ESI

EMULSION STABILISATION BY COMPLEXES OF OPPOSITELY CHARGED SYNTHETIC POLYELECTROLYTES

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Figure S1. Potentiometric titration of a 1 g L⁻¹ PAANa solution against 0.1 M HCl (open points). The pH of the initial PAANa solution was increased to \approx 11.5 with NaOH to evaluate the full pH range. The curve that connects the filled points corresponds to the derivative of the pH as a function of the volume of titrating agent (dpH/dV). Inset plot: degree of ionisation *versus* pH obtained from the titration curve.



Figure S2. Variation of the average particle diameter with x_{PAANa} for aqueous PEC dispersions prepared from 0.1 g L⁻¹ individual PEL solutions at different pH.



Figure S3. Variation of (a) average diameter and (b) zeta potential *versus* charge ratio $Z_{-/+}$ for aqueous PEC dispersions prepared from 0.1 g L⁻¹ individual PEL solutions at three extents of ionisation of PAANa calculated according to ref. 32.



Figure S4. Appearance of fresh aqueous PEC dispersions prepared from 5 g L⁻¹ PEL solutions at (a) pH = 2 and (b) pH = 6 at different x_{PAANa} (given). Scale bars = 1 cm. Optical microscope image of a drop of dispersion at (c) pH = 2, $x_{PAANa} = 0.57$ or (d) pH = 6, $x_{PAANa} = 0.57$.



Figure S5. TEM images of the diluted freshly prepared aqueous PEC dispersion ($x_{PAANa} = 0.5$) prepared from 5 g L⁻¹ PEL solutions at pH = 10 at different magnifications. The sample was negatively stained with uranyl acetate.



Figure S6. TEM images of aqueous PEC dispersion ($x_{PAANa} = 0.5$) prepared from 5 g L⁻¹ PEL solutions at pH = 10 at different magnifications. First row - unstained sample, second row - negatively stained sample.



Figure S7. Appearance of dodecane-in-water emulsions ($\phi_o = 0.20$ added in one step) from aqueous PEC dispersions ([PEL] = 5 g L⁻¹, $x_{PAANa} \approx 0.50$) at different pH (given). Appearance of the emulsions 11 days after preparation is also shown. Scale bar = 1 cm.



Figure S8. Appearance of dodecane-in-water emulsions ($\phi_o = 0.20$ added in one step) stabilised by PAANa at pH = 2 and different concentrations (given in g L⁻¹) at various times. Scale bar equals to 1 cm.



Figure S9. Appearance of emulsions immediately after homogenisation prepared with dodecane ($\phi_o = 0.2$) and 5 g L⁻¹ PEL solution at pH = 10 for PAANa and PDADMAC separately. Scale bar = 1 cm.



Figure S10. (a) Appearance of aqueous PEC dispersion prepared from 30 g L⁻¹ PEL solutions at pH = 10, $x_{PAANa} = 0.5$. A white dispersion coexists with a viscous gelatinous phase as seen on the inverted vial. (b) Appearance of dodecane-in-water emulsion immediately after homogenisation (left, $\phi_o = 0.20$ in one step); right - corresponds to the same vial after removal of the gelatinous phase on top. Scale bar = 1 cm. Optical microscope image of (c) white dispersion in (a), (d) gelatinous phase in (a), (e) aqueous dispersion separated after emulsification in (b).



Figure S11. Appearance of o/w emulsion ($\phi_o = 0.20$, added stepwise) with (a) isopropyl myristate and (b) squalane from aqueous PEC dispersion ([PEL] = 5 g L⁻¹, pH = 10, x_{PAANa} = 0.5) at different times. Scale bars = 1 cm.



Figure S12. (a) Appearance of PDMS-in-water emulsion ($\phi_o = 0.20$, added stepwise) from the aqueous PEC dispersion ([PEL] = 5 g L⁻¹, pH = 10, $x_{PAANa} = 0.5$) with time. Scale bar = 1 cm. (b) Optical microscope images of the above emulsion once creaming halted.



Figure S13. (a) Appearance of toluene-in-water emulsion ($\phi_o = 0.20$, added stepwise) from aqueous PEC dispersion ([PEL] = 5 g L⁻¹, pH = 10, $x_{PAANa} = 0.5$) with time. Scale bar = 1 cm. (b) Optical microscope images of the above emulsion once creaming halted.

