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Light Scattering Study of Ionomer Solutions. 3. Dynamic Scattering from Sulfonated Polystyrene Ionomers in a Polar Solvent (Dimethylformamide)

Jhi-Li Wu and Masanori Hara*

Department of Mechanics and Materials Science, Rutgers,
The State University of New Jersey, Piscataway, New Jersey 08855-0909

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ABSTRACT: Dynamic light scattering experiments were conducted on samples of a random ionomer, partially sulfonated polystyrene (SPS) (Na salt), which had small amounts of ionic groups (less than 4 mol %), dissolved in an aprotic, polar solvent, dimethylformamide (DMF). For high molecular weight ionomers (MW: 200 000 and 400 000), the (effective) diffusion coefficient, D_{eff}, obtained from the methods of cumulants, increases significantly with polymer (ionomer) concentration and bends over at high ionomer concentration. The D_{eff} increases with ion content of the ionomers at fixed polymer concentration. These results are consistent with those found for the same ionomers by low-angle light scattering: i.e., the reciprocal reduced scattered intensity increases significantly with ionomer concentration, becomes almost horizontal at higher concentration, and, at fixed ionomer concentration, increases with ion content. Those results reflect a significant increase in inverse osmotic compressibility with polymer concentration, which arises from long-range electrostatic interactions among ionomer molecules in salt-free solution. For low molecular weight ionomer (MW: 50 000), quite contrasting dynamic behavior is observed: the D_{eff} is insensitive to polymer (ionomer) concentration, and, at fixed polymer concentration, the D_{eff} decreases with ion content. The effect of added salts (LiCl) on D_{eff} of ionomer solution was also studied: the D_{eff} increases linearly with polymer (ionomer) concentration over the salt concentration range studied (0.0001–0.1 M). The slope of the line in the diffusion coefficient vs concentration plot increases significantly with decreasing salt concentration. This is due to increased interactions between ionomer molecules caused by less screening on ionomer charges by added salts. The D_{eff} at infinite dilution is almost independent of added salt concentration, which suggests little change in ionomer size over the salt concentration range studied (0.0001–0.1 M).

Introduction

The solution behavior of polyelectrolytes with added salts is rather well understood and may be explained as neutral polymers in "very good" solvent. Theories initially developed for understanding solution behavior of neutral polymers such as the excluded volume theory[1] and the scaling theory[2] have been adapted to explain the behavior of polyelectrolytes with added salts.[3,4] In contrast, polyelectrolyte behavior observed for salt-free solution is still not well understood;[4] there still exist controversies with respect to the structure of salt-free solution and the essential factors causing the characteristic behavior. This is obviously due, in part, to the difficulty in accommodating long-range electrostatic interactions in the theory. Another reason lies in the difficulty in obtaining good, reliable data for salt-free polyelectrolytes in aqueous solutions, which are much more difficult to handle than added-salt systems.

Recently, it has been demonstrated that ionomers, which have a small amount of ionic groups (i.e., up to 10–15 mol %) along nonionic backbone chains, offer good model systems to investigate the characteristic behavior of salt-free polyelectrolyte solutions.[5] Because of the very small amounts of polar groups (ionic groups), ionomers are usually insoluble in water but dissolve in organic solvents. In is now well established that ionomers dissolved in organic solvents show two types of behavior, depending mainly on the polarity of the solvent:[6] one is aggregation behavior arising from association of ionic dipoles (i.e., ion pairs) in a nonpolar solvent, such as toluene ($\epsilon = 2.4$), and another is polyelectrolyte behavior due to ionic interactions among fixed ions and dissociated counterions in a polar solvent, such as DMF ($\epsilon = 37$); here, ϵ is the dielectric constant of the solvent. It should be cautioned, however, that the term *ionomer* is usually more connected to the aggregation behavior, since much work has been focused on the structure and properties of ionomer solids;[7–9] in the solid state, ionic groups are dispersed in a medium of low dielectric constant, such as polyethylene and polystyrene ($\epsilon = 2.5$); therefore, counterions are strongly bound to fixed ions of ionomers and practically all ionic groups exist at least as ion pairs and even form higher order aggregates, such as ionic clusters. In this work, we focus entirely on the *polyelectrolyte behavior* of ionomers observed in a polar solvent, where many of the counterions are dissociated.[10] Ionomer solutions may be used as simple model systems of more complex polyelectrolytes in aqueous solution.[11] It has been demonstrated that the polyelectrolyte behavior of ionomers observed in a polar solvent is essentially the same as that of polyelectrolytes observed in aqueous solution: properties investigated by such methods as viscosity,[10–17] static light scattering,[13,18,19] dynamic light scattering,[13,20] small-angle neutron[16] and X-ray[21,22] scattering and osmotic pressure[10] measurements all show basically similar behavior. A recent review on this subject is available.[5]

Some ionomers, such as the sodium salt of SPS, are readily dissolved in polar, aprotic, organic solvents, such as DMF and dimethyl sulfoxide (DMSO).[6] Use of an aprotic, organic solvent system reduces the problems associated with aqueous solution; e.g., in aqueous solution, autodissociation of water always produces small amounts of ions (H^+ and OH^-) and makes a salt-free system unavailable.[4] In some cases, complex water structures, such as ice structure and iceberg structure (relating to hydrophobic interactions), need to be considered to explain solution behavior, while those problems do not exist for an aprotic, polar solvent. Moreover, light scattering

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[*] To whom all correspondence should be addressed.

