Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Predicting the outcomes of interpolyelectrolyte neutralization at surfaces on the basis of complexation experiments and *vice versa*

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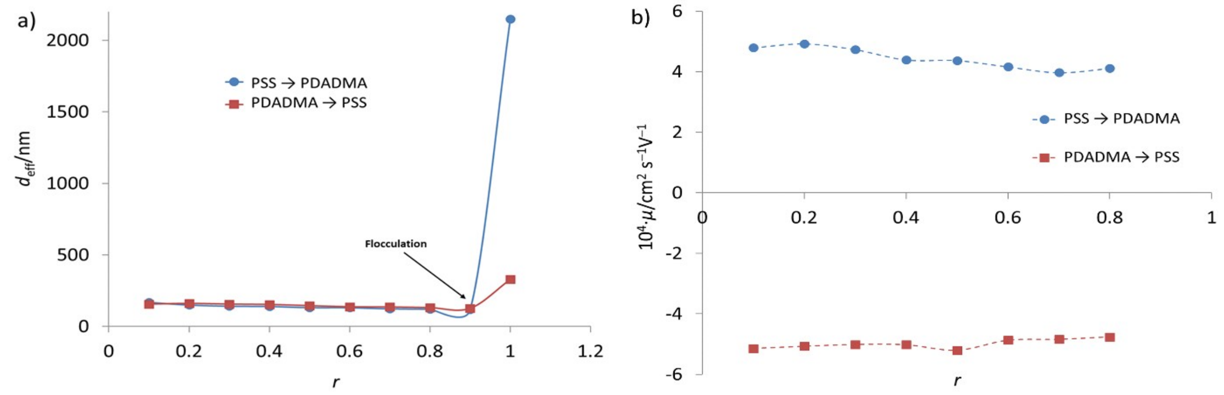


Figure S1. a) Mean effective hydrodynamic diameters and (b) electrophoretic mobilities of complexes prepared by titrations of PDADMA·Cl with Na·PSS and *vice versa* at 25 °C; c_m(titrand) = 1×10^{-3} mol dm^{-3}, c_m(titrant) = 2×10^{-2} mol dm^{-3}.

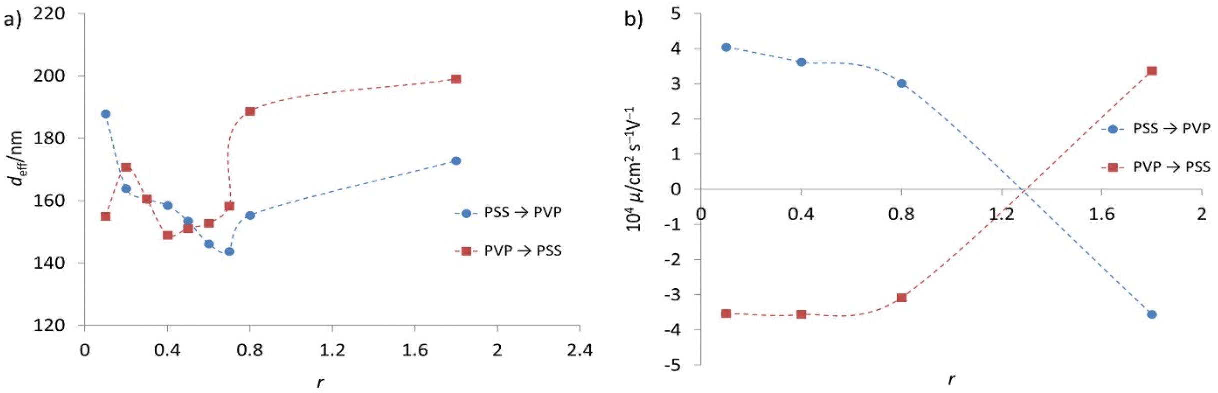
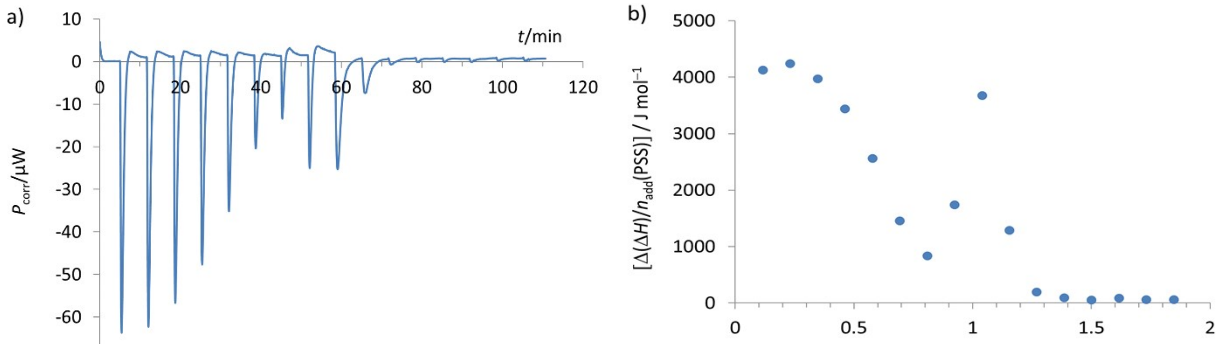


Figure S2. a) Mean effective hydrodynamic diameters and (b) electrophoretic mobilities of complexes prepared by titrations of PVP·Br with Na·PSS and *vice versa* followed by abrupt addition of one equivalent of titrant at 25 °C; c_m(titrand) = 1×10^{-3} mol dm^{-3}, c_m(titrant) = 2×10^{-2} mol dm^{-3}.



