Supporting Information

Equilibrium Overcompensation in Polyelectrolyte Complexes

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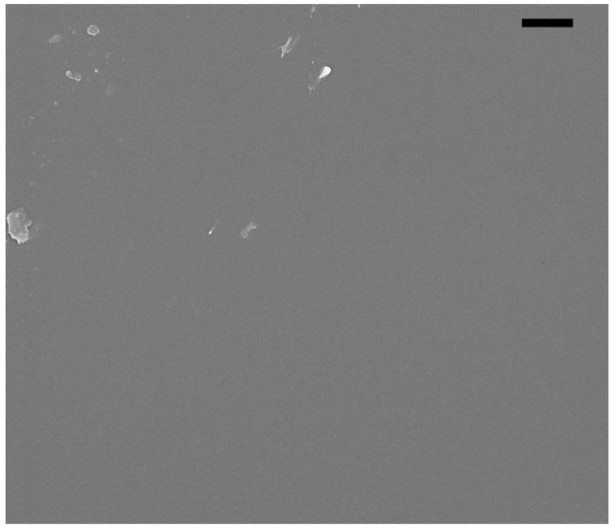

Figure S 1. SEM image of $(PDADMA/PSS)_{20}$ cycled 6 times between 30 min 2 M NaCl and 5 min 10 mM PSS79 in 1 M NaCl. Scale bar is 1 μm.

Table S1. Peak assignments for PDADMA/PSS films in transmission FTIR. Assignment is done based on separate and combined polymer spectra, and on the works of Yang et al.,[1] and Mwangi et al.[2]

Polymer	**Peak**	**Functional group**
PDADMA (obtained by subtracting 5% of 1010 and 1036 cm^{-1} PSS peaks combined area)	1473 cm^{-1}	C=C stretching (in a positively charged environment, contributed by the nitrogen)
PSS	1010 cm^{-1}	Aromatic ring
	1036 cm^{-1}	Sulfonate group
	1125 cm^{-1}	Aromatic ring
	1194 cm^{-1}	Sulfonate group
Nitrate	1345 cm^{-1}	

