# Rheology of Sulfonated Polystyrene Solutions

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*Received December 30, 1997; Revised Manuscript Received June 5, 1998*

ABSTRACT: We report the apparent viscosity of aqueous solutions of a well-characterized synthetic polyelectrolyte, the sodium salt of polystyrene sulfonate. Using two rheometers we measure the apparent viscosity over more than five decades of shear rate to determine the Newtonian viscosity and the onset of shear thinning, which is inversely proportional to the relaxation time. We study five decades of polyelectrolyte concentration, from the dilute to the entangled regimes, and three decades of added salt (NaCl) concentration, on a single polyelectrolyte sample. Much of the viscosity data in the literature are shown to be in the shear thinning regime and are not indicative of the Newtonian viscosity. Our data for viscosity and longest relaxation time are qualitatively consistent with a recent scaling theory. There are systematic deviations from this simple theory, including the failure of the well-established Fuoss law, which is shown to be obeyed by the apparent viscosity only at higher shear rates.

## I. Introduction

Charged polymer systems are abundant in nature and essential to life. Understanding polyelectrolytes is necessary for a fundamental understanding of biological systems and biological processes, since many biological polymers are polyelectrolytes, including DNA. Polyelectrolyte research also has many direct pragmatic industrial applications. Polyelectrolytes are used as thickeners for aqueous coatings and as flocculants for colloids and wastewater treatment and to control charge delivery in commercial electrolytic batteries. Owing to their large size in solution, polyelectrolytes exhibit shear thinning at particularly low shear rates, making them important industrial additives for a number of high-shear applications. For example, polyelectrolytes are added to slurries pumped into oil wells to aid in tertiary oil recovery from porous rock and as drag reducers. We report the principal results of a thorough experimental investigation of the shear-rate dependence of the apparent viscosity of a 1 200 000 molecular weight sodium salt of a 92% sulfonated polystyrene (NaPSS), over five decades of polymer concentration from below $c^*$, the overlap concentration, to far above $c_e$, the entanglement concentration, in both the presence and absence of added salt.

A polyelectrolyte in solution is surrounded by a cloud of counterions that exactly balance the large charge on the chain, so that the solution maintains charge neutrality. The interplay among the strong Coulombic repulsion between nearby charges on the polyelectrolyte, which tends to stretch the polymer chain, the screening of this Coulombic repulsion due to rearrangement of the ions in solution, and the large loss of entropy in localizing the counterion cloud ultimately determines the polyelectrolyte configuration. In turn, this configuration determines the dynamic response of the polyelectrolyte solution and the resultant rheological behaviors. The complex, long-range interactions which dominate the physics of polyelectrolytes give rise to a wealth of interesting behaviors.

Cursory inspection of the literature data on polyelectrolyte solution rheology indicates huge inconsistencies. We will show that most of the experimental inconsistencies are related to the new prediction of Dobrynin et al.[1,2] that *the relaxation time of semidilute linear polyelectrolyte solutions decreases as polyelectrolyte concentration increases*. This prediction comes from a new dynamic scaling theory based upon the original static scaling picture proposed by de Gennes et al.[3] For high molecular weight polyelectrolytes, strong shear thinning should be observed near the overlap concentration, where the viscosity is roughly twice that of the solvent, water. If this theory is correct, much of the literature data on high molecular weight polyelectrolyte Newtonian viscosity (the viscosity at zero shear rate) are erroneous and have actually been taken in the shear-thinning regime. We give direct experimental evidence supporting this assertion.

The static model of de Gennes et al.[3] extended to describe poor solvent[1] treats the configuration of the chain as globular at the smallest scales, where the poor solvent interaction dominates. At larger scales the electrostatic interaction stretches the chain into a directed random walk of globular electrostatic blobs. This extended configuration, which we loosely term "rodlike", extends to the correlation length. For scales larger than the correlation length, the electrostatic interaction is screened by the surrounding correlation blobs so the correlation blobs are flexibly connected and form a random walk. It is assumed by Dobrynin et al.[1,2] that the hydrodynamic interaction is also screened at the correlation length scale, so that Rouse dynamics are used to describe the motion of the chain of correlation blobs, while Zimm dynamics are used within the correlation blob. In this paper we will not review in detail the origin and derivation of the scaling theory of

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S0024-9297(97)01884-6 CCC: $15.00 
Published on Web 08/05/1998

polyelectrolytes, but instead we will refer the reader to previous works[1−3] so that we may instead focus upon comparing our experimental measurements and those in the literature with the predictions of the theory.

Polyelectrolyte solution rheology is complicated because polyelectrolytes are very sensitive to the presence of ions in solution. The dynamic properties are predicted to change markedly when the ionic concentration of the solution exceeds the concentration of dissociated counterions. Thus, even in the absence of added salt, the concentration of residual ions must be measured in order to distinguish dilution effects from effects of the residual salt. These characterization techniques are sorely lacking in previous studies of polyelectrolyte rheology. To avoid this pitfall, we have studied thoroughly the effect of added salt on our measurements and made measurements of the osmotic pressure and conductivity of our solutions which are described elsewhere.[4,5]

In contrast to previous studies, we thoroughly investigated the shear rate dependence of viscosity using two rheometers, a Contraves low shear 30 (LS30) rheometer at lower shear rates and a Rheometrics Fluids spectrometer (RFS) at higher shear rates, spanning nearly five decades of shear rate. For all of our samples we have measured the zero-shear (Newtonian) viscosity definitively without the need for extrapolation. In so doing, we discovered a violation of the long-accepted empirical Fuoss law,[6] describing the Newtonian viscosity of semidilute polyelectrolyte solutions. We were able to reproduce the law by measuring the apparent viscosity at higher shear rates, thereby explaining the wide applicability of the Fuoss law to literature data. We also determine the relaxation time from the onset of shear thinning of the apparent viscosity data. While these data agree with the scaling theory[1,2] qualitatively at moderate concentrations, they disagree with the scaling predictions at low concentrations.

In section II we will summarize the principal predictions of the dynamic scaling theory of Dobrynin et al.[1,2] and survey briefly the seminal experimental findings on the viscosity of polyelectrolytes in the literature in section III. Then we will discuss our experiments on NaPSS (section IV) and show our principle results compared to these predictions in section V. Finally, we compare and contrast our results to the large collection of literature data on NaPSS in section VI.

## II. Background: Theory

The scaling model of the static configuration of polyelectrolytes balances the poor solvent interaction within an electrostatic blob, which favors a collapsed, globular configuration, with the strong electrostatic interaction between charges, which tends to stretch the chain into a highly extended configuration. While this model predicts a globular structure on small scales (inside the electrostatic blob), the crucial feature of this scaling description in semidilute solutions is that the chain is rodlike up to the correlation length but flexible beyond the correlation length due to the screening of surrounding chains. Thus the persistence length is assumed to be proportional to the correlation length. In semidilute solution this model yields a simple expression for the correlation length $\xi$ in terms of the monomer number density $c$, the monomer size $b$, and the parameter $B$, which is the ratio of the fully extended length to the actual end-to-end distance in dilute solution with no added salt ($B \cong 3$ for NaPSS).

$$\xi = (B/cb)^{1/2} \tag{1}$$

We have followed the notation of Dobrynin et al.[2] who calculate $B$ in the poor solvent limit

$$B \cong (A^2 b/l_B)^{2/3} \tag{2}$$

where $A$ is the effective number of monomers between uncondensed charges assuming a simplified two state model for counterion condensation ($A \cong 4$ for NaPSS[5]), $l_B$ is the Bjerrum length ($l_B = 7$ Å in water). It has been shown that this model is slightly oversimplified in that a single monomer size $b$ is insufficient to describe precisely both the PSS monomer size and volume.[4] A simple refinement introducing a small scale persistence blob corrects this deficiency but does not affect the concentration dependence of the scaling results.[4]

From dynamic scaling, one can determine characteristic rheological properties, such as relaxation time, modulus, Newtonian viscosity, and diffusion coefficient, given a static model describing the configuration of a polymer chain. The critical length scale controlling dynamics is the correlation length, $\xi$, which delineates the onset of hydrodynamic and electrostatic screening. Inside of the correlation length, the modes of the polymer chain are hydrodynamically coupled and described by the Zimm model. Beyond this scale they are uncoupled and described by the Rouse model.

