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Dynamic light scattering and rheology of associating sulfonated polystyrene ionomers in non-polar solvents

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Dynamic light scattering and reduced viscosity measurements on dilute solutions of sodium sulfonated polystyrene (NaSPS) ionomers of molecular weight 1×10^5 g mol^{-1} and sulfonation levels of 0, 0.62, 0.95 and 1.39 mol% in xylene are described and compared with earlier static light and small-angle neutron scattering studies. The unsulfonated polystyrene and 0.62 mol% ionomer are present in dilute xylene solutions as single expanded chains. The 0.95 mol% ionomer, however, forms an equilibrium between single chains and aggregates of three chains in the concentration range studied (i.e. closed association). The dimensions of both the aggregates and single chains with the latter ionomer are closer to those observed for polystyrene under theta conditions rather than in xylene. With the 1.39 mol% ionomer single chains are found to be in equilibrium with aggregates of all sizes (i.e. open association). The single chains are more compact than expected for polystyrene even in a theta solvent. The aggregates, however, are lower density structures. The viscosities of the ionomer solutions were found to be determined by the total volumes occupied by the single chains and aggregates only in very dilute solutions (< 0.4 g dl^{-1}). Comparison of the behaviour of these ionomers dissolved in xylene with previous rheological and light scattering studies on different ionomers dissolved in a range of other solvents suggest that the variations in the extent of single-chain collapse and aggregation behaviour with charge level observed in this work could be a common feature of randomly charged ionomers in non-polar solvents. The charge levels at which transitions between different types of behaviour occur are determined primarily by the strengths of the ionic interactions and the dielectric constant of the solvent. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The addition of a few ionic groups to non-polar polymers to produce an ionomer has profound effects on the properties of the polymer[1]. The purpose of this work is to interpret some of the effects of the addition of these ionic groups on the viscosities of such polymers in non-polar solvents by using monodiperse sodium sulfonated polystyrene ionomers (NaSPS) of molecular weight 1×10^5 g mol^{-1} in xylene as a model system. In an earlier work, a large number of measurements on the dilute solution viscosity of polydisperse sulfonated polystyrene ionomers with a molecular weight of the order of 2.6×10^5 g mol^{-1} and neutralized with a range of different bases in several non-polar solvents were reported[2]. In those measurements it was observed that as the sulfonation level increased, the intrinsic viscosity decreased. It was found that all the intrinsic viscosities (i.e. reduced viscosity extrapolated to zero concentration) could be scaled to fit a master curve given by

$$[\eta] = [\eta]_{PS} F(\xi) \qquad (1)$$

where

$$\xi = a_s a_a y$$

y is the mole fraction of ionic groups and $[\eta]_{PS}$ is the intrinsic viscosity of the parent polystyrene in the same solvent as the ionomer. a_s is a solvent factor given by

$$a_s = \varepsilon_{toluene}/\varepsilon$$

where ε and $\varepsilon_{toluene}$ are the relative dielectric constants of the solvent and toluene (used as an arbitrary solvent standard), respectively. a_a was dependent upon the counterion for the ionomer and was set equal to 1 for the sodium counterion. Below $\xi = 0.4$, $F(\xi)$ is close to 1. For $\xi > 0.4$, $F(\xi)$ decreases as ξ is raised until the ionomer becomes insoluble at critical values of $\xi_c = 1.6$ and $F(\xi)_c = 0.18$. These critical values for sodium sulfonated polystyrene (NaSPS) are calculated to be at sulfonation levels of 1.6, 1.5 and 5.1 mol% in toluene, *p*-xylene and tetrahydrofuran (THF), respectively [by using equation (1) with $\varepsilon_{toluene} = 2.37$, $\varepsilon_{xylene} = 2.27$ and $\varepsilon_{THF} = 7.6$]. Ionomer solutions with ξ values close to the critical value will often gel in the semi-dilute concentration range. The variations of reduced viscosities with concentration in dilute solution, however, have previously

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been much more difficult to interpret or scale than the intrinsic viscosities.

Rheological studies with other molecular weight ionomers include those on monodisperse SPS ($M_w = 4 \times 10^5$ g mol^{-1}) neutralized with sodium[3] and other counterions[4] in tetrahydrofuran (THF). Intrinsic viscosities close to values expected from the master curve derived by Agarwal *et al.*[2] were also observed in these cases. Studies on ionomers with backbones other than polystyrene, such as sulfonated EPDM in xylene[5] and methacrylic acid-*co*-methyl methacrylate in THF[6], show similar trends in rheological properties, indicating that the types of behaviour described above are common to many ionomers in non-polar solvents.

