Chain Stiffness and Excluded-Volume Effects in Sodium Poly(styrenesulfonate) Solutions at High Ionic Strength

Eigo Hirose, Yoshimi Iwamoto, and Takashi Norisuye*

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

Received May 24, 1999; Revised Manuscript Received September 3, 1999

ABSTRACT: Sixteen narrow-distribution samples of sodium poly(styrenesulfonate) (NaPSS) ranging in weight-average molecular weight M_w from 2.6×10^3 to 6.5×10^5 were prepared by the radical polymerization of sodium-*p*-styrenesulfonate, followed by repeated fractional precipitation, and were studied by static light scattering, sedimentation equilibrium, and viscometry in 0.5 M aqueous NaCl at 25 °C and in 4.17 M aqueous NaCl at 16.4 °C, the Θ point, where the light scattering second virial coefficient vanished for high M_w. The characteristic ratio (i.e., the mean-square radius of gyration at the Θ point divided by the degree of polymerization) for high-molecular-weight NaPSS was found to be considerably smaller than that for polystyrene in cyclohexane. Data for the intrinsic viscosity $[\eta]$ in 4.17 M aqueous NaCl at Θ were analyzed by the theory of Yoshizaki et al. (*Macromolecules* **1988**, *21*, 165) for the wormlike chain, a special limit of the helical wormlike chain, to obtain 0.23 (± 0.03), 0.69 (± 0.07), and 1.2 (± 0.1) nm for the monomeric contour length, the persistence length q, and the chain diameter, respectively. This q value is much smaller than the intrinsic persistence length of 1.2 nm widely used in the literature for experimental tests of available theories for the electrostatic persistence length. At the lower NaCl concentration of 0.5 M where intramolecular excluded-volume effects were significant, the molecular weight dependence of $[\eta]$ was explained quantitatively by a combination of Yoshizaki et al.'s theory and the quasi-two-parameter theory with a larger q of 1.5 nm and an excluded-volume strength parameter of 1.6 nm.

Introduction

Sodium poly(styrenesulfonate) (NaPSS) has long been used as a typical polyelectrolyte for studies of electrostatic excluded-volume and stiffness effects in aqueous salt solutions,[1−14] but its molecular characteristics at high ionic strength, primarily important to the understanding of those effects, still remain to be explored. More than 30 years ago, Takahashi et al.[1] found from phase separation experiments that this polyelectrolyte attains the Θ state in 4.17 M aqueous NaCl at 25 °C. Although not remarked upon in their paper, the relation between $[\eta]$ (the intrinsic viscosity) and M_w (the weight-average molecular weight) determined under this solvent condition is far below that for polystyrene in cyclohexane at the Θ point,[15] suggesting that NaPSS in aqueous NaCl has a lower intrinsic stiffness than that of the nonionic polymer in the organic solvent. The suggestion is inconsistent with the widely accepted intrinsic persistence length q_0 of 1.2 nm for NaPSS in aqueous NaCl, because the polystyrene chain modeled by the wormlike chain[16] has a smaller persistence length q of 1.0 nm.[17] This q_0 value, obtained by two independent methods,[2,4] relies on some assumptions and does not seem decisive. On the other hand, none confirmed the $[\eta]-M_w$ relation or even the Θ condition reported by Takahashi et al. Beer et al.[14] recently remarked that NaCl solutions of their NaPSS samples did not exhibit solubility or precipitation behavior consistent with the presence of the Θ state.

The present study was undertaken to determine molecular characteristics of NaPSS in aqueous NaCl at high ionic strength, with interest in the estimation of the chain stiffness of the polyelectrolyte in the Θ state. Our solubility tests showed that 4.17 M aqueous NaCl solutions of NaPSS samples, transparent at room temperature, became turbid on cooling below 10 °C. On the basis of this information, we first determined the Θ temperature for the polymer in the aqueous salt by static light scattering and then made viscosity measurements at that temperature for 16 samples covering a broad range of M_w from 2.7×10^3 to 6.5×10^5. Viscosity data were also obtained at a lower NaCl concentration of 0.5 M (at 25 °C) to examine excluded-volume and stiffness effects. Separate estimation of these two effects in polyelectrolyte solutions is another important problem to be settled.

In the work reported below, we analyze the $[\eta]$ data in 4.17 M aqueous NaCl at the Θ temperature and in 0.5 M aqueous NaCl at 25 °C on the basis of the wormlike chain with or without excluded volume. This model is a special limit of the helical wormlike (HW) chain,[18] and thus, as is the case in all previous studies, our analysis assumes that possible helical nature of the NaPSS molecule is weak.

Experimental Section

Preparation of Samples. NaPSS samples were prepared by the radical polymerization[19] of sodium-*p*-styrenesulfonate in water containing potassium peroxodisulfate (1.3−14% per monomer) and sodium hydrogen sulfite (0.7−7% per monomer) at 45 or 55 °C. The monomer concentration was varied from 14 to 25 wt %. After being stirred for 4−12 h under nitrogen atmosphere, the reaction mixture was concentrated, mixed with a small quantity of 0.5 N aqueous NaOH, and poured into a large quantity of 99% ethanol to precipitate the polymer. The product collected on a glass filter was washed with ethanol three times and dried in a vacuum. The monomer was recrystallized with a water−methanol mixture (1:1).

