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Small-Angle Neutron Scattering from Sulfonate Ionomer Solutions. 1. Associating Polymer Behavior

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ABSTRACT: Small-angle neutron scattering (SANS) experiments have been carried out on a series of sulfonated polystyrene solutions. At a fixed sulfonation level, polymer concentrations in perdeuterated tetrahydrofuran ranging from 0.5 to 4.0 g dL^{-1} were studied. Even at the lowest concentration, intermolecular association of ionomer coils was observed. By use of a mixed-labeling technique, the radius of gyration of a single chain within these aggregates was determined. The results provide a molecular basis for the understanding of the solution behavior of ionomers in nonionizing solvents.

Introduction

Ionomers such as lightly sulfonated polystyrene are long-chain flexible polymers with a few ionic groups randomly spaced along the backbone. These ionic groups interact strongly with one another. The morphology and properties which result from ionic interactions in solid-state ionomers have been widely studied, as evidenced by an extensive literature.[1–3]

Previous solution viscosity studies[4–7] have revealed several unusual phenomena in dilute and semidilute ionomer solutions. These phenomena are due to the presence of polar ionic groups in the polymer and hence are highly dependent upon solvent polarity. This study focuses on sulfonated polystyrene ionomers dissolved in a relatively nonpolar solvent where available evidence indicates that the salt groups exist as contact ion pairs.

Ionomers dissolved in these nonionizing solvents exhibit a marked reduction in solution viscosity as the dilute concentration regime is approached. This has previously been interpreted as due to coil collapse. As polymer concentration is increased, the solution viscosity increases dramatically and gelation eventually occurs due to extensive intercoil associations. At an intermediate concentration, the ionomer solution viscosity is the same as that of an equivalent solution of unmodified polymer. This has previously been understood as a delicate balance between inter- and intrachain associations.

The provision of a molecular basis for the observed viscometric phenomena is clearly of interest. To this end, small-angle neutron scattering measurements (SANS) have been performed on a model system. Specifically, sodium salts of lightly sulfonated polystyrene (SPS) with a narrow molecular weight distribution have been studied in tetrahydrofuran (THF). This nonionizing solvent ($\epsilon = 7.6$) was used in its perdeuterated form to provide sufficient contrast for the neutron scattering experiment and to reduce incoherent background scattering. When we consider the ionomer chains in solution, it is reasonable to assume that aggregation occurs due to the strong tendency of the chains to associate. Due to these strong interactions, a conven-

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tional SANS experiment will not yield single-chain conformations. We may, however, consider the solution as a dilute or semidilute solution of aggregated *clusters* of chains and use conventional SANS data to extract the average values of the molecular weight and radius of gyration of these clusters. A second set of experiments including known amounts of perdeuteriated chains in the polystyrene ionomers then makes it possible, as discussed in the formalism below, to extract M_w and R_g values for *single chains* within the clusters. Measurements were made on materials of fixed sulfonation level and molecular weight and are compared with the unmodified polystyrene precursor results. These SANS experiments are the first of their kind on ionomer solutions. The results clarify the previously reported solution viscosity behavior for sulfonated ionomers and are expected to apply in general to ionomer solutions in low polarity solvents.

Experimental Section

Polymer Preparation. Anionically polymerized styrene and perdeuteriostyrene were purchased from Polymer Laboratories, Ltd. for these studies. The number average molecular weights of the hydrogenous polymer and its perdeuteriated analogue were 1.00×10^5 and 1.04×10^5 daltons, respectively. The polydispersity index was less than 1.05 in both cases.

The sulfonated polymers were prepared by methods previously described.[8,9] In general, these polymers were sulfonated in 1,2-dichloroethane by using acetyl sulfate. Following reaction at 50 °C, the polymers were neutralized with sodium acetate and precipitated into water/methanol mixtures. The solution was subsequently filtered and the polymer was isolated as the sodium 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 sulfur analysis and was used to calculate the sulfonate content.

A sulfonate content of 4.2 mol % was determined for the hydrogenous sulfonated polystyrene; the analogous perdeuteriated material contained 4.0 mol % sulfonation. 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.

Polymer solutions 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 before dilution to ensure complete dissolution.

Solution viscosity measurements were made 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 measurement. Reproducible flow rates were obtained, and the measurements were repeated (typically five times) with the average value given in the text.

