Preparation and Characterization of Hydrosoluble, Partially Charged Poly(styrenesulfonate)s of Various Controlled Charge Fractions and Chain Lengths

Damien Baigl, Thomas A. P. Seery,[†] and Claudine E. Williams*

Laboratoire de Physique de la Matière Condensée, CNRS URA 792, Collège de France,
11, place Marcelin Berthelot, 75231 Paris Cedex 05, France

Received October 1, 2001; Revised Manuscript Received December 4, 2001

ABSTRACT: A series of hydrophobic polyelectrolytes with narrow molecular weight distributions and well-characterized fractions of charged monomers on the hydrophobic backbone has been prepared. These polymers are derived from the controlled sulfonation of a series of polystyrene standards with low polydispersity indices. We have used a gentle sulfonation method that had previously been designed for ionomers. Because we wished to push this reaction to higher sulfonation levels, a careful characterization of the product materials was necessary. The sulfonation level of each sample has been determined by NMR and elemental analysis, and the efficacy of NMR for this purpose has been demonstrated. Size exclusion chromatography (SEC) measurements in mixtures of acetonitrile and water have shown that under nearly all sulfonation conditions tested here the mass distribution of the resulting copolymer was the same as that of the parent standard material. The sulfonation reaction has been optimized and characterized according to the dependence of sulfonation level on reaction time, initial reagent concentrations, and molecular weight of precursor polystyrene.

1. Introduction

The study of ion-containing hydrophobic polymers has long emphasized the behaviors of either fully charged molecules, those possessing a charged moiety on every hydrophobic monomer, or molecules where not more than about 10% of monomers are charged. The former, called polyelectrolytes,[1−3] are soluble in water whereas the latter are only soluble in organic nonpolar solvents and are called ionomers.[4,5] Sulfonated polystyrene (PSS) has had the rare privilege of serving as a model system to study polyelectrolyte behavior when fully charged as well as ionomer characteristics at low charge. The large gap in the range of chemical structures from ionomers to fully charged polyelectrolytes is the domain of hydrophobic polyelectrolytes. In this range partially charged PSS may also be considered as a model for natural[6,7] and bio-molecules[8] but also as polymer material used in many applications such as waste treatment, cosmetology, and pharmacology.

The behavior of hydrophobic polyelectrolytes is governed by the percentage of charges along the polymer backbone. For PSS the charge fraction is equal to the sulfonation level f, which is expressed as the percentage of sulfonated monomers in a chain (e.g., $f = 50\%$ means that every second monomer is sulfonated on average). The range of interest here is $30\% \leq f \leq 95\%$. This is also the range where PSS is soluble in water at room temperature. However, the charge fraction macroscopically observed is less than f; it is called the effective charge fraction and abbreviated f_{eff}. The reduction of f_{eff} can be quite large. In the case of classical polyelectrolytes where the behavior is dominated by electrostatic interactions (in practical terms, when the uncharged monomers are hydrophilic), the effective charge fraction in the Manning counterion condensation model[9,10] is predicted to be $f_{\mathrm{eff}} \sim 36\%$ for all values of f superior to 36%. Experimental data have confirmed this effect of charge renormalization to a constant value in dilute solution[11,12] and more recently at higher concentration for classical polyelectrolytes such as PAMAMPS (poly(acrylamide-*co*-sodium 2-acrylamido-2-methylpropanesulfonate).[13] For hydrophobic polyelectrolytes in aqueous solution such as PSS sodium salts, abbreviated NaPSS, the situation is more complex mostly due to the hydrophobic nature of the backbone.[14] In this case, the properties are due to a competition between electrostatic interactions and hydrophobic ones. Charge renormalization is also observed, but it leads to a linearly increasing value of f_{eff} from 0 (for $f = 27\%$) to about 30% (for $f = 100\%$),[11] where f_{eff} approaches the prediction of Manning condensation theory. When $f < 27\%$, NaPSS (parent PS of $M_{\mathrm{w}} = 250$ kg mol^{-1}) is insoluble in water. Thus, the sulfonation level f is an extremely important parameter because it will influence the fundamental and practical physicochemical properties of hydrophobic polyelectrolytes such as NaPSS.

A recent review[15] of sulfonation methods for polymers covers a range of conditions that include both homogeneous and heterogeneous sulfonating agents. Methods of preparation for highly charged sodium poly(styrenesulfonate) (NaPSS) often rely on harsh conditions[16] in which case one must be concerned with degradation or cross-linking in the product materials. These problems should be less severe with the milder methods that exist for preparing ionomers. Makowski's method[17] had been previously adapted[18] to obtain higher charge contents without any apparent degradation. Because of the recent strong interest in well-defined (i.e., controlled charge content and mass distribution) hydrophobic polyelectrolytes,[19−23] it has proved necessary to fine-tune this method.

With this perspective we have prepared a series of poly(styrenesulfonate)s with $30\% \leq f \leq 95\%$ for samples spanning $2^{1}/_{2}$ decades of molecular weight. This was

---

[†] Permanent address: Polymer Program and Department of Chemistry, University of Connecticut, Storrs, CT 06269.

10.1021/ma011707o CCC: $22.00

Table 1. Properties of Parent PS

	characterization according to the manufacturer				SEC measurements results[d]			
name	M_n[a] (g mol^{-1})	M_w[b] (g mol^{-1})	M_w/M_n	DP$_w$[c]	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n	DP$_w$
PS122	12 900	13 500	≤1.06	130	11 000	12 700	1.15	122
PS410	45 500	47 900	≤1.06	461	38 200	42 600	1.11	410
PS1320	145 000	152 000	≤1.06	1470	124 000	137 000	1.11	1320
PS2360	231 000	245 000	1.06	2360	*e*	*e*	*e*	*e*
PS2520	275 000	289 000	≤1.06	2780	241 000	262 000	1.09	2520

[a] Number-average molecular weight determined by SEC in THF for PS from Polymer Source (PS2360) and by membrane osmometer in THF and SEC in THF for PS from Pressure Chemicals Co. [b] Weight-average molecular weight determined by SEC in THF for PS from Polymer Source (PS2360) and by low-angle light scattering in THF and by SEC in THF for PS from Pressure Chemicals Co. [c] Weight-average degree of polymerization DP$_w$ = M_w/104. [d] SEC measurements are performed at LPMC laboratory, ESPCI, Paris. [e] No data.

obtained by optimizing the experimental conditions of the sulfonation reaction after a systematic study of the following parameters: reaction time, initial reagents concentration, and molecular weight of the precursor polystyrene. To characterize precisely the synthesized polyelectrolytes, the mass distribution was determined by careful SEC measurements in mixtures of acetonitrile and water, and the sulfonation level was determined by NMR.