In this way, 13 NaPSS samples with intrinsic viscosities ranging from 6 to 46 cm^3 g^{-1} in 0.5 M aqueous NaCl at 25 °C were prepared. They were each divided into several parts by fractional precipitation with 0.5 N aqueous NaOH as the

10.1021/ma990813b CCC: $18.00

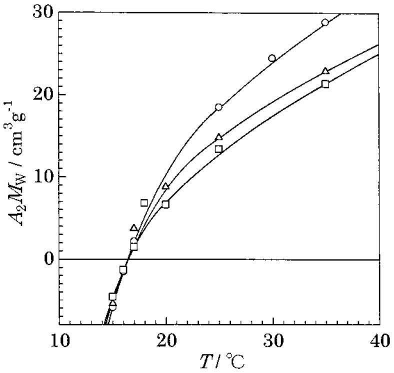

Figure 1. Temperature dependence of A_2M_w for NaPSS samples F-1(circles), F-2 (triangles), and F-4 (squares) in 4.17 M aqueous NaCl.

solvent and 99% ethanol as the precipitant.[1] Each product reprecipitated from a 0.5 N NaOH solution into ethanol was washed with ethanol three times and dried in a vacuum. Fractions having nearly identical intrinsic viscosities (in 0.5 M aqueous NaCl at 25 °C) were combined and again fractionated. This procedure was further repeated 2−4 times, and from 60 fractions thus obtained, the 16 middle ones designated below as F-1−F16 in order of decreasing molecular weight were chosen for the present study. Full sulfonation was confirmed by elementary analysis for arbitrarily chosen fractions.

Each of the 16 fractions was dissolved in deionized water and passed through a mixed-bed ion exchanger (Amberlite IR-120 + IR-400). The solution (pH ∼ 2) was then neutralized with 0.05 N aqueous NaOH. Its pH was monitored by a Beckman ϕ 70 pH meter. All of the Na salt samples thus obtained were freeze-dried over more than 4 days. They were further dried in a vacuum for several days before use. Test solutions were prepared by dissolving a given NaPSS sample directly in 4.17 or 0.5 M aqueous NaCl.

Light Scattering. To determine the Θ temperature where the second virial coefficient vanishes for high molecular weight, preliminary light scattering experiments were carried out on three NaPSS samples F-1, F-2, and F-4 in 4.17 M aqueous NaCl at different temperatures T between 15 and 35 °C on a Fica-50 light-scattering photometer in an angular range from 30 to 150°, using vertically polarized incident light of 436 nm wavelength. Pure benzene of 25 °C was used to calibrate the apparatus. Its Rayleigh ratio for unpolarized light at 436 nm was taken as 46.5×10^{-6} cm^{-1},[20] and its depolarization ratio was determined to be 0.406 by the method of Rubingh and Yu.[21] The excess reduced scattering intensity R_θ, determined as a function of scattering angle θ and polymer mass concentration c, was analyzed by the square-root plot. Test solutions were made optically clean by filtration through a 0.45 μm Millipore filter, followed by a 4 h centrifugation at $2.5 \times 10^4 g$ in a Sorvall RC 5C centrifuge.

Figure 1 shows that the light scattering second virial coefficients A_2 for the three samples in 4.17 M aqueous NaCl identically vanish at 16.4 °C. On the basis of this, our light scattering measurements in the aqueous salt were made at 16.4 °C on seven higher molecular weight samples (F-1−F-7) in the manner described above; M_w's for the rest were determined by sedimentation equilibrium in 0.5 M aqueous NaCl at 25 °C as the solvent.

Excess refractive indices of 0.5 and 4.17 M aqueous NaCl solutions of NaPSS were measured at 25 and 16.4 °C, respectively, for the wavelengths of 436 and 546 nm using a modified Schulz−Cantow-type differential refractometer. Data for undialyzed solutions of different fractions showed that the specific refractive index increments ($\partial n/\partial c$) of NaPSS in both solvents are essentially independent of molecular weight, at least, in the range of our interest. This was also the case with the partial specific volume or the density increment ($\partial \rho/\partial c$) in 0.5 M aqueous NaCl (see below for the measurement of solution densities ρ). On the basis of these findings, 0.5 M NaCl solutions of sample F-7 and 4.17 M NaCl solutions of sample F-5 were dialyzed against the corresponding solvents at 25 and 16.4 °C, respectively, using the apparatus[22] described previously. The values of $(\partial n/\partial c)_\mu$ obtained for the dialyzed solutions (i.e., at fixed chemical potentials μ of diffusible components) were 0.1760 cm^3 g^{-1} at 436 nm and 0.1678 cm^3 g^{-1} at 546 nm in 0.5 M aqueous NaCl at 25 °C and 0.1505 cm^3 g^{-1} at 436 nm and 0.1437 cm^3 g^{-1} at 546 nm in 4.17 M aqueous NaCl at 16.4 °C.

