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Effect of aggregation on the single-chain dimensions of sulfonated polystyrene ionomers in xylene

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Small-angle neutron scattering has been used to determine the dimensions of single chains within the aggregates formed in the solvent *p*-xylene by a sodium sulfonated polystyrene ionomer (SPS). This polymer has a molecular weight of 10^5 g mol^{-1} and sulfonation level of 1.25 mol %. The dimensions were obtained by using a mixture of normal and deuterated polymer to achieve contrast match of the overall polymer in a mixed normal and deuterated solvent. As the concentration of the ionomer was raised, the average single-chain radius of gyration increased. This rise occurs as a result of an increase in the ratio of aggregates to single chains. The isolated ionomer chains collapse to dimensions smaller than for the 'parent' polystyrene in a theta solvent. Within an aggregate, however, each individual ionomer chain expands to a size larger than that for the equivalent polystyrene in *p*-xylene (a good solvent for the 'parent' polymer). Using an open association model to quantify the extent of aggregation as a function of concentration, the single-chain dimension both in the aggregates and as collapsed chains have been estimated. The average radius of gyration of a single chain was found to be 60 Å for an isolated chain but rose to a maximum value of 144 Å within an aggregate. It is suggested that the entropy change that occurs on aggregation arises primarily from the single-chain expansion. The models developed have also been used to explain previous measurements of the single-chain dimensions of other ionomers in non-polar solvents. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Ionomers are macromolecules containing a small number (typically < 10 mol %) of ionic groups chemically bound to a non-polar chain. Several reviews describing their properties in both the solid state and solution[1,2], as well as theories on their state of aggregation[3,4] and industrial applications of these polymers[5], are available. Their industrial importance stems from the very dramatic effects of the presence of low levels of charged groups on the properties of non-polar polymers. The addition of a few charged groups to polyethylene, for example, greatly improves its clarity. The charged groups can also substantially increase the miscibility of the non-polar polymer with polar additives or other polymers, and improve tensile properties. In non-polar solvents the addition of a few charged groups can make a soluble, non-polar polymer surface-active and under some conditions greatly enhance its solvent viscosifying properties. Many uses for ionomers in various lubricants as stabilizers and viscosifiers have therefore been found. The initial aim of our work, however, was to gain a fundamental understanding of how these charged groups affect the rheological properties of non-polar polymers in low polarity solvents.

In low polarity solvents such as xylene, toluene and tetrahydrofuran, the reduced viscosity of dilute ionomer solutions usually decreases as the level of charged groups on the ionomer is raised. It was initially suggested (since the reduced viscosity is proportional to the volume occupied by the polymer chains) that this is as a result of single-chain collapse via intramolecular ion pair associations. In the semi-dilute concentration regime, however, an increase in viscosity is observed as the level of charged

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groups is raised. At a critical charge level the ionomer becomes insoluble. Just below this charge level, the semi-dilute solutions of the ionomer often 'gel'. The gelation was attributed to intermolecular associations forming at the expense of intramolecular ones as the ionomer concentration was raised. This would cause single-chain expansion, aggregation and network formation[6–8].

However, use of light and neutron scattering indicated that even in very dilute solution many of the single ionomer chains are aggregated in non-polar solvents[9,10]. The reduced viscosity in dilute solution is therefore dependent not only on the single-chain dimensions, but also on the compactness of the aggregates and the ratio of single chains to aggregates at any given concentration. More recent work has shown that the 'open' and 'closed association models'[11] can be used to determine (from detailed light and neutron scattering studies) both the ratio of single chains to aggregates at a given concentration and their individual dimensions in dilute solution[12,13]. In the open association model it is assumed that single chains are in equilibrium with aggregates of all sizes. In the closed association model, however, only single chains and aggregates of one size are considered to be present in solution[11].