In Table 1 we summarize the results for the concentration ($c$) and degree of polymerization ($N$) dependences of the dynamic scaling theory for polyelectrolytes, as described by Rubinstein et al.[2] (refer there for more details). In the first column we give the rheological predictions in terms of the correlation length, $\xi$. Using these expressions, the dynamic scaling results from any static model with a single length scale can easily be determined by substituting the static predictions for the correlation length. In the second column we substitute the correlation length calculated from the de Gennes electrostatic blob model in the absence of added salt. In the third column we show how these predictions change in the presence of excess salt. For comparison, the neutral polymer results in good solvent are given

**Table 1. Summary of the Dynamical Predictions,[1,2] Calculated from the Static Correlation Length ($\xi$), for the Dependences on Polymer Concentration ($c$), Salt Concentration ($c_s$) and Degree of Polymerization ($N$) of Polyelectrolytes (Charged) under both High Salt ($c_s \gg c/2A$) and Low Salt ($c_s \ll c/2A$) Conditions, using the de Gennes[3] Electrostatic Blob Scaling Theory, and Neutral Polymers in Good Solvent**

| | charged | | |
|---|---|---|---|
| unentangled semidilute | low salt $\xi \sim c^{-1/2}$ | high salt $\xi \sim c^{-3/4}\, c_s^{1/4}$ | neutral $\xi \sim c^{-3/4}$ |
| relaxation time $\tau \sim \xi^{-3} c^{-2} N^2$ | $c^{-1/2} N^2$ | $c^{1/4} c_s^{-3/4} N^2$ | $c^{1/4} N^2$ |
| modulus $G \sim cN^{-1}$ | $cN^{-1}$ | $cN^{-1}$ | $cN^{-1}$ |
| viscosity $\eta \sim \xi^{-3} c^{-1} N$ | $c^{1/2} N$ | $c^{5/4} c_s^{-3/4} N$ | $c^{5/4} N$ |
| diffusion coeff $D \sim \xi^2 cN^{-1}$ | $N^{-1}$ | $c^{-1/2} c_s^{1/2} N^{-1}$ | $c^{-1/2} N^{-1}$ |

| | charged | | |
|---|---|---|---|
| entangled semidilute | low salt $\xi \sim c^{-1/2}$ | high salt $\xi \sim c^{-3/4}\, c_s^{1/4}$ | neutral $\xi \sim c^{-3/4}$ |
| relaxation time $\tau \sim \xi^{-6} c^{-3} N^3$ | $N^3$ | $c^{3/2} c_s^{-3/2} N^3$ | $c^{3/2} N^3$ |
| modulus $G \sim \xi^{-3}$ | $c^{3/2}$ | $c^{9/4} c_s^{-3/4}$ | $c^{9/4}$ |
| viscosity $\eta \sim \xi^{-9} c^{-3} N^3$ | $c^{3/2} N^3$ | $c^{15/4} c_s^{-9/4} N^3$ | $c^{15/4} N^3$ |
| diffusion coeff $D \sim \xi^5 c^2 N^{-2}$ | $c^{-1/2} N^{-2}$ | $c^{-7/4} c_s^{5/4} N^{-2}$ | $c^{-7/4} N^{-2}$ |

in the fourth column. We will compare these predictions for viscosity, relaxation time, and modulus directly with our experiments.

## III. Background: Experiments

Polyelectrolytes exhibit a number of anomalous, characteristic properties when compared to neutral polymer solutions and have been extensively studied, over the past forty years.[7−10] Polyelectrolytes exhibit unique rheological properties, as evidenced by their reduced viscosity which shows both a maximum at low concentrations[11−21] and a minimum at high concentrations.[22,23] There are many studies in the literature of these rheological properties but the results are often contradictory, as detailed in Section VI for NaPSS.

In 1951 Fuoss proposed a phenomenological equation, the Fuoss law,[6] which describes the viscosity data for a number of polyelectrolyte solutions without added salt.

$$\eta_{red} = \eta_{sp}/c = (\eta - \eta_s)/\eta_s c = A/(1 + Bc^{1/2}) \qquad (3)$$

The first two equalities define the reduced viscosity ($\eta_{red}$) and the specific viscosity ($\eta_{sp}$) in terms of the solution viscosity ($\eta$) and the solvent viscosity ($\eta_s$). The final equality is the statement of the Fuoss law where $A$ and $B$ are constants and $c$ is the concentration of the polyelectrolyte. Equation 4 predicts that a plot of $1/(\eta_{red})$ vs $c^{1/2}$ should be linear, with intercept $1/A$ and slope $B/A$. Fuoss established that this phenomenological form could describe data for a number of polyelectrolyte systems.[24,25]

Tam and Tiu[21] used the Fuoss law to generate master curves for describing the shear thinning of several polyelectrolytes, including three molecular weights of polyacrylamide, a substituted poly(ethylene oxide), and a carboxycellulose sample. While incorporating the Fuoss law into the reduced variable approach of Graessley[26] was remarkably successful for describing the low molecular weight samples, discrepancies from the master curve increased with increasing molecular weight. In addition, they studied a much broader concentration range than Fuoss, and found that two different values of $B$ from eq 3 were needed in the dilute and semidilute regimes to get reasonable agreement.

In 1954 Eisenberg and Pouyet[11] extended viscosity measurements to lower concentration, and found a maximum in the reduced viscosity. Later Cohen et al.[16] made very careful measurements investigating the behavior of this peak. They showed that the concentration at the peak is independent of molecular weight for NaPSS between 16 000 and 690 000 at a constant temperature of 300K. They also established that the concentration at the peak is proportional to the added salt concentration.[16] Both of these observations suggest that the peak in the reduced viscosity is caused by the presence of residual salt. They measured a pH of 5.4 which they argue is evidence that the residual salt level in their "salt-free" solutions is $4 \times 10^{-6}$ M due to dissociation of carbon dioxide from the air.[16] Using conductivity[4,5] and osmotic pressure measurements,[4] we have supported this assertion, as the residual conductance of 1.3 $\mu$S/cm and concentration of $5 \times 10^{-6}$ M are consistent with the known conductance of carbonic acid (details are discussed elsewhere[4]).

One drawback of Cohen et al.'s[16] measurements is that they used an Ubbelohde-type viscometer which had an effective shear rate of approximately 500 $s^{-1}$. They could investigate the shear-dependence of their viscosity measurements only down to about 300 $s^{-1}$. Not surprisingly, in this limited range of shear rates they did not detect large shear-thinning effects. However, they definitely are in the shear-thinning regime for their higher molecular weight samples and have thus measured non-Newtonian apparent viscosities.