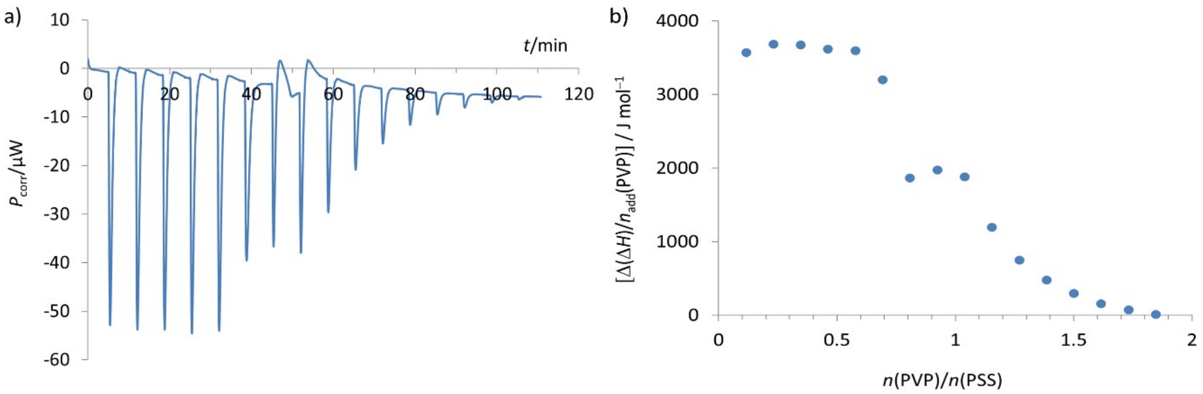


Figure S4. a) Corrected (stacked) thermograms and, b) successive normalized enthalpy changes (divided by amount of titrant monomer added) obtained during Na·PSS (c_m = 5×10^{-3} mol dm^{-3}, V = 1.3 mL) titration with PVP·Br, (c_m= 5×10^{-2} mol dm^{-3}), ϑ = 25.0 °C.

Table S1. Enthalpies of PVP-PSS primary complex formation at 25.0 ºC.

($\Delta_r H_{PSS\rightarrow PVP}$ ± SE)/kJ mol^{-1}	($\Delta_r H_{PVP\rightarrow PSS}$ ± SE)/kJ mol^{-1}
1.95 ± 0.03	0.90 ± 0.03

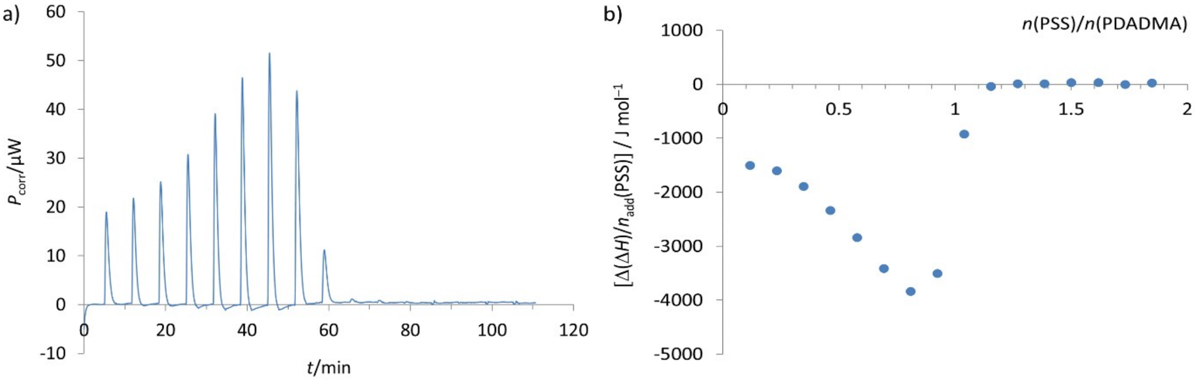


Figure S5. a) Corrected (stacked) thermogram and, b) successive normalized enthalpy changes (divided by amount of titrant monomer added)obtained during PDADMA·Cl titration (c_m = 5×10^{-3} mol dm^{-3}, V = 1.3 mL) with Na·PSS (c_m= 5×10^{-2} mol dm^{-3}), ϑ = 25.0 °C.

