Supporting Information to

Structure and dynamics of polyelectrolyte complex coacervates studied by scattering of neutrons, X-rays and light

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1 Scattering length densities of PDMAEMA and PAA

Table 1: Neutron scattering length densities of PDMAEMA and PAA used in this study on the structure of polyelectrolyte complex coacervates. ρ is the bulk density of the polymers ($\rho = M/v_{\mathrm{m}}N_{\mathrm{Av}}$, with M the molar mass and v_{m} the molecular volume of a monomeric unit) and ρ_{N} is the coherent neutron scattering length density.

Polymer	ρ (kg/m^3)	ρ_{N} (10^{-6} Å^{-2})	Note
d-PAA (acidic D form)	1.095	5.05	Assuming equal molecular volumes compared to the hydrogenated form of PAA and correcting for the increase in mass due to deuterium.
d-PAA (acidic H form)	1.095	4.20	
d-PAA (K-salt)	1.45	4.26	Assuming that the molecular volume of d-PAAK is the combined volume of a d-PAA and a K^+ ion ($v_{\mathrm{m}} = 1.14\times10^{-28}+1.47\times10^{-29}$ m^3) [1].
d-PAA (K-salt)	1.095	3.22	Assuming that the density of d-PAAK is the same as the density of d-PAAH. Note: the true density of d-PAAK will be intermediate between these two values (1.45 and 1.095).
d-PAA (with 1 KCl associated)	1.45	3.81	See d-PAA (K-salt)
d-PAA (with 1 KCl associated)	1.095	2.88	See d-PAA (K-salt)
d-PDMAEMA (amine form)	1.023	6.23	Assuming equal molecular volumes compared to the hydrogenated form of PDMAEMA and correcting for the increase in mass due to deuterium. The alternative assumption of equal densities of h-PDMAEMA and d-PDMAEMA would yield $\rho_{\mathrm{N}} = 5.7\times10^{-6}$ Å^{-2} [2].
d-PDMAEMA (HCl form)	1.113	5.78	Assuming that the molecular volume of d-PDMAEMA-HCl is the combined volume of a d-PDMAEMA and a HCl molecule ($v_{\mathrm{m}} = 2.79\times10^{-28}+3.10\times10^{-29}$ m^3).
d-PDMAEMA (DCl form)	1.113	6.08	See d-PDMAEMA (HCl).

2 Match point of complex coacervate scattering length

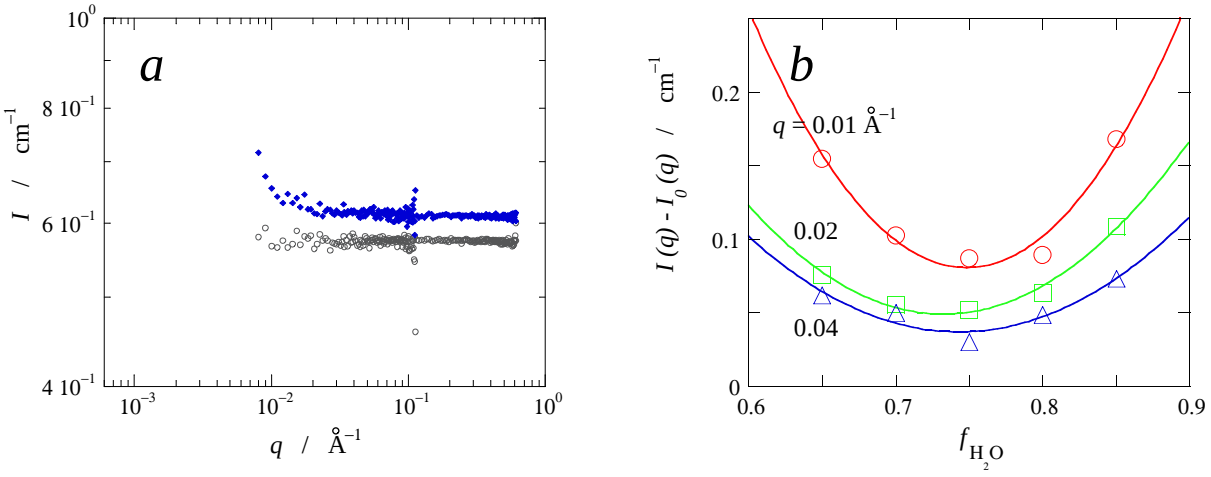

Figure 1: (a) Small angle neutron scattering curves of h-PDMAEMA$_{574}$/h-PAA$_{550}$ complex coacervates in 75% H_2O / 25% D_2O (v/v), pH 6.5, containing 1.2 M KCl (blue diamonds) and the corresponding solvent (gray circles). (b) The point of closest contrast matching is determined by averaging the absolute difference between scattering intensity form complex coacervates and the corresponding solvent at three different wave numbers q.