The reduced viscosities of dilute polymer solutions are primarily dependent upon the dimensions of (or volumes occupied by) the polymer chains. In THF, NaSPS ionomers of molecular weights 1.0×10^5, 9.0×10^5 and 18.0×10^5 g mol^{-1} with sulfonation levels of the order of 1 mol% were found to have single-chain hydrodynamic radii (as determined by dynamic light scattering) comparable with those of polystyrene[7]. This is as might be expected from the rheological studies of Agarwal *et al.*[2] since $\xi \approx 0.3$ and $F(\xi) \approx 1$. For ionomers with higher sulfonation levels, however, the apparent hydrodynamic radii determined by dynamic light scattering were all much larger than those for the unsulfonated polymer, contrary to what might be initially expected from the rheological studies. Static light scattering results described in the same study[7] indicated, however, that the large apparent sizes were a result of the polymer chains exhibiting an increasing tendency to aggregate as their concentration is raised. It has been proposed that the aggregation is caused by intermolecular ion–pair associations. Both a_s and a_a could be taken as a measure of the strength of these associations. In order to explain the rheological properties of the aggregating ionomers the aggregate molecular weights, weight fractions and dimensions as a function of concentration are needed in order to determine the total volumes occupied by the polymer. This unfortunately requires[8] small-angle neutron scattering measurements (or very careful light scattering studies) to be made over a broader concentration range than previously measured for the aggregating ionomers in THF[7].

In earlier studies we have determined the extent of aggregation of several monodipserse NaSPS ionomers (molecular weight 10^5 g mol^{-1}) in xylene by means of static light[9] and small-angle neutron[10–12] scattering. These measurements were obtained over a sufficiently broad concentration range such that the 'open' and 'closed' association models[8] could be fitted to the results (see later for a detailed description of these models). By using these models, the aggregate and single-chain radii of gyration were determined as well as the relative weight fractions of aggregates and single chains at different concentrations. In this work, the hydrodynamic radii of the ionomers obtained by dynamic light scattering are compared with the previously obtained radii of gyration. The viscosities of the model ionomers in xylene are also described and compared with that expected from the single-chain and aggregate, hydrodynamic and gyration, radii.

THEORY

Aggregation of NaSPS ionomers in xylene

Much of the early work on the viscosity of ionomer solutions was carried out in the concentration range of 0.1 to 1 g dl^{-1}. In this concentration range the extent of aggregation of sodium sulfonated polystyrene ionomers of molecular weight 10^5 g mol^{-1} in xylene varies with sulfonation level in the manner described below.

0.62 mol% NaSPS. Preliminary static light scattering results suggest that aggregation of 0.62 mol% NaSPS in xylene ($\xi = 0.67$) is negligible at low concentrations[13] as observed previously with other ionomer solutions with low ξ values. The ionomer radius of gyration, however, can only be roughly estimated owing to the polymer size being close to the meausurement limit of the latter techniques. Futher measurements using other methods are therefore required to confirm the lack of aggregation of this ionomer in xylene and determine its dimensions.

0.95 mol% NaSPS. Small-angle neutron scattering (SANS) data from 0.95 mol% NaSPS ionomers in xylene ($\xi = 0.99$) can be interpreted by assuming a closed association model in which single chains are in equilibrium with aggregates consisting of three chains only[11,12], i.e.

$$3P_1 \Leftrightarrow P_3$$

where P_1 represents a single chain and P_3 a three-chain aggregate. The equilibrium constant for this aggregation is given by

$$^{n}K_c = [P_3]/[P_1]^3$$

where $[P_3]$ and $[P_1]$ are the molar concentrations of aggregates and unimers, respectively. From SANS it was found that $^{n}K_c = 1.63 \times 10^{11}$ dl^2 mol^{-2}. The weight fractions of single chains at a given total polymer concentration, c, can be calculated from

$$w_1 = (3 - x)/2 \qquad (2)$$

where x is the ratio M_w/M_1, M_w being the weight-average molecular weight of the single chains and aggregates and M_1 the molecular weight of the single chains. x varies with the total ionomer concentration according to the expression

$$c^2 = (2M_1)^2[x - 1]/[3 - x]^3/(3^{n}K_c) \qquad (3)$$

The weight fraction of aggregates $(1 - w_1)$ is plotted against concentration in *Figure 1*. From *Figure 1* it is clear that in the concentration range where many previous measurements on ionomer solution viscosities have been obtained

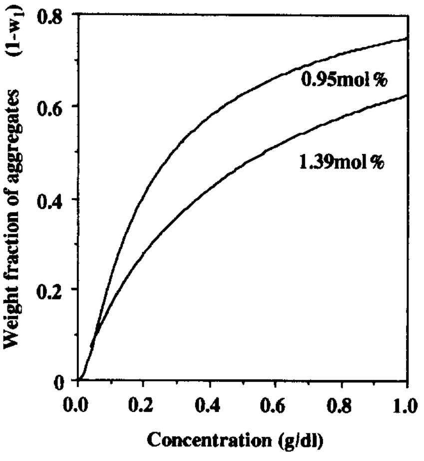

Figure 1 Calculated weight fractions of aggregates $(1 - w_1)$ *versus* concentration for 0.95 and 1.39 mol% SPS in xylene [from equations (2) and (3) and equations (5) and (6)]

(0.1 to 1 g dl^{-1}) there is a large variation in the relative concentrations of single chains and aggregates. This should therefore be taken into account when analysing the rheological results.