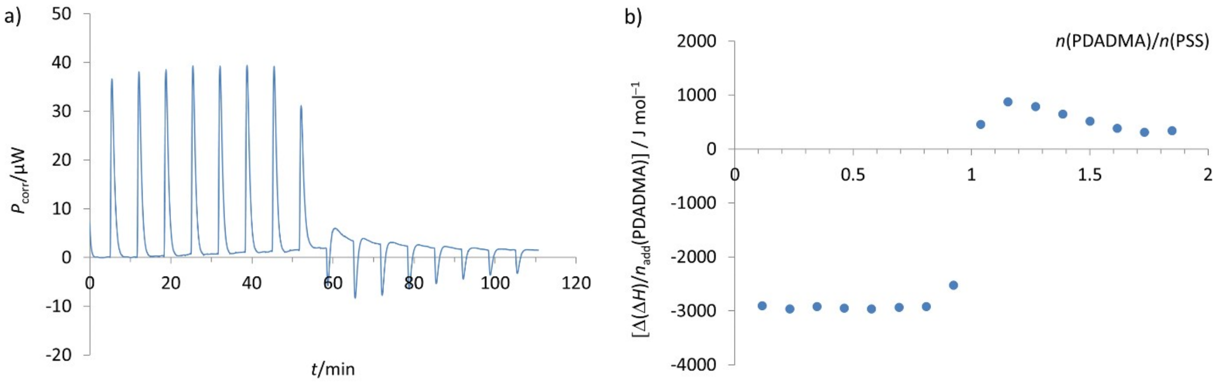


Figure S6. a) Corrected (stacked) thermograms and, b) successive normalized enthalpy changes (divided by amount of titrant monomer added) obtained during Na·PSS ($c_m = 5\times10^{-3}$ mol dm^{-3}, $V = 1.3$ mL) titration with PDADMA·Cl ($c_m = 5\times10^{-2}$ mol dm^{-3}), $\vartheta = 25.0$ °C.

Table S2. Enthalpies of PDADMA-PSS primary complex formation at 25.0 ºC.

($\Delta_r H_{PSS\rightarrow PDADMA}$ ± SE)/kJ mol^{-1}	($\Delta_r H_{PDADMA\rightarrow PSS}$ ± SE)/kJ mol^{-1}
–2.89 ± 0.01	–2.60 ± 0.09

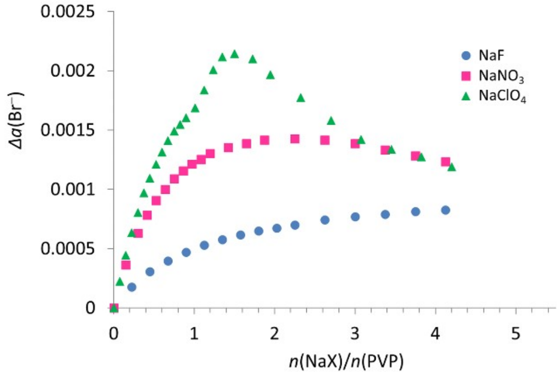


Figure S7. Potentiometric titration of PVP·Br with sodium salt solutions containing different anions; c_m(PVP·Br) = 3×10^{-3} mol dm^{-3}, V(PVP·Br) = 40 mL, c(NaX) = 0.9 mol dm^{-3}, $\vartheta = 25.0$ °C.

The peculiar decrease in Br$^-$ activity above approximately 1:1 monomolar ratio in the case of PVP titration with NaClO$_4$ is induced by precipitation of PVP·ClO$_4$ salt. -The formation of precipitate changes the ionic strength of solution thereby affecting the activity or released bromides.

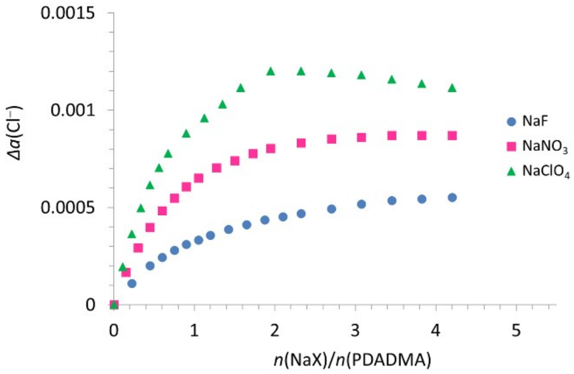


Figure S8. Potentiometric titration of PDADMA·Cl with sodium salts solutions containing different anions; c_m(PDADMA·Cl) = 3×10^{-3} mol dm^{-3}, V_0(PDADMA·Cl) = 40 mL, c(NaX) = 0.9 mol dm^{-3}, ϑ = 25.0 °C.

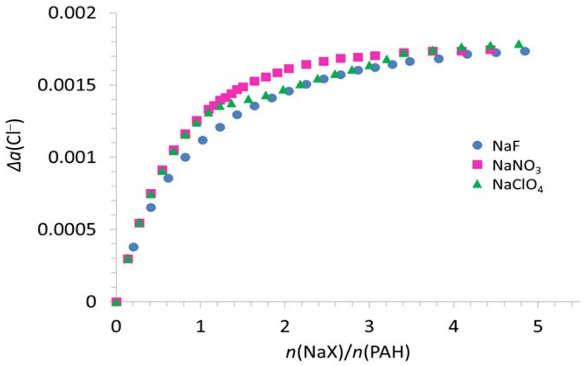


Figure S9. Potentiometric titration of PAH·Cl with sodium salt solutions containing different anions; c_m(PAH·Cl) = 3×10^{-3} mol dm^{-3}, V(PAH·Cl) = 40 mL, c(NaX) = 0.9 mol dm^{-3}, ϑ = 25.0 °C.

