Supporting Information: Entanglement properties of polyelectrolytes in salt-free and excess salt solution

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MATERIALS AND METHODS

Three sodium carboxymethyl cellulose samples with varying molar mass (M_w) and degree of substitution (DS) were purchased from Sigma-Aldrich, their main characteristics are listed in Table SI. Samples CMC240k and sample CMC1.2M were purified to remove residual salts. Sample CMC90k was only measured in excess salt and was therefore not purified. NaCl and NaOH were purchased from Sigma-Aldrich and VWR respectively. Deionised water was obtained from a milli-Q source.

Solutions were prepared gravimetrically and stored in plastic vials to avoid ion contamination from glass. We assume a residual salt concentration of $c_S = 5 \times 10^{-6}$ M from carbonic acid picked up from the air.

Rheological measurements were performed on two stress controlled rheometers: A Kinexus pro (Malvern) and a HR3 (TA) using cone and plate geometries of 40 mm or 60 mm and 1° angle. The temperature was regulated using a Peltier plate. A solvent trap was employed to reduce evaporation.

	Supplier		Measured	
	M_w (g/mol)	DS	M_w (g/mol)	DS
CMC90k	9×10^4	0.7	–	–
CMC240k	2.5×10^5	1.2	2.4×10^5 [a]	1.3 [a]
CMC1.2M	7×10^5	0.8-0.95	1.2×10^6 [a]	–

Table S I. Properties of NaCMC samples used in this study. [a] See reference [1]

I. EXPERIMENTAL RESULTS

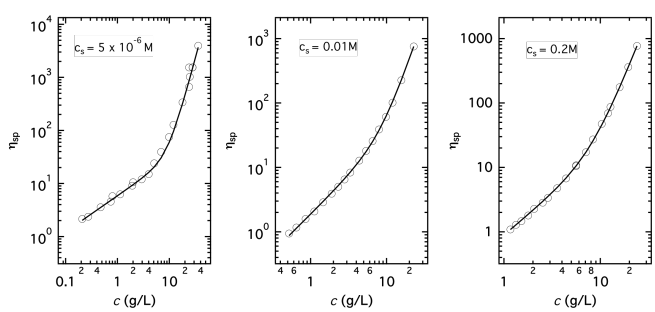

Figure S 1. Determination of entanglement concentration for CMC sample with $M_w \simeq 3.2 \times 10^5$ g/mol and DS $\simeq 1.2$. Data are from reference [1,2]. Lines are fits to Eq. 4 of the main text.

Figure 1 shows the viscosity of NaCMC as a function of polymer concentration in aqueous solutions with different amounts of added salt along with fits to Eq. 4 of the main paper.

Figure 2 plot the loss (G'') and storage (G') modulus of NaCMC solutions of different concentrations in salt-free water. The plateau modulus (G_p) is approximated from the crossover point between G' and G''.

