

**Complexation between polyallylammonium cation and polystyrenesulfonate
anion; the effect of ionic strength and electrolyte type**

SUPPORTING INFORMATION

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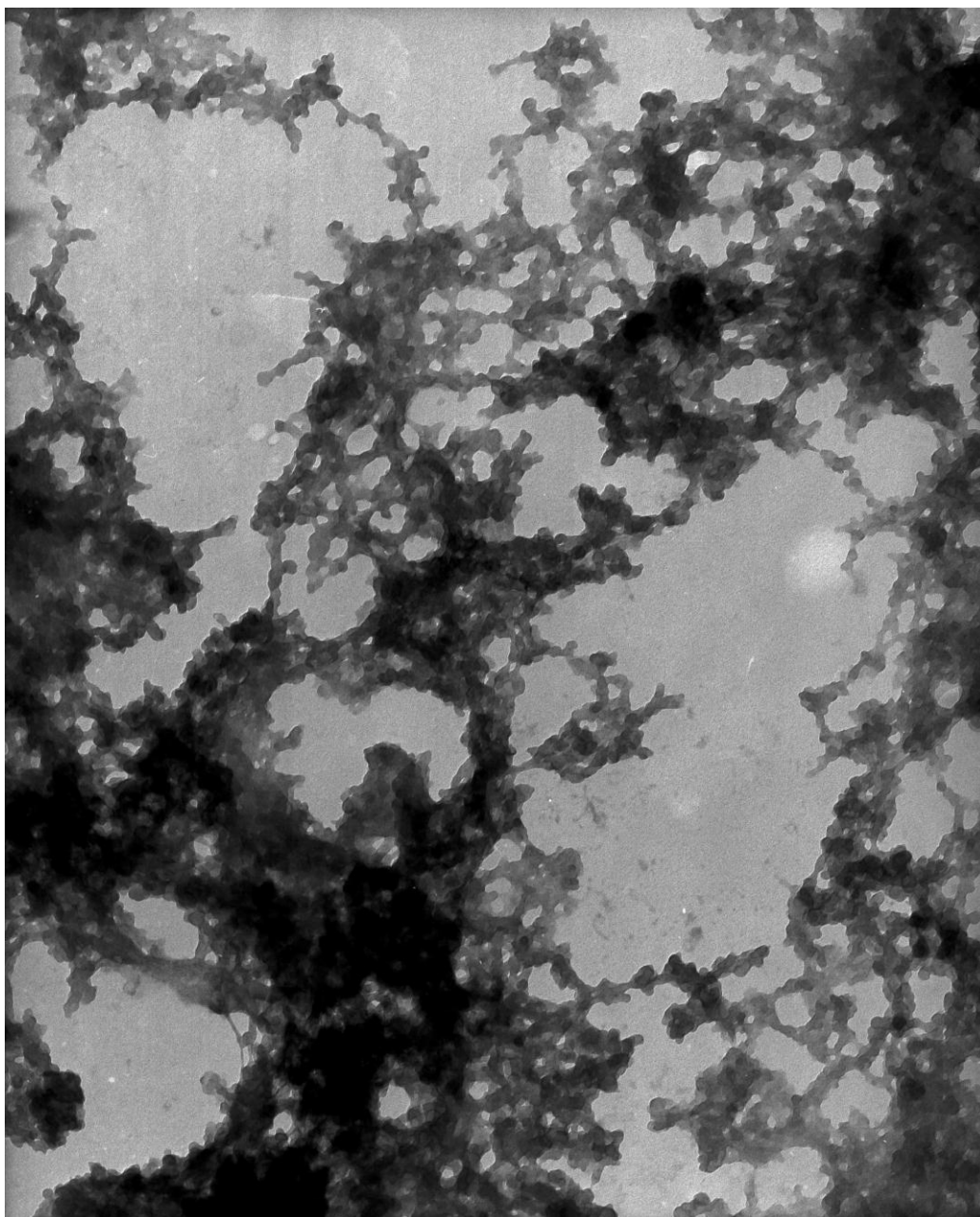


Figure S1. TEM photography of precipitate obtained by titration of sodium polystyrenesulfonate with polyallylammonium chloride at $r = 1$.

