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Small-Angle Neutron Scattering from Sulfonate Ionomer Solutions. 2. Polyelectrolyte Effects in Polar Solvents

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ABSTRACT: Dimethylformamide solutions of lightly sulfonated polystyrene (SPS) ionomers have been studied. These SPS polymers possess a narrow molecular weight distribution and are in the form of sodium salts. A combination of reduced viscosity and small-angle neutron scattering (SANS) measurements reveal polyelectrolyte effects in these solutions. Mixed-labeling experiments were performed to provide a molecular basis for understanding these effects.

Introduction

Solutions of charged macromolecules may exhibit a wide variety of properties depending on the solvent quality and polarity and the charge density of the solute. One particularly interesting case is ionomer solutions. Ionomers such as lightly sulfonated polystyrene are flexible long-chain polymers that contain a few ionic groups spaced randomly along the backbone. These ionic groups interact strongly with one another in a manner which is highly dependent on the choice of solvent. This study focuses on sulfonated polystyrene ionomers dissolved in a polar (ionizing) solvent.

In solvents of high polarity, ionomers exhibit solution viscosity behavior that is reminiscent of classical polyelectrolytes.[1,2] That is, a marked upsweep in reduced viscosity is observed as polymer concentration is decreased. It is rather unusual that materials of such low ionic content can display this characteristic polyelectrolyte effect. With suitable choice of solvent, the same ionomeric materials can also behave as associating polymer systems.[3–5]

The molecular basis for classical polyelectrolyte solution behavior remains unknown. To establish such a basis for ionomer solutions, small-angle neutron scattering measurements (SANS) have been carried out on a model ionomer system. Specifically, lightly sulfonated polystyrene (SPS) of narrow molecular weight distribution was used in its sodium salt form and dissolved in dimethylformamide (DMF). This polar solvent ($\epsilon = 36.1$) was used in its perdeuteriated form to reduce incoherent background in the scattering experiment. Because of the large extent of the polyelectrolyte chains, the system studied was no longer in the dilute regime and consequently a conventional SANS determination of single-chain parameters such as the radius of gyration was not possible. However, by replacing known amounts of the hydrogenous chains with perdeuteriated ones, it was also possible to calculate the coherent scattering from a single macromolecule at semidilute concentrations and thus to obtain single-chain parameters. Measurements were made on materials with a variety of molecular weights and sulfonation levels, and the results are compared with those of the unmodified polystyrene precursor. The results clarify the previously reported solution viscosity behavior of sulfonated polystyrene ionomers and are expected to apply generally to ionomers dissolved in ionizing solvents.

Experimental Section

Polymer Preparation. Anionically polymerized styrene and perdeuteriostyrene were purchased from Polymer Laboratories Ltd. The number average molecular weights of the (undeuteriated) polymer ranged from 3.50×10^4 to 1.15×10^5 daltons. The corresponding perdeuteriated polymers had molecular weights greater by ~8%. For the mixed-labeling experiments, the perdeuteriated polymers and hydrogenous polymers mixed had the same average number of monomer units. In what follows, the "molecular weight" will refer to the undeuteriated chains. The polydispersity index was less than 1.05 in all cases. The sulfonated polymers were prepared by previously described methods.[4,6,7] In general, these polymers were modified in 1,2-dichloroethane by using acetyl sulfate as the sulfonating agent. The sulfur content was determined analytically and used to calculate the sulfonate content. Sulfonate contents ranged between 0 and 10 mol %; i.e. zero to ten out of every hundred repeat units were modified.

Polymer solutons were prepared volumetrically by using magnetic stirrers for agitation. Freshly opened solvents were used as received to prepare stock solutions for serial dilution. These stock solutions were stirred for a minimum of 24 h to ensure complete dissolution.

The reduced viscosity [defined as $(\eta - \eta_0)/\eta_0 c$ where η is the viscosity of the polymer solution, η_0 is the viscosity of the solvent, and c is the polymer concentration] was measured with a standard Ubbelohde viscometer. Viscosity measurements were made at 25 ± 0.05 °C in a thermostated bath.

Neutron Scattering. SANS measurements were performed at both the Brookhaven National Laboratory (BNL) in New York and the Oak Ridge National Laboratory (ORNL) in Tennessee. At BNL, a sample-to-detector distance of 1.9 m and neutrons of 7.5 Å wavelength were used. At ORNL, 4.75-Å wavelength neutrons and a sample-to-detector distance of 4 m were chosen. In all experiments, the polymer solutions were held in tightly capped quartz cells with the sample area defined by circular diaphragms. The incoherent scattering from a water sample under identical conditions was used for detector normalization. Background corrections were made by subtracting the scattering due to the cell and solvent. Standard corrections were made for sample transmission. In the ORNL experiments, the incoherent background scattering was estimated from measurements at higher angles.

