Quiz 3 Polymer Physics January 31, 2020

A polymer coil in dilute solution (where the chains can be considered isolated) contains a fixed concentration of monomers which is called c-star or the overlap concentration and written c^* . This concentration has the same dependence on size and mass as the inverse of the density discussed in class for fractal objects, $1/\rho$. A related concentration is the entanglement concentration, c_e , which is the concentration above which entanglements are observed in rheology. In solution, c_e is determined from a transition in the scaling of the specific viscosity with concentration, $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η_0 is the viscosity of the solvent. η_{sp} is used rather than the viscosity because below $\eta_{sp} = 1$ the solution viscosity plateaus at the solvent viscosity. As a general rule of thumb, c^* is reached in increasing concentration where η_{sp} reaches 1 or where $\eta = 2\eta_0$. Carlos G. Lopez, Macromolecules **52** 9409-15 (2019) *Scaling and Entanglement Properties of Neutral and Sulfonated Polystyrene*, studied the effect of adding salt on the overlap concentration for polyelectrolytes in water. Adding salt causes Debye charge screening so that at high salt content the polymers act as if they are uncharged. (*In soaps this is called "salting out"*) Lopez found that c_e is only weakly impacted by charge screening while c* has a strong dependence shown in Figure 3 below left (*top line high salt; low line no salt*).



polymerization. Black symbols are for salt-free solution in degree of symbols for 0.5 M NaCl. c^* in salt-free solution is estimated from the crossover between $q^* \propto c^{1/3}$ to $q^* = 1.7c^{1/2}$ (SAXS and LS) and from $\eta_{\rm sp}$ (c^*) = 1 (viscosity). Estimates are made from the data from refs 3, 12, 31–34.

a) For the three cases shown in the figure to the right above, 1) describe the three structures,
2) what is their mass fractal dimension, *d*_f, and 3) how does *c** depend on *N*, the mass of the chain.

Salt-free polyelectrolyte

(v ≈ 1)

b) For a randomly branched chain, such as created by irradiation of a polymer with γ -rays, the good solvent scaling displays $\nu = 0.5$. If the chain contour path, p, follows the same convolution as the linear chain in a good solvent, so that $1/d_{\min} = 0.6$, what is the connectivity dimension, c? The number of branches is given by $n_{\text{br}} = (N^{1+5/(2df)-5/(2c)}-1)/2$.

The mole fraction branches is given by

 $\phi_{\rm br} = (N-p)/N = 1 - N^{(1/c)-1}$. The average branch length is given by $N_{\rm br} = N \phi_{\rm br}/n_{\rm br}$. For a randomly branched chain with N = 250, calculate these values and sketch the branched polymer using these values. [Macromolecules 42, 4746-50 (2009)]

- c) Calculate the *N* dependence of c^* for the same molecular weight branched and linear polymer. Which c^* is larger?
- d) Explain the results shown in Figure 3.
- e) Lopez uses $G_e \sim kTc/N_e$ to obtain the molecular weight between entanglements in a melt, N_e , from the plateau modulus for solutions of variable concentration, *c*. Explain the origin of this equation. Note that c = 1 for a polymer melt.

Topisa Gourrion Gil dy=2 Y=0.5 Q) Middleisa Geod Schuert Exponded (cil df = 5/3 V=0.8 Bettern i ran exended chain /ved de= 1 v=1 $C^{\star} = \frac{N}{R^3} = \frac{N}{N^3/d_r} = N^{1-3/d_{+}}$ $R = N^{n/d} + = N^{n/d}$ Gaussian Gil cx = NO.5 Geodolat (il C* = N = N = N $C = N^{1-3} = N^{-2}$ Rod 5) $C = \frac{d_{f}}{T_{m1}} = \frac{2^{0}}{T} = \frac{6}{T} = 1.2$ $n_{Br} = (250 - 1) = 0.75$ One brough fer 1.3 chains I ALL $\frac{1}{2d_{\perp}} = \frac{5}{2c} + 1 = 0.167$ 618 \$Br=1-250^(5/6-1)=0.602 Not every Chaib hasabrough <Nor = 250 (0.602)/0.75 = 201

CX ~ N° Lorger cX-0,063 Brachd CX ~ N° Smaller CX ~ 0,012 Cinen ~ N° Smaller CX ~ 0,012 Fr $\langle \rangle$ For likeou chain (*~ N-2 (abeco) d)Fu GSchein, CX~N (ahrap) $P(R) = k_1 \exp\left(\frac{-3R^2}{2ne^2}\right) - \frac{5KTR^2}{5chain - 2ne^2}$ $P(R) = k_2 \exp\left(\frac{-E}{K_0T}\right)$ e) $FdR = dE = \left(\frac{3kT}{nP2}\right)R$ G~ 347~ K/ In solution loss enterport, at lows C. Me ~ ckt Fe vou putelule Icucis G

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Scaling and Entanglement Properties of Neutral and Sulfonated **Polystyrene**

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Supporting Information

ABSTRACT: We study the rheological properties of sodium polystyrene sulfonate in salt-free and excess added salt solution. The overlap concentration scales as $c^* \propto N^{-2}$ (DI water) and $c^* \propto N^{-0.77}$ (excess salt), corresponding to rodlike and expanded coil conformations, respectively. A comparison of small-angle X-ray scattering and viscosity data reveals that c^* in salt-free solution may be quantitatively estimated as the point at which the viscosity of a NaPSS solution is $\simeq 5/3$ that of the solvent. The entanglement crossover and entanglement density are found to be approximately independent of the concentration of the added salt, and similar to those of neutral polystyrene in good or θ solvents. These results indicate that polymer conformation has a weaker effect on entanglement



formation in solution than expected by packing models of polymer entanglement.

