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Aggregation Behavior of ω- and α,ω-Metal Sulfonato Polystyrene in Toluene

P. Vanhoorne[†] and R. Jérôme*

Center for Education and Research on Macromolecules (CERM), Université de Liège, Sart-Tilman B6, B-4000 Liège, Belgium

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ABSTRACT: The aggregation behavior of ω- and α,ω-metal sulfonato polystyrene in toluene has been investigated by static and dynamic light scattering. Monofunctional chains reversibly associate into small reverse micelles. Lithium-based ionic aggregates contain an average of 12 ion pairs, which corresponds to a preferential structure for the ionic cores. When the molecular weight of the chains is increased, polymer–solvent interactions progressively distort the ionic aggregates, and above a critical molecular weight, estimated to be 50 000 in toluene, the multiplets collapse into smaller aggregates of an average of 3 ion pairs. Traces of polar solvents do not strongly affect the aggregation number, but do weaken the dipole–dipole interactions. Structure of the ionic cores strongly depends on the nature of the ion pairs, which suggests that this structural feature is a key parameter in the control of the structure–property relationships in ionomers. The aggregation behavior of the difunctional chains is complex, due to the occurrence of a closed association mechanism for the individual multiplets and an open association of reverse micelles into larger aggregates.

Introduction

For the last three decades, special attention has been paid to the phase morphology of ionomers, i.e. hydrocarbon chains containing less than 15 mol % of ionic groups. It is now well established[1,2] that the original properties of ionomers compared to those of the nonionic precursors result from a microphase separation of the ionic groups. The ionic microdomains act as thermoreversible physical cross-links and are responsible for improved ultimate mechanical properties.[3] However, the precise shape and size of the ionic microdomains still remain unsolved. Direct imaging by electron microscopy has only been reported in a few specific cases,[4–7] and most experimental studies are currently based on indirect methods. Extensive studies by dynamic mechanical analysis (DMA),[2,8] dielectric spectroscopy,[9–12] and X-ray (SAXS)[13–18] or neutron (SANS)[19–21] small angle scattering have given rise to a wide range of models accounting for the structure and properties of ionomers.[2,22] All models refer to the ion pair association in two kinds of structures, called multiplets and clusters. Multiplets contain a few ion pairs, whereas clusters are larger structures rich in ion pairs, phase-separated from the polymer matrix and responsible for the original mechanical properties.[22]

A better understanding of the ionomer morphology has resulted from the synthesis of model compounds, i.e. halato-telechelic polymers (HTP's), which are linear chains selectively capped at both ends with an ionic group.[16–18,23–26] Many characteristic features can be modified at will and the influence of parameters, such as molecular weight and T_g of the polymeric backbone, nature of the ion pairs, etc., can be investigated in a straightforward way. Recently, dielectric[27] and solid-state NMR[28] investigations of these model ionomers have reported strong experimental support of the model proposed by Eisenberg *et al.* for the structure of ionomers.[22] In this model, the ionic groups phase-separate via formation of small multiplets containing about 10 ionic groups. The mobility of the chain segments directly attached to multiplets is restricted which builds up a shell of "rigid" segments around the multiplets. The thickness of this shell would be at least the persistence length of the chains. Whenever the ionic content is high enough for the low-mobility regions to overlap each other (this might already happen below 5 mol % ions), there is formation of continuous regions of restricted mobility, i.e. clusters, the T_g of which is higher than that of the base polymer. Of course, in contrast to dynamic mechanical measurements, electron microscopy cannot discriminate the two phases which are of the same chemical nature.

However, the actual size and shape of the multiplets are still unanswered questions, and the assumption that multiplets contain a small number of ion pairs has not been ascertained. Recently, SAXS investigations of bulk ω- and α,ω-metal sulfonato polystyrenes has shown that multiplets are essentially the same for both mono- and difunctional compounds and are distributed in a liquid-like manner throughout the polymer matrix.[29,30] Moreover, multiplets are not affected by dissolution of the polymers in apolar solvents, such as toluene, and they keep their size and shape unchanged in the investigated concentration range (from bulk down to 5 wt %). Simple geometrical considerations show that these multiplets should contain about 12 ion pairs, but this estimation is based on several approximations.[30] A detailed study of dilute solutions is expected to provide more accurate aggregation numbers. Due to the ion pair aggregation, however, HTP's readily form gels at concentrations as low as a few weight percent. This explains why the preparation and analysis of these solutions can be problematic. This problem can be overcome by using ω-functional chains (halato-semitelechelic polymers, HSTP's), since the ion pair aggregation results in micelle formation rather than in a cross-linked material. Since the aggregation number is the same in both HTP's and HSTP's, the latter compounds thus provide a unique opportunity for an accurate determination of the average aggregation number.[31]

In this paper, we report on light-scattering measurements on dilute toluene solutions of ω-metal sulfonato polystyrene. In contrast to X-ray scattering, light scattering, in both the static and dynamic modes, is a

