

Supporting Information: Scaling and Entanglement properties of neutral and sulfonated polystyrene.

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I. THE OVERLAP CONCENTRATION IN SALT-FREE SOLUTION

In this section we discuss the estimation of the power-law of the overlap concentration with the degree of polymerisation according to different methods. We begin by considering the various ways of estimating c^* , then discuss the possible sources of experimental error and the range over which we expect scaling to hold. Finally we provide estimate for the scaling exponents in salt-free solution.

A. Estimation methods

Table S I lists three estimates for the overlap concentration: 1) c_η^* , estimated viscosimetrically using the $\eta_{sp}(c^*) = 1$ criterion put forward by Colby and co-workers¹. 2) c_{SAXS}^* , which is identified as the crossover point between $q^* \propto c^{1/3}$ and $q^* \propto c^{1/2}$. 3) $c_{LS/SAXS}^*$, which follows the same procedure as for c_{SAXS}^* , but the dilute solution q^* data are from light scattering measurements.

For methods 2) and 3), the q^* vs. c relation is calculated by fitting dilute solution data to:

$$q^* = Bc^{1/3} \quad (S1)$$

where B is a fit parameter listed in Table S I, q^* is in nm^{-1} and c in units of moles of repeating units per dm^3 . For q^* in semidilute solutions, we use Kaji et al's² relation:

$$q^* = 1.7c^{1/2} \quad (S2)$$

The overlap concentration is estimated as the crossover between Eqs. S1 and S2:

$$c_{SAXS}^* = \left(\frac{B}{1.7}\right)^6 \quad (S3)$$

Estimates of c_{SAXS}^* for which no values of B are listed in Table I are read of from the crossover between $q^* \propto N^{1/3}$ to $q^* \propto N^0$ in Ref. [2].

B. Sources of error

The relaxation times of polyelectrolytes in salt-free solution increase with decreasing concentration, meaning that in order to obtain the zero-shear values of the viscosity, low shear-rates, often below what is typically achievable by capillary viscosimetry must be used. A significant part of the literature suffers from shear thinning effects. This issue has been discussed extensively in references^{1,3-5}. The data selected for this study are expected to correspond to the zero-shear rate limit, following the criteria explained in the aforementioned references.

The high exponent in Eq. S3 means small errors in B can lead to relatively large errors in c^* . Aqueous solution of NaPSS always contain a finite amount of residual salt. Carbon dioxide from the air dissolves in water to form carbonic acid with a concentration of $c_S \simeq 5 \times 10^{-6}$ M. Additional contamination may arise from leaching of ions from glass containers or from residual salt being present in the polymer powder, see references [1,6] for a discussion of this topic. The effect of added salt is to shrink polyelectrolyte chains, thereby increasing c^* . Viscosity measurements show the increase in c_η^* with increasing c_S , see for example refs. [1,4,7-9]. Scaling expects:

$$c^*[1 + 2c_S/(fc^*)]^{-1.5} = b'^{-3}N^{-2} \quad (S4)$$

where the various symbols have the same meaning as in the main text. According to Eq. S4, the effect of c_S on c^* becomes significant when $c_S \gtrsim fc/2$, i.e. when the number of salt ions exceeds that of free counterions.

The effect of residual salt on estimates for the overlap concentration using Eqs. S1-S3 is less clear. Addition of salt is known to shift q^* to lower values¹⁰, decreasing the value of B in Eq. S1. This in turn results in a lower value of c_{SAXS}^* when calculated from Eq. S3. This increase is of course artificial as c^* always increases with added c_S . All the values of c_{SAXS}^* are for $fc \gg 2c_S$ where the effect of residual salt is expected to be negligible. For some of the estimates of $c_{SAXS/LS}^*$ on the other hand $fc \sim 2c_S$, and the effect of residual salt could be significant. We are at present unable to provide a quantitative estimate for the effect of c_S on $c_{SAXS/LS}^*$.

C. Range of validity of scaling

A final question before we determine the power-law exponent of c^* with N is the range over which scaling

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Table S I. Values for the overlap concentration in salt-free solution used in Figure 2 of the main text.