## IV. Experimental Section

Our polystyrene sulfonate sample was obtained from Scientific Polymer Products (Webster, NY) Catalog No. 628, Lot No. 02. Size exclusion chromatography and light scattering yield a weight-average molecular weight $M_w = 1.20 \times 10^6$ with $M_w/M_n < 1.2$. Elemental analysis reported by the manufacturer indicates that 92% of the monomers are sulfonated. To remove salt impurities and any other low molecular weight contaminants, we extensively dialyzed the sample using a 20 000 molecular weight cutoff Amicon membrane. Water from a Millipore deionization system with conductivity less than 0.8 $\mu$S/cm was forced through a chamber by high-pressure nitrogen gas (30 psi). The sample was flushed with water for over 2 weeks, until the conductivity of the emerging dialyzate was constant (1.0 ± 0.2 $\mu$S/cm). To avoid contamination by ions from glass, all solutions were stored in cleaned polyethylene bottles. Serial dilutions were made with each subsequent dilution being a factor of 2 lower in concentration. The concentrations of all solutions were then checked by UV absorption at 262 nm. The extinction coefficient $\epsilon = 383 \pm 18$ L/(mol cm) was established from multiple determinations of solids concentrations by drying to constant mass. A sodium ion concentration determined via ion chromatography confirmed the concentration of polyelectrolyte determined from UV absorption measurements and proved that the counterion was indeed sodium. UV absorption was also checked on solutions after rheology, and minimal concentration changes were found.

An important characterization tool missing from previous studies is a systematic way of quantifying the ionic content of the polyelectrolyte solutions, particularly in the absence of added salt. In an attempt to rectify this oversight we measured the conductivity and osmotic pressure of our test solutions. Both of these measurements are sensitive to the free ion concentration. There are literature data on both of these properties, but not on a single well-characterized sample over such a broad range of polymer and salt concentrations. Both measurements were consistent with a residual salt content of approximately $5 \times 10^{-6}$ M, as described in detail elsewhere.[4] The hydrogen ion content was determined noninvasively using pH paper in a small volume of solution which was discarded after measurement. This procedure was employed because it required less volume of solution than a pH meter, and conductivity measurements done before and after using a pH meter indicated that the pH meter increased significantly the residual ionic content of the solution. The pH was found to be 5.4 ± 0.1 indicating a hydrogen ion content of $4 \times 10^{-6}$ M. This is exactly the value expected due to dissociation of dissolved atmospheric carbon dioxide, and in agreement with the measurements of Cohen et al.[16]

A Contraves low shear 30 viscometer was used to measure apparent viscosity of the lower viscosity samples ($\eta < 200$ cP) at low shear rates in the range $0.01 < \dot{\gamma} < 128.5$ $s^{-1}$. We used a concentric cylinder geometry (of outer diameter 12.0 mm and inner diameter 11.1 mm) in steady shear. The apparatus was modified to minimize evaporation from the sample by placing a truncated plastic cone over the sample cell. In addition, the sample temperature was maintained at 25.0 ± 0.2 °C by adding a temperature controlled water bath surrounding the sample cell. After calibration, the viscosity of standard oils (7.87, 30.3, 45.9, and 101.5 cP) were reproduced to better than 3%.[4] The LS30 has remarkable sensitivity, and is able to measure the viscosity of air yielding 0.0188 ± 0.0003 cP accurately over almost a decade and a half of shear rates (3−120 $s^{-1}$). This value is within error bars of the literature value

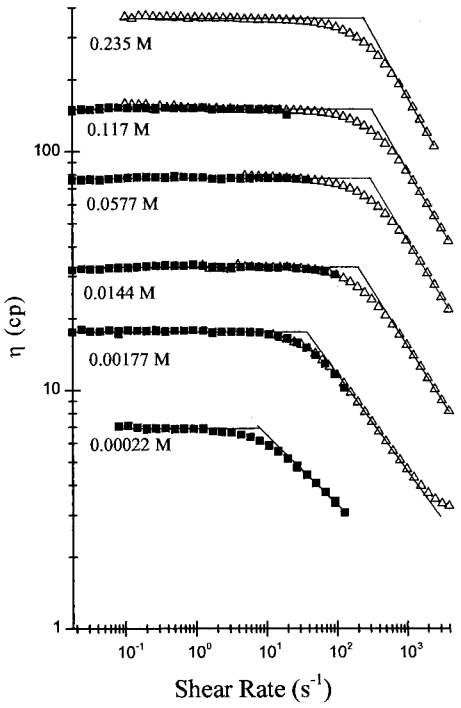


**Figure 1.** Shear rate dependence of apparent viscosity for selected NaPSS solutions with no added salt (concentrations indicated on plot). Filled squares are Contraves LS30 data, and open triangles are Rheometrics Fluid Spectrometer data.

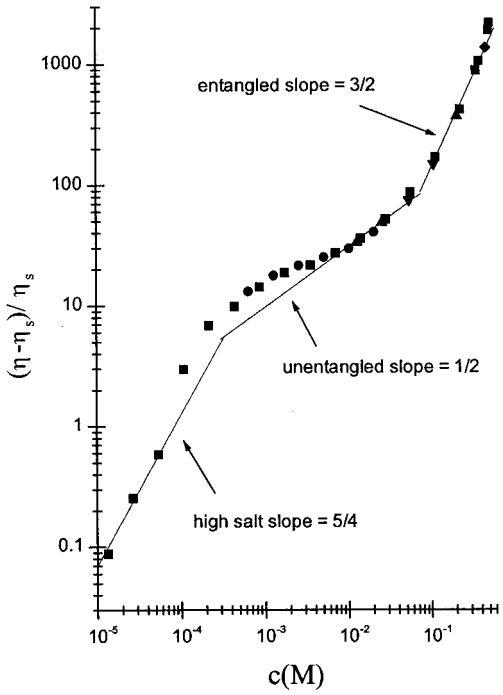


**Figure 2.** Concentration dependence of Newtonian specific viscosity $(\eta - \eta_s)/\eta_s$ for NaPSS with no added salt (squares) and with added NaCl corresponding to the low-salt limit of the scaling theory (circles have $10^{-5}$ M NaCl, triangles have $10^{-4}$ M NaCl, inverted triangles have $10^{-3}$ M NaCl, and diamonds have $10^{-2}$ M NaCl). Solid lines are the predictions of the scaling theory (See Table 1).

at 25 °C of 0.0185 cP. Using this rheometer, at least 1 decade of shear rate independent apparent viscosity was measured for our NaPSS solutions, even for low viscosity samples which were shear thinning at quite low shear rates.

A Rheometrics Fluids spectrometer (RFS) with a cone and plate geometry (50 mm diameter truncated stainless steel cone with a 0.02 rad cone angle and a 50 mm diameter stainless steel plate) was used in steady shear to measure the shear rate dependence of the apparent viscosity for solutions in the range from 1 to 3000 $s^{-1}$. This rheometer extended by over a decade the range of shear rates we could access, thus allowing a more complete probe of the shear thinning behavior. The RFS can use either of two transducers differing in torque sensitivity by a factor of 10 (10 cm and 100 gm cm). In this geometry, using the more sensitive transducer (10 gm cm) allows reliable measurement of moderate viscosity fluids, down to about 20 cP. Using the higher torque range transducer (100 gm cm) we were able to measure high viscosity samples (greater than 200 cP), which could not be measured in the LS30, over a broad range of shear rates. The sample temperature was maintained at 25.0 ± 0.2 °C with a circulating water bath.