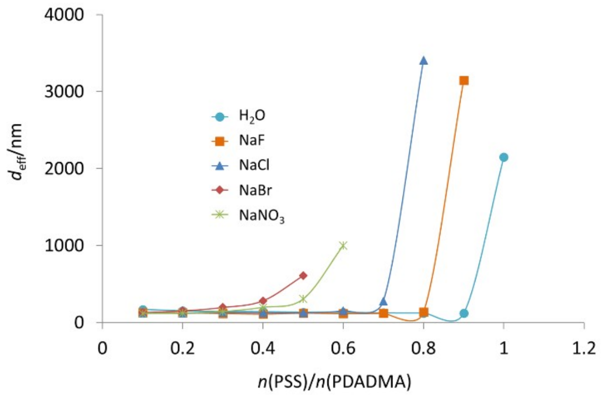


Figure S10. Mean effective hydrodynamic diameters of complexes prepared by titration of PDADMA·Cl (c_m = 1.0×10^{-3} mol dm^{-3}, V_0 = 2.0 mL) with Na·PSS (c_m = 2.0×10^{-2} dm^{-3}) in 0.1 mol dm^{-3} salt solutions at 25 °C.

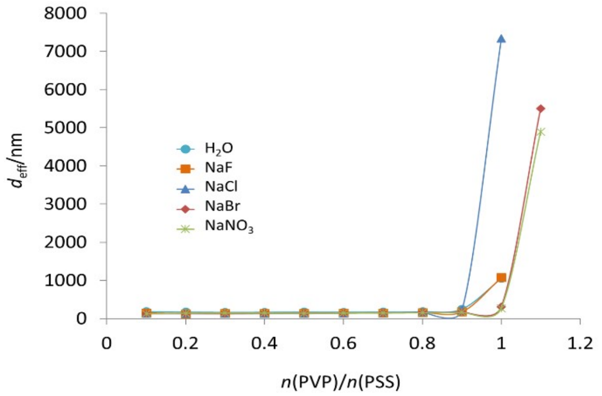


Figure S11. Mean effective hydrodynamic diameters of complexes prepared by titration of Na·PSS (c_m = 1.0×10^{-3} mol dm^{-3}, V = 2.0 mL) with PVP·Br (c_m = 2.0×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} salt solutions at 25 °C.

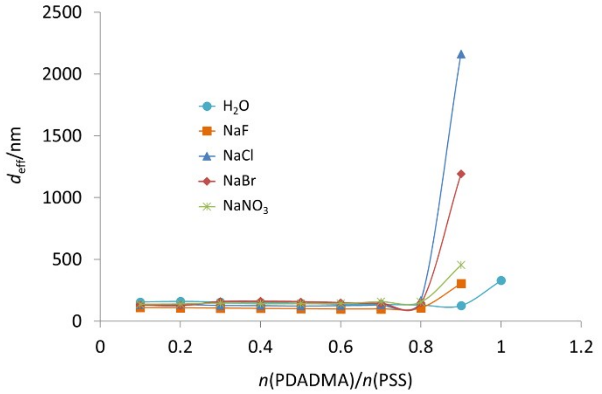


Figure S12. Mean effective hydrodynamic diameters of complexes prepared by titration of Na·PSS (c_m = 1.0×10^{-3} mol dm^{-3}, V = 2.0 mL) with PDADMA·Cl (c_m = 2.0×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} salt solutions at 25 °C.