INTRODUCTION

The entanglement of polyelectrolytes in solution is a major open question in the physics of charged polymers.^{1,2} Strong disagreements between experimental results and theoretical expectations for salt-free solutions were noted over two decades ago,^{3,4} and relatively little progress in our understanding of the problem has been made since then.⁵⁻⁸ Beyond its importance to fundamental polyelectrolyte science, understanding polyelectrolyte dynamics is of interest in many industrial applications, where polyelectrolytes are used as rheology modifiers (e.g., cosmetic or food products), and biology.

The conformational range that polyelectrolytes can adopt far exceeds that of uncharged polymers. By way of example, the end-to-end distance of chains in dilute solution scales as $R \simeq$ $l_{\rm K} N_{\rm k}^{\nu}$ with $\nu \simeq 0.5 - 0.59$ for uncharged polymers, where ν is the solvent quality exponent. $l_{\rm K}$ and $N_{\rm K}$ are the Kuhn length and number of Kuhn segments in a chain, respectively. Polyelectrolytes extend this range to $\nu = 1$ in salt-free solutions because of the long-ranged nature of electrostatic forces.^{1,5,7,9} It is possible to effect a crossover between the salt-free polyelectrolyte ($\nu = 1$) and the good solvent ($\nu = 0.59$) universality classes by increasing the added salt concentration, as shown schematically in Figure 1.

Earlier studies have found that nonentangled polyelectrolyte dynamics are similar to those of nonionic polymers^{6-8,10-12} (i.e., Rouse-Zimm) once conformational changes induced by charge repulsion are accounted for.

Various theories predict that entanglement density in solution for $\nu = 0.5-0.59$ is independent of solvent quality for most experimentally accessible systems.¹³ Polyelectrolytes



Figure 1. Schematic of different universality classes for polymer conformation. End-to-end sizes are approximately to scale for NaPSS with the degree of polymerization $N \simeq 1000$.

in a salt-free solution on the other hand are expected to display markedly different properties.¹⁴ In this article, we study the entanglement of flexible polyelectrolyte sodium polystyrene sulfonate (NaPSS). We show that the entanglement and critical molar masses of NaPSS are nearly identical to those of nonionic polystyrene, despite differences in their conformation.

Polyelectrolyte Conformation and Nonentangled **Dynamics.** The overlap concentration (c^*) marks the onset of the semidilute regime and can be estimated as¹⁵

$$c^* \simeq \frac{N}{R^3} \simeq \frac{1}{l_K^{3(1-\nu)} b'^{3\nu} N^{3\nu-1}}$$
(1)

Received: July 30, 2019 Revised: September 1, 2019 Published: November 27, 2019 where *N* is the degree of polymerization, *b'* is the effective monomer size, $l_{\rm K}$ is the length of a Kuhn monomer, and ν is the solvent quality exponent. For $c < c^*$, scaling expects $\eta_{\rm sp} \sim (R^3/M)c \sim [\eta]c$, where $[\eta] \simeq 1/c^*$ is the intrinsic viscosity.

In nonentangled solution, the terminal modulus of both uncharged polymers and polyelectrolytes is predicted by the Rouse model to be kT per chain or G = kTc/N, where k and T are the Boltzmann constant and absolute temperature, respectively.^{1,6,15} The Rouse viscosity and the longest relaxation time of the salt-free polyelectrolytes are expected to scale as¹⁴

$$\eta_{\rm sp,R} = \eta_{\rm sp} (c^*) (c/c^*)^{1/2}$$
(2a)

$$\tau_{\rm R} = \frac{\eta_{\rm s} [R(c^*)]^3}{kT} (c/c^*)^{-1/2}$$
(2b)

where η_s is the solvent viscosity.

According to Dobrynin et al.'s model,¹⁴ addition of salt modifies the properties of solutions as

$$X(c_{\rm S}) = X(0)[1 + 2c_{\rm S}/(fc)]^{\varsigma}$$
(3)

where $c_{\rm S}$ is the concentration of the added monovalent salt, *f* is the fraction of dissociated counterions, and ζ is an exponent that depends on the property *X* and the concentration regime (Table 2).

Entangled Dynamics. The plateau modulus (G_e) is related to the degree of polymerization of an entanglement strand (N_e) as¹⁵

$$G_{\rm e} \simeq \frac{kTc}{N_{\rm e}}$$
 (4)

The theory of Colby and Rubinstein^{13,15,19–21} (which modifies the Lin–Noolandi–Kassavalis conjecture^{16–18} for polymer melts) expects an entanglement to form when a fixed number of binary contacts between chains occurs in a fixed volume. The density of binary contacts between chains is expected to be proportional to the number density of correlation blobs (ξ^{-3}) . Milner's extension²¹ of the Colby–Rubinstein model will be considered in a forthcoming study. These assumptions lead to two important predictions: first, the entanglement tube diameter (*a*) is proportional to the correlation length; second, the entanglement concentration is proportional to the overlap concentration¹⁴

$$c_{\rm e} \propto \begin{cases} N^{-0.77} \text{ good solvent} \\ N^{-2} \text{ salt} - \text{free polyelectrolyte} \end{cases}$$
 (5)