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measurements are easier to conduct for ionomers in organic solvents due to the stronger scattering (or due to the smaller interference effect) and lower viscosity of ionomer solutions (optical clarification by filtration or centrifugation is easier). For example, the excess scattered intensity, R_θ, from SPS ionomers dissolved in DMF is (1–20) × 10^{-6} (cm^{-1}),[18] while that from poly(sodium methacrylate) with comparable molecular weight dissolved in water is (0.1–1) × 10^{-6} (cm^{-1}).[23] Here, R_θ is the difference in reduced scattered intensity between solution and solvent, and the reduced scattered intensity is defined by $i_\theta r^2/I_0V$ for vertically polarized incident light, where i_θ is the scattered light intensity at scattering angle θ, I_0 is the intensity of the incident light, r is the distance between the sample and the detector, and V is the scattering volume. Moreover, foreign particles that exist in solution in some amount even after careful optical clarification contribute less to the overall scattering, because the refractive index of some organic solvent (e.g., 1.43 for DMF) is much closer than water (e.g., 1.33) to that of many foreign particles[24] and because the excess scattered intensity from foreign particles is proportional to the square of the refractive index difference between the foreign particles and the solvent.

In this work, we conducted dynamic light scattering experiments for SPS ionomers in DMF. These random ionomers, in which ionic groups are randomly distributed along backbone chains, have been used extensively for the study of solution behavior. We used these ionomers previously for viscosity[15,17,25] and low-angle light scattering[18,19] experiments to study polyelectrolyte behavior, especially the characteristic behavior of salt-free solution. The purpose of this work is to obtain additional information on the dynamics of SPS ionomer in DMF and to compare these data with those obtained for polyelectrolytes in aqueous solution, especially those for salt-free solution.

Experimental Section

Samples. Lightly sulfonated polystyrene (SPS) was prepared by sulfonation of polystyrene with a sulfonating agent, acetyl sulfate, according to the procedure reported by Makowski et al.[26] The starting polystyrenes (PS) were PS standards (Pressure Chemical Co.) (MW: 50 000, 200 000, and 400 000) with narrow molecular weight distributions ($M_w/M_n = 1.06$). After the reaction was terminated by adding methanol, polymer (acid form) was recovered by steam stripping in boiling water. The acid copolymers were then dissolved in a solvent mixture (benzene/methanol, 90/10 v/v), freeze-dried, and dried under vacuum at room temperature for at least a week to remove residual solvent. The acid content of the copolymer samples was determined by titration of the sulfonic acid groups using a standard sodium hydroxide solution with phenolphthalein as an indicator in a solvent mixture, benzene/methanol (90/10 v/v). Acid copolymers were then converted to ionomers (sodium salt) by adding a calculated amount of methanolic sodium hydroxide in benzene/methanol (90/10 v/v), freeze-dried, and dried under vacuum at room temperature for at least a week. This drying procedure was preferable to vacuum drying at high temperature (e.g., 80 °C for 1 day) to avoid potential undesirable reactions such as cross-linking and degradation. The details of the polymer samples are summarized in Table 1.

Polymer solutions were prepared by dissolving the freeze-dried ionomer samples in DMF (Fisher: Spectranalyzed grade) under stirring for 1 day at room temperature. Ionomer samples were easily dissolved: polymer disappeared as soon as DMF was added. Since DMF was used immediately after opening a new bottle, the content of water was kept to a minimum (<0.15%). Lithium chloride (LiCl) (Fisher) was used as an added simple salt, since a wide range of salt concentration (0.0001–0.1 M) was covered in this study and LiCl had a much higher solubility than NaCl in DMF.

Measurements. Each light scattering cell (12-mm round cell) for dynamic light scattering experiments was dedusted by flushing the cell for 2 h with dust-free condensing acetone vapors and condensate using a Thurmond-type instrument.[27] This is a very effective method to prepare dust-free cells.[28] The optical clarification of the solution was carried out by passing the solution through two membranes, whose pore sizes were 0.5 and 0.2 μm, in succession (Fluorepore Filter: Millipore Co.). Most of the sample preparation, including dilution of stock solution and an optical clarification of the solution, was conducted inside a dust-free hood (Class 100K Hood: Laminare Co.) to avoid contamination by dust particles.

Table 1. Molecular Characteristics of Polymers

mol wt[a]	M_w[b]	M_w/M_n[a]	ion content[c] (mol %)
400 000	4.0 × 10^5	1.06	0
			1.9
			2.6
200 000	2.3 × 10^5	1.06	0
			1.9
			3.0
50 000	5.0 × 10^4	1.06	0
			2.0
			4.0

[a] Data from Pressure Chemical Co. [b] Determined by low-angle light scattering. [c] Determined by titration.

Dynamic light scattering measurements were conducted with a BI-200 photogoniometer (Brookhaven) and a BI-2030 digital correlator (Brookhaven) at a wavelength of 633 nm from a 30-mW He–Ne laser (Spectra-Physics). Measurements were conducted at nine angles from 30 to 150° at 25 ± 0.1 °C. The channel numbers were 64 and the scattering data from the correlator were transferred to a microcomputer for analysis.