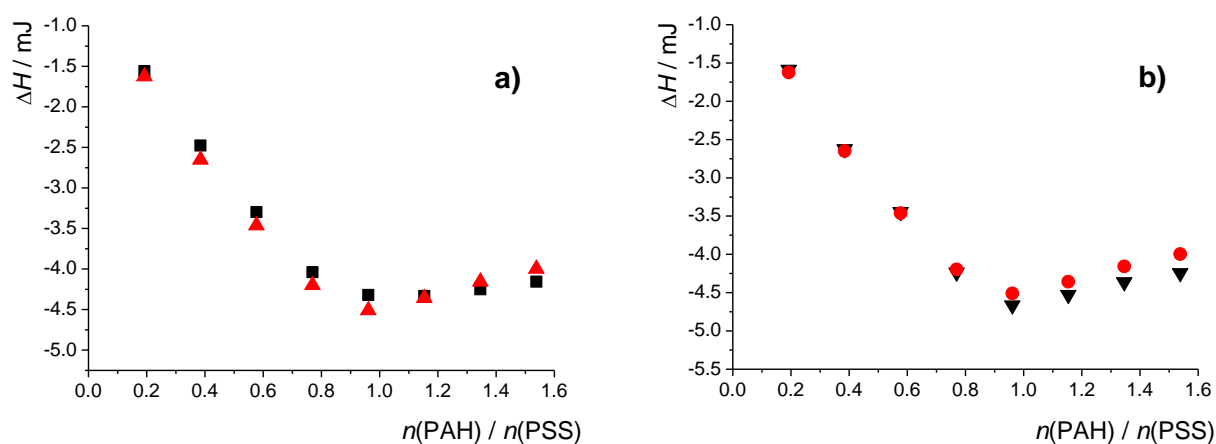


Figure S2. a) Cumulative enthalpy changes obtained by titration of sodium polystyrenesulfonate ($c_m = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $V_0 = 1.3 \text{ mL}$) with polyallylammonium chloride ($c_m = 5 \times 10^{-2} \text{ mol dm}^{-3}$) at different stirring rates (■ – 50 rpm, ▲ – 300 rpm), titrant delivery rate: $300 \mu\text{l min}^{-1}$, $\theta = (25.0 \pm 0.1) \text{ }^\circ\text{C}$.

b) Cumulative enthalpy changes obtained by titration of sodium polystyrenesulfonate ($c_m = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $V_0 = 1.3 \text{ mL}$) with polyallylammonium chloride ($c_m = 5 \times 10^{-2} \text{ mol dm}^{-3}$) at different titrant delivery rates (● – $50 \mu\text{l min}^{-1}$, ▼ – $300 \mu\text{l min}^{-1}$), stirring rate: 300 rpm, $\theta = (25.0 \pm 0.1) \text{ }^\circ\text{C}$.

