Supporting Information

Scattering Neutrons along the Polyelectrolyte Complex/Coacervate Continuum

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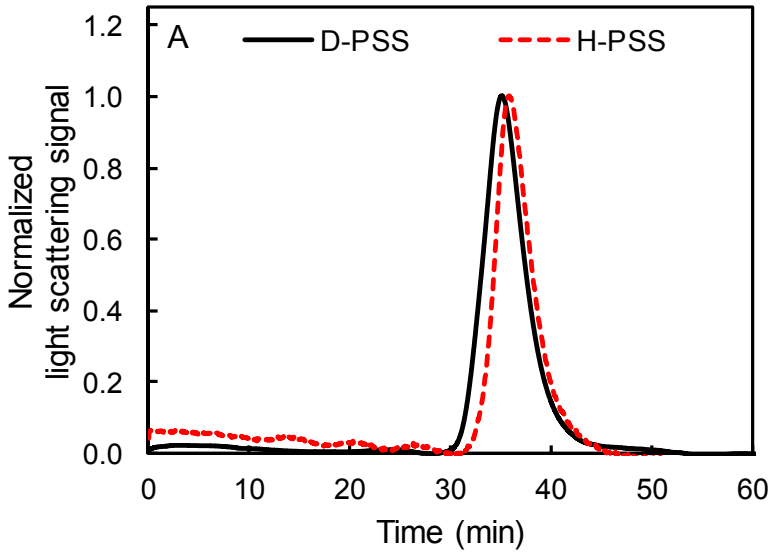

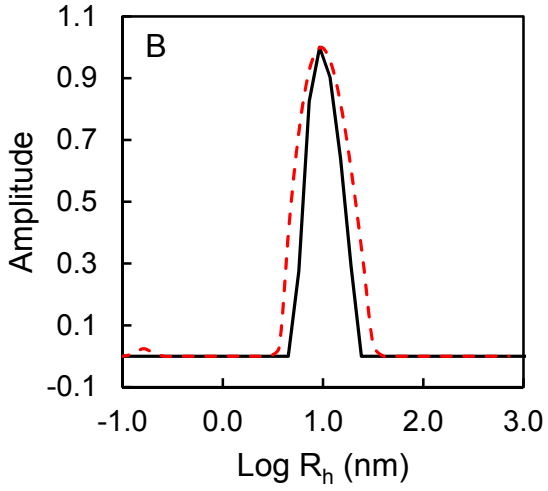

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GPC analysis	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n	N, number of repeats	R_h in 0.1 M KBr (nm)
H-PSS	104 200	103 300	1.01	501	9.7 ± 0.7
D-PSS	111 300	109 600	1.02	515	10.3 ± 0.3

Figure S 1. (A) Normalized light scattering signal obtained from gel permeation chromatography (GPC) to determine PSS molecular weights. (B) Dynamic light scattering (DLS) analysis showing the hydrodynamic radius, R_h, of H-PSS (red dashed) and D-PSS (black solid) in 0.1 M KBr. (C) Summary table showing the mass average (M_w), number average (M_n) molar masses, polydispersity indices (M_w/M_n), and R_h of H-PSS and D-PSS, sulfonated from H-PS and D-PS, obtained by GPC and DLS.

