$$s_{ij} = \sigma_i/\sigma_j \qquad (A5)$$

Estimations for σ_k have been obtained from Bondi's work.[26]

Values for g_{ef} calculated from equilibrium swelling data depend on the choice of V_b (monomeric or trimeric methanol, or toluene) as well as on the model used for front factors A and B. In modern views on rubber elasticity one encounters the possibility for A and B to depend on the swelling ratio.[44] The relations are complex and implicit and we have checked on the effect such dependencies will have on the interaction parameters using as a first approximation

$$A = A_1 + A_2\phi; \qquad B = B_1 + B_2\phi \qquad (A6)$$

and setting $A = {}^1/_3$, $B = 0$ at $\phi = 0$, and $A = 1$, $B = {}^2/_3$ at $\phi = 1$. Equation A4 has to be amended and changes into

$$\ln (1 - \phi) + \phi + m_1\chi_{ef}\phi^2 + \nu_e m_1 V_b\{A_1\phi^{1/3} - B_1\phi + A_2\phi(3\phi - \phi^{1/3})/2 - B_2\phi^2(1 + \ln \phi)\} = 0 \qquad (A7)$$

Registry No. (Desmodur RF)(PPG) (copolymer), 88546-51-4.

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Light Scattering Studies of Ionomer Solutions

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ABSTRACT: The molecular parameters responsible for the solution properties of poly(styrenesulfonate) ionomers in both a polar and a relatively nonpolar solvent have been studied. The second virial coefficients, apparent molecular weights, and diffusion coefficients have been measured by a combination of static and quasi-elastic light scattering techniques. Solution viscosities have also been measured. From this combination of scattering and rheological information, a more detailed description emerges of ionomer solution behavior over a range of solvent polarities, polymeric molecular weights and ionic contents, and concentrations.

Introduction

Rheological properties of flexible long-chain polymers can be dramatically altered by introducing a very small fraction of ionic groups along the hydrocarbon backbone. A frequently observed manifestation of this ionic effect is the significant change in the melt-flow behavior of bulk ion-containing polymers.[1,2] Polymers containing up to 10 mol % of such groups are commonly called ionomers. Recently, solution viscosity studies have revealed several unusual properties in dilute and semidilute ionomer solutions.[3-9] This behavior must have its origins in the conformations of the individual chains and the interactions induced by the presence of the salt groups. The conformation of a single ionomer chain in solution is determined by a complicated balance of forces. These forces can include charge repulsion and screening, van der Waals in-

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teractions, the entropic driving force for mixing, and chain elasticity. As a result, the molecular conformation and hence the solution properties of ionomers are expected to vary with solvent, ionic content and type, temperature and history, and polymer molecular weight and concentration.

It has been shown that solvent polarity plays a major role in determining the solution viscosity behavior of flexible-chain ionomers.[10,11] Hence the solution properties of ion-containing polymers naturally divide into two categories: high- and low-polarity solvent systems. In this context, a high-polarity solvent is taken to mean one in which the salt groups ionize, while a low-polarity solvent is one that will solvate ion pairs but not actually dissociate them.

In the case of ionomers dissolved in an ionizing solvent, a marked increase in solution viscosity is observed as the dilute concentration regime is approached. This behavior is characteristic of polyelectrolytes. Conversely, a dramatic reduction in solution viscosity is seen at the same ionomer concentration in nonionizing solvents. As the polymer concentration is increased, the solution viscosity increases and eventually gelation occurs. This behavior is typical of associating polymers.

To investigate further these two classes of solution behavior, solution quality and solute size have been measured in ionomer solutions by a combination of static and quasi-elastic light scattering methods. Although the goal must ultimately be an understanding of ionomer solutions over the complete range of environments, this study is restricted to a single class of ionomers: sulfonated polystyrenes (SPS) of narrow molecular weight distribution containing less than 10 mol % ionic groups. Specifically, the effects of solvent type, molecular weight, sulfonation level, and counterion and polymer concentration have been examined. It is expected that the results from this model system will also apply to other sulfonate ionomers in particular and to ionomer solutions in general.

Experimental Section

Anionically polymerized styrene used in these studies was purchased from Polymer Laboratories Ltd. and Pressure Chemical Corp. These polymers had number-average molecular weights of 1.00×10^5, 1.15×10^5, 9.00×10^5, and 1.80×10^6 Da with polydispersities less than 1.05 in all instances.

