BUTTERWORTH HEINEMANN

*Polymer* Vol. 36 No. 4, pp. 691-697, 1995

0032-3861/95/$10.00+0.00

# Effect of sulfonation level on the single chain dimensions and aggregation of sulfonated polystyrene ionomers in xylene

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*(Received 18 July 1994; revised 21 September 1994)*

Small angle neutron scattering has been used to determine the dimensions and extent of aggregation of dilute solutions of sodium sulfonated polystyrene (SPS) ionomers of molecular weight $10^5\,\mathrm{g\,mol^{-1}}$ and sulfonation levels of 0.95 and 1.65 mol% in *p*-xylene. At concentrations below $0.1 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$ the 0.95 mol% SPS was present as mainly single chains of considerably smaller dimension than that of the 'parent' polystyrene. Above this concentration small compact aggregates consisting of three chains were formed. These data could be analysed using the closed association model. The higher sulfonation level ionomer was present as even more compact single chains in very dilute solution. It associated, however, to form a distribution of much less dense aggregates with an average size that increased as the polymer concentration was raised. This type of behaviour was interpreted using the open association model and used to explain why semi-dilute solutions of this latter ionomer can gel.

**(Keywords: ionomer; aggregation; dimensions)**

## INTRODUCTION

Ionomers are macromolecules containing a small number (typically < 10 mol%) of ionic groups chemically bound to a non-polar chain. Addition of these charged groups can widely modify the properties of the polymer; for example, tensile strength of the ionomer and miscibility with other polymers can be greatly increased[1-5]. The presence of low levels of charged groups also has large affects on the properties of the polymer when in solution. Some of the novel effects that have been observed with these polymers have led to new applications. These range from adhesives and compatibilizers to more recently, for oil-based oil and gas drilling fluids, as both a viscosity modifier and stabilizer[1]. The purpose of this work is to understand more fully the properties of ionomers in solution.

When dissolved in polar solvents such as dimethylformamide or dimethylsulfoxide lightly sulfonated polystyrene (SPS) ionomers behave in a similar manner to polyelectrolytes for which the reduced viscosity increases rapidly with decreasing polymer concentration. This effect becomes more pronounced as the sulfonation level is raised and is generally thought to be caused by solvation of the counterions resulting in negative charges along the polymer backbone and chain extension[5-7].

Inversely, in less polar solvents such as xylene, toluene and tetrahydrofuran, these ionomers usually have less effect on the solution viscosities at low concentration than the same amount of the unsulfonated 'parent' polystyrene. This was initially believed to be caused by contraction of the ionomer chains as a result of intramolecular ion-pair associations. In the semi-dilute concentration regime, however, the ionomers have much greater effects on viscosity than polystyrene and in some cases cause the solutions to gel. This is as a result of intermolecular associations[7,8]. More recently it was shown by light scattering, however, that ionomers associate via intermolecular ion-pair interactions even in very dilute solution. It was therefore proposed that in dilute solution the aggregates must be more compact than the single polystyrene chains thereby reducing their effect on viscosity[9].

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In earlier work we studied the dilute and semi-dilute solution properties of sodium SPS ionomers with a molecular weight of $10^5$ and sulfonation level of 1.39 mol% in *p*-xylene using light and neutron scattering[10–12]. In this case, single chains which were much more compact than those of the parent unsulfonated polystyrene were found to be present in dilute solution. As the ionomer concentration was raised, however, intermolecular associations formed at the expense of intramolecular and an equilibration between single collapsed chains and aggregates of increasing average size was observed. The open association model was found to explain the apparent increase in molecular weight with concentration of these ionomers in this solvent extremely well. It is a model that has been used extensively and successfully in the past to understand the aggregation of both polymers[13] and surfactants[14] in solution. It was therefore extended so as to extract both the single chain and the two-chain aggregate dimensions of the ionomers from the variation in apparent average size of the polymer with concentration. The aggregates were found to be of relatively low density contrary to the previous suggestion in reference 9. In this case, therefore, the reduced viscosity was expected and observed to be very sensitive to the ratio of single chains to aggregates. The lack of temperature dependence of the aggregation process suggested that the position of equilibrium is dominated by an increase in entropy on forming the aggregates from single collapsed chains.

Neutron scattering studies on semi-dilute solutions showed that within the aggregates the single chains can become extended. At concentrations above 2.5 g dl$^{-1}$ very large aggregates formed which resulted in the viscosity of the solution becoming very high. At these concentrations, however, the results are very dependent upon sample preparation and the rate of attainment of any equilibrium is extremely slow[10]. In this paper we shall continue this work by reporting the effects of varying sulfonation level on chain collapse and aggregation of these ionomers in xylene.