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technique appropriate to the study of aggregation in dilute solutions.[32,33] Provided that the multiplets are stable down to the dilute concentration regime, the scattering curves are dominated by the form factor of the individual starlike multiplets, and contribution of the intermultiplet interferences is negligible.[32] Light scattering thus gives access to the size and shape of the individual reverse micelles, from which the aggregation number can be calculated.[31-34]

Experimental Section

Polymer Synthesis. ω- and α,ω-sulfonato polystyrene samples were synthesized by living anionic polymerization of styrene followed by deactivation with 1,3-propanesultone, as reported elsewhere.[30] Functionally was systematically better than 90%, as checked by potentiometric titration of the acid end groups with a standard solution of tetramethylammonium hydroxide in a toluene/methanol (9/1 v/v) mixture. Molecular weight and molecular weight distribution were measured by size exclusion chromatography of a polymer sample picked out before deactivation of the living chains by 1,3-propanesultone.

Lithium sulfonate terminated polymers were purified by a repeated precipitation in methanol. Cation exchange was conducted as follows: lithium sulfonate terminated polymers were converted into the sulfonic acid counterparts by a twice repeated precipitation in methanol containing at least 20 equiv of perchloric acid and a final reprecipitation in pure methanol. (Semi)telechelics were kept in the acid form in a toluene/methanol solution. Sulfonic acid end groups were neutralized by 1.05 equiv of the appropriate metal acetate. Methanol and acetic acid were removed by the azeotropic distillation of the solvent (regularly replaced by dry toluene), until no polar compound could be detected in the distillate by gas chromatography and/or potentiometric titration. Solvent was finally removed by distillation and the polymer was dried at 160 °C under vacuum for 16 h.

Stock solutions were prepared by dissolving, in tight flasks, weighed amounts of polymer in precise volumes of toluene (analytical grade). The solutions were subsequently stirred for 24 h at 25 °C.

Light Scattering. Static and dynamic light-scattering measurements were conducted with a BI-200 photogoniometer (Brookhaven Instruments) equipped with a BI-2030 128 channel digital correlator (Brookhaven) and an Ar-ion laser (Spectraphysics) emitting vertically polarized light at the wavelength $\lambda = 488$ nm. All the measurements were conducted at 25 ± 0.1 °C, and the data were transferred from the correlator to a microcomputer for analysis. The specific refractive index increment, d*n*/d*c*, was measured with a home-built differential refractometer operating at a wavelength of 488 nm at 25 ± 0.1 °C.

The light-scattering cells (12 mm round cells) were cleaned in sulfochromic acid and carefully rinsed with deionized water (MilliQ grade). The optical clarification of the solutions was carried out by repeated filtration through a 0.22 μm filter (Anotop filter, Alltech). Most of the sample preparation, including dilution of the stock solution and optical clarification, was conducted inside a dust-free hood, to avoid contamination by dust particles.

Results and Discussion

Molecular characteristics of the investigated samples are summarized in Table 1. The molecular weight distribution does not exceed 1.2, and the functionality in sulfonate is systematically better than 90% and 185% for mono- and difunctional samples, respectively. The specific refractive index increment of the functional chains has been measured at 488 nm, and no significant difference has been reported in comparison to the unfunctionalized polystyrene chains. The values increase slightly with molecular weight, from d*n*/d*c* = 0.104 mL/g ($\bar{M}_n$ = 1000) to d*n*/d*c* = 0.117 mL/g ($\bar{M}_n$ = 49 000), which is in complete agreement with literature data.[35]

Table 1. Molecular Characteristics of the ω- and α,ω-Metal Sulfonato Polystyrenes

$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Fty[a]	d*n*/d*c* (mL/g)[b]	*C** (wt %)
1 000	1 100	1.10	0.92	0.104 ± 0.002	83.1
3 000	3 300	1.10	0.95		35.1
7 200	8 000	1.11	0.95	0.106 ± 0.002	17.5
13 000	14 000	1.08	0.96	0.115 ± 0.003	11.3
38 500	39 000	1.02	0.93	0.112 ± 0.002	5.1
49 000	50 000	1.02	0.91	0.117 ± 0.003	4.2
97 000	99 000	1.02	0.90	0.112 ± 0.003	2.4
7 500	9 000	1.20	1.90	0.115 ± 0.003	16.0
23 500	25 000	1.06	1.86	0.117 ± 0.002	7.2

[a] Average number of sulfonate end groups per chain. [b] Measured at $\lambda = 488$ nm.

Intermediate Concentration Regime. SAXS of ω-barium sulfonato polystyrenes could not be carried out at concentrations smaller than 5 wt % due to a lack of contrast.[29,30] This concentration is typically 5–10 times higher than the usual concentrations for static light-scattering measurements. In a concentration range from 1 to 5 wt %, however, dynamic light scattering can be used to measure the hydrodynamic radius of HSTP aggregates. Actually, the experimental correlation function, Γ, is related to the translational diffusion coefficient D_T by eq 1, where $q = (4\pi/\lambda)$ sin

$$D_T q^2 = \Gamma \tag{1}$$

$(\theta/2)$ is the scattering vector.[33] D_T is the actual diffusion coefficient in solutions below the critical overlap concentration C^*,[36] defined as

$$C^* = \frac{M}{\frac{4}{3}\pi R_g^{\,3} N_A} \tag{2}$$

where R_g is the gyration radius of the chains, M is their (weight) average molecular weight and N_A is Avogadro's number. Using R_g values reported in the literature,[37] C^* has been calculated and reported in Table 1. The requirement that C^* be higher than 5 wt % is fulfilled for $\bar{M}_w$ smaller than 39 000. Accordingly, dynamic light-scattering measurements have been conducted in this range of molecular weight.