The sulfonated polymers were prepared by procedures similar to those described previously.[12,13] In general, these polymers were sulfonated in 1,2-dichloroethane with acetyl sulfate as the sulfonating agent. Following reaction at 50 °C, the polymers were neutralized with either sodium or zinc acetate and precipitated into water–methanol mixtures. The solution was subsequently filtered and the polymer was isolated as either the free acid or the sodium or zinc salt via steam stripping. The sulfonated polymer was vacuum dried for 24–48 h at 80 °C. The sulfur content of the polymers was determined by Dietert sulfur analysis and was used to calculate the sulfonate content.

The sulfonated polystyrenes ranged in sulfonate content from about 0.50 to about 4.7 mol %. In this nomenclature, sulfonate content is based on the average number of repeat units of the polymer chain. Therefore, in the case of polystyrene, 1 mol % refers to an average of one out of every 100 repeat units functionalized. The resulting materials are listed in Table I.

Polymer solutions were prepared volumetrically by using magnetic stirrers for agitation. Freshly opened solvents were used as received to prepare stock solution for serial dilution. These stock solutions were stirred for a minimum of 24 h before dilution to ensure complete dissolution. Prior to use, the solutions were carefully filtered through 0.5 and 0.2 μm filters.

A Chromatix KMX-6 low-angle laser light scattering photometer was used in all static light scattering measurements. This apparatus includes a He–Ne laser of wavelength 633 nm, a silica cell, a series of annuli to determine the forward scattering angle, and a highly linear photomultiplier. The 6–7° annulus was used for the measurements reported here. A Chromatix KMX-16 laser differential refractometer was used to measure the refractive index increments. These measurements were made at a temperature of 25 °C.

Table I
Materials

mol wt	sulfonation level wt %	mol %	counterion
100 000	0	0	
100 000	0.35	1.15	Na
100 000	0.91	3.05	Na
100 000	1.39	4.75	Na
900 000	0	0	
900 000	0.15	0.5	Na
900 000	0.52	1.72	Na
900 000	0.95	3.20	Na
1 800 000	0	0	
1 800 000	0.21	0.68	Na
1 800 000	0.70	2.30	Na
1 800 000	1.14	3.80	Na
115 000	0.75	2.49	H, Na, Zn

Table II
Static Light Scattering Results: Polystyrene/DMF

mol wt	measd M_w	$A_2 \times 10^6$, dL mol g^{-2}
100 000	95 000 ± 9 500	3.8 ± 0.4
900 000	952 000 ± 95 000	1.9 ± 0.2
1 800 000	1 877 000 ± 198 000	1.8 ± 0.2

A Brookhaven Instruments BI-2030 with a digital correlator was used in the quasi-elastic light scattering measurements. Again a He–Ne laser (Spectra Physics Model 124B) operating at 35-mW power with a wavelength of 633 nm was used as the light source. Measurements were made at 25 °C and a scattering angle of 90°. Sample and duration times were adjusted to give reproducible results for each solution.

Solution viscosities were measured with a standard Ubbelohde capillary viscometer in a temperature-controlled water bath at 25 °C. The solutions were temperature equilibrated for approximately 20 min prior to viscosity measurement. The measurement was repeated (typically 5 times) with the average values shown.

Results and Discussion

Ion-Containing Polymers in Ionizing Solvents. The solution viscosity behavior of lightly sulfonated polystyrene ionomers in ionizing solvents has been reported[10,11] for materials of broad molecular weight distribution. The current study included similar measurements on material of narrow molecular weight distribution. The polymers used have been described in the preceding section and the solvent chosen was dimethylformamide (DMF). In this highly polar nonaqueous media, a sufficient number of salt groups are ionized to increase the hydrodynamic volume of the chain via repulsion of like charges, i.e., sulfonate groups. A distinguishing characteristic of this increase in polymer dimensions is an enhancement of viscosity in relatively dilute solutions. As expected, this "polyelectrolyte effect" is proportional to sulfonation level (Figure 1) at a constant molecular weight, and the effect increases with molecular weight at a constant sulfonation level. In order to investigate this behavior, the static and quasi-elastic light scattering properties of these particular ionomer solutions were measured. Typical static light scattering results from a series of sulfonated polystyrenes in DMF are presented in Figure 2 and Table II. These results are compared directly with the unfunctionalized polystyrene precursor. Light scattering from polymer solutions is usually interpreted according to eq 1.[14] K is