2. Experimental Section

2.1. Analytical Measurements. a. Sulfonation Fraction. Proton NMR measurements were performed with a Bruker AM-200 spectrometer (200 MHz). A lyophilized NaPSS sample was placed in a 5 mm Wilmad NMR tube and dissolved in 1 mL of dimethyl-d_6 sulfoxide (DMSO-d_6) from Aldrich Chemical Co. or deuterium oxide, D_2O, from the SDS Co. (France). Lightly sulfonated samples were dissolved in deuterated chloroform $CDCl_3$ (Aldrich). The concentration of NaPSS in deuterated solvent was precisely known by weight measurement. The best compromise to have good signal while minimizing viscosity effects on relaxation times corresponded to a polymer concentration of 0.5 wt % in the NMR solvent. The chemical shifts were referenced to the following residual solvent peaks $\delta_{\mathrm{DMSO}} = 2.49$ ppm, $\delta_{\mathrm{H_2O}} = 3.5$ ppm, and $\delta_{\mathrm{CHCl_3}} = 7.26$ ppm. Typical NMR spectra were obtained by averaging of 32 acquisitions, and integration was performed using the Bruker supplied software where the aliphatic band ($\delta = 0.8-2$ ppm) was given an area of 3, corresponding to the number of aliphatic protons per monomer.

Elemental analyses performed at Service Central d'Analyse of C.N.R.S. provided the weight percentage of carbon (% C), sodium (% Na), and sulfur (% S) in 30 mg samples of lyophilized NaPSS. In this way, the sulfonation level could be easily determined by taking into account the relative masses of atoms in a monomer unit: $f_{/\mathrm{S}} = (96/32) \times (\%\ \mathrm{S}/\%\ \mathrm{C}) \times 100\%$ according to the sulfur carbon ratio, or $f_{/\mathrm{Na}} = (96/23) \times (\%\ \mathrm{Na}/\%\ \mathrm{C}) \times 100\%$ by using the sodium amount. The error for this measurement is estimated to be 5%.

b. Molecular Weight Distribution. Molecular weight distributions were determined by size exclusion chromatography (SEC) measurements. The SEC measurements of parent PS were performed in THF at Laboratoire de Physico-Chimie Macromoléculaire (ESPCI, Paris, France). The SEC measurements of hydrophobic NaPSS were performed at Laboratoire des Systèmes Complexes Chargés (DRECAM/CEA, Saclay, France). They were made using a Shimadzu LC-9A pump (Tokyo, Japan) and a Knauer differential refractometer (Berlin, Germany) as detector. The exclusion column set was made up of four Shodex OHpak columns, SB-806, 805, 804, and 803 HQ, and a protective precolumn, Ohpak SB-800P (Showa Denko Japan). Samples with concentrations of approximately 1 mg mL^{-1} were introduced into the exclusion columns with a 200 μL loop valve injector, Rheodyne 7125 (Cotati).

The eluent for the hydrophobic polyelectrolytes was a mixture of aqueous 0.1 M sodium nitrate and acetonitrile in either 80/20 or 60/40 ratio. The importance of the nature of the eluent is discussed below. The flow rate was set at 1.0 mL/min and measurements were performed at room temperature. The calibration was established for each solvent condition from the injection of four low-polydispersity, fully charged NaPSS standards ranging in molar weight from 8×10^3 to 5×10^5 g mol^{-1} obtained from Sopares (Paris, France) and Polymer Laboratories (Shropshire, UK).

2.2. NaPSS Preparation. a. Chemicals. Five parent polystyrene (PS) standards have been used in the synthesis of our hydrophobic polyelectrolytes: PS122, PS410, PS1320, and PS2520 from Pressure Chemicals (Pittsburgh, PA) and PS2360 from Polymer Source (Dorval, Canada). The manufacturer certified characteristics are shown in Table 1 along with results from our own analysis.

Sulfuric acid (H_2SO_4) from Merck Co. (Darmstadt, Germany) was certified 95−97% (sulfuric acid fraction) and analysis grade. 1,2-Dichloroethane (DCE) from SDS Co. (Peypin, France) was synthesis grade (purity ≥99%). Acetic anhydride from Fluka Co. was synthesis grade (purity ≥99.5%). Sulfonations were performed under a nitrogen blanket, U grade from Air Liquide (France). Liquid nitrogen was also obtained from Air Liquide Co. Triply distilled water, conductivity 5 μS cm^{-1}, was produced in a quartz distillation column. Milli-Q water was produced by the Milli-Q RG system from Millipore Co.; its quality was checked by conductivity measurement to be less than 10^{-1} μS cm^{-1}.

b. NaPSS Synthesis. *Sulfonation.* The synthesis is derived from the procedure developed by F. Lafuma and W. Essafi[18] based on Makowski's method.[17] A Quickfit three-neck, round-bottom glass flask with angled necks was charged with 1 g of parent PS (9.6×10^{-3} mol of monomer). The middle neck was topped by a water-cooled condenser, and gaseous nitrogen was introduced through the right-hand neck with pressure and flow rate controlled by a gas valve. Liquid reagents were introduced through the left-hand neck from a capped dropping funnel with pressure-equalization arm and Teflon stopcock. The tank reactor was immersed in a stirred water bath at a controlled temperature. The sulfonation reaction was run under a slight overpressure of nitrogen flowing through a bubbler that was attached to the top of the condenser. Each sulfonation reaction was performed under a dry nitrogen atmosphere in order to minimize the desulfonation reaction initiated by the presence of water.

The parent PS was first dissolved in 14 mL of DCE, and it was then stirred for 1 h under a nitrogen atmosphere at 50 °C. A quantity of acetic anhydride was added slowly through the dropping funnel; it was subsequently charged under flowing nitrogen with the required amount of H_2SO_4, which was added in the same way. For all reactions the volume ratio of acetic anhydride to sulfuric acid was held at 1.5, which corresponds approximately to an equimolar ratio of those two reagents (molar ratio: $n_{\mathrm{H_2SO_4}}/n_{\mathrm{AA}} = 1.1$). The reaction mixture was maintained at 50 °C throughout the reaction time that could be as long as 15 h. The reaction was quenched by placing the hot reaction vessel in a cold water bath at 10 °C.

Isolation. The reaction workup and isolation of the polymer were complicated by the fact that the polymer solubility is a strong function of the sulfonation level. One of two procedures was used depending on the state of the cooled reaction mixture. If the reaction mixture was homogeneous, which occurred for short reaction times (≤30 min) that yielded $f < 30\%$, the organic solvent DCE was removed by rotary evaporation at

40 °C until boiling of DCE in the vacuum flask stopped. If the state of the polymer solution after the reaction was heterogeneous, i.e., the modified polymer had precipitated during the reaction which is typical of $f \geq 30\%$, then DCE was easily removed by decantation. The organic phase was demonstrated to be free of polymer by evaporation. In both cases the resulting polymer was poly(styrene-*co*-styrenesulfonic acid) (HPSS) and had the appearance of chewing gum.