1.39 mol% SPS. For NaSPS ionomers in xylene with sulfonation levels of 1.25, 1.39 and 1.65 mol%, the open association model can explain both static light[9] and small-angle neutron[10] scattering results. This model assumes that single chains are in equilibrium with aggregates of all sizes, i.e.

$$P_1 + P_1 \Leftrightarrow P_2, \quad K_2$$

$$P_1 + P_2 \Leftrightarrow P_3, \quad K_3$$

$$P_1 + P_n \Leftrightarrow P_{n+1}, \quad K_{n+1}$$

where 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.

$$^{n}K_0 = K_2 = K_3 = [P_2]/[P_1]^2 \qquad (4)$$

where $[P_1]$ and $[P_2]$ are the molar concentrations of the single chains and two-chain aggregates, respectively. In this case

$$w_1 = \left(M_1/{}^{n}K_0 c\right)[(x-1)/(x+1)] \qquad (5)$$

and

$$x^2 = 1 + \left(4^{n}K_0 c/M_1\right) \qquad (6)$$

The equilibrium constant, $^{n}K_0$, varies little for sulfonation levels between 1.25 and 1.65 mol%[11]. For 1.39 mol% (ξ = 1.5 for the ionomer in xylene) it was found to equal 1.1×10^5 dl mol^{-1}. Using this with equations (5) and (6), the weight fraction of aggregates ($1 - w_1$) *versus* concentration given in *Figure 1* for 1.39 mol% NaSPS was calculated. At concentrations below 0.4 g dl^{-1} most of the aggregates consist of two chains so that the approximation

$$w_2 \approx 1 - w_1 \qquad (7)$$

can be made. This approximation will be used in the following analysis of rheological and dynamic light scattering data from this ionomer.

Dynamic light scattering

For non-aggregating polymers in dilute solution, a concentration-independent z-average diffusion coefficient, D_z, can be obtained from dynamic light scattering (see below). The hydrodynamic radius of the polymer can then be determined from the Stokes–Einstein equation

$$R_h = k_B T/\left(6\pi\eta D_z\right) \qquad (8)$$

where k_B is the Boltzmann constant, T the temperature and η the solvent viscosity. For a polydisperse system the z-average diffusion coefficient is then given by

$$D_z = \sum w_i M_i D_i / \sum w_i M_i \qquad (9)$$

If a polymer is aggregating, however, then D_z can be taken to vary with concentration. In this case, provided the concentration of the solutions is small so that interaction terms between the aggregates can be considered negligible, a diffusion coefficient dependent only upon the relative weights of aggregates and single chains and their sizes can be determined. For a solution of two species only—monodisperse single chains and n-chain aggregates—equation (9) would give the z-average diffusion coefficient as

$$D_z x = \left[D_1 + (1 - w_1)(nD_n - D_1)\right] \qquad (10)$$

where D_1 and D_n represent the diffusion coefficients of the single chains and n-chain aggregates, respectively. Combining equations (8) and (10) gives

$$x/R_h = \left[1/R_{h,1} + (1 - w_1)(n/R_{h,n} - 1/R_{h,1})\right] \qquad (11)$$

where $R_{h,1}$ and $R_{h,n}$ are the single-chain and aggregate hydrodynamic radii. The ratio $x = M_w/M_1$ and weight fractions of single chains, w_1, can be calculated at a given concentration using equations (2) and (3) for the 0.95 mol% ionomer (where $n = 3$). For the 1.39 mol% ionomer equations (5) and (6) can be used, but equation (11) is predicted to be valid at low concentrations only where the concentrations of aggregates consisting of more than two chains can be considered negligible. In these cases a plot of x/R_h *versus* ($1 - w_1$) should be linear provided there are no interactions between the aggregates.