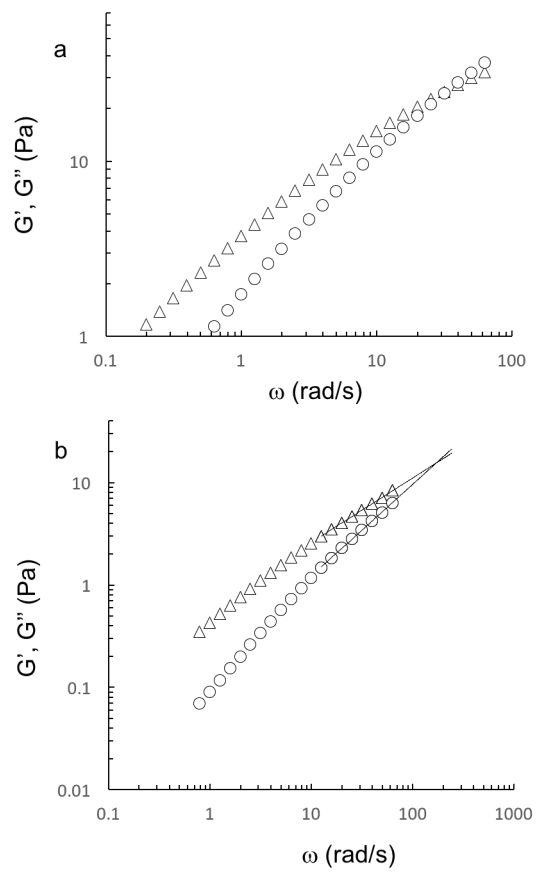

Figure S 2. Oscillatory rheology results for sample CMC1.2M in salt-free water. Loss modulus (triangles) and storage modulus (circles). Top and bottom curves are for 9 g/L and 4.5 g/L solutions. $T = 298$ K for both measurements. Lines are extrapolation to crossover point. Data were acquired on the Kinexus Rheometer.

II. COMPARISON WITH THE ROUSE MODEL

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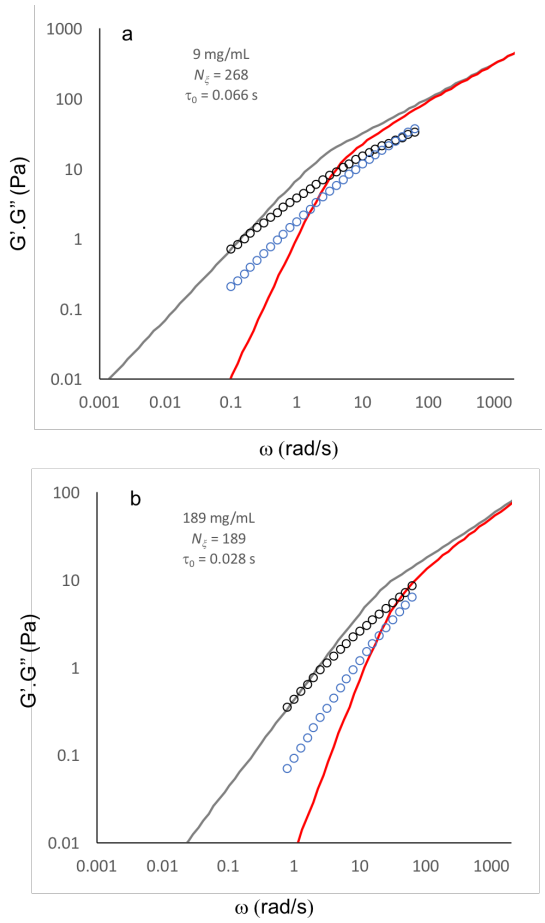

Figure S 3. Oscillatory rheology NaCMC (circles). Red and grey lines are Eqs. S1 and S2 respectively. Data for sample CMC1.2M in salt-free solution, $N = 5300$.

Semidilute non-entangled polyelectrolyte solutions are known to follow Rouse dynamics. The Rouse model predicts the loss and storage moduli of polymer chains to vary as:

$$G' = \frac{cRT}{M}\sum_{p=1}^{N_R}\frac{(\omega\tau_p)^2}{1+(\omega\tau_p)^2} \tag{S1}$$

$$G'' = \frac{cRT}{M}\sum_{p=1}^{N_R}\frac{\omega\tau_p}{1+(\omega\tau_p)^2} \tag{S2}$$

where N_R is the number of Rouse segments in a chain, $\tau_p = \tau_1[sin(\pi/2N_R)/sin(p\pi/2N_R)]^2$ is the relaxation time of the pth mode and τ_1 is the longest relaxation time of the chain. Eqs S1 and S2 predict a crossover in G' and G'' for polymer chains with a small number of Rouse segments. We therefore wish to verify that the cross-overs observed for the data in Figure 3 of the main text are due to entanglement and not due to the finite number of Rouse segments.

For non-entangled polymers in semidilute solution, N_R may be identified with the number of correlation blobs per chain N_ξ. SANS measurements of the correlation length of NaCMC in salt-free solution have been reported in earlier publications[2,3], the number of Rouse segments may then be estimated as $N_R = N_\xi = L/\xi$, where L is the contour length of a chain.