Purification. This material was dissolved in 100 mL of triply distilled water. DMSO could be used instead of water in the following steps if the polymer was not soluble in water (i.e., $f < 30\%$). HPSS was converted into NaPSS by slowly adding NaOH until the solution pH reached 10 in order to make sure that every sulfonic group was converted into the sodium salt form. At this step the polymer solution usually looked slightly cloudy. It was made transparent by evaporating the DCE traces presumably sequestered by the hydrophobic parts of the polymer in a rotavapor. The importance of this step on the reaction yield will be discussed later. The clear solution was then filtered under vacuum through a poly(vinylidene difluoride) (PVDF) membrane (Durapore membrane 0.45 μm from Millipore) in a Millipore filtration unit in order to remove insoluble residual parts from the solution. No insoluble material was seen for sulfonation levels $f \geq 40\%$, and the small amounts found at lower levels are presumed to be unsulfonated polymer. Then the volume of the filtered solution was reduced by rotary evaporation to between 50 and 100 mL, depending on the polymer solubility. The concentrated solution was loaded into a dialysis membrane bag and dialyzed against 2.0 L of triply distilled water to remove the bulk of the ions (NaOH in excess, sulfates, acetates). A molecular weight cutoff of 6800 g mol^{-1} was used for polymers derived from PS13.5 while a cutoff of 12 000−14 000 g mol^{-1} was used with all higher molecular weights. This initial dialysis was followed by successive dialyzes against 2.0 L volumes of Milli-Q water in capped polypropylene funnels. The purification efficiency was monitored by a continuous conductivity measurement where data acquired by an Inolab 2 conductivity meter (WTW Co., Germany) was collected by computer via a RS232 interface and treated using custom software. A TetraCon 325 conductivity cell with four graphite electrodes (cell constant 0.475 cm^{-1}) was used for higher conductivities (100 μS to 1 S cm^{-1}) and a LR 325/01 conductivity cell (cell constant 0.100 cm^{-1}) for conductivities less than 100 μS cm^{-1}. In this way the progress of the dialysis could be tracked, and the water outside the membrane bag could be replaced by pure Milli-Q water whenever its ionic strength had reached a constant level. This procedure was repeated until the Milli-Q water outside the dialysis bag had the same equilibrium conductivity as a control volume of pure Milli-Q water. This procedure took 2 weeks on average depending on the volume ratio between the dialysis bag and the outside water and on the frequency of changes of dialysis solvent. Finally, the dialyzed solution was frozen under atmospheric pressure in liquid nitrogen prior to lyophilization. The dried sulfonated polymers were stored in screw-capped polypropylene bottles.

3. Results and Discussion

Our goal at the outset of this study was to prepare a series of NaPSS of narrow molecular weight distribution and well-characterized charge fraction for future studies. Therefore, our minimal requirements were that we should be able to vary the charge fraction and to measure it conveniently and precisely even if we could not predetermine this number via control of the reaction conditions. Furthermore, we hoped to demonstrate that the chain length distribution was not affected by the sulfonation procedure. Elemental analysis has been the standard method for assessing the fraction of sulfonated monomers, *f*, and is fairly robust to the most common impurity found in charged polymers, which is water. A varying amount of water hydrates the sulfonate moieties to a degree that depends on local humidity and that requires heroic efforts to remove. However, elemental analysis is a destructive method of analysis that is typically performed offsite and is affected by the second most common impurity in these samples, Na_2SO_4. Therefore, we wished to develop a standard procedure for characterizing the percentage, *f*, using common spectroscopic tools of organic synthesis such as NMR and IR.

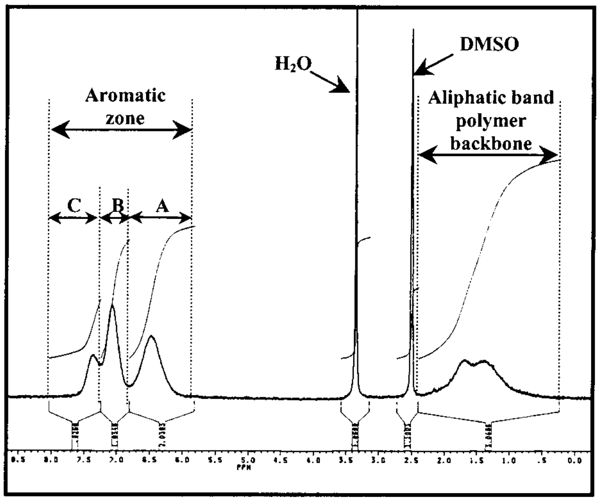

Figure 1. Typical ^{1}H NMR spectrum of NaPSS ($DP_w = 410$, $f = 39\%$) in DMSO-d_6 showing the aromatic zone, the solvent peaks, and the aliphatic band corresponding to the polymer backbone.

3.1. NMR Measurement. a. Spectra Analysis. A typical ^{1}H NMR spectrum of partially sulfonated NaPSS in DMSO-d_6 is shown in Figure 1. It is composed of a broad band ($\delta = 0.8-2$ ppm) corresponding to the three aliphatic protons of the polymer backbone, a sharp peak corresponding to the residual protons from the imperfect deuteration of the solvent DMSO ($\delta = 2.49$ ppm), a second sharp peak attributed to water ($\delta = 3.35$ ppm), and three broader peaks with roughly Gaussian shapes in the aromatic region of the spectrum. We have labeled the latter three peaks A (maximum at $\delta = 6.5$ ppm), B (maximum at $\delta = 7.1$ ppm), and C (maximum at $\delta = 7.35$ ppm).

Peaks assignments in the aromatic zone were done by comparison between different spectra.

Figure 2 shows a spectrum of the parent PS in $CDCl_3$ (a), a partially sulfonated polystyrene in DMSO-d_6 (b), and a fully sulfonated NaPSS (obtained by polymerization of styrene sodium sulfonate) in D_2O (c) over the range 5.5−8.5 ppm. Peak A was attributed to the two ortho protons on the pendant aromatic ring; it was visible in the same position in all spectra for all sulfonation levels. Furthermore, the relative area of this peak is roughly in a 2 to 3 ratio to the aliphatic protons in the broad band between 0.8 and 2.0 ppm for all sulfonation levels.

Peak B was observed in the parent PS spectrum and corresponds to meta and para protons on unsulfonated aromatic rings which are indistinguishable from each other due to the naturally broadened spectrum of a polymer. The ratio of the area of this peak to peak A is 3:2. The identification of this peak was confirmed by its absence in the spectra of fully sulfonated NaPSS where the sulfonate group shifts the resonances of the meta protons upfield. In partially sulfonated NaPSS the relative area of peak B was always less than 3 due to the reduction in the fraction of unsulfonated rings.

