{1}{(1-\lambda)(1-f)}$ and $N^2_{charged} = \frac{1+f+\lambda(1-f)}{(1-\lambda)^2(1-f)^2}$. Red dots are simulation results. The $\langle ... \rangle$ denotes ensemble average over all chains.

2 The importance for experimental study to maintain same charge density f for polyanions with different λ values in order to verify computational and theoretical results

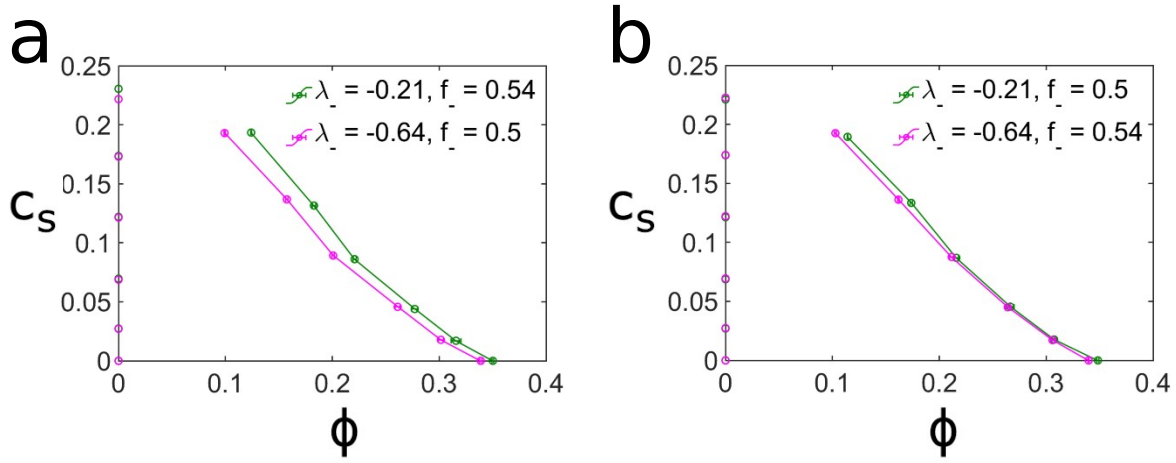

Figure S2: Simulation binodal curves for coacervates formed by fully charged polycations ($f_+ = 1$) and polyanions with charge density f_- and sequence λ_-. a: Simulation results for the conditions of our initial experimental attempt. b: Simulation results for the conditions similar to a, but reversing the f_- of the two systems. Comparing a and b shows that besides λ_-, f_- also affects coacervation behavior which needs to be controlled more preciously.