$$Kc/R_\theta = 1/M_w + 2A_2c \qquad (1)$$

an optical constant incorporating the refractive index of

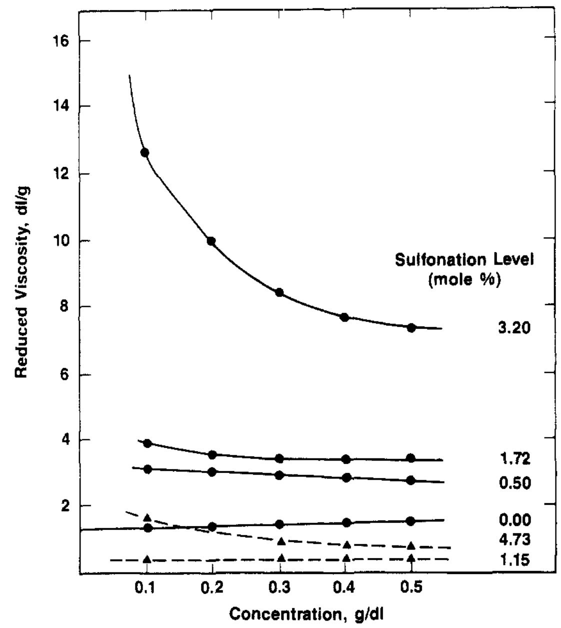

Figure 1. Reduced viscosity–polymer concentration relationships of sodium-neutralized sulfonated ionomers in dimethylformamide (DMF) at different sulfonation levels and different backbone molecular weights: (▲) 100 000; (●) 900 000.

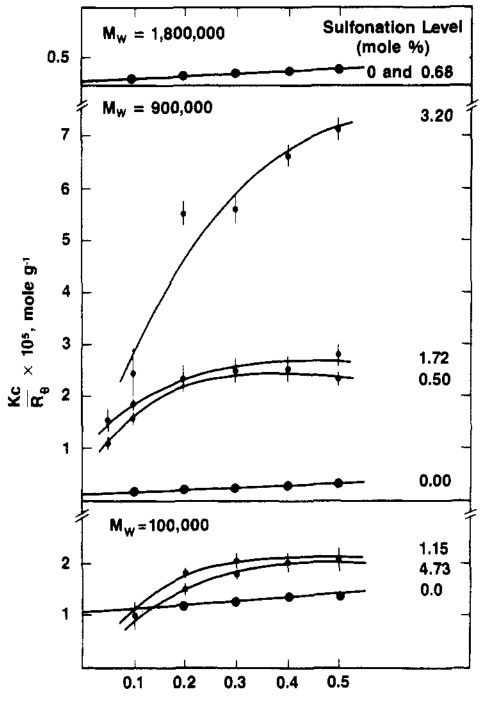

Figure 2. Low-angle light scattering data showing Kc/R_θ as a function of polymer concentration for a series of monodisperse sodium-neutralized sulfonate ionomers in dimethylformamide (DMF).

the solvent and the specific refractive index increment, M_w is the weight-average molecular weight of the dissolved polymer, and A_2 is the z-average second virial coefficient. From such plots, the molecular weight is obtained from the intercept while A_2 is directly related to the slope.

The data in Figure 2 clearly reveal the significant effect of incorporating even a few mole percent of sodium sulfonate groups along the polystyrene chain. Deviations from linearity occur in these plots, even at sulfonation levels as low as 0.50 mol %. Such curvature is indicative of polyelectrolyte behavior[15] and makes the evaluation of A_2 impossible. It suggests that considerable chain expansion is present and therefore the resulting scattering is no longer described by the conventional quadratic approximation to the virial equation. Such curvature may alternatively be explained by a continuous change in polymer coil size over the concentration range studied. This latter possibility is refuted by the diffusion coefficient values shown in Figure 3.