## V. Results and Discussion

**A. Viscosity with No Added Salt.** For each concentration of NaPSS, a plot of apparent viscosity vs shear rate was analyzed, containing both sets of data (from the LS30 and the RFS). In Figure 1 we plot the apparent viscosity as a function of shear rate for NaPSS solutions of various concentrations with no added salt. Note that there is a dramatic shear-thinning effect, at a shear rate which decreases with dilution in the semidilute unentangled regime, qualitatively confirming the scaling predictions.[1,2] Below 20 cP, the RFS viscosity data are systematically 10−20% low relative to the LS30 data sets and thus the RFS data have been shifted slightly on the viscosity scale to match the LS30 data. This mild geometry effect will be the subject of a future publication. Note the excellent agreement between the two rheometers for the samples above 10 cP viscosity. For the samples with viscosity below 10 cP; in the absence of added salt, the RFS appears to be unreliable, never showing any Newtonian behavior and failing to overlap with the LS30, which is still well within its optimal operating range. In this range ($c < 5 \times 10^{-4}$ M), the viscosity is determined entirely from the LS30 data. Apparent viscosity as a function of shear rate was measured at higher added salt concentrations as well. As salt was added, the solutions showed less dramatic shear thinning and had much lower osmotic pressures. These factors may have contributed to the improved viscosity data agreement between the LS30 and the RFS, which we observed as we increased the salt concentration.

The horizontal fitted line in Figure 1 is the best fit Newtonian viscosity. Also shown is the best-fit power law in the shear-thinning regime. The shear rate at the onset of shear thinning was determined by finding the intersection of these two least-squares fit lines. The reciprocal of the shear rate at the onset of shear thinning defines a relaxation time $\tau$ of the polyelectrolyte.

The Newtonian viscosity data without added salt are plotted in Figure 2. In addition, we have plotted the data points from the other added salt concentrations that satisfy the condition $c \gg 2Ac_s$, indicating that they are in the low salt limit (many more free counterions than salt ions). The data in Figure 2 span more than four decades of concentration and clearly show the transition to entangled behavior at a concentration of 0.07 M NaPSS and a viscosity of 75 cP. Empirically, the crossover to dilute solution behavior usually occurs at about twice the solvent viscosity ($\eta_s$ = 0.89 cP for water at 25 °C). This corresponds to an overlap

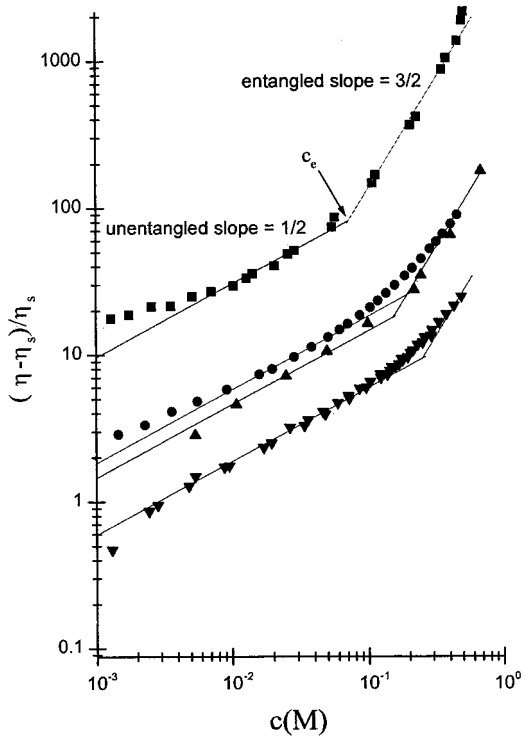


**Figure 3.** Comparison of our salt-free specific viscosity data (squares, with $c_e = 0.071$) with literature data of Prini and Lagos[22] for M = 300 000 (triangles, with $c_e = 0.16$ M) and data of Oostwal[23] for $M = 398\,000$ (circles, with $c_e = 0.2$ M) and for $M = 199\,000$ (inverted triangles, with $c_e = 0.25$ M). Solid lines have the slopes predicted by the scaling theory (see Table 1).

concentration, $c^*$, of approximately $7 \times 10^{-5}$ M (~14 ppm). Above 0.01 M concentration, the data support the scaling theory. For about a decade the scaling prediction of $\eta \sim c^{1/2}$ for the unentangled semidilute regime gives a fine description of the data. Below 0.01 M, though, there is a shoulder in the data which is not described by the theory. In the entangled regime the data follow the predicted $\eta \sim c^{3/2}$ dependence for nearly an entire decade. At very high concentrations (~0.5 M), the data systematically deviate upward from this prediction.

By plotting the specific viscosity, we remove the effect of the solvent viscosity so that we can look for scaling behaviors in the low concentration range as well. Long-range electrostatic interactions should dominate at low concentrations and continue to couple the chains even when they are no longer physically overlapping because the distance between chains is a weaker function of concentration than the electrostatic screening length. However, the experimental data indicate that the electrostatic interaction is screened in this dilute regime by the presence of the residual salt. To our surprise we find that $\eta_{sp} \sim c^{5/4}$ for dilute NaPSS. This concentration dependence is predicted by theory for semidilute unentangled polyelectrolytes in the high salt limit. The residual salt concentration is higher than the counterion concentration in our dilute solutions with no added salt, but we do not understand why the semidilute scaling prediction appears to work in dilute solution.

In Figure 3 we show all of the NaPSS viscosity data in the literature that are taken at high enough concentrations to see the transition to entangled behavior. Our data and those of Fernandez et al.[22] clearly show both the unentangled semidilute scaling of $\eta \sim c^{1/2}$ and the entangled semidilute scaling of $\eta \sim c^{3/2}$ so that the concentration at the crossover, $c_e$, can unambiguously be determined. In contrast, Oostwal[23] does not quite measure high enough concentrations to get beyond the crossover region and measure the expected scaling in the entangled regime. We have fitted asymptotic curves to the Oostwal data, but our error bars in determining $c_e$ reflect the uncertainty in this extrapolation. It is noteworthy that Oostwal's data for 398 000 show the same lower slope as our data in the unentangled regime at low concentrations.

Figure 4a shows how the experimentally determined overlap concentration $c^*$ and the entanglement onset concentration $c_e$ vary with the degree of polymerization $N$. The experimental overlap concentration is found from the X-ray scattering data of Kaji et al.[28] when the concentration scaling of the peak of the scattering function crosses from a one-third to one-half scaling exponent (squares). The overlap concentration is found phenomenologically when the specific viscosity is twice the solvent viscosity from literature viscosity data (circles). The fitted power law of $c^* \sim N^{-2.0}$ describes the data well for more than $2^1/_2$ decades of $N$ and is in excellent agreement with the prediction of the scaling theory[1]. We find that the entanglement concentration, $c_e$, as determined from viscosity data (inverted triangles) scales with the degree of polymerization as: $c_e \sim N^{-0.6}$. One might be tempted to not put too much credence in this result since clearly the slope of $-0.6$ is being determined principally by only two data points, our data and the data of Fernandez Prini and Lagos.[22] However, from the self-diffusion measurements of Oostwal[29] we get a second determination of $c_e$ (triangles) which shows a consistent slope. It is not very surprising that there is a prefactor between the $c_e$ determined from the diffusion coefficient and that determined from viscosity. It is quite reasonable that topological constraints could begin to hinder diffusion before significantly affecting the viscous dissipation. The experimental slope of $-0.6$ is markedly different than the scaling theory prediction[1] of $c_e \sim N^{-2}$. While the exponents predicted in each regime for the viscosity are in reasonable agreement with the data, clearly the criterion used for polyelectrolyte entanglement is incorrect.