Rheology

The reduced viscosity of dilute, non-aggregating polymer solutions can be given by the Huggins equation for $[\eta]c \ll 1$:

$$\eta_{sp}/c = [\eta]\left(1 + k_H[\eta]c\right) \qquad (12)$$

where k_H is the Huggins constant, $[\eta]$ the intrinsic viscosity and η_{sp} the specific viscosity. The intrinsic viscosity is dependent upon the volume occupied by the polymer chains. For polydisperse systems it is given by[14]

$$[\eta] = \sum w_i[\eta]_i \qquad (13)$$

where $[\eta]_i$ is determined by the volume of the species of molecular weight M_i. In the dilute ionomer solutions where single chains and aggregates of one size only are present, if the concentration is low enough (i.e. so that all other interactions other than the aggregation can be considered negligible), then from equation (13) the reduced viscosity might be expected to be given by

$$\eta_{sp}/c \approx w_1[\eta]_1 + (1 - w_1)[\eta]_n = [\eta]_1 + (1 - w_1)\left([\eta]_n - [\eta]_1\right) \qquad (14)$$

In this case $[\eta]_1$ and $[\eta]_n$ will be constants dependent upon the volumes occupied by the single chains and aggregates, respectively. This result suggests that if measurements can be obtained in a dilute concentration regime (so that inter-aggregate interactions can be considered negligible) where the weight fraction of aggregates also varies strongly with concentration, then a plot of reduced viscosity *versus* ($1 - w_1$) should be a straight line from which both $[\eta]_1$ and $[\eta]_n$ can be obtained.

Expansion factors

In order to compare the hydrodynamic radii and $[\eta]_1$ and $[\eta]_n$ terms with the previously determined radii of gyration of single chains and aggregates, three expansion factors can be defined. These are given by

$$\alpha_s = R_g/R_{g,\theta} \qquad (15)$$

for the radii of gyration,

$$\alpha_h = R_h/R_{h,\theta} \qquad (16)$$

for the hydrodynamic radii, and

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \qquad (17)$$

for the viscosities. The subscript θ represents unperturbed values. Relationships between these expansion factors have been the focus of many theoretical and experimental studies[14–16]. The relationship

$$\alpha_\eta = \alpha_h = 0.596\alpha_s + 0.404 \qquad (18)$$

has been found to be valid for polystyrene in cyclohexane and a range of other linear polymer/solvent systems. It has also been justified theoretically.

In the following work, expansion factors for the single chains and aggregates of the ionomers will be estimated by using the expected dimensions of polystyrene in cyclohexane at 34.5°C (theta temperature) as the unperturbed values. The latter were estimated from the following expressions calculated from previous data in Refs. [17–19], respectively:

$$R_{g,\theta}\ (\text{Å}) = 0.288M^{0.5} \qquad (19)$$

$$R_{h,\theta}\ (\text{Å}) = 0.221M^{0.5} \qquad (20)$$

and

$$[\eta]_\theta\ (\text{dl g}^{-1}) = 8.6 \times 10^{-4} M^{0.5} \qquad (21)$$

(where M is expressed in g mol^{-1} and is taken as M_1 or nM_1 for the single chains and aggregates, respectively).

If the ionomer viscosity expansion factors for all the single chains and aggregates equal the hydrodynamic factors, then this indicates that the viscosities are determined primarily by the total volumes occupied by the polymer chains. Large deviations in the relationship between the hydrodynamic and gyration expansion factors predicted by equation (18) could indicate that the ionomer structures are very different from those of a linear non-associating polymer (for example, the ionomer structures might have denser cores or the aggregates be more rod-like). Alternatively, they might indicate that the assumption that inter-aggregate interactions are negligible as assumed in the theory sections above is not valid in the concentration ranges measured.

EXPERIMENTAL

Sample preparation

Polystyrene samples of molecular weight 115 000, 100 000 and 105 000 g mol^{-1} with polydispersity index (M_w/M_n) of less than 1.05 were sulfonated to levels of 0.62, 0.95 and 1.39 mol%, respectively, following methods as described in several previous publications[20,21]. Briefly, the procedure involves sulfonation of the polymer in 1,2-dichloroethane with acetyl sulfate followed by neutralization with sodium acetate. The process results in a randomly sulfonated polymer whose sulfur content is determined by Diertert sulfur analysis.

Dynamic light scattering

From dynamic light scattering measurements the dynamic structure factor $S(q,t)$ is obtained. In the following this was analysed by using a cumulant expansion

$$\ln S(q,t) = \ln S(q) - \Gamma t + v\Gamma^2 t^2/2 \qquad (22)$$

where v is a coefficient that describes the polydispersity of the system and Γ is the first cumulant. From Γ, diffusion coefficients were determined using

$$\Gamma/q^2 = D_c = D_z(1 + k_D c)(1 + Cq^2) \qquad (23)$$

where k_D and C are constants and q is the wavevector given by

$$q = (4\pi n_D/\lambda) \sin \theta/2$$

n_D is the refractive index of the solvent, λ is the wavelength of the laser and θ is the angle of scatter. According to equation (23) an apparent diffusion coefficient

$$D_{app} = D_z(1 + k_D c) \qquad (24)$$

can be obtained from a plot of D_c *versus* q^2. For non-aggregating polymers D_z and k_D can then be determined from a plot of D_{app} *versus* concentration. For the aggregating polymers it was assumed (as a first approximation) that the interaction term $k_D c$ in equation (24) could be taken as negligibly small so that