Reference	N	c_η^* (M)	c_{SAXS}^* (M)	$c_{LS/SAXS}^*$ (M)	Notes
Uzum et al [11]	367	0.018			
Uzum et al [11]	155	0.227			
Uzum et al [11]	64	0.353			
Uzum et al [11]	32	0.635	0.305		c_η^* extrapolated from $c < 0.3$ M data, B calculated from $c = 0.08$ - 0.2 M
Uzum et al [11]	20		1.1		B calculated from $c = 0.01$ - 0.1 M
Lopez and Richtering [5]	145.5	0.13			
Lopez and Richtering [5]	319	0.027			
Lopez and Richtering [5]	740	0.0045			
Lopez and Richtering [5]	1305	0.0011			
Oostwal and Odijk [12]	155	0.09			
Oostwal and Odijk [12]	440	0.014			
Oostwal and Odijk [12]	885	0.0021			c_η^* extrapolated from data for $c = 0.027$ M $< c < 0.047$ M
Pavlov et al [13]	620	0.019			Sample 6, M_w recalculated from $[\eta]$ in 0.2M NaCl and MHS relation from Iwamoto et al ¹⁴
Pavlov et al [13]	420	0.0445			Sample 7, M_w recalculated as above.
Pavlov et al [13]	265	0.0765			Sample 8, M_w recalculated as above.
Boris and Colby [1]	6060	0.00008			
Chen et al [15]	5942				
Chen et al [15]	4005	0.0003			
Chen et al [15]	2925	0.0005			
Chen et al [15]	1310	0.00078			
Yang [16]	1070	0.0115			
Yang [16]	445	0.095			
Cohen et al [6]	1060	0.0010			
Cohen et al [6]	885	0.0036			Extrapolated from $c < 0.0025$ M
Cohen et al [6]	690	0.0055			Extrapolated from $c < 0.005$ M
Ganter et al [17]	77000	0.000028			M_w corrected to $\simeq 15000$ kg/mol from $[\eta]$ in 0.1 M and Takahashi et al's ¹⁸ MSK relation, see also [5,19].
Kaji et al [2]	9		1.3		Extracted from Fig. 5 of ref. [2]
Kaji et al [2]	23		1.25		Extracted from Fig. 5 of ref. [2]
Kaji et al [2]	40		0.73		Extracted from Fig. 5 of ref. [2]
Kaji et al [2]	66		0.5		Extracted from Fig. 7 of ref. [2]
Kaji et al [2]	84		0.3		Extracted from Fig. 7 of ref. [2]
Kaji et al [2]	90		0.135		Extracted from Fig. 5 of ref. [2]
Kaji et al [2]	110		0.2		Extracted from Fig. 7 of ref. [2]
Kaji et al [2]	155		0.1		Extracted from Fig. 7 of ref. [2]
Kaji et al [2]	210		0.05		Extracted from Fig. 7 of ref. [2]
Kaji et al [2]	300		0.025		Extracted from Fig. 7 of ref. [2]
Krause et al [20]	1770			8.8×10^{-4}	$B = 0.5252$, full c range
Krause et al [20]	5300			5×10^{-3}	$B = 0.479$, $c < 0.00018$ M
Johner et al [21]	500			5.3×10^{-3}	$B = 0.7121$ full c range
Johner et al [21]	1000			8.3×10^{-4}	$B = 0.5206$ full c range
Johner et al [21]	2000			3.4×10^{-4}	$B = 0.4478$ full c range

expects Eq. S4 to apply. In principle, no obvious upper limit is expected, at least within the experimental range of N considered in this study. According to Dobrynin et al's model, Eq. S4 should not hold when the end-to-end distance of NaPSS chains is smaller than the size of a thermal blob ξ_T . The latter has been estimated as $\simeq 1$ nm from scattering measurements of the lateral chain dimensions of NaPSS^{22,23}. Note that this value is smaller than the intrinsic Kuhn length of NaPSS and scaling ex-

pects ξ_T to always be larger than the monomer size.²⁴ Another way of estimating ξ_T is as the value of ξ at which Eq. S2 breaks down and a new scaling of $q^* \propto c^{1/4}$. This presumably corresponds to the value at which the concentrated regime sets in. This crossover has been measured by SAXS as $c_D = 1.2$ M,²⁵ and gives $\xi_T \simeq 3.3$ nm. A problem with this estimate is that in the concentrated regime, the chain size is expected to be independent of concentration, which is not observed experimentally.¹⁹