This experimental result indicates that details of the entanglement model used in the literature[1] need refinement. The problem could lie in the assumption that a universal number of overlapping chains, $n$, is necessary to form an entanglement. Instead, $n$ may vary with the persistence length of the chain. This follows from the simple intuition that flexible segments may entangle more easily than rigid ones. For neutral polymers this would be largely unimportant to the polymer physicist, since it is determined by chemical constraints of the chain and renormalized by the effective Kuhn segment. However, for polyelectrolytes the persistence length is asserted to be proportional to the correlation length, which changes with concentration. This hypothesis would introduce a concentration dependence in the $n$ parameter that cannot be simply rescaled as a prefactor of the theory.

We can determine the empirical chain length dependence of $n$, the number of overlapping chains necessary to form an entanglement, from the experimental result that $c_e \sim N^{-0.6}$, and the experimentally verified prediction that $c^* \sim N^{-2}$.

$$n \approx \left(\frac{c_e}{c^*}\right)^{1/4} \approx N^{0.35} \qquad (4)$$

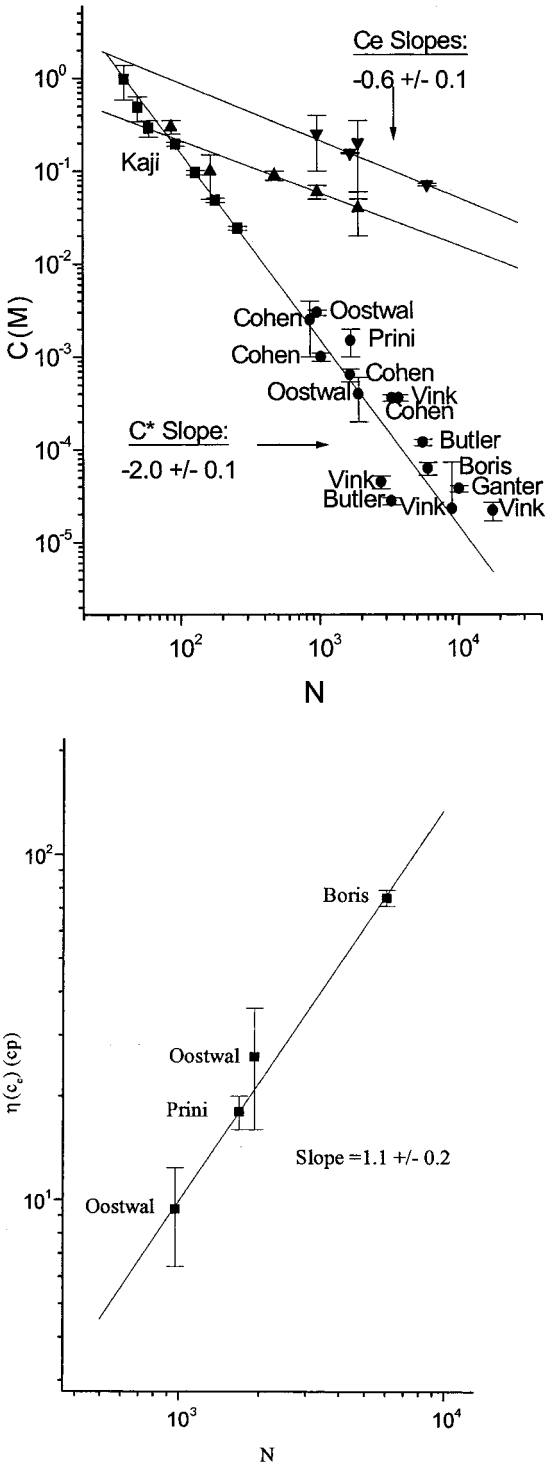





**Figure 4.** (a) Overlap concentration from X-ray scattering data of Kaji et al.[28] (squares), overlap concentration from viscosity data[12,16,19,20,22,23] (circles), entanglement concentration from viscosity[22,23] (inverted triangles), and entanglement concentration from diffusion[29] (triangles) as a function of degree of polymerization for NaPSS with no added salt. (b) Viscosity at the entanglement concentration[22,23] (squares) as a function of degree of polymerization for NaPSS with no added salt.

If the theory is self-consistent, then the value of the entangled viscosity at the entanglement concentration $c_e$, will satisfy the scaling relation: $\eta(c_e) \sim n^2 \sim N^{0.7}$. In Figure 4b we plot the chain length dependence of the viscosity at the entanglement concentration $\eta(c_e)$ and find that this consistency check fails. In fact, the viscosity at the onset of the semidilute entangled regime scales as $\eta(c_e) \sim N^{1.1}$. A better theoretical understanding of entanglement formation in polyelectrolytes is needed.

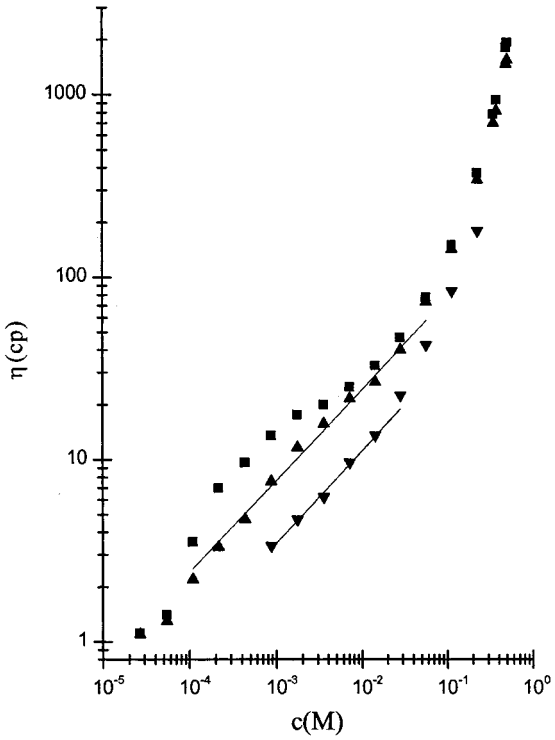


**Figure 5.** Concentration dependence of Newtonian viscosity (squares) and non-Newtonian apparent viscosities at shear rates of 100 $s^{-1}$ (triangles) and 1000 $s^{-1}$ (inverted triangles). Solid lines have the $^1/_2$ slope anticipated by the Fuoss law (eq 3) and the unentangled semidilute dynamic scaling theory (Table 1).

The Fuoss law has been "verified" by many other researchers. In fact, until this study it was considered to be one of the defining characteristics of polyelectrolyte behavior. By actually measuring viscosity all the way through the semidilute regime, we have demonstrated that the Fuoss law is violated. It is quite interesting to note that at either end of the semidilute regime the data appear to obey the Fuoss law, as was seen by the other researchers (i.e., the initial slope at both ends of the unentangled semidilute regime is $\eta \sim c^{1/2}$). However, the Fuoss law does not adequately describe the viscosity of the entire unentangled semidilute regime.