Figure 3 compares the relaxation spectra for some of the least concentrated (i.e. least entangled) samples in Figure 3 of the main text with Eqs S1 and S2. For these two samples, the Rouse model does not expect a crossover in the storage and loss modulus in the frequency range studied. The disagreement between Eqs S1 and S2 observed in Figure 3 is expected due to the influence of entanglements on the dynamics of NaCMC chains.

III. CHAIN DIMENSIONS OF NaCMC IN SEMIDILUTE SOLUTION.

A possible way of quantifying the degree of entanglement of NaCMC in solution would be to compare the tube diameter ($a \simeq (k_BT/G_p\xi)^{1/2}$) with the end-to-end distance of chains (R). Due to the lack of commercially available deuterated NaCMC, no direct measurement of the chain size of NaCMC have been reported in semidilute solution. Dobrynin's scaling model[4] allows us to obtain an estimate of $R(c, c_S)$ from the correlation length data are available for salt-free solutions[2,3]:

$$R \simeq (\xi N_\xi^{1/2})[1 + 2c_S/(fc)]^{-1/8} \tag{S3}$$

where ξ and N_ξ are the correlation length and number of correlation blobs per chain[33] in salt-free solution respectively, c is the polymer concentration, c_S is the added salt concentration and f ($\simeq 1/2^6$) is the fraction of dissociated counter-ions. The term in round brackets is the end-to-end chain size in salt-free solution and the term in square brackets accounts for the decrease in R due to electrostatic screening by added salt ions. Using Eq. S3 we find $R > a$ for all data considered in Figure 3 of the main paper, as expected for entangled solutions. However, Eq. S3, which was derived for intrinsically flexible polyelectrolytes, yields values of R that are smaller than the θ dimensions of NaCMC as estimated by Hoogendam et al[7], which may arise from the limited applicability of Dobrynin's theory to semiflexible polyelectrolytes and/or due to errors in the estimation of chain dimensions of NaCMC in reference [7]. Additionally, as discussed in the main text, the approximation $G_p \simeq G_c$ underestimates the value of the plateau modulus which further limits the reliability of this method to assess the degree of entanglement for our system. Both factors lead to an underestimation of the degree of entanglement.