The hydrodynamic radius of the aggregates, R_H, can be calculated from the Stokes–Einstein relationship (eq 3), if the infinite dilution diffusion coefficient, D_0, is

$$D_0 = \frac{kT}{6\pi\eta_0 R_H} \tag{3}$$

assumed to be equal to the experimental diffusion coefficient D_T. In eq 3, k is the Boltzmann constant, T is absolute temperature, and η_0 is solvent viscosity. This method is widely used for particle size measurement,[33] and it has previously been applied to random ionomer solutions in both polar[36] and apolar[38] solvents. Figure 1 reports the typical dependence of the hydrodynamic radius of aggregates on concentration. The aggregate size does not change at all in the concentration range from 0.1 to 5 wt %. Although the hydrodynamic radius of a starlike molecule is not very sensitive to the number of arms beyond six to eight arms,[39] these data are in favor of the invariance of multiplet size and shape down to 0.1 wt % in toluene. Moreover, the size distribution

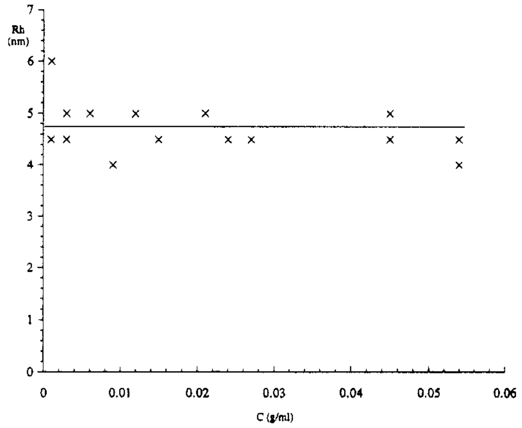

Figure 1. Dependence of the hydrodynamic radius of ω-barium sulfonato polystyrene ($\bar{M}_w$ = 14 000) on concentration in toluene. The full line is the average value.

of the aggregates is in all cases very narrow, which is in favor of a well-defined aggregation number corresponding to a thermodynamically stable structure for the aggregates. This interpretation has been confirmed by static light scattering and will be discussed later.

Since previous SAXS measurements[29,30] have shown that the size and shape of multiplets of ω-metal sulfonato polystyrenes are not affected by dilution from bulk down to 5 wt % in toluene, these results show that the weight average aggregation number of multiplets in bulk HSTP's can be calculated from the absolute molecular weight of multiplets as measured by static light scattering in dilute solution.

Dilute Solution Behavior. Static light scattering is a very useful technique for measuring the absolute molecular weight of polymers in a wide range of solvents. However, the molecular weight of aggregating species may depend on concentration, and the scattering curves may accordingly deviate from the classical Zimm law and require a more sophisticated treatment of the experimental data.[32]

Light-scattering evidence for aggregation of random ionomers has been reported in several solvents,[36,38,40] and the open model has been found to describe properly solutions of randomly sulfonated polystyrene in xylene.[21] Sulfobetaine zwitterionic[41] and metal carboxylato[31] HSTP's, which will be discussed later, have also been investigated. Möller[42,43] and Burchard[34] have reported on the aggregation of two high molecular weight ω-lithium sulfonato polystyrene samples in cyclohexane and toluene. Depending on the data analysis, the reported aggregation numbers vary from 3 to 12. The effect of the molecular weight and the nature of the counterion has however been disregarded. Thus, a more precise picture of the aggregation behavior of ω-metal sulfonato polystyrene in apolar solvents requires a more detailed study.

1. Aggregation Models. The aggregation numbers of all ionomers investigated to the present are clearly concentration dependent.[21,31,34,41-43] The aggregation behavior can be described by two completely different modls, i.e. the open and closed association models.[32] The closed association model states that free chains are in equilibrium with only one N-mer, the aggregation number of which, N, is unambiguously defined. Below the so-called critical micelle concentration (cmc), the system mainly consists of free chains. For concentrations well above the cmc, the concentration of free chains is exceedingly small, and the system contains mainly N-mers. Equation 4 depicts the closed model, where M_1

