SAXS Study of ω- and α,ω-Metal Sulfonato Polystyrenes in Toluene Solution

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ABSTRACT: Solutions of ω- and α,ω-barium sulfonato polystyrenes in toluene have been investigated by SAXS as a function of concentration. A characteristic ionic peak is displayed over the whole investigated concentration range. The experimental data are in favor of the ion pair aggregation into small stable multiplets homogeneously distributed throughout the material. The characteristic distance is related to the average intermultiplet distance d. A general law has been derived for the dependence of d on molecular weight, functionality, and concentration of the polymer. The size of the multiplets does not depend significantly on polymer concentration and molecular weight. Below a critical concentration which depends on the chain length, solutions of difunctional samples display a constant average intermultiplet distance. This behavior has been attributed to the partial multiplet dissociation by the fully extended chains. Sample preparation and subsequent thermal treatment have no influence on the position of the ionic peak but can affect the intensity of the peak and the upturn in scattered intensity at very small angles.

Introduction

For the past two 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 actual composition, shape, and space distribution of the ionic microdomains are still unanswered questions. The small size (2-10 Å) and lack of long-range order of the ionic microphases have precluded any reliable characterization by electron microscopy.[4,5] Rather, the phase morphology of ionomers has been studied by small-angle scattering of either X-rays (SAXS)[6-14] or neutrons (SANS).[15-17] Typical scattering profiles display a fairly broad peak, designated as the "ionic" peak, at s values of 0.07-1 nm^{-1}, corresponding to Bragg distances of 1-15 nm. Furthermore, a strong upturn in the scattered intensity is observed at very small angles (typically below 0.08 nm^{-1}). The nature of the polymer backbone, ion pair, ion pair content, and sample history have an effect on the characteristic features of the SAXS profile.

A better understanding of the ionomer morphology has resulted from the synthesis of model compounds, i.e., halato-telechelic polymers, which are linear chains selectively capped at both ends with an ionic group.[12-14,18-22] 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. The model recently proposed by Eisenberg et al. for the structure of ionomers fits much of the experimental data available for both ionomers and halato-telechelic polymers.[23] In this model, ionic groups phase separate with formation of small multiplets (containing less than 10 ionic groups), and intermultiplet interference is at the origin of the scattering maximum in the SAXS profiles. The mobility of chain segments directly attached to multiplets is restricted, which builds up a shell of "rigid" segments around the multiplets, the thickness of which would be approximately the persistence length of the chains. When the ionic content is high enough for the low-mobility regions to overlap each other (this might already happen below 5 mol % ions), there exist continuous regions of restricted mobility, 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. As far as the small-angle intensity upturn is concerned, its origin has been attributed to large-scale heterogeneities in the material, which have recently been related to the heterogeneous distribution of ion pairs by Cooper et al.[7,24] and MacKnight et al.[25,26] and to the liquid-like organization of the multiplets throughout the polymeric matrix.

It is, however, worth pointing out that evidence has been reported for a long-range organization in some halato-telechelic polymers, particularly for a polymeric backbone of a large cross section such as poly(*tert*-butyl acrylate).[13,14,27,28] Furthermore, Duplessix and Jalal[29] have investigated solutions of ω-barium carboxylato polystyrene in toluene at 25 °C by SAXS. According to these authors, semitelechelic polymers would be better models for ionomers than the parent telechelics (α,ω-functional). Indeed, when there is only one ion pair per chain, ion pair association is no longer perturbed by the formation of a three-dimensional polymer network, as occurs in ionomers and halato-telechelic polymers. Thus, in the absence of gelation, Duplessix and Jalal have reported for the first time a hexagonal-type of supramolecular structure in solution. There is accordingly a strong incentive to know whether that behavior is general, particularly in relation to the structure of the ion pairs. This is why ω- and α,ω-metal sulfonato polystyrenes have been synthesized and

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their solutions in toluene have been analyzed by SAXS in this paper.

