Effect of Sulfonation Level on Solubility and Viscosity Behavior of Low to Medium Charged Sulfonated Polystyrenes

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ABSTRACT: Theoretical treatments based on Fixman's theory and on the electrostatic wormlike theory are applied to sulfonated polystyrene (KSPS) with sulfonation levels ranging from 11 to 52 mol %. Good agreement between theory and experimental results was obtained for SPS with more than 19 mol % of ionic groups on the backbone. However, large deviations were observed for the data on KSPS with low sulfonation level, 11 mol %, which indicates the failure of the models—originally developed for strongly charged polyelectrolytes—to explain results for weakly charged polyelectrolytes (ionomers). Experimentally, SPS were prepared by the sulfonation of polystyrene with a milder method in homogeneous media so as to avoid chain degradation or cross-linking. Sulfur elemental analysis was used to calculate the sulfonation level while characterization using infrared and nuclear magnetic resonance spectroscopy confirmed that the SPS did not suffer cross-linking or degradation. Optimized conditions were established in solubility tests with THF/H_2O mixtures to obtain viscosity data using dilute capillary viscometry measurements. Counterion condensation was observed at several polymer concentrations in measurements of reduced viscosity in salt-free solution and of intrinsic viscosity in the presence of NaCl up to 0.2 M. A sharp increase in viscosity with the sulfonation level occurred up to 25 mol %, after which it remained constant.

1. Introduction

Polyelectrolyte solutions are among the least understood categories of condensed matter. Salt-free solutions of conventional polyelectrolytes, such as sodium poly(styrenesulfonate), are still not understood in terms of either the structure of the solutions or the main factors governing the polyelectrolyte behavior.[1] In the absence of added salts, polyelectrolyte solutions have their reduced viscosity increased upon dilution due to repulsion between charges in the backbone, which leads to an expansion of the chain.[2,3] The addition of low-molar-mass electrolytes decreases the reduced viscosity, which reflects the contraction of the polymer chains as the fixed charges in the polyion are shielded by counterions. The interest in polyelectrolyte solutions has been extended to ionomers and telechelic ionomers.[4−7] Ionomers comprise a nonpolar backbone chain with a relatively small number of covalently bonded ionic groups, up to 10−15 mol %, distributed along the polymer backbone. They are insoluble in water but can be dissolved in polar and in low-polarity solvents. When dissolved in low-polarity solvents, the ionic groups are not ionized, and the polymers exhibit intramolecular or intermolecular aggregation between the ion pairs. [8,9] When dissolved in polar solvents, they display a typical polyelectrolyte behavior due to the Coulombic repulsive forces of the ionic groups.[8−10] Ionomers may serve as model polyelectrolytes for salt-free polyelectrolyte solutions[4−7,11] and are also important for applications such as compatibilizers in polymer blending,[12−14] selective membranes, and polymer light-emitting devices.[15]

The influence of the sulfonation level on the physicochemical properties of polyelectrolytes can be predicted by the Manning counterion condensation model,[2,16] according to which the effective charge (in units of charge per monomer unit) has an upper bound, since a fraction, x, of the counterions condense and the effective charge is $1 - x$. Properties such as the dilute solution viscosity, which depend on the effective charge of the polyion, are therefore affected by the fraction of condensed counterions. For ionomers in a polar solvent with x below the onset point for counterion condensation, Lundberg and Philips[8] observed a linear increase in reduced viscosity with the ion content. The same continuity was observed by Essafi et al.[17] for sulfonated polystyrene (SPS) with sulfonation degree ranging from 30 to 100 mol %. For SPS in water, counterion condensation starts at approximately 35 mol % of sulfonation. Counterion condensation has been an important issue,[18,19] and a theory by Heath and Schurr[20] predicts that the onset for counterion binding is much more rapid than is predicted by Manning's theory. Sulfonated polystyrene is one of the most frequently studied charged polymers, and the investigation of intermediate range of sulfonate content, between ionomers and polyelectrolytes, which includes the onset point for counterion condensation, is of prime importance in the elucidation of ion condensation phenomena.

Sulfonated polystyrene is usually prepared by direct sulfonating polystyrene in solution with acetyl sulfate,[21,22] thus avoiding chain degradation or cross-linking. This procedure has been described as a gentle method of sulfonation, affording a sulfonation level higher than 34 mol % with no evidence of polymer degradation, notably when applied to polystyrenes of moderate molecular weights.[23]

In the present study we prepared sulfonated polystyrenes with various sulfonate contents and investigate effects from the ion content on their solubility and viscometric behavior. The sulfonation levels range from low (as in ionomers) to high values, characteristic of polyelectrolytes. SPS were prepared by sulfonation of polystyrene in solution by acetyl sulfate, resulting in

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sulfonation levels of 11, 19, 25, 40, and 52 mol %. These polymers were studied in dilute solution by viscometry, both in salt-free and in added salt solutions. The behavior of KSPS in solution was interpreted in terms of semiempirical models of polyion stiffness and by applying the electrostatic wormlike chain theory for polyelectrolytes and compared with published data for highly sulfonated polystyrene.