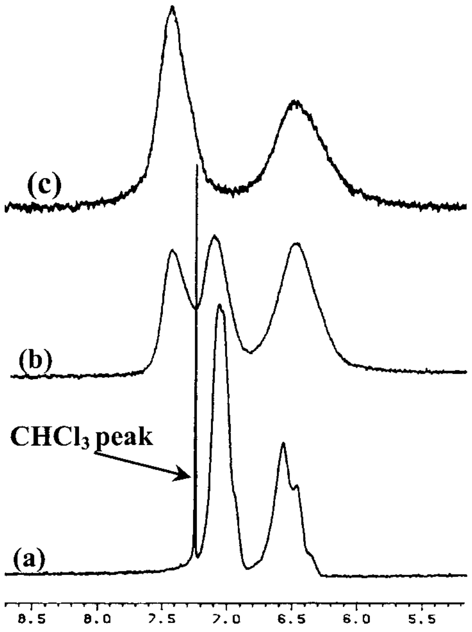

Figure 2. ^1H NMR aromatic zone of parent PS ($DP_w = 410$) in $CDCl_3$ (a), partially sulfonated NaPSS ($DP_w = 410$, $f = 56\%$) in DMSO-d_6 (b), and fully sulfonated NaPSS in D_2O (c).

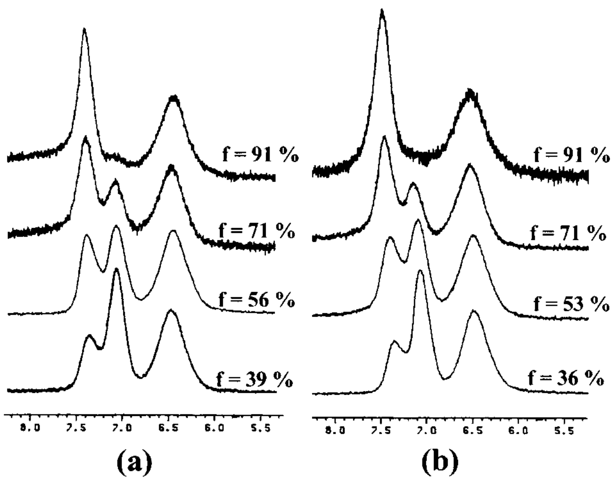

Figure 3. ^1H aromatic zone of NaPSS in DMSO-d_6 of two chain lengths $DP_w = 410$ (a) and $DP_w = 1320$ (b) of several sulfonation levels.

Peak C was observed for fully sulfonated NaPSS (maximum at $\delta = 7.35$ ppm) and did not appear in the parent PS spectrum, and it is thus due to meta protons on the sulfonated aromatic rings. The position of peak C was shifted from that of peak B ($\delta = 7.1$ ppm) due to the electron-withdrawing nature of the adjacent sulfonate group.

The influence of the sulfonation level in the aromatic part of spectrum is shown in Figure 3 where spectra of two series of four NaPSS with different sulfonation levels, as determined by elemental analysis, are presented in two stack plots. If we focus on a series, i.e., one chain length, it is clear that the ratio of peak C area over peak B area is increasing with the sulfonation level.

b. Comparison with Elemental Analysis. Protons corresponding to peaks A, B, and C are labeled H_A, H_B, and H_C, respectively, in the structure drawn in Figure 4 of partially sulfonated NaPSS of sulfonation level f ($f = 100x$, where x is the mole fraction of sulfonated monomers $0 \leq x \leq 1$). Using this nomenclature, areas of different peaks of NaPSS for a sulfonation level f will be proportional to: for aliphatic protons $I_{\text{aliphatic}} = 3$, for H_A protons $I_A = 2$, for H_B protons $I_B = 3(1 - x)$, and for H_C protons $I_C = 2x$.

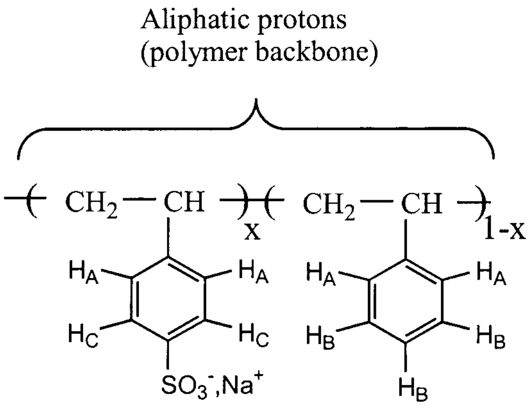

Figure 4. Representation of the average monomer of NaPSS of sulfonation level $f = 100x$ ($0 \leq x \leq 1$) with correspondence between protons and their position in the ^1H NMR spectrum.

The most straightforward way to obtain f would be $f = 100 I_C/I_A$. But that method provided inconsistent values of the sulfonation level. For example, for the fully sulfonated polystyrene shown in Figure 2 the ratio I_C/I_A is measured to be 1.2 instead of 1. This is probably the result of the ortho protons having a longer relaxation time than the aromatic protons that are farther from the chain backbone.

In view of this fact, it seemed more appropriate to use protons in the same position relative to the chain backbone but chemically different. Therefore, peaks B and C were used to estimate sulfonation levels. If α is the ratio $\alpha = I_C/I_B$, then the sulfonation level f determined by NMR, abbreviated f_{NMR}, is given by $f_{\text{NMR}} = 100x = 100[3\alpha/(2 + 3\alpha)]$. At this step, we used several methods of integration in order to obtain α. The first one took advantage of the integrator included in the Bruker spectrometer. However, it does not curve-fit the peaks but simply sums the spectrum between user specified values of δ. A more rigorous method consisted in fitting the aromatic region of the spectrum with a sum of three Gaussian peaks, $y(\delta) = a \exp[b(\delta - c)^2]$. In this way integration of a peak is proportional to $ab^{-1/2}$ where a corresponds to the height of the peak and b to its width. In this case α is given by $\alpha = (a_C/a_B)(b_C/b_B)^{-1/2}$. A third and simplest approach to estimate α consisted in measuring the height of the peaks only and setting $\alpha = h_C/h_B$, i.e., the ratio of peak heights. This last method could be improved upon by using some results of the Gaussian fits. According to the fit, results for several spectra $(b_C/b_B)^{-1/2}$ were approximately constant to 0.91 and not influenced by the sulfonation level or chain length. This last method thus finds $\alpha = 0.91 h_C/h_B$, and we will refer to this as a modified peak heights ratio.