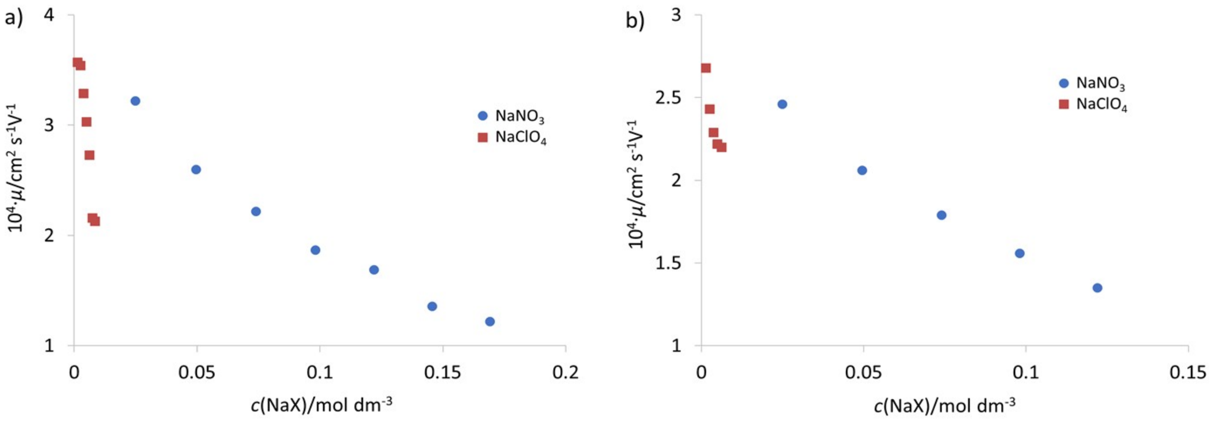


Figure S13. Electrophoretic mobility of particles obtained by titrating positive a) PDADMA-PSS and b) positive PVP-PSS complexes (n(PSS)/n(polycation) = 0.5) with $NaNO_3$ (c = 5 mol dm^{-3}) and $NaClO_4$ (c = 0.25 mol dm^{-3}) at 25 °C. Positive complexes were prepared by the addition of Na·PSS ($c_m = 5\times10^{-2}$ mol dm^{-3}) to solution containing either PDADMA·Cl or PVP·Br ($c_m = 1\times10^{-3}$ mol dm^{-3}, V = 2 mL).

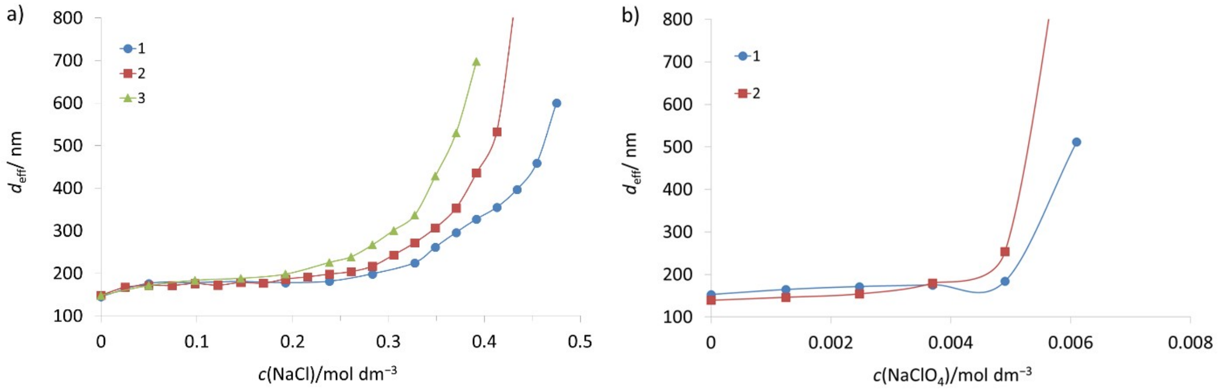


Figure S14. Mean effective hydrodynamic diameters of particles obtained by repetitive titrations of positive PVP-PSS complexes (n(PSS)/n(polycation) = 0.5) with a) NaCl (c = 5 mol dm^{-3}) and b) $NaClO_4$ (c = 0.25 mol dm^{-3}) at 25 °C. Positive complexes were prepared by the addition of Na·PSS ($c_m = 5\times10^{-2}$ mol dm^{-3}) to solution containing PVP·Br ($c_m = 1\times10^{-3}$ mol dm^{-3}, V = 2 mL).

Table S3. Time dependence of mean effective hydrodynamic diameter of particles obtained by titrating positive PVP-PSS complexes (n(PSS)/n(PVP) = 0.5) with NaCl and NaBr (c = 5 mol dm^{-3}) at 25 °C. Positive complexes were prepared by the addition of Na·PSS ($c_m = 5\times10^{-2}$ mol dm^{-3}) to solution containing PVP·Br ($c_m = 1\times10^{-3}$ mol dm^{-3}, V = 2 mL); CC- coagulation concentration.

			d_{eff}/nm			
salt	c(salt) /% CC	after preparation	1 h	24 h	3 d	5 d
NaCl	50	223	208	244	271	306
NaCl	80	253	312	448	518	aggregation
NaBr	50	205.4	192	200	202	216
NaBr	80	210.5	239	341	684	aggregation