Most of the detailed light and neutron scattering work has been carried out on sodium sulfonated polystyrene ionomers (SPS) that are randomly sulfonated and of molecular weight 10^5 g mol^{-1} in *p*-xylene[12,13]. These ionomers become insoluble in this solvent at charge levels greater than 1.7 mol %. In the range of ionic substitution between 1.25 and 1.65 mol % gelation of the semi-dilute solutions can be observed. In these later cases the aggregation in dilute solution follows the open association model and the average number of chains in an aggregate increases as the ionomer concentration is raised. If the sulfonation level is reduced to 0.95 mol %, however, just single chains and aggregates consisting of three chains only are ever present in dilute solutions (i.e. the aggregation follows the closed association model)[12,13]. The single isolated chains for the SPS ionomers with sulfonation levels from 0.95 to 1.65 mol % were all found to be very compact in xylene. The aggregates, however, were much less compact for the ionomers aggregating via the open association model (i.e. sulfonation levels of 1.25 to 1.65 mol %) than those formed by the 0.95 mol % ionomer. From the open association model it can be predicted that in the semi-dilute concentration regime the higher sulfonation level ionomers should form very large, low density aggregates which would explain the observation of gelation. Comparison of results for these ionomers with rheological measurements[6] and light scattering[9] results on other ionomers in non-polar solvents suggests that this change from a closed to open association model as the sulfonation level is raised to a critical level (at which the semi-dilute solutions can gel and beyond which the ionomer becomes insoluble) may be a common feature.

The aim of the present work is to understand what controls the type and extent of aggregation of ionomers in dilute solution and particularly why it should change so dramatically at critical charge levels. Neutron scattering results as a function of temperature have shown that the equilibrium position between single chains and aggregates for all the above SPS ionomers studied in xylene is determined primarily by the increase in entropy that arises on forming an aggregate, with relatively little enthalpy change of aggregation being observed[12,14]. For SPS ionomers with sulfonation levels between 1.25 and 1.65 mol % a 'simple' open association model, in which the entropy change is constant each time an aggregate increases in size by one chain, can explain all the results at low concentrations (below 1 g dl^{-1}) very well. In order to observe a system whose aggregation can be described by the closed association model (i.e. as with the 0.95 mol % SPS ionomer), the formation of one aggregate must result in slightly greater entropy than obtained with any other structure. It has been suggested that the entropy rise of the above polymers on aggregation is due to an increase in configurational entropy arising primarily from single-chain expansion on breaking intra- and forming intermolecular ion pair associations[12,14]. The expansion could also, however, affect the entropy of the solvent due to its better mixing with expanded rather than compact single chains.

It is possible to determine the single-chain dimensions within aggregates using neutron scattering and a contrast match method. This technique uses partially deuterated polymers and matches the scattering of the aggregates to that of the solvent, but leaves a contrast between individual polymer molecules and their environment. It gives an average single-chain size for all the polymer chains, both aggregated and isolated in solution. The average single-chain dimensions in solutions of a partially deuterated 0.98 mol % SPS ionomer in xylene at concentrations between 1 and 3 g dl^{-1}, where most of the single chains are expected to be in three-chain aggregates, are of similar size to those observed for the 'parent' unsulfonated polymer at the same concentration. This size is very much larger than that observed for the isolated chains in dilute solution of any of the above-described ionomers in xylene. Preliminary results have also shown that in semi-dilute gelled xylene solutions of 1.25 mol % SPS, the average single-chain dimensions are much more expanded than the isolated chains[15]. The purpose of this work is to confirm that this single-chain expansion also occurs as a result of aggregation with the 1.25 mol % SPS ionomer in dilute solution (where the aggregation can be explained by the open association model). If single-chain expansion does occur on forming intermolecular associations at the expense of intramolecular associations, then the single-chain dimensions in dilute solution should increase with concentration in a systematic manner dependent upon the ratio of single chains to aggregates. A model to predict these changes with concentration will also be given.

