Electrostatic Contributions to Chain Stiffness and Excluded-Volume Effects in Sodium Poly(styrenesulfonate) Solutions

Yoshimi IWAMOTO, Eigo HIROSE, and Takashi NORISUYE

*Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan*

(Received November 22, 1999)

ABSTRACT: Intrinsic viscosities for sodium poly(styrenesulfonate) in aqueous sodium chloride at 25°C have been determined for 15 samples ranging in weight-average molecular weight from 3.8×10^3 to 6.5×10^5 at five salt concentrations C_s between 0.05 and 2 M. Their molecular weight dependence at each C_s is fairly satisfactorily explained by the theory of Yoshizaki *et al.* for unperturbed wormlike chains combined with the quasi-two-parameter theory for excluded-volume effects. The estimated persistence length q and excluded-volume strength B both increase with decreasing C_s . This increase in q is not quantitatively described by the known theories for the electrostatic persistence length when the previously determined q of 0.69 nm in 4.17 M aqueous NaCl at the theta point is used for the intrinsic persistence length. It is also shown that the values of B computed on the conventional bead model and the rodlike segment model in the Debye–Hückel approximation with the ion condensation hypothesis are too large compared to the experimental estimates at lower C_s of 0.05 and 0.1 M though the latter model gives considerably smaller B than does the former one.

KEY WORDS Polyelectrolyte / Poly(styrenesulfonate) / Wormlike Chain / Chain Stiffness / Electrostatic Persistence Length / Excluded-Volume Effect /

According to the current polyelectrolyte theory,^{1–4} the persistence length q of a charged linear polymer, modeled by the Kratky–Porod wormlike chain,⁵ in aqueous salt increases with lowering salt concentration C_s . Although much experimental work on this electrostatic stiffening effect has been reported in the past two decades, our understanding of it still leaves much to be desired, at least, for intrinsically flexible or weakly stiff polyelectrolytes.⁶ The problem^{7,8} is that the effects of chain stiffness and volume exclusion in those polymers can hardly be separated without resort to a relevant excluded-volume theory, but no such theory is, of course, as yet known. In this situation, it is intriguing and probably significant to estimate q and the excluded-volume strength B (or the binary cluster integral) from data for the intrinsic viscosity $[\eta]$ or the radius of gyration with the aid of the quasi-two-parameter (QTP) theory^{9–11} for uncharged wormlike or helical wormlike chains,⁹ since the theory is capable of almost quantitatively explaining the radius and viscosity expansion factors for nonionic polymers, both flexible⁹ and stiff.¹²

In a series of previous studies,^{7,13–15} we made such attempts for aqueous NaCl solutions of sodium hyaluronate, a charged polysaccharide with a q of about 4 nm at high ionic strength and a linear charge density of 1 nm^{-1} , and drew the following conclusions. 1. The QTP scheme is applicable to this polysaccharide down to $C_s = 0.01 \text{ M}$. 2. The electrostatic contribution to q obtained as a function of C_s is considerably larger than predicted by the known theories.^{1–4} 3. The dependence of estimated B on C_s is in moderate agreement with the Fixman–Skolnick theory¹⁶ for the excluded volume of a pair of charged rodlike segments. On the other hand, the conventional bead model gives too large B compared to the experimental estimate.

The present paper reports a viscometric study undertaken for poly(styrenesulfonate) (NaPSS) in aqueous NaCl at 25°C as an extension of the previous work on Na

hyaluronate. Its primary purpose is to see whether the $[\eta]$ data obtained for this typical polyelectrolyte lead to conclusions similar to those derived for the polysaccharide. These polymers differ largely in intrinsic flexibility and charge density. In fact, NaPSS has a small q of 0.69 nm in 4.17 M aqueous NaCl at 16.4°C,⁸ the theta point, when modeled by the wormlike chain (a special limit of the helical wormlike chain⁹), and its linear charge density is roughly four times as high as that of Na hyaluronate. In the work reported below, we analyze the measured $[\eta]$ at different salt concentrations between 0.05 and 2 M by a combination of Yoshizaki *et al.*'s theory¹⁷ for unperturbed wormlike chains and the QTP theory, assuming that possible helical nature of NaPSS is weak. We then discuss the C_s dependence of estimated q and B in relation to theoretical predictions.^{1–4,16}