Neutron Scattering. SANS experiments were performed at the Institut Laue Langevin (ILL) in Grenoble using the D11 spectrometer.[10] The polymer solutions were held in tightly capped 0.5-cm quartz cells with the sample area defined by a 1.0-cm diaphragm. The incoherent scattering from a water sample under the same conditions was used for detector normalization. Background corrections were made by subtracting the scattering due to the cell and solvent. Conventional corrections for sample transmissions were made. The incoherent background was estimated from measurements at larger angles. The radii of gyration measurements were carried out with a sample-to-detector distance of 10 m and neutrons of 8-Å wavelength.

Analysis. The intensity of scattered neutrons at a given scattering angle, θ, is determined as the radially averaged scattering at a distance d from the neutron beam center. In the limit of low angles, the scattering angle is approximated by d/D where D is the sample-to-detector distance. The scattering vector q is then calculated as

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

where λ is the wavelength of the incident neutrons.

Let us suppose that the solute consists of a random mixture of hydrogenous and perdeuteriated chains. The angular dependence of the intensity $I(q)$ scattered by the polymer solution is determined by the following summation

$$I(q) = K \sum_{\alpha\beta ij} a_{i\alpha} a_{j\beta} \exp[i\vec{q}\cdot(\vec{r}_{i\alpha} - \vec{r}_{j\beta})] \qquad (2)$$

In eq 2, the summation indices i and j refers to individual scattering units that are located along chains α and β. The separation between scatterers i and j is given by the vector distance $\vec{r}_{i\alpha} - \vec{r}_{j\beta}$. The magnitude of scattered intensity will be determined by the amount of contrast $a_{i\alpha}$ and by the prefactor K which contains machine parameters and other constants.

The contrast factor $a_{i\alpha}$ can be described as the average contrast $\bar{a}$ plus the local deviation from the average $\delta a_{i\alpha}$. That is

$$a_{i\alpha} = \bar{a} + \delta a_{i\alpha} \qquad (3)$$

Here "contrast" is defined as total neutron scattering length per monomer relative to the global average over the solution. Substituting this relationship into eq 2 yields the following collection of sums for a solution that contains both hydrogenous (H) and perdeuteriated (D) polymer chains.

$$I(q) = K\bar{a}^2 \sum_{i,j,\alpha,\beta} \exp[i\vec{q}\cdot(\vec{r}_{i\alpha} - \vec{r}_{j\beta})] + \\ K[c_{\mathrm{H}}\delta a_{\mathrm{H}}^2 + (1 - c_{\mathrm{H}})\delta a_{\mathrm{D}}^2 \sum_{i,j} \exp[i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)] \qquad (4)$$

In eq 4, the fraction of hydrogenous polymer is c_{H} and the fluctuation in scattering power is defined as

$$\delta a_{\mathrm{H}} = (a_{\mathrm{H}} - a_{\mathrm{D}})(1 - c_{\mathrm{H}}) \qquad (5)$$

The quantity of interest is the scattering form factor $f(q)$ for a single chain; this is defined as

$$f(q) = \sum_{i,j} \exp[i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)] \qquad (6)$$

To obtain the scattering due to a single chain in nondilute conditions, two solutions of the same polymer concentration but with different hydrogen/deuterium ratios are measured. This provides two expressions in the form of eq 4 which may be algebraically combined and solved for $f(q)$. This mixed-labeling technique is applicable to a broad range of solution concentrations, as recently demonstrated by Ullman et al.[11,12]

In the case of scattering from dilute solutions of hydrogenous polymers in perdeuteriated solvents, eq 2 reduces directly to the single-chain scattering form factor since α and β are equal (i.e. all the chains are hydrogenous). The single-chain scattering form factor is related to the radius of gyration of the polymer chain as shown by Zimm.[13] Since a series approximation is involved, this model is only applicable over the range $qR_g \ll 1$. When these qualifications are met, the scattering from a dilute polymer solution with concentrations C_p is

$$\frac{K'C_p}{I(q)} = \frac{1}{M}\left[\frac{1 + q^2\langle R_g^2\rangle}{3}\right] + 2A_2C_p \qquad (7)$$

In eq 7, M is the polymer molecular weight and A_2 is the second virial coefficient. The constant K' contains machine parameters and contrast factors. The radius of gyration R_g can be determined from the slope of a linear $C_p/I(q)$ vs q^2 plot and is independent of normalization and the constant K'. The molecular weight is derived from the intercept and is therefore less accurate due to its dependence on absolute intensity and contrast factors.