EXPERIMENTAL

Sample preparation

The ionomer used in this study has been described previously (sample A in ref. 15). In order to prepare this ionomer, 80 wt % hydrogenous polystyrene of molecular weight 105 300 g mol^{-1} was first mixed with 20 wt % deuterated polystyrene of molecular weight 108 000 g mol^{-1}. For both polymers $M_w/M_n < 1.05$. This polymer mixture was then sulfonated to a level of 1.25 mol % using the method detailed in ref. 15. Briefly, this sulfonation procedure consists of reacting the polymer in 1,2-dichloroethane with acetic anhydride and concentrated sulfuric acid. The acid form of the randomly sulfonated ionomer obtained is then neutralized with sodium acetate and isolated from the solvent by steam stripping. The sulfonation level is determined by Diertert sulfur analysis. The ionomer obtained can cause gelation of xylene at polymer concentrations $>2.0\,\mathrm{g\,dl^{-1}}$ (ref. 15). Its aggregation in dilute xylene solutions was also found by light scattering to be identical to that of ionomers of similar sulfonation level containing no deuterated polymer[16]. These results are a good indication that the deuterated and normal polystyrene are sulfonated to the same extent. After sonication for about 30 min in a sonic bath, all the ionomer solutions used in the following experiments were left for 2 weeks to allow time for equilibrium to be reached.

Small-angle neutron scattering

Small-angle neutron scattering (SANS) experiments were performed using the D17 spectrometer at the Institut Laue Langevin, Grenoble, France. The samples were measured in 2 mm path length quartz cells at 25°C. The use of a large beam, high neutron flux and long sample times allowed measurements to be made on unusually dilute contrast matched solutions (down to $0.1\,\mathrm{g\,dl^{-1}}$). 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 $q = (4\pi/\lambda)\sin\theta$. λ is the incident wavelength (15 Å in this case), the sample-to-detector distance was 3.4 m and the scattering angle is 2θ. 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 as a measure of the detector response. The resulting intensity represents the polymer scattering that is mainly coherent but with a very small (and in this case negligible) flat incoherent component.

THEORY

Analysis of scattering data

The intensity (as a function of the scattering vector q) due to the coherent scattering from a solution containing both deuterated and hydrogenous polymer molecules can be written as

$$I(q) = \kappa Mc[AS_\mathrm{s}(q) + BS_\mathrm{p}(q)]$$

The constant κ can be calculated from the intensity of scattering from water and the known scattering cross-section of water. $S_\mathrm{s}(q)$ and $S_\mathrm{p}(q)$ are the single-chain and pair (or cross term) scattering functions, respectively, and the constants A and B are given by

$$A = (N_\mathrm{A}/m_0^2)\,[(a_\mathrm{D} - a_\mathrm{s}^*)^2 x + (a_\mathrm{H} - a_\mathrm{s}^*)^2(1 - x)]$$

and

$$B = (N_\mathrm{A}/m_0^2)\,(a_\mathrm{P} - a_\mathrm{s}^*)^2$$

where

$a_\mathrm{P} = a_\mathrm{D}x + a_\mathrm{H}(1 - x)$;
N_A is Avogadro's number;
c is total polymer concentration in $\mathrm{g\,dl^{-1}}$;
M is polymer molecular weight;
m_0 is molecular weight of a monomer unit of the polymer;
a_H and a_D are scattering lengths referring to the hydrogenous and deuterated monomers, respectively;
a_s^* is scattering length for the solvent corrected for the difference between the volume of a solvent molecule and the volume of a monomer unit in the polymer; and
x is mole fraction of deuterated polymer.

The above polymer was therefore dissolved in a mixture of 67 wt % hydrogenous/33 wt % deuterated *p*-xylene. Under these conditions $a_\mathrm{P} = a_\mathrm{s}^*$, making B zero, so that single-chain scattering only is then observed. In this case for $qR_\mathrm{g} < 1$, the Zimm expression

$$A\kappa c/I(q) = 1/M[1 + (qR_\mathrm{g})^2/3] \tag{1}$$

can be used to obtain the mean-square single-chain radius of gyration, R_g, of the monodisperse ionomer. Alternatively, using the Debye model for Gaussian chains[17] gives

$$I(q)/(A\kappa c) = M(2/u^2)\,[\exp(-u) - 1 + u] \tag{2}$$

where $u = (qR_\mathrm{g})^2$. This later expression can be used over the full q range measured. In the following, both the above functions were fitted to the scattering data in order to obtain R_g as a function of the ionomer concentration.