EXPERIMENTAL

Samples

The previously investigated NaPSS samples,⁸ F-1, F-2, ..., and F-15, ranging in weight-average molecular weight M_w from 3.8×10^3 to 6.5×10^5 were used for the present work. They had been prepared by the radical polymerization of *p*-styrenesulfonate followed by repeated fractional precipitation, and their M_w 's had been determined by light scattering (for samples F-1 to F-7) or sedimentation equilibrium (for samples F-8 to F-15). The *z*-average to weight-average molecular weight ratios determined by sedimentation equilibrium were about or less than 1.10.⁸

Viscometry

Viscosities of aqueous NaCl solutions of NaPSS with $C_s = 0.05, 0.1, 0.2, 1,$ and 2 M were measured at 25°C using conventional capillary viscometers of the Ubbelohde type. As in our previous work,⁸ the relative viscosity was evaluated by taking into account the difference be-

Figure 1. Concentration dependence of reduced viscosity η_{sp}/c for indicated NaPSS samples in 0.005 M aqueous NaCl at 25°C. The values of η_{sp}/c for sample F-2 (at zero shear rate) were obtained by use of a low-shear four-bulb capillary viscometer.

tween the solution and solvent densities. Except for a few low molecular weight samples at $C_s = 1$ and 2 M, Huggins' constants k' estimated were in the range between 0.31 and 1.0 and tended to increase with decreasing M_w .

At an early stage of our experiment, we attempted to determine $[\eta]$ down to $C_s = 0.005$ M as in the work of Takahashi *et al.*¹⁸ for high molecular weight NaPSS ($4 \times 10^5 < M_w < 2.4 \times 10^6$). However, our measurements at $C_s = 0.005$ and 0.01 M showed unexpected concentration dependence of reduced viscosity η_{sp}/c for low molecular weight samples and did not allow the determination of $[\eta]$ over the molecular weight range of our interest. Here, η_{sp} and c denote the specific viscosity and the polymer mass concentration, respectively.

Figure 1 shows that the Huggins plot for high molecular weight sample F-2 ($M_w = 5.39 \times 10^5$) in 0.005 M aqueous NaCl is normal ($k' = 0.40$) as reported by Takahashi *et al.*, whereas those for low molecular weight ones F-11 ($M_w = 1.83 \times 10^4$) and F-13 ($M_w = 9.71 \times 10^3$) in the same solvent have negative slopes as typically observed for polyelectrolyte solutions of very low ionic strength. The indicated curve for sample F-9 ($M_w = 5.10 \times 10^4$) exhibits different behavior that, as c decreases, η_{sp}/c slightly rises and then sharply drops. Similar concentration dependence was also observed at $C_s = 0.01$ M. These findings suggest that the chain expansion of a macroion accompanying a decrease in c is not directly responsible for the negative slope of the Huggins plot,

Table I. Weight-average molecular weights and intrinsic viscosities for NaPSS samples in aqueous NaCl at 25°C

Sample	$M_w/10^4$ ^a	$[\eta]/10^2 \text{ cm}^3 \text{ g}^{-1}$				
		C_s/M				
		0.05	0.1	0.2	1	2
F-1	65.0	2.86	2.19	1.68	0.854	0.525
F-2	53.9	2.48	1.87	1.46	0.728	0.470
F-3	49.4	2.33	1.77	1.37	0.706	0.444
F-4	35.9	1.72	1.35	1.04	0.554	0.352
F-5	26.5	1.34	1.04	0.830	0.444	0.286
F-6	21.0	1.07	0.839	0.670	0.379	0.235
F-7	13.8	0.722	0.564	0.464	0.270	0.177
F-8	9.22	0.510	0.397	0.345	0.208	0.138
F-9	5.10	0.300	0.247	0.219	0.131	0.0972
F-10	2.76	0.174	0.148	0.128	0.0864	0.0647
F-11	1.83	0.129	0.110	0.0990	0.0687	0.0543
F-12	1.41	0.111	0.0905	0.0805	0.0565	0.0470
F-13	0.971	0.0790	0.0662	0.0583	0.0437	0.0373
F-14	0.610	0.0610	—	—	0.0344	0.0305
F-15	0.383	0.0464	0.0409	0.0358	0.0282	0.0267

^a Taken from ref 8.

Figure 2. Dependence of $[\eta]$ on salt concentration C_s for NaPSS samples (F-1, F-2, ..., and F-15 from top to bottom) in aqueous NaCl at 25°C. The data at $C_s = 0.5$ M (25°C) and 4.17 M (16.4°C) have been taken from ref 8.

since, if responsible, a higher molecular weight sample undergoing a larger dimensional change should show a more pronounced upswing of η_{sp}/c . In other words, another physical factor may have to be considered in order to explain such negative slopes.

