Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Prediction of solvent-induced morphological changes of polyelectrolyte diblock copolymer micelles

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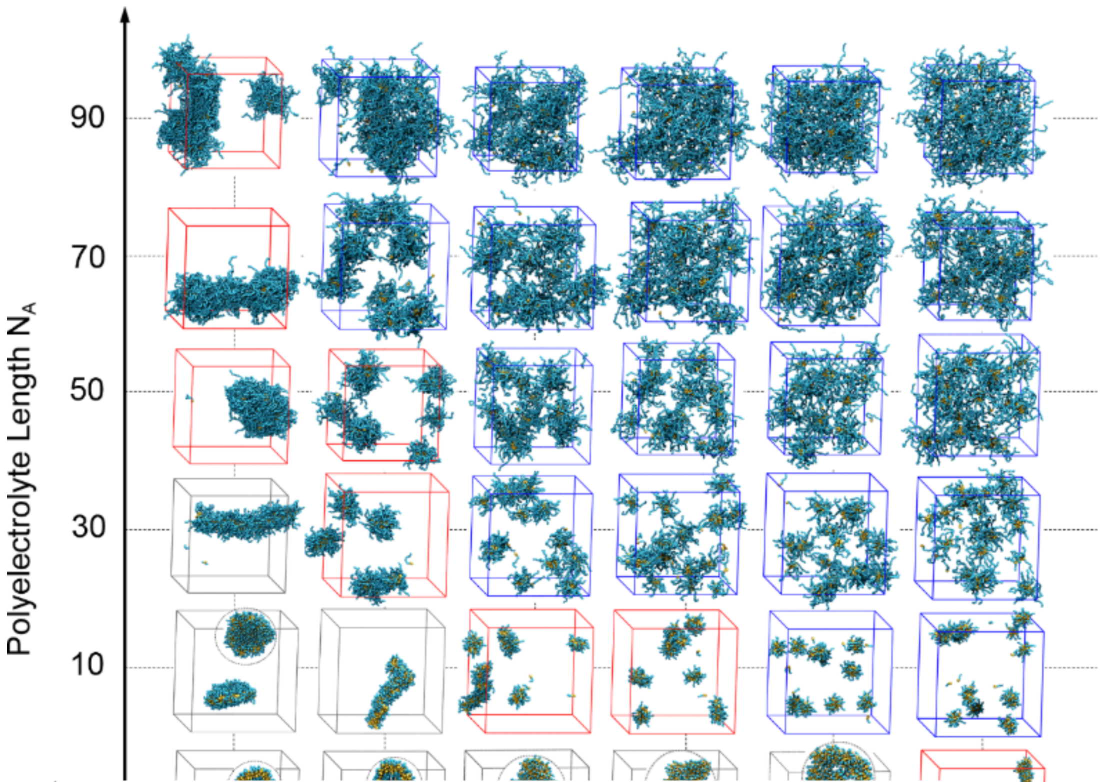
Methods: The properties of DPD system are expressed using dimensionless quantities in units of the cutoff r_c, the energy scale k_BT and the bead mass m_0. As a result, the unit of time, τ, is $\tau = \sqrt{r_c^2 m_0/k_BT}$. k_B=1.381*10^{-23} J/K is the Boltzmann constant, and T is the reference temperature in Kelvin.

In order to map the DPD model to the self-assembly system of single stranded DNA (ssDNA) amphiphiles , the above simulation parameters can be related to physical length and time scales by examining the properties of a single polyelectrolyte model in aqueous solutions.

The averaged bond length between successive beads from simulations of a single polyelectrolyte in aqueous solution is 0.2748±0.09913 when a_{elec} =15. The average segment length of polyT is approximately 6.5 Å according to the atomistic simulations of single stranded DNA [H. S. Kim et.al., In preparation], when the salt concentration is 0.5 M. This value can be used to establish a dimensional length scale in the DPD simulations and gives r_c= 2.3 nm. When we map one DPD polyelectrolyte bead with one monomer in polyT, the mass of one monomer is what the mass unit m_0 represented, which is 5.35*10^{-22} g. As a result, $\tau = 0.26*10^{-10}$ s.