In θ solvent, which we will not consider here in detail, the Colby–Rubinstein theory predicts $c_e \propto N^{-0.77} \ll c^*$. Scaling theories give a good description of the experimental data for flexible polymers in melts and solutions^{22–25} but do not reproduce experimental findings for semiflexible polymers (e.g., polysaccharides^{26–28}). Combining the above arguments on entanglement formation with the reptation model, the plateau modulus, longest relaxation time, and specific viscosity are predicted to be

$$\tau_{\rm rep} \propto N^3 [1 + 2c_S / (fc)]^{-1.5}$$
 (6a)

$$G_{\rm e} \propto kTN^0 c^{1.5} [1 + 2c_{\rm S}/(fc)]^{-0.75}$$
 (6b)

$$\eta_{\rm sp} \propto N^3 c^{3/2} [1 + 2c_{\rm S}/(fc)]^{-2.25} \tag{6c}$$

Equations 6aa–6c correctly describe the polymer concentration dependences of η , τ , and G, respectively, in the high-salt limit but do not work well in a salt-free solution.⁸ Assuming that the entanglement density is independent of the solvent quality exponent and that it scales as $\rho_e \propto c^{2.3}$ leads instead to a revised scaling of

$$c_{\rm e} = B^{-0.77} N^{-0.77} c_{\rm S}^0$$

where *B* is a polymer–solvent specific parameter. The reptation time of a chain can be estimated as $\tau_{\rm rep} \simeq \tau_{\rm R}(N/N_{\rm e})$, where $N/N_{\rm e}$ is independent of $c_{\rm S}$. Entangled dynamics of polyelectrolytes are then expected to follow⁸

$$\tau_{\rm rep} \propto N^3 c^{0.8} [1 + 2c_{\rm S}/(fc)]^{-0.75}$$
 (7a)

$$G_{\rm e} \propto Bc^{2.3}c_{\rm S}^0$$
 (7b)

$$\eta_{\rm sp} \propto N^3 c^{3.1} [1 + 2c_{\rm S}/(fc)]^{-0.75}$$
 (7c)

Beyond a concentration c_D , various theories expect the size of polyelectrolytes to be independent of concentration. While there is evidence from small-angle X-ray scattering (SAXS)²⁹ and osmotic pressure³⁰ of a crossover at $c \simeq 1.2$ M, the chain size of NaPSS decreases with concentration of at least up to $c \simeq 4$ M.¹¹

MATERIALS AND METHODS

NaPSS samples were purchased from Polymer Standard Services (Mainz, Germany), see Table S1 for more details. Deionized (DI) water with a conductivity of 0.06 μ S cm⁻¹ was obtained from a Milli-Q source. NaCl was purchased from VWR. Rheological measurements were performed on a Kinexus-Pro (Malvern) stress-controlled rheometer with cone-and-plate geometry (40 mm diameter, 1° angle). The temperature was controlled with a Peltier plate. A solvent trap was employed to minimize evaporation. Solutions were stored in plastic vials to avoid ion contamination from glass.

RESULTS AND DISCUSSION

The concentration and shear rate $(\dot{\gamma})$ dependences of the viscosity of selected samples are plotted in Figure 2. The shear rate dependence of the viscosity is fitted to a constant value at low shear rates and to a power law at a high shear, as shown in Figure 2b. The intercept between these two lines corresponds to $\dot{\gamma}_c = 1/\tau$. Fits to the Carreau model give similar results for the longest relaxation time τ at low concentrations.¹¹ For high molar mass, high-concentration samples, the Carreau model does not adequately describe the measured flow curves, and we therefore employ the fitting method in Figure 2b for all samples.

Dilute Solution Conformation. Figure 3 plots the overlap concentration of NaPSS in DI water and 0.5 M NaCl solution. In the salt-free condition, we estimate c^* as the crossover from $q^* \propto c^{1/3}$ to $q^* \propto c^{1/2}$, where q^* is the peak in the scattering intensity, reported in refs 31–34. Details are given in the Supporting Information (SI). We further estimate c^* from the viscosity data using $\eta_{sp}(c^*) = 1$, as proposed by Colby and coworkers.^{3,14} The two methods differ by a factor of ≈ 2 . Agreement between the viscosity and SAXS estimates can be achieved if $\eta_{sp}(c^*) = 0.67$ is assumed instead. A more detailed discussion on this topic is provided in the SI. The data are consistent with the scaling prediction of $c^* \propto N^{-2}$ for rodlike structures in dilute solution. The observed values of c^* are



Figure 2. (a) Specific viscosity of NaPSS in DI water. Symbols are for different molar masses, from top to bottom: 2×10^6 , 9.7×10^5 , 6.7×10^5 , 4.4×10^5 , 2.8×10^5 , 1.45×10^5 , 6.7×10^4 , and 2.9×10^4 g/mol. Data for low molar masses and at low concentrations are from refs 11 and 12. (b) Shear rate dependence of the viscosity of NaPSS at c = 1 M and variable $c_{\rm S}$.