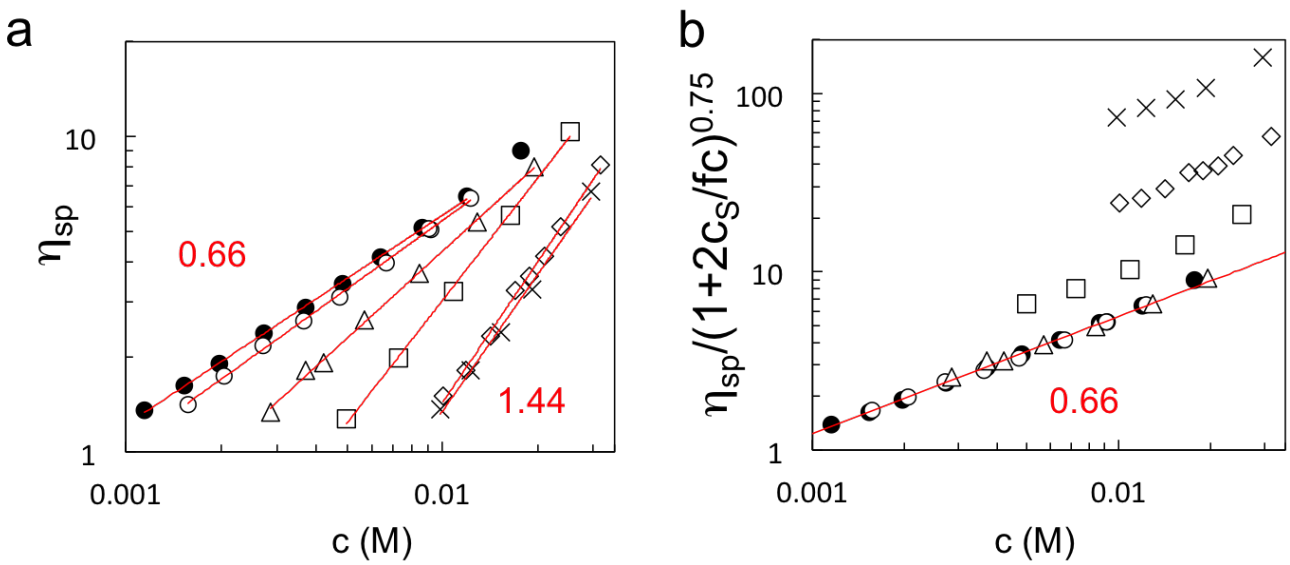

Figure S 4. a: Specific viscosity of NaCMC240k in DI water (•) and in aqueous NaCl solution: 10^{-4} M (○), 10^{-3} M (△), 10^{-2} M (□), 10^{-1} M (◇), 0.5 M (×). Lines are best fit power-laws, see Table SII for the values of the exponents. b: Specific viscosity divided by $(1 + c_S/(fc_p))^{3/4}$ following Dobrynin et al's theory.

IV. SOLVENT QUALITY EXPONENT AS A FUNCTION OF ADDED SALT

Measurements for sample 240k were made in DI water and in aqueous NaCl solution. The results are plotted in Figure S4a. Power-law exponents are compiled in Table SII. It is possible that the viscosity data do not follow a power-law but instead are relation of the type $\eta_{sp}(c_S) = \eta_{sp}(0)[1 + c_S/(fc_p)]^{-3/4}$ applies, as predicted by Dobrynin et al[4]. Figure S4b suggests this may be the case at low added salt concentrations, but our data are insufficient to clearly establish this. At higher added salt concentrations, the scaling law proposed by Dobrynin et al is seen not to work, in agreement with earlier results on a similar sample[1].

c_S	exponent
5×10^{-6}	0.68
1×10^{-4}	0.72
1×10^{-3}	0.92
1×10^{-2}	1.29
1×10^{-1}	1.48
5×10^{-1}	1.44

Table S II. Exponents for the power-law dependence of the specific viscosity of sample 240k as a function of added salt.

Values of the Flory exponent ν as a function of c_S plotted in Figure 1 of the main text are calculated from the viscosity data of reference [1,2] and this work, the SANS data of references [2,3], and intrinsic viscosity data from references [1,2,6,8–25], see reference 1 for a discussion of data selection and M_w estimation for some of the samples.

V. COMPARISON WITH OTHER SYSTEMS

We next examine rheology data for other polyelectrolyte systems from the literature, and compare the results with the predictions of the Dobrynin model and the revised scaling laws outlined in the main text.

A. Poly(isobutylene-alt-maleate) (IBMA)

Figure S5 plots the viscosity concentration exponent of three IBMA polymers of varying molar mass as a function of the polymer concentration divided by $c_{e,Dobrynin}$, where $c_{e,Dobrynin}$ corresponds to the crossover between $\eta_{sp} \propto c^{1/2}$ and $\eta_{sp} \propto c^{3/2}$, as determined in reference [26]. The $\eta_{sp} \propto c^{3/2}$ dependence predicted by Dobrynin et al's model[4] for entangled polymer solutions is not observed over any significant concentration range. By contrast, Eq. 4 of the main text gives a reasonably good description of the data and suggests that all data are in the non-entangled regime except for perhaps the highest concentration data-point for the $M_w = 410$ kg/mol sample. This interpretation is consistent with the N dependence of the viscosity of these samples. At the highest concentration studied $c = 0.45$ M, corresponding to $c \simeq 3 - 6c_{e,Dobrynin}$, a power-law fit gives $\eta_{sp} \propto N^{1.9}$, which is incompatible with the reptation exponent and consistent with the idea that samples are near, but below, the entanglement crossover, and that the apparent exponent of $\eta_{sp} \propto c^{3/2}$ arises from a cross-over between

$\eta_{sp} \sim c^{0.5}$ and $\eta_{sp} \sim c^{3.1}$. Similar behaviour is observed for NaCMC in water[1].