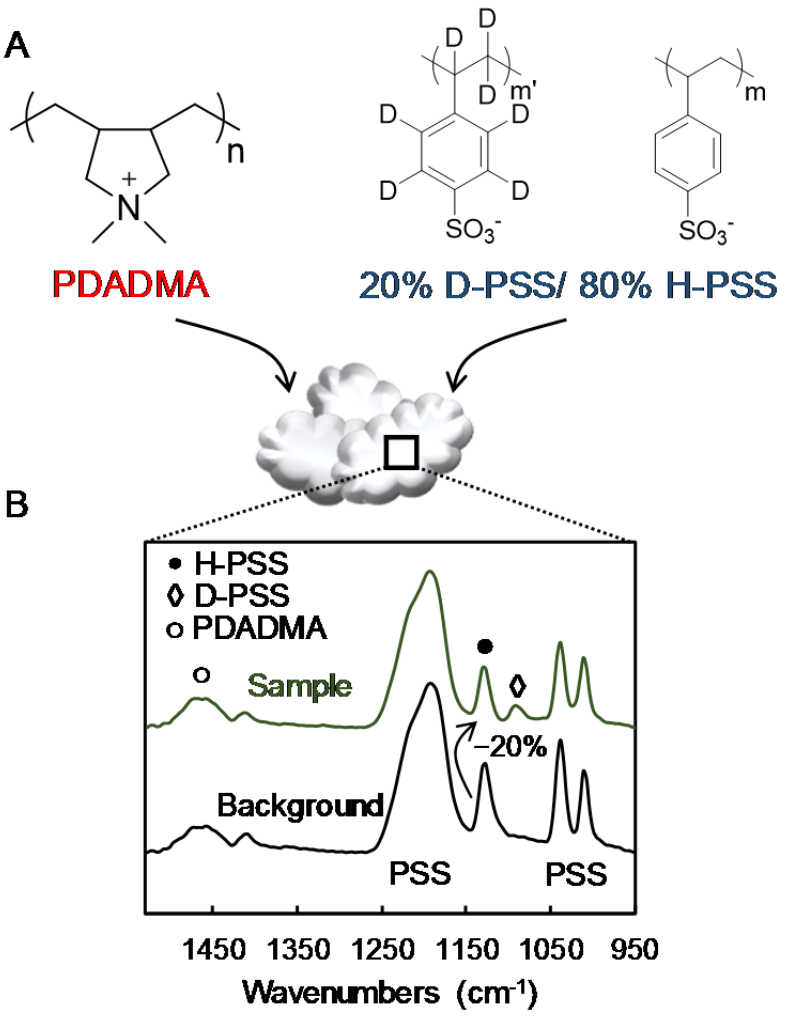

Figure S 2. (A) Structures of poly(diallyldimethylammonium) (PDADMA) and poly(styrenesulfonate) (PSS) (protiated and deuterated). (B) Background and sample spectra of PDADMA/PSS PEC. H-PSS area in background = 0.152; H-PSS area in sample = 0.120; Percent decrease = 21%.