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Analysis. The intensity of scattered radiation at a given scattering angle, θ, is determined as the radially averaged scattering at a distance d from the beam center. For small angles, the scattering vector q is calculated as

$$q = \frac{4\pi \sin(\theta/2)}{\lambda} \sim \frac{2\pi d}{\lambda D} \tag{1}$$

where λ is the wavelength of the incident neutron beam and D is the sample-to-detector distance.

The angular dependence of the scattered intensity $I(q)$ is determined by the summation over all possible vectorial combinations. In the case of dilute hydrogenous polymer solutions, this reduces to the single chain form factor $f(q)$.

$$I(q) = Ka^2 \sum_{ij} \exp[i\vec{q}(\vec{r}_i - \vec{r}_j)] = Ka^2 f(q) \tag{2}$$

In eq 2, the summation is performed over all scatterers i and j whose separation is given by the vector distance $\vec{r}_i - \vec{r}_j$. The magnitude of scattered intensity will be determined by the amount of contrast "a" for a single monomer and by the prefactor K which contains molecular weight terms and machine parameters.

To obtain the single-chain form factor in nondilute conditions, a mixed-labeling method was employed. This technique was described in the earlier paper in this series,[5] and an analogous method has been applied to the neutron scattering from classical polyelectrolyte solutions.[8,9] In general, two solutions of the same polymer concentration but with different hydrogen/deuterium ratios are measured. This provides two equations that can be algebraically combined and solved for $f(q)$.

Once the single chain scattering is known, the radius of gyration R_g and weight-average molecular weight M_w can be calculated as shown by Zimm.[10] Since a series approximation is involved, this model is only applicable to a limited angular range (for $qR_g \ll 1$). When these qualifications are met, the single-chain scattering from a solution with polymer concentration C_p is

$$\frac{K'C_p}{I(q)} = \frac{1}{M_w}\left[1 + \frac{q^2\langle R_g^2\rangle}{3}\right] + 2A_2C_p \tag{3}$$

where A_2 is the second virial coefficient of the polymer solution. The radius of gyration can be determined from the slope of a linear $C_p/I(q)$ vs q^2 plot and is independent of normalization. The moleular weight is derived from the intercept of such a plot and is therefore less accurate due to the uncertainity in calibrating K' with absolute intensity and contrast factors.

The functional form for the single-chain factor was derived by Debye with the assumption of a Gaussian random walk for the polymer chain conformation.[11] The resulting relationship is

$$f(q) = \frac{2}{u^2}[e^{-u} - 1 + u] \tag{4}$$

where $u = q^2\langle R_g^2\rangle$. The value of R_g can be obtained by fitting the single-chain scattering with this functional form, and the polymer molecular weight can be determined from the scattered intensity extrapolated to zero angle. As discussed below, eq 4 does not apply to the sulfonated polystyrene ionomers which are not Gaussian coils but may be applied to pure polystyrene in dilute solution as a check of the method of extracting single-chain parameters.

Results and Discussion

Reduced viscosity measurements of lightly sulfonated polystyrene ionomers dissolved in polar solvents have been previously reported[1,12] for materials of broad molecular weight distribution. Significant upturns in viscosity at low concentrations are observed which are characteristic of polyelectrolytes. The current study includes similar measurements on materials of narrow molecular weight distribution. The concentration dependences of reduced viscosity for sodium salts of SPS dissolved in DMF are shown in Figure 1. The characteristic polyelectrolyte effect is apparent in these materials as it was with the polydisperse materials. Presumably, the upturn in reduced viscosity at low concentrations is due to an expansion of the ionomer chain. In this highly polar nonaqueous medium, a sufficient number of salt groups must be ionized to cause an increase in the hydrodynamic volume (and hence in the viscosity) by repulsion of like charges. As expected, this polyelectrolyte effect is proportional to sulfonation level at a given molecular weight and the effect increases with increasing molecular weight at constant ionic content.