Open association model for the aggregation of 1.25 mol % SPS in xylene

In order to determine if single-chain expansion occurs as a result of ionomers forming intermolecular ion pair associations at the expense of intramolecular ones, a model of how the single-chain dimensions might be expected to rise with concentration as the ratio of single chains to aggregates increases is required. Details of previous known properties of the ionomer to be studied in this work will, therefore, first be described.

In xylene, SPS ionomers with ionic substitution levels between 1.25 and 1.65 mol % of molecular weight $10^5\,\mathrm{g\,mol^{-1}}$ follow an open association type aggregation process, the extent of which varies little with the sulfonation level[12,13,16]. This process can be represented by

$$\begin{array}{ll} \mathrm{P_1 + P_1 \Leftrightarrow P_2} & K_2 \\ \mathrm{P_1 + P_2 \Leftrightarrow P_3} & K_3 \\ \mathrm{P_1} + \mathrm{P}_n \Leftrightarrow \mathrm{P}_{n+1} & K_{n+1} \end{array}$$

where P_i is an aggregate consisting of i chains. If the equilibrium constants for each step can be considered invariant to increases in the size of the aggregates, i.e.

$$^nK_0 = K_2 = K_3 = [\mathrm{P_2}]/[\mathrm{P_1}]^2 \tag{3}$$

where $[\mathrm{P_1}]$ and $[\mathrm{P_2}]$ are the molar concentrations of the single chains and two-chain aggregates, respectively, then the weight-average molecular weight of the single chains and aggregates as a function of concentration is given by[11]

$$(M_\mathrm{w})^2 = (M\,)^2[1 + (4\,^nK_0c/M\,)] \tag{4}$$

This expression fits the variation in weight-average molecular weight with concentration of the 1.25–1.65 mol % SPS in xylene obtained by both light[16,18] and non-contrast matched neutron scattering[12,13] very well. $^nK_0$ was found to equal $1.1(\pm 0.2) \times 10^4\,\mathrm{l\,mol^{-1}}$. The number-average molecular weight M_n of the single chains and aggregates is then given by[11]

$$M_\mathrm{n}/M = 1 + {}^nK_0c/M_\mathrm{n}$$

On multiplication of both sides by (M_n/M) and rearrangement, this gives the quadratic

$$(M_n/M)^2 - (M_n/M) - {}^nK_0 c/M = 0 \tag{5}$$

which can be solved to obtain M_n/M at any concentration c, since ${}^nK_0$ is known. This will be used later in this paper.

The free energy change on the addition of a single chain on to an aggregate or another single chain is given by

$$\Delta G = -RT \ln {}^nK_0 \tag{6}$$

Since ${}^nK_0$ is independent of temperature, this suggests that the free energy must be primarily entropic in nature. From the variation in average aggregate dimensions with concentration, the isolated single-chain radius of gyration of these ionomers has been shown to be only 58(±3) Å. This compares with a value of 130 Å for the 'parent' non-sulfonated polystyrene at infinite dilution[12]. Both the hydrodynamic radius (from dynamic light scattering[18]) and radius of gyration (from SANS[12]) of the two-chain aggregates, however, are between two and three times greater than the values obtained for the single collapsed chains.

A schematic model for the aggregation behaviour of these ionomers is shown in *Figure 1*. The figure is only two-dimensional and the exact number of ion pairs that associate together in each cluster within a single chain or aggregate is unknown. However, the figure does show a schematic mechanism for aggregation that takes into account all the above known properties of these ionomers.