RESULTS

The present $[\eta]$ data for NaPSS samples in aqueous NaCl at 25°C are summarized in Table I, along with the previously determined molecular weights,⁸ and are plotted double-logarithmically against C_s in Figure 2, which includes our previous data⁸ at $C_s = 0.5$ M (at 25°C) and 4.17 M (at the Θ temperature of 16.4°C). As expected, $[\eta]$ for a higher molecular weight sample increases more remarkably with decreasing C_s . The increase is more pronounced in the region of C_s above 1 M, differing from what was observed previously for Na hyaluronate⁷

Figure 3. Molecular weight dependence of $[\eta]$ for NaPSS in aqueous NaCl with $C_s = 0.05, 0.1, 0.2, 1$, and 2 M (from top to bottom) at 25°C .

whose $[\eta]$ increased more remarkably at lower C_s .

Figure 3 illustrates the molecular weight dependence of $[\eta]$ for NaPSS at five NaCl concentrations. Except for $C_s = 2$ M, all the curves are essentially linear down to $M_w \approx 3 \times 10^4$ and bend appreciably up with decreasing M_w below 1×10^4 ; the linear relation for $C_s = 2$ M is limited to M_w above 10^5 . The viscosity exponents in the linear region are 0.69 at $C_s = 2$ M and 0.90 at $C_s = 0.05$ M, the latter of which exceeds the limiting value of 0.80 predictable for nonionic flexible chains in good solvents^{9,19} and is considerably higher than the value 0.72 early determined at the same C_s by Takahashi *et al.*¹⁸ for M_w between 4×10^5 and 2.4×10^6 .

DISCUSSION

Analysis of Viscosity Data and Comparison with Theory

The theory of Yoshizaki *et al.*¹⁷ for the unperturbed intrinsic viscosity $[\eta]_0$ of a wormlike touched-bead chain contains three parameters, λ^{-1} (the Kuhn segment length or more generally the static stiffness parameter in the helical wormlike chain⁹), L (the contour length), and d (the hydrodynamic bead diameter). The first parameter is related to the persistence length by $\lambda^{-1} = 2q$ and the second one, to the molecular weight M by $L = M/M_L$, with M_L being the molar mass per unit contour length of the chain.

The cube of the viscosity expansion factor, $\alpha_\eta^3 (\equiv [\eta]/[\eta]_0)$, in the QTP scheme⁹⁻¹¹ may be expressed by

$$\alpha_\eta^3 = (1 + 3.8\bar{z} + 1.9\bar{z}^2)^{0.3} \quad (1)$$

if the Barrett function²⁰ is adopted. Here, $\bar{z}$ is the scaled excluded-volume parameter defined by^{9,11}

$$\bar{z} = (3/4)K(\lambda L)z \quad (2)$$

with

$$K(\lambda L) = (4/3) - 2.711(\lambda L)^{-1/2} + (7/6)(\lambda L)^{-1} \text{ for } \lambda L > 6$$

Figure 4. Comparison between the measured $[\eta]$ for NaPSS at $C_s = 0.05, 0.1, 0.2, 0.5, 1, 2$, and 4.17 M (from top to bottom) and the theoretical values calculated from the theory of Yoshizaki *et al.*¹⁷ for unperturbed wormlike chains and the QTP theory⁹⁻¹¹ for excluded-volume effects with the parameters in Table II. For clarity, the theoretical values (discrete for low M) are represented by continuous lines.

$$= (\lambda L)^{-1/2} \exp[-6.611(\lambda L)^{-1} + 0.9198 + 0.03516 \lambda L] \text{ for } \lambda L \leq 6 \quad (3)$$

and

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \quad (4)$$

The excluded-volume strength in eq 4 is defined for the wormlike chain by

$$B = \beta/a^2 \quad (\text{wormlike chain}) \quad (5)$$

with β and a being the binary cluster integral and the bead spacing (along the chain contour), respectively.