(a)


90
70
50
30
10
Polyelectrolyte Length N_A
0

(b)

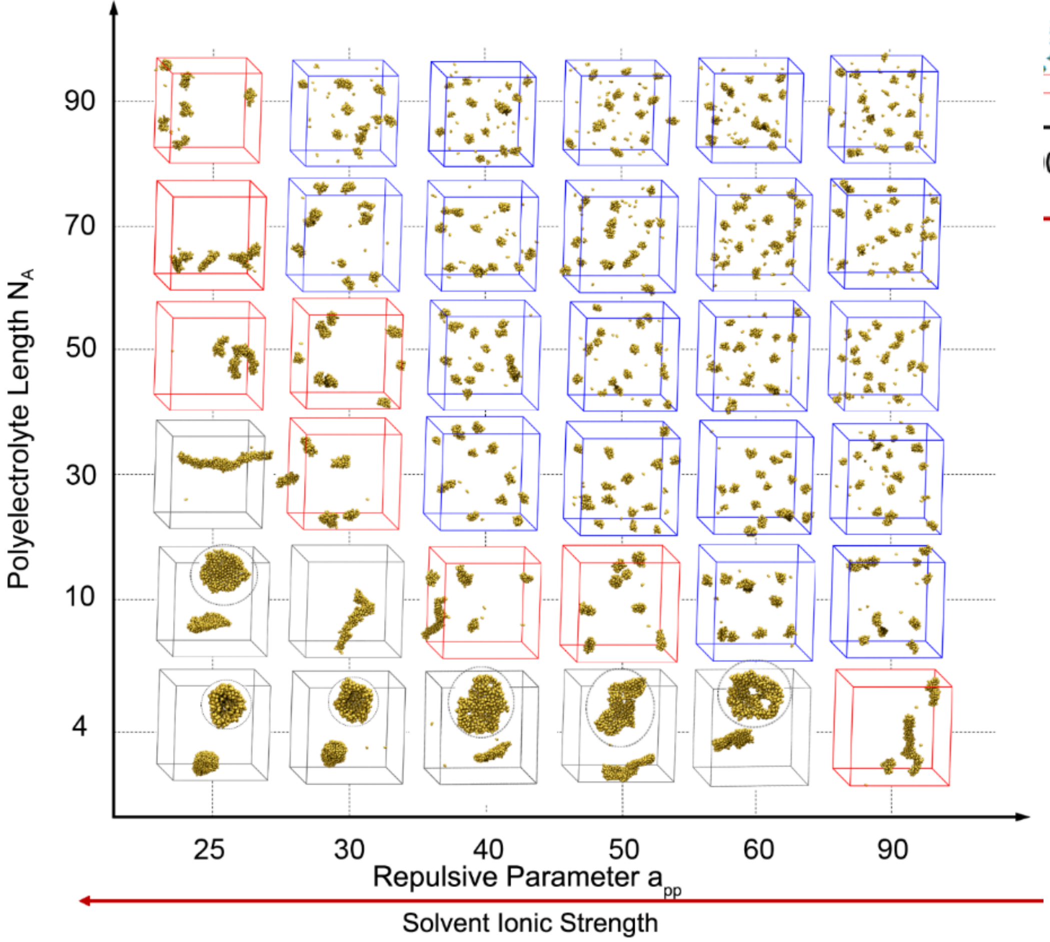

90
70
50
30
10
4
Polyelectrolyte Length N_A
25
30
40
50
60
90
Repulsive Parameter a_{pp}
Solvent Ionic Strength

Figure S1. Phase diagrams of dilute aqueous solution of polyelectrolyte diblock copolymers obtained by DPD simulations. Both hydrophobic and polyelectrolyte beads are displayed in (a) and only hydrophobic beads are displayed in (b). Aggregates formed by all 300 chains, including vesicles, lamellar shape or pretzel shape are outlined with a black box, wormlike/cylindrical micelles with a red box, and spherical micelles with a blue box. The section view for vesicles and side view for lamellar shapes are displayed in dash circle.