Sedimentation Equilibrium. Sedimentation experiments were performed for samples F-8−F-16 in 0.5 M aqueous NaCl at 25 °C to determine M_w and M_z/M_w (the z-average to weight-average molecular weight ratio). A Beckman model E ultracentrifuge with a Kel-F 12 mm double-sector cell was used. The liquid column was adjusted to 1.2−2.0 mm, and the rotor speed was chosen so that the ratio of the equilibrium polymer concentration (c_b) at the cell bottom to that (c_a) at the meniscus became about 3. For the two lowest molecular weight samples, however, this ratio was considerably lower than 3 and did not allow M_z/M_w to be estimated with reasonable accuracy (see elsewhere[23] for the procedure of data analysis).

Densities of 0.5 M aqueous NaCl solutions of NaPSS at 25 °C were determined by a bicapillary pycnometer with 30 cm^3 capacity. The value of $(\partial \rho/\partial c)_\mu$ obtained for dialyzed solutions of sample F-7 was 0.356.

Viscometry. Viscosity measurements were made on all NaPSS samples in 0.5 M aqueous NaCl at 25 °C and in 4.17 M aqueous NaCl at 16.4 °C by using conventional capillary viscometers of the Ubbelohde type. The relative viscosity was evaluated by taking into account the difference between the solution and solvent densities. Values of ρ for undialyzed 4.17 M NaCl solutions of NaPSS were calculated with the partial specific volume 0.599 cm^3 g^{-1} (determined for undialyzed 0.5 M NaCl solutions) and literature density data for 4.17 M aqueous NaCl at 16.4 °C.

Results

Parts a and b of Figure 2 illustrate the light scattering envelopes for NaPSS sample F-3 in 4.17 M aqueous NaCl at 16.4 °C, where K denotes the optical constant. In Figure 3 is shown the concentration dependence of $(Kc/R_0)^{1/2}$, i.e., the zero angle value of $(Kc/R_\theta)^{1/2}$, for all of the samples studied by light scattering. The straight lines fitting the data points for the respective samples are almost horizontal, confirming that A_2 is essentially zero in 4.17 M aqueous NaCl at 16.4 °C. This can be seen more clearly in Table 1, in which our light scattering results are summarized ($\langle S^2\rangle_z$ denotes the z-average mean-square radius of gyration). The A_2 data convince us that the Θ point for fully sulfonated NaPSS in 4.17 M aqueous NaCl is 16.4 °C. This temperature is considerably lower than that (25 °C) determined long ago by Takahashi et al.[1] from phase separation experiments on synthesized NaPSS samples. The contradictory observations by Beer et al.[14] mentioned in the Introduction might be due to their samples that were not fully substituted NaPSS (these authors reported that the degree of substitution was higher than 90%). With regard to our Θ point from light scattering, the following remark may be pertinent.

For a monodisperse sample of molecular weight M in a binary solvent, A_2 obtained by use of $(\partial n/\partial c)_\mu$ differs slightly from the osmotic second virial coefficient $A_{2,\mathrm{OS}}$; i.e., $A_2 = A_{2,\mathrm{OS}} + \Delta/M + O(M^{-2})$,[24] with Δ being a constant for a given polymer + mixed solvent system. This relation indicates that, if nonzero $A_{2,\mathrm{OS}}$ happens to be compensated by Δ/M, A_2 can be zero at a temperature other than the "true" Θ point where $A_{2,\mathrm{OS}}$ vanishes for high molecular weight. In such a case (i.e., for $|A_{2,\mathrm{OS}}| > 10^{-5}$ mol g^{-2} cm^3), however, A_2 should be dependent discernibly on molecular weight. Our data

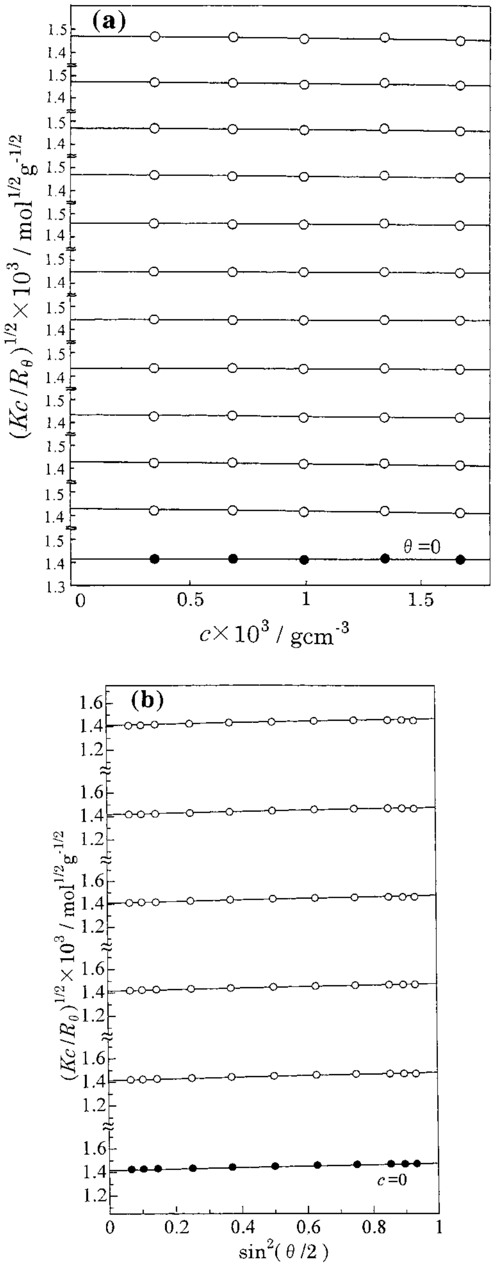

Figure 2. Concentration dependence of $(Kc/R_\theta)^{1/2}$ at fixed scattering angles (a) and angular dependence of $(Kc/R_\theta)^{1/2}$ at fixed polymer concentrations (b) for NaPSS sample F-3 in 4.17 M aqueous NaCl at 16.4 °C.