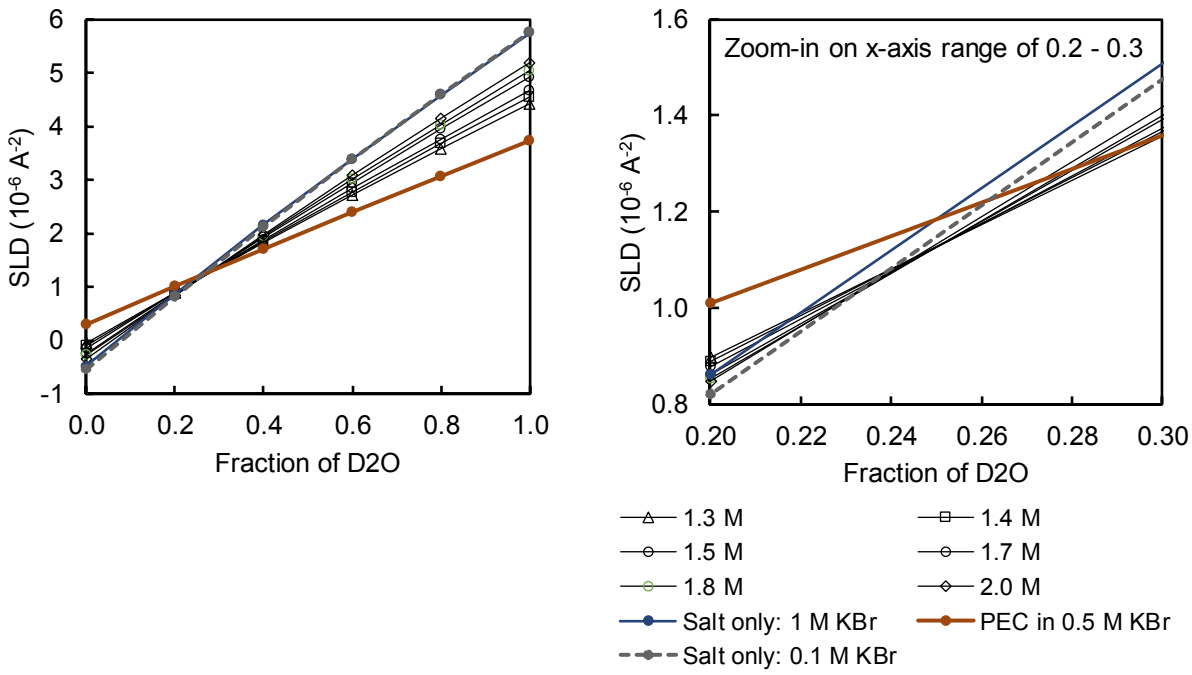

Figure S 3. Scattering length densities (SLDs) of different compositions of solid polyelectrolyte complex (in 0.5 M KBr), coacervates (in 1.3 – 1.8 M KBr), solution (in 2.0 M KBr), as well as KBr in water. Compositions were estimated from the phase diagram established by Wang and Schlenoff.[1] The NIST Center for Neutron Research online calculator was used to calculate the SLDs (https://www.ncnr.nist.gov/resources/activation/). The right diagram is a zoom-in on the x-axis range of 0.2 – 0.3 from the plot on the left.

The strategy in the current work was to match the SLDs of all components except the deuterated PSS, allowing a focus on the structural properties of this one component. In theory, the nondeuterated components could also be matched, but the PDADMA employed here had a broad molecular weight distribution, which would complicate analysis (e.g. would provide a range of coil diameters).

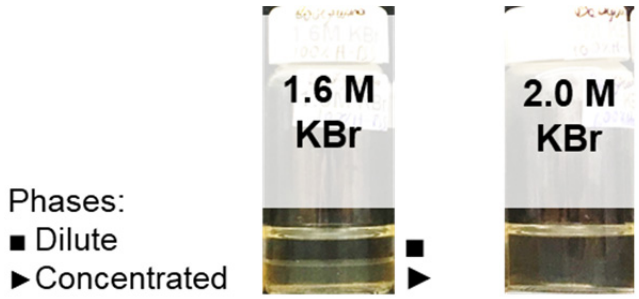

Figure S 4. Comparison between the phase-separated coacervate at 1.6 M KBr and the uniform polyelectrolyte complex solution at 2.0 M KBr.