Insight into the prevalence of the Fuoss law is found when one analyzes the apparent viscosity at higher shear rates, typical of the capillary viscometers employed by many other researchers. In Figure 5, we show our data in the zero shear limit and at 100 and 1000 $s^{-1}$ shear rates. The best fit slopes at these higher shear rates obey the Fuoss law! Evidently the Fuoss law is a relation obeyed by the apparent viscosity over a wide range of shear rates (100−1000 $s^{-1}$). This is probably the best explanation for why the Fuoss law has been observed so pervasively in the literature. It is possible that the Fuoss law is obeyed in the Newtonian regime for lower molecular weight samples.

**B. Viscosity with Added Salt.** The Newtonian viscosity data of NaPSS with added NaCl are shown in Figure 6. As more salt is added, the viscosity departs from the no-salt viscosity at progressively higher NaPSS concentrations, as expected by the scaling theory. The fact that the $10^{-5}$ M NaCl data have similar viscosities

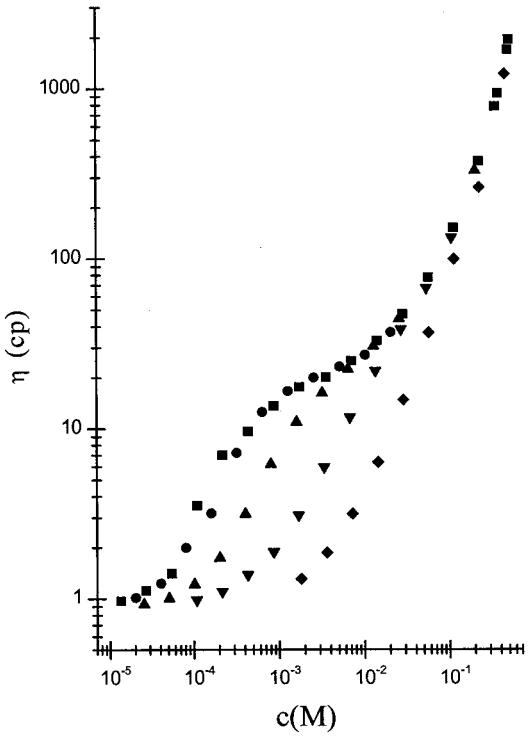


**Figure 6.** Concentration dependence of Newtonian viscosity for NaPSS solutions with no added salt (squares), with $10^{-5}$ M NaCl (circles), with $10^{-4}$ M NaCl (triangles), with $10^{-3}$ M NaCl (inverted triangles), and with $10^{-2}$ M NaCl (diamonds).

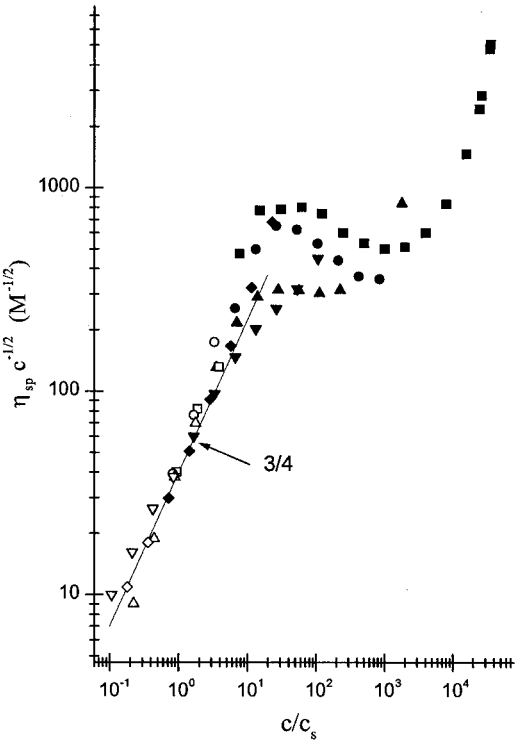


**Figure 7.** Viscosity data plotted in the scaling form for unentangled semidilute polyelectrolytes in the high salt limit (see Table 1), using a residual salt concentration of $5 \times 10^{-6}$ M. Symbols are the same as Figure 6. Open symbols indicate that the sample is below the overlap concentration ($c < c^*$). The solid line is the $^3/_4$ slope predicted by the theory, which is consistent with the data with $c/c_s < 2A \cong 8$.

to the data with no added salt gives further support for the "salt free" data having a residual salt concentration of approximately $10^{-5}$ M.

Below the concentration where each data set departs from the data with no added salt, there are more salt ions than free counterions ($2c_s >$ c/A). The fact that these data are consistent with the unentangled high salt predictions of the dynamic scaling theory (Table 1) is demonstrated in Figure 7, where we plot $\eta\, c^{-1/2}$ against $c/c_s$. The scaling theory predicts this plot will be universal for all salt concentrations (in the high salt limit, where $c < 2Ac_s$) with a slope of $^3/_4$. This prediction of the dynamic scaling theory is verified remarkably well, using the residual salt concentration of $5 \times 10^{-5}$ M determined from conductivity and osmotic pressure data.[4,5] It is surprising, however, that this theory continues to work even below the overlap concentration.

**C. Relaxation Time and Terminal Modulus.** The simplest method to determine the relaxation time from our apparent viscosity data was to find the intersection of the constant Newtonian viscosity measured at low shear rates with the power law fit to the apparent viscosity at high shear rates in the shear thinning regime. Taking the reciprocal of this shear rate gives us the characteristic relaxation time $\tau$. Alternate definitions of the relaxation time based upon finding the shear rate at which the apparent viscosity has fallen to a fixed percentage of its Newtonian value (95% and 90% were used) differed by constant factors from $\tau$, giving us considerable confidence in our method. In the semidilute unentangled regime, neutral polymers have a relaxation time that increases with increasing concentration as $\sim c^{1/4}$. In contrast, polyelectrolytes have a relaxation time which is predicted to decrease with increasing concentration as $\sim c^{-1/2}$. In the entangled regime, a neutral polymer's relaxation time increases as $\sim c^{3/2}$ while a polyelectrolyte's relaxation time is predicted to be independent of concentration. In Figure 8, we compare the experimentally determined scaling laws for the relaxation time to those predicted by theory.

Clearly the agreement is only reasonable in the $1^1/_2$ decade concentration range from 0.007 to 0.2 M, showing both the predicted unentangled and entangled semidilute scaling. However, for concentrations lower than 0.007 M, the data show a stronger than predicted concentration dependence of $c^{-0.90 \pm 0.02}$ down to a concentration of 0.0002 M. This same dependence of relaxation time on concentration is seen in poly(α-glutamate) solutions (another polyelectrolyte system) using frequency domain dielectric spectroscopy by Bordi et al.[30] This gives us considerable confidence in these results and indicates that this dependence is likely a universal feature of polyelectrolyte behavior. These data, which cover $1^1/_2$ decades of concentration, *are not explained by the scaling theory*. However, it is worth noting that the relaxation time is larger than predicted by theory in the same range of concentration that the viscosity is larger than predicted (see Figure 2). These data indicate that there is a fundamental flaw in our understanding of polyelectrolyte dynamics in this concentration range.

The data below 0.0002 M have larger error bars due to experimental difficulties. These data show a definitive downturn and scale with a slope of $c^{1.4 \pm 0.2}$. Assuming the maximum in $\tau$ corresponds to the crossover from the low salt limit at high concentration ($c \gg 2Ac_s$) to the high salt limit at low concentration ($c \ll 2Ac_s$) the scaling theory predicts a much weaker dependence on concentration: $\tau \sim c^{1/4}$.