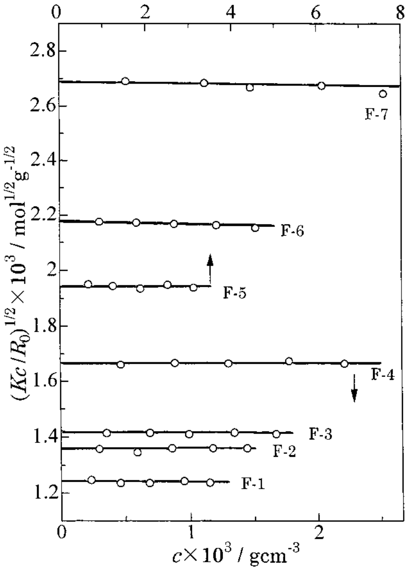

Figure 3. Concentration dependence of $(Kc/R_0)^{1/2}$ for the indicated NaPSS samples in 4.17 M aqueous NaCl at 16.4 °C (the Θ point).

Table 1. Results from Light Scattering and Sedimentation Equilibrium Measurements on NaPSS Samples in Aqueous NaCl

	light scattering in 4.17 M NaCl at 16.4 °C (Θ)			sedimentation equilibrium in 0.5 M NaCl at 25 °C		
sample	M_w ($\times10^4$)	10^6A_2 (mol g^{-2} cm^3)	$\langle S^2\rangle_z$ (nm^2)	M_w ($\times10^4$)	10^4A_2 (mol g^{-2} cm^3)	M_z/M_w
F-1	65.0	0	190			
F-2	53.9	0	160			
F-3	49.4	0	150			
F-4	35.9	0	110			
F-5	26.5	0				
F-6	21.0	−7				
F-7	13.8	−5				
F-8				9.22	4.6	1.03
F-9				5.10	6.8	1.01
F-10				2.76	12	1.04
F-11				1.83	19	1.07
F-12				1.41	5	1.04
F-13				0.971	41	1.10
F-14				0.610	43	1.06
F-15				0.383	70	
F-16				0.266	58	

in Table 1 show no such dependence, at least, above 2.65 × 10^5, and their extrapolation to $1/M_w = 0$ gives $A_{2,\mathrm{OS}}$ (at infinite molecular weight) a rough value of 0 to − 3 × 10^{-6} mol g^{-2} cm^3, which can be regarded as practically zero. Hence, our Θ temperature of 16.4 °C from light scattering must be essentially the same as that from osmometry.

The $\langle S^2\rangle_z$ values in Table 1 are proportional to M_w, yielding a constant of 3.0 × 10^{-4} nm^2 for $\langle S^2\rangle_z/M_w$. This Gaussian behavior is consistent with the vanishing of A_2, although our $\langle S^2\rangle_z$ data are limited to a very narrow molecular weight range. Importantly, the unperturbed dimension of 3.0 × 10^{-4} nm^2 is much smaller than the $\langle S^2\rangle_z/M_w$ value[25,26] of 8.35 × 10^{-4} nm^2 known for polystyrene in cyclohexane at the Θ point.

Figure 4 displays sedimentation equilibrium data for samples F-8−F-16 in 0.5 M aqueous NaCl at 25 °C as the plot of ${M_{\mathrm{app}}}^{-1}$ (the reciprocal of the apparent molecular weight) against the mean concentration $\bar{c}$ [≡ $(c_b + c_a)/2$]. The values of M_w and the sedimentation second virial coefficient evaluated from the indicated straight lines are presented in Table 1, in which the latter quantity (equated to A_2) is seen to be positive and large. The values of M_z/M_w also included in the table indicate narrow molecular-weight distribution of our samples (F-8−F-14), although they may contain errors of about 10%.

The data of [η] in 0.5 M aqueous NaCl at 25 °C and in 4.17 M aqueous NaCl at the Θ point are summarized in Table 2, along with those of k' (Huggins' constant), and they are plotted double-logarithmically against M_w in Figure 5. The curve fitting the data points in the Θ solvent shows the expected Gaussian behavior of slope 0.5 only for $M_w > 2 \times 10^5$ and markedly bends upward with decreasing molecular weight, as may be seen from the dot−dashed line of the slope 0.5 drawn as a eye guide. In the range of M_w between 10^4 and 10^5, the slope of the experimental curve is roughly 0.4. On the other