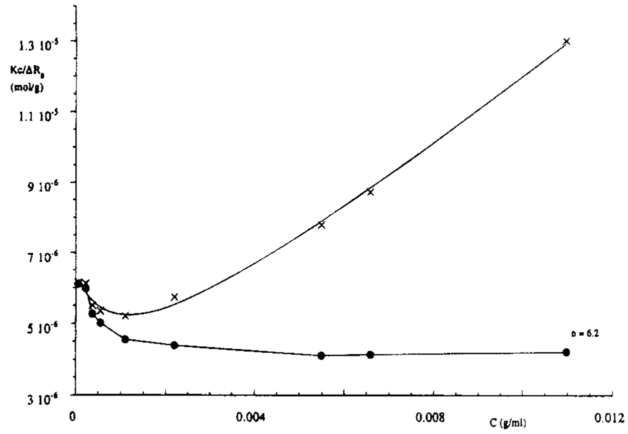

Figure 2. Reciprocal reduced scattered intensity at zero angle, $Kc/\Delta R_0 = 1/\bar{M}_w$, as a function of concentration for ω-lithium sulfonato polystyrene ($\bar{M}_w$ = 39 000) in toluene, before (×) and after (●) correction for polymer–solvent interactions.[34] Full lines are guides for the eyes.

$$N M_1 \rightleftharpoons M_N \qquad {}^{n}K_0 = \frac{[M_N]}{[M_1]^N} \tag{4}$$

is a free chain, and M_N is an aggregate of N chains. The closed model thus describes an all-or-none process.

In the open association model, the unimers are assumed to be in equilibrium with dimers, which in turn are in equilibrium with trimers, etc. There is thus a continuous distribution of multimers of all finite values ranging from 1 up to infinity. As an approximation, all the equilibrium constants are currently assumed to be equal to the dimerization constant. In spite of this hypothesis, the model has been shown to provide a good description for a wide range of systems.[32]

Equation 5 schematizes the open association model, which, however, fails in predicting a well-defined cmc.

$$\begin{array}{l}
M_1 + M_1 \rightleftharpoons M_2 \\
M_2 + M_1 \rightleftharpoons M_3 \\
M_3 + M_1 \rightleftharpoons M_4 \quad {}^{n}K_0 = \dfrac{[M_2]}{[M_1]^2} = \dfrac{[M_3]}{[M_2][M_1]} = \dots = \dfrac{[M_N]}{[M_{N-1}][M_1]} \qquad (5) \\
\text{- - - - - - - - - - - - -} \\
M_{N-1} + M_1 \rightleftharpoons M_N
\end{array}$$

More elaborated models may be built by combining the two extreme open and closed association models, as detailed elsewhere.[32]

Interestingly enough, Elias[32] has calculated the typical light-scattering curves for each of the two extreme models and has proposed mathematical tools for discriminating the open and closed models from the experimental data. These calculations are, however, restricted to ideal systems, in which no polymer–solvent interaction occurs ($A_2 = 0$). In the case of good solvents, a more complex mathematical treatment, as discussed by Burchard,[34] is required.

2. Metal Sulfonato–Halato–Semitelechelic Polymers in Toluene. Figure 2 reports the typical concentration dependence of the reciprocal reduced scattered intensity, $Kc/\Delta R_0$, for ω-metal sulfonato polystyrene in dilute toluene solutions. Upon an increase in concentration, the reciprocal reduced scattered intensity first decreases, passes through a minimum, and then rises sharply at higher concentrations. Since scattered intensity is related to the molecular weight of the scattering particles, such typical behavior unambiguously shows a dependence of the aggregation number on concentration.

From the previous observation of the size and shape invariance of the multiplets at concentrations higher than 0.1 wt %, closed association behavior is expected. This is supported by the failure of the Elias equation for the open model[32] to describe the experimental curves, even when polymer–solvent interactions are taken into account (the fitting procedure is not convergent). Therefore, the experimental curves have been analyzed according to Burchard's method[34] which is valid for the closed association model. In this method, the reciprocal reduced scattered intensity is assumed to be given by

$$\frac{Kc}{\Delta R_0} = \frac{1}{\bar{M}_{\mathrm{w,app}}} = \frac{1}{\bar{M}_{\mathrm{w}}(c)}(1 + 2A_2(c)\bar{M}_{\mathrm{w}}(c)c + 3gA_2(c)\bar{M}_{\mathrm{w}}^2(c)c^2 + ...) \qquad (6)$$

where c is the concentration (g/mL), ΔR_0 is the excess reduced scattered intensity extrapolated at zero angle, A_2 is the (osmotic) second virial coefficient, and K is the optical constant for vertically incident polarized light, defined as

$$K = \frac{4\pi^2 n_0^{\,2}(\mathrm{d}n/\mathrm{d}c)^2}{\lambda_0^{\,4} N_{\mathrm{A}}} \qquad (7)$$

where n_0 is the refractive index of the solvent. In eq 6, g is a proportionality factor between the second and third virial coefficients, defined by

$$A_3\bar{M}_{\mathrm{w}}c^2 = g(A_2\bar{M}_{\mathrm{w}}c)^2 \qquad (8)$$

For starlike aggregates, g is close to $1/3$, and eq 6 can then be rearranged into

$$\sqrt{\frac{K_{\mathrm{c}}}{\Delta R_0}} = \sqrt{\frac{1}{\bar{M}_{\mathrm{w}}(c)}}\,(1 + A_2\bar{M}_{\mathrm{w}}(c)c) \qquad (9)$$