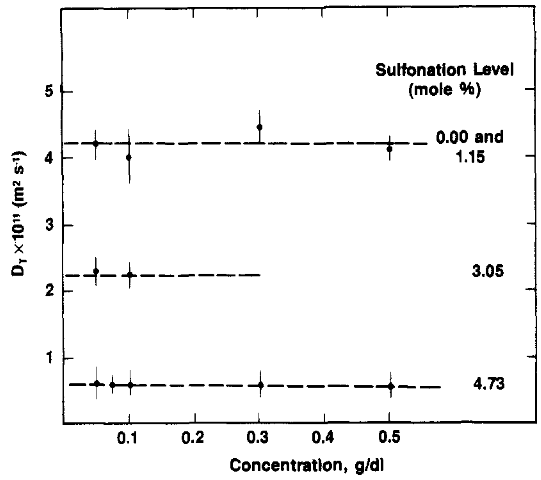

Figure 3. Diffusion coefficients (obtained from QELS) as a function of polymer concentration for a series of monodisperse sodium-neutralized sulfonate ionomers in dimethylformamide (molecular weight: 100 000).

It is apparent from Figure 3 that the diffusion coefficients remain invariant over the concentration range of interest. This indicates that the effective polymer size is not changing to any significant extent. The diffusion coefficient D_T was measured by quasi-elastic light scattering. This quantity is related to the measured correlation function Γ by

$$D_T q^2 = \Gamma \tag{2}$$

where q is the scattering vector $q = (4\pi/\lambda) \sin (\theta/2)$.

An important consideration in the interpretation of the quasi-elastic scattering data is whether the measured diffusion coefficient may be ascribed to free diffusion of the polymer chain. Equivalently, it must be considered whether the solution is dilute. If the solution has a concentration greater than c^*, then free diffusion of the polymer chain is no longer possible. Rather, it is the motion of a characteristic section ξ of the overlapping polymers which determines D_T. One complication is the calculation of c^* itself. Recent theoretical advances have been made in estimating c^* for polyelectrolyte solutions in the absence of added low molar mass electrolyte.[16-18] However, it is not yet possible to decide where the transition from dilute to semidilute really lies. The presence of polyelectrolyte phenomena in these solutions suggests that interference between ionomer chains may be important, even at these low concentrations. This is supported by preliminary small-angle neutron scattering measurements on analogous solutions.[19] Importantly, the data in Figure 3 show that the diffusion coefficient decreases dramatically with increasing sulfonation level. This strongly suggests significant chain expansion as a function of ionic content.

An additional aspect of this study of lightly sulfonated polystyrene ionomers in DMF is the dependence of solution properties on the nature of the counterion. Hara and co-workers[7,8] have investigated the effect of counterion size for a series of monovalent counterions. In the present study, the effect of valency was examined by measuring the static light scattering from the sulfonic acid and its zinc

Table III
Quasi-Elastic Scattering for SPS/DMF with a Molecular Weight of 115 000 and a Sulfonation Level of 2.49 mol %

counterion	$D_T \times 10^7$, cm^2 s^{-1}
Na	2.8 ± 0.2
Zn	2.0 ± 0.2
H	2.3 ± 0.2

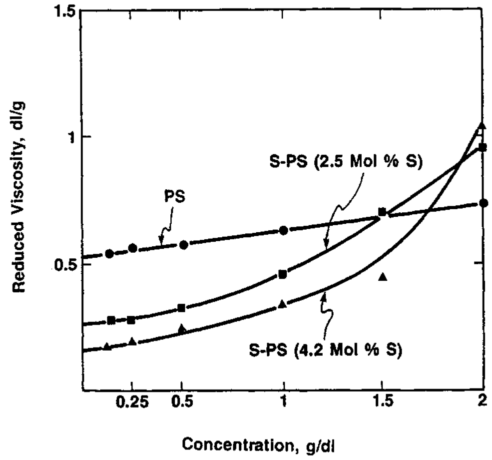

Figure 4. Reduced viscosity–concentration profiles of polystyrene and its sulfonated sodium salt in tetrahydrofuran.

and sodium salts—each ionomer having a fixed ionic content of 2.49 mol % and a molecular weight of 115 000. The preliminary data suggest that the sulfonic acid, zinc salt, and sodium salt each display polyelectrolyte behavior. Presumably, DMF is sufficiently polar to ionize each of these three forms. Chain expansion then occurs due to the resulting charge repulsion. This expansion is again indicated by the low diffusion coefficients as measured by quasi-elastic scattering. The amount of chain expansion increases in the order Na < H < Zn. These results are consistent with other measurements on sulfonate-based ionomers.[9] The specific data are collected in Table III.

