Light Scattering from Sulfonate Ionomers in Xylene

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ABSTRACT: Static and dynamic light scattering measurements have been made on dilute sodium sulfonated polystyrene ionomer/xylene solutions. The extent of aggregation via intermolecular ion pair interactions has been shown to be controlled by an equilibrium between single contracted chains and multichain clusters and can be modeled by the "open association" model. The single-chain dimensions of the ionomers at infinite dilution were found to be approximately 20% smaller than the single-chain dimensions of the unfunctionalized polystyrene of the same molecular weight in the same solvent. This contraction is thought to be due to intramolecular ion pair associations.

Introduction

Ionomers are macromolecules containing a small number (typically less than 10 mol %) of ionic groups chemically bound to a nonpolar chain. The addition of ionic groups to the polymer can cause large differences in the polymer properties due to microphase separation of the ionic groups in the nonpolar matrix. These properties can be controlled broadly through changes in the counterion structure and the concentration of ionic groups. The solution properties are of particular interest since the rheology of fluids can be modified in a rather facile manner with changes in the chemical structure. In addition, unexpected and technologically useful phenomena, such as marked viscosity enhancement with increase in concentration, temperature, and shear rate (shear thickening), have been observed.

In polar or high dielectric constant (ϵ) solvents, such as dimethylformamide and dimethyl sulfoxide, ionomers behave in a similar manner to polyelectrolytes.[1] However, ionomers with low levels of ionic groups are also soluble in less polar solvents, such as tetrahydrofuran (THF, $\epsilon = 7.4$). In this solvent it has been observed that sulfonation of polystyrene results in a decrease in the intrinsic viscosity of the solution.[2] At higher concentrations the ionomers were found to be aggregated, causing network formation and highly viscous solutions. It was suggested that at low ionomer concentrations single ionomer chains contracted via intramolecular ion pair associations but that at the single-chain overlap concentration intermolecular ion pair associations were formed at the expense of intramolecular associations. However, it was recently observed by light scattering[3] that even in very dilute solution, sulfonated polystyrene ionomers aggregated in THF. It was therefore suggested that the reduction in the intrinsic viscosity was due to a larger density within the aggregate compared with the density within the single polystyrene chains. This would result in a reduction in the volume occupied by the ionomer chains and therefore a reduction in the viscosity.

In the nonpolar solvent xylene, sulfonated polystyrene ionomers up to a sulfonation level of approximately 1.5 mol % will dissolve. However, in this solvent very interesting solution properties are observed even at these modest sulfonation levels. In the semidilute regime the solution viscosities have been seen to be time and shear rate dependent,[4,5] i.e., shear thickening and thinning. In this regime very high viscosities are observed for relatively dilute solutions due to network formation, but an equilibrium situation does not appear to be reached. In more dilute solution, equilibrium is formed after several days, and as in THF, the intrinsic viscosity of the ionomers is lower than that of polystyrene. In order to help explain the more concentrated solution properties, we have described in this paper light scattering measurements from dilute solutions of sodium sulfonated polystyrene (Na-SPS) ionomers (1.39 mol %) in a low dielectric constant solvent (xylene, $\epsilon = 2.2$).

Experimental Section

Sodium sulfonated polystyrene ionomers were prepared as described in refs 5 and 6 by using anionically polymerized polystyrene. The molecular weight and polydispersity of the unfunctionalized polystyrene were 105 000 g/mol and less than 1.05, respectively. Solutions were prepared at least 1 week before measurements were made to allow time for equilibrium to be reached. After this length of time, sample or time dependencies could not be observed at these concentrations. All solutions were filtered through 0.5- or 0.8-μm Nucleopore filters three times before filtering into dust-free light scattering cells.

Static and dynamic light scattering measurements were made simultaneously at 20 °C by using a wavelength $\lambda_0 = 488$ nm and an angular scan of 20–150° in steps of 10 deg. Details of the instrument are described in a paper by Bantle et al.[7] The refractive index increments dn/dc (0.120 for SPS and 0.108 for PS at 488 nm) were measured by using a Brice Phoeniz differential refractometer.