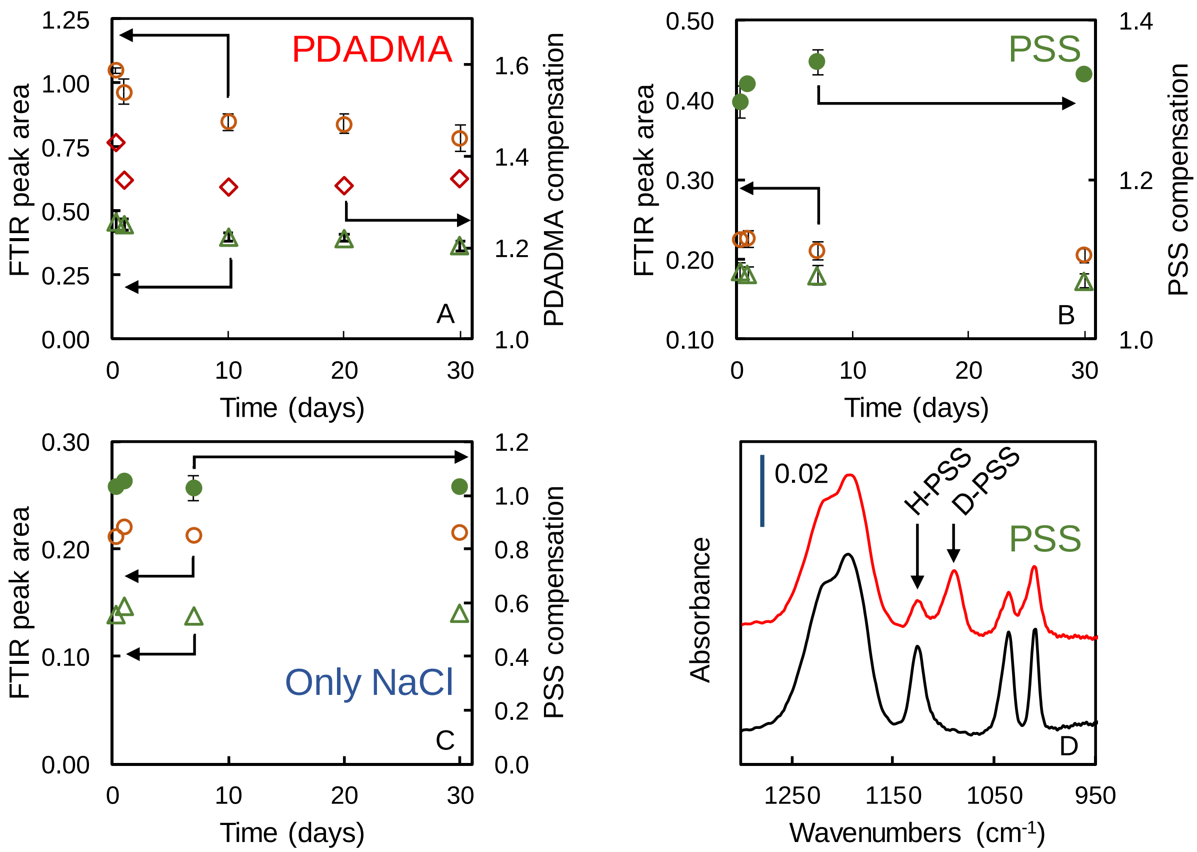

Figure S 2. (A) FTIR peak areas of PDADMA (○), PSS (△), and PDADMA/PSS (◇) ratio when the $(PDADMA/PSS)_{20}$ cycled film is soaked in 10 mM PDADMA500 in 1 M NaCl for an extended duration. (B) FTIR peak areas of PDADMA (○), PSS (△), and PSS/PDADMA (●) ratio when a stoichiometric $(PDADMA/PSS)_{10}$ film is soaked in 10 mM PSS79 in 1 M NaCl for an extended duration. (C) Stoichiometric $(PDADMA/PSS)_{10}$ soaked in 1 M NaCl (only salt) for an extended duration. (D) Lower spectrum (black): $(PDADMA/PSS)_{10}$ film, made and cycled with PSS127, then soaked in PSS127 in 1.4 M NaCl for 4h until overcompensation equilibrium is reached. Upper spectrum (red): After overcompensation equilibrium is reached, the same film is immersed in deuterated PSS, D-PSS110, for 30 days showing exchange of PSS by D-PSS (a decrease in the H-PSS peak and an increase in the D-PSS peak).