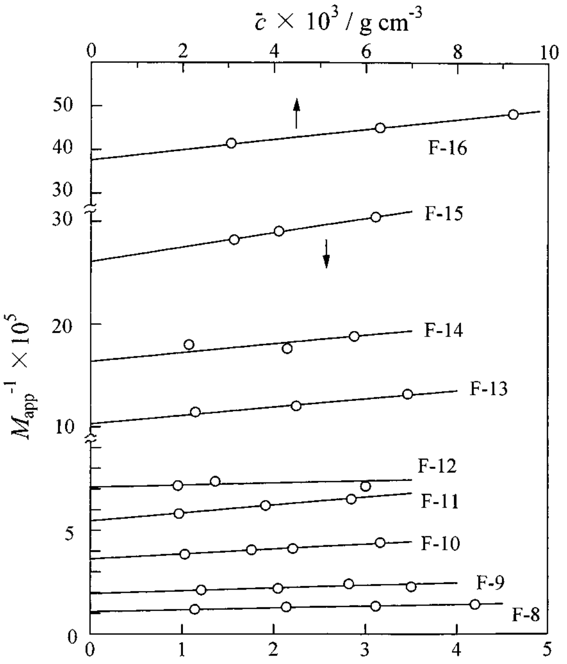

Figure 4. Plots of M_{app}^{-1} vs $\bar{c}$ for the indicated NaPSS samples in 0.5 M aqueous NaCl at 25 °C.

Table 2. Results from Viscosity Measurements on NaPSS Samples in Aqueous NaCl

	in 4.17 M NaCl at 16.4 °C (Θ)		in 0.5 M NaCl at 25 °C	
sample	$[\eta]$ (cm^3 g^{-1})	k'	$[\eta]$ (cm^3 g^{-1})	k'
F-1	17.9	0.88	116	0.32
F-2	16.1	1.0	101	0.37
F-3	15.0	1.3	95.5	0.34
F-4	13.0	1.5	74.4	0.38
F-5	11.4	1.8	60.5	0.34
F-6	10.3	1.7	49.7	0.33
F-7	8.68	1.8	35.5	0.35
F-8	7.80	1.7	26.9	0.36
F-9	5.90	2.3	17.0	0.43
F-10	4.66	2.5	10.6	0.46
F-11	4.02	2.9	8.20	0.44
F-12	3.69	2.8	6.94	0.50
F-13	3.25	2.8	5.38	0.53
F-14	2.91	2.7	3.96	0.96
F-15	2.61	3.0	3.30	0.99
F-16	2.27	2.8	2.29	0.97

hand, the curve for 0.5 M aqueous NaCl is linear with a much higher slope of 0.76 for $M_w > 3 \times 10^4$ and approaches that for the Θ solvent with decreasing M_w. The intrinsic viscosities (about 2.3 cm^3 g^{-1}) at the lowest M_w in the two solvents are slightly larger than the Einstein sphere value 1.5 cm^3 g^{-1} calculated with the partial specific volume 0.599 cm^3 g^{-1} as the specific volume.

In Figure 5, Takahashi et al.'s earlier data[1] for high-molecular-weight NaPSS samples ($4.9 \times 10^5 \le M_w \le 2.3 \times 10^6$) in 0.5 M aqueous NaCl at 25 °C and in 4.17 M aqueous NaCl at the Θ point (25 °C), shown by dashed lines (only for M_w below 10^6), appear somewhat below our relations in the respective solvents. Their $[\eta]/M_w^{1/2}$ value (0.0204 cm^3 g^{-1}) at the Θ point is about 8% lower than ours (0.0220 cm^3 g^{-1}). In any event, both are much smaller than the literature value[15,25] of 0.088 cm^3 g^{-1} for polystyrene in cyclohexane at the Θ point, being consistent with the above-mentioned difference in unperturbed dimension.

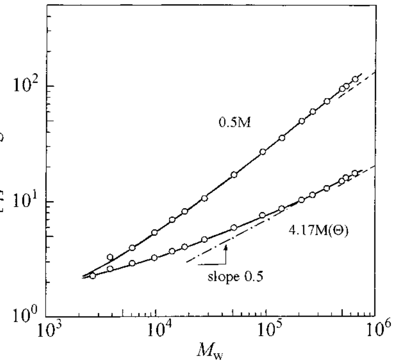

Figure 5. Molecular weight dependence of $[\eta]$ for NaPSS in 0.5 M aqueous NaCl at 25 °C and 4.17 M aqueous NaCl at 16.4 °C (the Θ point). The dashed lines represent the data of Takahashi et al.[1] in the respective solvents (see the text). The dot–dashed line is drawn as an eye guide to show the asymptotic slope 0.5 in the Θ state.

Discussion

Data Analysis and Comparison with Theory. We analyze the data in Figure 5 by a combination of the Yoshizaki–Nitta–Yamakawa theory[27] for the intrinsic viscosity $[\eta]_0$ of an unperturbed HW chain[18] and the quasi-two-parameter (QTP) theory[28–30] for excluded-volume effects, confining ourselves to the wormlike chain limit of the HW chain. The former theory to be applied to the data in 4.17 M aqueous NaCl contains three parameters: λ^{-1} (the stiffness parameter), L (the contour length), and d (the hydrodynamic chain diameter in the touched-bead model). The first parameter in the wormlike chain limit is related to the persistence length by

$$\lambda^{-1} = 2q \text{ (wormlike chain)} \quad (1)$$

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

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

if the Barrett function[31] is adopted. Here, $\tilde{z}$ is the scaled excluded-volume parameter defined by[30]

$$\tilde{z} = (^3/_4)K(\lambda L)z \quad (3)$$

with

$$\begin{aligned} K(\lambda L) &= (^4/_3) - 2.711(\lambda L)^{-1/2} + (^7/_6)(\lambda L)^{-1} \quad \text{for } \lambda L > 6 \\ &= (\lambda L)^{-1/2} \exp[-6.611(\lambda L)^{-1} + 0.9198 + 0.035\,16\lambda L] \quad \text{for } \lambda L \le 6 \end{aligned} \quad (4)$$

and

$$z = (^3/_2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \quad (5)$$

wherein B denotes the excluded-volume strength. Equation 2 is known to accurately describe α_η^3 data for nonionic linear polymers, either flexible[18] or stiff,[32] and for Na hyaluronate[33–35] in aqueous NaCl with salt concentrations higher than 0.01 M.