In Figure 5, these four approaches to analyzing the NMR data are compared with the results of elemental analysis. Results are presented for two lengths of chain (a and b: $DP_w = 410$; c and d: $DP_w = 1320$). To characterize the relative accuracy of elemental analysis, two ratios of weight percentage in atom are used to determine the sulfonation level: % S/% C and % Na/% C. Each graph gives the sulfonation level determined by NMR using all four methods of integration (black symbols) vs the sulfonation level given by elemental analysis (according to % Na/% C ratio in Figure 5a,c

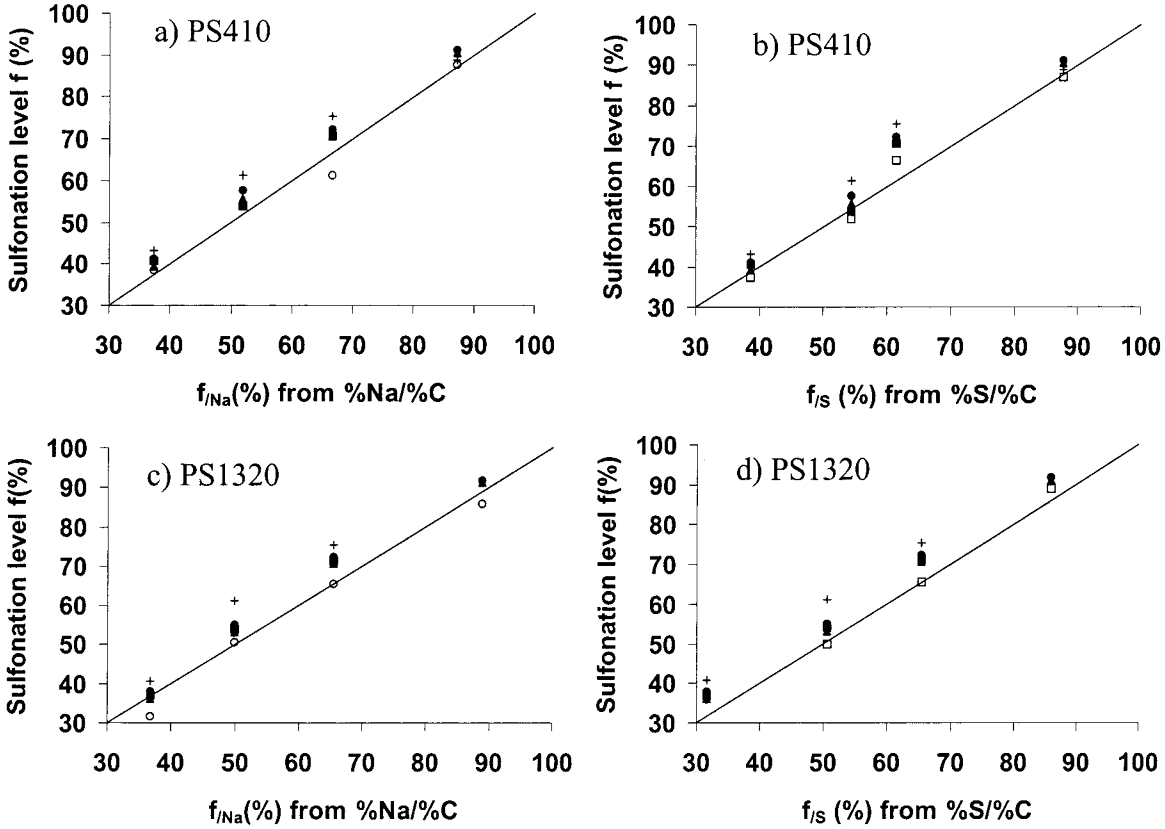

Figure 5. Comparison between ^{1}H NMR and elemental analysis determinations of sulfonation level for two molecular weights of parent polymer (a, b: PS410, $M_w = 42.6$ kg/mol; c, d: PS1320, $M_w = 137$ kg/mol). Each graph plots sulfonation level, *f*, from all four methods of integrating the NMR spectra against the *f* determined by elemental analysis (■, Gaussian fit; +, Bruker integrator; ●, peak heights ratio; ▲, modified peak heights ratio). The *f* determined from the second possible atomic ratio is also included to compare the NMR accuracy to the self-consistency of the elemental analysis data (○, % S/% C; □, % Na/% C). Lines are drawn on each graph with a slope of 1.

and to % S/% C ratio in Figure 5b,d). In each graph, the result given by using the same elemental analysis but the other element ratio is added (white symbol) in order to compare the accuracy of NMR method with elemental analysis.

Because NMR peaks are slightly overlapping, it is clear that using the Bruker integrator without separating peaks cannot give a precise measurement, and the sulfonation level is always overestimated (from 10% to 20% overestimation). For example, in Figure 5c the integrator provided an *f* value of nearly 60% vs 50% for the elemental analysis, a 10% difference that is 20% of the actual sulfonation level.

The three other methods (Gaussian fitting, peak heights ratio, and modified peak heights ratio) gave very close results which demonstrate the robustness of NMR and the sulfonation levels determined by these methods are in good agreement with those obtained by elemental analysis. The difference between results given by NMR and elemental analysis using a specific ratio of atoms is comparable to the variation observed in elemental analysis results from one ratio of atoms to the other, indicating that NMR is at least as accurate as elemental analysis.

The easiest calculation of α is from the peak heights ratio but this method systematically overestimated *f*. The Gaussian fit gave good results, but it is cumbersome because one must scan and digitize the spectra or access lesser known functions on the NMR computer. The quality of Gaussian fits degraded at high sulfonation levels (around 90%) because it was difficult to fit peak B when the amplitude was very low. The modified peak heights ratio method gave excellent results at any sulfonation level; it is very easy to perform since only the heights of peaks are needed once influence of the width has been determined.

c. Influence of the Chain Length. In Figure 3a the influence of sulfonation level on the aromatic region is shown for one chain length ($DP_w = 410$). Shapes of these spectra can be compared with those shown in Figure 3b obtained for roughly the same sulfonation levels at another chain length ($DP_w = 1320$). Qualitatively, the shape and amplitude of the aromatic region are determined by sulfonation level alone and are insensitive to the chain length. Quantitative comparison is presented in Figure 5 where the accuracy of an NMR determination of *f* is shown not to depend on the length of the chain. It can be understood by the fact that NMR relaxation times are local phenomena and do not depend on the long-range connectivity between monomers at these molecular weights.

d. Influence of the NMR Solvent. For NaPSS polymers that were soluble in both water and DMSO (i.e., sulfonation levels from 30 to 95%), the sulfonation level determined by ^{1}H NMR was exactly the same for either DMSO-d_6 or D_2O. Although homopolymers of styrene are not soluble in DMSO, the hydrophobic polyelectrolytes of NaPSS form clear solutions for $18\% \le f \le 95\%$. The fact that the solvent had no influence on the sulfonation level determination is further evidence of the robustness of NMR for determining *f*. For fully sulfonated NaPSS (obtained by polymerization of styrenesulfonate) D_2O was used as NMR solvent.

e. Conclusion about NMR Measurements. The determination of the sulfonation level by NMR was found to be at least as accurate as elemental analysis. It is also a quicker and easier analytical method because it can be performed on the spot where an NMR spectrometer is available. Furthermore, it is a nondestructive method (contrary to elemental analysis) because the polymer can be easily recovered by dialysis against water followed by freeze-drying. As a measure of purity, NMR is a reasonable tool for detecting organic impurities such as residual solvent in the 1−2% range particularly because small molecule peaks are much sharper than the polymer peaks. Proton NMR is also insensitive to the presence of aprotic mineral impurities since only protons are detected contrary to elemental analysis. Last, it needs less material (5 mg vs 30 mg).