These results from DMF solutions of narrow molecular weight distribution ionomers clarify the previous solution viscosity studies on polydisperse ionomers in ionizing solvents. Polyelectrolyte effects and chain expansion are observed with the inclusion of remarkably low levels of ionic groups. It is unusual to observe such effects in nonaqueous media and at such low ionic contents.

Ion-Containing Polymers in Nonionizing Solvents. A particularly intriguing aspect of ionomer solution behavior is the case of viscometric properties in nonionizing solvents. To illustrate this behavior, typical solution viscosity data for sulfonated polystyrene in tetrahydrofuran (THF) are reproduced in Figure 4. Similar results have been reported for carboxylate-base ionomers.[7]

In solvents such as THF, a majority of the salt group exists as solvated ion pairs. At low polymer concentrations, these ion pairs are expected to associate intramolecularly, resulting in a reduction in coil size relative to the unfunctionalized polystyrene precursor. This is suggested by the observed decrease in solution viscosity relative to unmodified polystyrene at low concentrations (Figure 4).

At higher concentrations, the ionomer coils are in sufficiently close proximity to interact, and a dramatic increase in solution viscosity is observed due to intermolecular associations of the ion pairs. As concentration is increased further, gelation occurs. At an intermediate concentration c^*, characterized by the intersection of the viscosity curves for the ionomer and the precursor, a balance may exist between inter- and intramolecular associations.

Table IV
Static Light Scattering Results: Na Salts/THF

mol wt	sulfonation level, mol %	measd M_w	$A_2 \times 10^6$, dL mol g^{-2}
100 000	1.15	91 000 ● 9 000	6.5 ± 0.7
100 000	3.05	284 000 ± 28 000	0.0 ± 0.7
100 000	4.73	543 000 ± 54 000	0.7 ± 0.7
900 000	0	1 023 000 ± 100 000	5.0 ± 0.4
900 000	1.72	5 208 000 ± 520 000	3.2 ± 0.7
900 000	3.20	insoluble	
1 800 000	0	2 000 000 ± 200 000	5.0 ± 0.4
1 800 000	0.68	2 000 000 ± 200 000	5.0 ± 0.4
1 800 000	2.30	bluish, not filterable	
1 800 000	3.80	insoluble	

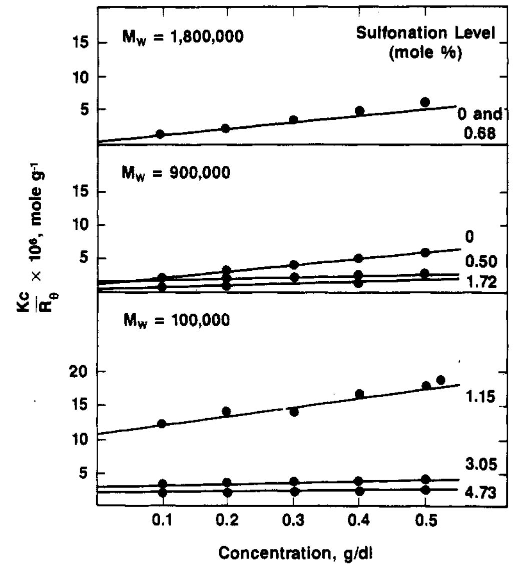

Figure 5. Low-angle light scattering data showing Kc/R_θ as a function of polymer concentration for a series of monodisperse sodium-neutralized sulfonated polystyrenes dissolved in tetrahydrofuran.

In order to investigate this crossover phenomenon in greater depth, a combination of static and quasi-elastic light scattering was used to determine the molecular behavior of this model ionomer system. Materials of narrow molecular weight distribution were chosen so that the effects of association could be seen more clearly in the absence of a large distribution of individual ionomer chain lengths. The solvent of choice was THF. The results yield values for the polymer solvent interaction parameter A_2 as well as the molecular weight and effective size of a single scattering entity. Solution viscosity measurements were also performed.

Typical static light scattering results from a series of lightly sulfonated polystyrenes in THF are shown in Figure 5 and Table IV. The results are directly compared with the unmodified polystyrene precursor. The data are presented as Kc/R_θ vs. polymer concentration as explained in the preceding section.