Because the contour length is related to M by $L = M/M_L$, with M_L being the molar mass per unit contour length, the $[\eta]$ versus M_w relation for NaPSS in 4.17 M aqueous NaCl may be determined by q, M_L, and d. We estimated these parameters in the Θ solvent by curve

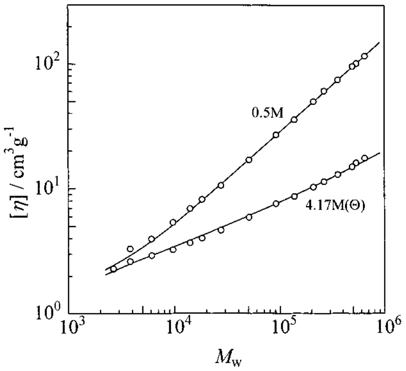

Figure 6. Comparison of the experimental $[\eta]$ for NaPSS in 0.5 and 4.17 M aqueous NaCl with the theoretical values calculated from the theory of Yoshizaki et al.[27] for unperturbed wormlike chains and the quasi-two-parameter theory for excluded-volume effects (eq 2) with the parameters in Table 3.

Table 3. Wormlike Chain Parameters for NaPSS in Aqueous NaCl

salt concn, T	q (nm)	M_L (nm^{-1})	d (nm)	B (nm)
4.17 M, 16.4 °C (Θ)	0.69	880	1.2	0
0.5 M, 25 °C	1.5	860	1.25	1.6

fitting, with the result that $q = 0.69 \pm 0.07$ nm, $M_L = 880 \pm 90$ nm^{-1}, and $d = 1.2 \pm 0.1$ nm. We note that a number of parameter sets within the indicated ranges of uncertainty lead to almost equally close fits but yield nearly identical values (7.8×10^{-4} nm^2) for the ratio q/M_L determining the asymptotic Gaussian behavior of $[\eta]$ or the unperturbed mean-square radius of gyration $\langle S^2\rangle_0$ (see eq 6).

As may be seen from eqs 1−5, perturbed $[\eta]$ is characterized by M_L, q, B, and d, but all four parameters cannot be determined from the present data in 0.5 M aqueous NaCl. In expectation of the insensitivity of M_L and d to NaCl concentration, we attempted to estimate a set of q and B in the aqueous salt with M_L and d fixed to 880 nm^{-1} and 1.2 nm, respectively. It turned out, however, that for any q between 1.2 and 1.8 nm, there is a B value (in the range between 1.2 and 2.0 nm) leading to an almost equally good fit when M_L and d are allowed to change slightly from the input values. This large uncertainty of the parameters ($q = 1.5 \pm 0.3$ nm and $B = 1.6 \pm 0.4$ nm) is attributable to the theoretical fact that in the limited range of M studied here, the effects of stiffness and excluded volume increase $[\eta]$ of the perturbed flexible chain in essentially the same fashion. It should be emphasized, however, that consideration only of excluded-volume effects gives somewhat poor agreement between theory and experiment.

The "best-fit parameters" obtained for the two aqueous salts are summarized in Table 3 with omission of their uncertainty, and the theoretical $[\eta]$ values calculated for the parameters are shown by continuous lines in comparison with the experimental data in Figure 6. The agreement between theory and experiment is good throughout the entire range of molecular weight studied. Notably, the Yoshizaki−Nitta−Yamakawa theory[27] is capable of explaining the very weak M_w dependence of experimental $[\eta]$ in the Θ solvent. Theoretically, a large d relative to q leads to a weak M dependence of $[\eta]$.

The wormlike chain parameters ($q = 0.69 \pm 0.07$ nm and $M_L = 880 \pm 90$ nm^{-1}) in 4.17 M aqueous NaCl give $\langle S^2\rangle_0/M$ a constant of 2.6×10^{-4} nm^2 for M above 2×10^5 when use is made of the expression[36]

$$\langle S^2\rangle_0 = (qL/3) - q^2 + (2q^3/L) - (2q^4/L^2)[1 - \exp(-L/q)] \quad (6)$$

for the unperturbed wormlike chain. This $\langle S^2\rangle_0/M$ is smaller by 15% than the experimental value 3.0×10^{-4} nm^2. The difference is attributable partially to small polydispersity effects but mainly to shortcomings of the viscosity theory of Yoshizaki et al.[27] in the coil limit and hence of the Kirkwood−Riseman (KR) theory[37] for Gaussian chains, both of which are known to overestimate the Flory viscosity factor Φ_0 [$\equiv [\eta]_0 M/(6\langle S^2\rangle_0)^{3/2}$] by 3−22% depending on the polymer + solvent system.[18,38] In other words, the present $\langle S^2\rangle_z$ and $[\eta]$ data in the Θ solvent are consistent with the currently known behavior of uncharged linear flexible chains in the unperturbed state. Using $\langle S^2\rangle_z/M_w = 3.0 \times 10^{-4}$ nm^2 with $M_L = 880$ ($\pm$90) nm^{-1} and $M_z/M_w = 1.05$ (the mean of the ratios in Table 1), we obtain $q = 0.75$ ($\pm$0.08) nm, which is to be compared to $q = 0.69$ ($\pm$0.07) nm from $[\eta]$.