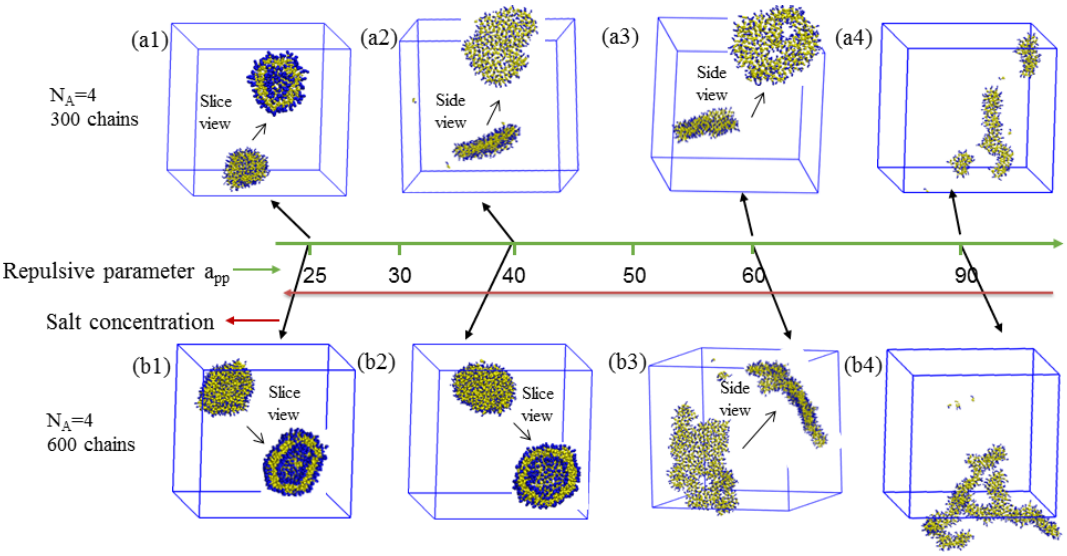
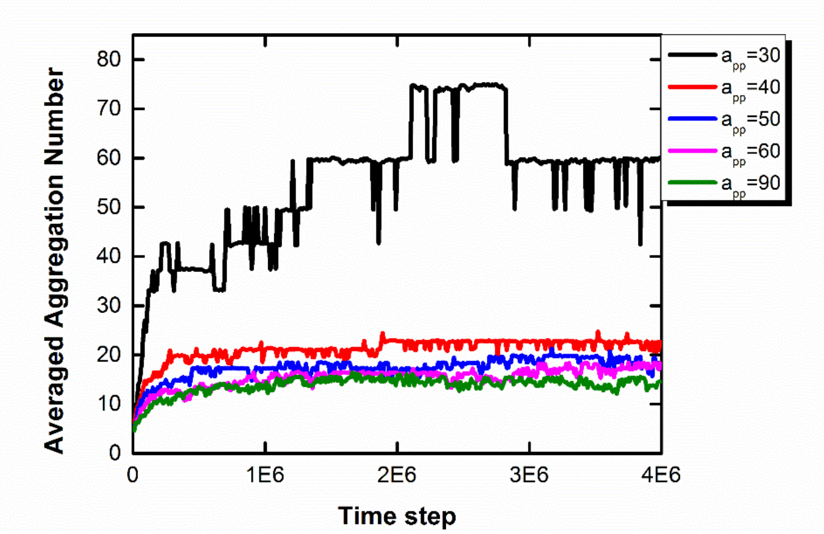


Figure S2. Typical snapshots of polyelectrolyte block copolymers in aqueous solution at N_A=4. Total number of chains is 300 (a1, a2, a3 and a4) and 600 (b1, b2, b3 and b4).

To reveal the effect of PDC concentration on the morphology of larger aggregates, we also performed simulations at higher copolymer concentrations, i.e., with 600 chains. Figure S2 shows the equilibrium snapshots of copolymer aggregates ($N_B = N_A = 4$) with respect to a_{pp}. With a relatively short hydrophilic block, the transition from wormlike/cylindrical micelles to lamellar-like aggregates and further to vesicles, was observed upon an increase in the ionic strength (decreasing a_{pp}), which is consistent with experimental observations.[1] Upon increasing the total chain number to 600, a further growth of the cylindrical micelles into network-like structures with Y-junctions was found (Figure S2b4). An intermediate morphology between cylindrical micelles and lamellae was also present (Figure S2a3).