3.2. IR Absorption.

In addition to NMR, we used IR spectroscopy to characterize these hydrophobic polyelectrolytes. Determining the sulfonation level using IR absorption measurement is possible, but this approach is hampered by the effects of water. Because water strongly absorbs at IR wavelengths, all measurements must be taken at the same humidity level or water must be excluded to generate a calibration curve. Unless the molar extinction coefficients are known for individual chromophores, the absorption of IR radiation is not simply related to the molar concentrations of various monomers in our study. We attempted to generate such curves using the ratio of the intensity of the alkyl stretch at 2925 cm^{-1} to the sulfonate stretch at 1100 cm^{-1}. The error within a set of determinations made on a single day was >10%, and slopes of calibration curves prepared on different days or using different methods (cast films on NaCl plates vs KBr pellets) varied by as much as a factor of 2. This is most likely the effect of the variable hydration of the sulfonate moiety on the extinction coefficient of the S=O stretch. Therefore, this method cannot be considered as a primary tool for establishing sulfonation levels unless water can be completely eliminated during sample preparation and measurement.

3.3. Characterization of the Sulfonation Reaction.

In this part the preparation of NaPSS according to the procedure described above is analyzed. Sulfonation levels have been determined by ^{1}H NMR using the modified peak heights ratio method.

a. Influence of Reaction Time. The sulfonation level is the parameter that will be used to characterize the extent of reaction. To follow the time course of the reaction, individual batches of NaPSS were quenched at different times. Results for two initial sulfonating agent concentrations and one molecular weight of parent PS (PS2360, $M_w = 245 \times 10^3$ g mol^{-1}) are shown in Figure 6. The initial sections of these kinetics curves (between 0 and 2 h) have second-order shape with an exponentially increasing progress of sulfonation. After 2 h of reaction, the degree of sulfonation goes through a broad maximum before seemingly decreasing because of a probable desulfonation process. We did not explore the range of equilibrium sulfonation levels in this study. We also did not attempt to extract rate constants from these kinetic data as the heterogeneous reaction conditions would have made any interpretation questionable. To observe the effects of changing various reaction conditions, we chose to run the remaining reactions for 2 h before quenching in order to maximize sulfonation levels and minimize any side reactions that might accompany the onset of desulfonation.

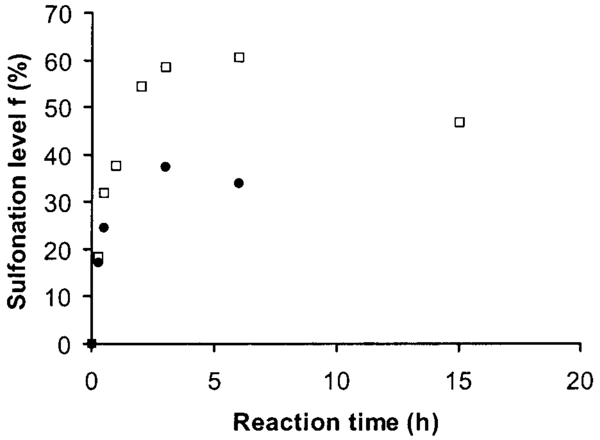

Figure 6. Kinetics of postsulfonation reaction of one parent PS (PS2360, M_w = 245 kg/mol) with two initial sulfonating agent concentrations (□, $[AA]_{t=0}$ = 0.61 mol/L; ●, $[AA]_{t=0}$ = 0.32 mol/L).

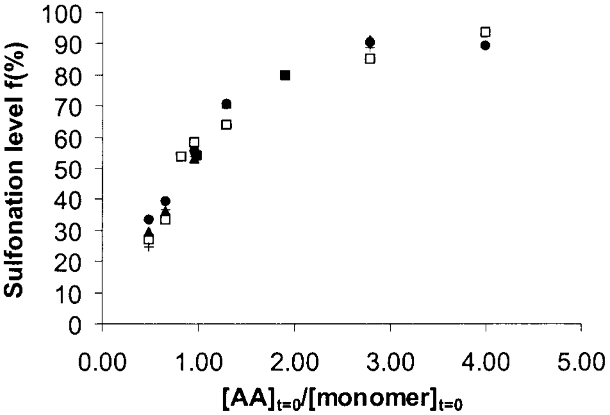

Figure 7. Influence of the ratio of initial sulfonating agent concentration (i.e., acetic anhydride concentration in mol/L) over initial parent PS concentration (in moles of monomer per liter) on sulfonation level after a 2 h reaction for different chain lengths (□, DP_w = 122; ●, DP_w = 410; ▲, DP_w = 1320; ■, DP_w = 2360; +, DP_w = 2520).

b. Influence of Initial Sulfonating Agent Concentration. The strong dependence of the maximum sulfonation level on the concentration of sulfonating agent shown in Figure 6 led us to examine this variable in some detail. Several reactions were run for each of the different parent PS (i.e., different lengths of chain) with 2 h reaction times and for several initial sulfonating agent concentrations in order to obtain the entire range of sulfonation levels. The actual sulfonating agent in this reaction is reported to be acetyl sulfate,[15] which is formed in situ from the mixture of acetic anhydride and sulfuric acid with a 1:1 stoichiometry. One mole of the acetyl sulfate can generate one sulfonic acid group on the polymer. Because H_2SO_4 was in slight excess in the sulfonating mixture, the initial sulfonating agent amount is proportional to the initial concentration of acetic anhydride $[AA]_{t=0}$. In Figure 7 the sulfonation level f (%) is plotted vs the ratio of initial concentration of acetic anhydride $[AA]_{t=0}$ over concentration of parent PS (in monomers) in the initial mixture. The sulfonating agent concentration is reduced by the monomer concentration (although this is held constant) so that the graph can be considered to depict the efficacy of the sulfonating agent at a 2 h reaction time. It is interesting to recall that this reaction has primarily been used to prepare ionomers but that we can, nonetheless, obtain nearly

Table 2. Size Exclusion Chromatography Results for Sulfonated Polystyrenes in Mixed Solvents; Molecular Weights and PDI's Are Calculated from Chromatograms Using Fully Sulfonated Polystyrene Standards in Mixed Solvents Containing Either 20% or 40% Acetonitrile in Water with 0.1 M Sodium Nitrate