2. Experimental Section

2.1. Polymer Preparation. The sulfonated polystyrenes were prepared by sulfonation of polystyrene with acetyl sulfate, which was produced in situ by the reaction of acetic anhydride and sulfuric acid.[22] The reaction was carried out by progressive addition of acetic anhydride and 98% sulfuric acid to a 5% w/w solution of polystyrene in 1,2-dichloroethane. The homogeneous mixture was stirred for 12 h at 25 °C and left to stand overnight at room temperature. Five SPS samples were prepared by the addition of sulfuric acid sufficient to produce theoretical sulfonation levels of 12, 22, 44, 65, and 85 mol %, assuming total conversion of the sulfuric acid. In all reactions the acetic anhydride/sulfuric acid molar ratio was fixed at 2:1. Once the reaction was complete, 150 mL of ethyl ether was added to each SPS solution to precipitate the polymer. These polymers were isolated and washed with 100 mL of ethyl ether, dried at reduced pressure at 35 °C, and redissolved in a THF/H_2O mixture (1:2, v/v). This solution was neutralized with 0.1 N KOH solution. The polymers were precipitated twice in ethyl alcohol and dried at reduced pressure (6 mmHg) at 60−70 °C for 72 h. The starting polystyrene was obtained by solution polymerization and had a number-average molecular weight of 32 000 and weight-average molecular weight of 77 000, as determined by high-performance size exclusion chromatography.

2.2. Characterization. Sulfur elemental analyses of KSPS were performed in a LECO model SC 132 sulfur analyzer. Infrared spectra were obtained from KBr pellets (200 mg of KBr and 1.5 mg of polymer) in conventional spectrometers. H^1 nuclear magnetic resonance spectra of 10% w/w solutions of the KSPS samples in DMSO-d_6 were recorded in a Bruker model AC 200 spectrometer at 200 MHz and 25 °C. Solubility tests were performed in THF/H_2O mixtures with compositions of 0, 20, 50, 80, 99, and 100 vol % THF. The experiments were conducted in 4×100 mm glass test tubes with a rubber stopper. The polymers were weighed directly into the tubes, and the solvent mixture was added in small portions. To accelerate the dissolution, the tubes with the mixture of polymer and solvent were placed in a cleaning ultrasound bath for 12 h. If the sample was completely dissolved, the test was stopped and the total volume of solvent used was recorded; otherwise, more solvent was added and the test was repeated.

The dilute solution viscosity was determined with a semi-micro-Cannon-Ubbelohde number 100 dilution viscometer at 25 ± 0.02 °C in a thermostatic bath. These measurements were conduced in THF:H_2O 1:1 v/v solution, both in the absence of added salt and in the presence of NaCl at concentrations of 0.01, 0.02, 0.05, 0.10, and 0.20 mol/L. As the viscosity measured data are low, below approximately 4 dL/g, it is possible to consider the viscosity as independent of the rate of shear, with the shear rate being near zero.[24]

3. Results and Discussion

3.1. Preparation and Characterization. The sulfonation levels of the polymers were calculated by sulfur elemental analysis, and the data are presented in Table 1 together with the expected sulfonation level for complete reaction between sulfuric acid and polystyrene. Up to the expected sulfonation level of 22%, the conversion is almost 100%. However, for higher levels, the degree of sulfonation deviates from the expected value, indicating that sulfonation becomes more difficult as the degree of sulfonation rises. This is probably the result of a decrease in solubility of SPS formed, causing a contraction of the chains. The weight-average molecular weights (M_w) calculated from the experimental data on degree of sulfonation and from the M_w of the parent polystyrene are presented as M_w-KSPS in Table 1. The infrared spectra of the polymers, after sulfonation, showed the typical absorption pattern of the polystyrene backbone, with two absorption bands attributed to O−S−O stretching, at 1190 cm^{-1} (asymmetric) and at 1032 cm^{-1} (symmetric). The ^1H NMR spectra of the five KSPS samples are very similar, except for the intensity of the signals. The spectra exhibit peaks at about 1.4 ppm for CH_2 and ca. 1.7 ppm for CH protons. The peaks from aromatic protons appear at about 6.5 ppm for protons in the ortho position and about 7.0 ppm for those in meta and para positions. The aromatic protons of SPS units in ortho positions with respect to the sulfonic groups appear at about 7.5 ppm. The spectra obtained in this work are similar to those published by Natansohn and Eisenberg[25] for SPS ionomers with 10 mol % sulfonic groups.

Table 1. Properties of Potassium Sulfonated Polystyrenes[a]

identification	sulfonation level (mol %) expected	sulfonation level (mol %) found[b]	M_w KSPS[c]
KSPS1	12	11	86 565
KSPS2	22	19	93 551
KSPS3	44	25	98 790
KSPS4	65	40	111 888
KSPS5	85	52	122 366

[a] Parent polystyrene has a weight-average molecular weight, $M_w = 77\ 000$; weight-average degree of polymerization $DP_w = 740$; monomer length $b = 2.52$ Å; contour length $L_c = 1865.8$ Å. [b] Degree of sulfonation determined by sulfur element analysis. [c] Weight-average molecular weight of the KSPS calculated as $M_{wKSPS} = (x \cdot DP_w \cdot 222) + ((1 - x) \cdot DP_w \cdot 104))$, where x is the mole fraction of sulfonated styrene units.