## EXPERIMENTAL

### *Sample preparation*

Sodium SPS ionomers of molecular weight 100 000 and 105 000 with a polydispersity $M_w/M_n < 1.05$ and sulfonation levels of 0.95 and 1.65 mol%, respectively, were prepared as described previously[10]. Then, 0.4 g of each ionomer was dissolved in 1,2-dichloroethane (8 g) and methanol (0.4 g) and left for 48 h at room temperature. This procedure allows time for the break up of any aggregates formed during preparation. The ionomers were isolated from the solvent by steam stripping and dried at 100°C in a vacuum oven for 2 days. The ionomers were then dissolved in deuterated xylene at the desired concentration, sonicated and left for 2 weeks to allow time for equilibration.

### *Small angle neutron scattering*

Small angle neutron scattering experiments were performed using the D17 spectrometer at the Institut Laue Langevin, Grenoble, France. The samples were measured in 5 mm path length quartz cells at 25°C. The use of a large beam, thick samples and a high neutron flux allowed measurements to be made on unusually dilute solutions (down to $7 \times 10^{-}$ g ml$^{-1}$). The data were collected on a 64 × 64 cm detector. Since the intensity of scattering was isotropic, it was radially averaged to give intensity *versus* scattering vector $q = (4\pi/\lambda)\sin\theta$. Here $\lambda$ is the incident wavelength (15 Å in this case), the sample to detector distance was 3.4 m and the scattering angle is $2\theta$. The data were corrected for background and incoherent scattering using the scattering from the empty cell and solvent. The scattering from water in a 1 mm cell was used as an intensity standard and to measure detector response. The resulting intensity represents the scattered intensity of the polymer molecules that is mainly coherent but with a very small (and in this case negligible) flat incoherent component.

## DATA ANALYSIS

### *Coherent scattering from associating polymer solutions*

In this work the apparent molecular weight ($M_{app}$) and radii of gyration ($R_{g,app}$) of the ionomers in solution were determined as described previously[12] from the coherent scattering from the polymer. Using the Zimm expression in the scattering range $qR_g < 1$

$$\kappa c/I = \{1/M_w[1 + (qR_g)^2/3]\} + 2A_2c \qquad (1)$$

Then

$$1/M_{app} = 1/M_w + 2A_2c \qquad (2)$$

and

$$R^2_{g,app} = R^2_g M_{app}/M_w \qquad (3)$$

$\kappa$ is a known constant, $c$ is the gram polymer concentration and $I$ is the intensity of scattered radiation as a function of $q$. $M_w$ and $R_g$ are taken as the true weight average molecular weight and $z$ average radii of gyration, respectively, of all the polymer molecules and aggregates in the solution. The second virial coefficient, $A_2$, then accounts for the non-ideality of the system arising from interactions of the solution components with the polymer molecules but excludes non-ideal effects due to the inter-polymer interactions that result in aggregation. For further details see reference 13. When all terms contributing to this $A_2$ cancel, the system may be considered to be in a theta state. In this case the $M_{app}$ measured equals the weight average of all the molecules and aggregates in the solution. Also, if the solution is very dilute, then the virial term can be assumed to be negligible and ignored. In this work at higher concentrations, however, it is assumed that $A_2$ can be taken as a constant for a given ionomer. This is a simplification because it ignores the possibility of variation of interaction between polymer and solvent with aggregation. For the following, however, $2A_2c$ becomes significant only after most of the chains are aggregated. The value obtained for $A_2$ is therefore expected to be primarily as a result of interactions between the solvent and aggregates.

## MODEL FITTING

### *Variation of molecular weight with concentration for aggregating polymers*

Two models, the open association and closed association models, have routinely been used to explain how the $M_{app}$ of associating species varies with concentration[13,14].