The Φ_0 values of $(2.9 \pm 0.2) \times 10^{23}$ mol^{-1} calculated from our data in the Θ solvent happen to be very close to the KR value 2.86×10^{23} mol^{-1}. This coincidence should not be taken as experimental support to the KR theory, because the rotational friction of the individual beads[27] in a chain (ignored in the KR theory) contributes to $[\eta]_0$ even for $M = 6.5 \times 10^5$, the highest molecular weight studied in this work.

Molecular Characteristics. The monomeric contour length h for NaPSS in 0.5 or 4.17 M aqueous NaCl is estimated to be 0.23 ($\pm$0.03) nm from $M_L = 880$ ($\pm$90 nm^{-1}) with the monomer molecular weight 206. This h is comparable to or slightly smaller than the value 0.25 nm calculated on the assumption that the NaPSS chain assumes the all-trans conformation. The estimated hydrodynamic diameter 1.2 ($\pm$0.1) nm also seems reasonable, in that it is comparable to the molecular diameter expected from the chemical structure of the polyelectrolyte.

The stiffness of the NaPSS chain in 4.17 M aqueous NaCl, expressed in terms of q ($= 0.69 \pm 0.07$ nm from $[\eta]$ or 0.75 ± 0.08 nm from $\langle S^2\rangle$), is appreciably lower than that of polystyrene ($q = 1.0$ nm)[17] in cyclohexane. In the chain model adopted in the present analysis, this is a direct reflection of the characteristic ratio $\langle S^2\rangle_z/n_w$ of 6.2×10^{-2} nm^2 (for high M_w) smaller than that (8.7×10^{-2} nm^2) for the nonionic polymer (n_w denotes the weight-average degree of polymerization). The smaller $\langle S^2\rangle_z/n_w$ value for NaPSS gives theorists an interesting problem to be solved, because it can hardly be reconciled with the usual notion that the presence of sulfonate groups should more sterically hinder the internal rotation of main-chain C−C bonds to increase $\langle S^2\rangle_z/n_w$. At present, we presume that the hydrophobicity of styrene is responsible for the smaller characteristic ratio of the polyelectrolyte, although its effect on the molecular size is unclear under the Θ condition where attractions and repulsions between monomeric units are compensated.

Our q value for NaPSS in 4.17 M aqueous NaCl must essentially be equal to or can be slightly larger than the intrinsic persistence length defined as q at infinite ionic strength. Nonetheless, it is much smaller than the widely accepted q_0 of 1.2 nm mentioned in the Introduction. This q_0 value was obtained by Weil and Maret[2] from magnetic birefringence (at NaCl concentrations lower than 2 M) and independently by Nierlich et al.[4] from small-angle neutron scattering for salt-free semidilute solutions. Our comments on these studies are as follows.

Weil and Maret[2] assumed appropriate values for the optical and magnetic anisotropies whose product is directly proportional to q for sufficiently long chains. Hence, the estimated q and q_0 build entirely on the assumed anisotropy values. On the other hand, in their analysis of scattering curves, Nierlich et al.[4] ignored possible effects of excluded volume and chain thickness and extrapolated the estimated q ($= 3.8-5.4$ nm at $c_p^{-1/2} = 1.38-2.18$ $M^{1/2}$) to infinite c_p, invoking the linear relation between q and $c_p^{-1/2}$ (c_p denotes the total monomer concentration in the aqueous solution). Such a linear relation down to $c_p^{-1/2} = 0$ is not established, so that the extrapolated q can hardly be appreciated even though it happens to agree perfectly with Weil and Maret's result. It is likely that this coincidence has tempted other workers to optimistically accept $q_0 = 1.2$ nm in later studies on the electrostatic persistence length[39,40] q_{el} ($= q - q_0$) of NaPSS in aqueous NaCl.

When the solvent condition is changed to 0.5 M aqueous NaCl, q increases to about 1.5 nm. Such an increase in q is in line with the current theories[39-42] for q_{el}, although we could not determine a precise value at this salt concentration owing to the strong correlation between q and B in fitting the viscosity data. The ambiguity in the separate evaluation of excluded-volume and stiffness effects may be specific to highly flexible, perturbed chains at high ionic strength, because this problem was not encountered in our previous work[33-35] on Na hyaluronate, an intrinsically stiffer polyelectrolyte with q_0 of about 4 nm. Further work on these two effects in NaPSS solutions at different NaCl concentrations is in progress in this laboratory. The ionic strength dependences of q and B will be discussed in relation to theoretical predictions when systematic data are accumulated.