$$D_{app, c \to 0} = D_z \qquad (25)$$

In this work dynamic light scattering experiments were carried out with both an instrument described in a paper by Bantle *et al.*[22] and repeated on a commercial Malvern 4700 instrument. Both used lasers with a wavelength λ = 488 nm. Measurements were performed at temperatures ranging between 25 and 60°C and scattering angles from 30–130°. To confirm that equilibrium had been obtained in the ionomer solutions, the experiments were repeated by using several different methods of solution preparation. The variations included changing the lengths of time of sonicating, heating and stirring the solutions before measurement. The time required for equilibration of the solutions depends strongly upon the particular ionomer and its exact history and can vary from just a few hours to, in some cases, several days or even weeks[23]. 'Excess scattering' appeared often to be obtained at the lower angles despite careful filtering of all solutions several times into dust-free cells. This excess scatter tends to decrease if the solutions are sonicated or stirred for much longer periods prior to measurement and is usually most noticeable in the more concentrated solutions. It is thought to result from the presence of just a few larger aggregates that are difficult to break up or an inter-aggregate scattering effect. Data from larger scattering angles, θ, between 70–130° only will be described in this report as these results attained equilibrium values much more readily.

Viscosity measurements

Viscosity measurements were obtained with Ubbelohde-type capillary viscometers. Efflux times of the solvent were always above 100 s and all measurements were carried out in a constant-temperature bath regulated to ± 0.2°C or better. Typically, measurements were obtained on solutions varying in concentration between 0.05 and 1 g dl^{-1} and temperatures ranging from 25 to 70°C. The errors involved were estimated from the variability in results obtained for the base polystyrenes (molecular weights of 100 000, 105 300 and 115 000 g mol^{-1}) and the reproducibility of the ionomer results on varying the solution preparation procedures as described for the dynamic light scattering measurements above.

Table 1 Dimensions and intrinsic viscosities of single chains for SPS ionomers in xylene at 25°C

Sulfonation level (mol%)	$R_{g,1}$ (Å)	$R_{h,1}$ (Å)	$[\eta]_1$ (dl g^{-1})	α_s	α_h	α_η
0.0	120 ± 5	83 ± 2	0.44 ± 0.02	1.32	1.19	1.18
0.62	140 ± 20	88 ± 5	0.46 ± 0.02	1.54	1.26	1.19
0.95	78 ± 5	61 ± 4	0.35 ± 0.03	0.86	0.87	1.09
1.39	55 ± 3	62 ± 4	0.18 ± 0.02	0.60	0.89	0.87

RESULTS

Dynamic light scattering

0.62 mol% SPS and polystyrene. For 0.62 mol% NaSPS and polystyrene, the relatively small size of these molecules meant that, within the errors of the technique, negligible variation with angle of the apparent diffusion coefficients was observed. For both these polymers the apparent diffusion coefficients varied linearly with concentration so equation (24) was used to interpret the results and obtain the z-average diffusion coefficient by extrapolation to zero concentration. k_D for SPS 0.62 mol% was found to be 0 ± 0.1 cm^3 g^{-1}, which compares with a value of 20 cm^3 g^{-1} for polystyrene. The infinite dilution hydrodynamic radii for these polymers obtained from the z-average diffusion coefficients are compared in *Table 1* with radii of gyration estimated from previous static light[9,13] and neutron[10] scattering work. The effect of temperature on the hydrodynamic radii between 25 and 60°C for both polymers was found to be negligible. The hydrodynamic radius of the 0.62 mol% ionomer is slightly larger than that of the polystyrene. This result may be a consequence of a slight stiffening of the polymer near the charged groups. It is difficult to completely rule out the possibility that the apparent larger size is due to the presence of just a few aggregated chains. It is clear, however, from combined dynamic and earlier static[13] light scattering results that there is neither substantial aggregation nor single-chain collapse of the 0.62 mol% ionomer in xylene.

0.95 mol% SPS. The angular dependencies of D_c [defined in equation (23)] were observed to be slightly greater for 0.95 mol% SPS than for polystyrene, so the apparent diffusion coefficient [equation (24)] was obtained by extrapolation of D_c *versus* q^2 to zero scattering angle. At low concentrations reproducible results for 0.95 mol% SPS were quite readily obtained. At concentrations above 0.6 g dl^{-1}, however, the apparent diffusion coefficients at a given concentration varied significantly with solution preparation procedure, indicating that with this particular ionomer the higher concentration solutions are slow to reach equilibrium. Apparent radii at concentrations above 0.6 g dl^{-1} are not therefore considered in the following discussion of the results in terms of equilibrium models. Apparent hydrodynamic radii obtained from the apparent diffusion coefficients with equation (8) are compared with values for SPS 0.62 mol% and PS in *Figure 2*. At low concentrations the hydrodynamic radii for 0.95 mol% SPS increase rapidly with concentration but at high concentrations show less dependence on concentration. The variation is as might be expected from the calculated weight fractions of aggregates as a function of concentration (compare *Figure 1* with *Figure 2*).