*Open association model.* In the open association model single chains are assumed to be in equilibrium with aggregates of all sizes, i.e.

$$\mathrm{P}_1+\mathrm{P}_1 \Leftrightarrow \mathrm{P}_2 \qquad \mathrm{K}_2$$

$$\mathrm{P}_1+\mathrm{P}_2 \Leftrightarrow \mathrm{P}_3 \qquad \mathrm{K}_3$$

$$\mathrm{P}_1+\mathrm{P}_n \Leftrightarrow \mathrm{P}_{n+1} \qquad \mathrm{K}_{n+1}$$

where $\mathrm{P}_i$ is an aggregate consisting of $i$ chains. If the interacting groups are far apart on the ionomer chain then the equilibrium constants for each step can be considered invariant to increases in the size of the aggregates, i.e.

$$ {}^{n}\mathrm{K}_0=\mathrm{K}_2=\mathrm{K}_3=[\mathrm{P}_2]/[\mathrm{P}_1]^2 \tag{4}$$

$[\mathrm{P}_1]$ and $[\mathrm{P}_2]$ are the molar concentrations of the single chains and two chain aggregates, respectively. Then if the polymer is monodisperse and has a single chain molecular weight, $M_1$[13]

$$(M_\mathrm{w})^2=(M_1)^2[1+(4\,{}^{n}\mathrm{K}_0 c/M_1)] \tag{5}$$

If this model explains the data then a plot of molecular weight squared *versus* concentration should be linear. The molar concentration of single chains is then

$$[\mathrm{P}_1]=(1/{}^{n}\mathrm{K}_0)(M_\mathrm{w}-M_1)/(M_\mathrm{w}+M_1) \tag{6}$$

which leads to a weight fraction of single chains

$$w_1=[\mathrm{P}_1]M_1/c \tag{7}$$

*Closed association model.* In the closed association model single chains are assumed to be in equilibrium with aggregates of one size only, i.e.

$$n\mathrm{P}_1 \Leftrightarrow \mathrm{P}_n$$

where $n$ is the number of chains in the aggregate. With the closed association model the equilibrium constant ${}^{n}\mathrm{K}_c$ is given by

$${}^{n}\mathrm{K}_c n(c/M_1)^{n-1}=(n-1)^{n-1}[x-1]/[n-x]^n \tag{8}$$

where $x=M_\mathrm{w}/M_1$[13]. In order to fit this equation to the data curves of $x$ *versus* $c$ for various values of ${}^{n}\mathrm{K}_c$ and $n$ were calculated by computer and the best fit to the results chosen. In this case the equilibrium constant

$${}^{n}\mathrm{K}_c=[\mathrm{P}_n]/[\mathrm{P}_1]^n \tag{9}$$

The weight average molecular weight will be given by

$$M_\mathrm{w}=\Sigma w_i M_i=w_1 M_1+(1-w_1)nM_1 \tag{10}$$

where $w_i$ is the weight fraction of species consisting of $i$ chains. This equation on rearrangement gives the weight fraction of single chains

$$w_1=(n-x)/(n-1) \tag{11}$$

*Free energy of aggregation*

For the open association model the free energy change on the formation of an aggregate of $n$ chains is given by

$$\Delta G_n=-(n-1)RT\ln {}^{n}\mathrm{K}_o \tag{12}$$

where ${}^{n}\mathrm{K}_o$ is defined in units of mol l$^{-1}$. (Note, this defines the standard state as 1 mol l$^{-1}$ as used in ref. 13.) With the closed association model this expression becomes

$$\Delta G_n=-RT\ln {}^{n}\mathrm{K}_c \tag{13}$$

*Variation of radius of gyration with concentration for aggregating polymers*

The $z$-average radius of gyration is given by

$$R_\mathrm{g}=\Sigma w_i M_i R_{\mathrm{g}_i}/\Sigma w_i M_i \tag{14}$$

With the open association model at low concentration it can be assumed that only single chains and two chain aggregates are present. Then

$$w_2=1-w_1 \tag{15}$$

Using this with equation (14) gives

$$R_\mathrm{g}(M_\mathrm{w}/M_1)=[R_{\mathrm{g}_1}+(1-w_1)(2R_{\mathrm{g}_2}-R_{\mathrm{g}_1})] \tag{16}$$

where $R_{\mathrm{g}_1}$ and $R_{\mathrm{g}_2}$ are the single chain and two-polymer chain aggregate radii of gyration, respectively. In this case $w_1$ can be calculated from equations (5)–(7) once ${}^{n}\mathrm{K}_0$ is known. $R_{\mathrm{g}_2}$ and $R_{\mathrm{g}_1}$ can then be found from the intercept and initial gradient of a plot of $R_\mathrm{g}(M_\mathrm{w}/M_1)$ *versus* $(1-w_1)$.