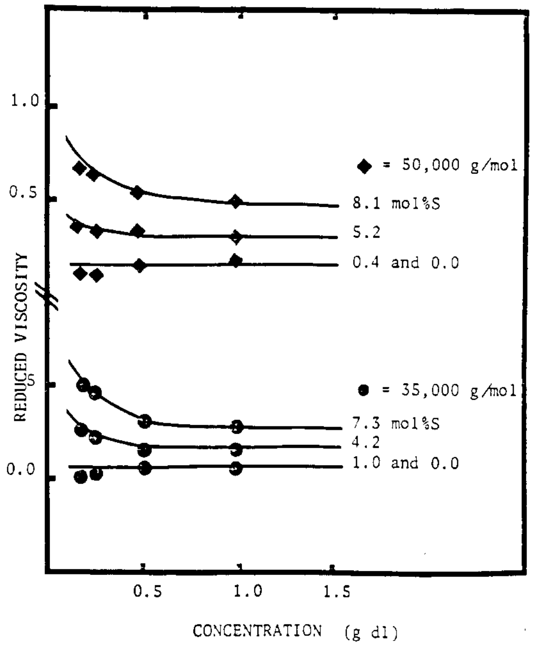

Figure 1. Concentration dependence of reduced viscosity for sulfonated polystyrene ionomers dissolved in dimethyl formamide (◇, 50000 g/mol; ○, 35000 g/mol).

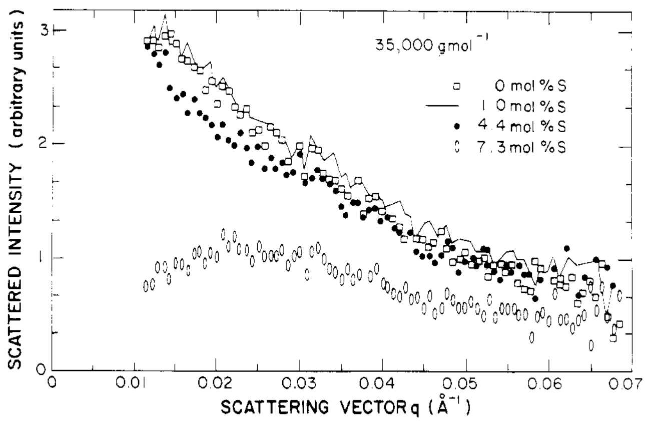

Figure 2. Wave vector, **Q**, dependence of scattered intensity of hydrogenous SPS ionomers dissolved in perdeuteriated DMF (M = 35000 g/mol; C = 0.5 g/dL) (□, 0; —, 1.0; ●, 4.2; ○, 7.3 mol % S).

In order to investigate this behavior further, the small-angle neutron scattering from analogous solutions of hydrogenous polymer in perdeuteriated DMF was measured at a fixed concentration. The resulting scattering curves are shown in Figures 2–4. The presence of a peak in the small-angle scattering is consistent with the behavior of known polyelectrolytes.[13,14] This peak moves to smaller angles with increasing molecular weight and is no longer observable in the accessible q range for the highest molecular weight. Its occurrence at the highest sulfonation level suggests that interference effects are present which may not be negligible at lower ionic contents. Though several theories have been developed to explain the polyelectrolyte peak,[15-19] it is not possible to derive

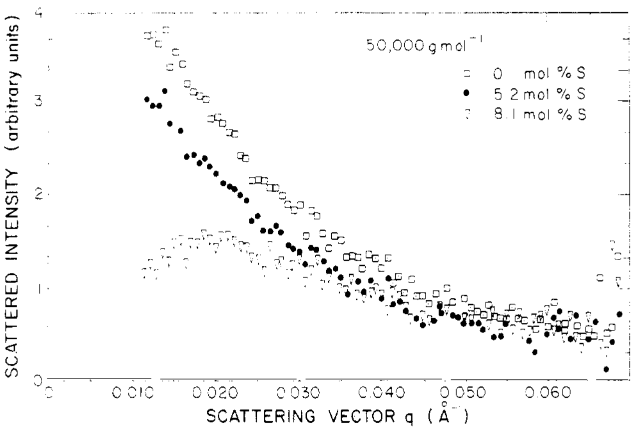

Figure 3. Q dependence of scattered intensity for hydrogenous SPS ionomers dissolved in perdeuteriated DMF (M = 50 000 g/mol; C = 0.5 g/dL) (⊡, 0; ●, 5.2, ▽, 8.1 mol % S).

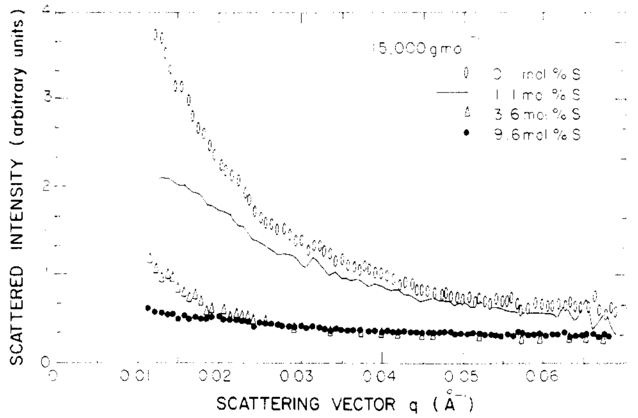

Figure 4. Q dependence of scattered intensity of hydrogenous SPS ionomers dissolved in perdeuteriated DMF (M = 115 000 g/mol; C = 0.5 g/dL) (○, 0; —, 1.1; △, 3.6, ●, 9.6 mol % S).