Theory

(a) Static Light Scattering. In light scattering experiments, the apparent weight-average molecular weight is

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Table I
Light Scattering Results on Na-SPS and Its Nonionic Precursor

sample	$10^{-5}(M_1)_w$, g/mol^{-1}	$10^{-4}K_0$, L mol^{-1}	10^4A_2, mol cm^3 g^{-2}	$10^7D_{c\to0}$, cm^2 s^{-1}	$R_{H,c\to0}$, Å
polystyrene	1.07 ± 0.05		4.8 ± 0.1	4.0 ± 0.1	83 ± 2.0
Na-SPA (1.39 mol %)	1.17 ± 0.05	1.0 ± 0.2		5.3 ± 0.2	62 ± 4.0

defined by[8]

$$(M_w)_{app} = R_0/Kc \qquad (1)$$

where

$$K = \frac{4\pi^2}{N_A\lambda_0^4}(dn/dc)^2n_0^2 \qquad (2)$$

c is the polymer concentration (in g cm^{-3}), R_0 the Rayleigh ratio at observation angle zero, λ_0 the wavelength of light, and n_0 the refractive index of the solvent. The concentration dependence of the apparent weight average molecular weights of nonmultimerizing solutes is at sufficiently low c normally expressed by

$$\frac{1}{(M_w)_{app}} = \frac{1}{M_w} + 2A_2c \qquad (3)$$

where A_2 is the second virial coefficient and M_w the true weight-average molecular weight.

To interpret the concentration dependence of apparent molecular weights for multimerizing polymers a physical model is required.[9] For this ionomer system, the "open association" model appears to properly explain the data. This term was coined by Elias and Lys[10] but has also been called random polymerization or indefinite self-associations. In this model, the aggregation process is assumed to be controlled by a series of equilibria between single chains and multichain aggregates:

$$\begin{array}{ll} M_1 + M_1 \rightleftharpoons M_2 & K_2 \\ M_1 + M_2 \rightleftharpoons M_3 & K_3 \\ M_1 + M_i \rightleftharpoons M_{i+1} & K_{n+1} \end{array} \qquad (4)$$

where M_i is an aggregate consisting of i chains. If the interacting groups on the ionomer chain are far apart, then the equilibrium constant K_i for each step can be considered invariant to increases in the size of the aggregates,[9] i.e.

$$K_0 = K_2 = K_3 = K_{n+1}$$

Then the concentration of aggregates consisting of i chains (in mol L^{-1} units) is given by

$$M_i = K_0^{i-1}[M_1]^i \qquad (5)$$

It was shown that for $K_0[M_1] < 1$ the weight-average molecular weight is given by

$$(M_w)^2 = (M_1)_w^2 + (4 \times 10^3)K_0[(M_1)_w^2/(M_1)_n]c \qquad (6)$$

where $(M_1)_n$ and $(M_1)_w$ are the number- and weight-average single-chain molecular weights. The concentration of single chains is then

$$[M_1] = (1/K_0)[M_w - (M_1)_w/(M_w + (M_1)_w)] \qquad (7)$$

(b) Dynamic Light Scattering. In dilute solution, the time-dependent correlation function measured by dynamic light scattering can be expressed in terms of the electric field correlation function $g(t)$. This function is related to the dynamic structure factor $S(q,t)$ by[14,15] $g(t) = S(q,t)/S(q)$. Using a cumulant expression of $S(q,t)$ gives

$$\ln S(q,t) = \ln S(q) - \Gamma t + v\Gamma^2t^2/2 \qquad (8)$$

where v is a coefficient that describes the polydispersity of the system and Γ is the first cumulant. The z-average diffusion coefficient is then given by

$$D_z = \Gamma/q^2 \quad \text{at} \quad q = 0 \qquad (9)$$

from which the hydrodynamic radius can be calculated by using the Stokes–Einstein relationship

$$R_H = kT/6\pi\eta_sD_z \qquad (10)$$

From the definition of a z-average, the diffusion coefficient ($D_z = \sum w_iM_iD_i/\sum w_iD_i$) of a solution containing aggregates of molecular weight M_1, $2M_1$, $3M_1$, ... will be given by

$$D_z = \frac{M_1}{M_w}(w_1D_1 + 2w_2D_2 + 3w_3D_3 + ... + iw_iD_i) \qquad (11)$$

where w_i and D_i are the weight fraction and diffusion coefficient of an aggregate consisting of i chains.

At low ionomer concentrations where most chains exist as either single chains or aggregates consisting of two chains, this can be simplified and rearranged to give

$$D_z\frac{M_w}{M_1} = D_1(c=0) + (1 - w_1)[2D_2(c) - D_1(c=0)] \qquad (12)$$

Assuming that at low ionomer concentrations D_1 and D_2 are concentration independent, the single-chain diffusion coefficient at infinite dilution can be estimated from the intercept of a plot of $D_z(M_w/M_1)$ against $(1 - w_1)$ and D_2 from the gradient.