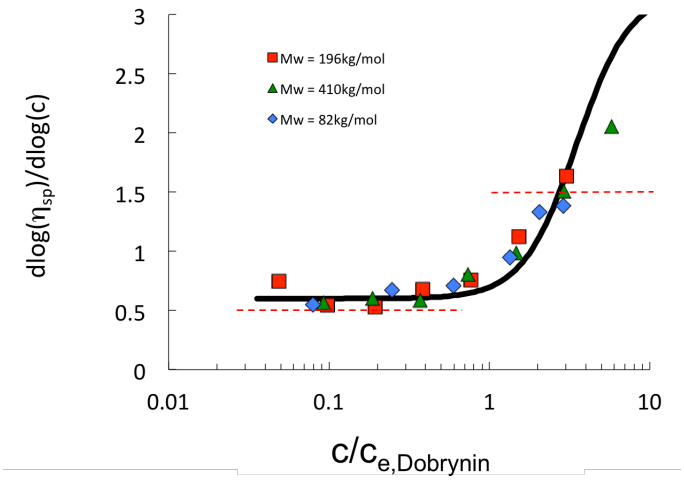

Figure S 5. Viscosity-concentration power-law exponent as a function of $c/c_{e,Dobrynin}$ for IBMA polymers with three different molar masses. $c_{e,Dobrynin}$ is determined from the crossover of $\eta_{sp} \propto c^{1/2}$ and $\eta_{sp} \propto c^{3/2}$, see reference [26]. Data are from reference 26. Dashed red lines are Dobrynin's prediction for non-entangled ($\eta_{sp} \propto c^{1/2}$) and for entangled solutions ($\eta_{sp} \propto c^{3/2}$). Black line is Eq. 4 of the main text with $\eta_{Rouse} \propto c^{0.6}$ and $c_e = 4c_{e,Dobrynin}$.

B. Quaternized Poly(2-vinyl pyridine)

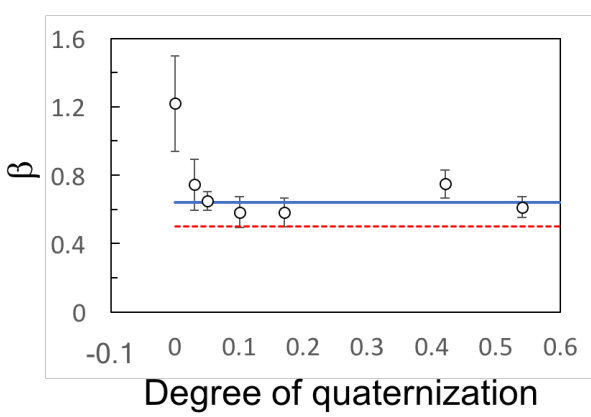

Figure S 6. Viscosity concentration exponent in the non-entangled regime for P2VP as a function of degree of quaternization. Viscosity-concentration data are from ref.[27]. Red line is Dobyrnin et al's prediction and blue line is best fit value (0.64).

Dou and Colby investigated the rheological properties of poly(2-vinyl pyridine) quaternized with methyl iodide to different degrees (0-54%) in ethylene glycol. Figure S6 plots the non-entangled viscosity exponent as a function of degree of quaternization, which decreases from $\eta_{sp} \propto c^{1.25}$ for the neutral polymer, as predicted by scaling theory to $\eta_{sp} \propto c^{0.64\pm0.03}$ for the polyelectrolyte samples.[34] The polyelectrolyte viscosity exponent is higher than the value expected by the Dobyrnin model and consistent with what has been found for other polyelectrolyte systems, including NaCMC.[1–3,29]