A combination of mixed-labeling experiments have been performed in this investigation to measure the size of an independent association of ionomer coils and the dimensions of a single chain within such an aggregated cluster.

Results and Discussion

As mentioned in the Introduction, ionomers dissolved in nonionizing solvents act as associating polymers. Above a certain concentration, aggregation phenomena are observed in solution viscosity measurements.

Solutions of lightly sulfonated polystyrene (SPS) sodium salts with 0 and 19% perdeuteriated chains were studied

Table I
Molecular Parameters Determined from Zimm Analysis

system	concn, g dL^{-1}	total scattering			single-chain scattering		
		R_g, Å	R_g^c,[a] Å	M_w, g mol^{-1}	R_g, Å	R_g^c,[a]	M_w, g mol^{-1}
SPS (4.2 mol % S)	4.0	790 ± 120		1 164 000 ± 233 000	104 ± 10	91 ± 10	135 000 ± 20 000
	2.5	390 ± 40		471 000 ± 71 000	124 ± 12	109 ± 12	190 000 ± 29 000
	1.0	226 ± 23		299 000 ± 45 000	110 ± 10	97 ± 10	184 000 ± 28 000
	0.5	230 ± 23		317 000 ± 48 000	128 ± 11	112 ± 13	
PS	0.5	134 ± 13	118 ± 13	assumed 100 000	113 ± 11	99 ± 11	104 000 ± 15 000

[a] The values of R_g^c have been corrected for the finite range of qR_g according to ref 18, as discussed in the text.

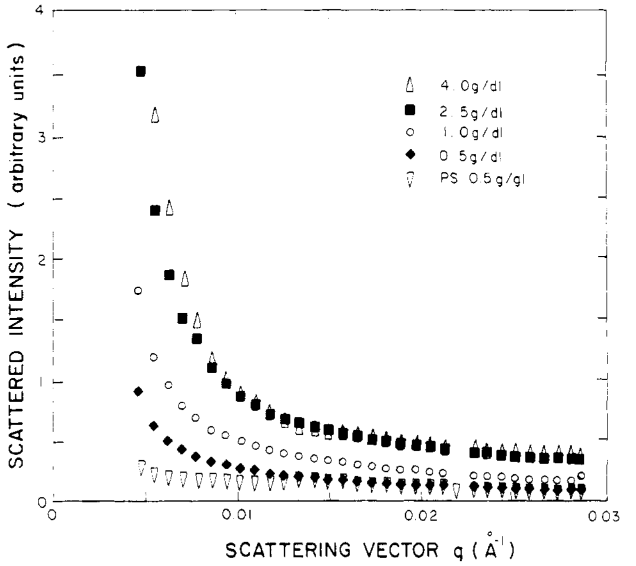

Figure 1. Scattered intensity for SPS ionomers (4.2 mol % S) in THF-d_6.

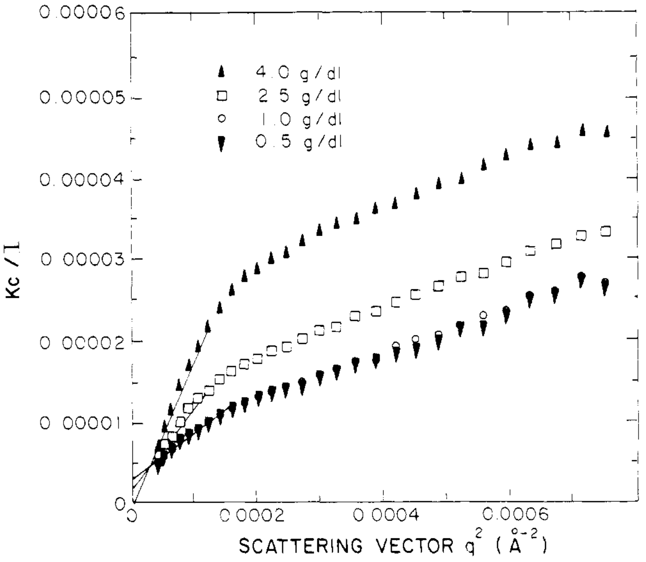

Figure 2. Zimm plot of data from Figure 1.

throughout a concentration range of 0.5–4.0 g dL^{-1} in perdeuteriated tetrahydrofuran (THF-d_6). A 0.5 g dL^{-1} solution of unmodified polystyrene (PS) was also measured for comparison.