Above cmc, $\bar{M}_{\mathrm{w}}(c)$ is expected to be constant, and according to eq 9, a plot of $(Kc/\Delta R_0)^{1/2}$ versus c is linear (see Figure 3). The intercept of the straight line allows the molecular weight of the micelle to be calculated to a first approximation, while the slope makes the second virial coefficient attainable. From the molecular weight of the micelle and that of the precursor, a first estimate of the aggregation number can be extracted. From the approximate value of the aggregation number, the precise value of g can be determined,[34] and the experimental points are then corrected for the contribution of polymer–solvent interactions in agreement with eq 6. The corrected values can then be used for a more precise determination of the aggregation number.[34]

The corrected curve in Figure 2 shows a constant aggregation number as soon as the concentration is higher than a few mg/mL. This is strong evidence for a closed association for ω-metal sulfonato polystyrene in toluene. Whenever enough experimental data are available in the dilute solution regime, cmc can be estimated.[42]

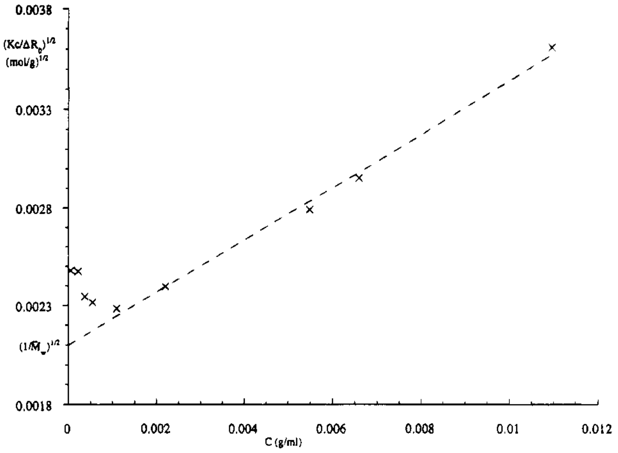

Figure 3. Square root of the reciprocal reduced scattered intensity, $(Kc/\Delta R_0)^{1/2}$, as a function of concentration for ω-lithium sulfonato polystyrene ($\bar{M}_{\mathrm{w}}$ = 39 000) in toluene. Linear regression above cmc (dashed line) yields a first estimate of the aggregate molecular weight.[34]

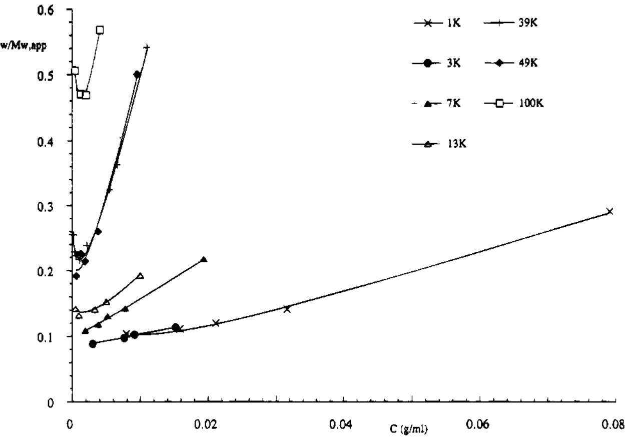

Figure 4. Normalized reciprocal reduced scattered intensity, $(\bar{M}_{\mathrm{w}})_{\mathrm{l}}/(\bar{M}_{\mathrm{w}})_{\mathrm{ag}}$, versus concentration for a series of ω-lithium sulfonato polystyrenes in toluene. The numbers are molecular weight in thousands. Lines are guides for the eyes.

Table 2. Molecular Parameters of the Ionic Aggregates for a Series of ω-Lithium Sulfonato Polystyrenes in Toluene[a]

$(\bar{M}_{\mathrm{w}})_{\mathrm{I}}$	$(\bar{M}_{\mathrm{w}})_{\mathrm{ag}}$	$\bar{N}_{\mathrm{w}}$	10^4A_2 [(mol·mL)/g^2]	$10^4A_{2,0}$ [(mol·mL)/g^2]
1 100	18 000	16.4	7.84	21.7[c]
3 300	43 000	13	4.38	14.6[c]
8 000	87 000	10.9	2.78	
14 000	125 000	8.9	2.31	
31 500[b]	295 000	9.4	1.87	6.2
39 000	242 000	6.2	2.80	
50 000	350 000	7	2.32	5.8[c]
97 000	265 000	2.8	1.58	6.0[c]
312 000[b]	1 020 000	3.2	1.35	3.2

[a] $(\bar{M}_{\mathrm{w}})_{\mathrm{I}}$ and $(\bar{M}_{\mathrm{w}})_{\mathrm{ag}}$ are the weight average molecular weights of single chains and aggregates, respectively, $\bar{N}_{\mathrm{w}}$ is the weight average aggregation number, and A_2 and $A_{2,0}$ are the second virial coefficients for the aggregates and the nonfunctional chains, respectively. [b] From ref 34. [c] From ref 37.