As may be seen from the above relations, $[\eta]$ for a given M is determined by M_L , q (or λ^{-1}), B , and d , but all four parameters for NaPSS at a fixed C_s cannot uniquely be determined from the present $[\eta]$ data. In expectation of the insensitivity of M_L and d to NaCl concentration, we attempted to estimate a set of q and B at each C_s by curve fitting with M_L and d fixed to the previously determined values⁸ 880 nm^{-1} and 1.2 nm , respectively, in the Θ state (*i.e.*, in 4.17 M aqueous NaCl at 16.4°C). It was found that a number of different sets of q and B , each within a certain range, led to equally close agreements between the measured and calculated $[\eta]$ at high salt concentrations of 1 and 2 M . Large uncertainties of ± 20 to 30% in these parameters arose from the theoretical fact that in the molecular weight range studied here, the effects of chain stiffness and excluded volume increase $[\eta]$ in essentially the same fashion with respect to the change in M . At $C_s \leq 0.2 \text{ M}$, on the other hand, satisfactory agreement was not found between the measured and calculated $[\eta]$ for $M_L = 880 \text{ nm}^{-1}$ and $d = 1.2 \text{ nm}$, and thus in the curve-fitting procedure, M_L and d were allowed to change successively from these initial values until the closest fit was reached.

The best-fit theoretical curves thus obtained are compared with the $[\eta]$ data in Figure 4, in which the results from our previous analysis⁸ for 0.5 and 4.17 M NaCl solutions are also shown. The agreement is generally good, though the curves tend to deviate slightly upward for M_w between 2×10^4 and 1×10^5 and slightly downward for

Table II. Wormlike chain parameters and excluded-volume strength for NaPSS in aqueous NaCl at 25°C

C_s/M	M_L/nm^{-1}	q/nm^c	d/nm	B/nm^c
0.05	800	2.5 (± 0.2)	1.5	4.0 (± 0.4)
0.1	820	2.3 (± 0.2)	1.4	2.6 (± 0.4)
0.2	830	2.0 (± 0.2)	1.3	2.1 (± 0.4)
0.5 ^a	860	1.5 (± 0.3)	1.25	1.6 (± 0.4)
1	880	1.2 (± 0.2)	1.2	1.2 (± 0.3)
2	880	0.80 (± 0.2)	1.2	0.64 (± 0.19)
4.17 ^{a,b}	880	0.69 (± 0.07)	1.2	0

^a Taken from ref 8. ^b At 16.4°C (the theta temperature). ^c Except for $C_s = 4.17$ M, the uncertainty is estimated with M_L and d fixed to the given values.

M_w above 3×10^5 .

The parameters used for the calculations are summarized in Table II. As C_s decreases, q and B monotonically increase, thus substantiating that both stiffness and volume effects are responsible for the increases in $[\eta]$ with decreasing C_s , observed in Figure 2. On the other hand, M_L in the table little changes with C_s . Its average 840 (± 40) nm^{-1} yields a value of $0.25 (\pm 0.02)$ nm for the monomeric contour length h ($= M_0/M_L$, with M_0 being the monomer molecular weight 206). This h is quite close to the value calculated on the assumption that the NaPSS molecule assumes the all-*trans* conformation. The hydrodynamic diameter of about 1.2 nm at high C_s also seems reasonable if compared to the molecular diameter expected from the chemical structure of the polymer. However, the systematic change in d can hardly be explained unless the degree of hydration increases with lowering C_s .

As remarked by Hagerman²¹ on the basis of the Odijk-Skolnick-Fixman (OSF) theory,^{1,2} a decrease in M down to a certain value at a fixed C_s should lower the "apparent value" of the electrostatic persistence length q_{el} and hence that of q owing to the diminished total electrostatic interaction energy on the chain. If $[\eta]$ is influenced by such an end effect, its M -dependence is no longer described by a single stiffness parameter. However, the above analysis shows a single q to explain the molecular weight dependence of $[\eta]$ for NaPSS even at the lowest C_s of 0.05 M. In the Appendix, we show that this finding does not contradict Hagerman's remark, by further analyzing the present $[\eta]$ data with end effects incorporated.