The scattering from the solution of fully hydrogenous PS in THF-d_6 was used to scale the scattered intensity to absolute values. In order to determine molecular weight, corrections must be made for the effects of the second virial coefficient A_2 in eq 7. The literature value[14] of A_2 = 5.5 × 10^{-4} cm^3 mol g^{-2} was used for the PS/THF-d_6 solutions. The apparent second virial coefficient for SPS/THF solutions has been shown[15] to be zero under these conditions, and so no correction was necessary for the ionomer solutions.

The scattering from fully hydrogenous SPS in THF-d_6 over a range of concentrations is shown in Figure 1. The presence of aggregates larger than single chains is immediately evident from the upturn in intensity at low angles. When eq 7 is used to analyze the scattering, the plots shown in Figure 2 are obtained. The values of radius of gyration and molecular weight that result from the low q limit are listed in Table I.

The molecular weight values listed in Table I indicate that interchain association is present even at concentrations as low as 0.5 g dL^{-1}. As concentration is increased to 4.0 g dL^{-1}, the weight-average number of chains per aggregate rises from 3 to 12. It is important to emphasize that this is an average degree of aggregation. Though the individual ionomer chains make up a narrow molecular weight distribution ensemble, there is no reason to anticipate a narrow distribution of aggregate sizes. In fact, the strong downward curvature present in the plots of Figure 2 is consistent with a polydispersity greater than 2.[16,17] Curvature is also expected when the low-angle limit is exceeded. For this reason, only the initial portions of the $K'C_p/I(q)$ plots can be used.

The range of q values over which eq 7 has been used does not always satisfy the required criterion $qR_g \ll 1$ for the obtained R_g. This is a common occurrence in the field of SANS studies of polymer conformations. For values of qR_g up to ~4, the values for the molecular weight and R_g obtained from eq 7 may be corrected for using the method of Ullman,[18] who also takes polydispersity into account. As is well-known, and as Ullman's calculations show, increasing the polydispersity *reduces* the error due to qR_g not being ≪1. Since, as discussed above, the aggregates are likely to be quite polydisperse, we have *not* corrected the R_g listed in Table I for the "finite qR_g" effect as we expect them to be accurate to 10%, except for one case. This is the case of the highest polymer concentration (4.0 g dL^{-1}) where $3.2 < qR_g < 8.7$. For this concentration the R_g and M_w obtained from the data are not reliable but may be taken only as semiquantitative estimates of these quantities. Note that the quantity M_w extracted from the data represents the weight-average molecular weight and R_g represents the Z-averaged radius of gyration.

Concomitant with the increase in molecular weight, the radius of gyration of an aggregate increases with concentration. These values also appear in Table I. At the lowest concentration of this study, the results may be compared with previous light scattering measurements.[15] Although the identical system has not been studied, it is possible to interpolate the light scattering results and predict an approximate hydrodynamic radius of 380 Å and an approximate average aggregate molecular weight of 4.00 × 10^5 g mol^{-1} for the 4.2 mol % ionomer of Table I at 0.5 g/dL concentration. These results are in reasonable agreement with the present measurements.

At first sight these results are unexpected in light of the solution viscosity behavior shown in Figure 3. The reduced viscosity at 0.5 g dL^{-1} is markedly higher for PS than

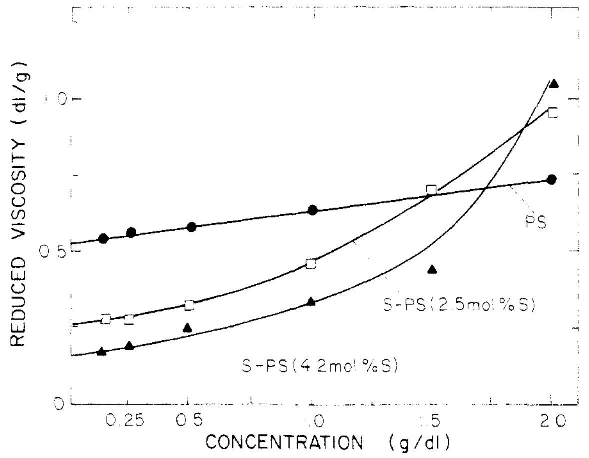

Figure 3. Solution viscosity of PS and SPS in THF.

for its sulfonated analogue, and yet PS has a smaller radius than the sulfonated aggregate. However, the solution viscosity of a molecularly dispersed solution can be greater than that of an aggregated solution if the density of material within a viscometric particle changes.