Low-angle light scattering measurements were conducted with a KMX-6 low-angle laser light scattering photometer (Chromatix) at a wavelength of 633 nm at 25 ± 0.5 °C. This instrument was designed only for low-angle (2–7°) measurements but with high precision; absolute scattered intensity is directly calculated by geometrical parameters and the ratio of radiant power, without using standard materials (e.g., benzene).[29] The optical clarification of the sample solution was carried out by passing the solution with a constant flow rate using a syringe pump through two membranes with 0.5 and 0.2 μm, in succession. The measurements were conducted through at least three different points of a cell window to minimize the effect of roughness of the cell window on total scattering. The specific refractive index increment, dn/dc, was measured at a wavelength of 633 nm at 25 ± 0.1 °C by using a KMX-16 differential refractometer (Chromatix). The details of low-angle light scattering experiments are described elsewhere.[19]

Light Scattering Equations. The method of cumulants[30] was used to analyze the dynamic scattering data:

$$\ln[C(\tau)/B - 1]^{1/2} = \ln b^{1/2} - \bar{\Gamma}\tau + \mu_2\tau^2/2 + \ldots \qquad (1)$$

Here, $C(\tau)$ is the measured intensity (time) autocorrelation function, B is the base line, and b is an optical constant. $\bar{\Gamma}$ represents the first cumulant, μ_2 is the second cumulant, and τ is the delay time. An effective (apparent) diffusion coefficient, D_{eff}, was calculated by the following equation:

$$\bar{\Gamma} = D_{\text{eff}}q^2 \qquad (2)$$

where $q = (4\pi n/\lambda_0)\sin(\theta/2)$ is the magnitude of the scattering vector, n is the refractive index of the solution, λ_0 is the wavelength of the light in vacuo, and θ is the scattering angle.

When the higher terms in eq 1 are negligible, as in the case for standard polystyrene (PS) with a sharp molecular weight distribution, the correlation function is reduced to a single-exponential function:

$$C(\tau) = B(1 + be^{-2\bar{\Gamma}\tau}) \qquad (3)$$

It is common to use the normalized second cumulant or quality factor, Q, as a measure of deviation from single exponentiality of the autocorrelation function,[30] which is defined by

$$Q = \mu_2/\bar{\Gamma}^2 \tag{4}$$

Values of 0.02 or less are generally obtained for clean monodisperse samples.[31] Large Q values may arise from the molecular weight polydispersity for a dilute solution of neutral polymers,[30] and they may also arise from long-range electrostatic interactions for a dilute solution of ionic polymers.[32,33]

For monodisperse, nonaggregating polymers, the mutual translational diffusion coefficient as a function of polymer concentration, $D(c)$, is given by a generalized Stokes–Einstein relation[1,34,35]

$$D(c) = \frac{M(\partial\pi/\partial c)}{N_0 f(c)}(1 - \nu c) \tag{5}$$

where M is the molecular weight of the polymer, N_0 is Avogadro's number, $\partial\pi/\partial c$ is the inverse (isothermal) osmotic compressibility, ν is the partial specific volume of the polymer, c is the weight concentration (g/cm^3) of the polymer solution, and $f(c)$ is the frictional coefficient of the polymer molecule.

When the interaction is relatively weak, as is the case for neutral polymres and for polyions with large amounts of added salts in dilute solution, both $\partial\pi/\partial c$ and $f(c)$ can be expanded in terms of c:[1]

$$\frac{\partial\pi}{\partial c} = \frac{RT}{M}(1 + 2A_2Mc + \ldots) \tag{6}$$

$$f(c) = f_0(1 + k_f c + \ldots) \tag{7}$$

where T is absolute temperature, A_2 is the (osmotic) second virial coefficient, and f_0 is the frictional coefficient of the polymer at infinite dilution. Therefore, from eqs 5–7

$$D(c) = \frac{kT}{f_0}[1 + (2A_2M - k_f - \nu)c + \ldots] \tag{8}$$

$$= D_0(1 + k_D c + \ldots) \tag{9}$$

where D_0 ($=kT/f_0$) is the mutual translational diffusion coefficient at infinite dilution, k_D ($=2A_2M - k_f - \nu$) is the diffusion virial coefficient, and k is the Boltzmann constant. The behavior of unmodified standard PS and SPS ionomers with large amounts of added salts (LiCl) may be explained by these equations.

When the interaction is strong, as is the case for a salt-free polyion solution, a virial expansion may not be sufficient to describe the interference effect. In these strongly interacting systems, which naturally exclude solutions with very low polymer concentration or with high ionic strength, the concentration dependence of $\partial\pi/\partial c$ in eq 5 is much stronger than that of $f(c)$ and $(1 - \nu c)$;[35] therefore, the diffusion coefficient for strongly interacting systems is roughly proportional to $\partial\pi/\partial c$

$$D(c) \propto \partial\pi/\partial c \tag{10}$$

It is also known from the fluctuation theory of static light scattering that the reciprocal scattered intensity at zero angle is written[1] as

$$\frac{Kc}{R_0} = \frac{\partial\pi/\partial c}{RT} \propto \frac{\partial\pi}{\partial c} \tag{11}$$

where R_0 is the excess reduced scattered intensity extrapolated to zero angle and K is the optical constant for vertically polarized incident light, defined by