Electrostatic Contribution to the Persistence Length

The circles in Figure 5 show that the experimental q increases fairly steeply and then gradually with increasing $C_s^{-1/2}$. This C_s dependence is compared with the predictions from the Le Bret³ and OSF^{1,2} theories for q_{el} (the curves) in the figure, with the intrinsic persistence length q_0 ($= q - q_{el}$) taken as 0.69 nm, i.e., the q value at $C_s = 4.17$ M; the former theory, essentially the same as Fixman's,⁴ is based on the complete Poisson-Boltzmann equation, while the latter theory uses the Debye-Hückel (DH) approximation. In evaluating Le Bret's q_{el} (tabulated in his paper), we have taken the following parameters: the linear charge density σ ($= h^{-1}$) = 4.0 nm^{-1} , the ratio of the dielectric constant of the polymer to that of water = 0, and the chain radius = 0.5 nm (a value slightly smaller than the estimated hydrodynamic radius of 0.6–0.75 nm). On the other hand, we have

Figure 5. Experimental values (circles) of the persistence length q for NaPSS in aqueous NaCl at 25°C compared with the Le Bret theory³ (see the text for the parameters used) and the Odijk-Skolnick-Fixman theory^{1,2} with ion condensation. The intrinsic persistence length is taken as 0.69 nm.

calculated OSF's q_{el} from $q_{el} = (4\kappa^2 Q_B)^{-1}$ by invoking the ion condensation hypothesis,²² where Q_B is the Bjerrum length (0.714 nm for water at 25°C) and κ is defined by $\kappa^2 = 8\pi Q_B N_A C_s / 1000$ for aqueous 1-1 electrolyte, with N_A being the Avogadro constant (C_s is expressed in units of M). Note that the charge parameter σQ_B for NaPSS ($= 2.9$) exceeds unity.

It can be seen in Figure 5 that in the limited range of C_s studied, the Le Bret theory overestimates q_{el} while the OSF theory with ion condensation underestimates it. This differs from our previous finding¹³ on Na hyaluronate that both theories considerably underestimate q_{el} of the polysaccharide. If literally taken, the deviations of Le Bret's q_{el} from the two experimental relations imply that his theory predicts too strong dependence of q_{el} on σ . In the previous comparison with the OSF theory, we considered no ion condensation for the polysaccharide whose σQ_B is about 0.7. For NaPSS, the OSF expression ($q_{el} = \sigma^2 Q_B / 4\kappa^2$) without ion condensation gives q values (not shown here) that are fairly close to the experimental points up to $C_s^{-1/2} = 2.5 \text{ M}^{-1/2}$ but much larger than them for $C_s^{-1/2} > 3 \text{ M}^{-1/2}$ (for example, $q = 6.0$ nm at $C_s = 0.05$ M). In short, the current q_{el} theories fail to explain the present q data for NaPSS in aqueous NaCl as well as those for Na hyaluronate and appear to be only applicable to intrinsically rigid (long) polyelectrolyte chains such as DNA.³

The experimental q_{el} for NaPSS, when plotted double-logarithmically against C_s between 0.05 and 1 M, varies roughly linearly with a much smaller, negative slope of $-0.40 (\pm 0.08)$ than the value of -1 predicted by the OSF theory with or without ion condensation. Interestingly, however, it is almost parallel with what is predicted by the Le Bret theory. We previously found a similar agreement in the slope of the $\log q_{el}$ vs. $\log C_s$ plot (about -0.6) for Na hyaluronate in aqueous NaCl.⁷ It should be noted that, though slopes of about -0.5 were reported for several intrinsically flexible or weakly stiff polyelectrolytes,^{23,24} they were derived from q data estimated without consideration of excluded-volume effects.

Excluded-Volume Strength

We first compare the B data in Table II with what is

predictable from the conventional bead model in which each small bead has a charge at its mass center. Separating the total interaction potential into hard-core (w_c), electrostatic (w_{el}), and attractive (w_a) potentials, we have¹⁶

$$\beta = \beta_c + \beta_{el} + \beta_a \quad (6)$$

for the three contributions to β appearing in eq 5, where

$$\beta_c = (4\pi/3)d_c^3 \quad (7a)$$

$$\beta_{el} = 4\pi \int_{d_c}^{\infty} r^2 [1 - \exp(-w_{el}/k_B T)] dr \quad (7b)$$

$$\beta_a = 4\pi \int_{d_c}^{\infty} r^2 \exp(-w_{el}/k_B T) \times [1 - \exp(-w_a/k_B T)] dr \quad (7c)$$

In these equations, d_c is the hard-core diameter of each bead, k_B and T are the Boltzmann constant and the absolute temperature, respectively, and r is the bead-bead distance. Note that β_{el} and β_a (the electrostatic and attractive contributions) have been separated from the function $\{1 - \exp[-(w_{el} + w_a)/k_B T]\}$ for $r > d_c$ where $w_c = 0$. Because of the presence of the term $\exp(-w_{el}/k_B T)$ in eq 7c, β_a abruptly diminishes with decreasing ionic strength and is often ignored in the evaluation of β or B of polyelectrolytes.^{7,16} However, its importance is apparent for NaPSS at high C_s where β approaches zero.