Figure 3. Overlap concentration of NaPSS as a function of degree of polymerization. Black symbols are for salt-free solution and red symbols for 0.5 M NaCl. c^* in salt-free solution is estimated from the crossover between $q^* \propto c^{1/3}$ to $q^* = 1.7c^{1/2}$ (SAXS and LS) and from $\eta_{\rm sp}$ (c^*) = 1 (viscosity). Estimates are made from the data from refs 3, 12, 31–34.

approximately five times larger than those calculated by the scaling theory ($c^* = b'^3 N^{-2} \simeq 340 N^{-2}$ with $b' = 1.7 \text{ Å}^{11,14}$) and suggest that chain dimensions at the overlap are $\simeq 1.7$ smaller than the conformation at infinite dilution, in agreement with the simulation data of ref 35 for flexible polyelectrolytes.

In excess salt solution, we estimate the overlap concentration as $c^* = [\eta]^{-1}$ (values reported in refs 40, 41). A weaker dependence of $c^* \simeq 23N^{-0.77}$ is observed. This value is similar to the exponent observed for neutral polymers in good solvent, indicating that polyelectrolytes in excess added salt adopt expanded coil conformations. 42

Dilute solution viscosity and SAXS data are consistent with the crossover between rodlike and expanded coil conformations shown in Figure 1. The value of the solvent quality exponent ν can also be estimated from the concentration dependence of various properties in a semidilute solution. Table 1 compiles the ν values calculated from diffusion, viscosity, and chain size data in a semidilute solution, all of which are consistent with $\nu \simeq 1$.

Figure 4 plots the *N* dependence of the specific viscosity of NaPSS for c = 0.009 M in a salt-free solution. A single power law of $\eta_{sp} \propto N^{1.27\pm0.05}$ describes both the dilute and semidilute data. This behavior is at odds with scaling, which expects a crossover from Zimm ($\eta_{sp} \propto N^2$) to Rouse ($\eta_{sp} \propto N$) dynamics at $c = c^*$.

Entanglement and Critical Molar Masses. We estimate the entanglement crossover by fitting data at a fixed molar mass or fixed concentration to

$$\eta_{\rm sp} = \eta_{\rm sp,R} [1 + (c/c_{\rm e})^{\rho}]$$
(8a)

$$\eta_{\rm sp} = DN^{\alpha} [1 + (N/N_{\rm C})^{\gamma}]$$
(8b)

where $\beta = 2.7$ and $\alpha = 1.24$ follow the earlier work^{8,11,12} and $\gamma = 2.4$ from the reptation theory.¹⁵ $\eta_{sp,R}$ is the nonentangled viscosity, which we take as $Ac^{1/2}e^{1.4c^*}$ in a salt-free solution, where *A* is an adjustable parameter, chosen to match the data at low *c*, where $\eta_{sp} \propto c^{1/2}$.¹² We consider only the semidilute data ($c^* < c < 1.2$ M).

Figure 5 shows fits of eqs 8a and 8b to experimental data. We could only fit eq 8a to the two highest-molar-mass samples because $c_{\rm e}$ is close to $c_{\rm D}$ for other samples and a fitting eq 8a over a narrow concentration range becomes problematic. Therefore, for lower molar masses, we employ an approximate method to estimate $c_{\rm e}$ by noting that according to eq 8a, $\eta_{\rm sp}(c_{\rm e}) \simeq 2\eta_{\rm sp,R}$. Equation 8b was applied at c = 1 M and c = 0.45 M. At lower concentrations, no significant deviations from the nonentangled power law were observed, see also Figure 4. Extrapolating the entanglement molar at the two highest concentrations down to 0.009 M using $c_{\rm e} \propto N^{-2}$ and $c_{\rm e} \propto N^{-0.77}$, we obtain $N_{\rm e} \simeq 3 \times 10^4$ and $N_{\rm e} \simeq 1 \times 10^6$. The data in Figure 4 suggest that $N_{\rm e} > 7.5 \times 10^4$, thus favoring the $c_{\rm e} \propto N^{-0.77}$ scaling.

The entanglement crossovers estimated from eqs 8a and 8b agree within the experimental error, suggesting that the onset of $\eta_{sp} \propto N^3$ coincides with that of $\eta_{sp} \propto c^3$, as observed for NaCMC/water.^{7,8} However, due to the limited N and c range studied, we cannot clearly verify this. We discuss the experimental determination of β further in Section 3.4.

The reduced modulus, GN/(kTc), of NaPSS solutions is plotted as a function of polymer concentration in Figure 6a. In the nonentangled regime, $G \simeq 0.6k_{\rm B}Tc/N$ is observed. The lower value compared to the Rouse prediction likely is an artefact of the method employed to estimate *G* from the steady shear viscosity data.⁴⁶

At $c \simeq 1.1$ M, the plateau modulus is independent of the molar mass as expected for entangled solutions. The $G \propto N^0$ relation suggests that solutions are entangled down to at least $N \simeq 2000$. The fact that for $N \lesssim 4000$, we observe that G/c < kT/N again suggests that $G = \eta/\tau$, where τ is obtained following the method in Figure 2, underestimates G by a factor of $\simeq 2$.

Table 1. Estimates for ν from Semidilute Data

"We use the exponent calculated from a plot of ξ/L vs c/c^* (inset of Figure 6 of ref 43). "The exponent is artificially small because of the influence of the intrinsic Kuhn segment, which weakens the *c* dependence of R_g . In the next row, we subtract $b'l_{K,0}$ (b' = 1.7 Å and $l_{K,0} = 22$ Å) to remove the influence of intrinsic stiffness.



