Supporting Information: Screening lengths and osmotic compressibility of flexible polyelectrolytes in excess salt solutions

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SANS configurations

Table S1 lists the different instrument configurations used for the experiments along with the q range covered.

Instrument	Wavelength (Å)	Sample to detector distance (m)			q range (Å^{-1})
		Low	Middle	High	
NGB 10m	5	-	5	1.5	0.01-0.4
NGB 30m	6	13.4	4.5	1.5	0.003-0.4
NGB 30m	6	13.4	4	1.5	0.003-0.4
D11	6	-	8	1.5	0.008-0.4

Table S1: Configurations of different SANS instruments employed.

Typical acquisition times were 3-5 minutes for the high q configurations and 5-15 minutes for the middle q configurations. Samples were run in 1 mm or 2 mm path length Hellma cells.

Contrast of polymer, counter-ions and co-ions

The scattering intensity of a salt-free polyelectrolyte solution is given by:

$$I(q)/\rho = b_m^2 S(q)_{mm} + b_c b_m S(q)_{mc} + b_{cc}^2 S(q)_{cc}$$

where ρ is the number density of particles, b is the contrast factor and $S(q)$ is the structure factor. The subscripts b and m refer to the monomers and counterions respectively. Table S2 lists the coherent scattering lengths (b_{coh}) and partial molar volumes (V) of the different scattering species in solution along with the contrast factors. The main source of contrast is expected to arise between the monomers and the solvent, with the counterions and added salt ions having only a minor effect on the scattering intensity. We therefore approximate:

$$\frac{I(q)}{\rho} \approx b_m^2 S(q)_{mm}$$

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Component	b_{coh} (fm)	V (cm^3/mol)	$b_i = b_{coh} - b_{D2O}[V/V_{D2O}]$ (fm)
D_2O	19.1	18.1	-
PSS^-	47.2	114.8	5470
Na^+	3.6	3.63	0.053
$NaCl$	13.2	16.6	18.63

Table S2 lists the coherent scattering lengths, partial molar volumes and contrast factors of the various components of the NaPSS solutions. The contrast between polymer and solvent is seen to dominate over the ion-solvent.

Fitting procedure

Figure S1a shows a representative scattering profile of NaPSS in 3 M NaCl solution before the background has been subtracted along with a fit to:

$$P(q) = \pi/(b'q)e^{-q^2R_C^2/4} + Bkgd \qquad\qquad (S1)$$

Where the b' is the effective monomer size, R_C is the cross-sectional radius of the chain and $Bkgd$ is the background terms, which includes both coherent and incoherent q-independent scattering contributions. We use $b' = 2$Å and $R_C = 4$Å as discussed in the main text, and leave the background as a free parameter. The background subtracted intensity $[I(q) - Bkgd]$ is plotted in Figure S1b.
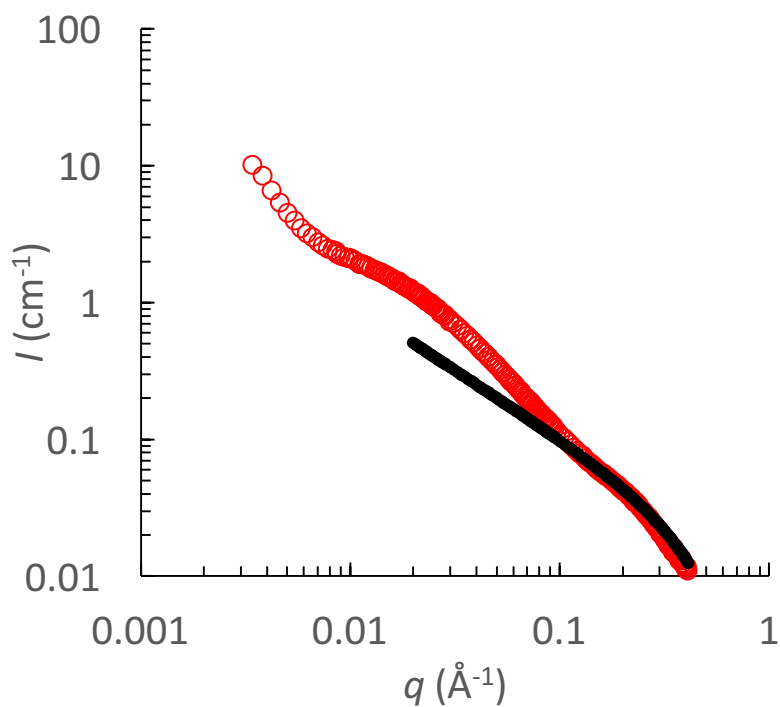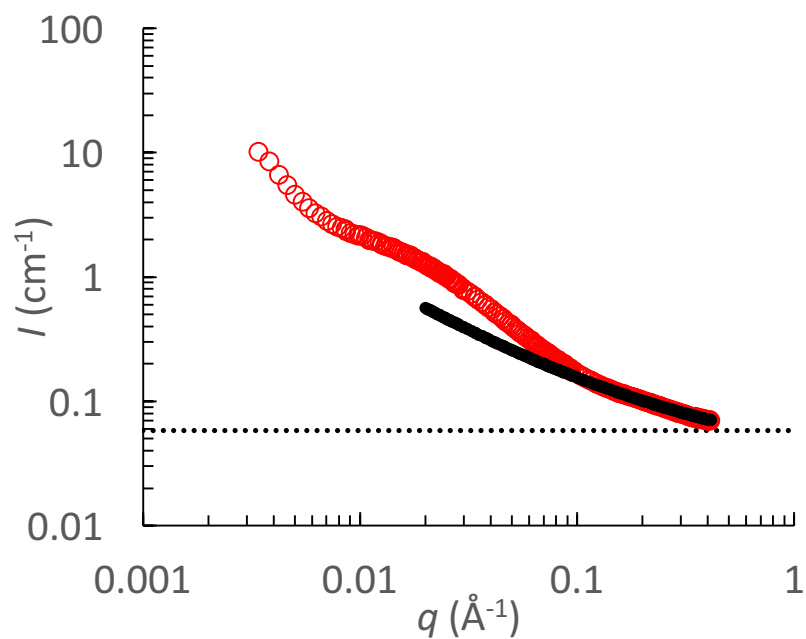
Figure S1: Top: scattering intensity prior to background subtraction, indicated by dashed line. Bottom: background subtracted scattering intensity. Black lines are fits to the worm-like chain form factor at high q, given by Eq. S1.

A Debye plot of the background subtracted scattering intensity is shown in Figure S2a. A linear region can be observed for $0.0001 \text{ Å}^2 < q^2 < 0.002 \text{ Å}^2$, with a downturn caused by aggregates

occurring at low q^2. The full line is a fit to Eq. 9 of the main text over the linear region.

Alternatively, the clustering contribution may be removed by subtracting a power-law:

$$I(q)_{clust} = Cq^{-m}$$

where C is a pre-factor and m is an exponent related to the fractal dimension of the clusters. The inverse scattering intensity after subtraction of the clustering term is shown in Figure S2b along with a fit to Equation 9 of the main text. Values obtained from both methods do not typically differ beyond a few percent. For the results presented in the paper, we have adopted this second method to extract $I(0)$ and ξ.
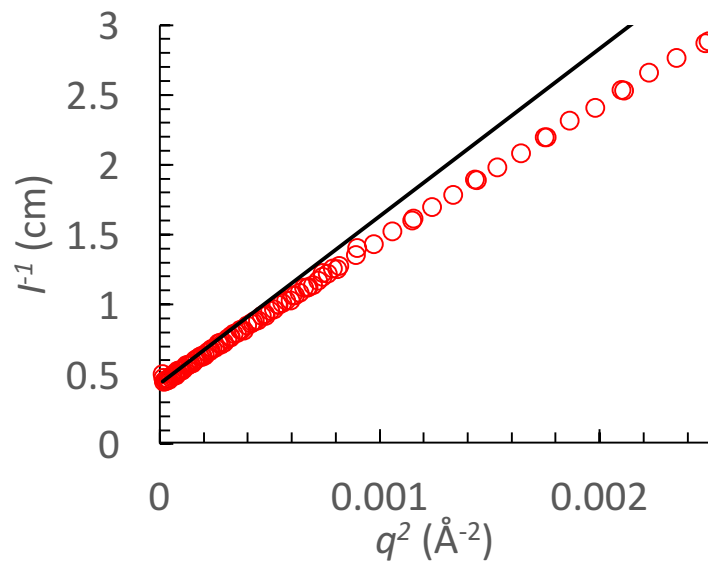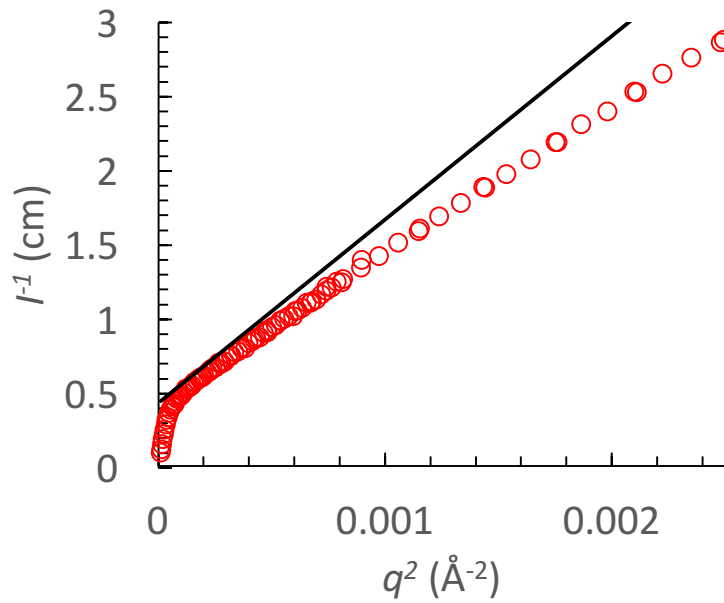
Figure S2: Inverse scattering intensity as a function of q^2. Top: Background subtracted scattering intensity. Bottom: Background and clustering subtracted scattering intensity. Lines are fits to Eq. 9 of the main text.

Best fit power-laws for ξ and *I(0)/c* vs. *c*

Table S2 lists the various power-laws and confidence intervals (95%) for the various fits in Figure 3 as well as additional c_S concentrations not included in the figure. The calculation of the confidence intervals was carried out using standard linear regression analysis, see below for more details.

c_S (M)	ξ vs. c exponent	$I(0)$ vs. c exponent
3	-0.43 ± 0.05	-0.76 ± 0.11
2.25	-0.50 ± 0.08	-0.87 ± 0.19
1.5	-0.57 ± 0.10	-0.95 ± 0.17
0.75	-0.63 ± 0.10	-0.82 ± 0.11
0.375	-0.69 ± 0.11	-1.1 ± 0.17

Table S3: Power-law exponents for correlation length and reduced zero-angle scattering intensity dependence on concentration. Errors are 95% confidence intervals, calculated as explained below.

Best fit power-laws for ξ and vs. c_S

c (M)	ξ vs. c_S exponent	c_S range (M)
0.2	0.48 ± 0.19	0.75-3
0.1	0.29 ± 0.08	0.3-3
0.05	-0.28 ± 0.07	0.15-3

Table S4: Power-law exponents for the added salt dependence of the correlation length in excess salt. Errors are 95% confidence intervals, calculated as explained below.