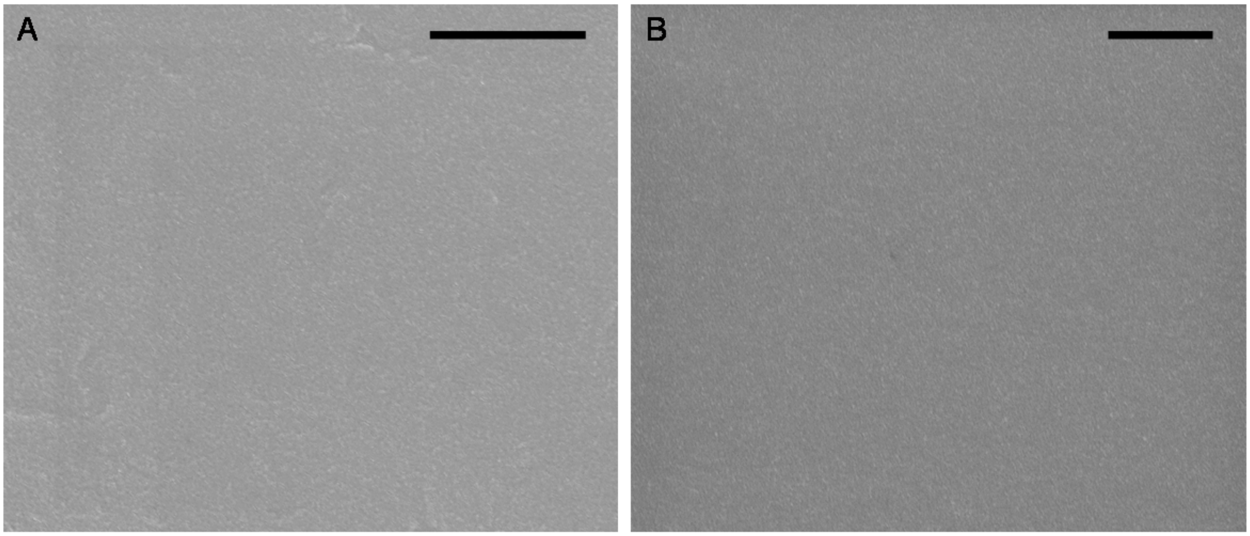

Figure S 3. (A) SEM image of $(PDADMA/PSS)_{20}$ after 3 h in 10 mM PDADMA500 in 1 M NaCl. (B) SEM image of $(PDADMA/PSS)_{20}$ after 2 h in 10 mM PSS79 in 1.4 M NaCl. Scale bars are 1 µm. Scratches were from repetitive manipulation.

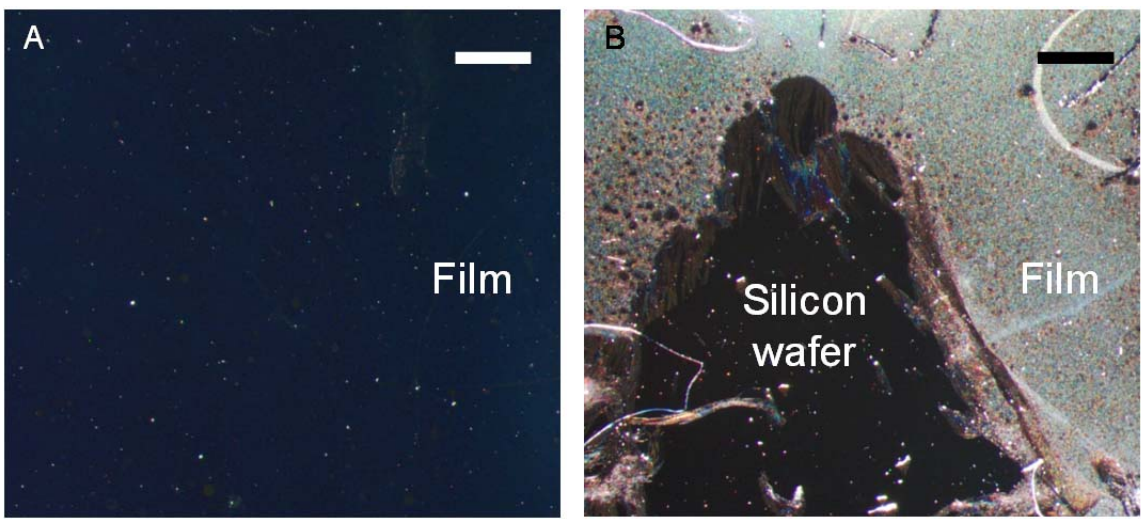

Figure S 4. (A) Representative image of a PSS overcompensated 20 layer film after 2 h in 10 mM PSS79 in 1 M NaCl. (B) Image of a PSS overcompensated film showing the effect of erosion after 2 h in 10 mM PSS600 in 1.4 M NaCl. Scale bars are 1 mm.

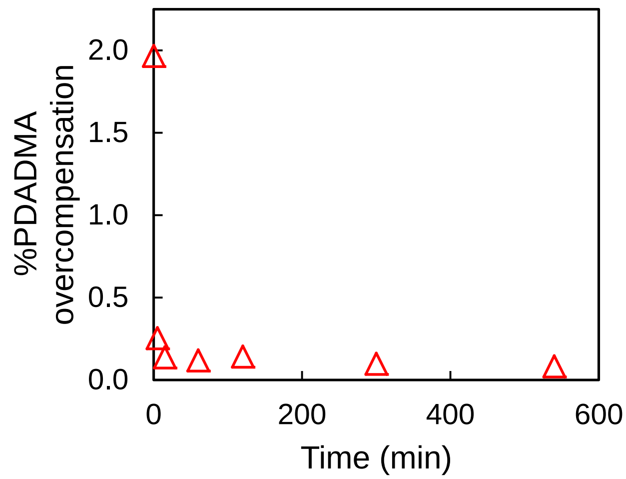

Figure S 5. ^{22}NaI radiolabeling during the addition of 10 mM PDADMA in 1 M NaCl to a stoichiometric $(PDADMA/PSS)_{20}$ film. The ^{22}Na, taken here as percent of PDADMA overcompensation, is used to show that no neutral salt enters the film during overcompensation.