Results and Discussion

(a) Static Light Scattering. In Table I, values of the apparent weight-average molecular weight and the second virial coefficient obtained for polystyrene in xylene are shown. These values are in reasonable agreement with the GPC molecular weight and virial coefficients, respectively, for polystyrene in similar solvents.[16] At low ionomer concentrations since only small aggregates are formed and the apparent molecular weights are fairly small, the intensity of scattering was almost independent of angle. Therefore to obtain the apparent molecular weights, an average intensity over angles between about 40° and 90° was used.

Figure 1 shows a plot of apparent molecular weight squared versus concentration for the ionomer. The values of K_0 and $(M_1)_w$ obtained from this plot by using eq 6 are shown in Table I. The linearity of this plot and the good agreement between the obtained and expected single-chain molecular weights suggest that the "open association" model is a good model for the data and that the second virial coefficient is very small.

In THF,[17] it has been shown that on increasing the sulfonation level, the virial term decreases. In theoretical calculations,[18,19] it was suggested that the second virial coefficient for ionomers is composed of two parts, $A_2 = A'_2 + f^2A''_2$, where f is the ion content, A'_2 is the sec-

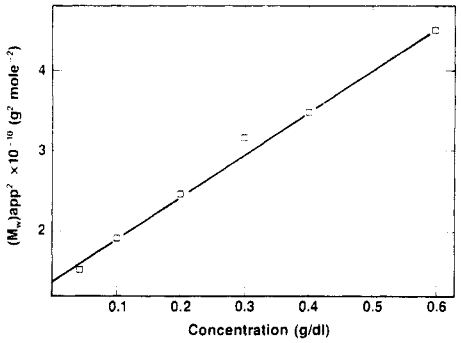

Figure 1. Apparent molecular weight squared versus concentration of sodium sulfonated polystyrene ionomer (1.39 mol %) in xylene.

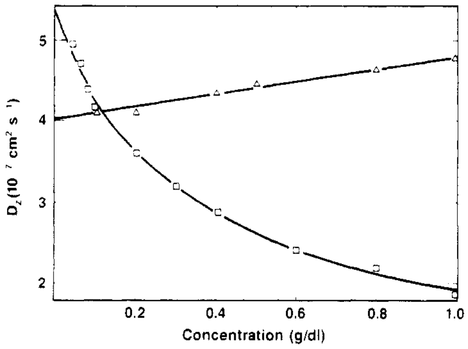

Figure 2. z-average diffusion coefficient versus concentration in xylene [□ Na-SPS (1.39 mol %); △ PS].

ond virial coefficient due to the excluded volume of the backbone chains, and A''_2 is the second virial coefficient due to attractions between dipoles. For this system $f^2A''_2$ is accounted for by using the "open association" model so the second virial term that we obtain should only be a measure of the excluded volume.[9] This virial term is expected to be smaller for the ionomer compared with polystyrene due to the interactions between ionic groups and the nonpolar solvent xylene. The insolubility of ionomers with higher sulfonation levels than about 1.5 mol % and the observation of single-chain collapse (see dynamic results later) give further evidence that the term A'_2 for this system is very small. $(M_w)_{app}$ in eq 3 therefore equals M_w at low concentrations.

From the equilibrium constant K_0 and eqs 5–7, the weight fractions of aggregates of different sizes at any concentration can be estimated. At the lower concentrations, most of the ionomer chains exist as single chains or in aggregates consisting of only two chains. At higher concentrations, more of the larger aggregates are formed.

(b) Dynamic Light Scattering. As with the static light scattering measurements, within experimental error, no angular dependence of the apparent diffusion coefficients could be observed between 40° and 90°. The average diffusion coefficients over this angular range for both the ionomer and polystyrene are shown in Figure 2. For polystyrene, a linear dependence of the diffusion coefficient on concentration is observed with the gradient divided by the intercept, k_0 = 20 cm^3 g^{-1}. The diffusion coefficient extrapolated to infinite dilution and the corresponding calculated hydrodynamic radius are shown in Table I. These results are in good agreement with other values for polystyrene in similar solvents, such as toluene[16,20] and benzene.[16] The polydispersity correction term for polystyrene (Figure 3) is small. According to Brown et al.,[21] $\upsilon = (1/4)(M_z/M_w - 1)$ if $M_z/M_w < 1.25$. This suggests that for this polystyrene sample $M_z/M_w \simeq 1.056$.