With the closed association model

$$w_n=1-w_1$$

should be valid over the whole concentration range. Then, as with equation (16) above

$$R_\mathrm{g}(M_\mathrm{w}/M_1)=[R_{\mathrm{g}_1}+(1-w_1)(nR_{\mathrm{g}_n}-R_{\mathrm{g}_1})] \tag{17}$$

In this case the weight fraction of single chains $(w_1)$ can be calculated from equations (8) and (11) above once $n$ and ${}^{n}\mathrm{K}_c$ are known. In this case a plot of $R_\mathrm{g}(M_\mathrm{w}/M_1)$ *versus* $(1-w_1)$ should be linear over the whole concentration range if the closed association model explains the results well.

## RESULTS

*Apparent molecular weights*

In *Table 1* the $M_\mathrm{app}$ and $R_{\mathrm{g}_\mathrm{app}}$ values [i.e. values obtained assuming the term $2A_2c$ in equation (1) is zero] for SPS 1.65 mol% in xylene are given for a range of concentration. When the apparent molecular weight squared is plotted against concentration a straight line is obtained almost over the whole range measured (*Figure 1*). This suggests that, as observed previously with 1.39 mol% SPS in xylene[11,12], equation (5) and the open

**Table 1** Molecular weights and radii of gyration of SPS (1.65 mol%) in xylene

| | Apparent dimensions | | Calculated dimensions$^a$ | | |
|---|---|---|---|---|---|
| $10^2c$ (g ml$^{-1}$) | $10^{-5}M_\mathrm{app}$ (g mol$^{-1}$) | $R_{\mathrm{g}_\mathrm{app}}$ (Å) | $10^{-5}M_\mathrm{w}$ (g mol$^{-1}$) | $R_\mathrm{g}$ (Å) | $w_1{}^b$ |
| 1 | 2.87 | 169 | 2.57 | 160 | 0.331 |
| 0.6 | 2.11 | 133 | 2.01 | 130 | 0.439 |
| 0.4 | 1.75 | 114 | 1.70 | 112 | 0.531 |
| 0.2 | 1.43 | 100 | 1.41 | 99 | 0.682 |
| 0.1 | 1.31 | 83 | 1.31 | 83 | 0.805 |
| 0.075 | 1.25 | 80 | 1.25 | 80 | 0.844 |
| 0.05 | 1.16 | 79 | 1.16 | 79 | 0.889 |
| 0.025 | 1.12 | 71 | 1.12 | 71 | 0.941 |

$^a$Calculated using equations (2) and (3) with $A_2=-0.2\times10^{-4}$ ml mol g$^{-2}$

$^b$Calculated using equations (5)–(7) with the equilibrium constant given in *Table 2*

**Table 2** Dimensions and equilibrium constant for SPS (1.65 and 1.39 mol%)

| Sulfonation level | $10^{-5} M_1$ (g mol$^{-1}$) | $10^{-4}\,{}^{n}K_0$ (l mol$^{-1}$) | $-\Delta G_2/RT$ | $10^4 A_2$ (ml mol g$^{-2}$) | $R_g$ (Å) | $R_g$ (Å) |
|---|---|---|---|---|---|---|
| 1.65 | 1.05 ± 0.05 | 1.3 ± 0.2 | 9.5 | −0.2 | 58 ± 3 | 154 ± 20 |
| 1.39[a] | 1.15 ± 0.05 | 1.1 ± 0.2 | 9.3 | 0.0 | 57 ± 3 | 175 ± 25 |

[a] From previous data in reference 12

**Table 3** Molecular weights and radii of gyration of SPS (0.95 mol%) in xylene

| | Apparent dimensions | | Calculated dimensions[a] | | |
|---|---|---|---|---|---|
| $10^2c$ (g ml$^{-1}$) | $10^{-5} M_{\mathrm{app}}$ (g mol$^{-1}$) | $R_{\mathrm{g,app}}$ (Å) | $10^{-5} M_{\mathrm{w}}$ (g mol$^{-1}$) | $R_{\mathrm{g}}$ (Å) | $w_1$[b] |
| 1.0 | 1.39 | 120 | 2.59 | 164 | 0.20 |
| 0.6 | 1.61 | 126 | 2.38 | 153 | 0.29 |
| 0.4 | 1.76 | 129 | 2.30 | 147 | 0.37 |
| 0.2 | 1.66 | 122 | 1.87 | 129 | 0.53 |
| 0.1 | 1.60 | 116 | 1.69 | 119 | 0.70 |
| 0.075 | 1.40 | 106 | 1.45 | 108 | 0.78 |
| 0.070 | 1.44 | 117 | 1.49 | 119 | 0.79 |
| 0.035 | 1.03 | 96 | 1.04 | 96 | 0.93 |
| 0.014 | 1.00 | 86 | 1.00 | 86 | 0.99 |
| 0.007 | 1.03 | 81 | 1.03 | 81 | 1.00 |