A close examination of Figure 5 shows that the second virial coefficient is rapidly reduced as the level of sulfonation is increased. This decrease in the value of A_2 corresponds to a decrease in solvent quality. Θ conditions (where $A_2 = 0$) are approached at very low sulfonation levels. In general, for higher molecular weights lower charge densities are required to approach Θ conditions. This effect can also be seen in Table IV where the higher molecular weight materials are soluble over a more limited range of sulfonation levels. The measured decrease in second virial coefficient with increasing ionic content is consistent with recent theoretical predictions of Cates and

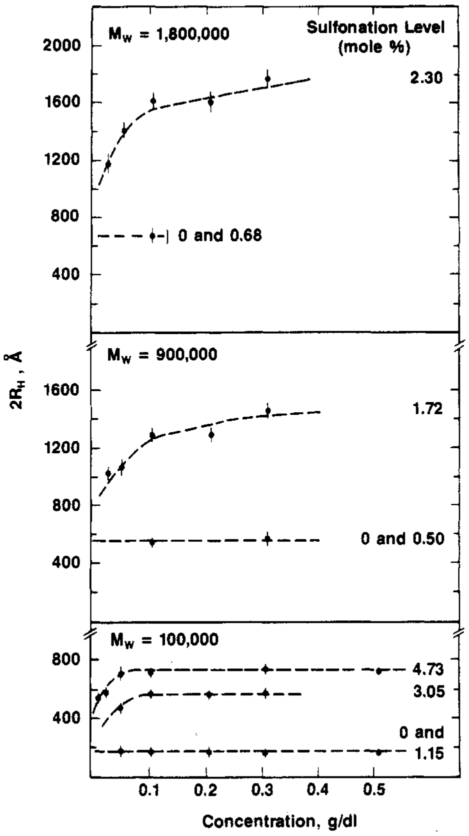

Figure 6. Effective hydrodynamic radii as a function of polymer concentration for a series of sodium sulfonated polystyrenes in tetrahydrofuran.

Witten.[20] Conditions similar to those found for ordinary chains near the Flory Θ temperature have been predicted for idealized materials where the number of monomers between associating groups is large and the associating interaction is both local and very strong. A wider range of molecular weights and ionic contents must be studied to evaluate the scaling predictions of this model. In the present study, the molecular weight of the scattering entity increases with increasing sulfonation level. It should be noted that the data for the highest molecular weight materials in Figure 6 appear to be insensitive to very low levels of sulfonation. This is probably erroneous and caused by the filtering process. The larger aggregates (>0.2 μm) will not pass through the filter. In the lower molecular weight series, the aggregates are smaller and are able to pass through the filter, thus contributing to the scattering. This aggregation phenomenon is apparently due to the inability of the metal sulfonate groups to interact in a purely intramolecular manner. As a result, a small number interact intermolecularly. At sufficiently high sulfonation levels, these intermolecular associations lead to insolubility.

The values of A_2 obtained from the static low-angle scattering measurements are presented in Table IV. The second virial coefficient has previously been measured[21] for unmodified polystyrene dissolved in THF and is in reasonable agreement with the values determined in this study. In addition, calculation of Kc/R_θ requires the measurement of the specific refractive index increment, dn/dc. This quantity was measured for a number of the ionomer solutions and the results are compiled in Table V.

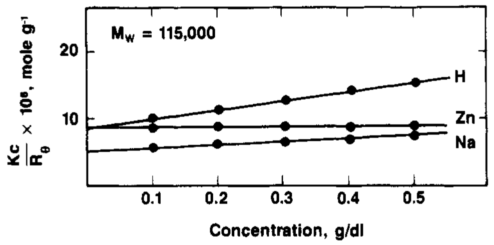

Figure 7. (Kc/R_θ)–polymer concentration relationships of sulfonated polystyrene (molecular weight of 115 000) in acid, zinc and sodium forms in tetrahydrofuran.

