Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplemental Information for:

The influence of ionic strength and mixing ratio on the colloidal stability of PDAC/PSS polyelectrolyte complexes

Yanpu Zhang[a], Erol Yildirim[b], Hanne S. Antila[b], Maria Sammalkorpi[b], Luis D. Valenzuela[a], and Jodie L. Lutkenhaus*[a]

[a]Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States

[b]Department of Chemistry, Aalto University, P.O. Box 16100, 00076 Aalto, Finland

Part 1. Experimental data

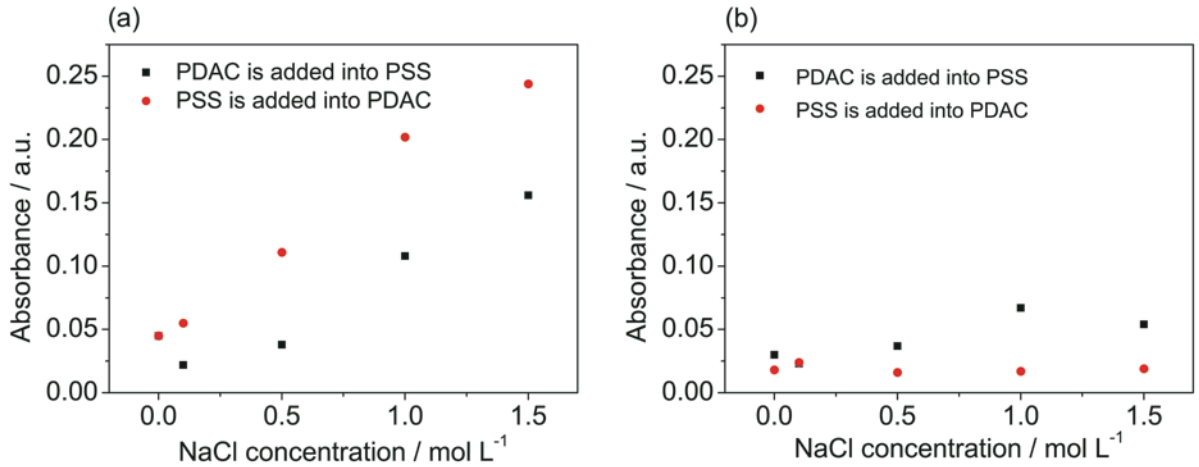

Figure S1. Turbidity of newly prepared complexes with different mixing order. The complex are prepared from (a) 20 mol% PDAC, (b) 80 mol% PDAC, respectively.

The order of mixing is another factor that affects the PEC formation, suggestive of a kinetically trapped state . The overall trend is similar regardless of mixing order but the exact

turbidity value varies, which is consistent with Chen's work.[1] Here, PDAC was always added into PSS to eliminate the effect of this variable.

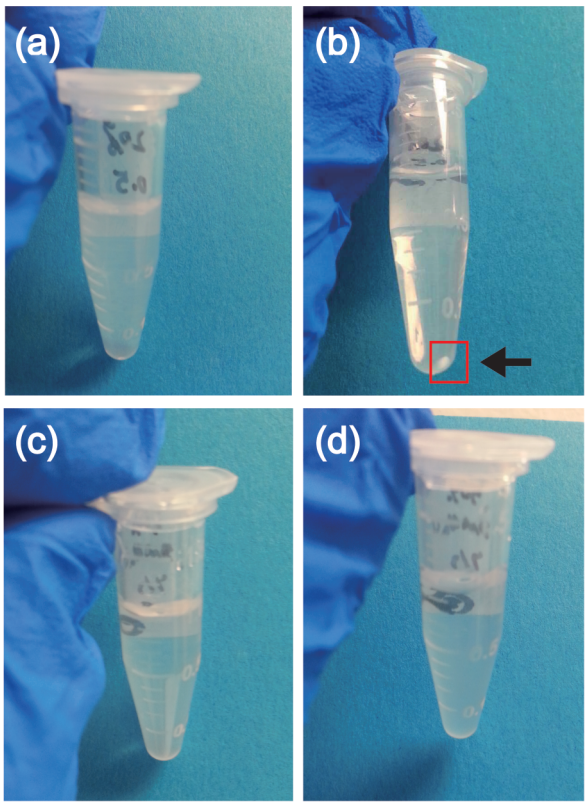

Figure S2. Optical images of PEC aged for 24hs. 20 mol% PDAC, 0.5 M NaCl (upper panel) before (a) and after (b) centrifugation. 50 mol% PDAC, 3.0 M NaCl (lower panel) before (c) and after (d) centrifugation. Centrifugation parameters: 8500 rpm, 15 min. The black arrow and red square help to observe the white precipitate of complex.

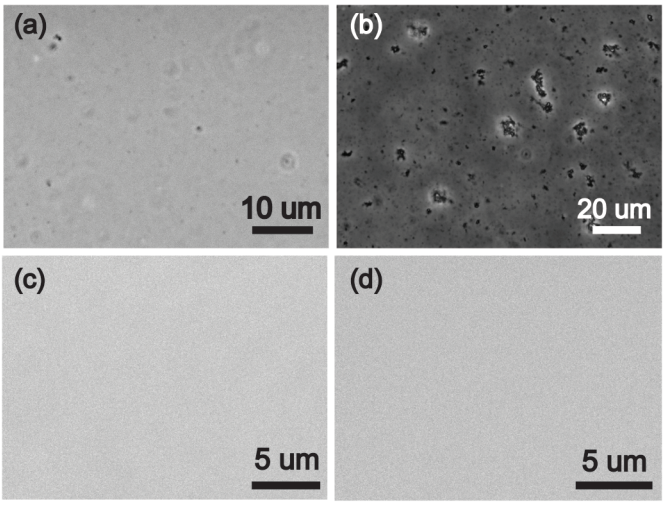

Figure S3. Optical microscope images of PECs aged for 24hs. 20 mol% PDAC, 0.5 M NaCl (upper panel) before (a) and after (b) centrifugation. 50 mol% PDAC, 3.0 M NaCl (lower panel) before (c) and after (d) centrifugation.