Figure 4. Viscosity of NaPSS in a salt-free solution at c = 0.009 M. Data are from this work and refs 3, 11, 12, 34, 36–39.

Effect of Added Salt. Figure 7 plots the change in the specific viscosity of NaPSS upon the addition of NaCl as a function of c_S/c , data are from ref 3.⁴⁷ The results are in moderate agreement with Dobrynin et al.'s model.¹⁴ Similar agreement is found for other properties (Table 2). The origin of the larger exponent is not clear to us. Other flexible polyelectrolyte systems in aqueous solution display lower exponents: $\zeta_{\eta} = -0.70 \pm 0.05$ for polyacrylic acid⁴⁸ and $\zeta_{\eta} = -0.8$ for acrylamide co-polymers.⁴⁹ One possible explanation is that counterion condensation is increased by the addition of salt, which would mean that *f* decreases with increasing c_S . Such a behavior could lead to artificially high values of the exponent ζ_{η} .

The specific viscosity, longest relaxation time, and plateau modulus for the data presented in Figure 2b are plotted as a function of added salt in Figure 8. For this sample, $\eta_{\rm sp} \simeq 20\eta_{\rm sp,R}$, and it is therefore in the entangled regime. Estimates for the plateau modulus based on the crossover in G' and G'' are approximately 30% higher than those obtained from the shear rate dependence of the viscosity, see also Table S2.^{51,52} $\eta_{\rm sp}$ and τ are seen to decrease with increasing $c_{\rm S}$, while the G remains constant within the experimental error. The data are in agreement with eqs 7a–7c and contradict the Dobrynin et al.'s model for entangled polyelectrolytes (eqs 6a–6c). These results are in line with experimental observations for sodium carboxymethyl cellulose in aqueous NaCl solution, where a dependence of $G \propto c_{\rm S}^{\rm S}$ is also observed.⁸

The flow curves presented in Figure 2b for c = 1 M and different added salt concentrations can be superposed into a single flow curve by imposing a horizontal (a_{τ}) and vertical shift (a_n) , which is consistent with the idea that the addition of



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Figure 5. (a) Concentration dependence of η_{sp} on NaPSS with $M = 2.07 \times 10^6$ g/mol in a salt-free solution. (b) N dependence of the specific viscosity on different concentrations. Solid lines are fits to eqs 8a and 8b, and dashed lines are the nonentangled term.

salt modifies the Rouse times but not the entanglement density. Viscosity vs shear rate data measured at different temperatures can also be superposed following a similar procedure (Table S3). The modulus varies proportionally with temperature, as expected by eq 4 if N_e is independent of T.

Comparison of NaPSS with Neutral Polystyrene. Figure 9 compares the entanglement and critical degree of polymerization of polystyrene in good and θ solvents, and polystyrene sulfonate in salt-free and 0.1 M NaCl solutions. Data points for the critical molar mass correspond to either $(N_{\rm C}, c)$ values obtained using eq 8b or $(N, c_{\rm e})$ values obtained from eq 8a. For neutral polystyrene, data by Delsanti and co-workers⁵³ and Kulicke and co-workers⁵⁴ were fitted to eqs 8a and 8b, respectively, to estimate $N_{\rm C}$, with $\eta_{\rm sp,R} \propto Nc^{1.25}$ (good solvent) or $\eta_{\rm sp,R} \propto Nc^2$ (θ -solvent). Viscosity data in toluene were normalized by solvent friction following ref 55. The



Figure 6. Left: reduced modulus (GN/(kTc)) as a function of polymer concentration. Dashed line is G = kTc/N and full line G = 0.6kT/N. All points are estimated as $G = \eta/\tau$. Right: reduced modulus as a function of polymer molar mass for $c \simeq 1.1$ M. Hollow symbols estimated from $G = \eta/\tau$ and full points from crossover in loss and storage modulus. Dashed line is nonentangled modulus expected by scaling theory.



Figure 7. Relative decrease of NaPSS solution viscosity as a function of $c/c_{\rm S}$ ratio. Dashed line is the prediction of the Dobrynin et al.'s model for nonentangled solutions (eq 3 with $f = 0.2^{50}$ and $\zeta_{\eta} = -0.75$). Full line is a fit to eq 3, the best fit parameters are f = 0.2 and $\zeta_{\eta} = -0.95$. Data are from 3.

Table 2. Comparison of Predicted Exponents (Dobrynin et al.'s Model¹⁴) with Experimental Results

	$\zeta_{ m theo}$		Ç _{exp}	
X	$c < c_{\rm e}$	$c > c_e$	$c < c_{\rm e}$	$c > c_e$
$\eta_{ m sp}$	-3/4	-9/4	-0.9	-0.9
τ	-3/4	-3/2		-0.9
G	0	-3/4	0	0
D	1/2	5/4	0.3 ^a	
^a Estimate m	ade from diffu	sion data in ref	44.	

entanglement degree of polymerization was estimated using eq 4 and $G_e = \eta/\tau$, with the values of τ and η tabulated in ref 53. We also include data by Ganter et al.⁵⁶ for NaPSS in 0.1 M NaCl. The conformational properties for polystyrene in different solvents are summarized in Table 3. Parameter *B'* is the excluded volume strength, defined as $B' = \beta_c/l_K^2$, where β is the binary cluster integral between two Kuhn segments.