If the ion condensation hypothesis with $\sigma Q_B = 2.9$ is invoked, the average number of effective charges for NaPSS is estimated to be roughly one for three monomer units. We may thus take three monomers as one bead and d_c as 0.75 nm, i.e., $d_c = a$; this d_c is slightly smaller than the chain diameter (about 1 nm) expected from the partial specific volume⁸ of the polymer. We numerically evaluated β_{el} and β_a for this simplified model using the DH screened Coulomb potential $(Q_B/r)e^{-\kappa r}$ for $w_{el}/k_B T$ and the familiar potential function $-A/r^6$ for $w_a/k_B T$. In so doing, $\exp(A/r^6)$ was approximated by $1 + (A/r^6)$ and the positive constant A (assumed to be independent of C_s) was determined to be 0.179 nm^6 in such a way that β becomes zero at $C_s = 4.17 \text{ M}$ where $\beta_{el} \approx 0$. We note that this approximation with the adjusted A introduces no substantial error in the evaluation of β_a .

In Figure 6, the calculated values of B are shown by curve 1 in comparison with the experimental estimates. This curve deviates conspicuously upward from the plotted points for $C_s^{-1/2} > 2 \text{ M}^{-1/2}$ (i.e., $\kappa^{-1} > 0.6 \text{ nm}$), the deviation being too large to be attributed to the crudeness of the present bead model or the rough approximations employed in the evaluation of β_{el} . We may add that without ion condensation, β_{el}/a^2 for a pair of beads with $a = 0.25 \text{ nm}$, i.e., the electrostatic contribution to B , is as large as 200 nm at $C_s = 0.05 \text{ M}$. These findings lend support to the idea¹⁶ that the conventional bead model is not directly applicable to the evaluation of β_{el} for polyelectrolytes at low ionic strength where κ^{-1} is comparable to or even larger than the bead spacing. Note that the pseudo (or short-range) potential used for excluded-volume interactions in the QTP theory should be immaterial for large κL .

Figure 6. Values of the excluded-volume strength B for NaPSS in aqueous NaCl at 25°C compared with the theoretical curves 1 and 2 for the bead model (eq 6 and 7 with $a = d_c = 0.75 \text{ nm}$) and the rodlike segment model¹⁶ (eq 8 and 9 with $d_c' = 1.0 \text{ nm}$), respectively, both with the ion condensation hypothesis. The filled circle refers to 4.17 M aqueous NaCl at 16.4°C (the theta point).

Fixman and Skolnick¹⁶ proposed replacing a set of beads by a rodlike segment with line charge distribution, and evaluated the electrostatic contribution β_{el}' to the excluded volume β' for a pair of segments with length l and hard-core diameter d_c' in the DH approximation. If the attractive contribution β_a' is incorporated into their theory, $B = (\beta'/l^2)^{1/2}$ to be compared with our data is expressed as

$$B = (\pi/2)d_c' + (2/\kappa)R(y) + \beta_a'/l^2 \quad (8)$$

where the first and second terms represent the hard-core and electrostatic contributions, respectively, $R(y)$ is a known function¹⁶ of $y [= 2\pi(Q_B\kappa)^{-1}\exp(-\kappa d_c')]$ if ion condensation is considered, and the attractive contribution is given by (cf. eq 7c)

$$\beta_a'/l^2 = \int_0^\pi \sin^2 \theta d\theta \int_{d_c'}^\infty \exp(-w_{el}'/k_B T) [1 - \exp(-w_a'/k_B T)] dx \quad (9)$$

with

$$w_{el}'/k_B T = (y/\sin \theta) \exp[-\kappa(x - d_c')] \quad (10a)$$

$$w_a'/k_B T = -A'/(x^4 \sin \theta) \quad (10b)$$

(each prime symbol refers to the rodlike segment model). In eq 10, x is the shortest distance between the two rod axes, θ is the angle between them, and A' is a positive constant to be determined as done above for the bead model; eq 10b has been derived by use of the r^{-6} function (per unit contour length) for the attraction between two points on the respective rod axes.²⁵ As may be seen in eq 8 with eq 9, l need not be specified in the evaluation of B . We also note that end effects, ignored in the above equations, may not be very important (unless C_s is too low) since both ends of each segment are linked to the adjacent segments.