[a] Calculated using equations (2) and (3) with $A_2 = 1.65 \times 10^{-4}$ ml mol g$^{-2}$
[b] Calculated using equations (8) and (11) with the equilibrium constant given in *Table 4*

association model describe the results well. The data deviate from a straight line slightly at the highest concentration but this can be accounted for by introducing a small negative second virial coefficient as in equation (2) (*Figure 1*). The equilibrium constant, ${}^{n}K_0$, and single chain molecular weight, $M_1$, were calculated from the gradient divided by the intercept and intercept of this plot, respectively, using equation (5). These terms are given with $A_2$ in *Table 2*. The equilibrium constant is similar in magnitude to that obtained previously with ionomers with a sulfonation level of 1.39 mol% in xylene[12] (*Table 2*) and the single chain molecular weight in good agreement with the expected value. Molecular weights and radii of gyration corrected using the $A_2$ given are shown in *Table 1*. Also given in *Table 1* are the weight fractions of single chains calculated using equations (5)–(7).

The $M_{\mathrm{app}}$ values for 0.95 mol% SPS in xylene *versus* concentration are given in *Table 3*. In this case in order to make a plot of molecular weight squared *versus* concentration linear a large $A_2$ value must be assumed using equation (2). Even then the fit of equation (5) is poor even at low concentration where negligible effect of any virial term will be expected (*Figure 1*). The variation of apparent inverse molecular weight with concentration can, however, be much better described by equation (8) at low concentration but not over the whole range measured (*Figure 2*). It was therefore again assumed that the $M_{\mathrm{app}}$ values at high concentration could be corrected for a single $A_2$ using equation (2). The effect of a range of virial coefficients on the data was calculated by computer. Good agreement of the closed association model with the whole data set was found only when $A_2$ was taken as $1.7 \times 10^{-4}$ ml mol g$^{-2}$ (*Figure 2*). The best fit of equation (8) then gave the number of chains in the aggre-

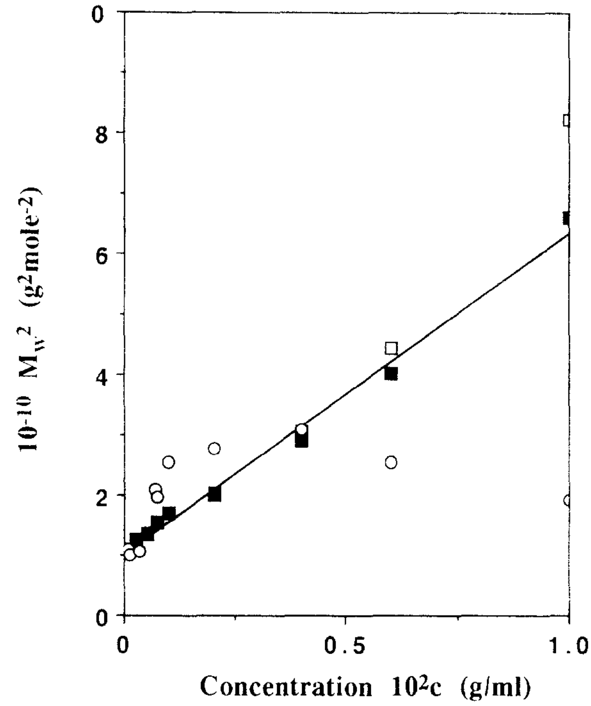

**Figure 1** Apparent molecular weight squared *versus* concentration in xylene: (□) 1.65 mol% SPS; (○) 0.95 mol% SPS; (■) molecular weight squared for 1.65 mol% ionomer corrected for a second virial coefficient of $-0.2 \times 10^{-4}$ ml mol g$^{-2}$ using equation (2)