Figure 4 shows the effect of molecular weight on the scattering curves, normalized by the molecular weight of the unimers. Clearly, the aggregation number decreases with increasing molecular weight of the chains. Moreover, polymer–solvent interactions are stronger for the longest chains, as can be inferred from the steeper slope at high concentrations. Molecular weight, aggregation number $\bar{N}_{\mathrm{w}}$, and second virial coefficient are listed in Table 2 for a series of ω-lithium sulfonato polystyrenes in toluene. It is obvious that the aggregation number decreases from 16 to 3, when the molecular

Table 3. Aggregation Parameters for a Series of ω-Metal Sulfonato Polystyrenes ($\bar{M}_w$ = 3300) in Toluene

cation	$(\bar{M}_w)_{ag}$	$\bar{N}_w$
Li	43 000	13.0
Na	40 000	12.1
K	50 000	15.2
Mg	64 500	19.5
Ca	38 300	11.6
Ba	18 500	6.0

weight of single chains increases from 1000 to 300 000. These aggregation numbers are consistent with spherical starlike aggregates, in complete agreement with previous SAXS data.[29,30] There is an apparent contradiction between the constant multiplet size reported by SAXS in the limited molecular weight range from 3000 to 18 000,[29,30] and the moderate decrease in the aggregation number over the same molecular weight range (from 13 to 9), as observed by light scattering. This difference might merely reflect the inaccuracy of the SAXS data.

A_2 values are systematically lower for the aggregates than for the parent unfunctionalized polystyrene chains, which also qualitatively agrees with the proposed starlike structure for the multiplets. Experimental data did not allow cmc values to be accurately determined. In all cases, however, cmc is lower than 1 mg/mL, which is quite small and supports the formation of very stable reverse micelles.

The dependence of the aggregation number on molecular weight is reported in Figure 5. For molecular weights below 50 000 $\bar{N}_w$ slowly decreases with increasing molecular weight, and the following power law is observed:

$$\bar{N}_w = K\bar{M}_n^{-0.22} \tag{10}$$

Above this molecular weight, there is a discontinuity and the aggregation number drastically decreases to ca. 3 chains per aggregate where it remains constant. This behavior is in favor of the preferred packing model for the ion pair organization in the ionic core.[44,45] According to this model, ion pairs tend to arrange themselves in an ordered structure, resulting in a well-defined aggregation number and a minimum in electrostatic energy. Upon an increase in chain length, the polymer–solvent interactions progressively distort this preferred structure to the point where it collapses. Then the model assumes that the chains remain unassociated, although an alternate hypothesis might be the formation of smaller and less distorted aggregates.

A clear picture is now emerging for the aggregation of ω-sulfonato polystyrene in apolar solvents. Lithium sulfonate ion pairs tend to aggregate into stable multiplets containing approximately 12 ion pairs. In toluene, polymer–solvent interactions progressively destabilize this preferred structure, as reflected by a decreasing aggregation number of the multiplets when molecular weight is increased. Above a molecular weight of 50 000, distortion is strong enough to break down the aggregates into smaller multiplets containing an average of three ion pairs. The observation that a preferred packing of ion pairs prevails gives strong support to a closed association model for their aggregation. This means that aggregates smaller or larger than an optimum size are less stable and tend to rearrange into the "ideal" multiplets. The aggregation number is thus well-defined and only a small fraction of free chains is in equilibrium with a single type of N-mers. In the absence of polymer–solvent interactions, multiplets are expected to maintain the preferred size independently of molecular weight. This is in agreement with results by Möller *et al.*,[42,43] who reported a constant aggregation number of 12, regardless of molecular weight, for ω-lithium sulfonated polystyrene in cyclohexane. Cyclohexane is a θ solvent for these polymers at room temperature, and accordingly, the polymer–solvent interactions are then vanishingly small.[42]

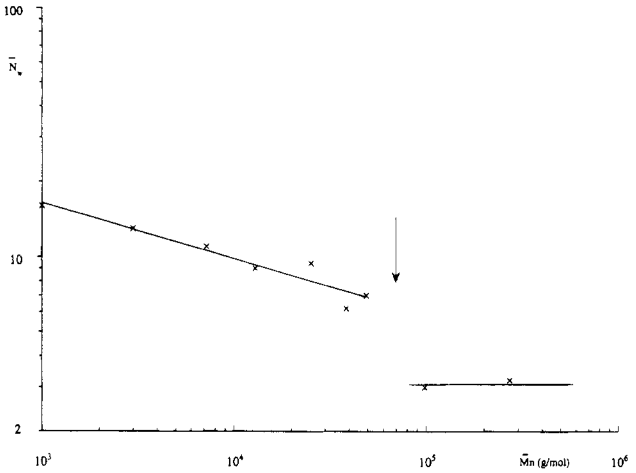

Figure 5. Dependence of the multiplet average aggregation number, $\bar{N}_w$, on molecular weight for a series of ω-lithium sulfonato polystyrenes in toluene. Lines are guides for the eyes. The arrow indicates a critical molecular weight above which multiplets collapse (see text).