Table V
Refractive Index Increments: SPS Ionomers

mol wt	sulfonation level, mol %	solvent	dn/dc, mL/g
1 800 000	0	THF	0.20 ± 0.01
900 000	1.72	THF	0.20 ± 0.01
900 000	1.72	DMF	0.15 ± 0.01

Table VI
Variation of Counterion in THF for the Polymer with a Molecular Weight of 115 000 and a Sulfonation Level of 2.49 mol %

counterion	measd M_w	$A_2 \times 10^6$, dL mol g^{-2}	$D_T \times 10^7$, cm^2 s^{-1}
Na	190 000 ± 19 000	2.2 ± 0.7	5.4 ± 0.2
Zn	116 000 ± 12 000	0.0 ± 0.7	4.7 ± 0.2
H	123 000 ± 12 000	7.3 ± 0.7	5.6 ± 0.2

In order to determine the size of the individual polymer coils or aggregates, the diffusion coefficient D_T was measured by quasi-elastic light scattering. As in the previous section, eq 2 was used. After this correlation function Γ was measured, the effective diffusion coefficient D_T was determined. Using the Stokes–Einstein relation (eq 3)

$$D_0 = \frac{kT}{6\pi\eta_0 R_H} \tag{3}$$

allows the calculation of an effective hydrodynamic radius R_H for the polymer coils. In eq 3, kT is thermal energy and η_0 is the solvent viscosity. The infinite dilution diffusion coefficient D_0 was assumed equal to the measured diffusion coefficient. These resulting values of R_h are shown in Figure 6. From the results, it is again readily observed that aggregation occurs at the higher sulfonation levels. It should be noted that the data for the highest sulfonation level of the 1 800 000 Da series is indicative of this trend but is of lower accuracy than the other data points since the aggregated species are too large to filter (see Table IV). This aggregation is apparent from the severalfold increase in effective size with increasing sulfonation.

It is especially interesting to note that these aggregates can be "broken up" by dilution. This is most clearly seen in the case of 100 000 molecular weight polystyrene with 4.73 mol % sulfonation as shown in Figure 6. The scattering from this solution was measured at concentrations as low as 1 × 10^{-6} g dL^{-1}, the experimental limit of our apparatus. The continuous change in effective size below concentrations of 1 × 10^{-5} g dL^{-1} is evidence of the dynamic nature of the aggregation process. At lower concentrations, less aggregation occurs. Similar trends are seen in the 900 000 and 1 800 000 molecular weight series as well.

An additional aspect of this study of lightly sulfonated polystyrene ionomers in a relatively nonpolar solvent is the variation of solution properties with counterion. Hara and co-workers[8] have correlated the degree of aggregation with counterion binding for a series of monovalent salts. The effect of counterion valency is considered here. To this end, the static and quasi-elastic scattering from the sulfonic acid and its sodium and zinc salt forms are compared at a fixed molecular weight of 115 000. The variation in static scattering with concentration is shown in Figure 7 and the results are given in Table VI. As observed earlier, the sodium salt has a lower value of A_2, indicating poorer solvent quality compared to unmodified polystyrene dissolved in THF. This effect is even more dramatic in the case of the zinc-neutralized ionomer. Neither the salt forms nor the acid is significantly aggregated in solution at this level of sulfonation. This is shown by the molecular weight measured via static light scattering and by the effective diffusion coefficient determined from quasi-elastic scattering.

These results from narrow molecular weight distribution materials extend the previous solution viscosity measurements on sulfonated polystyrene solutions with broad molecular weight distributions. It is apparent that polymer–solvent interactions, concentration, and ionic content strongly influence the balance between inter- and intramolecular associations in a nonpolar solvent system. These associations, in turn, have a marked effect on the macroscopic solution viscosity.

Conclusions

Ionomers dissolved in dimethylformamide (DMF) exhibit a pronounced polyelectrolyte effect. This is manifested by nonlinear relationships in reduced viscosity–concentration profiles and in the static light scattering data. Thus, even in this nonaqueous solvent, a sufficient degree of ionization occurs to cause chain expansion via the mutual repulsion of negatively charged sulfonate groups. The quasi-elastic light scattering measurements confirm this intepretation.

In comparison to the marked ionomer chain expansion observed in dimelthylformamide, ionomer coil association is observed at low concentrations in tetrahydrofuran (THF). As concentration increases, intramolecular associations are gradually re-formed intermolecularly, resulting in aggregation and eventually gelation. This aggregation phenomenon is clearly observable by quasi-elastic light scatering. It is also manifested by the decrease in the second virial coefficient as measured by static light scattering.

Finally, it should be noted that these results from narrow molecular weight distribution sulfonated polystyrene ionomers clarify, to a great extent, the previously reported solution viscosity measurements on polydisperse materials. It is anticipated that these findings will be useful in interpreting the solution properties of ion-containing polymers in general and sulfonate-based ionomers in particular.

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