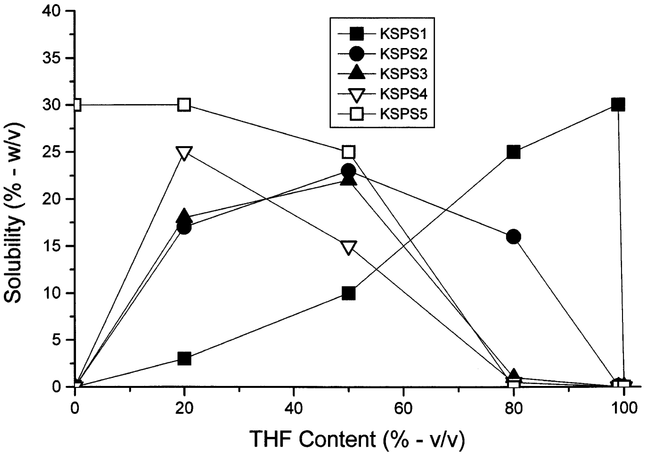

Figure 1. Solubility of (a) KSPS1, (b) KSPS2, (c) KSPS3, (d) KSPS4, and (e) KSPS5 in THF/H_2O mixture at room temperature.

3.2. Solubility in THF/Water Mixtures. The solubility diagram of SPS in THF/H_2O mixtures is presented in Figure 1 as a function of solvent composition and shows a considerable variation in the solubility of the polymers. The least sulfonated polymer, KSPS1, displays its maximum solubility, approximately 30 wt %, in 99% THF solution, although it is insoluble in 100% THF. This abrupt fall in the solubility can be attributed to the specific interaction of water with the sulfonated groups. Lundberg[8] reported that sulfonated polystyrene

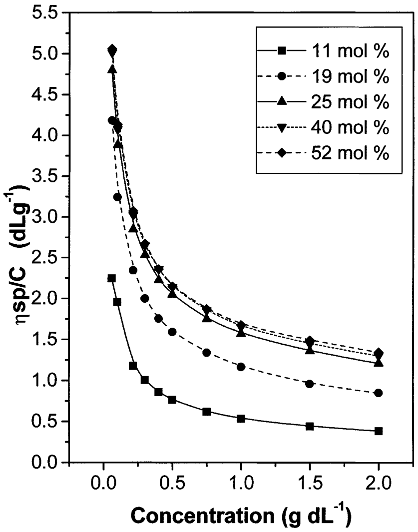

Figure 2. Reduced viscosity η_{sp}/c vs polymer concentration for the five KSPS samples prepared, in salt-free THF:H_2O 1:1 v/v mixture.

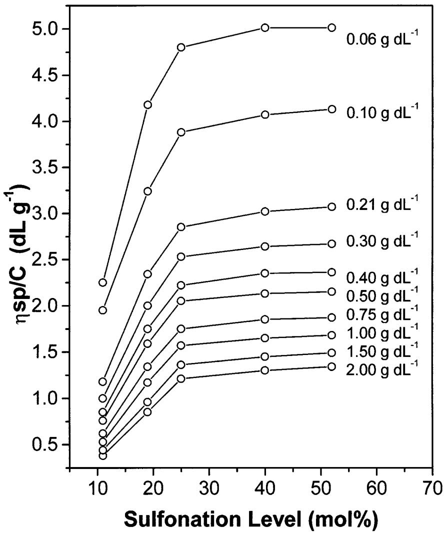

Figure 3. Reduced viscosity η_{sp}/c vs sulfonation level of sulfonated polystyrenes in THF:H_2O 1:1 v/v solvent.

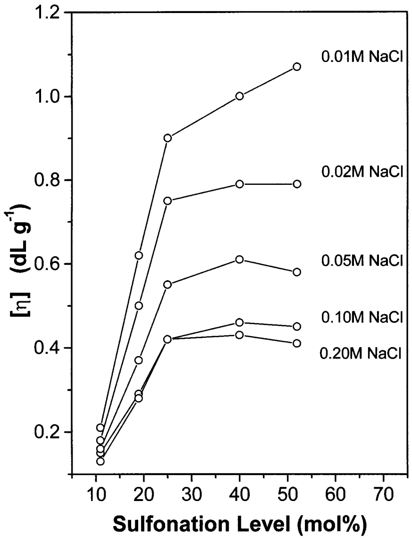

Figure 4. Intrinsic viscosity vs sulfonation level of sulfonated polystyrene at several NaCl concentrations in THF:H_2O 1:1 v/v solvent.