As expected from equation (11), a plot of x/R_h *versus* $(1 - w_1)$ is linear below 0.6 g dl^{-1} for 0.95 mol% SPS (see *Figure 3*). This suggests that the closed association equilibrium model can explain the variation in apparent diffusion coefficients with concentration as well as previous static light and small-angle neutron scattering results for this ionomer[11,12]. The hydrodynamic radii of the single chains and aggregates consisting of three chains calculated with *Figure 3* and equation (11) are shown in *Tables 1 and 2*, together with radii of gyration that were previously determined by neutron scattering[11]. The dimensions of the single chains are clearly much smaller than those of the polystyrene. Those of the aggregates will be discussed later.

1.39 mol% SPS. Also given in *Figure 3* are the hydrodynamic radii for 1.39 mol% SPS from previous measurements[9]. Repeated measurements on a 1 g dl^{-1} 1.39 mol% SPS solution indicated that the results with this ionomer

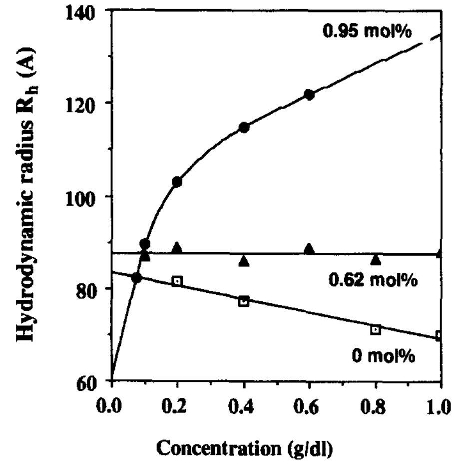

Figure 2 Apparent hydrodynamic radii *versus* concentration for PS, 0.62 and 0.95 mol% SPS in xylene (lines are a guide to the eye that have been extrapolated to the single-chain values)

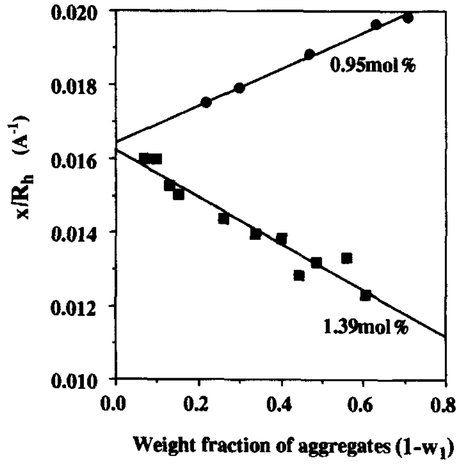

Figure 3 Plot of x/R_h *versus* weight fraction of aggregates $(1 - w_1)$ for 0.95 and 1.39 mol% SPS in xylene

Table 2 Dimensions and intrinsic viscosities of aggregates of SPS ionomers in xylene at 25°C

Sulfonation level (mol%)	Aggregate size (n)	$R_{g,n}$ (Å)	$R_{h,n}$ (Å)	$[\eta]_n$ (dl g^{-1})	α_s	α_h	α_η
0.95	3	150 ± 10	141 ± 10	0.47 ± 0.03	0.95	1.17	1.00
1.39	2	170 ± 20	201 ± 30	0.44 ± 0.03	1.32	2.03	1.05

were readily reproducible up to this concentration but they were found to be difficult to reproduce beyond 2 g dl^{-1}. Also, at low concentrations over the temperature range of 20 to 60°C the apparent hydrodynamic radii obtained showed no significant variation. The gradient of x/R_h *versus* $(1 - w_1)$ is negative for this ionomer and practically constant up to 1 g dl^{-1} (see *Figure 3*). This plot is expected to be linear up to concentrations of about 0.4 g dl^{-1} since in this range only single chains and aggregates of two chains are present in solution. To obtain a negative gradient at low concentrations according to equation (11), the hydrodynamic radius of the two-chain aggregate, $R_{h,2}$ would need to be greater than twice the single-chain radius. This could occur if the aggregates were much less dense than the single chains. Estimates of the single-chain and two-chain aggregate dimensions obtained from this plot are given in *Tables 1 and 2* together with previously determined radii of gyration[10]. The linearity of *Figure 3* for 1.39 mol% SPS above 0.4 g dl^{-1} indicates that either $n/R_{h,n}$ is independent of n for $n \geq 2$ or that neglecting the inter-aggregate term $k_D c$ [assumed when combining equations (10) and (25)] is not valid at the higher concentrations.