$$K = 4\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2/\lambda_0^4 N_0 \tag{12}$$

where n_0 is the refractive index of the solvent. Vrij and Overbeek[36] pointed out that fluctuation theory cannot be applied to low salt ($<10^{-3}$ M) polyion solution at finite angles, because of the interference effects between different volume elements. However, the fluctuation theory can still be applicable at 0° (extrapolated to zero angle), because the necessary condition, $2\sin(\theta/2)/(\kappa\lambda_0/n) \ll 1$, can be satisfied at 0°, where $1/\kappa$ is the Debye–Hückel screening length[37] defined by

$$\kappa^{-1} = \left(\frac{\epsilon kT}{4\pi\sum_i e_i^2 c_i}\right)^{1/2} \tag{13}$$

where ϵ is the dielectric constant of the solution and e_i and c_i are the charge and the concentration of the ionic species i.

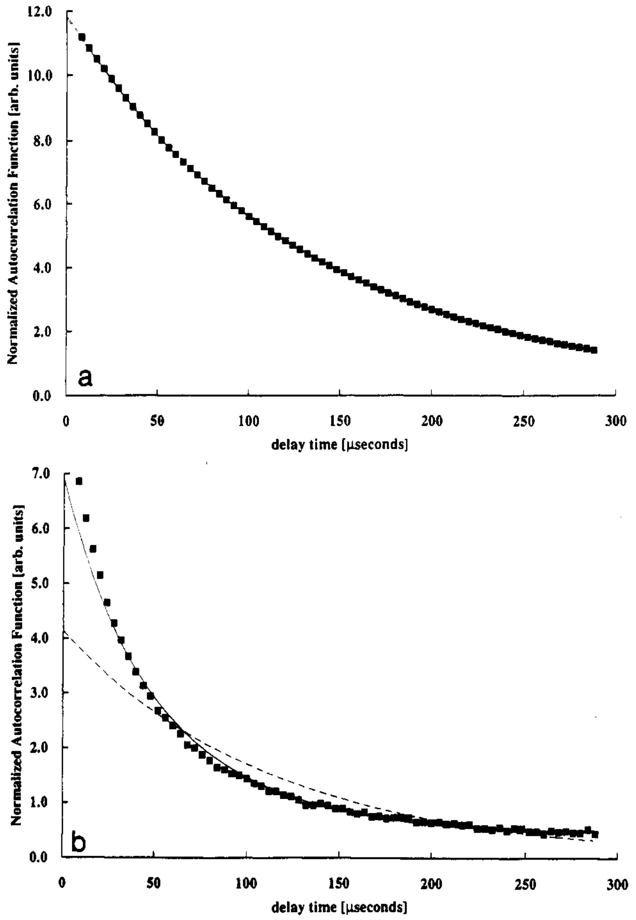

Figure 1. Autocorrelation function for (a) polystyrene and (b) SPS ionomer (MW: 400 000; ion content: 1.9 mol %): closed squares represent data points, dashed lines are the single-exponential fit, and solid lines are the cumulant fit.

From eqs 10 and 11, it is shown that the concentration dependences of the diffusion coefficient and of the reciprocal reduced scattered intensity for strongly interacting polymers are similar. This parallel relation can also be shown from microscopic discussions.[35] Ionomers without salts in a polar solvent may be explained by these equations.

For the added-salt system, a combination of eqs 6 and 11 can lead to a well-known relation

$$\frac{Kc}{R_0} = \frac{1}{M}(1 + 2A_2Mc + \ldots) \tag{14}$$

Comparison of eq 14 with eq 8 indicates that the concentration dependence of both the diffusion coefficient and the reciprocal reduced scattered intensity for an added-salt system is reflected in the $2A_2Mc$ term.

Results

Except for the case of unmodified standard PS (see Figure 1a), the cumulants fit is better than the single-exponential fit (see Figure 1b) and the χ^2 test shows consistently lower values; therefore, we used the method of cumulants for all the samples. The deviation of the correlation function from a single-exponential function may be caused by various factors, such as (i) polydispersity of particles in solution (e.g., ionomers in toluene) and (ii) electrostatic interactions (e.g., ionomers in DMF) as

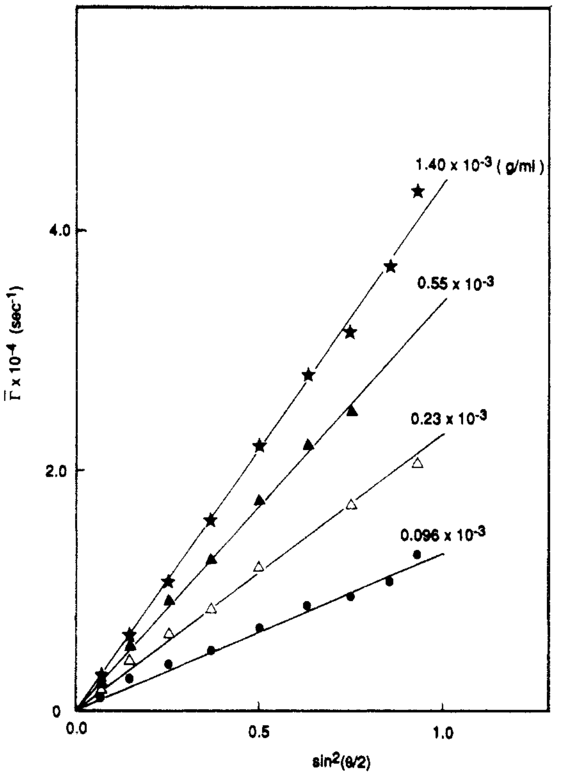

Figure 2. First cumulant, $\bar{\Gamma}$, against $\sin^2(\theta/2)$ for SPS ionomer (MW: 400 000; ion content: 2.6 mol %) for various polymer concentrations in DMF.