Table 2. Intrinsic Viscosity, [η], for KSPS at Several NaCl Concentrations in THF:H_2O 1:1 v/v Solution

	[η] (dL/g)				
C_s (mol/L) NaCl	KSPS1	KSPS2	KSPS3	KSPS4	KSPS5
0.2	0.15	0.29	0.42	0.43	0.41
0.1	0.13	0.28	0.42	0.46	0.45
0.05	0.16	0.37	0.55	0.61	0.58
0.02	0.18	0.50	0.75	0.79	0.79
0.01	0.21	0.62	0.90	1.00	1.07

ionomers in nonpolar solvents, to which very low quantities of a polar cosolvent (DMSO, H_2O) had been added, exhibited polyelectrolyte behavior. This was attributed to specific interactions between the cosolvent and the ionizable groups of the ionomer. As the sulfonation increased, in KSPS2 and KSPS3, the maximum solubility occurred at about 1:1 THF/H_2O (v/v), where these polymers have a solubility of 22−23 wt %. KSPS4 showed maximum solubility in 1:4 THF/H_2O (v/v) mixture, in which 24 wt % of the polymer dissolved. For the most sulfonated polymer, KSPS5, the maximum solubility was 30 wt %, which was achieved in pure water.

Figure 1 shows that the best choice of solvent system, which can be used satisfactorily for all polymers, is a 1:1 THF/H_2O (v/v) mixture. This composition of solvent was chosen for all the measurements of dilute solution viscosity.

3.3. Polyelectrolyte Behavior in Salt-Free Solution. The dependence of reduced viscosity on concentration of sulfonated polystyrene in 1:1 THF/H_2O (v/v) mixture is shown in Figure 2. The KSPS samples all show typical polyelectrolyte behavior, in which the reduced viscosity, η_{sp}/c, increases remarkably with dilution. In Figure 3, reduced viscosity is plotted against the ion content of the polymer at several polymer concentrations. For any given concentration, the reduced viscosity increases steeply with the sulfonation level up to 25 mol % and then remains almost constant at higher sulfonation levels. Hence, 25% can be taken as the onset point for counterion condensation predicted in Manning's theory.[18] This onset seems to be independent of polymer concentration in salt-free solutions. The linear increase of reduced viscosity with sulfonation level in the range between 11% and 25% was also described by Lundberg and co-workers for polystyrenesulfonate ionomers with sulfonation levels ranging from 1.7 to 6.05 mol % in polar solvents.[8] Hara and Wu[11] described a similar behavior for the effective hydrodynamic diameter, determined by light scattering, as a function of ion content, in polystyrenesulfonate ionomers in DMF solutions.

3.4. Viscosity Behavior in Added Salt Solutions. When low-molar-mass electrolytes are added to polyelectrolyte solutions, the interactions between the charges on the backbone are suppressed by the screening effect of the counterions and the macroions behave like neutral polymers. Consequently, the reduced viscosity can be expressed as a power series in concentration,[26] and plots of reduced viscosity against concentration become linear, allowing extrapolation to the intrinsic viscosity using Huggins's equation.[27] The data on intrinsic viscosity are presented in Table 2 and are plotted in Figure 4 as a function of ion content for several NaCl concentrations. The intrinsic viscosity increases notably with sulfonation degree, up to 25 mol %, beyond which it is almost unchanged, for all NaCl concentrations above 0.02 mol/L. This behavior is similar to that

Table 3. Structural Characteristics and Stiffness Parameters Obtained from Viscometric Measurements

			stiffness parameters		
identification	d^a (Å)	λ^b	$[\eta]_\infty$ (dL/g)	$S \times 10^2$	$[\eta]_{0.1}$
KSPS1	22.91	0.44	0.11	0.98	0.13
KSPS2	13.26	0.76	0.17	4.46	0.28
KSPS3	10.08	1.00	0.25	6.71	0.42
KSPS4	6.30	1.60	0.26	7.44	0.46
KSPS5	4.85	2.08	0.20	8.62	0.45

[a] Mean average distance between sulfonic groups calculated as $d = b/\alpha$ where α is the number of ionic groups per monomer length, b. [b] Charge density parameter calculated from eq 3 using dielectric constant of solvent $D = 57$.

observed in salt-free solutions, indicating again that counterion condensation starts at 25 mol %; i.e., at this point $\lambda = 1$. The onset for counterion condensation is not affected by salt concentrations from 0.02 to 0.2 mol/L.