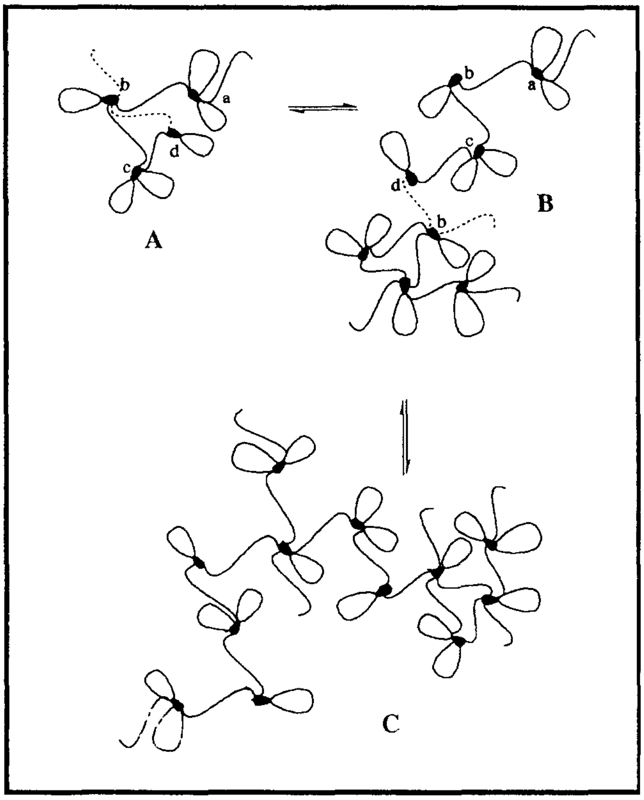

Figure 1 Schematic diagram showing the aggregation behaviour of SPS 1.25 mol % in xylene (for details see text)

Model for the variation of single-chain dimensions of 1.25 mol % SPS in xylene with concentration

In *Figure 1* collapsed single chains are represented by A and expanded two-chain aggregates by B. Part of the single chain A is shown dotted and the associations labelled to indicate how intermolecular association might occur at the expense of intramolecular association. Since the entropy change observed is the same whether a collapsed single chain joints another collapsed chain or an aggregate of any size (since the equilibrium constants in equation (3) are equal), a similar process must be occurring in all cases. In aggregate B, therefore, only one of the individual chains is shown expanded. In the three-chain aggregate C, two of the individual chains are expanded. This has been done to show simply and schematically how a constant increase in entropy (observed each time a single chain adds on to an aggregate or single chain) could be accounted for by a constant increase in single-chain expansion. This model means, however, that the average size of a single chain in an aggregate increases as the number of chains in the aggregate is raised. If the radius of gyration of a single isolated chain is R_{g_1} and its expansion on joining an aggregate x, then the average single chain size, R_{g_n}, in an aggregate of n chains will be

$$\begin{aligned} R_{g_2} &= [R_{g_1} + (R_{g_1} + x]/2 \\ R_{g_3} &= [R_{g_1} + (R_{g_1} + x) + (R_{g_1} + x)]/3 \\ R_{g_n} &= [nR_{g_1} + (n-1)x]/n = R_{g_1} + (n-1)x/n \end{aligned} \tag{7}$$

The average single-chain size in an infinitely large aggregate will be $R_{g_\infty} = R_{g_1} + x$.

Unfortunately, calculation of the mean-square single-chain radius of gyration as obtained from the scattering for the monodisperse but aggregating ionomers is complex if the above model for the single-chain sizes in an aggregate is used. It has been found in this work, however, that calculating instead the mean radius of gyration of the ionomer single chains greatly simplifies the mathematics of the problem. The difference between the two means of the single-chain dimensions was found to be negligibly small for this work. It shall, therefore, be taken that the measured contrast matched single-chain radius of gyration for the ionomers is given by

$$R_g \approx \sum_n c_n R_{g_n}/c \tag{8}$$

where c_n is the concentration of single chains that are within aggregates consisting of n chains. Combining equations (7) and (8) gives

$$R_g \approx \sum_n \{c_n[R_{g_1} + (n-1)x/n]/c\}$$

Expanding this expression gives

$$R_g \approx \sum_n (c_n R_{g_1}/c) + \sum_n (c_n x/c) - \sum_n (c_n x/nc)$$

Since $\Sigma_n c_n = c$ and R_{g_1}, x and c are constants that can be removed from the summation, all terms (except the final term) in the last equation simplify, leading to

$$R_g \approx R_{g_1} + x - (x/c)\sum_n (c_n/n) \tag{9}$$

But from ref. 11

$$(1/c)\sum_n (c_n/n) = (c_1 + c_2/2\ldots)/c = M/M_n \qquad (10)$$

where M_n is the number-average molecular weight of all the aggregates and single chains and can be calculated from equation (5) above for any given ionomer concentration. Then, combining equations (9) and (10)

$$R_g = R_{g_1} + x(1 - M/M_n) \qquad (11)$$

A plot of R_g (from contrast matched single-chain dimensions) *versus* $(1 - M/M_n)$ (calculated from ${}^nK_0$ obtained previously[12]) should, therefore, be linear with the intercept and gradient equal to R_{g_1} and x, respectively, if the above model describes the aggregation process well.