Experimental Section

Synthesis. ω- and α,ω-sulfonato polystyrenes were synthesized by living anionic polymerization of styrene, as reported elsewhere.[29,30] The end functionalization of the living chains was carried out according to the slightly modified Quirk procedure.[31] The living chains were first capped with 1,1-diphenylethylene, before being deactivated with a twofold molar excess of freshly distilled 1,3-propanesultone. The functionality was systematically better than 95%, 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 the functionalization step. 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. The 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 compounds could be detected in the distillate by gas chromatography and/or potentiometric titration. The solvent was finally removed by distillation and the polymer was dried at 160 °C under vacuum for 16 h.

Unless otherwise stated, solutions were prepared by dissolving a weighed amount of polymer in a precise amount of toluene (analytical grade) in tight flasks with stirring for 1 week at 25 °C. This procedure will be designated as the "swelling method" in the next section. Clearly, solutions have not been prepared in a previously dried solvent. Nevertheless, for the sake of comparison, some samples were prepared according to a second method, referred to as the "concentration method". The sulfonic acid terminated polymer was neutralized as explained before, and the final solution, free from any polar compound, was concentrated until the required concentration. The solution in toluene was kept under nitrogen for 1 week at room temperature. As a result, a dry solution was made available and the neutralized material was not previously annealed at 160 °C under vacuum as in the first method.

SAXS. Preliminary experiments were conducted at the Max-Planck-Institut für Polymerforschung (M.P.I.P.) at Mainz. Spectra were recorded under vacuum on a Kratky compact camera at the Cu Kα (1.54 Å) wavelength. The sample-to-detector distance was 23.9 cm. Quartz tubes (1 mm thick) were filled with the solution (short-term contact with the atmosphere) and sealed. The beam was 1 cm wide and 50 μm thick. A 256-channel linear detector (resolution 100 μm) collected the scattered intensity in the 0.03–0.5-nm^{-1} s range. Data were desmeared according to the Strobl procedure, and the absolute intensity was determined by the moving-slit technique. Due to the low intensity of the X-ray flux, only concentrated solutions (>40 wt %) of low molecular weight samples ($\bar{M}_n \le 7000$) were analyzed.

All other spectra were run at LURE (Orsay) on DCI D22 (λ = 1.381 Å) or D24 (λ = 1.608 Å) lines. The high X-ray flux of D24 was convenient for dilute solutions and high molecular weight polymers. The incident beam was always smaller than 1 mm^2, so that desmearing of the experimental data was not required. One-dimensional multichannel detectors were used (Xe–CH$_4$, resolution 200 μm on D22; Xe–CO$_2$, resolution 156 μm on D24). The sample-to-detector distance was adjusted to cover the s range from 0.02 to 0.38 nm^{-1} (86.1 cm on D22, 163 cm on D24). Special tight cells (ϕ 5 mm, 5 mm thickness) with Kapton windows were filled with solutions and pure toluene, respectively.

Data Analysis. Multiplets were assumed to be isolated and of negligible volume fraction (typically less than 1%), and Bragg's law ($d_{\text{Bragg}} = 1/s_{\max}$) was used to calculate the average center-to-center distance between multiplets. The average number of ion pairs per multiplet, $\bar{n}$, was approximated by simple space-filling calculations. On the basis of a model in which all the ion pairs were contained in multiplets organized according to a face-centered cubic lattice, $\bar{n}$ was related to d_{Bragg} as follows:

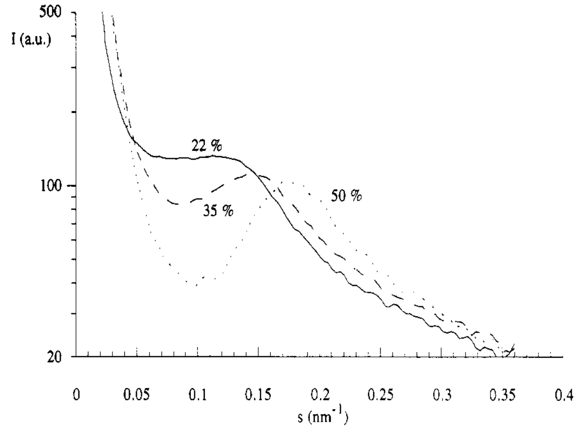

Figure 1. Effect of dilution on the SAXS profile of α,ω-barium sulfonato polystyrene (molecular weight 7000) in toluene.