M_w PS parent[a] (g mol^{-1})	M_w PSS, calcd[b] (g mol^{-1})	f (%)	20% ACN			40% ACN		
			M_w, SEC	PDI	M_w/M_{calc}	M_w, SEC	PDI	M_w/M_{calc}
12 700	16 800	34	9210	1.09	0.54	15 200	1.09	0.90
42 600	59 000	39	30 500	1.22	0.52	61 100	1.12	1.03
42 600	65 900	56	52 600	1.15	0.80	79 700	1.18	1.21
42 600	72 100	71	69 800	1.16	0.97			
42 600	80 400	91	76 200	1.27	0.95			
137 000	186 000	36	93 100	1.29	0.50	229 000	1.15	1.23
137 000	209 000	53	179 000	1.26	0.86	320 000	1.21	1.54
137 000	232 000	71	251 000	1.38	1.08			
137 000	260 000	91	298 000	1.19	1.14			
262 000	356 000	37	176 000	1.51	0.49	445 000	1.18	1.25
262 000	400 000	54	333 000	1.37	0.83			
262 000	490 000	89	384 000	2.1	0.78			

[a] Weight-average molecular weights, M_w, from SEC measurements reported in Table 1. [b] M_w for the sulfonated polystyrenes calculated from the values in column 1 and the sulfonation fraction, f (column 3), measured by NMR as described in the text.

quantitative conversion of the styrene rings to styrenesulfonic acid with a 3- or 4-fold excess of sulfonating agent. This is well within the range of commercially available samples of poly(styrenesulfonic acid). The second important feature demonstrated by this graph, when the literature on ionomers is considered as well, is that this synthesis provides fine control of sulfonation level over the entire range available.

c. Influence of the Molecular Weight of Parent PS. In Figure 7 one can see that data from several different molecular weights all fall on the same curve so that the sulfonation reaction is shown not to be dependent on chain length.

d. Yield of NaPSS Preparation. Here we define the yield of the preparation as the molar ratio (in percentage) of the final PSS to the initial PS. For 2 h reactions the yield was found to be more than 90% for all sulfonation levels, which is consistent with small transfer losses during workup. This is important for two reasons: first, it indicates that the sulfonation was not accompanied by significant degradation of the polymer, and second, it shows that the sulfonated products were fairly homogeneous and were not mixtures of components with greatly different sulfonation levels and thus different solubility. However, it is important to note that such high yields are obtained only if organic solvent residues (DCE) are removed by rotary evaporation before the filtration step. Yields were often below 50% when the evaporation of residual DCE was not performed. After dissolution of HPSS in water and neutralization, the resulting aqueous solution of NaPSS was usually cloudy as noted earlier. Cloudiness is believed to be due to sequestering of DCE molecules by hydrophobic parts of the polymers that can act as an emulsion. It was difficult to filter the solutions in this state with standard filtration devices, and some material can be lost during this step.

e. NaPSS Molecular Weight Distribution. It is important to establish whether the sulfonation reaction has a deleterious effect on the molecular architecture, i.e., in the present case the molecular weight and its distribution. While the absolute determination of average molecular weights for a series of samples such as these would be a laborious project outside the scope of the current effort, a calibrated measurement could be obtained from GPC. Attempts to elute the polymers using water with added salt as the solvent did not meet with success as the polymer, not surprisingly given its amphiphilic nature, did not exit the column. However, satisfactory elution curves were obtained with mixtures of water and acetonitrile. In fact, polymers over our entire range of sulfonation fraction were eluted using either 80/20 or 60/40 water/acetonitrile mixtures. The results from these chromatograms are summarized in Table 2. Figure 8 is a composite of the elution curves for the same polymers as shown in Figure 3 where the $DP_w = 410$ for the parent polymer and $f = 39$, 56, 71, and 91%. At the two highest sulfonation fractions the molecular weight calculated from the measured value of f and from the parent molecular weight corresponds almost exactly to the molecular weight of the equivalent poly(styrenesulfonate) standard. At the two lower sulfonation fractions there is a growing disparity between the hydrophobic polyelectrolytes and the fully sulfonated standard materials. This comparison is clearly seen in Table 2 where the ratio the calibrated to the calculated value of molecular weight is seen for several of our partially sulfonated polystyrenes. We can change the apparent molecular weight of these polymers by eluting with a less polar solvent. Figure 9 is a comparison of the elution curves for a $DP_w = 410$ polymer at $f = 39\%$ being eluted in an 80/20 and a 60/40 mixture of water/acetonitrile. The less polar environment provides a larger (nearly double) molecular weight as expected for the more hydrophobic polyelectrolyte. This implies that

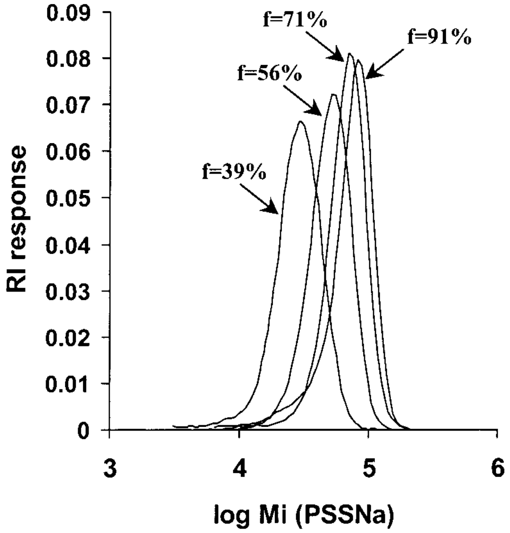

Figure 8. Size exclusion chromatograms of PS410 at four sulfonation levels (39, 56, 71, and 91%) eluted in 20% acetonitrile/80% 0.1 M sodium nitrate solution.

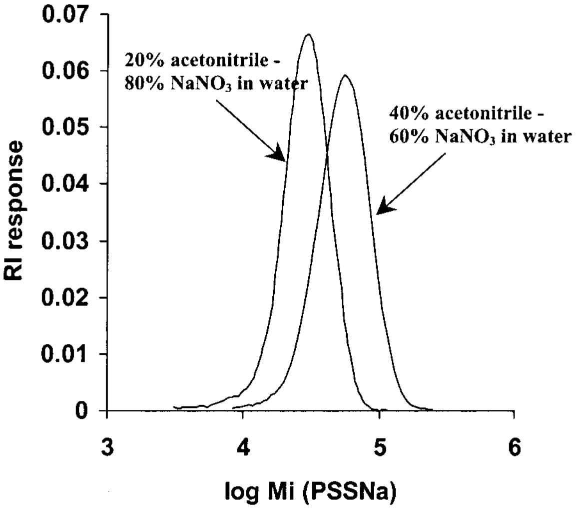

Figure 9. Size exclusion chromatograms of PS410 at 39% sulfonation level eluted in 20/80 and in 40/60 solutions of acetonitrile/0.1 M sodium nitrate, respectively.

partially sulfonated materials have conformations in solution that reflect some phase separation on short length scales (less than polymer dimensions) that is manifest as a differential swelling of the various components of a chain.