3 Dependence of coacervate density on λ for different neutral monomer sizes

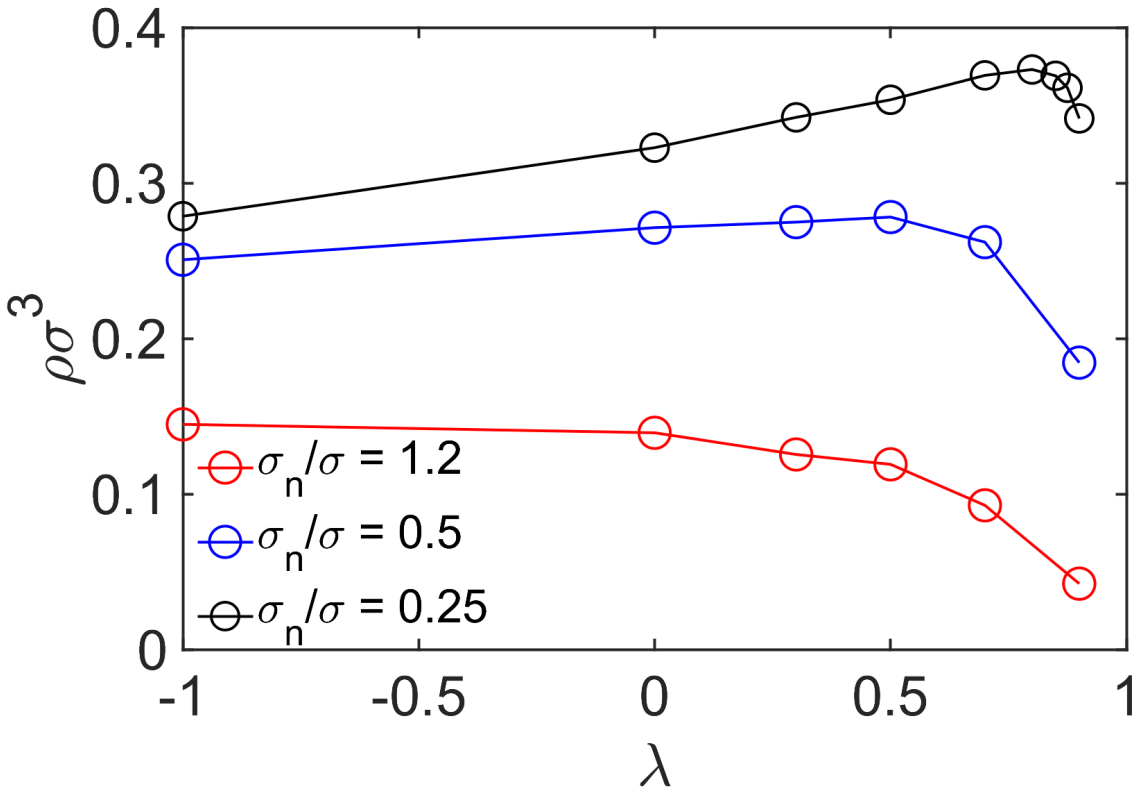

Figure S3: Dependence of the coacervate density on λ for different sizes of the neutral monomer, $\sigma_n/\sigma = 1.2$, 0.5, and 0.25. The errors are smaller than the circle symbols. Simulation parameters are equal to $f_+ = f_- = 0.5$, $N = 10^2$, and $l_B/\sigma = 1.68$; the solvent quality is good. Increasing the size of the neutral monomer facilitates microphase separation, and λ^* shifts to lower values.

4 Simulation snapshots of salt-free coacervate phases formed by charged block copolymers

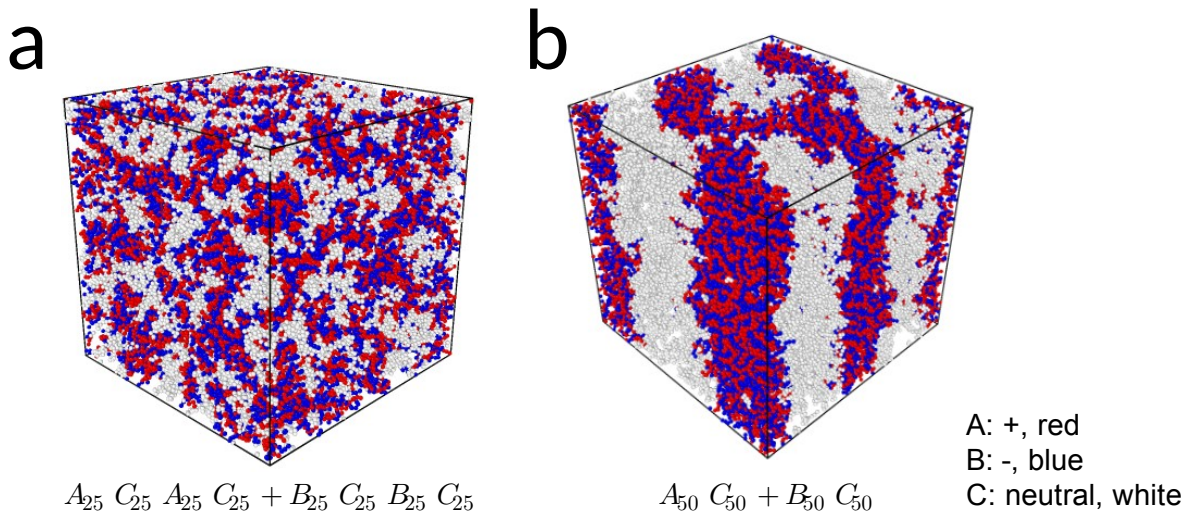

Figure S4: Simulation snapshots of salt-free coacervate phases formed by charged block copolymers using the same simulation parameters as statistical polyelectrolytes. Simulation parameters: $f_+ = f_- = 0.5$, $N = 10^2$, and $l_B/\sigma = 1.68$ (good solvent). a: For tetrablock copolymers, the coacervate phase is still microemulsion-like structure with high fluctuation but no obvious long range order. b: For diblock copolymers, there is a lamellar-like structure forming within coacervate phase.