For example, if the well-known Flory relation[19] is assumed and the intrinsic and reduced viscosities are considered comparable at low concentrations, then the solution viscosity may be roughly approximated by

$$\eta_{\text{red}} = K''(R_g)^{3/2}/M \tag{8}$$

If the data for PS shown in Figure 3 are now used to calculate the proportionality constant K'' and the measured radii of gyration and molecular weights of SPS at the two lowest concentrations are inserted in eq 8, then a reduction of up to 40% in η_{red} is predicted for the SPS solutions. Clearly, this naive calculation cannot be expected to predict solution viscosity precisely, but its implication is nonetheless of great importance: the presence of aggregation at low SPS concentrations in THF is not inconsistent with decreased solution viscosity.

It now remains to determine the dimensions of a single ionomer chain within an associated aggregate. To this end, the mixed-labeling technique described in the previous section was used. As demonstrated,[12] this technique can be used to isolate single-chain information without additional corrections for the second virial coefficient.

This subtraction technique was tested on solutions of unsulfonated polystyrene. The scattering from a 0.5 g dL^{-1} solution of 19% perdeuteriated PS in THF-d_6 was measured, and the results were combined with those of the fully hydrogenous polymer to calculate the single-chain scattering form factor $f(q)$. Since the solution is dilute for PS at this concentration and molecular weight, the subtraction technique should yield the same results as the fully hydrogenous chains (after these later have been corrected for A_2 as discussed earlier). The resulting values appear in Table I. As can be seen, the two measurements agree within experimental error and the correct molecular weight is measured by the subtraction technique.

Solutions of SPS containing 19% perdeuteriated chains were measured at the same concentrations as the completely hydrogenous ionomers. The results were combined to yield single chain information. An example of this combination is shown in Figure 4. The resulting single chain scattering patterns are shown in Figure 5. As with the overall scattering from the aggregates, eq 7 was used to determine the R_g and M_w of the single chain from the low q data. The appropriate plots are shown in Figure 6. The R_g's thus obtained satisfy the relationship $0.8 < qR_g < 2$ for the q range used to analyze the data. Since the individual chains are fairly monodisperse as discussed previously, a correction (of roughly 14%) has been made to the data by using the method of Ullman[18] and the corrected values are also displayed in Table I. Since the

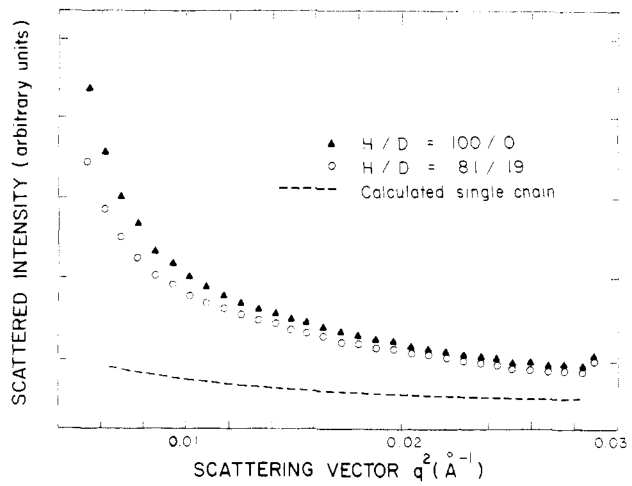

Figure 4. Mixed-labeling substraction technique.

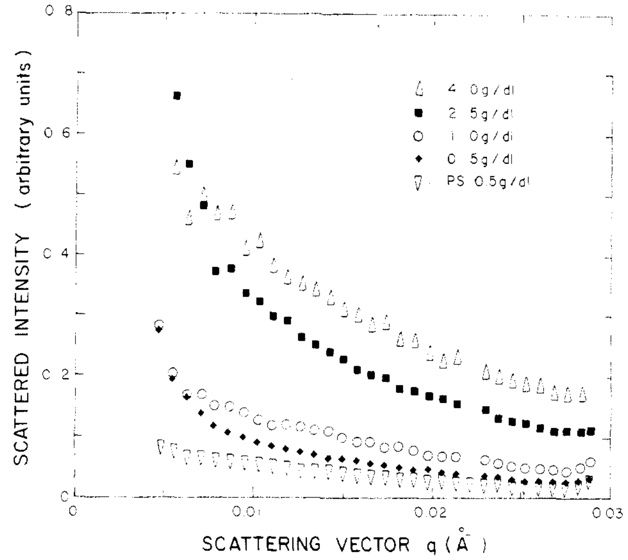

Figure 5. Calculated single-chain scattering for SPS ionomers (4.2 mol % S) in THF-d_6.