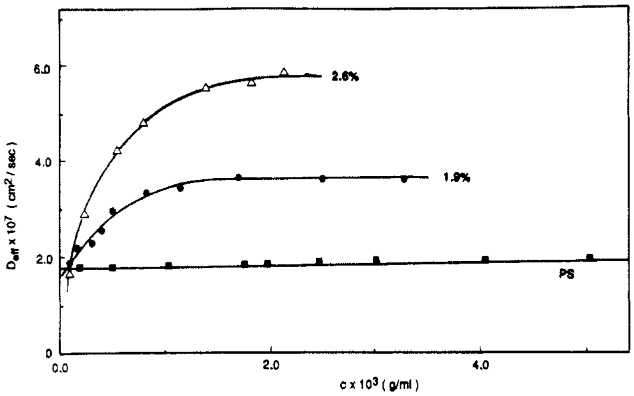

Figure 3. Effective (apparent) diffusion coefficient, D_{eff}, against polymer concentration for SPS ionomer (MW: 400 000) for various ion contents in DMF.

observed for salt-free polyelectrolytes in water.[32,33] For random ionomers in DMF, the polydispersity of the sample with respect to ion content (degree of sulfonation) may also cause such a deviation. Figure 2 shows an example of the relationship between the first cumulant, $\bar{\Gamma}$, and $\sin^2(\theta/2)$ for the high molecular weight (MW: 400 000) samples. All the lines intersect at the origin within experimental error. A similar linear relationship between $\bar{\Gamma}$ and $\sin^2(\theta/2)$ is observed for most of the samples studied in this work; therefore, the effective (apparent) diffusion coefficient, D_{eff}, was evaluated from the slopes of these lines by using eq 2. When a deviation from a linear line is observed at higher angles (typically over 90°), the slope of the line at lower angles is used to obtain D_{eff}.[38]

Figure 3 shows the relation between D_{eff} and polymer concentration for ionomer with high molecular weight (MW: 400 000) for different ion contents. The effective diffusion coefficient increases steeply at low concentration, bends over, and becomes almost horizontal at higher polymer concentration, while the value of unmodified PS is almost independent of concentration. It is also seen that the higher the ion content, the higher is the value of D_{eff} over most of the concentration range studied, except at very low polymer concentration, where this order seems to be reversed. At high polymer concentration, D_{eff} is around 2×10^{-7} cm^2/s for unmodified PS and is around 6×10^{-7} cm^2/s for 2.6 mol % ionomer. The same trend is observed for ionomer with molecular weight of 200 000 (see Figure 4).

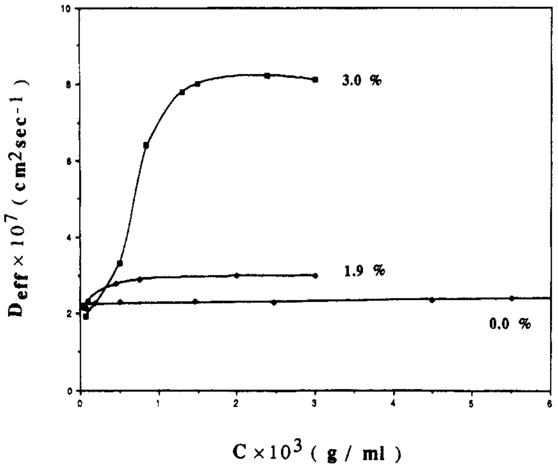

Figure 4. Effective (apparent) diffusion coefficient, D_{eff}, against polymer concentration for SPS ionomer (MW: 200 000) for various ion contents in DMF.

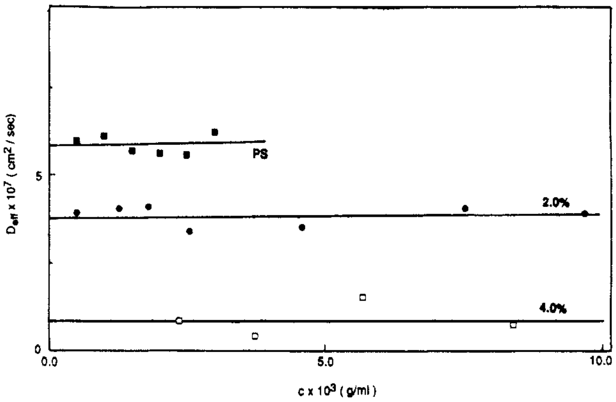

Figure 5. Effective (apparent) diffusion coefficient, D_{eff}, against polymer concentration for SPS ionomer (MW: 50 000) for various ion contents in DMF.