3.5. The Charge Density Parameter, λ. The effective influence of the ionic groups on the viscosity behavior can be quantified through the charge density parameter (λ), as defined by Lifson and Katchalsky.[28]

$$\lambda = \left(\frac{\alpha}{b}\right)\left(\frac{q_e^{\,2}}{Dk_bT}\right) \qquad (1)$$

where α/b is the number of ionic sites divided by monomeric unit length, b, q_e is the charge of the electron, D is the dielectric constant of the solvent, and k_bT is the Boltzmann term. The charge density parameter is a structural parameter, and according to Manning's theory[16] for counterion condensation, the effective charge parameter tends to a limit value, $\lambda_{\mathrm{eff}} = 1$. Therefore, for $\lambda > 1$, there is a fraction $(1 - 1/\lambda)$ of condensed counterions on the polyelectrolyte chain. Condensation of counterions occurs in polyelectrolyte solutions until the free energy of charge repulsion balances that arising from the entropy of a free counterion so that the distance between effective charges on the polyion is the Bjerrum length, Q. The Bjerrum length is a natural length scale for polyelectrolytes in solution and can also be defined as the distance between two elementary charges when the electrostatic energy equals the thermal energy, k_bT.

$$Q = \frac{q_e^{\,2}}{Dk_bT} \qquad (2)$$

Therefore, the charge density parameter may also be expressed as

$$\lambda = \frac{Q}{d} \qquad (3)$$

where $d = b/\alpha$ is the distance between two elementary charges, q_e.

The charge density parameter exerts a great influence on the macroion conformation and, as a consequence, on the hydrodynamic behavior of the polyelectrolytes in solution. To calculate λ, it is necessary to know the value of the dielectric constant of the solvent, which is not available in the case of THF/H_2O mixtures used in this work. Therefore, the dielectric constant was used as an adjustable parameter, using eq 1 for the case where $\lambda = 1$. This situation occurs when the reduced viscosity or the intrinsic viscosity does not increase with increasing ionic charge. Using the average distance between ionic groups calculated for KSPS3, which corresponds to a sulfonation degree of 25 mol % (see Figures 3 and 4), a dielectric constant of 57 was estimated. This value is intermediate between the relative dielectric constants for water $D_{\mathrm{water}} = 78.5$ and for THF $D_{\mathrm{THF}} = 7.6$. The values determined for the charge density parameter, λ, and for the distance between the ionic groups, d, are presented in Table 3.

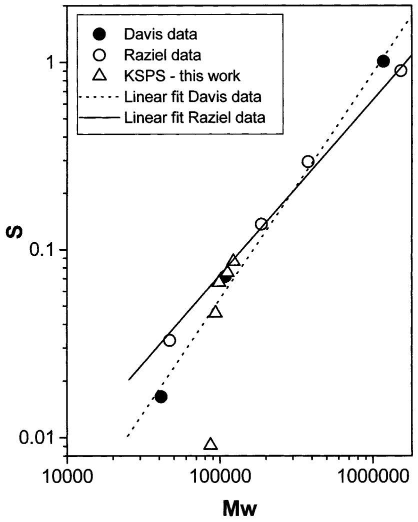

Figure 5. Dependence of S on M_w data from Davis and Raziel and for the potassium sulfonated polystyrenes prepared in this work.

3.6. Dependence of the Intrinsic Viscosity on the Ionic Strength. The Stiffness of the Macroion. The dependence of the intrinsic viscosity on the ionic strength has been expressed, for a series of polyelectrolytes,[29] by the empirical equation

$$[\eta]_\mu = [\eta]_\infty + S\mu^{-1/2} \qquad (4)$$

where $[\eta]_\mu$ is the intrinsic viscosity at an ionic strength (μ), $[\eta]_\infty$ is the intrinsic viscosity extrapolated to infinite ionic strength, and S is the slope of the straight line relating $[\eta]_\mu$ and $\mu^{-1/2}$. The values of $[\eta]_\infty$ and S are presented in Table 3. The values of $[\eta]_\infty$ may be interpreted as the viscosity at the theta condition $[\eta]_\theta$,[30] and the parameter S is proportional to the molecular weight of the polyelectrolyte.[29] A double-logarithmic plot of S against M_w is linear with a slope of unity according to Fixman's theory.[29,31] Figure 5 shows a double-logarithmic plot of S vs M_w for data taken from Davis and Russel[32] and Raziel and Eisenber[33] for sulfonated polystyrenes with high sulfonation level, showing good linearity in both cases, with slopes of 1.2 and 0.94, respectively. For KSPS samples in the present work, the variation of molecular weight is not sufficient to obtain good regression data from the S vs M_w plot, but it is possible to see that the data for the sulfonated polystyrenes with a sulfonation level higher than 19 mol % fall on the straight lines obtained for the data taken from the literature. On the other hand, KSPS1, with 11 mol % sulfonic groups, displayed a distinct behavior, which means that the relationship between S and M_w is not observed for low-charged KSPS.