RESULTS

In *Figure 2* examples of Zimm plots for contrast matched 1.25 mol% SPS in xylene are shown. Within experimental error, all the intercepts equal the inverse single-chain molecular weight as expected from equation (1). This result gives confidence that the solutions were correctly contrast matched. It can be seen from these plots that although some of the data are outside the $qR_g < 1$ region, the Zimm plot is almost linear over the whole q range measured. Including data at $qR_g > 1$ tends to result in values for R_g from the Zimm plot that are slightly too large. However, in this work, the values obtained were corrected for using data at too large q by dividing the radii of gyration obtained from the gradient of the Zimm plots by factors calculated by Ullman[19]. In *Figure 3* an example of the fit of the Debye model to the whole scattering curves is shown. This model clearly also fits the data very well and was found to give (within experimental error) identical radii of gyration to those obtained using the Zimm expression with correction factors. Radii of gyration obtained using the Zimm expression over several q ranges as well as the Debye model were averaged and are given in *Table 1* as a function of concentration. The errors in this table indicate the variation in radii of gyration obtained using different scattering models and q ranges.

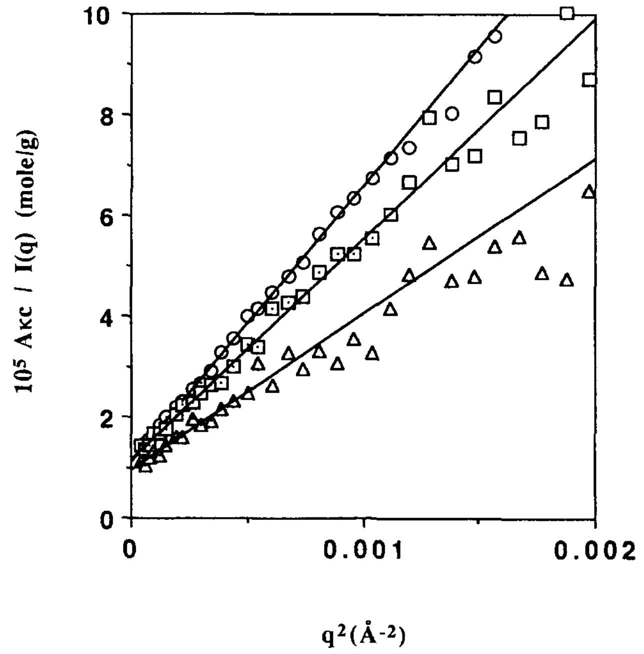

Figure 2 Normalised inverse coherent scattering intensity as a function of scattering vector squared (Zimm plot) for SPS 1.25 mol% in xylene; (△) 0.2 g dl^{-1}; (□) 0.5 g dl^{-1}; (○) 1.5 g dl^{-1} (the lines are the best straight line fits to the data at $q^2 < 0.001$)

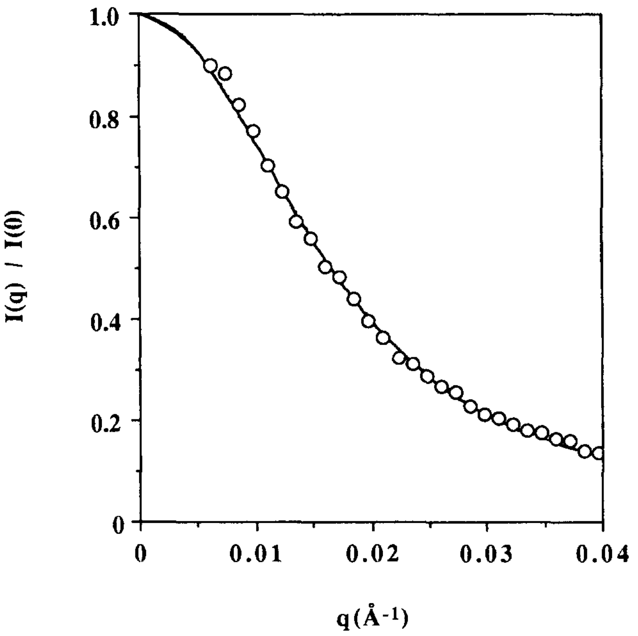

Figure 3 Coherent scattering for SPS 1.25 mol% at 1.5 g dl^{-1} in xylene as a function of the scattering vector q. (Curved line is the best fit of the Debye equation found with $R_g = 96$ Å)