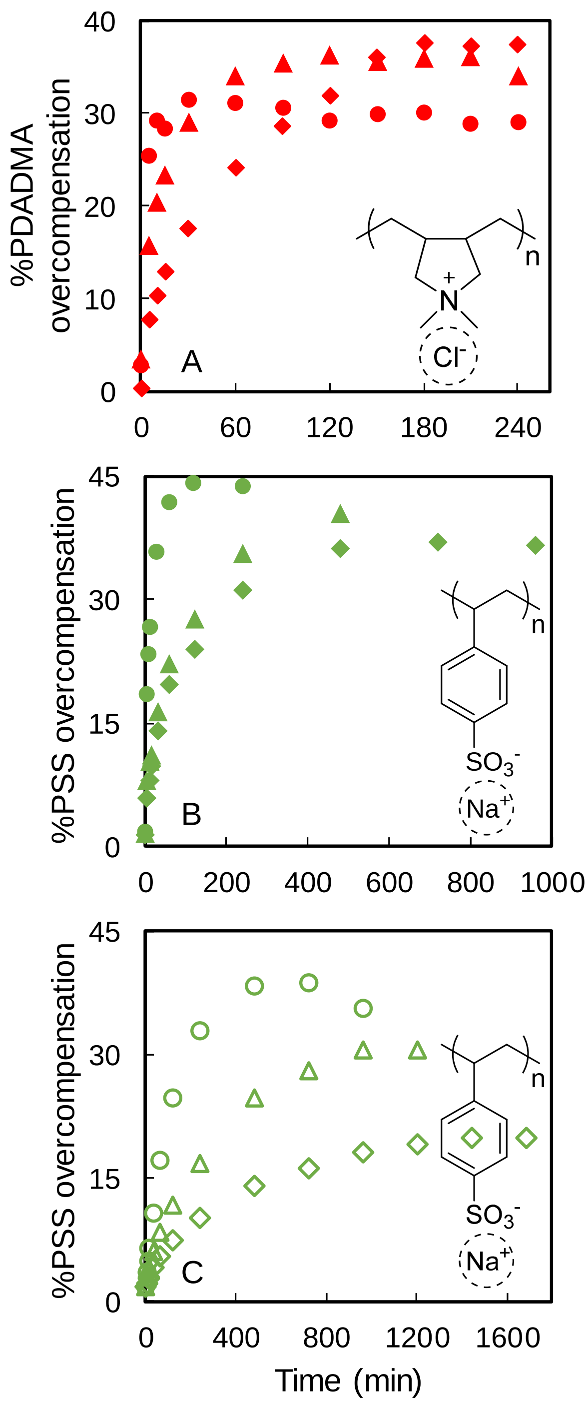

Figure S 6. (A) PDADMA percent overcompensation during addition of 10 mM PDADMA500 in 1 M NaCl to stoichiometric 20 (●), 30 (▲) and 40 (◆) layer (PDADMA/PSS) films. Precision is ± 4% on average. (B) PSS percent overcompensation during the addition of 10 mM PSS79 in 1.4 M NaCl to stoichiometric 20 (●), 30 (▲) and 40 (◆) layer (PDADMA/PSS) films, and (C) during addition of 10 mM PSS79 in 1 M NaCl to stoichiometric 20 (○), 30 (△), and 40 (◇) layers of the same type of films. Precision is ± 2% on average.