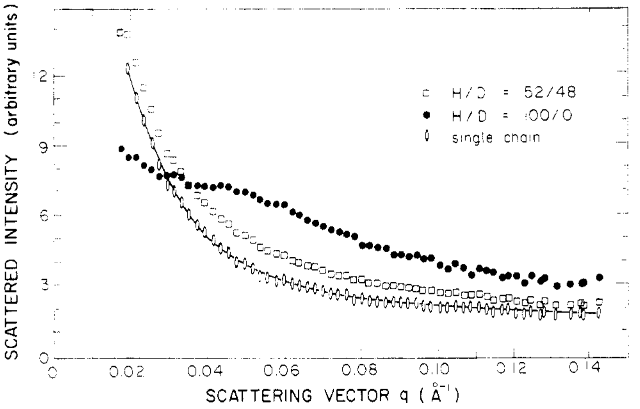

Figure 5. Mixed-labeling subtraction technique for SPS ionomer (M = 50 000 g/mol) (8.1 mol % S) dissolved in perdeuteriated DMF at 4.0 g/dL (●, H:D = 100:0; □, H:D = 5248; ○ single chain).

unambiguously single-chain information from the data in Figures 2–4.

In order to obtain single-chain information from these polyelectrolyte solutions, mixed-labeling experiments were performed. The procedure was similar to that discussed in a companion paper.[5] Ionomers of fixed molecular weight were studied over a range of sulfonation levels and polymer concentrations. An example of the mixed-labeling subtraction is shown in Figure 5 where the scattering from a solution of hydrogenous ionomers is compared with that of a solution containing both hydrogenous and perdeuteriated chains. These two scattering curves are combined to yield the single-chain form factor. The result shows clearly that the polyelectrolyte peak is due to interference between chains since it is absent from the single chain profile. This is in agreement with preliminary studies on aqueous solutions of classical polyelectrolytes.[9]

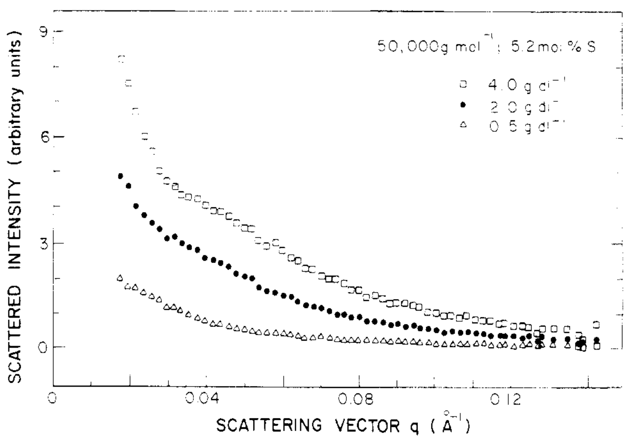

Figure 6. Q dependence of scattered intensity for hydrogenous SPS ionomers dissolved in perdeuteriated DMF (M = 50 000 g/dL; 5.2 mol % S) (□, 4.0; ●, 2.0; △, 0.5 g/dL).

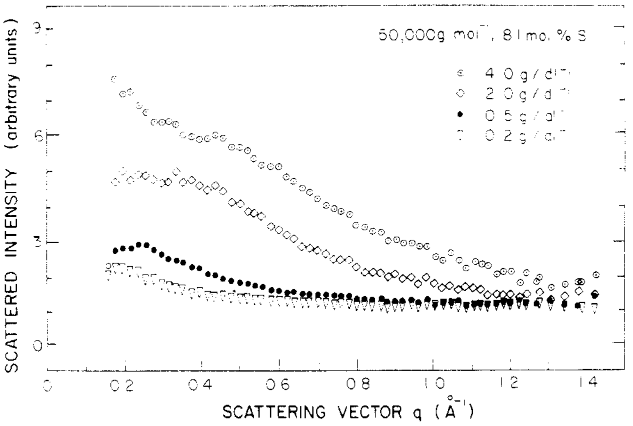

Figure 7. Q dependence of scattered intensity for hydrogenous SPS ionomers dissolved in perdeuteriated DMF (M = 50 000 g/dL; 8.1 mol % S) (○, 4.0; ◇, 2.0; ●, 0.5; ▽, 0.2 g/dL).