$$\bar{n} = \frac{10^{-19}\rho N_A f C (d_{\text{Bragg}})^3}{2^{1/2}\bar{M}_n} \qquad (1)$$

where ρ is the polymer density (g/cm^3), N_A is the Avogadro number, C is the polymer concentration (vol %), f is the end functionality of the chains (either 1 or 2), and $\bar{M}_n$ is the number-average molecular weight. Since no ion pairs were assumed to be isolated in the polymer matrix, the calculated values of $\bar{n}$ should be upper estimates and used for comparison.

Results and Discussion

A series of ω-barium sulfonato polystyrenes of various molecular weights ($\bar{M}_n$ = 2800, 6400, 7700, 13 200, and 18 400) were synthesized, and their solutions in toluene were analyzed by SAXS over a large concentration range from 5 up to 60 vol %. The SAXS profiles for the bulk samples were also recorded. Figure 1 typically illustrates the effect of dilution on the SAXS profile. The scattering maximum is continuously shifted toward lower s values as the dilution is increased. Thus, when the solution contains more solvent, the average distance between the ionic multiplets increases. In a parallel way, the ionic peak is not well defined, because of increasing overlap with the small-angle intensity upturn and decreasing signal-to-noise ratio. Except for combinations of dilute solutions (C < 10 vol %) and high molecular weight polymers ($\bar{M}_n$ > 15 000), the position of the ionic peak is clear and the mean distance between multiplets is accurately calculated. When the peak is observed as a shoulder of the small-angle intensity upturn, a suitable s^{-2} decreasing function is subtracted, which allows analysis of the scattering maximum.

The Bragg distance depends on the polymer concentration according to the power law (Figure 2)

$$d = KC^{\alpha} \qquad \alpha = -0.33\ (\pm 0.02) \qquad (2)$$

independently of the molecular weight, at least in the investigated range. α has been calculated by a least squares fitting of at least five experimental data. As will be discussed later, the experimental value of α is in favor of an isotropic organization of the mutually interacting multiplets. On the basis of a simple model, according to which dilution pushes the multiplets away from each other while keeping unchanged the structure and space distribution, the same effect might be anticipated to result from an increase in molecular weight at a constant dilution. Figure 3 gives credence to that model, since the same power law as before (except for the sign) is reported for the dependence of d_{Bragg} on the polymer molecular weight at

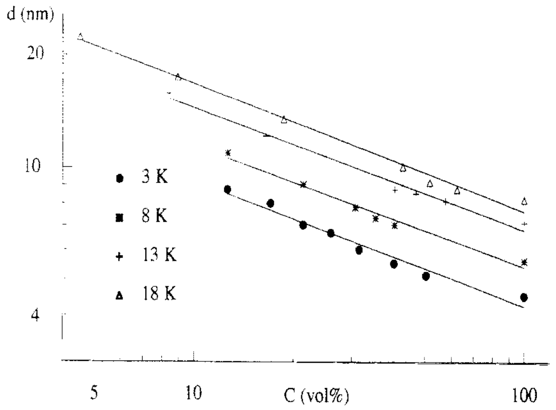

Figure 2. Effect of concentration on the average intermultiplet distance for ω-barium sulfonato polystyrene in toluene.

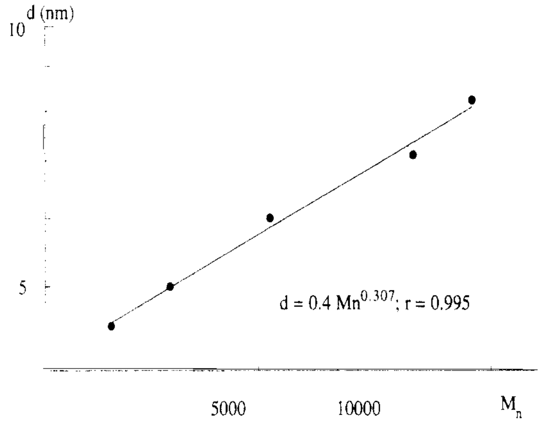

Figure 3. Effect of molecular weight on the average intermultiplet distance for ω-barium sulfonato polystyrene in bulk.