However, the opposite trend is observed for ionomer with lower molecular weight (MW: 50 000): Figure 5 shows that the D_{eff} decreases with increasing ion content. For example, D_{eff} is around 6×10^{-7} cm^2/s for unmodified PS and is around 1×10^{-7} cm^2/s for ionomer with 4.0 mol % ion content. A similar behavior to that of the low molecular weight sample was also reported for SPS ionomer (MW: 100 000) by using a single-exponential fit at 90° angle.[13] It is also noted for these low molecular weight ionomers that the D_{eff} is almost independent of ionomer concentration, as seen in Figure 5.

Figure 6 shows the effect of added salt (LiCl) on the diffusion coefficient of the ionomer (MW: 400 000) solution. The effective diffusion coefficient increases linearly with ionomer concentration over the salt concentration range studied (0.0001–0.1 M). At high salt concentration (0.1–0.01 M), the correlation function is a single exponential as is the case of standard PS (see Figure 1a) and Q values defined by eq 4 are very low (<0.05); these findings are in contrast to those obtained at lower salt concentration, where the correlation function deviates from a single-exponential function, as in the case of the salt-free solution (see Figure 1b), and Q values are high

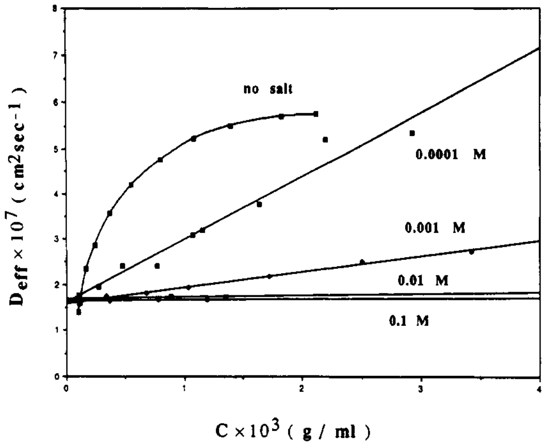

Figure 6. Effective (apparent) diffusion coefficient, D_{eff}, against polymer concentration for SPS ionomer (MW: 400 000; ion content: 2.6 mol %) for various salt concentrations in DMF.

Table 2. Diffusion Coefficient at Infinite Dilution, D_0, and Diffusion Virial Coefficient, k_D, for Sulfonated PS Ionomer (MW: 400 000; Ion Content: 2.6%) with Various Salt Concentrations in DMF

salt concn (M)	D_0 (cm²/s)	k_D (cm³/g)
0.0001	1.63×10^{-7}	828
0.001	1.58×10^{-7}	237
0.01	1.68×10^{-7}	21
0.1	1.65×10^{-7}	8
PS[a]	1.77×10^{-7}	22

[a] Taken as a reference.

(up to 0.15 for 0.001 M and up to 0.35 for 0.0001 M). This indicates nearly complete suppression of electrostatic interactions by the addition of 0.1–0.01 M LiCl. These results also suggest that the molecular weight distribution of the starting PS was little altered for low ion content samples during the sulfonation reaction due to undesirable side reactions such as chain scission or cross-linking.[39] Figure 6 also shows a significant increase in the effective diffusion coefficient with decreasing salt concentration, especially at low salt concentration level 0.0001 M), although the curvature as observed for salt-free solution does not seem to appear at this level of salt concentration. From these lines, the effective diffusion coefficient at infinite dilution, D_0, and the diffusion virial coefficient, k_D, are obtained by using eq 9 and are summarized in Table 2.

Figure 7a shows the results of low-angle light scattering for ionomers with high molecular weight (MW: 200 000): the reciprocal reduced scattered intensity of unmodified PS is almost independent of concentration, while it increases significantly at low concentration, bends over, and becomes almost horizontal at high polymer concentration for the ionomer solution. These results are generally observed for SPS ionomers in a polar solvent (see Figure 7b).[5,13,17-19]

The effect of ion content on the deviation from single exponentiality of the autocorrelation function is reflected in the value of the normalized second cumulant, Q. The Q value at 90° increases from less than 0.01 for PS to 0.2–0.5 for ionomers with 1.9 mol % ion content level and to 0.3–0.6 for ionomers with 2.6 mol % ion content level. The tendency is similar for other scattering angles. This significant increase in Q value may be again associated with increased electrostatic interactions with increasing ion content in salt-free ionomer solutions. A similar increase in Q values, due to an increase in ionic character, was reported for polyelectrolytes in water.[32,33] In addition, the polydispersity of the sample with respect to the degree of sulfonation may also contribute to some extent, as already pointed out.