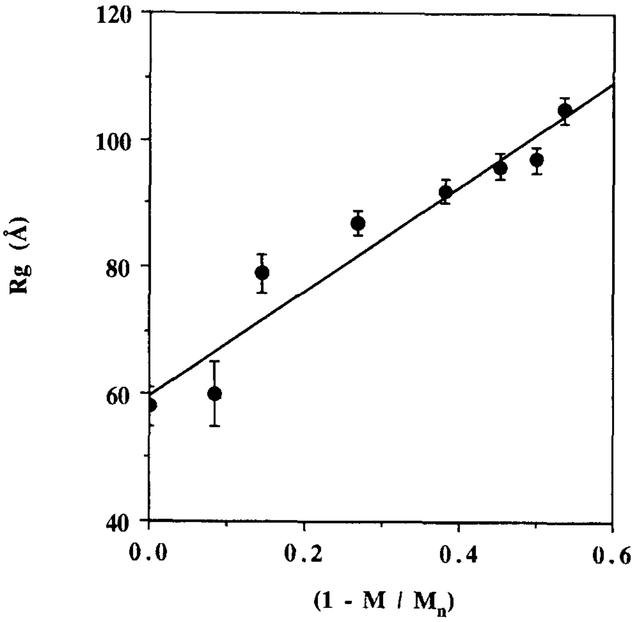

Figure 4 Single chain radius of gyration of SPS 1.25 mol% *versus* $(1 - M/M_n)$. (The error bars indicate the variation in R_g obtained using different scattering models and the straight line is the best linear fit through all the data)

Also in *Table 1* are values for M_n/M calculated using equation (5). R_g *versus* $(1 - M/M_n)$ is plotted in *Figure 4*. This plot is almost linear as expected from equation (11)

Table 1 Average single-chain dimensions of 1.25 mol % SPS in xylene, with calculated values for the number-average molecular weight as a function of concentration

c (g dl^{-1})	Average single-chain R_g (Å)	M_n/M[a]
0.0	58 ± 3[b]	1.000
0.1	60 ± 5	1.092
0.2	79 ± 3	1.171
0.5	87 ± 2	1.366
1.0	92 ± 2	1.618
1.5	96 ± 2	1.825
2.0	97 ± 2[c]	2.000
2.5	105 ± 2[c]	2.160

[a] Calculated using equation (5)

[b] Result obtained from non-contrast matched neutron scattering[13]

[c] Previous preliminary results from ref. 15

and gives from the intercept an isolated single-chain radius of gyration of 60 ± 5 Å, in agreement with earlier work[13]. The gradient x of *Figure 1* is 84 Å, which gives an average size of a single chain in an aggregate of infinite size as 144 ± 5 Å [from equation (7)]. This value is slightly larger than that obtained for the equivalent non-sulfonated polystyrene in this solvent at infinite dilution (130 Å)[12]. In an aggregate of two chains the average single-chain size will then be 102 Å [from equation (7)]. These results all agree well with the schematic representation of the aggregation process shown in *Figure 1*.

SUMMARY AND CONCLUSIONS

The above results give strong evidence for single-chain expansion of the 1.25 mol % SPS ionomer in xylene on forming intermolecular ion pair associations from intramolecular ones. The average radii of gyration of single chains in isolated compact single chains and aggregates of two chains were found to be 60 and 102 Å, respectively. In three-chain and infinitely large aggregates the average single-chain radii of gyration increased to 116 and 144 Å, respectively, according to the model developed in the above work. The extent of aggregation of ionomers in xylene has previously been shown to be entropy-dominated, with negligible enthalpy of aggregation being observed. With the expansion on aggregation is observed an increase in entropy of 77 and 154 J K^{-1} mol^{-1} for the formation of the two- and three-chain aggregates from single chains, respectively[12]. The expansion could affect both the configurational entropy of the polymer and the entropy of mixing with the solvent. In this case the aggregates are of low density, suggesting that the individual chains are not strongly interpenetrating within the aggregates.