(a)


Averaged Aggregation Number
80
70
60
50
40
30
20
10
0
0
1E6
2E6
3E6
4E6
Time step
a_{pp}=30
a_{pp}=40
a_{pp}=50
a_{pp}=60
a_{pp}=90

(b)

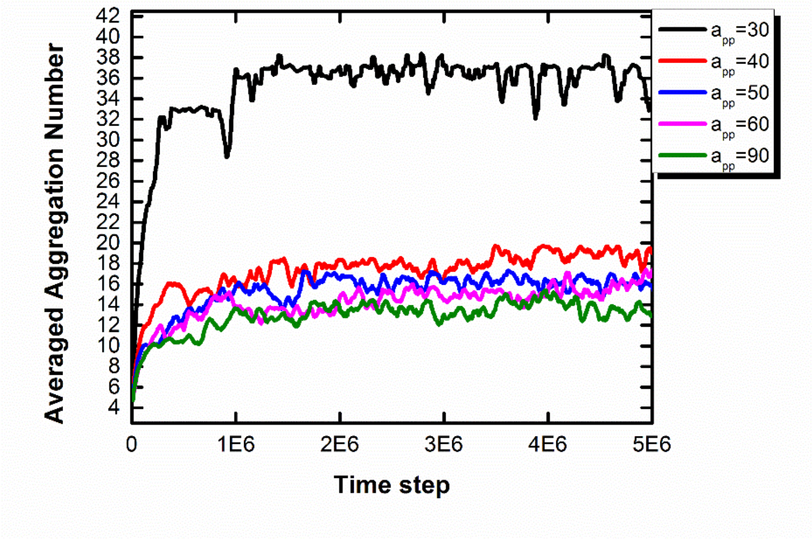


Figure S3. Temporal evolution of averaged aggregation number P for (a) N_A=30 and (b) N_A=50.

Figure S3 shows the typical variation of the averaged aggregation number P with time for N_A =30 and 50 with different a_{pp}. It can be seen that after 3.0E6 time steps, the aggregation numbers stay around a final value which indicates that the system has reached equilibrium. Evidently, after equilibrium, we have continually observed frequent exchanges of chains between micelles, and the outcome of the kinetic process guarantees true equilibrium.