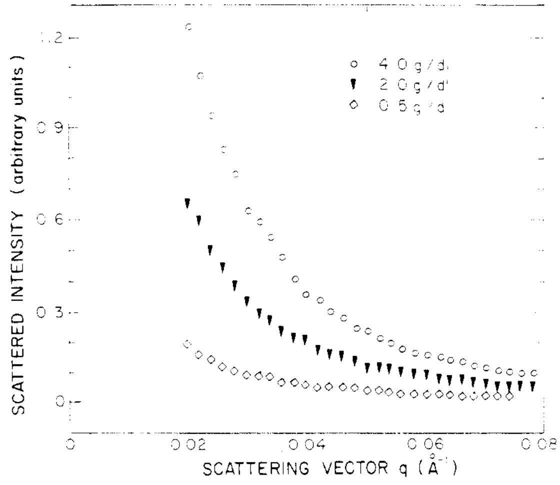

Figure 8. Q dependence of calculated single-chain scattering for solutions in Figure 6: ○, 4.0 g/dL; ▼, 2.0 g/dL; ◇, 0.5 g/dL.

The resulting scattering curves for the unlabeled ionomer solutions as a function of concentration are shown in Figures 6 and 7 while the corresponding single-chain scattering appears in Figures 8 and 9. This calculated single-chain scattering is uncoupled from A_2 effects.[20] The scattering from the unmodified polystyrene precursor was also measured for comparison. The scattering from PS of

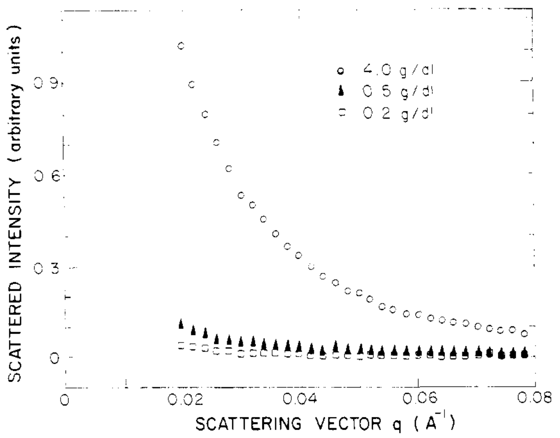

Figure 9. Q dependence of calculated single-chain scattering for solutions in Figure 7: ○, 4.0 g/dL; ▲, 0.5 g/dL; □ 0.2 g/dL.

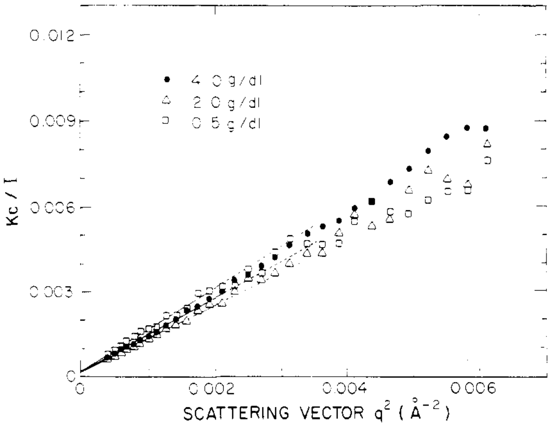

Figure 10. Zimm analysis of single-chain scattering for solutions in Figure 6: ●, 4.0 g/dL; △, 2.0 g/dL; □, 0.5 g/dL.

Table I
Single-Chain Parameters from Zimm Analysis

system	concn, g/dL	R_g, Å	M_w, g/mol	n
PS	0.5	57 ± 6[a]	assumed 50000	2.0
SPS (5.2%)	4.0	127 ± 26	40000 ± 8000	1.8
	2.0	119 ± 26	40000 ± 8000	1.8
	0.5	136 ± 26	40000 ± 8000	1.6
SPS (8.1%)	4.0	128 ± 26	40000 ± 8000	1.8
	0.5	189 ± 70	40000 ± 8000	1.7
	0.2	209 ± 70	40000 ± 8000	1.4

[a] This value is corrected for the (qR_g) range used in the analysis, using ref 21.

known molecular weight was used to scale the ionomer scattering curves in order to obtain absolute intensity data.