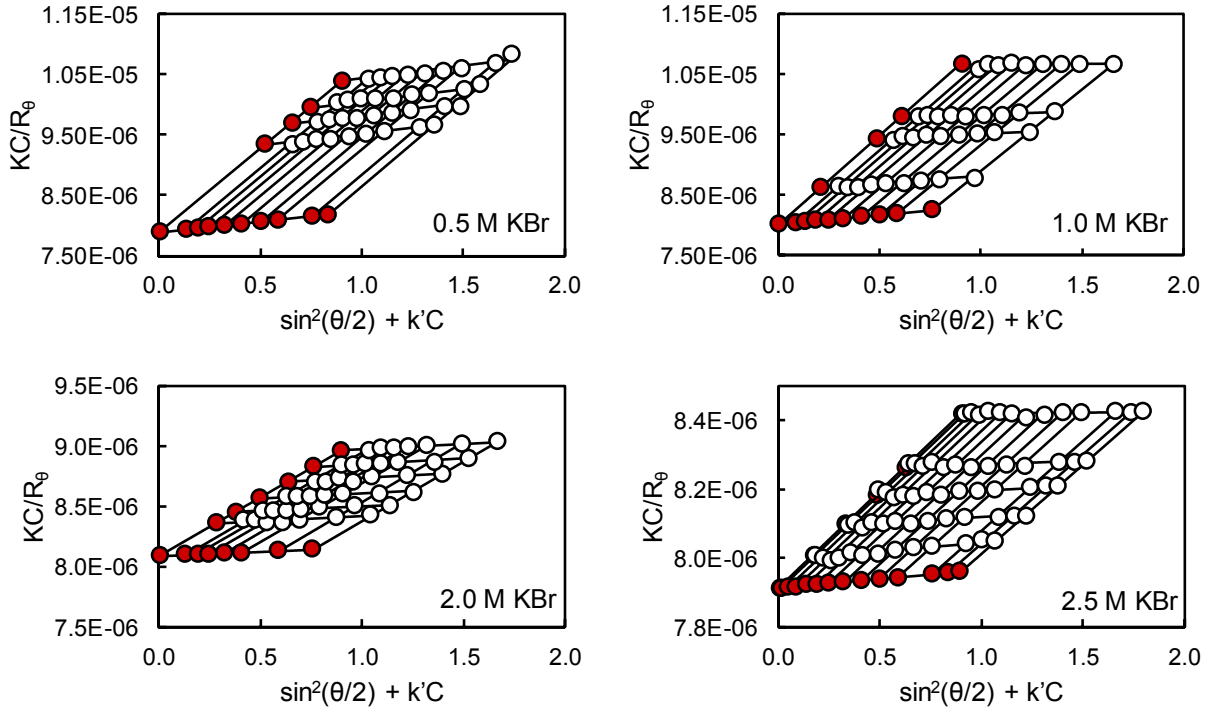

Figure S 5. Zimm plots obtained by fitting static light scattering data of H-PSS in 0.5, 1.0, 2.0 and 2.5 M KBr. The resulting R_g is shown in Figure 6 in the main text. The resulting molecular weights (M_w) and second virial coefficients (A_2) are shown in Figure S6 below.

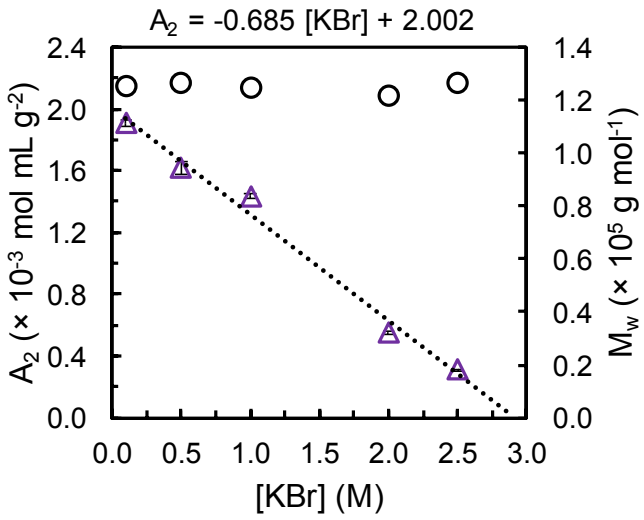

Figure S 6. Second virial coefficients (A_2, triangles) and molecular weights (M_w, circles) extracted from the Zimm plots for a series of H-PSS in 0.1 – 2.5 M KBr solutions, measured by static light scattering. The molecular weight here (around 123 000 g mol^{-1}) is larger than that observed in Figure S1 (104 200 g mol^{-1}) because the counterion to the PSS in this experiment is K^+ instead of Na^+. The dotted line shows the extrapolation of A_2 to 0 (theta conditions for [KBr] = 2.9 M).