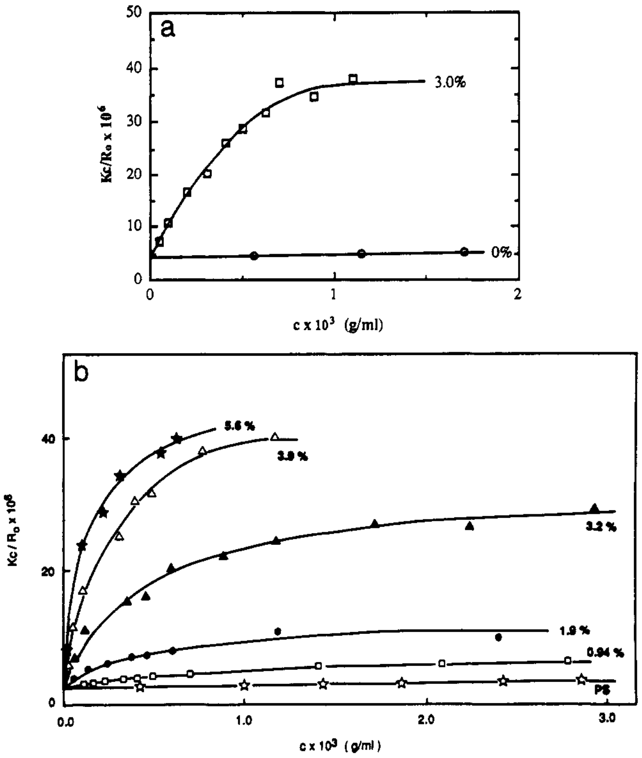

Figure 7. (a) Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for SPS ionomer (MW: 200 000; ion content: 3.0 mol %) in DMF. (b) Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for SPS ionomer (MW: 400 000) for various ion contents in DMF (from ref 18).

Discussion

Figures 3 and 4 show the concentration dependence of the effective diffusion coefficient, D_{eff}, of high molecular weight samples (MW: 200 000 and 400 000). It is seen that D_{eff} increases sharply at low concentration and bends over at higher concentration. This large concentration dependence arises from long-range electrostatic interactions that are reflected in the $\partial\pi/\partial c$ term[35] in eq 5. Since concentration dependence is dominated by the $\partial\pi/\partial c$ term, the effective diffusion coefficient should be roughly proportional to $\partial\pi/\partial c$ (eq 10). Similar curves are obtained from static low-angle light scattering experiments for the SPS ionomer in DMF:[18,19] Figure 7 shows that the reciprocal reduced scattered intensity, Kc/R_0, rises steeply at low concentration, bends over, and becomes nearly horizontal at higher concentration for ionomer (MW: 400 000 and 200 000) in DMF. Again, this large concentration dependence arises from long-range electrostatic interactions that are reflected in the $\partial\pi/\partial c$ term in eq 11. Equations 10 and 11 indicate that the D vs c curves and Kc/R_0 vs c curves should be similar in shape. Indeed, this is seen in our experiments. The fact that two entirely independent experiments lead to reasonable agreement indicates the reliability of the experiments. Thus, the parallel relation between mutual diffusion coefficient and reciprocal reduced scattered intensity in terms of the effect of *polymer concentration* and *ion content* is established for salt-free SPS ionomer solutions.

A parallel relation between diffusion coefficient and reciprocal reduced scattered intensity has been pointed out generally in terms of the effect of *added salt concentration* (or ionic strength) for ionic polymers, including bovine serum albumin (BSA), tRNA, and poly(L-lysine hydrobromide);[31,40] the effective diffusion coefficient measured by dynamic scattering rises sharply as the added salt concentration decreases, and the reciprocal scattered intensity increases (or total scattered intensity decreases) in a roughly proportional way; and D_0, the diffusion coefficient at zero concentration, is less than the one at high salt concentration. All these characteristics are also observed in our experiments for random ionomer solutions (see Figure 6 for dynamic scattering results and Figure 3 in ref 25 for low-angle scattering results).

Ionic charge density (or ion content) can also be altered by changing pH values for the protein (BSA) solution. BSA is considered to consist of hard spheres. Doty and Steiner[41] reported Kc/R_{90} vs c curves for salt-free BSA solution which are similar to those in Figure 7: i.e., with a decrease in pH, a linear line at pH 5.1 (isoelectric point) changed to a curve with a significant curvature at pH 3.2. Raj and Flygare[42] reported that the diffusion coefficient of BSA solution obtained from dynamic light scattering increased significantly with decreasing pH from 5.2 to 3.0 at low ionic strength. This is yet another example of a parallel relation between diffusion coefficient and reciprocal reduced scattered intensity in terms of the effect of *ionic charge density*.

It should be added that the characteristic diffusion coefficient vs polymer concentration curves as seen in Figures 3 and 4 are also reported for other ionic solutions: for example, the concentration dependence of the diffusion coefficient of sodium dodecyl sulfate (SDS) in salt-free aqueous solution[43] is quite similar to the curves seen in Figures 3 and 4. This may be attributed to electrostatic interactions between micelles (i.e., aggregated SDS molecules) with charges on the surface.[43] These characteristic behaviors and the parallel relationship between diffusion coefficient and reciprocal scattered intensity seem to be observed for ionic polymer solutions irrespective of their molecular shapes and charge density: spherical particles (e.g., BSA),[40-42] rigid rod particles (e.g., DNA),[44] flexible coils with high charge density (e.g., NaPSS), and flexible coils with low charge density (e.g., SPS ionomer). Since characteristic behavior is thermodynamically reflected in a significant concentration dependence of the inverse osmotic compressibility term, $\partial\pi/\partial c$, which arises from strong electrostatic interactions among ionic polymers, this observation should be naturally quite general.