5 Structure factors for lamellar phase of salt-free complex coacervate formed by charged diblock copolyelectrolytes

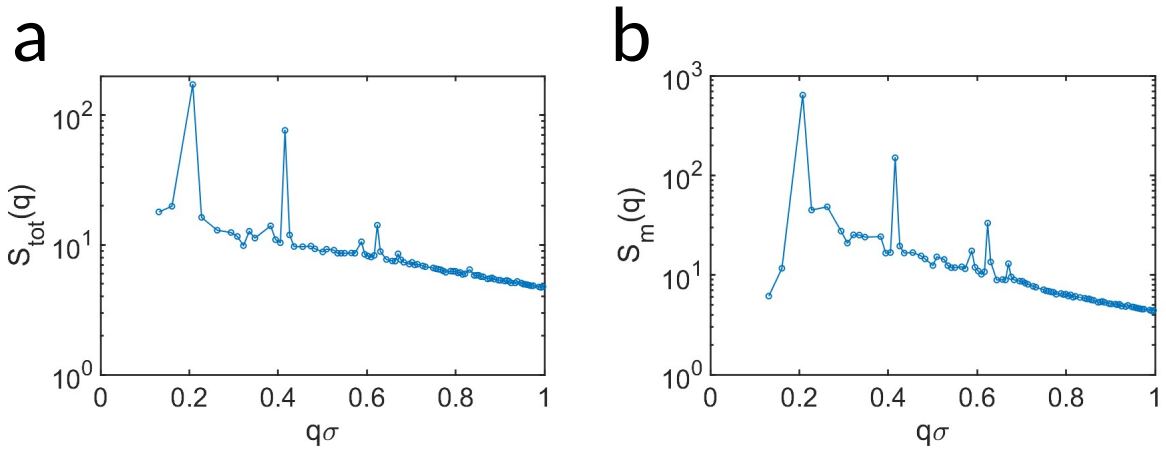

Figure S5: Structure factors for salt-free coacervates formed by oppositely charged diblock copolyelectrolytes (shown in Figure S4b). a: structure factor for all monomers, $S_{tot}(q)$ as a function of q in log-log scale. b: Structure factor of the density difference between neutral and charged monomers, $S_m(q)$ as a function of q in log-log scale. The peaks in structure factor plots are clear indications of lamellar-like structure within coacervate phase.

6 Structure factors for neutral and charged monomers of salt-free coacervate phases formed by polyelectrolytes with different λ values

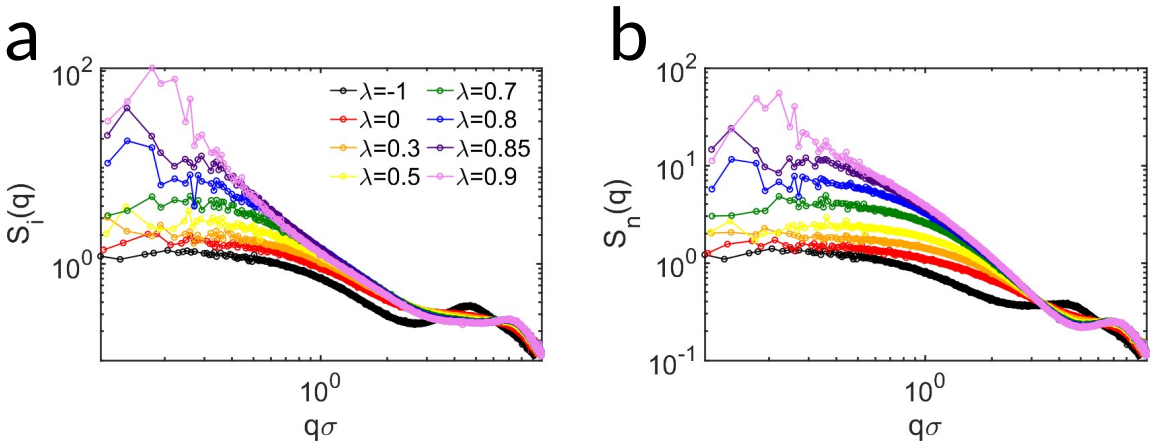

Figure S6: Structure factors for neutral and charged monomers within coacervate phases in log-log scale. Simulation parameters: $f_+ = f_- = 0.5$, $N = 10^2$, and $l_B/\sigma = 1.68$ (good solvent). a: Structure factor calculated for only ionic monomers, $S_i(q)$. b: Structure factors calculated for only neutral monomers, $S_n(q)$.