3 Tracer experiments

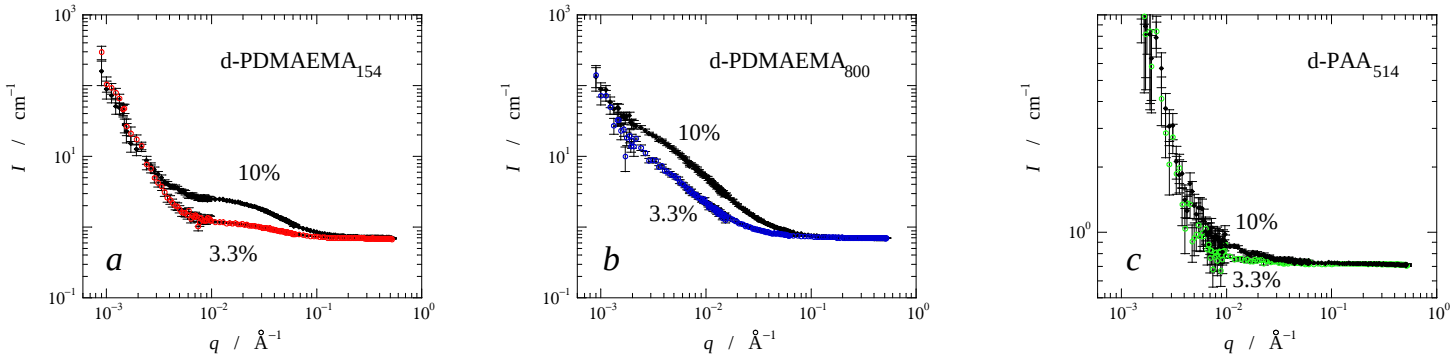

Figure 2: Raw SANS curves (no contrast matching correction) for the tracer experiments in Figure 3 in the main text for (a) d-PDMAEMA$_{154}$ tracers in complex coacervates of h-PDMAEMA$_{156}$/h-PAA$_{160}$ at 1.0 M KCl, (b) d-PDMAEMA$_{800}$ tracers in complex coacervates of h-h-PDMAEMA$_{574}$/h-PAA$_{550}$ at 1.2 M KCl and (c) d-PAA$_{514}$ tracers in complex coacervates of h-PDMAEMA$_{574}$/h-PAA$_{550}$ at 1.2 M KCl. For all samples, the curves of 3.3% tracers and 10% tracers are shown.

4 Structure factor of d-PDMAEMA$_{154}$ samples

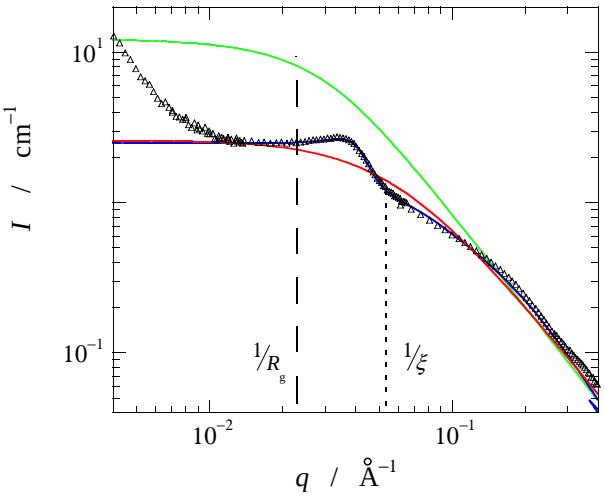

Figure 3: SANS curve of the complex coacervate of d-PDMAEMA$_{154}$/h-PAA$_{160}$ at 0.80 M KCl, with the theoretical structure factor for an Ornstein-Zernike law (solid red line), and the fitted structure factor for the Ornstein-Zernike law combined with a fraction of micelles (solid blue line). The solid green line is the corresponding form factor fit for d-PDMAEMA$_{154}$ single chains in the complex coacervates.

The scattering curve of d-PDMAEMA$_{154}$ samples is described best by a combination of two components: (1) a matrix of overlapping polymer chains, with a form factor given by Equation 1 in the main text and a structure factor given by Equation 2, and (2) micelles that are described as hard spheres (form factor [3]), which are homogeneously distributed in the complex coacervate matrix at an overall volume fraction ϕ_{m} (structure factor as given in the Sasfit manual with a Percus-Yevick closure [3]). The structure factors are included using the monodisperse approximation, in which the size-averaged form factor is multiplied directly with the structure factor to yield the differential scattering cross-sections. The two contributions to the total scattering cross-section are added: $\mathrm{d}\sigma/\mathrm{d}\Omega(q) = \sum_i \mathrm{d}\sigma_i/\mathrm{d}\Omega(q)$

References

[1] K. Hiraoka, T. Shirouzu, and T. Yokoyama, "Density measurements of poly(acrylic acid) potassium salts," *Rep. Tech. Eng. (Nagasaka)*, vol. 13, pp. 67–72, 1983.

[2] M. Moglianetti, P. Li, F. L. G. Malet, S. A. Armes, R. K. Thomas, and S. Titmuss, "Interaction of polymer and surfactant at the air-water interface: Poly(2-(dimethylamino)ethyl methacrylate) and sodium dodecyl sulfate," *Langmuir*, vol. 24, pp. 12892–12898, 2008.

[3] https://kur.web.psi.ch/sans1/SANSSoft/sasfit.pdf