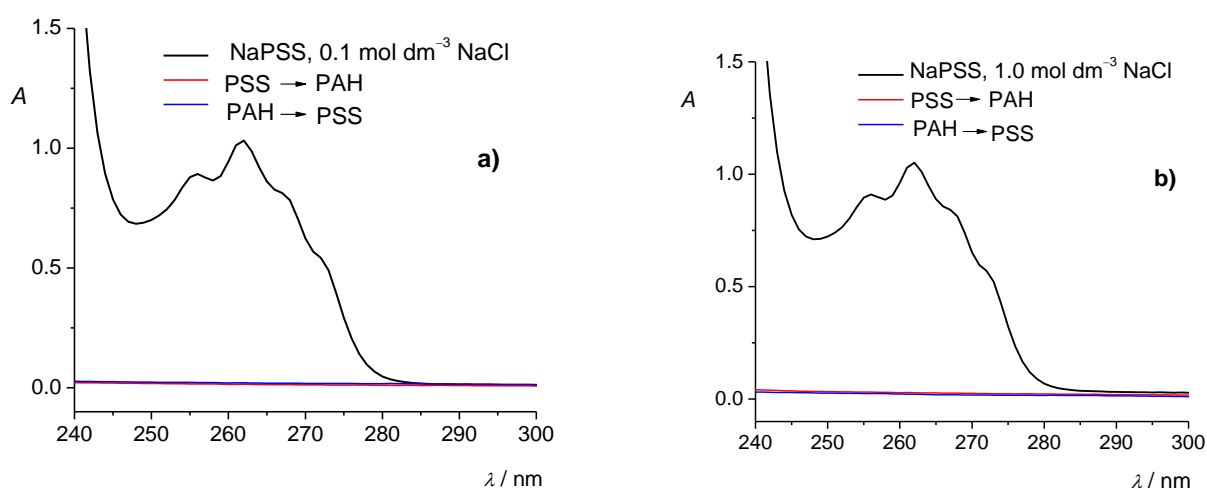


Figure S3. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS→PAH) and *vice versa* (PAH→PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$). (r – ratio of oppositely charged monomers. NaPSS - spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3} \text{ mol dm}^{-3}$), in NaCl ($c = 0.1 \text{ mol dm}^{-3}$) (a) and ($c = 1.0 \text{ mol dm}^{-3}$) (b).

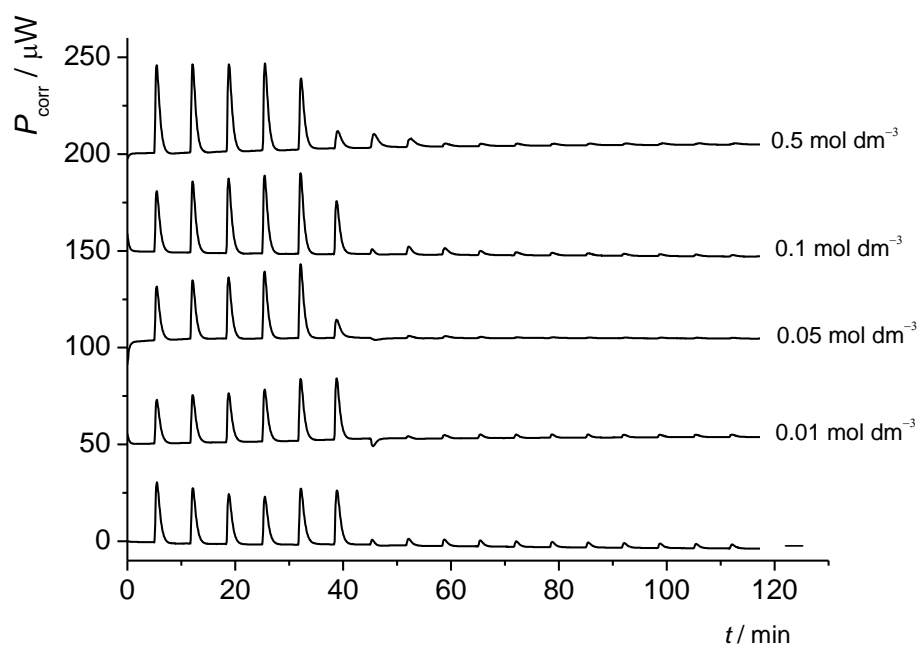


Figure S4. Thermograms obtained by titration polyallylammonium cation ($c_m = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $V = 1.3 \text{ mL}$) with polystyrenesulfonate anion ($c_m = 6 \times 10^{-2} \text{ mol dm}^{-3}$) in NaCl (aq), $\theta = (25.0 \pm 0.1)^\circ \text{C}$.