The dynamic behavior of low molecular weight samples (MW: 50 000) is quite different from that observed for higher molecular weight samples (MW: 200 000 and 400 000) (compare Figures 3 and 4 with Figure 5). Behavior similar to that of the low molecular weight samples was also reported by Lantman et al.[13] for SPS ionomers with molecular weight of 100 000. The higher the ion content, the lower the diffusion coefficient, which is opposite to the tendency observed for the higher molecular weight samples (MW: 200 000 and 400 000). In addition, almost no concentration dependence of the diffusion coefficient is observed for the low molecular weight ionomers. It is interesting to note that these results suggest that D_{eff} vs c curves that are independent of *ion content* may be obtained from ionomers of molecular weight between 50K and 200K.[45]

The effect of added salt on the mutual diffusion coefficient is clearly seen in Figure 6. When the salt concentration is high (0.1–0.01 M), the concentration dependence of the diffusion coefficient is very small. This is typical for neutral polymers such as monodisperse PS; the autocorrelation function is single exponential and the Q value is quite low, typically less than 0.02. This means that the $2A_2M$ term in eq 8 is close to the $(k_f + \nu)$ term. A simple example is demonstrated for spherical proteins: $2A_2M = 8$ and $(k_f + \nu) = 7.4$.[31] However, when the salt concentration decreases, A_2 increases significantly due to stronger electrostatic interactions, arising from less shielding effect by added salts on the ionic groups of ionomers. Therefore, k_D, the slope of D_{eff} vs c curves, increases significantly (with the $2A_2M$ term in eq 8). The added salt dependence of the effective diffusion coefficient at finite polymer concentration (1.5×10^{-3} g/cm^3) is plotted in Figure 8: a significant increase in the diffusion coefficient is seen below 0.001 M. This general trend is similar to the results reported recently for DNA solution,[44] which was explained in terms of the coupled mode theory considering electrostatic coupling between polyions and counterions.[46,47] Alternatively, this is explained in terms of the thermodynamics due to stronger interactions between ionomer molecules, as noted in high k_D values (Table 2) arising from high A_2 values at low salt concentration. A similar argument was used for explaining increased k_D values with decreasing NaCl concentration for DNA solution.[48] Almost similar values in D_0 suggest that ionomer size at infinite dilution is not significantly different, while the large change in k_D suggests a significant difference in intermolecular interactions. Interestingly, similar results were reported for rigid polyions, DNA, with NaCl in aqueous solution.[48]

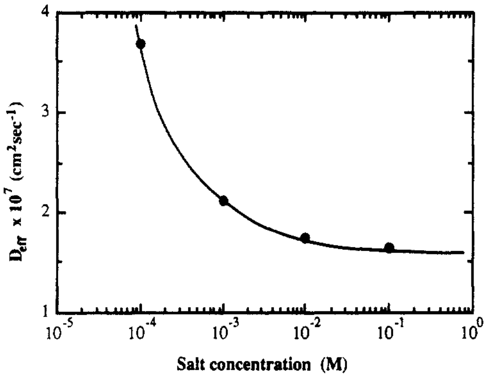

Figure 8. Effective (apparent) diffusion coefficient, D_{eff}, against added salt concentration for SPS ionomer (MW: 400 000; ion content: 2.6 mol %) in DMF at a polymer concentration of 1.5×10^{-3} (g/cm^3).

Conclusions

A dynamic light scattering study was conducted for sulfonated polystyrene ionomers, in which small amounts (<4 mol %) of ionic groups are randomly distributed, dissolved in an aprotic, polar solvent, DMF. The method of cumulants was used to analyze the data. For high molecular weight samples (MW: 200 000 and 400 000), characteristic behavior, arising from electrostatic interactions among ionomer molecules, is observed: i.e., the (effective) diffusion coefficient increases significantly at low ionomer concentration and bends over at high ionomer concentration. At a fixed ionomer concentration, the diffusion coefficient increases with ion content. This behavior is consistent with static (low-angle) light scattering results for the same ionomer solution: i.e., the reciprocal reduced scattered intensity changes in a similar fashion as the diffusion coefficient with respect to the effects of ionomer concentration and ion content. The dynamic behavior of small molecular weight ionomer (MW: 50 000) is in contrast to that observed for higher molecular weight ionomers (MW: 200 000, 400 000): the (effective) diffusion coefficient is almost independent of ionomer concentration and at fixed ionomer concentration, the diffusion coefficient decreases with ion content. The investigation of the reason behind this behavior is the subject of future work.[45] The addition of small salts (LiCl) significantly reduces the polymer concentration dependence of the diffusion coefficient. At low salt concentration (0.001–0.0001 M), the deviation from a single-exponential function is still significant, and the diffusion virial coefficient, k_D, is very high due to strong electrostatic interactions. At higher salt concentration (0.1–0.01 M), the behavior is quite similar to that of unmodified PS, which shows a single-exponential decay. Again, the random ionomers dissolved in an aprotic, polar solvent show characteristic polyelectrolyte behavior as observed by dynamic light scattering, as demonstrated by various experiments such as osmotic pressure, viscosity, low-angle light scattering, and small-angle neutron and X-ray scattering. Because of the stronger scattering power and easier optical clarification of an ionomer solution compared with a polyelectrolyte aqueous solution, the ionomer solution is especially useful to study the characteristic behavior of salt-free polyelectrolytes, where scattering is very weak and the effect of foreign particles is significant.

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$$D = \lim_{q\to 0} D_{\text{eff}} = \lim_{q\to 0} \frac{\bar{\Gamma}}{q^2} \propto \frac{\partial \pi}{\partial c}$$

This is consistent with eq 11, in which the static scattered intensity extrapolated to zero angle is used to correlate scattering data with thermodynamic relations.
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