The shape of the elution curves reveals narrow molecular weight distributions for all sulfonation levels of the three lowest degrees of polymerization, and for this series of polymers the polydispersity indices are all less than 1.4. However, the longest chain in this study, $DP_w = 2520$, shows significant broadening of the distribution at the highest sulfonation levels. There are two possibilities that we must consider: cross-linking and chain scission. Cross-linking reactions will lead to higher molecular weight materials while chain scission will lower the overall molecular weight. It is important to note at this point that the yield for the sulfonation reaction used to produce this material was not remarkably different from the other reactions. This rules out the possibility of cross-linking on a scale that would produce insoluble material that would be lost in the filtration step. We also note that the sulfonation level of these polymers is quite high, >90%, so that this broadened molecular weight distribution cannot be the result of polydispersity in the sulfonation level among the cohort of molecules in the sample. Because the sample is completely water-soluble, all the polymers must have $f \geq 30\%$, and at worst, a bimodal mixture that has an overall $f = 90\%$ could be composed of 1 part polymers with $f = 30\%$ and 6 parts polymers with $f = 100\%$. This would not be enough to produce the increase of PDI seen for these polymers. Indeed, we see a broader curve with a slightly lower average molecular weight so that the likely explanation is a combination of cross-linking and scission. As is well-known for polymers, the number of bond breaking or cross-linking reactions necessary to effect this type of change in the molecular weight distribution is on the order of 1 per chain or less than 0.05% change in the extent of reaction parameter for chains with DP = 2000. This level of degradation or cross-linking is not detectable by ordinary chemical or spectroscopic assays for the most part, and it demonstrates the extreme sensitivity of GPC to these chemical events as the effects of bond formation and degradation are multiplied by the long-chain connectivity of these molecules.

4. Conclusion

We have prepared a series of water-soluble partially sulfonated poly(styrenesulfonate)s with narrow molecular weight distributions and various sulfonation levels between $f \sim 30\%$ and 90%. The mass distribution of the synthesized NaPSS has been determined by SEC measurements. Mixtures of acetonitrile and water have proved to be adequate eluents for these amphiphilic molecules in the whole range of charge fractions. To measure sulfonation levels, we developed a method based on NMR measurement. It has been demonstrated as an accurate, quick, easy, and nondestructive method. Both SEC and NMR methods were used to characterize the dependence of the sulfonation reaction on reaction time, initial reagent concentrations, and molecular weight of parent polystyrene. Because the yield of the preparation was always found to be better than 90% and the mass distributions of NaPSS were observed to replicate ones of parent polystyrenes, the synthesis presented here was shown to be a gentle method of sulfonation in the case of not too high molecular weight of parent PS. However, when PS chains are very large ($DP_w > 6000$), some significant degradation was observed.

To conclude, we have presented in this paper a method well adapted to prepare hydrosoluble hydrophobic polyelectrolytes at any desired chemical charge contents and molecular weight distributions as long as the chains are not too large.

Acknowledgment. We thank J. Lesec and S. Mariot for having performed SEC measurements of parent PS in THF. We are highly grateful to M. Delsanti and P. Lixon in obtaining indispensable but nontrivial SEC measurements of partially sulfonated NaPSS in water–acetonitrile mixtures and to P. Guenoun, who brought this method to our attention. We acknowledge M.-A. Guedeau-Boudeville for her experienced support in practical chemistry. C.E.W. is very grateful to R. D. Lundberg and D. Peiffer, who first introduced her to the complexity of ionomer chemistry and for sharing with her their deep knowledge of the field. Fruitful discussions with R. A. Weiss are gratefully acknowledged.

References and Notes

(1) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120,* 51.
(2) Williams, C. E. In *Electrostatic Effects in Soft Matter and Biophysics*; Holm, C., Kékicheff, P., Podgornik, R., Eds.; Kluwer: Dordrecht, 2001.
(3) Barrat, J. L.; Joanny, J. F. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; Wiley: New York, 1996; Vol. XCIV.
(4) Kim, J. S.; Eisenberg, A. *Ionomers*; Wiley: New York, 1998.
(5) *Ionomers: Synthesis, Structure, Properties and Applications*; Tant, M. R., Mauritz, K. A., Wilkes, G. L., Eds.; Chapman & Hall: London, 1997.
(6) Schmitt-Kopplin, P.; Garrison, A. W.; Perdue, E. M.; Freitag, D.; Kettrup, A. *J. Chromatogr. A* **1998**, *807*, 101–109.
(7) Schmitt-Kopplin, P.; Garmash, A. V.; Kudryatsev, A. V.; Perminova, I.; Hertkorn, N.; Freitag, D.; Petrosyan, V. S.; Kettrup, A. *J. AOAC Int.* **1999**, *82*, 1594–1603.
(8) Radlinska, E. Z.; Gulik-Krzywicki, T.; Lafuma, F.; Langevin, D.; Urbach, W.; Williams, C. E.; Ober, R. In *Short and Long Chains at Interfaces*; Daillant, J., Guenoun, P., Marques, C., Muller, P., Trân Thanh Vân J., Eds.; Editions Frontières: Ville, 1995; pp 251–256.
(9) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(10) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(11) Essafi, W. PhD Thesis, Paris VI, 1996.
(12) Manning, G. S. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 909–922.

(13) Essafi, W.; Lafuma, F.; Williams, C. E. *Eur. Phys. J. B* **1999**, *9*, 261−266.
(14) Essafi, W.; Lafuma, F.; Williams, C. E. *J. Phys. II* **1995**, 1269−1275.
(15) Kuchera, F.; Jancar, J. *Polym. Eng. Sci.* **1998**, *38*, 783−790.
(16) Turbak, A. F. *Ind. Eng. Prod. Res. Dev.* **1962**, *1*, 275−279.
(17) Makowski, H. S.; Lundberg, R. D.; Singhal, G. S. US Patent 3 870 841, 1975, to EXXON Research and Engineering Co.
(18) Essafi, W.; Lafuma, F.; Williams, C. E. In *Macro-ion Characterization. From Dilute Solutions to Complex Fluids*; Schmitz, K. S., Ed.; American Chemical Society: Washington, DC, 1994; Chapter 21, pp 278−286.
(19) Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **1996**, *29*, 2974−2979.
(20) Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **1999**, *32*, 915−922.
(21) Micka, U.; Holm, C.; Kremer, K. *Langmuir* **1999**, *15*, 4033−4044.
(22) Carbajal-Tinoco, M. D.; Williams, C. E. *Europhys. Lett.* **2000**, *52*, 284−290.
(23) Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **2001**, *34*, 1964−1972.

MA011707O