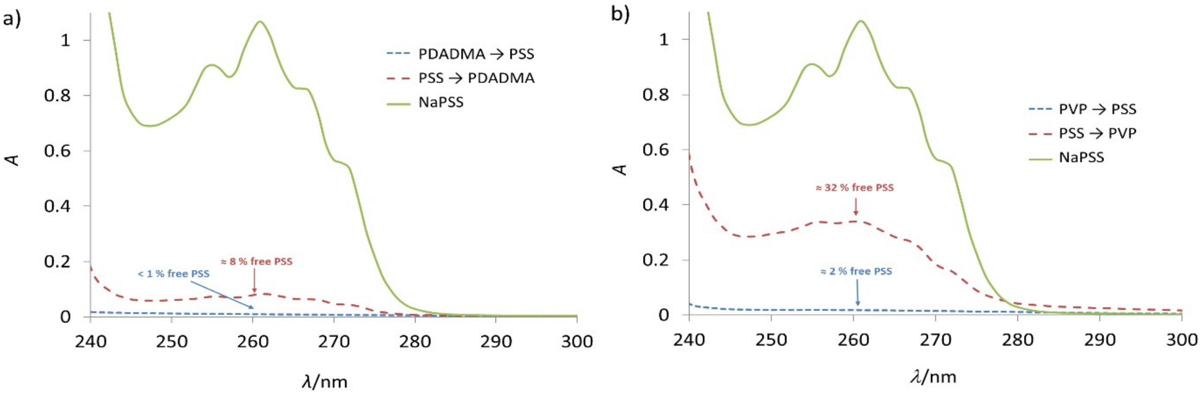


Figure S15. a) Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of PDADMA·Cl with Na·PSS and *vice versa* at equimolar monomer ratios ($c_m = 3.3\times10^{-3}$ mol dm^{-3}, $l = 1$ cm) in 0.1 mol dm^{-3} NaBr at 25 °C and b) corresponding results for PVP·Br-Na·PSS system in 0.5 mol dm^{-3} NaBr.

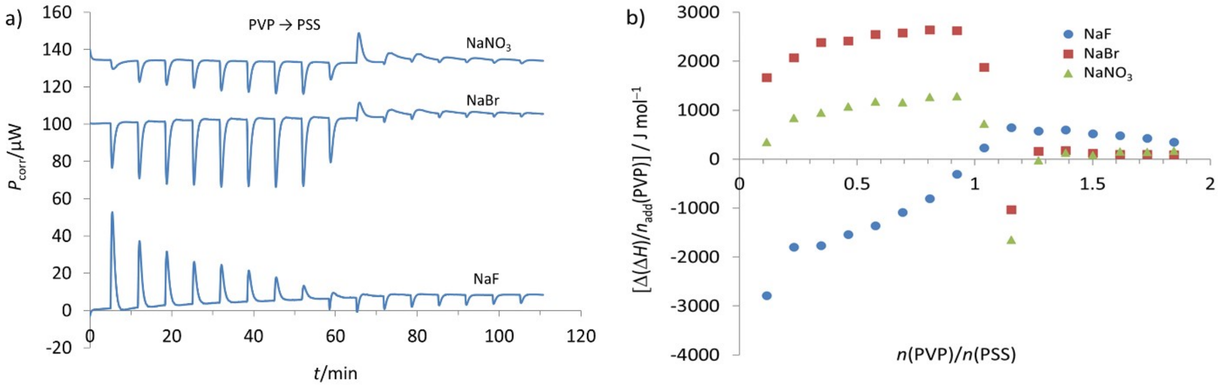


Figure S16. a) Corrected (stacked) thermograms and, b) successive normalized (divided by amount of titrant monomer added) enthalpy changes obtained during Na·PSS (c_m= 5×10^{-3} mol dm^{-3}, V= 1.3 mL) titration with PVP·Br (c_m= 5×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} NaX at 25.0 °C.

Table S4. Enthalpies of PVP-PSS primary negatively charged complex formation in 0.1 mol dm^{-3} NaX at 25.0 °C

NaX	($\Delta_r H_{\mathrm{PVP\rightarrow PSS}} \pm$ SE)/kJ mol^{-1}
NaF	−1.94 ± 0.09
$NaNO_3$	0.99 ± 0.03
NaBr	2.27 ± 0.07

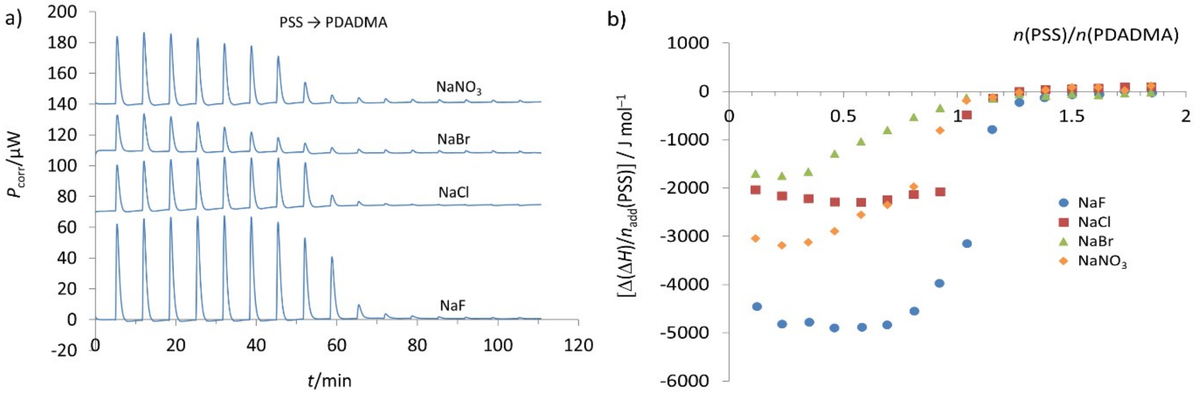


Figure S17. a) Corrected (stacked) thermograms and, b) successive normalized (divided by amount of titrant monomer added) enthalpy changes obtained during PDADMA·Cl (c_m= 5×10^{-3} mol dm^{-3}, V= 1.3 mL) titration with Na·PSS (c_m= 5×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} NaX at 25.0 °C.