Light microscope images acquired on Zeiss Axiophot microscope using 100x/1.3 oil immersion and a 40x/0.75 dry objectives, phase contrast optics and a Photometrics Coolsnap CF CCD camera. Image capture was controlled by Metavue v. 5 software (Media Cybernetics, USA). The features in Figure 4a and 4b are consistent with a complex precipitate. The lack of features in Figure 4c and 4d are consistent with the solution phase.

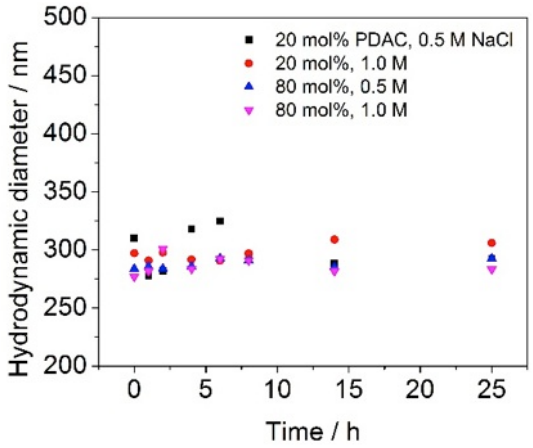

Figure S4. Time-lapsed hydrodynamic diameter of stable PECs.

Part 2. Simulation details and parameter values

In the molecular dynamics simulations, a cut-off distance of 12.5 Å was used for the van der Waals interactions and the Ewald summation method with accelerated convergence of lattice sums[2, 3] was used. The pressure was maintained at 1 atm by using the Andersen barostat method using a piston mass of 20 a.m.u[4]. The Nosé-Hoover-Langevin method[5] which is superior in thermostatting compared to the original Nosé thermostat, was used to maintain the temperature at 300 K with Q, mass of the time-scaling coordinate ratio of 10958 kcal/mol·ps^2. [6-8] Using this NPT ensemble setup, three different complex structures for each of the nine studied systems were relaxed for 1 ns after which data was collected for 100 ps at 5 ps intervals**.**

The initial configurations for the molecular dynamics simulations were initially generated within the Amorphous Cell tool in Accelrys Materials Studio Software. Amorphous Cell builds disorganized polymer conformations by employing a sampling method developed by Theodorou.[9] In this, a force-field defined distribution of polymer backbone torsion angles with the constraint that close contacts between atoms in a cell are minimized and no overlap or ring spearing exists are used. Out of 100 different generated stable complexes, three lowest energy structures for each composition were selected for further simulations. This procedure ensures relatively low energy, representative structures for the complexes. The obtained structures were then solvated by explicit water molecules in 8 nm^3 boxes with periodic boundary conditions. Finally, to obtain the initial configuration for the molecular dynamics simulations, the resulting 27 simulation systems were minimized in energy with conjugate gradient algorithm for 5000 steps.

Table S1. Summary of simulated systems. Subscript 40 refers to the number of monomers in each PSS or PDAC chain. Simulation box size is between (7.8 nm)^3 and (8.1 nm)^3 depending on the system. Na^+ and Cl^- columns show the total number of ions (counterions and excess salt). All systems are solvated by 15000 water molecules.

Simulated system	PSS/PDAC molar ratio	Excess salt	Na^+	Cl^-	H_2O
1 PSS_{40} -5 $PDAC_{40}$	0.167	none	40	200	15000

1 PSS_{40} -5 $PDAC_{40}$-1 M	0.167	1 M NaCl	340	500	15000
1 PSS_{40} -5 $PDAC_{40}$-2 M	0.167	2 M NaCl	640	800	15000
3 PSS_{40} -3 $PDAC_{40}$	0.500	none	120	120	15000
3 PSS_{40} -3 $PDAC_{40}$-1 M	0.500	1 M NaCl	420	420	15000
3 PSS_{40} -3 $PDAC_{40}$-2 M	0.500	2 M NaCl	720	720	15000
5 PSS_{40} -1 $PDAC_{40}$	0.833	none	200	40	15000
5 PSS_{40} -1 $PDAC_{40}$-1 M	0.833	1 M NaCl	500	340	15000
5 PSS_{40} -1 $PDAC_{40}$-2 M	0.833	2 M NaCl	800	640	15000

References

1. J. Chen, J. A. Heitmann and M. A. Hubbe, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2003, **223**, 215-230.
2. P. Ewald, *Ann. Phys*, 1921, **64**, ll.
3. N. Karasawa and W. A. Goddard III, *The Journal of Physical Chemistry*, 1989, **93**, 7320-7327.
4. H. C. Andersen, *The Journal of chemical physics*, 1980, **72**, 2384-2393.
5. A. A. Samoletov, C. P. Dettmann and M. A. Chaplain, *Journal of Statistical Physics*, 2007, **128**, 1321-1336.
6. P. H. Hünenberger, in *Advanced Computer Simulation*, Springer, 2005, pp. 105-149.
7. B. Leimkuhler, E. Noorizadeh and O. Penrose, *Journal of Statistical Physics*, 2011, **143**, 921-942.
8. N. Shuichi, *Progress of Theoretical Physics Supplement*, 1991, **103**, 1-46.
9. D. N. Theodorou and U. W. Suter, *Macromolecules*, 1985, **18**, 1467-1478.