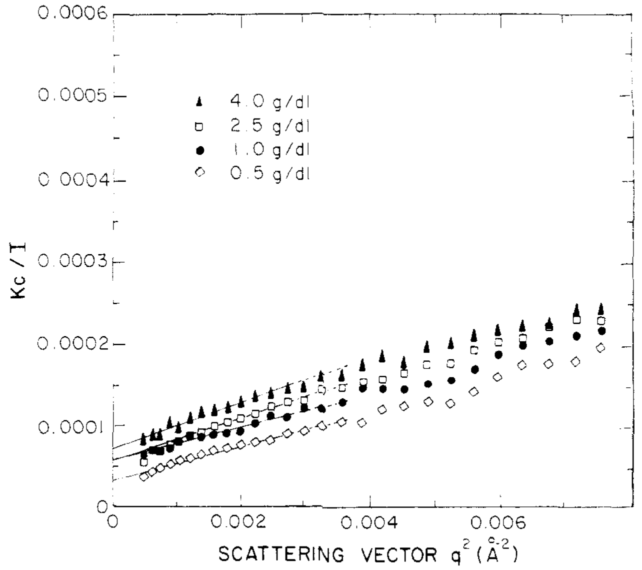

Figure 6. Zimm plot of data from Figure 5.

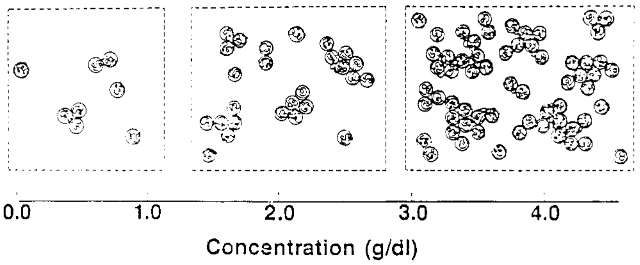

Figure 7. Association phenomenon in SPS/THF solutions.

M_w's are normalized relative to polystyrene chains assumed to have $M_w = 1.00 \times 10^5$ and with roughly the same R_g values, no correction is necessary for the values of M_w.

The molecular weight of a single chain should, of course, be constant with variation in concentration. As can be seen in Table I, the molecular weights are roughly constant within experimental error. The values are somewhat greater than expected, reflecting the uncertainty in determining absolute scattered intensity. In this case, different diaphragms were used for the polymer and ionomer solutions. The resulting attempts at cross-normalizing the two geometries led to an overcalculation of the ionomer molecular weight.

It is important to note that the radius of gyration of a single ionomer chain also remains constant within experimental error as concentration increases. There is no evidence for significant coil collapse throughout the concentration range studied. Coil collapse might be observed at even lower concentrations where light scattering studies suggest that these aggregates dissociate and intrachain associations should dominate. Significantly, there is no evidence for single coil expansion as concentration is increased. The resulting picture of ionomer solutions, schematically shown in Figure 7, is one where single coils associate into aggregates without significant changes in individual size. Interestingly, the radius of gyration of a single ionomer chain within such an aggregate is very comparable to dimensions measured in the bulk.[20]

It is to be emphasized that these results apply to solutions of sodium-neutralized SPS at a specific sulfonate level. "Softer" cations such as zinc have exhibited less aggregation as measured by light scattering in dilute solution. Further studies with other cations and different sulfonate levels are in progress.

Conclusions

These SANS studies of sodium salts of lightly sulfonated polystyrene in perdeuteriated tetrahydrofuran verify the presence of associating polymer behavior in ionomer solutions with nonionizing solvents. The results provide a molecular basis for the understanding of solution viscosity behavior. Individual ionomer coils are observed to retain constant dimensions while associating to form multicoil aggregates. At this low level of sulfonation, the single coil dimensions within an aggregate are not significantly different from those of unmodified polystyrene. Interchain associations are found to persist to unexpectedly low concentrations. The extent of aggregation is observed to be very dependent on concentration in agreement with light scattering and solution viscosity studies. These measurements on SPS solutions are expected to apply in general to ionomer solutions in low polarity solvents with appropriate considerations for polymer architecture and counterion structure.

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Registry No. Neutron, 12586-31-1.

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