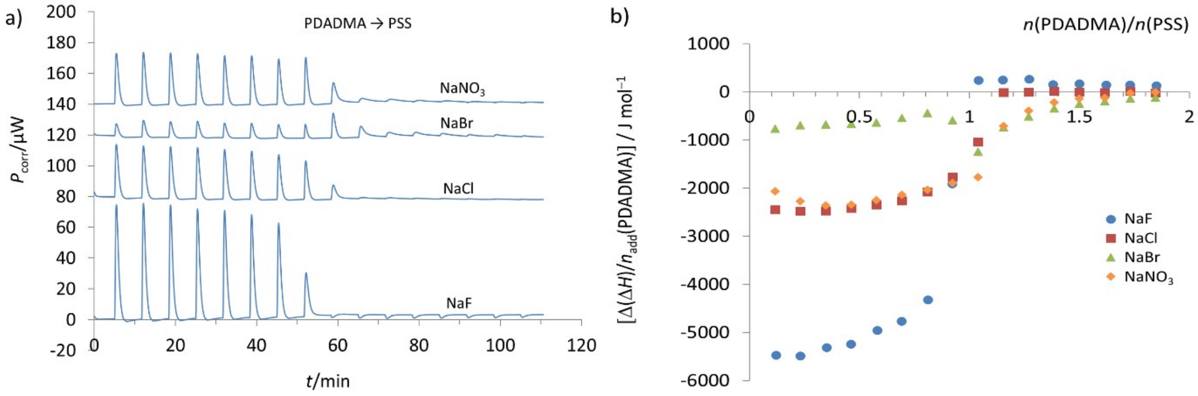


Figure S18. a) Corrected (stacked) thermograms and, b) successive normalized (divided by amount of titrant monomer added) enthalpy changes obtained by Na·PSS (c_m= 5×10^{-3} mol dm^{-3}, V= 1.3 mL) titration with PDADMA·Cl (c_m= 5×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} NaX at 25.0 °C.

Table S5. Enthalpies of PDADMA-PSS primary positively and negatively charged complex formation in 0.1 mol dm^{-3} NaX at 25.0 °C

salt	($\Delta_r H_{PSS\rightarrow PDADMA} \pm$ SE)/kJ mol^{-1}	($\Delta_r H_{PDADMA\rightarrow PSS} \pm$ SE)/kJ mol^{-1}
NaF	–4.45 ± 0.05	–4.81 ± 0.09
NaNO$_3$	–2.86 ± 0.07	–2.08 ± 0.02
NaCl	–2.14 ± 0.04	–2.25 ± 0.03
NaBr	–1.25 ± 0.01	–0.64 ± 0.01

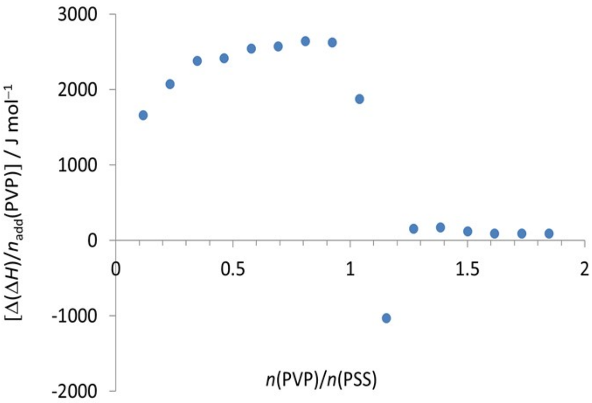


Figure S19. successive normalized (divided by amount of titrant monomer added) enthalpy changes obtained by Na·PSS (c_m= 5×10^{-3} mol dm^{-3}, *V*= 1.3 mL) titration with PVP· Br (c_m= 5×10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} NaBr at 25.0 °C.