Molecular parameters were determined by use of eq 3. The resulting plots are shown in Figures 10 and 11, and the values of R_g and M_w obtained are listed in Table I. Due to the nature of the subtraction technique, no correction for A_2C_p is required for the single-chain data. This is not true of the total scattering from the unmodiifed PS dissolved in perdeuteriated DMF, however, The value of $A_2 = 3.8 \times 10^{-4}$ cm^3 mol g^{-2} was estimated for this solution from light scattering measurements.[4] As a check, the SANS data were also fit with eq 4 which does not require an estimate of A_2. Initial estimates of base-line and zero-angle intensity were iteratively refined, and the resulting fit is shown in Figure 12. It yields a value of 70 Å for R_g which is in excellent agreement with that calculated with the estimated A_2 value and listed in Table I.

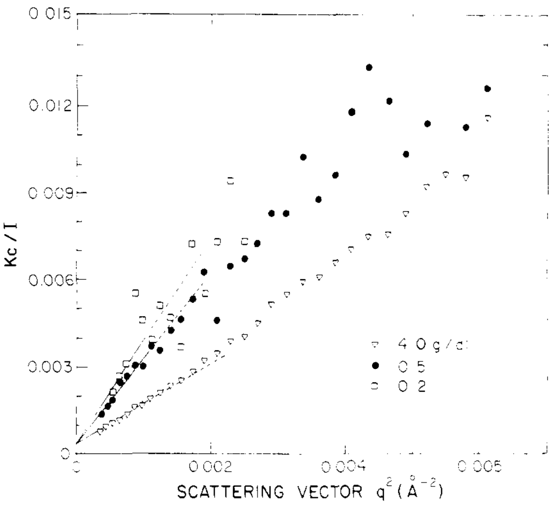

Figure 11. Zimm analysis of single-chain scattering for solutions in Figure 7: ▽, 4.0 g/dL; ●, 0.5 g/dL; □, 0.2 g/dL.

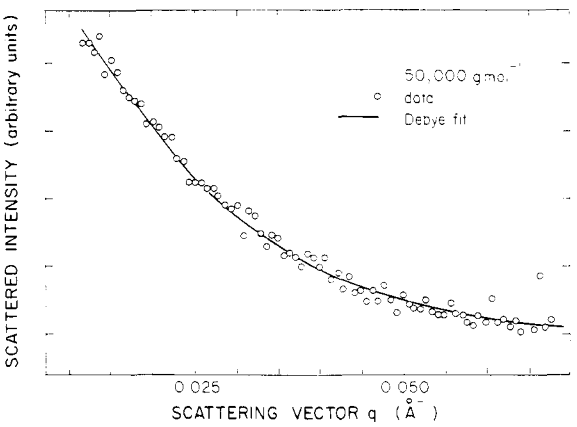

Figure 12. Q dependence of scattered intensity for hydrogenous PS dissolved in perdeuteriated DMF (M = 50000 g/dL; C = 0.5 g/dL) (○, data; —, Debye fit).

The q range used for the Zimm analysis (0.016 Å^{-1} < q < 0.034 Å^{-1}) was such that the values of (qR_g) do not lie in the range of validity of eq 3. However, the values for R_g and M_w may be corrected for this effect using the method of Ullman.[21] Ullman's calculations are strictly speaking for Gaussian coils. Corrections for the case of rigid rods have also been given by Ullman.[22] Since the corrections are roughly equal and opposite for Gaussian coils and rods and since, as we shall see below, the single sulfonated chains have characteristics of both, we have not made corrections for the qR_g range used in Table I, except for the pure polystyrene chains. However, the errors reflect the estimated 20% accuracy of the results, except for the most dilute cases, where qR_g is sufficiently large that the error is estimated at 35%. The molecular weight of a single ionomer chain should, of course, be independent of concentration. A value which is constant within experimental error is obtained by the subtraction technique as can be seen in Table I. The values of R_g in Table I indicate that chain expansion does indeed occur at sufficiently low polymer concentrations. This is consistent with the reduced viscosity measurements shown in Figure 1.