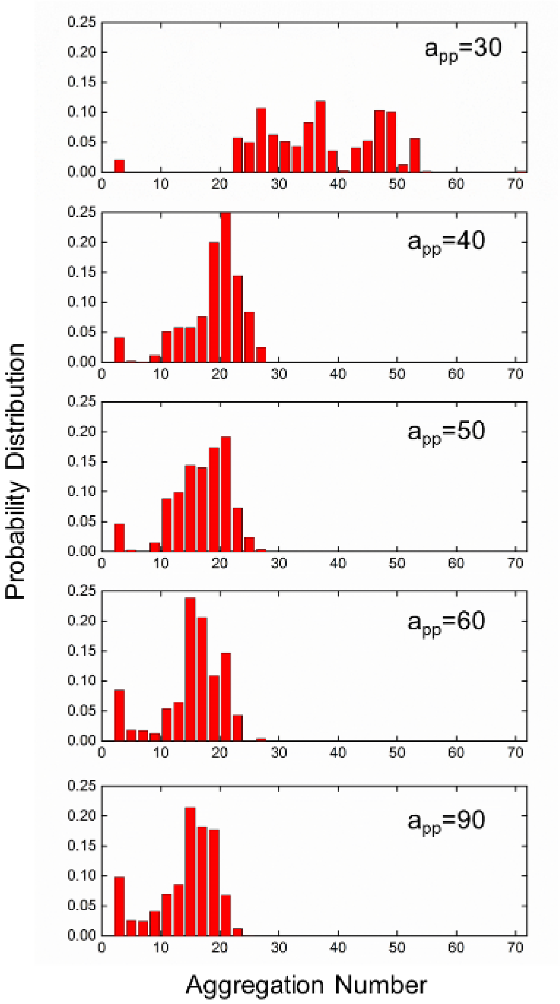


Figure S4. Probability distribution of the aggregation number when N_A=50

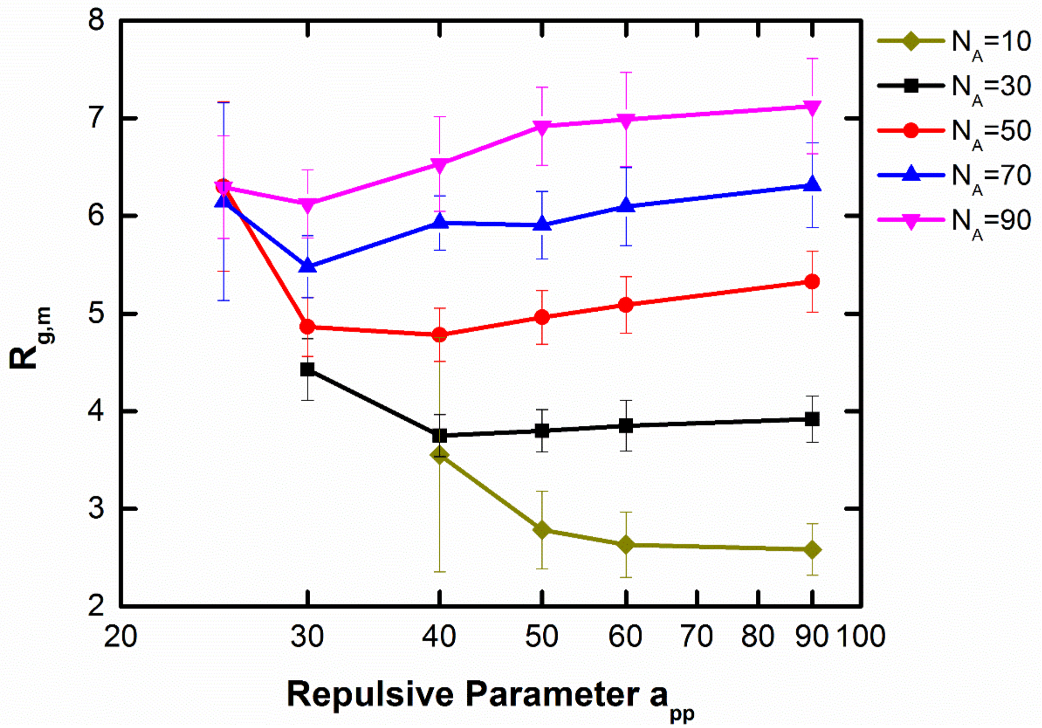


Figure S5. Radius of gyration of the micelles $R_{g,m}$ from DPD simulations as a function of repulsive parameter a_{pp}.