As for other flexible neutral polymer systems, $^{25} N_e \simeq 2N_C$ is found, in contrast to the values of $N_e \simeq 0.5N_C$ found in melts of flexible polymers. The entanglement and critical molar masses are seen to be largely independent of the solvent quality for the polymer–solvent systems considered. The results in Figure 9 are consistent with the independence of the G on c_S observed in Figure 8, which also suggests that N_e is independent of c_S (and therefore of ν).



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Figure 8. Salt dependence of specific viscosity (left), longest relaxation time (middle), and plateau modulus (right) for NaPSS with $M_w = 2 \times 10^6$ g/mol and c = 1 M. The plateau modulus is estimated as $G = \eta/\tau$ (\Box) and from the crossover point in the storage and loss modulus (O). Red lines are predictions of the Dobrynin et al.'s model (eqs 6a-6c), adjusted to match the experimental data in a salt-free solution. Black lines are expected by revised scaling (eqs 7a-7c).



Figure 9. Entanglement (circles) and critical (triangles) degree of polymerization of polystyrene in good solvent (open symbols: black are for toluene and gray for benzene), θ solvent (decalin, 25 °C, upside down triangles), and sodium polystyrene sulfonate in a saltfree solution (full symbols) and in 0.1 M NaCl solution (patterned symbols). Lines are power laws with an exponent of -0.77. Data for polystyrene and PSS in 0.1 M NaCl are from this work and refs 53, 54, 56, 61.

Most of the values in Figure 9 for NaPSS in DI water are estimated without assuming a value of β , relying instead on the criterion $\eta_{sp}(c_e) \simeq 2\eta_{R}$. Equation 8a for $c \gg c_e$ reduces to $\eta_{sp,ent}$

Table 3. Conformational Parameters for Different Polystyrene–Solvent Systems Studied

system	ν	l _K (nm)	<i>B'</i> (nm)
PS/tol ^a	0.59 ^b	2.1	0.54
PS/benzene ^a	0.59 ^b	2.1	0.51
PS/decalin ^a	0.5	2.1	$\simeq 10^{-3}$
PSS/DI	1	$2 + 4.1c^{-1/2}$	d
PSS/0.1 M NaCl	0.59 ^b	4.6 ^e	2.3 ^e

^{*a*}See refs 57–59 for estimates of $l_{\rm K}$ and *B'*. ^{*b*}Refers to the $N \gg N_{\rm T}$, where $N_{\rm T}$ is the degree of polymerization of a thermal blob. ^{*c*}*c* in units of moles per liter, see ref 11. ^{*d*}Chains are Gaussian on all length scales above $l_{\rm K}$. ^{*e*}*c* \rightarrow 0 limit.⁶⁰

 $\propto N^{1.2}(c/c_e)^{\beta}$. If we require the reptation exponent to hold (i.e., $\eta_{\rm sp,ent} \propto N^{3-3.4}$) and use the $c_e \sim N^{-0.77}$ relation from Figure 9, we obtain $\beta \simeq 2.3-2.9$, in agreement with the value assumed earlier based on ref 8.

CONCLUSIONS

We have examined the rheology of polystyrene sulfonate in salt-free and excess salt solutions. The overlap concentration in DI water, as evaluated from SAXS and viscosity data scales as $c^* \propto N^{-2}$, consistent with the scaling prediction that polyelectrolytes are rodlike in the dilute salt-free solution. In the nonentangled regime, the concentration, added salt, and degree of polymerization dependences of various rheological properties are in moderately good agreement with scaling theory. In entangled solution, strong deviations from theoretical predictions are observed. In particular, a comparison with neutral polystyrene reveals that the entanglement concentration and entanglement density are independent of added salt and of the solvent quality exponent.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b01583.

Analysis of c^* vs N, tabulated rheology data (PDF)

(PDF)

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Notes

The author declares no competing financial interest.

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REFERENCES

(1) Colby, R. H. Structure and linear viscoelasticity of flexible polymer solutions: comparison of polyelectrolyte and neutral polymer solutions. *Rheol. Acta* **2010**, *49*, 425–442.

(2) Dobrynin, A. V. Theory and simulations of charged polymers: From solution properties to polymeric nanomaterials. *Curr. Opin. Colloid Interface Sci.* 2008, 13, 376–388. (3) Boris, D. C.; Colby, R. H. Rheology of Sulfonated Polystyrene Solutions. *Macromolecules* **1998**, *31*, 5746–5755.

(4) Krause, W. E.; Tan, J. S.; Colby, R. H. Semidilute solution rheology of polyelectrolytes with no added salt. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 3429–3437.

(5) Di Cola, E.; Plucktaveesak, N.; Waigh, T. A.; Colby, R. H.; Tan, J. S.; Pyckhout-Hintzen, W.; Heenan, R. K. Structure and Dynamics in Aqueous Solutions of Amphiphilic Sodium Maleate-Containing Alternating Copolymers. *Macromolecules* **2004**, *37*, 8457–8465.

(6) Dou, S.; Colby, R. H. Charge density effects in salt-free polyelectrolyte solution rheology. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2001–2013.

(7) Lopez, C. G.; Colby, R. H.; Graham, P.; Cabral, J. T. Viscosity and Scaling of Semiflexible Polyelectrolyte NaCMC in Aqueous Salt Solutions. *Macromolecules* **2017**, *50*, 332–338.

(8) Lopez, C. G. Entanglement Properties of Polyelectrolytes in Salt-Free and Excess-Salt Solutions. *ACS Macro Lett.* **2019**, 979–983.