Reduced viscosity

0.62 mol% SPS and polystyrene. Both the 0.62 mole% SPS and polystyrene itself showed a linear dependence of viscosity on concentration (see *Figure 4*). The results were therefore analysed with the Huggins equation [equation (12)]. As the temperature was raised from 25 to 60°C the reduced viscosities and k_H values decreased but the effects of temperature on the intrinsic viscosities were only very small (< 10% in all cases). The intrinsic viscosities obtained for the various polystyrene-based polymers (with molecular weights ranging from 100 000 to 115 000 gmol^{-1}) were in agreement to ± 5%. At a given temperature both the intrinsic viscosity and k_H were slightly larger for the 0.62 mol% ionomer than for the polystyrene samples. At 25°C k_H equalled 0.81 and 0.94 for PS and SPS, respectively. Intrinsic viscosities for these polymers at 25°C are given in *Table 1*.

0.95 mol% SPS. At low concentrations the viscosities of 0.95 mol% ionomer solutions are slightly below those of polystyrene solutions (see, for example, *Figure 4*). The reduced viscosities of the ionomer solutions vary only slightly between 0.1 and 0.6 g dl^{-1} but begin to rise more steeply with concentration above 0.6 g dl^{-1}. The effects of temperature were very small at low concentrations as expected, since previous neutron scattering results indicate no effect of temperature on the extent of aggregation or size of the ionomer structures[12] (see *Figure 5*). In order to interpret the results, the reduced viscosities of the 0.95 mol% SPS were plotted against $(1 - w_1)$ (see *Figure 5*). According to equation (14) this plot should be linear at low concentrations if inter-aggregate effects are small. The strong deviations of the plot from linearity at concentrations above 0.6 g dl^{-1} ($w_1 < 0.3$) could be due to either inter-aggregate interactions or non-equilibrium conditions. Dynamic light scattering results have previously indicated that attaining equilibrium at concentrations above 0.6 g dl^{-1} is particularly difficult with this ionomer. Values for $[\eta]_1$ and $[\eta]_3$ estimated by use of equation (14) with data for the ionomer at the lowest concentrations are given in *Table 1*. $[\eta]_1$ is comparable with the intrinsic viscosity obtained by a simple linear extrapolation of reduced viscosity *versus* concentration for $c < 0.4$ g dl^{-1} to zero concentration. Its value is smaller than observed for the intrinsic viscosity of polystyrene as would be expected from the smaller dimensions of the ionomer single chains. To explain the value obtained for $[\eta]_3$ the expansion factors will need to be considered (see later).

1.39 mol% SPS. At low concentrations the viscosities of 1.39 mol% ionomer solutions are considerably below those of the polystyrene solutions (see *Figure 4*). As the ionomer concentration is raised, however, the reduced

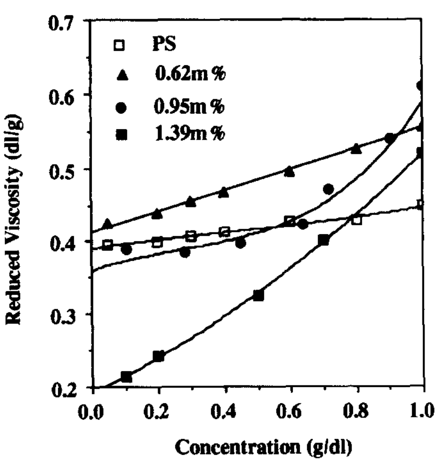

Figure 4 Reduced viscosity of polystyrene and NaSPS ionomers in xylene at 60°C

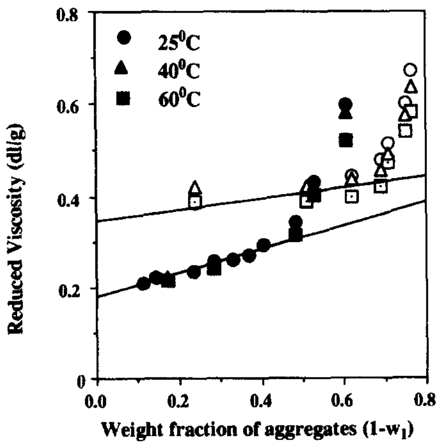

Figure 5 Reduced viscosity of 0.95 mol% (unfilled symbols) and 1.39 mol% (filled symbols) NaSPS *versus* the weight fraction of aggregates $(1 - w_1)$ [compare with equation (14)]

viscosities of 1.39 mol% SPS solutions increase rapidly. The reduced viscosity when plotted against $(1 - w_1)$ is linear up to concentrations of about 0.5 g dl^{-1} (see *Figure 5*). The deviations at higher concentrations from a straight line could arise partially from the formation of aggregates of three or more chains but are most probably primarily due to inter-aggregate interactions as solutions of this ionomer at concentrations above 2 g dl^{-1} will gel. $[\eta]_1$ obtained from the intercept of this plot is again close in value to the intrinsic viscosity obtained by a simple linear extrapolation of reduced viscosity *versus* concentration to zero concentration, as used with most previous reduced viscosity measurements on ionomers. $[\eta]_1/[\eta]_{PS} = F(\xi) \approx 0.5$, which is close to the value expected from the study by Agarwal *et al.*[2] for $\xi = 1.5$. $[\eta]_2$ estimated from the gradient of the plot in *Figure 5* using equation (14) will be discussed later.