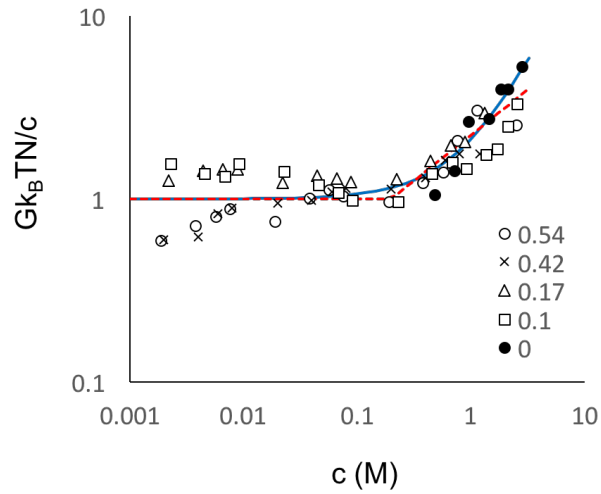

Figure S 7. Reduced modulus as function of polymer concentration for P2VP and its quaternized derivatives as a function of polymer concentration. The degree of quaternization is given in the legend. Full blue line is a cross-over function $G = k_BTc/N(1 + (c/c_e)^{1.25})$, expected by the revised scaling presented in the main paper with $c_e = 0.9$ M. Dashed red-line is $G = K_BTc/N$ for $c < 0.2$ M and $G = [k_BTc/N](c/0.2)^{1/2}$, as expected by the Dobrynin model for $c_e = 0.2$ M. Data are from ref [27]

The reduced modulus as a function of polymer concentration for the neutral P2VP and its quaternized derivatives is plotted as a function of polymer concentration in Figure S7. The modulus, which is a measure of the entanglement density is seen be be insensitive to the quaternization degree within the scatter of the data. This is consistent with the revised scaling presented in the main text. The Dobrynin prediction is also consistent with the experimental data for this system if a sharp cross-over at $c_e = 0.2$ M is assumed.

Figure S8 plots the viscosity-concentration exponent of P2VP and its quaternized derivatives as a function of polymer concentration. As for the maleate polymers, a region where the viscosity scales as $\eta_{sp} \propto c^{1.5}$ is not observed and instead the power-law exponent crosses over to higher values, never reaching a clear plateau. The apparent agreement with the Dobrynin model reported in reference[27] therefore was likely the result of the limited concentration range over which the $\eta_{sp} \propto c^{1.5}$ power-law was fitted. The power-law exponent expected by the revised scaling (Eq. 4 of the main text) also does not describe the experimental results adequately. The rea-

son for the high exponent ($\simeq 5$) observed at high polymer concentrations for both the neutral polymer and the polyelectrolyte remain unclear. Fitting Eq. 4 of the main text to viscosity data gives $c_e \simeq 0.5$ M, which is lower than that inferred in Figure S7, and consistent with the trends observed for other flexible neutral polymers in solution.[30]

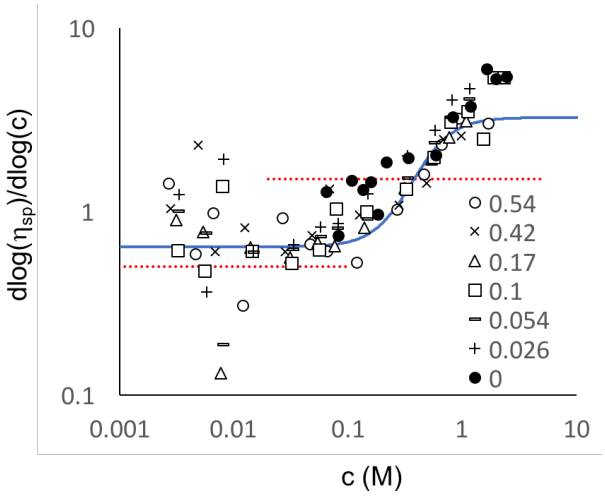

Figure S 8. Viscosity-concentration power law exponent as a function of polymer concentration for P2VP and its quaternized derivatives. Red lines are values of 0.5 and 1.5 predicted by Dobrynin et al[4] for non-entangled and entangled salt-free polyelectrolytes respectively. Blue line is calculated from Eq. 4 of the main text with $\eta_{Rouse} \propto c^{0.64}$ and $\beta = 2.4$ and $c_e = 0.5$ M.

C. Sodium polystyrene sulfonate

In a recent article, we have examined the concentration dependence of the viscosity-concentration exponent of polystyrene sulfonate, which was shown to be molar mass independent for most of the literature data available[31]. Unfortunately, there are not sufficient rheological data available at this point to test the two scaling frameworks considered in this study for this otherwise extensively studied system.

VI. REFERENCES

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