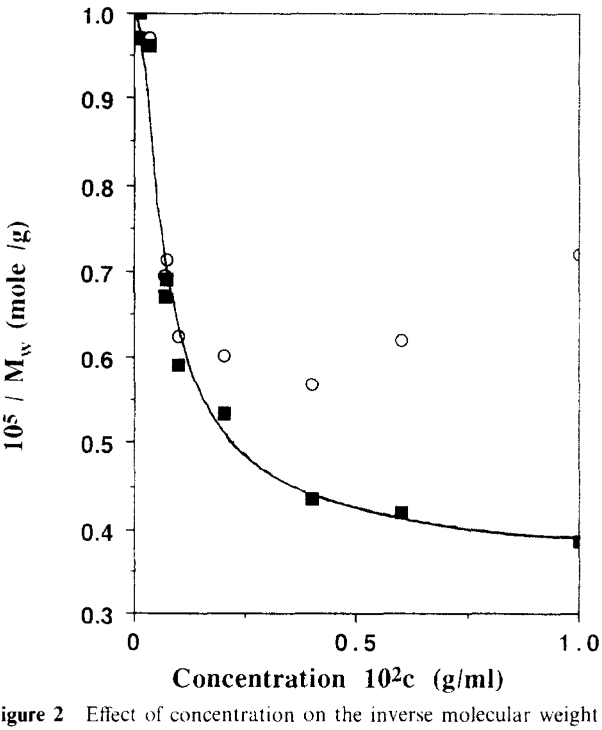

**Figure 2** Effect of concentration on the inverse molecular weight of 0.95 mol% SPS in xylene: (○) apparent inverse molecular weight; (■) inverse molecular weight corrected for a second virial coefficient of $1.7 \times 10^{-4}$ ml mol g$^{-2}$ using equation (2). Line is the best fit of equation (8) to the data

**Table 4** Dimensions and equilibrium constant for SPS (0.95 mol%) and polystyrene

| Sulfonation level | $10^{-5} M_1$ (g mol$^{-1}$) | $10^{-8\,n}K_c$ (l mol$^{-1}$)$^2$ | $-\Delta G_3/RT$ | $10^4 A_2$ (ml mol g$^{-2}$) | $R_{g1}$ (Å) | $R_{g3}$ (Å) |
|---|---|---|---|---|---|---|
| 0.95 | 1.0 ± 0.10 | 27 | 21.8 | 1.7 | 76 ± 5 | 163 ± 10 |
| 0.0[a] | 1.07 ± 0.05 | – | | 4.8 | 130 ± 5 | - |

[a] From previous data in references 11 and 12

gate as 3. The single chain molecular weight obtained from this fit is very close to the expected value. It is given with the equilibrium constant obtained in *Table 4*. True molecular weights and radii of gyration have been calculated using equations (1)–(3) assuming this $A_2$ and are tabulated in *Table 3* along with the weight fraction of single chains obtained using equations (8) and (11). These results indicate that above 1.39 mol% sulfonation these ionomers form aggregates of all sizes in xylene. With 0.95 mol%, however, single chains and aggregates consisting of primarily three chains are present in solution. It is possible that other association models might also fit the data particularly in this latter case. An example might be an open association type model where the equilibrium constants in equation (4) are not equal. It has been shown, however, that with this latter model, if $K_n$ [in equation (4)] *versus* $n$ has a peak with a maximum at $n_{max}$, then primarily single chains and aggregates consisting of $n_{max}$ chains will be observed in solution even if the peak is fairly broad. The use of the less complicated (fewer variables) closed association model in this case is then sufficient to explain the data in a crude manner[14]. The following provides further evidence to suggest that the models used interpret the scattering data well and give meaningful explanations of the bulk properties of the solutions.

### *Radii of gyration*

In *Table 1* the $R_{g,app}$ values are shown for the ionomer with 1.65 mol% sulfonation over the concentration range studied. These dimensions are also given in *Table 1* after correction [using equation (3)] for the $A_2$ obtained above. In *Figure 3* a plot of $R_g(M_w/M_1)$ against $(1-w_1)$ is shown. With this ionomer this plot [cf. with equation (16)] is only linear at low concentration. The strong deviation at higher concentration is as expected from the open association model and is due to the formation of aggregates consisting of more than two chains. With the equilibrium constant found for this ionomer an appreciable concentration of aggregates consisting of more than two chains (and therefore deviation in this plot) is predicted to occur when the concentration exceeds $2 \times 10^{-3}$ g ml$^{-1}$ (ref. 15).

In *Table 3* the apparent and corrected radii of gyration for the 0.95 mol% ionomer are given. In this case, as predicted by equation (17), a plot of $R_g(M_w/M_1)$ against $(1-w_1)$ is linear over the whole concentration range measured (*Figure 3*). This gives further evidence that the closed association model can interpret these results well.