Expansion factors

In *Tables 1 and 2* expansion factors calculated with equations (15)–(17) and equations (19)–(21) are shown for the ionomers and polystyrene. The hydrodynamic and viscosity expansion factors are plotted against the gyration factors in *Figure 6*. Also given in this figure is a plot of equation (18) to indicate how the hydrodynamic and viscosity expansion factors are related to the gyration expansion factors for polystyrene in cyclohexane. Since the gradient of this line is less than 1, this would suggest that the hydrodynamic and viscosity expansion factors might vary less with sulfonation level than the gyration expansion factors. With just one exception the hydrodynamic and viscosity expansion factors of the single chains and aggregates for all of the ionomers and polystyrene are, within experimental error, in agreement with the gyration expansion factors in that they all lie reasonably close to the line found for polystyrene in cyclohexane. This gives some confidence in the interpretation of the results by the methods described in this work. The exception are the results for the 1.39 mol% SPS aggregate for which the viscosity expansion factor is less than and the hydrodynamic radius much larger than the value expected from the gyration expansion factor. Solutions of the 1.39 mol% ionomer will gel when the polymer concentration exceeds 2 g dl^{-1}. Dynamic light scattering data on these ionomer gels indicate the presence of a very slow diffusion process. The gelation and slow diffusion process might arise because of inter-aggregate interactions. These types of interaction could also be complicating the interpretation of the dynamic light scattering studies even in the more dilute solutions.

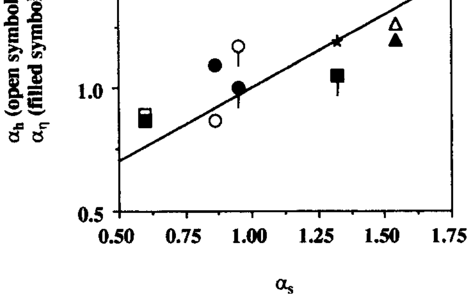

Figure 6 Hydrodynamic and viscosity *versus* gyration expansion factors for NaSPS ionomers and PS in xylene. Vertical pips indicate results for ionomer aggregates and the straight line is for PS in cyclohexane [equation (18)]

All the expansion factors for polystyrene and the 0.62 mol% ionomer are greater than 1, indicating that the chains are swollen by the solvent. With 0.95 mol% SPS both the single chains and aggregates have expansion factors close to 1. This suggests that both structures have similar densities to what would be observed for polystyrene in a theta solvent. With the 1.39 mol% ionomer, however, all the expansion factors for the single chains are much less than 1, indicating a very compact structure. Although the expansion factors for the 1.39 mol% ionomer two-chain aggregates have values ranging from 1 to 2, overall the results suggest that they are expanded structures. Gelation is probably as a result of interactions between these extended aggregates.

DISCUSSION AND CONCLUSIONS

This work has shown how aggregation of ionomers can make the interpretation of rheological data complex, even with very dilute solutions. The reasonable agreements between all but one of the single-chain and aggregate hydrodynamic and gyration radii and viscosity expansion factors obtained from dilute solution measurements, however, give confidence in the interpretation of all the data at low concentrations through the equilibrium association models described earlier in this work. They also confirm the suggestion that the viscosities of dilute ionomer solutions are dependent only upon the total volumes occupied by the polymer chains, whether in aggregates or as isolated molecules. Deviations of both the reduced viscosities and hydrodynamic radii from values expected from the equilibrium models at ionomer concentrations above 0.6 g dl^{-1} suggest that inter-aggregate interactions become significant at this concentration. Dynamic light scattering and rheological measurements appear to be more sensitive to these interactions than previous neutron scattering studies.

The above studies combined with previous light scattering results in THF[7] suggest that aggregation of ionomers in non-polar solvents does not occur until a critical level of charge on the ionomer has been reached. Comparison of scattering work with the earlier rheological measurements of Agarwal *et al.*[2] suggests that this critical level is dependent upon the strength of the ionic interactions. Below this charge level the ionomer dimensions are expanded and comparable with those of the base polymer in a good solvent. From these studies it appears that there is also a second critical charge level for SPS ionomers in xylene at which there is a dramatic transition in the type of aggregation. At present, owing to a lack of scattering studies, it is uncertain whether this second transition occurs in other systems although rheological measurements[2] are suggestive that it might.

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