Quantifying the stiffness of a polyelectrolyte chain, due to the electrostatic repulsion in solution, requires a parameter that gives a numerical value to this

Table 4. Parameters B and ν Determined Experimentally for the KSPS in This Study and Calculated for SPS from the Literature and B Values Taken from the Literature for Other Types of Polymer

identification	B	ν	reference
KSPS1	0.14[a]		
KSPS2	0.23[a]		
KSPS3	0.21[a]		this work
KSPS4	0.20[a]		
KSPS5	0.24[a]		
SPS Davis	0.17[b]	1.37	34
SPS Raziel	0.22[b]	1.10	35
polyphosphate	0.44[c]		31
polyacrylate	0.23[c]		31
carboxymethylamylose	0.20[c]		31
carboxymethylcellulose	0.065[c]		31
alginate	0.04[c]		31
DNA	0.0055[c]		31

[a] B values calculated from eq 7 with $\nu = 1.3$. [b] B and ν values determined graphically from viscometric data taken from the cited reference. [c] B values determined graphically reported in the literature, with ν varying from 1.2 to 1.4.

property. A successful stiffness parameter, B, employed by Smidsrød and Haug,[29] is based on the double-logarithmic plot of intrinsic viscosity at ionic strength 0.1 against S. A plot of intrinsic viscosity at $\mu = 0.1$, vs S, furnished nearly parallel straight lines, and the behavior of any particular polyelectrolyte can be expressed by

$$S = B([\eta]_{0.1})^{\nu} \tag{5}$$

As the exponent ν varies little over a great variety of polyelectrolytes, B is used as a characteristic measure for the response of $[\eta]$ to the addition of salt. Assuming an average value of 1.3 for ν, it is possible to calculate directly the value of B from S and $[\eta]_{0.1}$. However, if the polymer is available with several different molecular weights, B can be obtained more accurately by plotting S vs $[\eta]_{0.1}$ and extrapolating graphically to $[\eta]_{0.1} = 1.0$. This approach was applied successfully by Smidsrød and Haug to data they obtained for alginate samples and to data taken from the literature. As for KSPS in this work, the molecular weight variation is not sufficient to obtain a good relationship between S and $[\eta]_{0.1}$, and so the values of B were obtained with eq 5, using $\nu = 1.3$. These data are presented in Table 4, with B determined graphically from the data on intrinsic viscosity of sulfonated polystyrenes published by both Davis and Russel and Raziel and Eisenberg. Additionally, for the purpose of comparison, values of B given in the literature[29] for several other materials are also presented in Table 4. Except for KSPS1, B lies between 0.20 and 0.24, very close to the values obtained from the data of Davis and Raziel, namely 0.17 and 0.22, respectively. It seems that B does not depend on the degree of sulfonation, which certainly affects the hydrophobicity of the different KSPS, as was observed from their pattern of solubility. These results are consistent with those of Smidsrød and Haug,[29] who studied samples of nonacetylated and acetylated alginate, which, despite the fact they had different hydrophobicity, showed similar plots of S vs $[\eta]_{0.1}$, leading those authors to conclude that B is not very sensitive to changes in the degree of solvation of the chains. For KSPS1 B was 0.14, which is not far from the other values obtained for the more sulfonated samples. However, this indicates a more rigid polyion, since B increases with the flexibility of the polymer. The sulfonation level cannot explain this result, since less sulfonated samples should give more flexible polyions. This behavior remains unexplained and should be further investigated.

3.7. Application of the Electrostatic Wormlike Chain Theory. In this theory,[34,35] the polyion is modeled as a continuous space curve of length l (contour length) near the rod limit with N charges spaced equidistantly along the chain. The polyion in solution is characterized by a total persistence length $L_T = L_P + L_e$, where L_P is the intrinsic persistence length, which is the characteristic length of the backbone structure, independent of the electrostatic charge. L_e is the electrostatic persistence length, and its value increases as the electrostatic effect becomes stronger through intramolecular repulsions. The component L_P may be approximated by the ratio of the mean-square radius of gyration to the chain contour length at very high salt concentration C_s[36]

$$L_P = \frac{\langle S^2 \rangle}{l}; \quad C_s \rightarrow \infty \tag{6}$$

where l is the contour length.

The general result obtained by Odijk is

$$L_e = \frac{1}{12} Q N^2 h(kl) \tag{7}$$

where Q is the Bjerrum length, κ is the inverse Debye–Huckel screening length, and

$$h(y) = e^{-y}(y^{-1} + 5y^{-2} + 8y^{-3}) + 3y^{-2} - 8y^{-3} \tag{8}$$

In the limit of high ionic strength, where κl is large, the expression for L_e reduces to

$$L_e = \frac{Q}{4k^2 d^2} \tag{9}$$

where d is the linear charge spacing and the Debye screening length, k^{-1}, can be expressed as $\kappa^2 = 8\pi Q n$, where n is the concentration of 1:1 electrolyte (ion/cm^3).

To account for counterion[1] condensation, it is possible to combine eq 3 and eq 9 to give

$$L_e = \frac{\lambda^2}{4k^2 Q} \tag{10}$$

For charge spacing smaller than the condensation limit, $\lambda \geq 1$, the electrostatic persistence length is

$$L_e = \frac{1}{4k^2 Q} \tag{11}$$

with L_e being independent of charge density at high charge densities.