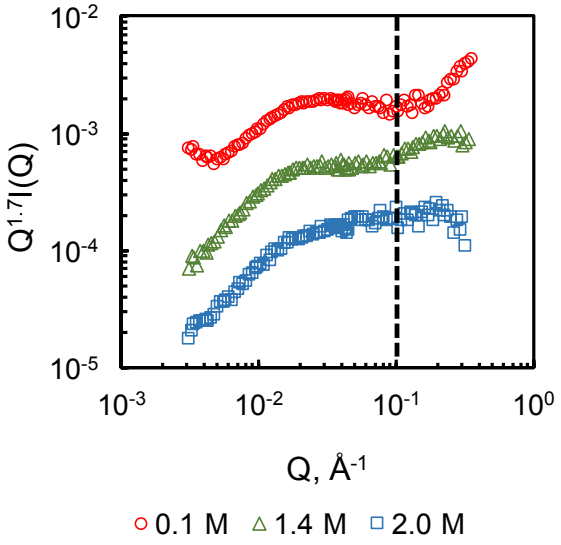

Figure S 7. $Q^{1.7}I(Q)$ versus (Q) plots to assess power scaling for PDADMA/PSS complexes in different morphologies: solid in 0.1 M KBr, gel-like coacervate in 1.4 M KBr, and liquid in 2.0 M KBr. The dashed line is added to show the limit of the slope dependence. The data to the right of it shows the effect of the high-Q peak on this scaling. The y-axis is in $Å^{-2}$ cm^{-1}.

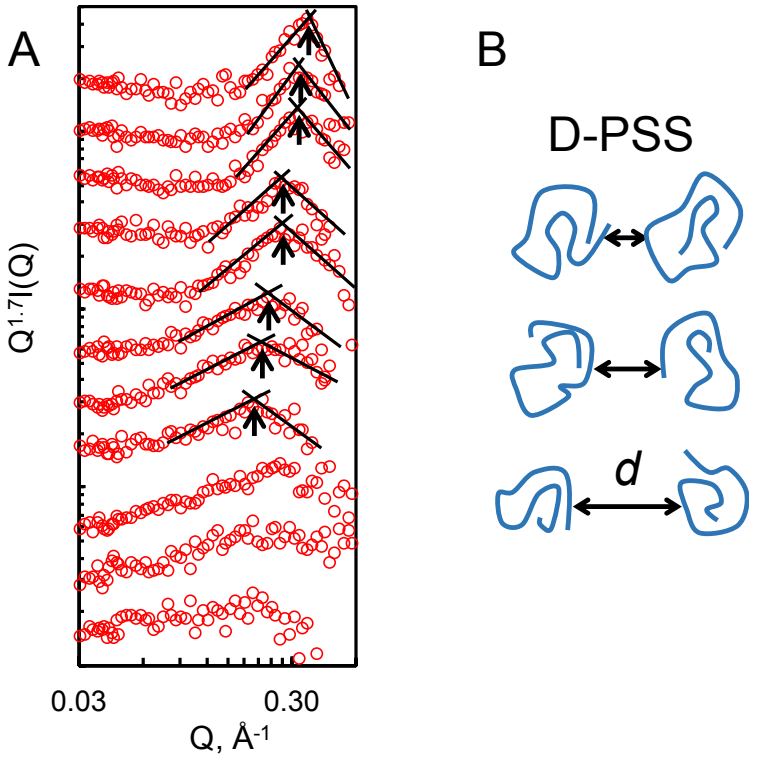

Figure S 8. (A) High Q correlation peak. The plots were obtained from the high Q region in $Q^{1.7}I(Q)$ plots. The black lines are added for the purpose of clarifying the position of the peak. The peak shifts towards lower Qs (higher distances) with the addition of salt, and progressively fades away in the coacervate regime. Samples are the same as mentioned before in increasing salt concentrations from top to bottom (0.1, 0.25, 0.5, 0.75, 1.0, 1.4, 1.5, 1.6, 1.7, 1.8 and 2.0 M KBr). (B) Schematic representation of the interchain distance between D-PSS.

Table S 1. Concentrations of total chains, total PSS, and D-PSS in the PDADMA/PSS PEC at different concentrations of KBr.

[KBr] (M)	[Chains] (M)	[PSS] (M)	[D-PSS] (M)
0.10	4.91	2.45	0.49
0.25	4.60	2.30	0.46
0.50	4.09	2.05	0.41
0.75	3.30	1.59	0.33
1.00	2.69	1.34	0.27
1.40	1.56	0.78	0.16
1.50	1.30	0.65	0.13
1.60	1.05	0.52	0.10
1.70	0.79	0.39	0.08
1.80	0.53	0.26	0.05
2.00	0.22	0.15	0.03

Reference

1. Wang, Q. F.; Schlenoff, J. B. The Polyelectrolyte Complex/Coacervate Continuum. *Macromolecules* **2014,** 47 (9), 3108-3116.