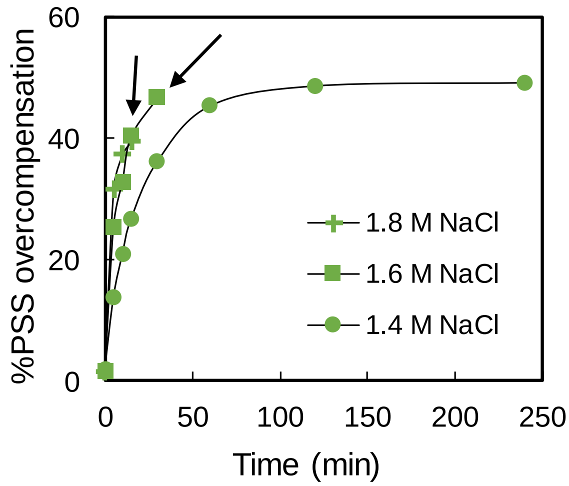

Figure S 7. PSS overcompensation during the addition of 10 mM PSS79 in 1.4 (●), 1.6 (■), and 1.8 M (+) NaCl to stoichiometric $(PDADMA/PSS)_{10}$ films. The arrows show the point where the films significantly erode and dissolve. Lines are a guide to the eye.

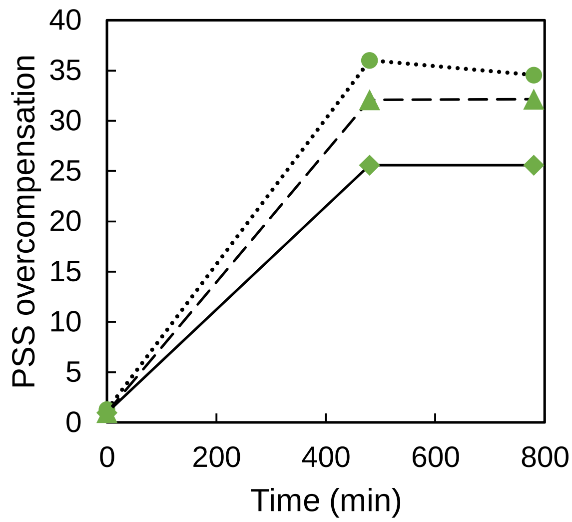

Figure S 8. PSS overcompensation obtained by $^{22}Na^{+}$ radiolabeling of stoichiometric 20 (●), 30 (▲) and 40 (◆) layer PEC films soaked in 10 mM PSS in 1.4 M NaCl for 8 and 13 h respectively.

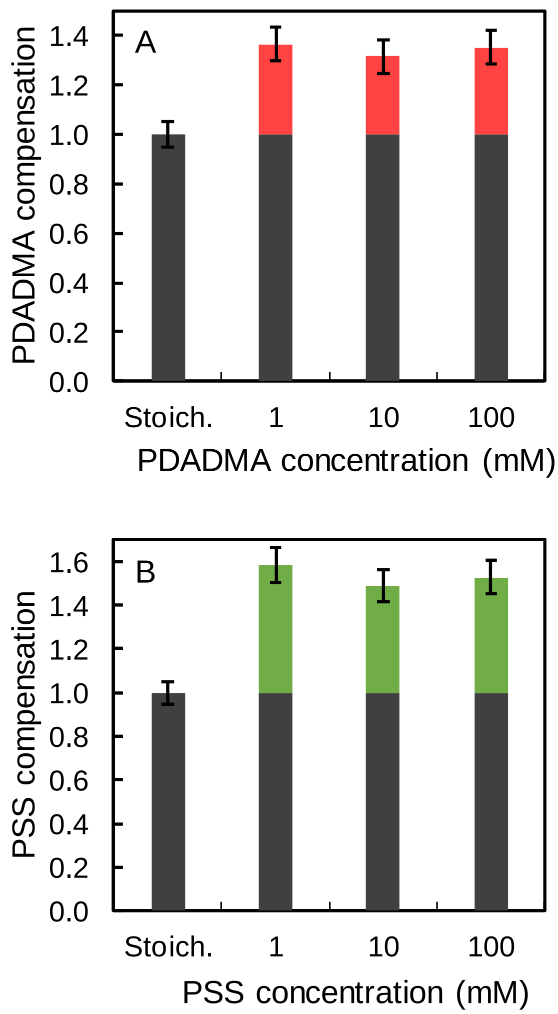

Figure S 9. (A) Normalized FTIR PDADMA/PSS peak areas in overcompensated films prepared by soaking stoichiometric $(PDADMA/PSS)_{20}$ in 1, 10 and 100 mM PDADMA500 in 1 M NaCl for 20 h. (B) Normalized FTIR PSS/PDADMA peak areas in overcompensated films prepared by soaking stoichiometric $(PDADMA/PSS)_{10}$ in 1, 10 and 100 mM PSS79 in 1.4 M NaCl for 4 h. Normalization is done relatively to the stoichiometric film.