(9) Stevens, M. J.; Kremer, K. The nature of flexible linear polyelectrolytes in salt free solution: A molecular dynamics study. *J. Chem. Phys.* **1995**, *103*, 1669–1690.

(10) Dou, S.; Colby, R. H. Solution Rheology of a Strongly Charged Polyelectrolyte in Good Solvent. *Macromolecules* **2008**, *41*, 6505–6510.

(11) Lopez, C. G.; Richtering, W. Conformation and dynamics of flexible polyelectrolytes in semidilute salt-free solutions. *J. Chem. Phys.* **2018**, *148*, No. 244902.

(12) Lopez, C. G.; Richtering, W. The Viscosity of Semidilute and Concentrated Non-Entangled Flexible Polyelectrolytes in Salt-Free Solution. *J. Phys. Chem. B* 2019, 5626–5634.

(13) Heo, Y.; Larson, R. G. Universal scaling of linear and nonlinear rheological properties of semidilute and concentrated polymer solutions. *Macromolecules* **2008**, *41*, 8903–8915.

(14) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. Scaling Theory of Polyelectrolyte Solutions. *Macromolecules* **1995**, *28*, 1859–1871.

(15) Rubinstein, M.; Colby, R. H. Polymer Physics; Oxford, 2003.

(16) Kavassalis, T. A.; Noolandi, J. New view of entanglements in dense polymer systems. *Phys. Rev. Lett.* **1987**, *59*, 2674.

(17) Kavassalis, T. A.; Noolandi, J. Entanglement scaling in polymer melts and solutions. *Macromolecules* **1989**, *22*, 2709–2720.

(18) Lin, Y. Number of entanglement strands per cubed tube diameter, a fundamental aspect of topological universality in polymer viscoelasticity. *Macromolecules* **1987**, *20*, 3080–3083.

(19) Colby, R. H.; Rubinstein, M. Two-parameter scaling for polymers in θ solvents. *Macromolecules* **1990**, *23*, 2753–2757.

(20) Colby, R. H.; Rubinstein, M.; Viovy, J. L. Chain entanglement in polymer melts and solutions. *Macromolecules* **1992**, *25*, 996–998.

(21) Milner, S. Predicting the tube diameter in melts and solutions. *Macromolecules* **2005**, *38*, 4929–4939.

(22) Richter, D.; Farago, B.; Butera, R.; Fetters, L.; Huang, J.; Ewen, B. On the origins of entanglement constraints. *Macromolecules* **1993**, 26, 795–804.

(23) Fetters, L.; Lohse, D.; Colby, R. *Physical Properties of Polymers Handbook*; Springer, 2007; pp 447–454.

(24) Heymans, N. A novel look at models for polymer entanglement. *Macromolecules* **2000**, *33*, 4226–4234.

(25) Heo, Y.; Larson, R. G. The scaling of zero-shear viscosities of semidilute Polymer solutions with concentration. *J. Rheol.* **2005**, *49*, 1117–1128.

(26) Horinaka, J.-i.; Urabayashi, Y.; Takigawa, T. Effects of side groups on the entanglement network of cellulosic polysaccharides. *Cellulose* **2015**, *22*, 2305–2310.

(27) Horinaka, J.-i.; Chen, K.; Takigawa, T. Entanglement properties of carboxymethyl cellulose and related polysaccharides. *Rheol. Acta* **2018**, 51–56.

(28) Lopez, C. G.; Colby, R. H.; Cabral, J. T. Electrostatic and hydrophobic interactions in NaCMC aqueous solutions: Effect of degree of substitution. *Macromolecules* **2018**, *51*, 3165–3175.

(29) Nishida, K.; Kaji, K.; Kanaya, T. High concentration crossovers of polyelectrolyte solutions. J. Chem. Phys. 2001, 114, 8671-8677.

Macromolecules

(30) Wang, L.; Bloomfield, V. A. Osmotic pressure of polyelectrolytes without added salt. *Macromolecules* **1990**, *23*, 804–809.

(31) Krause, R.; Maier, E.; Deggelmann, M.; Hagenbüchle, M.; Schulz, S.; Weber, R. Static light scattering by solutions of salt-free polyelectrolytes. *Phys. A* **1989**, *160*, 135–147.

(32) Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. Phase diagram of polyelectrolyte solutions. *J. Phys.* **1988**, *49*, 993–1000.

(33) Johner, C.; Kramer, H.; Batzill, S.; Graf, C.; Hagenbüchle, M.; Martin, C.; Weber, R. Static light scattering and electric birefringence experiments on saltfree solutions of poly (styrenesulfonate). *J. Phys. II* **1994**, *4*, 1571–1584.

(34) Üzüm, C.; Christau, S.; von Klitzing, R. Structuring of polyelectrolyte (NaPSS) solutions in bulk and under confinement as a function of concentration and molecular weight. *Macromolecules* **2011**, *44*, 7782–7791.

(35) Liao, Q.; Dobrynin, A. V.; Rubinstein, M. Molecular dynamics simulations of polyelectrolyte solutions: nonuniform stretching of chains and scaling behavior. *Macromolecules* **2003**, *36*, 3386–3398.

(36) Eckelt, J.; Knopf, A.; Wolf, B. A. Polyelectrolytes: Intrinsic viscosities in the absence and in the presence of salt. *Macromolecules* **2008**, *41*, 912–918.