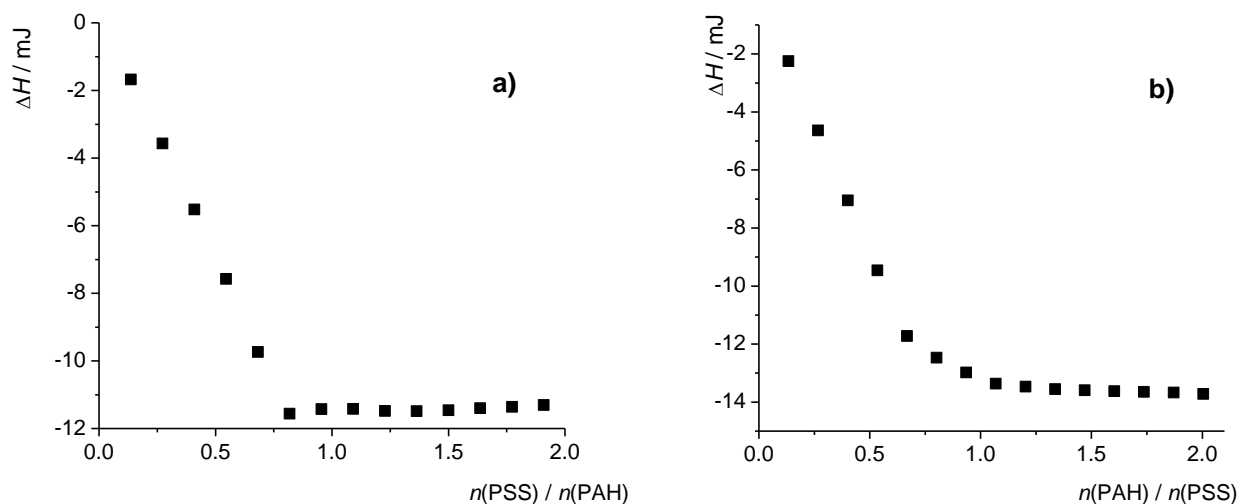


Figure S5. a) Cumulative enthalpy changes obtained by titration of polyallylammonium chloride ($c_m = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $V_0 = 1.3 \text{ mL}$) with sodium polystyrenesulfonate ($c_m = 6 \times 10^{-2} \text{ mol dm}^{-3}$) in 0.1 mol dm^{-3} NaCl, $\theta = (25.0 \pm 0.1)^\circ \text{C}$.

b) Cumulative enthalpy changes obtained by titration of sodium polystyrenesulfonate ($c_m = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $V_0 = 1.3 \text{ mL}$) with polyallylammonium chloride ($c_m = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$) in 0.1 mol dm^{-3} NaCl, $\theta = (25.0 \pm 0.1)^\circ \text{C}$.

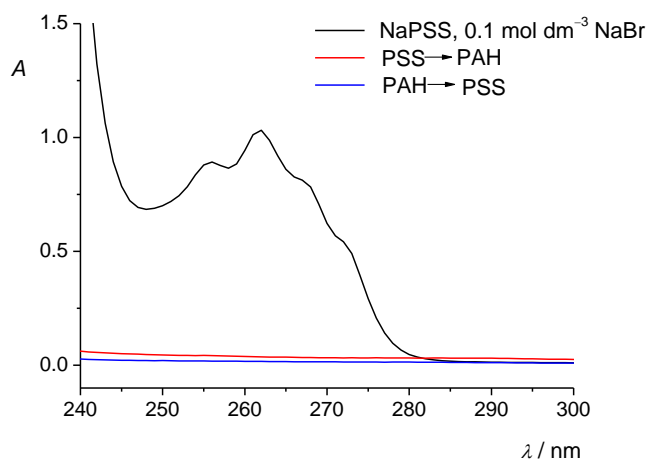


Figure S6. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS→PAH) and *vice versa* (PAH→PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1$ °C). (r – ratio of oppositely charged monomers. NaPSS - spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3}$ mol dm $^{-3}$), in NaBr ($c = 0.1$ mol dm $^{-3}$).

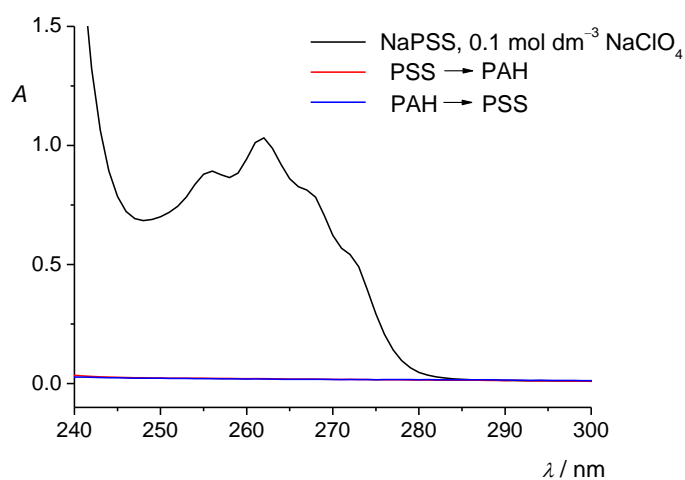


Figure S7. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS→PAH) and *vice versa* (PAH→PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1$ °C). (r – ratio of oppositely charged monomers. NaPSS - spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3}$ mol dm $^{-3}$), in NaClO $_4$ ($c = 0.1$ mol dm $^{-3}$).