The actual chain conformation is naturally of great interest. To estimate this geometry, the doubly logarithmic plots shown in Figure 13 were constructed. It should be recalled that at asymptomatically large q ($qR_g \geq 3$), the scattering from a polymer chain can be described by

$$I(q) \sim Aq^{-n} \tag{5}$$

where the exponent n has a value of 2 for a random coil and a value of 1 for a rigid rod.[23] The measured values of n are given in Table I. As can be seen, polystyrene exhibits the expected coil-like behavior in perdeuteriated

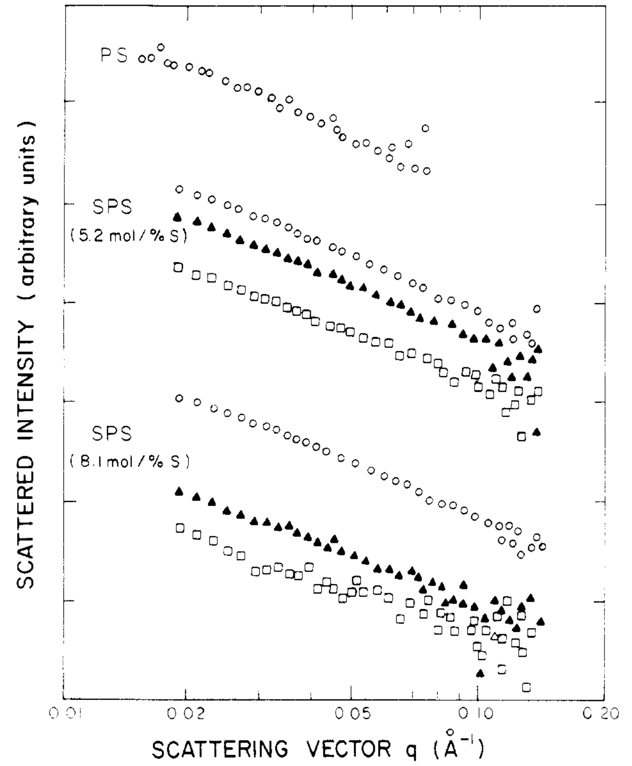

Figure 13. Double logarithmic plot of single-chain scattering for solutions in Figures 6, 7, and 12.

Table II
Infinite Dilution Dimensions

system	L, Å	R_g, Å	C^*, g/dL
SPS (5.2%)	840	240	0.014
SPS (8.1%)	1030	300	0.008

DMF. The ionomer chains, however, are intermediate between rods and coils and become more rodlike with decreasing polymer concentration.

These results can be used to model the ionomer chains in the following way. First the measured R_g of the PS chain is used to determine a statistical step length, l, for a PS random coil. Using the well-known relation[24]

$$\langle R\rangle_g^2 = nl/6^2 \tag{6}$$

where the number of steps n is set equal to the ratio of polymer to monomer molecular weight, yields a value of l = 7.5 Å. It is then assumed that each charge along an ionomer chain is separated by a random walk of m steps where m is the reciprocal of the average percent ionic content. Hence the ionomer will be locally "wiggly" on length scales less than $(ml^2)^{1/2}$ and stiff at larger length scales. In dilute polar conditions, electrostatic repulsions between charges would force the polymer chain to form a rod of length L where

$$L = \frac{n(ml^2)^{1/2}}{m} \tag{7}$$

This is depicted schematically in Figure 14. Knowing the molecular weight, sulfonation level and statistical step length, it is possible to calculate values for the infinite dilution rod length L. Once L is known, the order of mynitride of the overlap concentration C^* can be estimated as $C^* \sim M/(L)^3$. The radius of gyration for the infinite dilution limit can also be calculated as $R_g^2 = L^2/12$. The results of these calculations are given in Table II. With the assumptions of this model, the results show that even the lowest concentration studied is above the overlap concentration, consistent with the results of the scattering from the unlabeled and mixed-labeled chains.

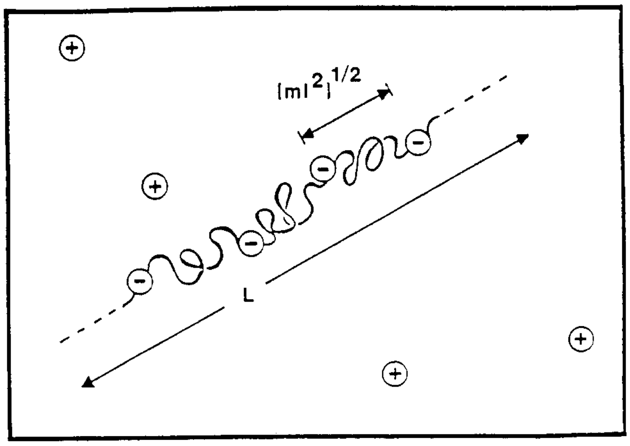

Figure 14. Schematic of an ionomer at infinite dilution in a polar solvent.