With $\exp(-w_a'/k_B T)$ again approximated by $1 - (w_a'/k_B T)$ and d_c' taken as 1.0 nm , the double integral in eq 9 was numerically evaluated to obtain B for the segment model as a function of C_s . The result represented by the curve 2 in Figure 6 comes far below the curve 1 and

closer to the plotted points for $C_s^{-1/2} > 3 \text{ M}^{-1/2}$. However, they are still too large in this low C_s region where β_{el}' is predominant. This was also the case for Na hyaluronate at C_s below 0.01 M, though the discrepancy was only about 30% at $C_s = 0.005 \text{ M}$.^{14,26} Apart from the poorer approximation to NaPSS that might be due to the high flexibility, the continuous charge distribution assumed in the Fixman-Skolnick theory may be worth to examine as a possible cause for these overestimates. At high C_s , the segment model underestimates B for NaPSS as in the case of the bead model, and the two curves have a strong upward curvature opposite to that of the experimental relation. The DH approximation with the ion condensation hypothesis is likely to underestimate w_{el}' at high ionic strength, thereby giving a smaller β_{el}' and a larger, negative β_a' .

In sum, our lengthy analysis ends up with pointing out difficulty in the theoretical explanation of B or β for polyelectrolytes, giving no definite conclusion. We hope that it stimulates further elaboration, theoretical and experimental, toward a better understanding of intramolecular excluded-volume effects in intrinsically flexible polyelectrolytes.

CONCLUSIONS

The theory of Yoshizaki *et al.*¹⁷ for the intrinsic viscosity of an unperturbed wormlike chain combined with the quasi-two-parameter theory⁹⁻¹¹ rather satisfactorily describes the molecular weight dependence of $[\eta]$ for Na poly(styrenesulfonate) (NaPSS) in aqueous NaCl with $C_s \leq 0.05 \text{ M}$ throughout the entire range (3.8×10^3 to 6.5×10^5) of M_w studied. The estimated persistence length and excluded-volume strength are decreasing functions of C_s , showing that both excluded-volume and chain-stiffening effects are responsible for the observed increases in $[\eta]$ of NaPSS with lowering ionic strength. However, neither of the electrostatic contributions to these parameters is explained by the available polyelectrolyte theories.

APPENDIX

Unless κL (the contour length relative to the Debye length) is much greater than unity, $q_{el,app}$ (the apparent value of q_{el} at a finite chain length) of a wormlike chain should decrease with decreasing chain length²¹ and may, in turn, influence theoretical $[\eta]$. The purpose of this appendix is to show by data analysis in the OSF scheme^{1,2} that $[\eta]$ for NaPSS in aqueous NaCl happens to be hardly affected by such effects in the C_s range studied here.

In the OSF scheme, the average ratio P of $q_{el,app}$ to q_{el} is given by^{1,21}

$$P \equiv q_{el,app}/q_{el} = 1 - (8/3)(\kappa L)^{-1} + (3\kappa L)^{-1}(8 + 5\kappa L + \kappa^2 L^2)e^{-\kappa L} \quad (\text{A-1})$$

so that q_{app} (the apparent value of q) may be expressed by

$$q_{app} = q_0 + (q - q_0)P \quad (\text{A-2})$$

where

$$q = \lim_{\kappa L \rightarrow \infty} q_{app} \quad (\text{A-3})$$

When applied to NaPSS in 0.05 M aqueous NaCl, these equations with $q_0 = 0.69 \text{ nm}$, $q = 2.5 \text{ nm}$, and $M_L = 800 \text{ nm}^{-1}$ (see Table II) give $q_{app} = 2.42$ and 1.16 nm for $M = 7 \times 10^4$ and 3×10^3 , respectively. Thus q_{app} begins to deviate appreciably from q at $M = 7 \times 10^4$ and becomes less than half at $M = 3 \times 10^3$. Similar calculations for other salt concentrations show that the deviation diminishes with increasing C_s and becomes practically negligible at $C_s = 0.5 \text{ M}$ in the range of M of our interest. We computed both $[\eta]_0$ and $[\eta]$ at $C_s = 0.05, 0.1$, and 0.2 M with the parameters in Table II but with q_{app} in place of q . The results may be summarized as follows.