The intrinsic viscosity $[\eta]$ may be written[36] as

$$[\eta] = [\eta]_{\infty} \left(\frac{L_T}{L_P} \right)^{3/2} \alpha_{\eta}^{3} \tag{12}$$

where $[\eta]_{\infty}$ is the intrinsic viscosity at infinite ionic strength and α_{η} is the expansion factor of viscosity which can be related to the expansion factor α_s[37] by

$$\alpha_{\eta}^{3} = (\alpha_s^{2})^{3/2} \tag{13}$$

Table 5. Debye Length, κ^{-1}, Square of the Expansion Factor, α_s^2, and Intrinsic Viscosity Calculated Using the Electrostatic Wormlike Chain Theory, at Several Electrolyte Concentrations, for KSPS1, KSPS2, and KSPS3−5[a]

			[η] (dL/g)		
C_s (mol/L) NaCl	κ^{-1}	α_s^2	KSPS1	KSPS2	KSPS3−5
0.2	5.790	1.9269	0.27	0.28	0.29
0.1	8.189	2.1961	0.34	0.36	0.39
0.05	11.581	2.4484	0.41	0.47	0.53
0.02	18.311	2.6475	0.51	0.68	0.88
0.01	25.895	2.6171	0.58	0.94	1.40

[a] The intrinsic viscosities were calculated assuming a persistence length L_P = 14 Å and $[\eta]_\theta \approx [\eta]_\infty$ = 0.10 dL/g.

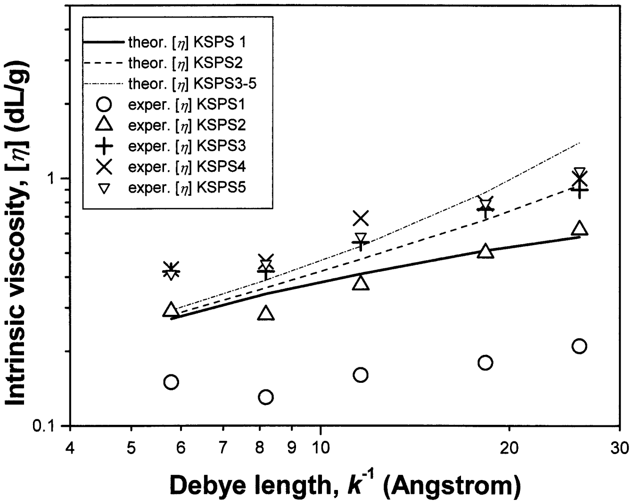

Figure 6. Double-logarithmic plot of experimental and theoretical values of intrinsic viscosity against Debye length.

Then α_s^2 is described by the excluded-volume parameter Z_{el} as[38]

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04Z_{el})^{0.46} \tag{14}$$

in which

$$Z_{el} = \frac{1}{32}\left(\frac{3}{\pi}\right)^{3/2}\beta_{el} l^{0.5} - L_T^{-3.5} \tag{15}$$

where β_{el} is the excluded volume, $\beta_{el} = 2\pi L_T^2 d_k$, d_k being the effective diameter of the Kuhn segment calculated by Fixman and Skolnick:[39]

$$d_k = k^{-1}\left(-\ln Qk + \ln 4\pi + \gamma - \frac{1}{2}\right) \tag{16}$$

where γ is the Euler constant (0.577 22).

The intrinsic viscosity was calculated from eq 12 using the mean value of $[\eta]_\infty$ = 0.10 g/dL, determined from the plots of [η] vs $C_s^{-1/2}$ extrapolated to infinite ionic strength, D = 57, Q = 9.84 Å, T = 298 K, and $\kappa^{-1} = 2.589C_s^{-1/2}$ (Å) if C_s is given in mol/L. The value of L_P = 14 Å was taken from the work by Davis and Russel.[32] The contour length l = 1865.8 Å was determined using the monomer length of 2.52 Å. The predictions for intrinsic viscosity based on eq 12 and the measured experimental values are presented in Table 5, with the values for k^{-1} and α_s^2. Figure 6 compares the predicted intrinsic viscosity with measured values for KSPS as a function of Debye length k^{-1}. The qualitative agreement is good for KSPS 2, 3, 4, and 5 (λ higher than 0.76) (see Figure 6). Especially at salt concentrations from 0.2 to 0.05, the predictions are good and deviate less than 30%. For a polyion with low charge, KSPS1, the theory fails, and for some salt concentrations it predicts values that deviate more than 100% from the measured values.

The failure to explain data for weakly charged polyelectrolytes (ionomers) points to the limitations of current theoretical treatments of polyelectrolytes, which have been developed for strongly charged polyelectrolytes.

4. Conclusions

Sulfonated polystyrenes with sulfonation levels from 11 to 52 mol % were prepared by sulfonation of polystyrene with acetyl sulfate. No evidence of degradation or cross-linking was observed. The linear charge density along the backbone plays an important role in the solubility of KSPS, so that the polystyrene with the highest sulfonation level, 52 mol %, is totally soluble in water whereas the polymer with the lowest sulfonation level is soluble in 99% THF. In the latter case, a small quantity of water is necessary for the polymer to dissolve, indicating a specific interaction between water and the sulfonic groups on the polymer backbone. Viscosity measurements were carried out in salt-free 50% THF solution, and the data showed the polyelectrolyte effect in all the polymers prepared. The plot of reduced viscosity vs polymer ion content showed an onset for counterion condensation at 25 mol % sulfonation. This value did not depend on the polymer concentration. Data for intrinsic viscosity in the presence of added salt also showed an onset for condensation at the same level of sulfonation, as predicted by Manning's theory for $\lambda = 1$. This behavior was independent of salt concentration at values higher than 0.02 mol/L. The stiffness parameter B determined for KSPS in THF 50% agrees with values from the literature.