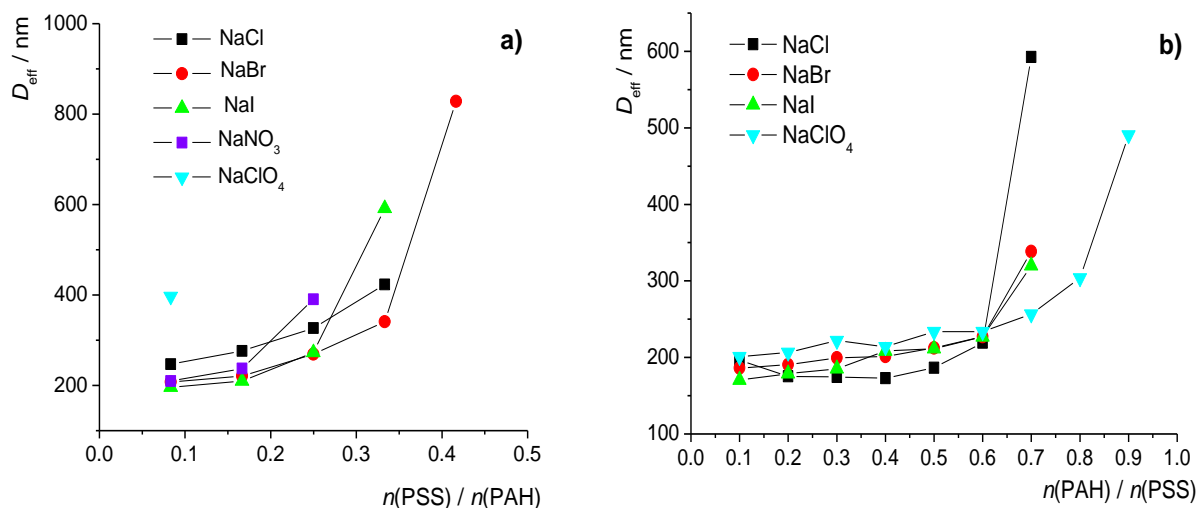


Figure S8.a) Hydrodynamic diameters of colloid complexes obtained by titration of polyallylammonium cation ($c_m = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $V = 2 \text{ mL}$) with polystyrenesulfonate anion ($c_m = 1.7 \times 10^{-2} \text{ mol dm}^{-3}$) in NaX (aq, $c = 1.0 \text{ mol dm}^{-3}$) at $25 \text{ }^\circ\text{C}$.

b) Hydrodynamic diameters of colloid complexes obtained by titration of polystyrenesulfonate anion ($c_m = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $V = 2 \text{ mL}$) with polyallylammonium cation ($c_m = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$) in NaX (aq, $c = 1.0 \text{ mol dm}^{-3}$) at $25 \text{ }^\circ\text{C}$.

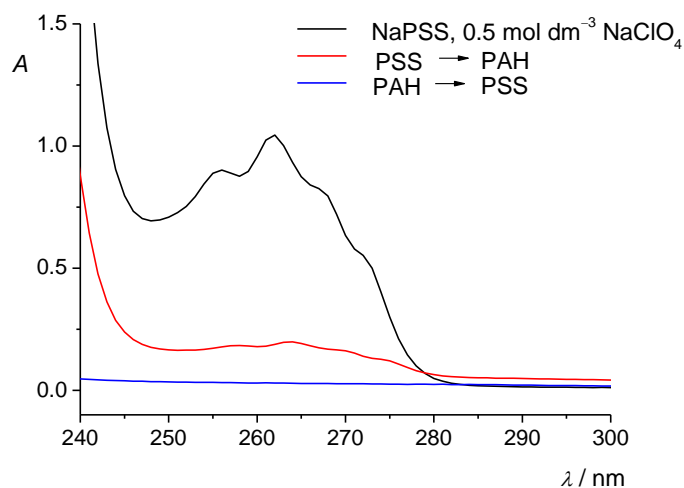


Figure S9. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS \rightarrow PAH) and *vice versa* (PAH \rightarrow PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$). (r – ratio of oppositely charged monomers. NaPSS – spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3} \text{ mol dm}^{-3}$), in NaClO_4 ($c = 0.5 \text{ mol dm}^{-3}$).