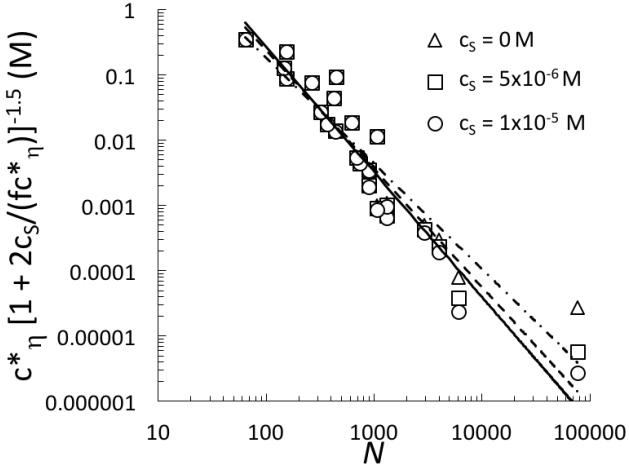


Figure S 1. Viscosimetric estimate of the overlap concentration corrected for the effect of residual salt according to Eq. S4. The different symbols correspond to different concentrations of residual salt, indicated on the legend. The lines are best fit power-laws. Full line: $c_s = 10^{-5}$ M, $c_{\eta}^*[1 + 2c_s/(fc_{\eta}^*)]^{-1.5} = 1800N^{-1.92}$. Dashed line: $c_s = 10^{-5}$ M, $c_{\eta}^*[1 + 2c_s/(fc_{\eta}^*)]^{-1.5} = 980N^{-1.81}$, dashed-dotted line: $c_s = 10^{-5}$ M, $c_{\eta}^*[1 + 2c_s/(fc_{\eta}^*)]^{-1.5} = 310N^{-1.62}$. Data are from references listed in Table S I.

From Fig. 2 of the main text, a crossover in the scaling of c^* with N is apparent around $c \simeq 1 - 1.2$ M or $N \simeq 40$. We therefore choose this as the N_{min} value for the following power-law fits.

D. Scaling of c_{η}^* with N

Figure 1 plots c_{η}^* multiplied by a factor of $[1 + 2c_s/(fc)]^{1.5}$ to correct for the effect of residual salt as a function of N . Three concentrations of residual salt are considered: $c_s = 0$ M, $c_s = 5 \times 10^{-6}$ M (the concentration expected from carbonic acid) and $c_s = 10^{-5}$ M. The best fit exponent for the variation of the corrected c_{η}^* depends strongly on the assumed concentration of residual salt, largely due to the influence of the highest N datum. For $N < 3000$, nearly no effect of added salt is expected. A fit over this N -region gives $c_{\eta}^* = 3690N^{-2.0 \pm 0.4}$, in agreement with Dobrynin et al's prediction.²⁴

E. Scaling of c_{SAXS}^* with N

For the reasons discussed above, it is difficult to assess the reliability of $c_{SAXS/LS}^*$. If we fit all $c_{SAXS/LS}^*$ and c_{SAXS}^* data for $N > 40$, $c_S^* = 787N^{1.84 \pm 0.25}$ is obtained, where the subscript S is used to indicate that the value refers to a combination of both SAXS and LS data, or $c_S^* = 1973N^{2.0 \pm 0.2}$ if we do not include the two highest N data points, which, following the earlier discussion, may be affected by the residual salt content in the solution.

These best fit exponent are, within error, in agreement with the viscosimetric estimate. If we restrict the fit to Kaji et al's data for $35 < N < 250$, $c_{SAXS}^* = 680N^{1.7 \pm 0.3}$ is obtained. All the error bars quoted are 95% confidence intervals. The relation given in Fig 3 of the main paper corresponds to the best fit for $40 < N < 2000$ with the exponent fixed at -2.

II. SAMPLES

Table S II lists the different samples employed in this study.

Table S II. Molecular weight of samples used in this study. The polydispersity (pd) and degree of sulfonation (D.S.) are estimated by the Polymer Standard Services as $pd < 1.2$ and D.S. $\simeq 0.95$ for all samples.