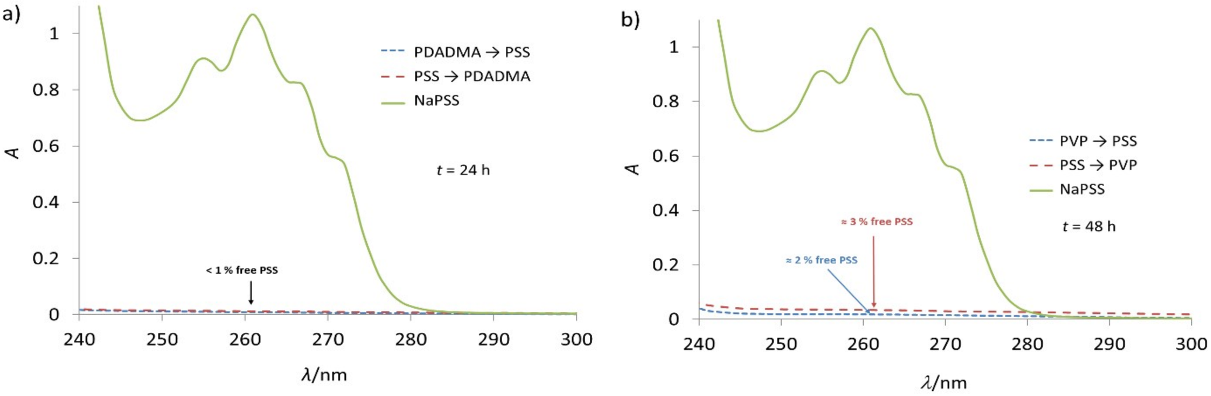


Figure S20. a) Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of PDADMA·Cl with Na·PSS and *vice versa* at equimolar monomer ratio (c_m = 3.3×10^{-3} mol dm^{-3}, l = 1 cm) in 0.1 mol dm^{-3} NaBr at 25 °C, 24 h after preparation and b) corresponding results for PVP·Br-Na·PSS system in 0.5 mol dm^{-3} NaBr at 25 °C, 48 h after preparation.

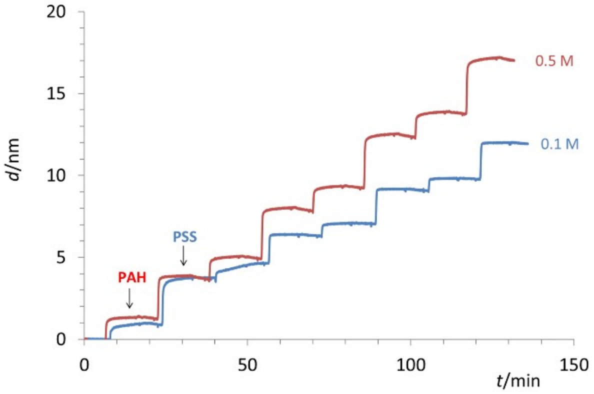


Figure S21. Thickness change during assembly of PAH/PSS (c_m(PAH) = c_m(PSS) = 1×10^{-3} mol dm^{-3}) multilayers in NaCl at 25 °C; flow rate = 150 µL min^{-1}.

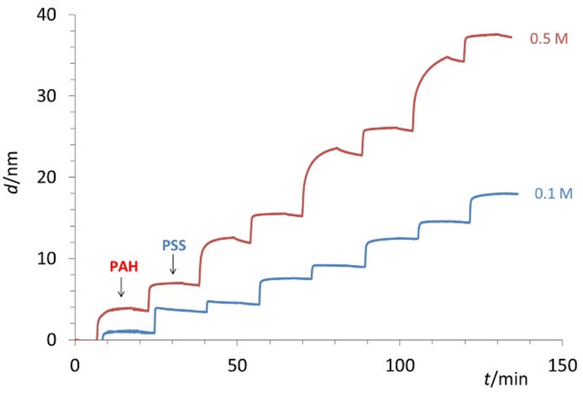


Figure S22. Thickness change during assembly of PAH/PSS (c_m(PAH) = c_m(PSS) = 1×10^{-3} mol dm^{-3}) multilayers in $NaClO_4$ at 25 °C; flow rate = 150 µL min^{-1}.

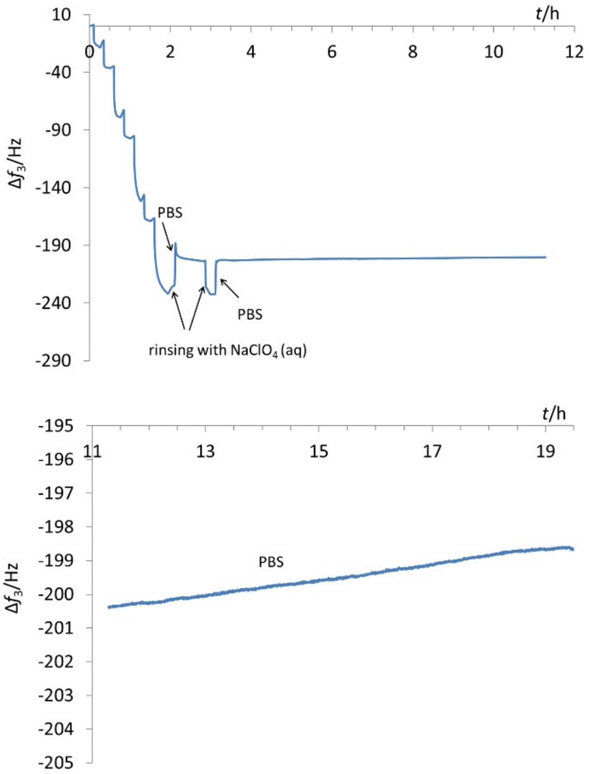


Figure S23. Frequency shift (third harmonic) of oscillating quartz crystal during assembly of PAH/PSS (c_m(PAH) = c_m(PSS) = 1×10^{-3} mol dm^{-3}) multilayers in 0.5 mol dm^{-3} $NaClO_4$ solution and their alternating rinsing with PBS buffer (c(PBS) = 0.15 mol dm^{-3}, pH = 7.4) and $NaClO_4$ (0.5 mol dm^{-3}), ϑ = 25.0 °C.