Since these ionomer solutions are sufficiently concentrated for one chain to be affected by the presence of another, it is expected that screening will cause the ionomer chain to deviate from purely rodlike behavior.[25] Hence the measured radius of gyration is expected to be less than the infinite dilution dimensions calculated above. At the highest concentration of this study (4.0 g dL^{-1}), this screening leads to comparable chain dimensions for both the 5.2 and 8.1 mol % ionomers. As polymer concentration decreases, the screening effect of the surrounding chains diminishes and hence the ionomer may traverse longer rodlike paths. The resulting increase in R_g is particularly evident at the higher sulfonation level in Table I. Even at the lowest concentration studied, however, the measured R_g does not attain the full theoretical value of an individual unscreened rod. The resulting picture of ionomers in polar solvents is one of partially stiffened chains that are forced to deviate from purely rodlike behavior by the screening of interactions by neighboring chains. This interpretation is consistent with the results in Figure 13 and with recent theoretical work.[15]

It should be noted that these results apply to SPS ionomers which are neutralized with sodium. Cations of different strength and valency may exhibit similar effects to different degrees. Further studies with other cations and sulfonate levels are in progress.

Conclusion

These SANS studies of lightly sulfonated polystyrene ionomers dissolved in perdeuteriated dimethylformamide verify the presence of polyelectrolyte behavior at low polymer concentrations. Within these semidilute solutions, single-chain information has been extracted by a mixed-labeling technique. The results reveal partial chain expansion upon dilution, in agreement with theoretical predictions. Presumably a sufficient number of the sodium salt groups are dissociated in this highly polar solvent to cause chain expansion. This chain expansion is shown to be mitigated by the presence of other ionomer coils; hence the purely rodlike limit is never observed. These results clarify the reduced viscosity behavior of sulfonated polystyrene ionomers and are expected to apply generally to ionomers dissolved in polar solvents with appropriate considerations for backbone architecture and counterion structure.

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An ESR Study of the Electrochemical Reduction and Oxidation of Poly(*p*-nitrostyrene)

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ABSTRACT: Electron spin resonance (ESR) spectroscopy is applied to study the electrochemical oxidation and reduction of poly(*p*-nitrostyrene) solutions in situ. The electrochemical reduction in dimethylformamide solution leads to production of the anion radical of poly(*p*-nitrostyrene). The ESR spectrum of the reduced polymer is unusual in that it consists of a single homogeneously narrowed line, with no observed hyperfine couplings. On the basis of the temperature and concentration behavior of the ESR spectrum, it is concluded that the electron spin is involved in an intramolecular hopping along the pendant nitrophenyl groups in the polymer. At room temperature the rate of this process is approximately 55 MHz. The activation energy for this process is 1.5 kJ/mol in solution and 0.18 kJ/mol in the solid state. Electrochemical oxidation of poly(*p*-nitrostyrene) gives rise to a radical with resolved hyperfine coupling to ^{14}N. The oxidized radical is evidently not a simple cation radical. The electrochemical oxidation is not reversible, and the same radical can be produced by oxidation in air.

Introduction

Charge transfer between two dissimilar powders forms the basis for the development step in conventional xerography. This transfer of charge is realized when the two materials are mixed such that there is contact between their surfaces, hence the name contact electrification or triboelectrification. In spite of the tremendous importance of this process, the mechanism for the charge exchange still remains basically unknown. We have focussed our efforts in the past few years on the feasibility of applying electron spin resonance (ESR) spectroscopy as a spectroscopic probe for detection of triboelectrification.

Our initial efforts have concentrated on electron transfer to and from a variety of pigments by using an in situ electrochemical cell to transfer electrons.[1] Pigments are known to play a significant role in the transfer of charge between toner and carrier particles in xerographic developers.[2] These experiments were done to determine whether pigments do undergo reversible electron-transfer reactions and whether ESR can detect these reactions. It turns out that carbon blacks can accept electrons reversibly. With chemically oxidized carbon blacks, the accepted electrons localize on surface sites giving rise to a narrow ESR signal.[1,3] With an unoxidized black, reduction leads to a narrow conduction ESR signal.[4] ZnO particles can also undergo electrochemical reduction, and these changes can be monitored by both the generation of an ESR signal and an increase in dielectric loss.[5] Finally the organic pigment, metal-free phthalocyanine (H_2Pc), undergoes both reduction and oxidation giving rise to ESR spectra which are readily differentiated.[6] Of course the polymers in both toner and carrier also play a significant role in both the direction and amount of charge transferred. It is therefore important to determine whether polymers can also accept or donate electrons and if we can detect these redox reactions with ESR. This present work then details our initial efforts at extending this study to polymers.

The utilization of electroactive polymers to chemically modify electrodes has been known for some time now.[7] Polymers such as poly(nitrostyrene),[8] poly(vinylferrocene),[9] poly(vinylanthraquinone),[10] and polyimide[11] have all been

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