The single chain and aggregate dimensions obtained from the above plots and equations (16) and (17) are given in *Tables 2* and *4*. The single chain radius of gyration is plotted as a function of sulfonation level in *Figure 4*. [Included in this Figure are also values at zero (for polystyrene) and 1.39 mol% sulfonation level from

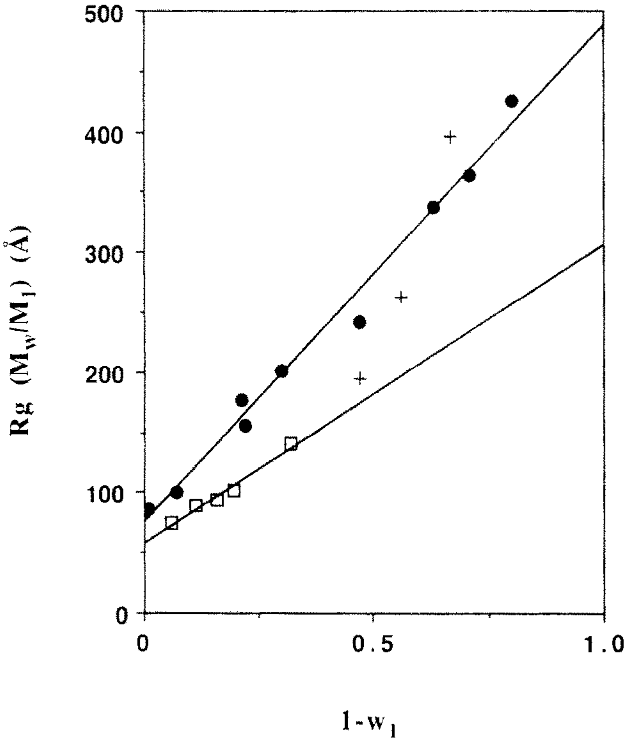

**Figure 3** Radii of gyration of SPS in xylene *versus* $(1-w_1)$: (●) sulfonation level of 0.95 mol%; (□, +) sulfonation level of 1.65 mol%. (The lines are the best straight line fits through the ● and □ data)

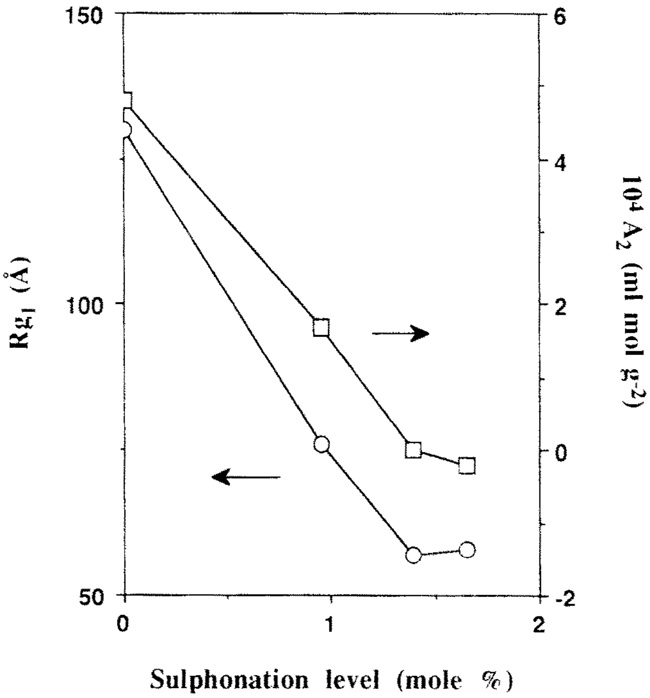

**Figure 4** Effect of sulfonation level on (○) the single chain dimensions and (□) second virial coefficient of SPS ionomers in xylene

ref. 12.) As the sulfonation level is reduced the single chain dimension decreases until a minimum value of ~55 Å. The three-chain aggregate dimension for the 0.95 mol% SPS is similar in magnitude to that obtained for the two-chain aggregates for the higher sulfonation level ionomers. This suggests that the aggregates for the lower sulfonation level ionomer are more compact.