In the concentration range from 0.03 to 0.2 M NaPSS, the phenomenological slope fit to the relaxation time

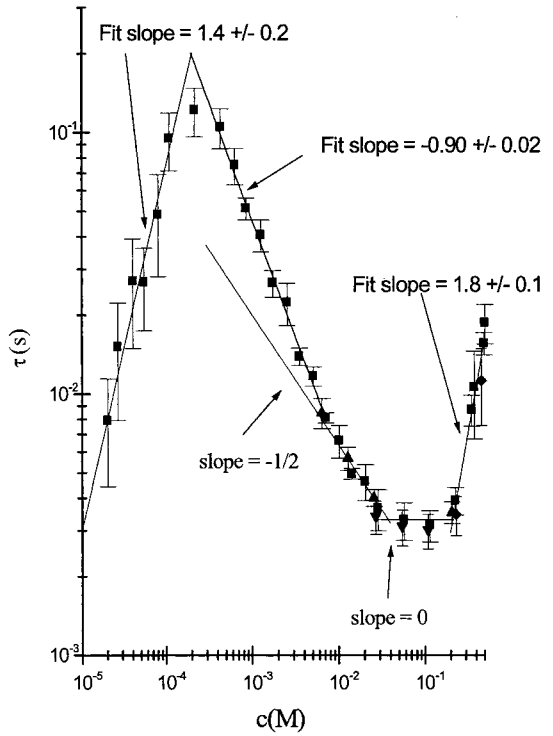


**Figure 8.** Concentration dependence of the relaxation time determined as the reciprocal of the shear thinning onset for NaPSS with no added salt (squares) and with added NaCl corresponding to the low salt limit of the scaling theory (symbols are the same as Figure 6). Solid lines are either the predictions of the scaling theory (see Table 1) or fitted power laws.

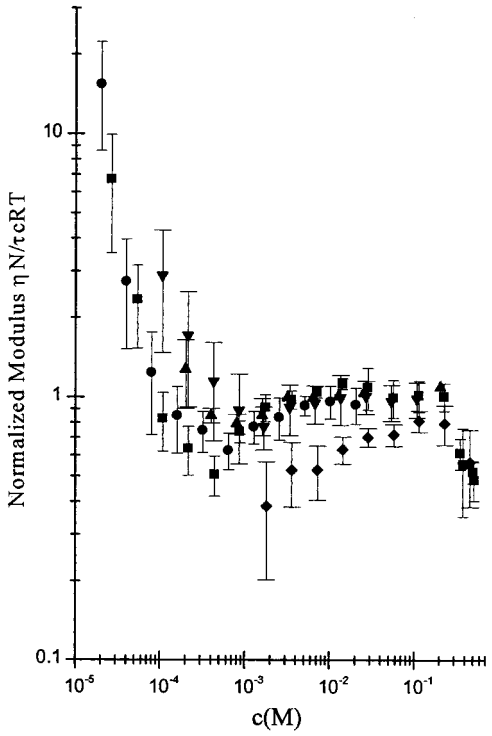


**Figure 9.** Concentration dependence of the normalized modulus for semidilute NaPSS solutions with and without added salt. Symbols are the same as Figure 6.

data is consistent, within error bars, with the predictions of the scaling theory, that the semidilute entangled relaxation time should be independent of concentration. The transition to entangled dynamics measured by the relaxation time data is quite sharp and indicates an entanglement onset concentration of $c_e \sim 0.032 \pm 0.004$ M. This entanglement concentration is lower than that determined from the scaling theory fit to the viscosity data in Figure 2 of $c_e = 0.071$ M. The entanglement concentration from the relaxation time is more consistent with the expectation based on extrapolating the entanglement concentration from diffusion (see Figure 4a).

At high concentrations, above 0.2 M, in what should be the semidilute entangled regime, there is a marked upturn in the relaxation time, which scales as $\sim c^{1.8}$ for about half a decade of concentration. This behavior is verified by nine independent measurements and is not predicted by theory. It is interesting to note that this concentration dependence is even stronger than the $c^{3/2}$ predicted for uncharged polymers in this regime. This finding is consistent with the measurements made on another polyelectrolyte system, poly(*N*-methyl-2-vinylpyridinium chloride), which also shows a very similar dramatic increase in the relaxation time in the same concentration range.[31] As concentration increases, the density of charges increases, so one would naturally expect the dielectric constant to increase. However, there is also a growing volume fraction of polystyrene which has a much lower dielectric constant. Properly incorporating both the effect of the increasing dielectric constant and the large solvation energy penalty for condensing charges within the poor solvent globules may allow an adequate description of this concentrated regime.

Although we did not measure directly the modulus of our polyelectrolyte solutions, it is quite interesting to use scaling to calculate the terminal modulus from the ratio of viscosity and relaxation time. Using the scaling relation that the terminal modulus is the ratio of the viscosity to the relaxation time we find

$$G \cong \frac{\eta}{\tau} \cong \frac{cRT}{N} \tag{5}$$

We therefore consider a normalized modulus $\eta N/cRT\tau$, which should be independent of concentration and of order unity over the entire unentangled semidilute regime. The normalized modulus should also exhibit a $c^{1/2}$ dependence in the entangled regime.

In Figure 9, we show the normalized modulus determined from our experimental Newtonian viscosity data and our relaxation time data. The dynamic scaling predicted for semidilute concentrations works for nearly 2 decades in the concentration range from 0.003 to 0.2 M, for all but the highest salt concentration. The normalized modulus is indeed normalized to unity and roughly independent of concentration over this range. This is surprising, since both viscosity and relaxation time data in the range from 0.07 to 0.2 M are indicating entanglement effects. However, the $c^{1/2}$ concentration dependence of the normalized modulus predicted in the entangled regime is *not* observed. In fact this prediction is not even qualitatively correct. Instead of increasing, the normalized modulus decreases with increasing concentration above 0.2 M in the entangled regime. The fitted power law in this regime has a concentration dependence of $c^{-0.8}$. Thus the (unnormalized) modulus increases with a power law of $c^{0.2}$, instead of the $c^{3/2}$ power predicted by the scaling theory in the entangled regime. It is difficult to interpret the normalized modulus being less than unity since this suggests that