7 Inverse structure factor calculated based on density difference between neutral and charged monomers for $\lambda = -1$ deviates severely from Ornstein-Zernike expression

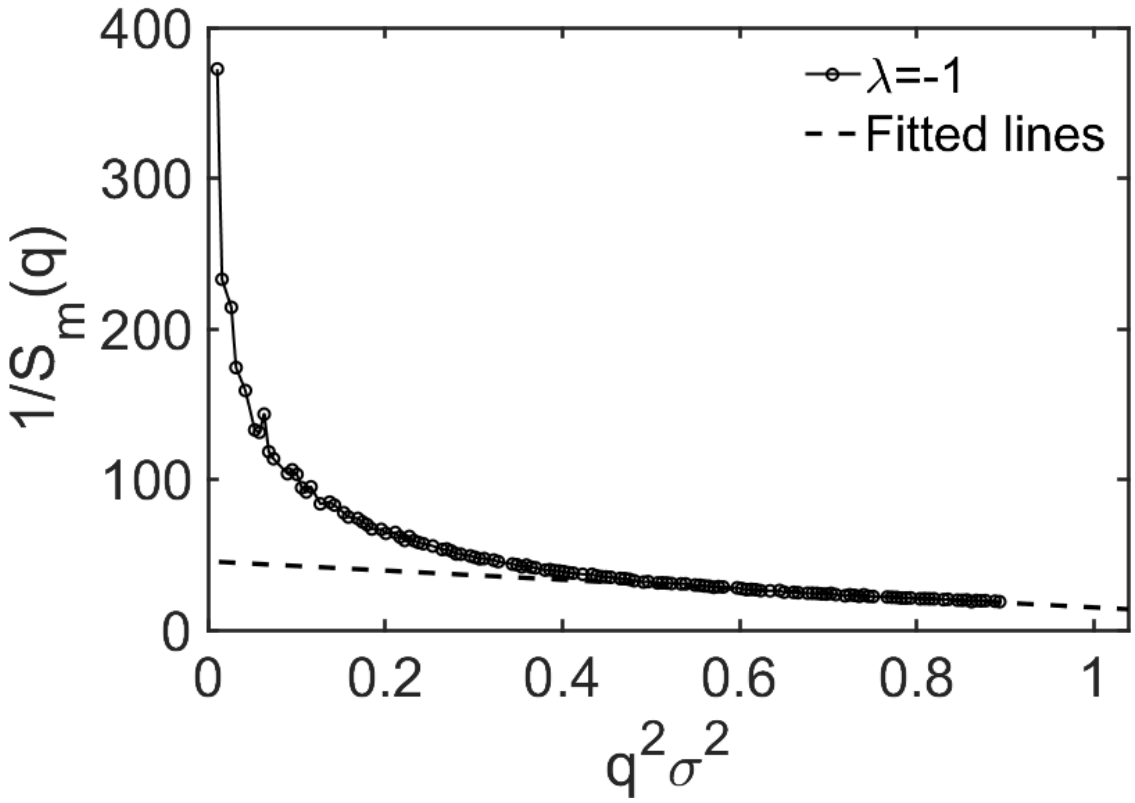

Figure S7: Inverse structure factors for $\lambda = -1$ as a function of q^2 fitted by Ornstein-Zernike expression. Simulation parameters: $f_+ = f_- = 0.5$, $N = 10^2$, and $l_B/\sigma = 1.68$ (good solvent).

8 Inverse structure factors calculated based on density difference between neutral and charged monomers for different λ values are fitted by microemulsion structure factor