Since the NaPSS chain is quite flexible even at the lowest C_s of 0.05 M, $[\eta]_0$ relative to that given by q significantly decreases as q_{app} lowers from q ; for $M < 4 \times 10^3$, it is insensitive to q_{app} since the chain is very short. The increased "apparent flexibility", however, leads to an increase in intramolecular excluded-volume effect, which, in turn, brings $[\eta]$ to nearly the same value as that given by q , with the maximum difference being only about 4%; for high M the difference between q_{app} and q is small (or negligible) and the slightly enhanced excluded-volume effects compensate for the small decreases of $[\eta]_0$. The $\log [\eta]$ vs. $\log M$ relations thus calculated for $C_s = 0.05$ and 0.1 M come slightly below the corresponding theoretical curves in Figure 4 for M between 7×10^3 and 7×10^4 but slightly above those for M below 6×10^3 , thus giving somewhat better fits to the experimental points. At $C_s = 0.2 \text{ M}$, virtually no change in the theoretical curve is observed before and after the consideration of the electrostatic end effect.

Since eq A-1 must be only approximate, we further examined other possible cases in which (1) q_{app} is closer to q than predicted by eq A-2 with eq A-1 and (2) contrarily, $1 - P$ is 2 to 3 times as large as that given by eq A-1 but P is necessarily positive. In both cases, the fits of the calculated $\log [\eta]$ vs. $\log M$ curves were as good as those found above from the analysis based on eq A-1, though the case (2) led to slightly better fits. Hence, we may conclude that the end effect on the electrostatic contribution to q does not alter the estimated model parameters for NaPSS in Table II.

Acknowledgment. This work was supported by a Grant-in-Aid (09450363) for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

REFERENCES

1. T. Odijk, *J. Polym. Sci.: Polym. Phys. Ed.*, **15**, 477 (1977).
2. J. Skolnick and M. Fixman, *Macromolecules*, **10**, 944 (1977).
3. M. Le Bret, *J. Chem. Phys.*, **76**, 6243 (1982).
4. M. Fixman, *J. Chem. Phys.*, **76**, 6346 (1982).
5. O. Kratky and G. Porod, *Rec. Trav. Chim.*, **68**, 1106 (1949).
6. See ref 7 and 8 and references cited therein.
7. K. Hayashi, K. Tsutsumi, F. Nakajima, T. Norisuye, and A. Teramoto, *Macromolecules*, **28**, 3824 (1995).
8. E. Hirose, Y. Iwamoto, and T. Norisuye, *Macromolecules*, **32**, 8629 (1999).
9. H. Yamakawa, "Helical Wormlike Chains in Polymer Solu-

- tions," Springer, Berlin, 1997.
10. H. Yamakawa and W. H. Stockmayer, *J. Chem. Phys.*, **57**, 2843 (1972).
11. J. Shimada and H. Yamakawa, *J. Chem. Phys.*, **85**, 591 (1986).
12. T. Norisuye, A. Tsuboi, and A. Teramoto, *Polym. J.*, **28**, 357 (1996).
13. K. Hayashi, K. Tsutsumi, T. Norisuye, and A. Teramoto, *Polym. J.*, **28**, 922 (1996).
14. K. Tsutsumi and T. Norisuye, *Polym. J.*, **30**, 345 (1998).
15. N. Mizukoshi and T. Norisuye, *Polym Bull.*, **40**, 555 (1998).
16. M. Fixman and J. Skolnick, *Macromolecules*, **11**, 863 (1978).
17. T. Yoshizaki, I. Nitta, and H. Yamakawa, *Macromolecules*, **21**, 165 (1988).
18. A. Takahashi, T. Kato, and M. Nagasawa, *J. Phys. Chem.*, **71**, 2001 (1967).
19. H. Fujita, "Polymer Solutions," Elsevier, Amsterdam, 1990.
20. A. J. Barrett, *Macromolecules*, **17**, 1566 (1984).
21. P. J. Hagerman, *Biopolymers*, **22**, 811 (1983).
22. G. S. Manning, *J. Chem Phys.*, **51**, 924 (1969).
23. M. Tricot, *Macromolecules*, **17**, 1698 (1984).
24. S. Ghosh, X. Li, C. E. Reed, and W. F. Reed, *Biopolymers*, **30**, 1101 (1990).
25. K. Kawakami and T. Norisuye, *Macromolecules*, **24**, 4898 (1991).
26. T. Norisuye, "Yamada Conference L Polyelectrolytes," I. Noda and E. Kokufuta, Ed., Yamada Science Foundations, Osaka, Japan, 1999, p 37.