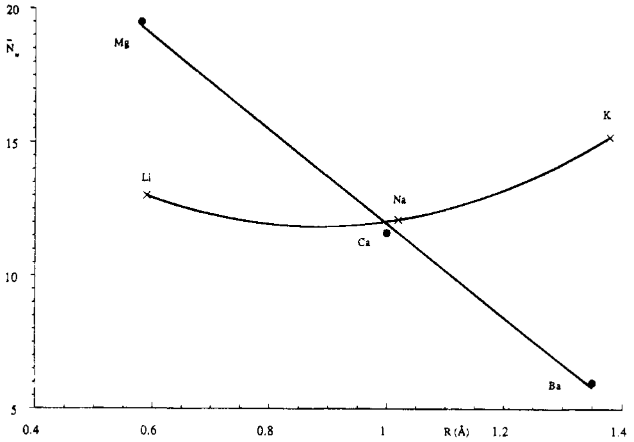

Figure 6. Dependence of the multiplet average aggregation number, $\bar{N}_w$, on the cation ionic radius, R, for a series of alkaline and alkaline-earth cations. Lines are guides for the eyes.

In the case of a preferred packing, the nature of the ion pairs is expected to have a decisive effect on the size and shape of the aggregates. As can be seen from Figure 6, the nature of the counterion is clearly a key parameter contributing to the magnitude of the aggregation number of ω-metal sulfonato polystyrenes. In the series of alkaline-earth cations, the aggregation number linearly decreases with the ionic radius of the cation, falling from $\bar{N}_w$ = 19.5 for magnesium to $\bar{N}_w$ = 6 for barium, whereas in the alkaline series the dependence is weaker and a minimum aggregation number is reached from sodium. Similar behavior has been previously reported for solutions of α,ω-carboxylato polybutadienes in xylene,[26] which stresses that the pronounced influence of the ion nature is not limited to sulfonate ion pairs. Wang[46] has reported the formation of *linear* aggregates for sulfobetaine HSTP's in toluene,

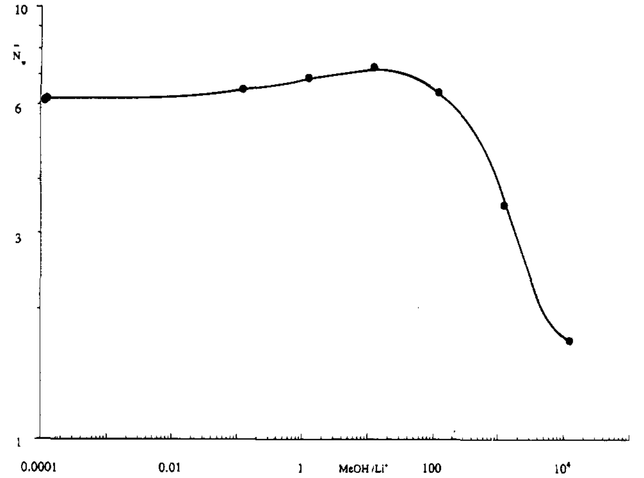

Figure 7. Average aggregation number, $\bar{N}_w$, as a function of methanol concentration, for an ω-lithium sulfonato polystyrene ($\bar{M}_w$ = 39 000) in toluene.

whereas Eisenberg *et al.*[31] have observed a significant effect of the cation nature on the size of ω-carboxylato polystyrene reverse micelles in cyclohexane, together with an *increase* in the aggregation number upon increasing molecular weight. The latter observation is in apparent contradiction with the theories proposed so far for the aggregation of HSTP's.[44,45] Nevertheless, the pronounced effect of the associating ion pairs on $\bar{N}_w$ is consistent with highly ordered ionic cores in the reverse micelles formed by HSTP's.

Influence of Methanol. Ion pair aggregation is known to be very sensitive to small amounts of polar compounds, such as water or alcohols.[2,21,26,47] The addition of 2% methanol, for example, has been reported to disrupt completely the ionic aggregates formed in apolar solvents.[21] No information is available, however, on the influence of much smaller amounts of this polar additive. This point might be of practical importance, since the removal of the last traces of polar compounds has proven to be a problem in ionomer preparation.[2,26] This is the reason why the influence of trace amounts of methanol on the aggregation behavior of ω-lithium sulfonato polystyrene has been investigated. Figure 7 shows the aggregation number as a function of the MeOH/Li$^+$ ratio for a representative ω-lithium sulfonato polystyrene. Interestingly enough, the size of the reverse micelles increases slightly with methanol concentration until 10 methanol molecules per lithium ion are added. Further addition of methanol rapidly decreases the aggregation number, but even 10 000 methanol molecules per ion pair cannot completely disrupt the reverse micelles. Accordingly, the multiplets appear to be extremely stable, as also supported by the small cmc values in the absence of any polar additive. The slight increase in the aggregation number upon addition of the first methanol molecules might be due to the partial solvation of the ion pairs, which would result in a rearrangement of the ionic core. The bulkier solvated ion pairs would form slightly larger ionic aggregates, which would be able to accommodate more polymer chains. This effect would persist till the point where the methanol molecules completely shield the dipole–dipole interactions between ion pairs. Beyond this point, further methanol addition would shift the equilibrium between free and aggregated solvated ion pairs toward the formation of single, fully solvated ion pairs. Accordingly, residual amounts of polar solvents are not expected to have a pronounced effect on the aggregation number of multiplets in ionomers. However, the strength of the ionic cross-links might be considerably more affected, since even traces of polar compounds have an influence on the internal structure of multiplets and may partially shield the dipole–dipole interactions between ion pairs.