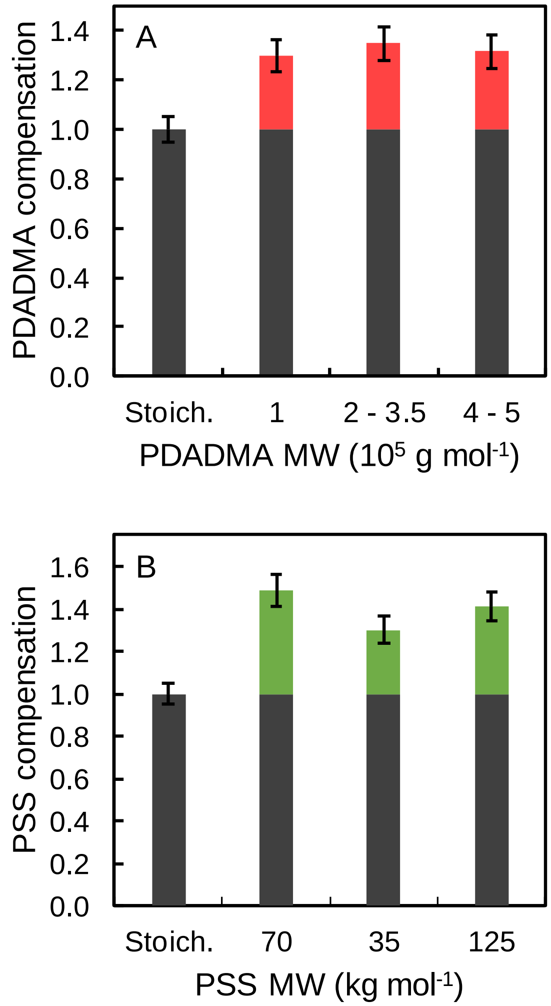

Figure S 10. (A) Normalized FTIR PDADMA/PSS peak areas in overcompensated films prepared by soaking stoichiometric $(PDADMA/PSS)_{20}$ in different wide molecular weight 10 mM PDADMA500 in 1 M NaCl for 20 h. (B) FTIR PSS/PDADMA peak areas in overcompensated films prepared by soaking stoichiometric $(PDADMA/PSS)_{10}$ in 10 mM PSS70 in 1.4 M NaCl for 4 h. Normalization is done relatively to the stoichiometric film.

Ion components – with Pol^+ overcompensating Pol^-:

Table S2. Components taken into consideration in the calculation of the concentration inside the films vs outside. The corresponding density values are used to obtain the final form of the equation.

Component	Symbol for density	Density used ($g\ L^{-1}$)	Molecular weight ($g\ mol^{-1}$)
Pol^+/Pol^- pair (intrinsic site)	ρ_{Pol^+/Pol^-}	1200	310 (PDADMA/PSS)
σ Pol^+ added	ρ_{Pol^+}	1000	126 (PDADMA)
σ A^- (overcompensation)	ρ_{A^-}	2000	35.5 (Cl^-)
y A^-, with y = k$[A^-]_{out}$ (doping), with k = sqrt of doping value (with concentrations)	ρ_{A^-}	2000	35.5 (Cl^-)
y C^+ (doping)	ρ_{C^+}	2000	23 (Na^+)
m H_2O for total water associated with Pol+/Pol- intrinsic site, doping water and overcompensation water	ρ_{H2O}	1000	18

References

1. Yang, J. C.; Jablonsky, M. J.; Mays, J. W. NMR and FT-IR studies of sulfonated styrene-based homopolymers and copolymers. *Polymer* **2002,** 43 (19), 5125-5132.

2. Mwangi, I. W.; Ngila, J. C.; Ndungu, P.; Msagati, T. A. M. Method Development for the Determination of Diallyldimethylammonium Chloride at Trace Levels by Epoxidation Process. *Water Air Soil Poll* **2013,** 224 (9).