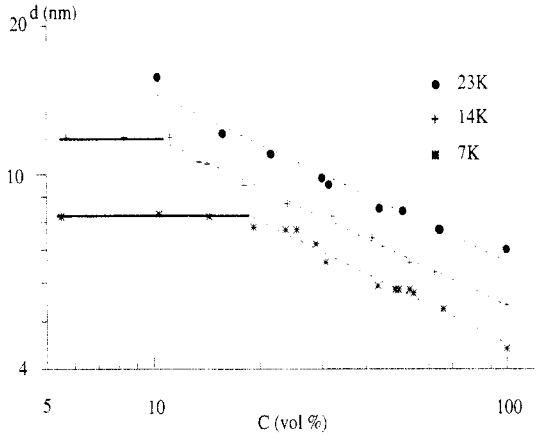

Figure 4. Effect of concentration on the average intermultiplet distance for α,ω-barium sulfonato polystyrene in toluene.

a constant concentration:

$$d = K'C^{\beta} \qquad \beta = 0.31\ (\pm 0.03) \tag{3}$$

It is thus clear that the general organization of ω-barium sulfonato polystyrenes in toluene remains unperturbed when the solution concentration or the chain length is changed.

Compared to ω-barium sulfonato polystyrenes, the solution behavior of the α,ω-functional counterparts shows a different distinct characteristic feature, as illustrated by Figure 4. Indeed, two concentration regimes are now clearly identified. At high concentrations ($C > 20$ vol %), a gel is formed and the average intermultiplet distance depends on concentration according to the same power law ($d = K''C^{\alpha}$, where $\alpha = -0.33 \pm 0.02$) as reported for the monofunctional samples. In contrast to ω-functional polystyrene, there is now a critical concentration which depends on the molecular weight and below which the Bragg distance is independent of dilution. This "plateau" extends to higher concentrations as the molecular weight of the polymer decreases. Conversely, the "plateau" can be unobserved when the chain length is exceedingly high, which does not necessarily mean that it has completely disappeared. The typical behavior of α,ω-barium sulfonato polystyrenes upon dilution suggests that, beyond a given degree of swelling, gels cannot accommodate more solvent and keep their phase morphology unchanged. In other words, a phase separation would occur into a gel phase and a toluene phase, although the samples appear to be homogeneous when observed with the naked eye.

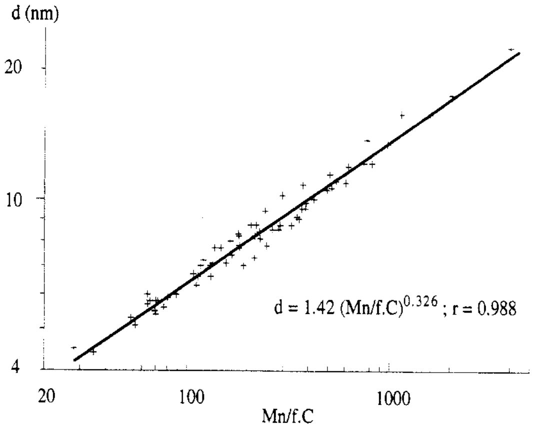

Figure 5. Average distance betweeen multiplets versus dilution for ω- and α,ω-barium sulfonato polystyrene in toluene.

Except for the concentration range in which the Bragg distance of the difunctional chains is constant, the experimental power laws from eqs 2 and 3 can be combined into a unique equation which describes the spatial organization of barium sulfonate dipoles attached to the extremities of polystyrene chains. This general law is as follows:

$$d = K_g\left(\frac{\bar{M}_n}{fC}\right)^{1/3} \tag{4}$$

where f is the end functionality (either 1 or 2) of polystyrene chains, C is the chain concentration (vol %) in toluene, $\bar{M}_n$ is the number-average molecular weight, and $(\bar{M}_n/f)$ is the $\bar{M}_n$ per ionic group. Figure 5 illustrates the validity of eq 4 for 65 experimental data points. It gives clear evidence that ω-functional chains are pertinent models for the space organization of the difunctional counterparts in solution, except for the "plateau" regime at high dilution.