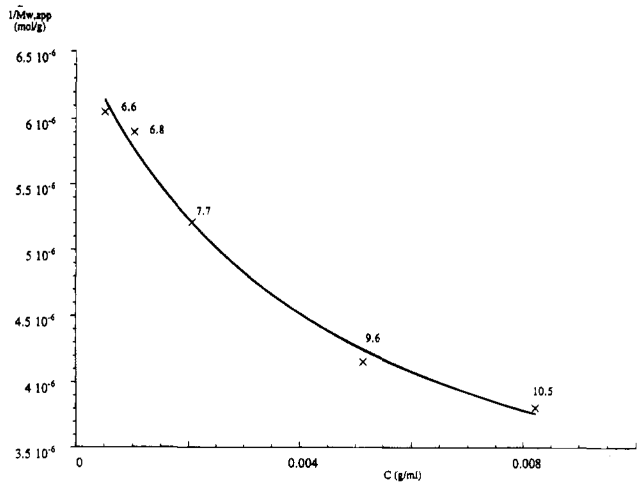

Figure 8. Reciprocal reduced scattered intensity at zero angle, $Kc/\Delta R_0 = 1/\bar{M}_w$, as a function of concentration for an α,ω-lithium sulfonato polystyrene ($\bar{M}_w$ = 25 000) in toluene. Numbers are weight average aggregation numbers. The line is a guide for the eyes.

Difunctional Chains. Although HTP's usually form a gel even at very low concentrations, α,ω-barium sulfonato polystyrenes form homogeneous solutions below 1 wt %.[29,30] Therefore, the aggregation behavior of one selected sample has been investigated by static light scattering. As can be seen from Figure 8, the difunctional sample shows clearly different behavior compared to that of monofunctional chains (see Figure 2). The second virial coefficient is seemingly negative, and the apparent molecular weight continuously decreases as concentration is decreased. Similar behavior has been reported for lightly sulfonated polystyrene in xylene, which could be described by an open association mechanism.[21] The aggregation behavior of HTP's thus seems to be inherently different from that of HSTP's. This apparent discrepancy might be rationalized as follows: in HSTP solutions the closed association model adequately describes the aggregation behavior of the individual multiplets. Since multiplets are the same in both HTP's and HSTP's, the closed model is expected to apply for the individual multiplets in HTP's. Difunctional chains, however, are able to link separate multiplets to form aggregates of several multiplets. This secondary aggregation process is expected to obey an open association model, since aggregates can grow indefinitely until gelation occurs. Light scattering would thus probe the two aggregation mechanisms, which would result in complex scattering curves. This is supported by the failure of both the open and the closed models to fit the data of Figure 8, and by recent SANS measurements on α,ω-sodium sulfonato polystyrene, which also suggest complex aggregation behavior.[48]

Conclusions

Combination of SAXS and dynamic light scattering has shown that multiplets formed by ω-metal sulfonato polystyrenes keep their size and shape unchanged from the bulk state down to 0.1 wt % in toluene. Under these conditions, static light scattering of dilute solutions of these polymers may give access to the actual aggregation number of the ionic multiplets. Light-scattering data have been reported for a series of ω-lithium sulfonato polystyrenes and analyzed according to the Burchard theory.[34] The results support an aggregation fitting a closed association model, and the critical micelle concentration is in all cases lower than 1 mg/mL. The aggregation number slowly decreases as the molecular weight increases, which favors a highly stable structure for the ionic cores. The most stable structure has been found to consist of 12 lithium sulfonate ion pairs. As molecular weight increases, polymer–solvent interactions progressively distort the preferred ionic core structure, and above a critical molecular weight, estimated at 50 000 in toluene, multiplets collapse into smaller aggregates of ca. 3 ion pairs. The preferred structure of the ionic cores depends strongly on the nature of the ion pairs, at least in the alkaline-earth series, and it is thought to be the key parameter in the control of the structure–property relationships in ionomers. Methanol preferentially solvates the ionic aggregates, which results in an internal rearrangement of the ion pairs. When added in trace quantities, methanol does not significantly change the aggregation number of the multiplets, although it is expected to weaken the strength of the ionic cross-links and hence the mechanical properties of the material.

When difunctional chains are considered, an open association of reverse micelles into aggregates is superimposed onto the closed aggregation behavior of the individual multiplets. This complex aggregation process makes the interpretation of the scattering curves very difficult.

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