(37) Cohen, J.; Priel, Z.; Rabin, Y. Viscosity of dilute polyelectrolyte solutions. *J. Chem. Phys.* **1988**, *88*, 7111–7116.

(38) Chen, S.-P.; Archer, L. A. Relaxation dynamics of salt-free polyelectrolyte solutions using flow birefringence and rheometry. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 825–835.

(39) Pavlov, G. M.; Okatova, O. V.; Gubarev, A. S.; Gavrilova, I. I.; Panarin, E. F. Strong linear polyelectrolytes in solutions of extreme concentrations of one-one valent salt. Hydrodynamic study. *Macromolecules* **2014**, *47*, 2748–2758.

(40) Takahashi, A.; Kato, T.; Nagasawa, M. The second virial coefficient of polyelectrolytes. J. Phys. Chem. A. **1967**, 71, 2001–2010.

(41) Hirose, E.; Iwamoto, Y.; Norisuye, T. Chain stiffness and excluded-volume effects in sodium poly (styrenesulfonate) solutions at high ionic strength. *Macromolecules* **1999**, *32*, 8629–8634.

(42) Note there is a slight difference between the data of Takahashi et al and those of Norisuye et al, probably due to the incomplete sulfonation of Takahashi's sample.

(43) Prabhu, V.; Muthukumar, M.; Wignall, G. D.; Melnichenko, Y. B. Polyelectrolyte chain dimensions and concentration fluctuations near phase boundaries. *J. Chem. Phys.* **2003**, *119*, 4085–4098.

(44) Oostwal, M.; Odijk, T. Novel dynamic scaling hypothesis for semidilute and concentrated solutions of polymers and polyelectrolytes. *Macromolecules* **1993**, *26*, 6489–6497.

(45) Oostwal, M.; Blees, M.; De Bleijser, J.; Leyte, J. Chain selfdiffusion in aqueous salt-free solutions of sodium poly (styrenesulfonate). *Macromolecules* **1993**, *26*, 7300–7308.

(46) This is consistent with estimates of G by the same method for polydisperse polyelectrolytes in salt-free solution, where the discrepancy between the estimates from steady shear and the expected modulus is even larger.^{28,62}

(47) The salt-free data were fit to a sixth order polynomial. This function was then used to interpolate values of $\eta_{sp,SF}$ to concentrations at which measurements with added salt were made.

(48) Konop, A. J.; Colby, R. H. Polyelectrolyte charge effects on solution viscosity of poly (acrylic acid). *Macromolecules* **1999**, *32*, 2803–2805.

(49) Kujawa, P.; Audibert-Hayet, A.; Selb, J.; Candau, F. Effect of ionic strength on the rheological properties of multisticker associative polyelectrolytes. *Macromolecules* **2006**, *39*, 384–392.

(50) Bordi, F.; Cametti, C.; Colby, R. H. Dielectric spectroscopy and conductivity of polyelectrolyte solutions. *J. Phys.: Condens. Matter* **2004**, *16*, R1423.

(51) The crossover method also underestimates the value of the plateau modulus, see ref 52 for a discussion.

(52) Liu, C.; He, J.; Van Ruymbeke, E.; Keunings, R.; Bailly, C. Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight. *Polymer* **2006**, *47*, 4461–4479.

(53) Adam, M.; Delsanti, M. Viscosity and longest relaxation time of semi-dilute polymer solutions. I. Good solvent. *J. Phys.* **1983**, *44*, 1185–1193.

(54) Kulicke, W.-M.; Kniewske, R. The shear viscosity dependence on concentration, molecular weight, and shear rate of polystyrene solutions. *Rheol. acta* **1984**, *23*, 75–83.

(55) Pickup, S.; Blum, F. D. Self-diffusion of toluene in polystyrene solutions. *Macromolecules* **1989**, *22*, 3961–3968.

(56) Ganter, J. L.; Milas, M.; Rinaudo, M. On the viscosity of sodium poly (styrene sulphonate), a flexible polyelectrolyte. *Polymer* **1992**, 33, 113–116.

(57) Konishi, T.; Yoshizaki, T.; Saito, T.; Einaga, Y.; Yamakawa, H. Mean-square radius of gyration of oligo-and polystyrenes in dilute solutions. *Macromolecules* **1990**, *23*, 290–297.

(58) Norisuye, T.; Nakamura, Y.; Akasaka, K. Reduced third virial coefficient for linear flexible polymers in good solvents. *Macro-molecules* **1993**, *26*, 3791–3794.

(59) Nakamura, Y.; Inoue, N.; Norisuye, T.; Teramoto, A. Ternary Cluster Integral for Polystyrene in trans-Decalin near the ϑ Point. *Macromolecules* **1997**, *30*, 631–636.

(60) Iwamoto, Y.; Hirose, E.; Norisuye, T. Electrostatic contributions to chain stiffness and excluded-volume effects in sodium poly (styrenesulfonate) solutions. *Polym. J.* **2000**, *32*, 428–434.

(61) Adam, M.; Delsanti, M. Viscosity and longest relaxation time of semi-dilute polymer solutions: II. Theta solvent. *J. Phys.* **1984**, *45*, 1513–1521.

(62) Lopez, C. G.; Richtering, W. Influence of divalent counterions on the solution rheology and supramolecular aggregation of carboxymethyl cellulose. *Cellulose* **2019**, *26*, 1517–1534.