Theoretical treatments based on Fixman's theory and on the electrostatic wormlike theory were applied to the data, with good agreement between the predicted and experimental behavior of sulfonated polystyrenes with more than 19 mol % of ionic groups on the backbone. Below this level (11 mol % ion content) a large deviation from the prediction was observed. The behavior of the less sulfonated polystyrenes, showing a poor agreement with empirical and theoretical models, suggests the limitation of current theories of polyelectrolytes, which have been derived for strongly charged polyelectrolytes, to deal with weakly charged polymers.

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References and Notes

(1) Hara, M. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993.
(2) Campos, A.; Garcia, R.; Suñer, I.; Figueruelo, J. *Polymer* **1997**, *38*, 3011−3016.
(3) Tong, Z.; Ren, B.; Gao, F. *Polymer* **2001**, *42*, 143−149.
(4) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(5) Hara, M.; Lee, A. H.; Wu, J. *J. Polym. Sci., Part B* **1987**, *25*, 1407−1418.
(6) Kupperblatt, G.; Hara, M.; Vanhoorne, P.; Jérôme, R. J. *Polymer* **1996**, *37*, 3741−3744.
(7) Young, A. M.; Garcia, R.; Higgins, J. S.; Timbo, A. M.; Peiffer, D. G. *Polymer* **1998**, *39*, 1525−1532.
(8) Lundberg, R. D.; Philips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143−1154.

(9) Hara, M.; Wu, J.; Lee, A. H. *Macromolecules* **1989**, *22*, 754−757.
(10) Güler, H.; Aras, L. *Br. Polym. J.* **1990**, *22*, 245−248.
(11) Hara, M.; Wu, J. L. *Macromolecules* **1988**, *21*, 402−407.
(12) Weiss, R. A.; Ghebremeskel, Y.; Charbonneau, L. *Polymer* **2000**, *41*, 3471−3477.
(13) Campos, A.; Garcia, R.; Suñer, I.; Figueruelo, J. E. *Polymer* **1997**, *38*, 3011−3016.
(14) VanderHart, D. L.; Feng, Y.; Han, C. C.; Weiss, R. A. *Macromolecules* **2000**, *33*, 2206−2227.
(15) Bodart, P.; Nunes, T.; Eisenberg, A.; Kim, J. S.; Amoureux, J. P. *Polymer* **1999**, *40*, 569−576.
(16) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924−933.
(17) Essafi, W.; Lafuma, F.; Williams, C. E. In *Macro-ion Characterization*; American Chemical Society: Washington, DC, 1994; Vol. 548, pp 278−286.
(18) Manning, G. S. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 909−922.
(19) Manning, G. S.; Ray, J. *J. Biol. Struct. Dyn.* **1998**, *16*, 461−476.
(20) Heath, P. J.; Schurr, J. M. *Macromolecules* **1992**, *25*, 4149−4159.
(21) Mita, K.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 504−508.
(22) Makowski, H.; Lundberg, R. D.; Simghal, G. H. US Patent 3 870 841, 1975.
(23) Baigl, D.; Seery, T. A. P.; Williams, C. E. *Macromolecules* **2002**, *35*, 2318−2326.
(24) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 310.
(25) Natansohn, A.; Eisenberg, A. *Macromolecules* **1987**, *20*, 323−329.
(26) Frisch, H. L.; Simha, R. In *Rheology: Theory and Applications*; Eirich, F. R., Ed.; Academic Press: New York, 1956; Vol. 1, Chapter 14.
(27) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716−2718.
(28) Lifson, S.; Katchalsky, A. *J. Polym. Sci.* **1954**, *13*, 43−55.
(29) Smidsrød, O.; Haug, A. *Biopolymers* **1971**, *10*, 1213−1227.
(30) Mandel, M. *Eur. Polym. J.* **1983**, *19*, 911−918.
(31) Fixman, M. *J. Chem. Phys.* **1964**, *41*, 3772−3778.
(32) Davis, R. M.; Russel, W. B. *Macromolecules* **1987**, *20*, 518−525.
(33) Raziel, A.; Eisenberg, H. *Isr. J. Chem.* **1973**, *11*, 183−199.
(34) Odijk, T.; Houwaart, A. C. *J. Polym. Sci.* **1978**, *16*, 627−639.
(35) Odijk, T. *Biopolymers* **1979**, *18*, 3111−3113.
(36) Tobitani, A.; Ross-Murphy, S. B. *Polym. Int.* **1997**, *44*, 338−347.
(37) Weill, G.; Des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99−105.
(38) Yamakawa, H. In *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(39) Skolnik, J.; Fixman, M. *Macromolecules* **1978**, *11*, 867−871.

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