### *Second virial coefficients*

For non-aggregating polymers as the quality of the solvent for the polymer decreases there is a reduction in both the $R_g$ of the polymer in dilute solution and $A_2$. The reduction in single chain dimensions with increasing sulfonation level observed in the previous section suggest that the virial coefficient for the non-aggregated chains should be small for all the ionomers studied. How this virial term might vary with aggregation, however, is more difficult to predict. *Figure 4* shows a plot of the observed $A_2$ *versus* sulfonation level including a value for polystyrene[11] at zero sulfonation. These results show a reduction in the $A_2$ as the number of sulfonate groups on the polymer chain is raised. In previous work the value obtained for $A_2$ for 1.39 mol% SPS could be split into the sum of an enthalpy ($A_{2,h}$) and entropy ($A_{2,s}$) term by determining the temperature dependence of the virial coefficient[12]. The value obtained for $A_{2,s}$ was comparable with that found for polystyrene. Changes in enthalpic interactions between the polymer aggregates and solvent are therefore the most likely primary cause of the observed reduction in $A_2$ on raising the sulfonation level. It should also be noted, however, that xylene becomes a non-solvent for these ionomers above ~2 mol% sulfonation. This gives further evidence that xylene should be a theta solvent (i.e. $A_2$ as defined above is close to zero and there is almost no free energy of mixing) for the 1.65 mol% SPS as observed.

### *Free energies of aggregation*

The free energies of aggregation for the 1.39[12] and 1.65 mol% SPS (*Table 2*) obtained using equation (12) are identical within experimental error. The lack of temperature dependence of the equilibrium constant observed previously with the 1.39 mol% ionomer suggests that in these cases the free energy change on aggregation arises mainly because of an increase in entropy[12]. This is most probably because within the aggregates the single chains can expand. Within the aggregates formed by both 1.25 and 0.98 mol% SPS ionomers the single chains have been shown by neutron scattering to expand to the same dimensions as the unsulfonated polymer[10,16].

Since the single chain of the 0.95 mol% ionomer is less compact than that of the higher sulfonation level ionomers it is likely that in this case less entropy would be gained on aggregation to form dimers of similar structure to those formed with the 1.39 and 1.65 mol% ionomers. These results suggest that this 0.95 mol% SPS can instead gain more free energy by forming a very different structured and more dense aggregate consisting of three chains. The free energy change on forming these aggregates (*Table 4*) is slightly more than twice the value obtained for the dimer of the higher sulfonation level ionomers. It is therefore also slightly larger than the free energy change on forming an aggregate of three chains with the 1.39 and 1.65 mol% ionomers [see equation (12)]. The formation of micelles of one preferred size is common with surfactants in water and is reasonably well understood[14]. Further work is, however, required to understand what controls the free energy changes on aggregation of these types of polymer in non-polar solvents.

## SUMMARY AND DISCUSSION

The aggregation behaviour of several SPS ionomers of molecular weight of $10^5\,\mathrm{g\,mol^{-1}}$ have been determined in *p*-xylene. As the sulfonation level is increased the free energy of solvation of the ionomers decreases until at ~2 mol% sulfonation the ionomer becomes insoluble. With ionomers of 1.39 and 1.65 mol% an equilibration between single collapsed chains and aggregates of all sizes occurs in this solvent. As the ionomer concentration is raised an increase in the average size of the aggregates is observed. The aggregates formed are of lower density than the single chains. Since the weight fraction of single chains decreases with raising the ionomer concentration this explains why the reduced viscosity of dilute solutions of these ionomers has been observed to rise rapidly with increasing concentration[16]. At concentrations exceeding $2\times10^{-2}\,\mathrm{g\,ml^{-1}}$ solutions of these ionomers can gel[10]. These results suggest this is because of the formation of very large low density aggregates.

With 0.95 mol% SPS in xylene single chains with dimensions in between those of polystyrene and the higher sulfonation level ionomers are observed. This explains why the intrinsic viscosity of these ionomer solutions has been observed[16] to be in between that of polystyrene and the above ionomers. In dilute solution these single chains equilibrate with aggregates consisting of three chains. The aggregates in this case were much more dense than those formed with the higher sulfonation level ionomers. This interprets why for this ionomer the reduced viscosity varies less with concentration in the dilute solution regime than observed with 1.39 mol% SPS.

It has been observed that the properties of this ionomer with 1.25 mol% sulfonation are very sensitive to the exact conditions of preparation. In some cases this ionomer will form a gel in xylene but at other times it forms only small aggregates and no gelation occurs[15]. This suggests that slight changes in the conditions of preparation of this ionomer can affect whether the ionomer behaves similarly to the 0.95 or the 1.65 mol% ionomers studied above. Further work is required in order to obtain a fuller understanding of the factors controlling the free energy changes on aggregation of ionomers in non-polar solvents. These results have shown, however, that both the single chain and aggregate dimensions are important in explaining the decrease in reduced viscosity of dilute ionomer solutions with raising the sulfonation level.

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