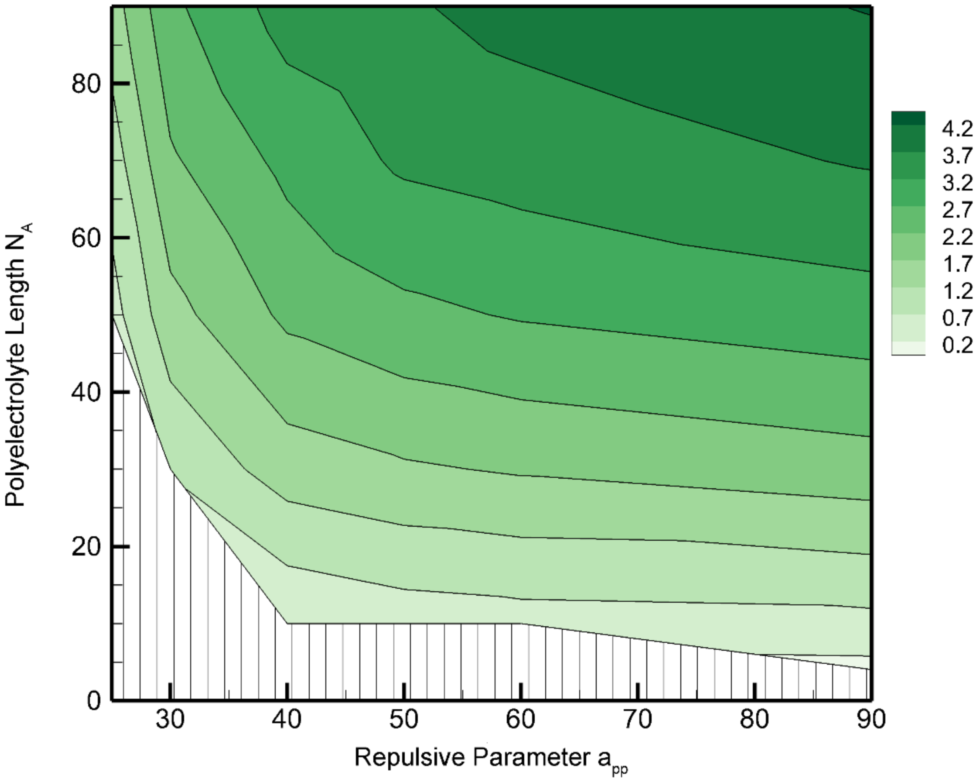


Figure S6. Contour plot of ratio of the thickness of corona H_{corona} to the radius of core $R_{g,c}$. The region with aggregates formed by all chains is shadowed.

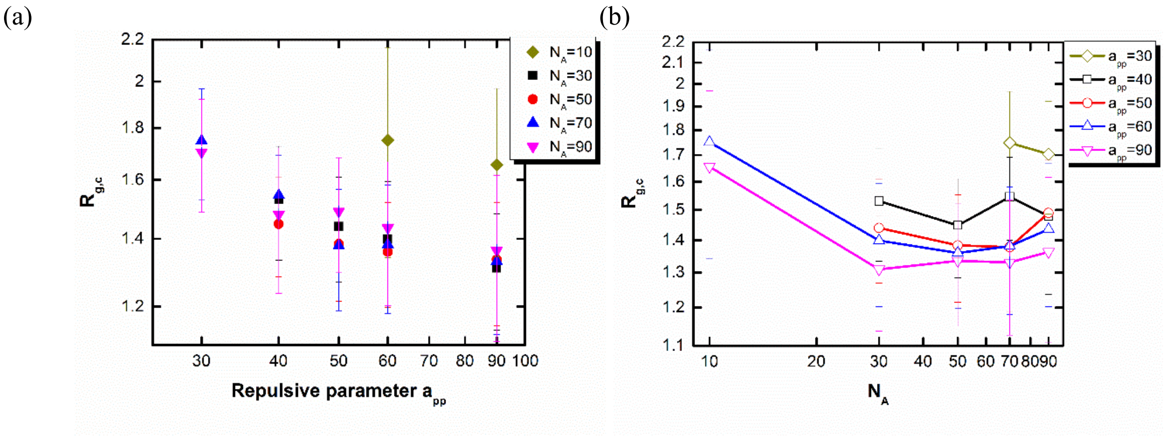


Figure S7. The radius of gyration of micellar core as a function of a_{pp} (a) and N_A (b).

Table S1. Micellar size from AFM images at different salt concentrations.

λ	6.1E-5	3.1E-3	3.1
Diameter / nm	25.2 ± 8.0	22.5 ± 9.0	28.5 ± 6.8
Height / nm	9.5 ± 2.7	7.3 ± 2.0	8.0 ± 1.8

Table S2. Experimental results.

λ / Charge Ratio	NaCl / [M]	Rg / nm
0.18904	5.44E-04	20.483±0.293
0.09443	0.00118	19.973±0.415
0.02656	0.00439	19.439±0.653
0.00366	0.032	16.726±0.515
0.0016	0.072	16.989±0.496
5.93E-04	0.15086	17.19±0.397
2.63E-04	0.30123	17.003±0.311
9.85E-05	0.70117	20.023±0.643
4.82E-05	1.23523	21.378±0.844
1.99E-05	2.20111	23.101±0.633

1. Regenbrecht, M.; Akari, S.; Förster, S.; Möhwald, H. Shape Investigations of Charged Block Copolymer Micelles on Chemically Different Surfaces by Atomic Force Microscopy. *The Journal of Physical Chemistry B* **1999**, 103, 6669.