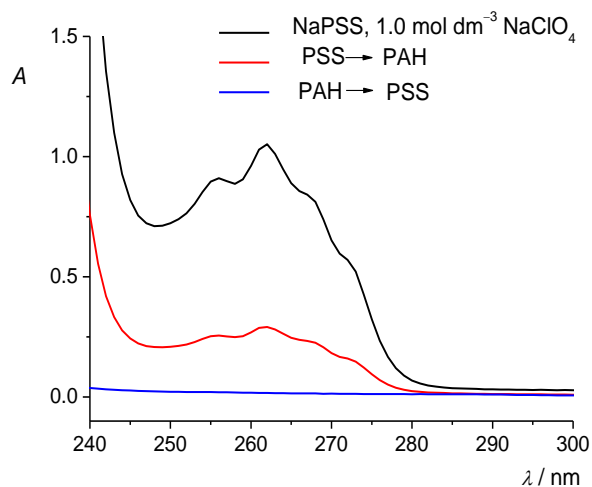


Figure S10. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS→PAH) and *vice versa* (PAH→PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1$ °C). NaPSS - spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3}$ mol dm⁻³), in NaClO₄ ($c = 1.0$ mol dm⁻³). The analytical concentration of positively and negatively charged monomers was always equal to monomer concentration in NaPSS.

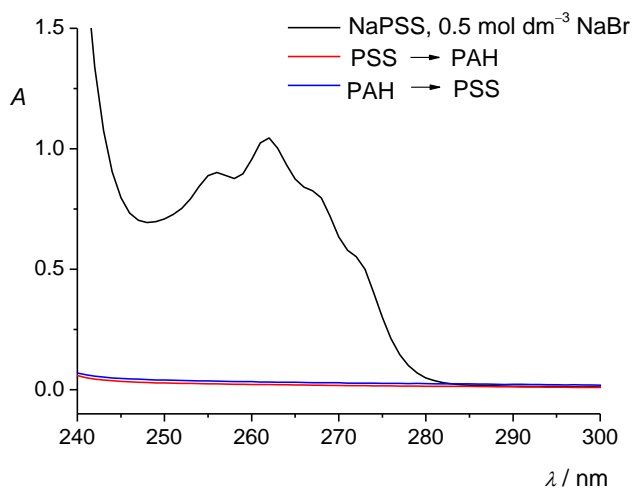


Figure S11. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS→PAH) and *vice versa* (PAH→PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1$ °C). (r – ratio of oppositely charged monomers. NaPSS - spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3}$ mol dm⁻³), in NaBr ($c = 0.5$ mol dm⁻³).

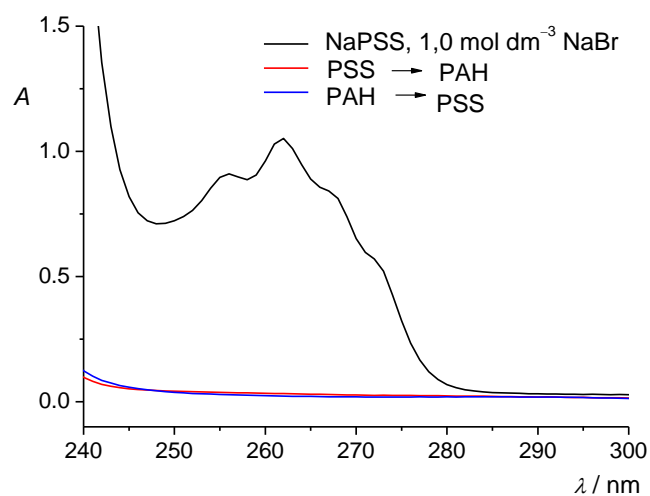


Figure S12. Spectra of supernatants obtained by centrifugation of suspensions prepared by titration of polycation with polyanion (PSS→PAH) and *vice versa* (PAH→PSS) at $r = 1$ ($\theta = 25.0 \pm 0.1$ °C). NaPSS - spectrum of sodium polystyrenesulfonate ($c_m = 3.3 \times 10^{-3}$ mol dm $^{-3}$), in NaBr ($c = 1.0$ mol dm $^{-3}$). The analytical concentration of positively and negatively charged monomers was always equal to monomer concentration in NaPSS.