By comparison, other work[14] has shown that with the 0.95 or 0.98 mol % SPS ionomer single chains expand from an average of about 78 Å in an isolated chain to 115 Å in their three-chain aggregates. In these cases a slightly larger increase in entropy of 176 J K^{-1} mol^{-1} is observed on forming a three-chain aggregate from single chains than observed with the 1.25 mol % SPS ionomer. With 0.95 mol % SPS, however, the aggregates formed are also very compact indicating that the expanded single chains are strongly interpenetrating within the aggregates. These results suggest that the type of structure of the aggregates (expanded or compact) as well as the extent of single-chain expansion are the main factors determining the entropy of aggregation of ionomers in xylene.

In conclusion, these types of study help gain a basic understanding of the factors controlling the aggregation of polymers in solution, particularly those with small numbers of randomly placed strongly associating groups. Associating polymers are found in a wide range of systems including biological fluids, foods, paints and lubricants. The study of model polymers like ionomers, therefore, where considerable control over the polymer polydispersity and number of associating groups can be achieved, will not only be of benefit in the application of the model system but also lead to an understanding of the factors controlling aggregation in general. This would enable better control over the use of any aggregating polymer system.

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REFERENCES

1 Tant, M. R. and Wilkes, G. L. *JMS Rev. Macromol. Chem. Phys.* 1988, **C28**(1), 1
2 Fitzgerald, J. J. and Weiss, R. A. *JMS Rev. Macromol. Chem. Phys.* 1988, **C28**(1), 99
3 Mauritz, K. A. *JMS Rev. Macromol. Chem. Phys.* 1988, **C28**(1), 65
4 Eisenberg, A., Hird, B. and Moore, R. B. *Macromolecules* 1990, **23**, 4098
5 Lundberg, R. D. in 'Structure and Properties of Ionomers' (Eds M. Pineri and A. Eisenberg), Reidel, Dortrecht, 1987, pp. 429–438
6 Agarwal, P. K., Garner, R. T. and Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 2095
7 Lundberg, R. D. and Makowski, H. S. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**(8), 1821
8 Peiffer, D. G., Kaladas, J., Duvdevani, K. and Higgins, J. S. *Macromolecules* 1987, **20**, 1397
9 Lantman, C. W., MacKnight, W. J., Peiffer, D. G., Sinha, S. K. and Lundberg, R. D. *Macromolecules* 1987, **20**, 1096
10 Lantman, C. W., MacKnight, W. J., Higgins, J. S., Peiffer, D. G., Sinha, S. K. and Lundberg, R. D. *Macromolecules* 1988, **21**, 1339
11 Elias, H. G. in 'Light Scattering from Polymer Solutions' (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch. 9
12 Pedley, A. M., Higgins, J. S., Peiffer, D. G. and Rennie, A. R. *Macromolecules* 1990, **23**, 2494
13 Young, A. M., Higgins, J. S., Peiffer, D. G. and Rennie, A. R. *Polymer* 1995, **36**, 691
14 Young, A. M., Timbo, A. Higgins, J. S., Peiffer, D. G. and Lin, M. Y. *Polymer* in press
15 Pedley, A. M., Higgins, J. S., Peiffer, D. G., Rennie, A. R. and Staples, E. *Polym. Commun.* 1989, **30**, 162
16 Pedley, A. M. *Ph.D. Thesis*, Imperial College, 1990
17 Debye, P. *J. Phys. Colloid Chem.* 1947, **51**, 18
18 Pedley, A. M., Higgins, J. S., Peiffer, D. G. and Burchard, W. *Macromolecules* 1990, **23**, 1434
19 Ullman, R. *J. Polym. Sci., Polym. Phys. Edn* 1985, **3**, 1477