Figure S3 plots the correlation length in excess added salt multiplied by $c^{1/2}$ [$\propto \xi(0)$] as function of $[1 + 2fc/c_S]^{0.25}$. The Dobrynin model expects this plot to reduce all points into a single line going through the origin, which is not observed experimentally.
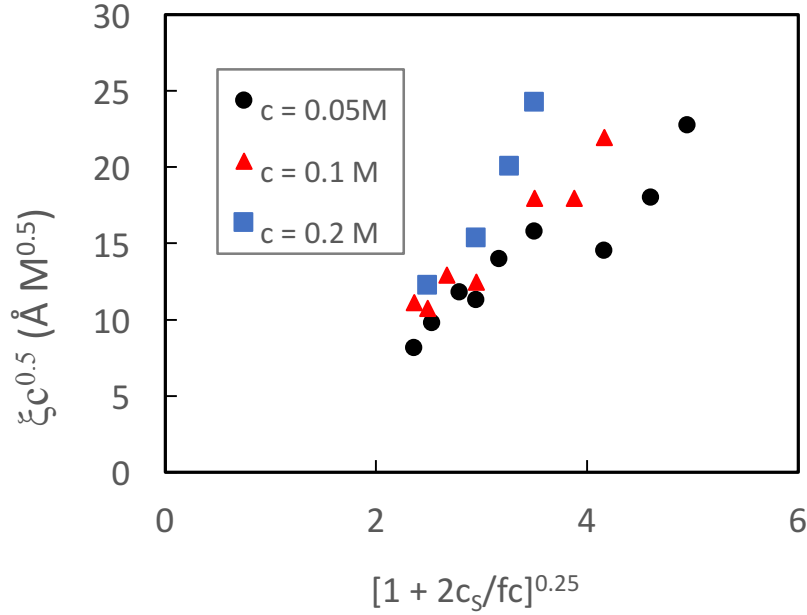
Figure S3, correlation length in excess added salt multiplied by $c^{1/2}$ as a function of $1 + 2fc/c_S]^{0.25}$. Polymer concentrations are indicated in the legend.

Estimates of confidence intervals

In order to fit experimental data to a power-law, for example $\xi = Kc^{\gamma}$, we use a standard linear regression method after linearizing the data. K and γ are therefore estimated as:

$$K = \log[\frac{\sum_{i=1}^{n} \log[\xi_i] - \gamma \sum_{i=1}^{n} \log[c_i]}{n}]$$

and

$$\gamma = \frac{n \sum_{i=1}^{n} \log[c_i] \log[\xi_i] - \sum_{i=1}^{n} \log[c_i] \log[\xi_i]}{n \sum_{i=1}^{n} (\log[c_i])^2 - (\sum_{i=1}^{n} \log[c_i])^2}$$

where n is the number of samples for each dataset, which varies between 6 and 11 for the data considered here. Confidence intervals (95%) for the exponents are estimated as:

$$E_{95\%} = \left[\frac{\frac{1}{n-1} \sum_{i=1}^{n} s_i^2}{\sum_{i=1}^{n} [Log c_i - avg(log c)]^2} \right]^{1/2}$$

where $avg(x)$ is the mean of n values of x, and $s_i = \log(\xi_i) - \log(K) - \gamma \log(c_i)$.

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Calculation of ξ_Π/ξ_{OZ}

The calculation of the osmotic correlation length is done as follows: Equations 5 and 8 of the main text are used to calculate the osmotic compressibilities of NaPSS as a function of polymer concentration at a fixed c_S. From these values, we subtract Eq. 4b to obtain the polymer contribution to the osmotic compressibility. Equation 4a is then fitted to these values, leaving A_Π as a free parameter and fixing γ to the value obtained from ξ_{OZ} vs. plots (i.e. the values listed in Table 2). The ratio ξ_Π/ξ_{OZ} is then calculated as A_Π/A.

Comparison of chain dimensions from SANS with light scattering data

In Figure 6a of the main text, we observed that the SANS measurements of the chain size of NaPSS exceeded those for the theta dimensions calculated from Norisuye and co-worker's light scattering data.