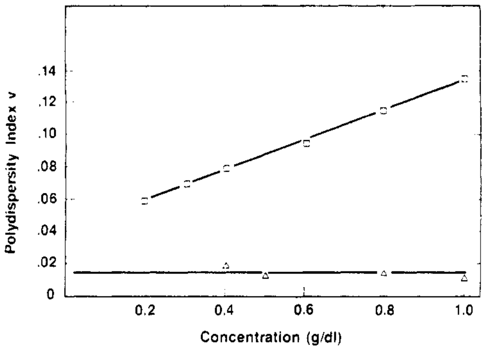

Figure 3. Polydispersity index, $\upsilon = 0.25 (M_z/M_w - 1)$, versus polymer concentration in xylene [□, Na-SPS (1.39 mol %); △ PS].

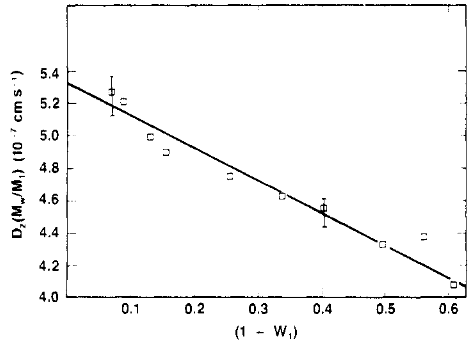

Figure 4. $D_z(M_w/M_1)$ versus $(1 - w_1)$ for Na-SPA (1.39 mol %) in xylene.

Figure 4 shows a graph of $D_z(M_w/M_1)$ for the ionomer against $(1 - w_1)$ (w_1 values are calculated from eq 7). From this plot, the single ionomer chain diffusion coefficient at infinite dilution can be obtained (cf. eq 12) and is shown in Table I. The hydrodynamic radius calculated from this diffusion coefficient is about 25% smaller than that of polystyrene in the same solvent. It is also slightly smaller than values for this molecular weight polystyrene in a Θ solvent (for example, R_H in cyclohexane, a Θ solvent, is 73 ± 5 Å).[22] From the gradient of Figure 4, we obtain (via eq 15) $D_2 \simeq 1.65 \pm 0.4 \times 10^{-7}$ cm^2 s^{-1}. Since the volume occupied is proportional to $R_H{}^3$ this would suggest that

$$\frac{\text{volume occupied per chain for single chains}}{\text{volume occupied per chain for two-chain aggregates}} = 2\frac{1.65^3}{5.3} = 0.06$$

and that upon aggregation, an increase in viscosity should occur, resulting in unusually high Huggins constants as observed in ref 5. However, since the concentration dependence of the diffusion coefficients is unknown for these ionomers, this value has a large uncertainty. At the highest concentration measured $D_z(M_w/M_1)$ versus $(1 - w_1)$ remains linear despite appreciable formation of aggregates consisting of more than two chains. This would occur if (see eq 14)

$$2D_2(c) \simeq 3D_3(c) \simeq 4D_4(c)$$

or if we assume at finite concentration the Stokes–Einstein relationship being valid that R_H increases proportional to the number of chains in the aggregates. Such behavior is expected for rodlike aggregation or is an indication of chain expansion as a result of aggregation. Possibly a local chain stiffening occurs around the cross-linking point.

The polydispersity term, v, for the ionomers was found to be linearly dependent upon the polymer concentration. As the polymer concentration increased, more larger aggregates are formed, so v is expected (and observed) to increase.

Conclusion

It has been found that in dilute sodium sulfonated polystyrene ionomer/xylene solutions, an equilibrium between single contracted chains and aggregates is formed. A contraction of the single ionomer chains of about 25% in the hydrodynamic radius compared with unfunctionalized polystyrene in the same solvent has been observed, explaining the marked reduction in intrinsic viscosity on increasing the sulfonation level. On forming aggregates, recent small-angle neutron measurements have shown that the single chains expand,[5] causing an increase in the volume occupied by each chain and, therefore, also in the viscosity. From the diffusion coefficient of an aggregate consisting of two chains compared with the diffusion coefficient of a single chain an increase in the volume occupied by the polymer is also expected with aggregation. This could explain why large Huggins coefficients are observed in reduced viscosity measurements on these[5] and other ionomer solutions.[25]

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