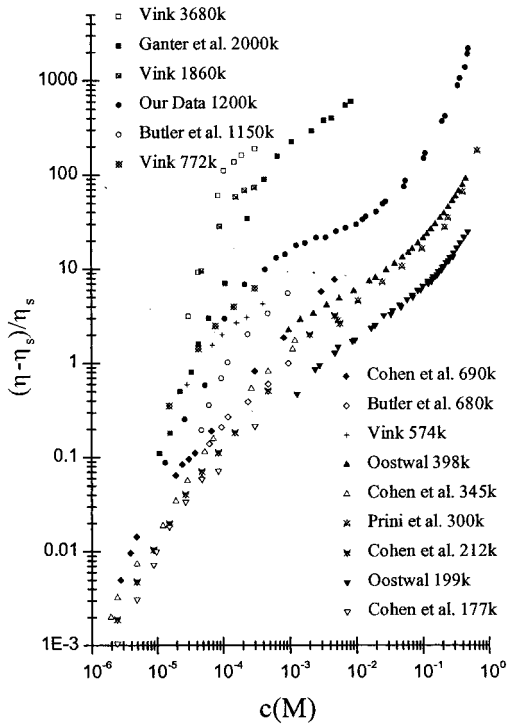


**Figure 10.** Specific viscosity of NaPSS with no added salt taken from the literature.[12,16,19,20,22,23]

*the terminal modulus at high concentration is less than kT per chain.*

## VI. Comparison to Rheological Data from the Literature

In Figure 10, we have assembled all literature data on the specific viscosity of NaPSS in salt-free aqueous solutions above 150 000 molecular weight. Studies which covered lower molecular weights or less than a decade of concentration were not included.[17] Cursory inspection of this plot shows that discrepancies are abundant in the literature data. At the highest molecular weights, both Ganter et al.[20] and Vink[19] observe transitions in the semidilute range above $c^*$, the overlap concentration (which occurs at approximately twice the solvent viscosity ($\eta \sim 2\eta_s$)). Ganter et al.[20] very carefully measured the shear rate dependence of the apparent viscosity and showed that they were near the Newtonian limit. Even at low concentrations, where they often measured less than a decade of Newtonian behavior, it is clear that the error in their reported Newtonian viscosities should be small. In contrast, Vink had to extrapolate his data to zero shear rate because he was unable to get to low enough shear rates, even with his custom-built variable driving head capillary rheometer which employed wall shear rates between 5 and 400 $s^{-1}$. At the two highest molecular weights, 3 860 000 and 1 860 000, he was unable to make any zero-shear limit extrapolation so these data are clearly non-Newtonian. It is appealing to assert that the single transition observed in each of the high molecular weight samples (2 000 000 by Ganter et al.[20] and both 3 860 000 and 1 860 000 by Vink[19]) is due to residual salt. However, this would require that the residual salt level is larger for higher molecular weight samples, a finding at variance with the original study of Cohen et al.[16] at 25 °C (the temperature used in both studies) but in agreement with the trend seen in a later study of Cohen and Priel[32] at slightly elevated temperatures.

Another disturbing conflict in the literature is the disagreement between the power law observed by Oostwal[23] of $\sim 1/3$ in the semidilute unentangled regime, compared to the $\sim 1/2$ power law seen by Fernandez Prini and Lagos[22] for samples relatively close in molecular weight (398 000 and 300 000 respectively). The Fuoss law and the scaling theory would predict the $1/2$ power law seen by Prini and Lagos;[22] however, their lowest concentration is not very far below the entanglement concentration and is probably still in the crossover regime. Our data supports the finding of Oostwal, and shows a power law smaller than $1/2$ in conflict with the Fuoss law and the prediction of scaling.

In the entangled regime these two data sets, at 398 000 (Oostwal[23]) and 300 000 (Fernandez Prini and Lagos[22]), also conflict. Fernandez Prini and Lagos[22] show a more dramatic upturn in viscosity, consistent with a $3/2$ power law. In fact their data appear to cross above that of Oostwal[23] despite being at a lower molecular weight. Oostwal measures the shear dependence ($1-300$ $s^{-1}$) of his samples but sees no shear thinning; in fact, he sees a gradual shear thickening which he subtracts out, claiming that it is also seen for pure solvent and is an artifact of his instrument. Since we expect a moderate shear thinning, this "artifact" is worrisome. If the sample is truly Newtonian, as he claims, it would validate the use of a capillary rheometer by Fernandez Prini and Lagos. This conflict, in principle, could be entirely due to the limited range of each of the data sets. Our findings on the viscosity of a higher molecular weight sample are consistent with the steeper slope of viscosity versus concentration measured by Prini and Lagos[22] in the entangled regime.

The data sets of Butler et al.[12] were taken at shear rates between 1 and 30 $s^{-1}$ where no shear dependence was reported, except for the highest molecular weight sample (1 150 000) which showed "a few percent" decrease. For this sample the zero-shear behavior was extrapolated. Our data taken over this range at a similar molecular weight (1 200 000) show dramatic shear thinning in comparison. We therefore conclude that the data of Butler et al.[12] at 1 150 000 molecular weight are not consistent with zero-shear behavior. In fact, their data are very similar to our data at higher shear rates. Another concern about their data is that the molecular weight distribution and percent sulfonation are not well quantified. Either of these concerns may also explain the low viscosities they measure compared to Cohen et al.[16] at nearly the same molecular weight (680 000 vs 690 000). Note that we already expect Cohen's viscosity data to be too low for these samples, because they are measured at a shear rate of 600 $s^{-1}$. Butler et al.[12] also report that solutions in glass vessels decreased in viscosity with time, due to leaching of ions. They ultimately stored their samples in polyethylene bottles to ensure reproducibility. Despite these precautions, their data still seem to indicate a fairly high level of residual salt.

The most alarming departure of the scaling predictions from the data in Figure 10 is seen in the prediction for chain length dependence of the viscosity. At a concentration of $2 \times 10^{-3}$ M, which, according to the scaling theory, corresponds to the semidilute unentangled regime for all chain lengths measured, a power law fit indicates $\eta_{sp} \sim N^{2.4}$. This is clearly a much stronger dependence than expected by the Rouse model ($\eta_{sp} \sim N$). For the longest chains the problem is more

severe, as shown by Ganter et al.[20] who measured more than 10 times our viscosity, with a molecular weight only a factor of 1.7 times larger. The best empirical function to describe the chain length dependence of viscosity is an exponential.

$$\eta_{sp} = 0.58 \exp(N/1600) \quad (6)$$

Such a strong dependence of viscosity on chain length is at odds with all current notions of polyelectrolyte dynamics.

## VII. Conclusions

We have measured a Newtonian viscosity, over at least a decade of shear rate, for aqueous solutions of a high molecular weight NaPSS as functions of polyelectrolyte concentration and salt concentration. The effect of added salt is in quantitative agreement with a simple scaling theory based on the Rouse model. However, the viscosity with no added salt only qualitatively agrees with the scaling predictions. In particular, the Fuoss law ($\eta \sim c^{1/2}$) was found to be valid only for constant shear rates that are in the shear thinning regime. The zero shear rate (Newtonian) viscosity data do not obey the Fuoss law and instead scale with a weaker power of concentration ($\eta \sim c^{0.35 \pm 0.02}$).

The terminal relaxation time of the polyelectrolyte chain increases as concentration is lowered in the semidilute unentangled regime, in qualitative agreement with the scaling theory. However, the observed concentration dependence is actually much stronger than predicted. This suggests that much of the literature data on high molecular weight polyelectrolyte solution viscosity do not represent the Newtonian limit. There is evidence that the relaxation time goes through a maximum at very low concentrations and then decreases sharply into the dilute regime. At very high concentrations, above the entanglement onset, the relaxation time appears to increase steeply. Neither of these features are described by current theories.

While the concentration dependencies of both viscosity and relaxation time are in reasonable agreement with the scaling predictions near the concentration onset of entanglements, the dependence of the entanglement concentration on chain length is much weaker than expected. Furthermore, the viscosity at the entanglement concentration, expected to be independent of chain length, is found to be roughly proportional to chain length. These observations indicate that polyelectrolytes entangle in ways that are quite different from entanglement in uncharged polymer solutions.

**Acknowledgment.** We thank the Eastman Kodak Company for financial support and hospitality during the course of this work. Discussions with Richard Connelly, Andrey Dobrynin, Tony Duong, Jeffrey Gillmor, Jehuda Greener, Lloyd Lobo, Charles Lusignan, Michael Rubinstein, Julia Tan, Thomas Whitesides, David Teegarten, Tom Mourey and Frank Saeva are acknowledged with gratitude. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

**Note Added in Proof.** The apparent rise at low concentration in Figure 9 is removed by using $\eta - \eta_s$ in place of $\eta$.

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