Sample	M_w (g/mol)	pd
PSS30k	3.3×10^4	1.2
PSS67k	6.7×10^4	1.2
PSS145k	1.45×10^5	1.2
PSS220k	2.1×10^5	1.2
PSS425k	4.25×10^5	1.2
PSS466k	4.66×10^5	1.2
PSS666k	6.66×10^5	1.2
PSS1M	9.76×10^5	1.2
PSS2M	2.07×10^6	1.2

III. DETERMINATION OF ENTANGLEMENT CROSS-OVER IN SALT-FREE SOLUTION

Table S III lists the data presented in Figure 5a of the main text. $\eta_{sp,NE}$ is the non-entangled viscosity, calculated following ref. [5]. The data for Figure 5b of the main text is compiled in Table S IV.

Table S III. Viscosity parameters for data in Fig. 5a of the main text.

c (M)	η_{sp}	$\eta_{sp,NE}$	$\eta_{sp}/\eta_{sp,NE}$	Eq. 8a
1.19	34800	2120	16.4	39500
1.00	20200	1500	13.5	18200
0.42	1520	428	3.54	874
0.28	628	288	2.19	388
0.17	347	196	1.77	215
0.041	101	79.1	1.28	79.3
0.031	74.8	67.7	1.11	67.8
0.022	61.4	56.8	1.08	56.8
0.016	52.4	48.5	1.08	48.5
0.011	42.8	40.0	1.07	40.0
0.011	42.3	39.2	1.08	39.2
0.0057	26.5	28.1	0.945	28.1

Table S IV. Specific viscosity data for Fig. 5b of the main text.

Reference	N	$c = 1 \text{ M}$	$c = 0.45 \text{ M}$	$c = 0.2 \text{ M}$	Notes
This work	10350	20200	1900	148.4	
This work	4995	2900	500	68.66	
This work	3330	860	178	35	
This work	2220	530	110	27.7	
Lopez and Richtering [5]	1400	210	49.8	13.8	
Lopez and Richtering [5]	740	57.8	18	5.41	
Lopez and Richtering [5]	335	20	7.32	2.18	
Lopez and Richtering [5]	150	8	2.95	0.65	
Uzum et al [11]	367	19.47 ^a	8		^a Extrapolated from $c < 0.5 \text{ M}$
Uzum et al [11]	155	5.11 ^a	1.95		^a Extrapolated from $c < 0.5 \text{ M}$
Uzum et al [11]	64	3.16 ^a	1.3		^a Extrapolated from $c < 0.5 \text{ M}$
Boris and Colby [1]	6060		1900	155	
Chen and Archer [15]	6063		1060	151	
Chen and Archer [15]	3890		246	55	
Chen and Archer [15]	2842		141	23	
Chen and Archer [15]	1275		34.96	10.2	
Oostwal and Odijk [12]	885		19.4 ^b	10	^b Extrapolated from $c < 0.437 \text{ M}$
Oostwal and Odijk [12]	440			4.8	
Oostwal and Odijk [12]	155			1.7	
Oostwal [26]	995		25		Values read from Ref. [1]
Oostwal [26]	1990		105		Values read from Ref. [1]
Prini et al [27]	1500		76	24	

IV. EFFECT OF TEMPERATURE AND ADDED SALT ON SOLUTION RHEOLOGY OF NAPSS

$c_S \text{ (M)}$	$\eta_0 \text{ (Pas)}$	$\tau \text{ (s)}$	$G_{int}^a \text{ (Pa)}$	$G_c \text{ (Pa)}$	G_{osc}/G_{int}
6×10^{-6}	18	0.055	327	450	1.35
8.8×10^{-2}	10	0.028	368	490	1.33
4.4×10^{-1}	4.6	0.0143	320	410	1.29
Average			340	450	1.3

Table S V. Rheological parameters for $c = 1 \text{ M}$ solutions of NaPSS with $M_w = 2 \times 10^6 \text{ g/mol}$. Steady shear parameters are estimated from fits in Fig. 2b. ^a $G_{int} = \eta/\tau$.

$T \text{ (K)}$	a_τ	a_η	$\frac{a_\eta/a_\tau}{T/298K}$
salt-free			
274	1.55	1.43	1.00
283	1.33	1.3	1.03
293	1.17	1.18	1.03
298	1	1	1
$c_S = 0.44 \text{ M}$			
274	1.8	7	1.02
298	1	1	1

Table S VI. Shift factors to reduce viscosity data in Figure 2b onto a single flow curve. a_η and a_τ are the vertical and horizontal shift factors respectively.

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