Conclusions

The following conclusions have been derived from the present work on NaPSS in 0.5 and 4.17 M aqueous NaCl.

(1) NaPSS attains the Θ state in 4.17 M aqueous NaCl as found earlier by Takahashi et al.[1] from phase separation. However, the Θ temperature 16.4 °C determined in this work from the light scattering second virial coefficient is appreciably lower than that (25 °C) reported by them.

(2) The molecular weight dependence of $[\eta]$ for this polyelectrolyte in the Θ state is almost quantitatively explained by the theory of Yoshizaki et al. for the unperturbed wormlike chain with a monomeric contour length of 0.23 nm, a chain diameter of 1.2 nm, and a persistence length q of 0.69 nm. The unperturbed radius of gyration gives q a slightly larger value of 0.75 nm when the monomeric length from $[\eta]$ is used.

(3) The q value of 0.69−0.75 nm is much smaller than the intrinsic persistence length 1.2 nm widely used for experimental tests of available theories for the electrostatic persistence length, and good agreements between theory and experiment often observed with this q_0 value must be fortuitous (see, for example, Nishida et al.[13]).

(4) When the NaCl concentration is lowered to 0.5 M (at 25 °C), q increases to about 1.5 nm, and the monomeric contour length and the chain diameter stay almost unchanged. The quasi-two-parameter theory quantitatively explains significant excluded-volume effects on $[\eta]$ at this salt concentration.

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 and Notes

(1) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(2) Weil, G.; Maret, G. *Polymer* **1982**, *23*, 1990.
(3) Tricot, M. *Macromolecules* **1984**, *17*, 1698.
(4) Nierlich, M.; Boue, F.; Lapp, A.; Oberthür, R. C. *Colloid Polym. Sci.* **1985**, *263*, 955.
(5) Ragnetti, M.; Oberthür, R. C. *Colloid Polym. Sci.* **1986**, *264*, 32.
(6) Wang, L.; Yu, H. *Macromolecules* **1988**, *21*, 3498.
(7) Peitzsch, R. M.; Burt, M. J.; Reed, W. F. *Macromolecules* **1992**, *25*, 806.
(8) Borochov, N.; Eisenberg, H. *Macromolecules* **1994**, *27*, 1440.
(9) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 53.
(10) Spiteri, M. N.; Boue, F.; Lapp, A.; Cotton, J. P. *Phys. Rev. Lett.* **1996**, *77*, 5218.
(11) Tanahatoe, J. J.; Kuil, M. E. *Macromolecules* **1997**, *30*, 6102.
(12) Tanahatoe, J. J.; Kuil, M. E. *J. Phys. Chem. A* **1997**, *101*, 8389.
(13) Nishida, K.; Urakawa, H.; Kaji, K.; Gabrys, B.; Higgins, J. S. *Polymer* **1997**, *38*, 6083.
(14) Beer, M.; Schmidt, M.; Muthukumar, M. *Macromolecules* **1997**, *30*, 8375.
(15) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.
(16) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(17) Norisuye, T.; Fujita, H. *Polym. J.* **1982**, *14*, 143.
(18) Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions*; Springer: Berlin, 1997.
(19) Wiley: R. H.; Smith, N. R.; Ketterer, C. C. *J. Am. Chem. Soc.* **1954**, *76*, 720.
(20) Deželić, Gj.; Vavra, J. *Croat. Chem. Acta* **1966**, *38*, 35.
(21) Rubingh, D. N.; Yu, H. *Macromolecules* **1976**, *9*, 681.
(22) Sato, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1983**, *16*, 185.
(23) Norisuye, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 547.
(24) Takashima, K.; Nakae, K.; Shibata, M.; Yamakawa, H. *Macromolecules* **1974**, *7*, 641.
(25) Miyaki, Y. Ph.D. Thesis, Osaka University, Japan, 1981.
(26) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(27) Yoshizaki, T.; Nitta, I.; Yamakawa, H. *Macromolecules* **1988**, *21*, 165.
(28) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(29) Yamakawa, H.; Shimada, J. *J. Chem. Phys.* **1985**, *83*, 2607.
(30) Shimada, J.; Yamakawa, H. *J. Chem. Phys.* **1986**, *85*, 591.
(31) Barrett, A. J. *Macromolecules* **1984**, *17*, 1566.
(32) Norisuye, T.; Tsuboi, A.; Teramoto, A. *Polym. J.* **1996**, *28*, 357.
(33) Hayashi, K.;. Tsutsumi, K.;. Nakajima, F.; Norisuye, T.; Teramoto, A. *Macromolecules* **1995**, *28*, 3824.
(34) Hayashi, K.;. Tsutsumi, K.; Norisuye, T.; Teramoto, A. *Polym. J.* **1996**, *28*, 922.
(35) Tsutsumi, K.; Norisuye, T. *Polym. J.* **1998**, *30*, 345.
(36) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(37) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(38) Fujita, H. *Polymer Solutions*; Elsevier: Amsterdam, 1990.
(39) Odijk, T. *J. Polym. Sci*: *Polym. Phys. Ed.* **1977**, *15*, 477.
(40) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(41) Le Bret, M. *J. Chem. Phys.* **1982**, *76*, 6243.
(42) Fixman, M. *J. Chem. Phys.* **1982**, *76*, 6346.

MA990813B