This discrepancy is not surprising given that in semidilute solutions the chains are expected to feel excluded volume interactions between the thermal blob size and the correlation length. For polyelectrolytes, the thermal blob size, that is, the length-scale at which excluded volume begins to perturb the polymer conformation is:

$$\xi_T = l_K^2/B$$

where l_K is the Kuhn length of the polyelectrolyte, which is a function of the solution ionic strength and B is the excluded volume strength, defined as

$$B = \beta/l_K^2$$

where β is the binary cluster integral between a pair of Kuhn segments. From Norisuye and co-workers' analysis of light scattering data for NaPSS in excess added salt, we estimate of the excluded volume strength of $B \approx 5$ Å, $l_K \approx 15$ Å and we calculate the thermal blob size to be $\xi_T \approx 45$ Å, containing 9 Kuhn segments and corresponding to a radius of gyration of $45/6^{1/2} \approx 18$ Å. Excluded volume is expected to perturb the chain for distances larger than ξ_T and up to the correlation length. The radius of gyration of a correlation blob for $c = 0.4$ M is ≈ 61Å. The chain dimensions of NaPSS in 3 M and at c = 0.4 M are then expected to be ≈ 8 Å^2, we have assumed that the chain end-to-end distance scales as $N^{0.59}$ for length-scales in the range $\xi_T < d < \xi$.

The value of $R_g^2/N \approx 8$ Å^2 is significantly smaller than the measured values for semidilute solutions in Fig 6a. The discrepancy could arise due to excluded volume persisting at length-scales larger than the correlation length.

Comparison with NaPSS prepared by sulfonation of polystyrene

Figure S4 compares the correlation length of NaPSS prepared by polymerisation of styrene sulfonate as described in the main text and by sulfonation of polystyrene. The latter samples were

purchased from polymer standard services (Mainz, Germany) and had molar masses of 900kg/mol and 2070 kg/mol. The data for both molar masses overlap within error.

The NaPSS samples prepared by different methods display similar values of the correlation length as a function of polymer concentration. The slightly larger values for NaPSS prepared by sulfonation of polystyrene are consistent with earlier studies by Takahashi et al and Hirose et al which showed that the θ salt concentration is lower ($\approx$ 3.1 M vs 4.2 M) for NaPSS prepared by sulfonation of polystyrene due to the influence of $\approx$ 5% non-sulfonated monomers which make the polymer backbone more hydrophobic, see references 68 and 77 of the main text for more details.
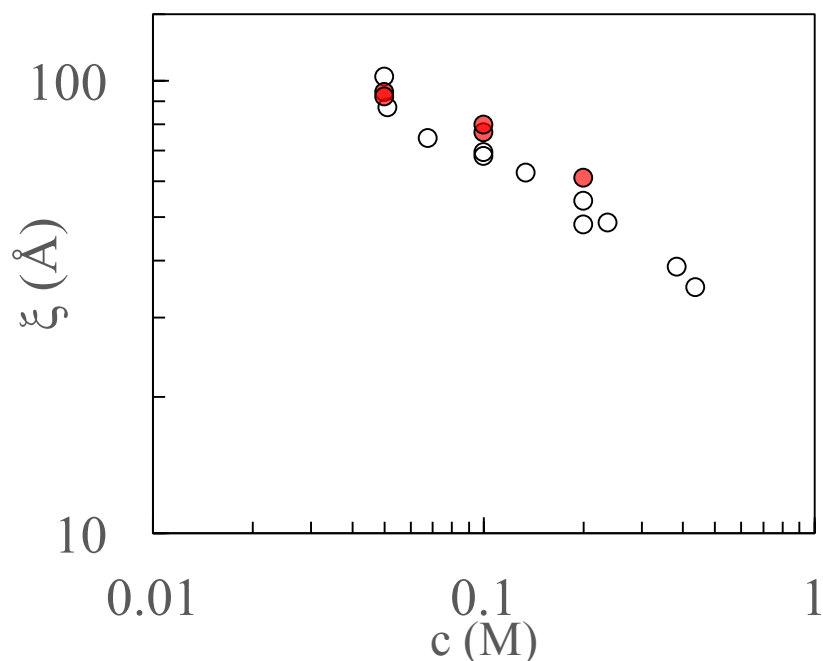

Figure S4. Comparison of ξ in c_S = 3 M salt solution. White symbols are for NaPSS prepared by polymerisation of styrene sulfonate and red points are for NaPSS prepared by sulfonation of polystyrene.