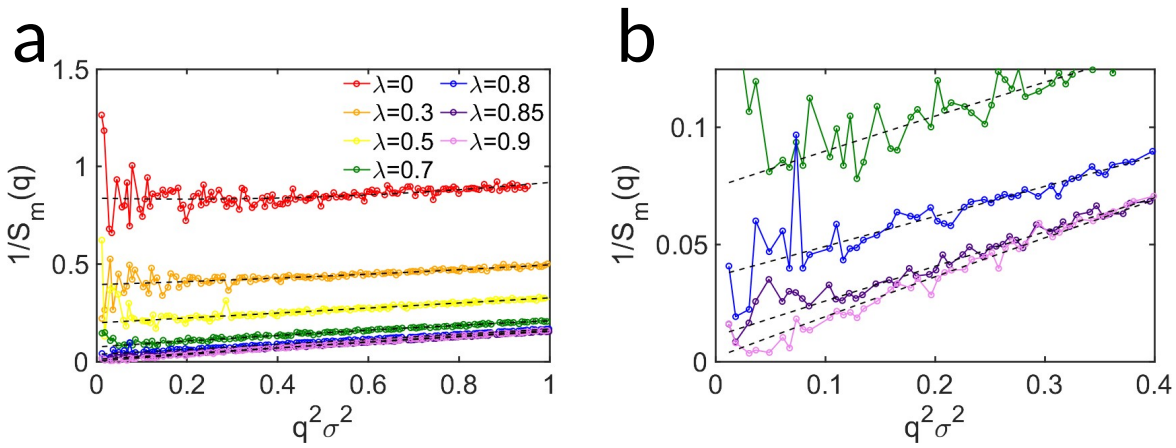

Figure S8: Inverse structure factors, $1/S_m(q)$ for different λ values as a function of q^2 fitted by microemulsion structure factor: $1/S(q)_m = c_0q^4 + c_1q^2 + c_2$. Dash lines are fitted lines. a: full plot with $0 < 1/S_m(q) < 1.5$ and $0 < q^2\sigma^2 \leq 1$; b: partially enlarged plot of a with $0 < 1/S_m(q) < 0.125$ and $0 < q^2\sigma^2 \leq 0.4$. Simulation parameters: $f_+ = f_- = 0.5$, $N = 10^2$, and $l_B/\sigma = 1.68$ (good solvent).

Table S1: Fitted coefficients of microemulsion structure factor for Figure S8.

λ	c_0	c_1	c_2
0	0.132	-0.051	0.838
0.3	0.030	0.072	0.394
0.5	0.004	0.124	0.198
0.7	-0.022	0.156	0.074
0.8	0.003	0.127	0.036
0.85	-0.008	0.151	0.011
0.9	-0.020	0.176	0.002

9 Inverse structure factors calculated based on density difference between neutral and charged monomers for different λ values are fitted by Porod's law

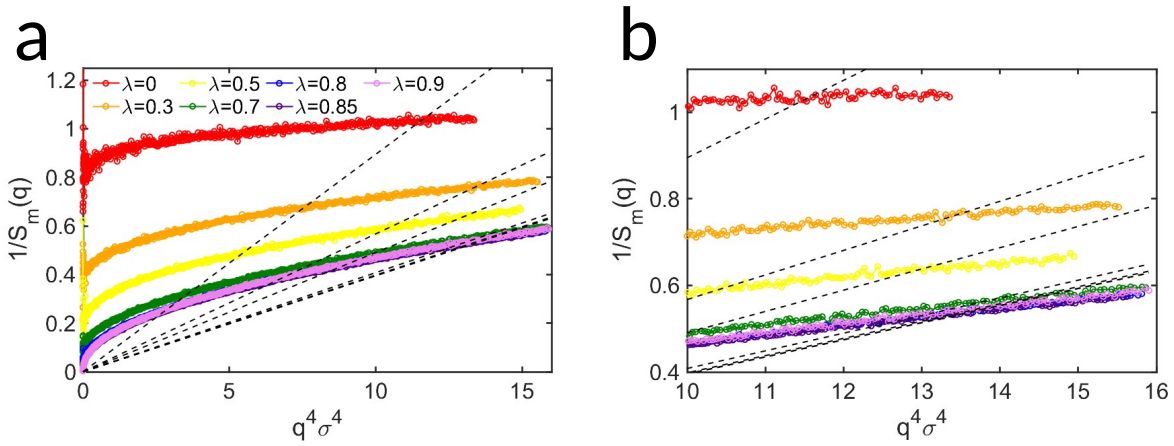

Figure S9: Inverse structure factors, $1/S_m(q)$ for different λ values as a function of q^4 fitted by Porod's law: $1/S(q)_m = c_0 q^4$ at high q regime ($10 < q^4\sigma^4 < 16$). Dash lines are fitted lines. a: full plot with $0 < 1/S_m(q) \leq 1.2$ and $0 < q^4\sigma^4 < 16$; b: partially enlarged plot of a with $0.4 \leq 1/S_m(q) \leq 1.2$ and $10 < q^4\sigma^4 < 16$. Simulation parameters: $f_+ = f_- = 0.5$, $N = 10^2$, and $l_B/\sigma = 1.68$ (good solvent).