Although it has often been disregarded, the effect of sample preparation on the final morphology and properties of ionomers has been pointed out by some authors.[2,9,10] It explains why some polymer solutions have been prepared according to two independent methods and investigated by SAXS. Dissolution has been carried out by the "concentration" and "swelling" methods described in the Experimental Section. Let us, however, point out that most of the solutions have been prepared by the "swelling" method and that the dissolution time might have an effect, particularly where gel-forming difunctional chains are concerned. To clear up that point, several equilibration times from 16 h (period of time required for getting a macroscopically homogeneous sample) up to 2 weeks have been considered. Figure 6 compares the SAXS profiles and shows that the equilibration time has no significant effect on the position of the scattering maximum. Thus, the experimental data which have been collected for a

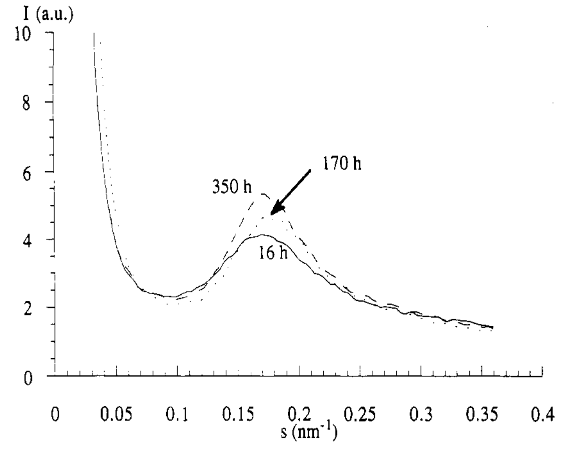

Figure 6. Influence of sample equilibration time on the SAXS profile of α,ω-barium sulfonato polystyrene (molecular weight 7000, 50 wt % in toluene).

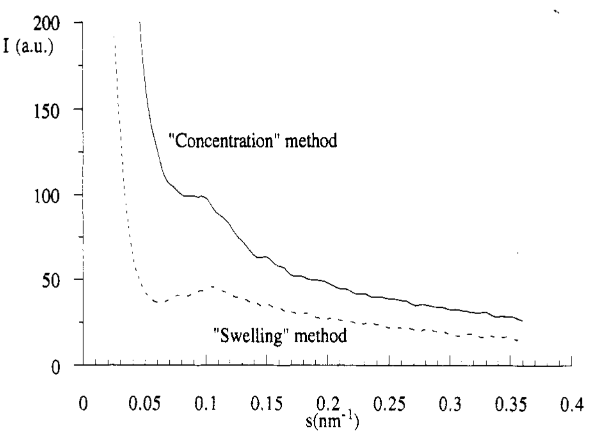

Figure 7. Influence of dissolution method on the SAXS profile of α,ω-barium sulfonato polystyrene (molecular weight 23 500, 35 wt % in toluene).

1-week equilibration period of time are quite reliable and cannot explain, for instance, the invariance of d_{Bragg} below a critical concentration for difunctional samples. Although Figure 6 shows that the peak position is independent of time, the shape of the SAXS profile does change upon increasing equilibration time. The peak becomes sharper and more intense, which indicates a narrower distribution of the intermultiplet distance. It is thus clear that increasing equilibration time has a favorable effect on the homogeneity of the space distribution of multiplets.

When solutions are prepared by the so-called "concentration" method, the position of the peak is in agreement with that reported by the "swelling" method. Nevertheless, Figure 7 shows that the peak is broader and the small-angle intensity upturn originates at a higher angle, whatever the equilibration time (up to 2 weeks). From this comparison, it is obvious that the "swelling" method gives rise to more homogeneous solutions and more uniform intermultiplet distances.

In agreement with previously published data,[9,13] substitution of barium by sodium and magnesium, all other conditions being the same, has no significant effect on the SAXS profile. Since the incoming beam intensity was not measured at LURE, the effect of cation substitution on the scattered intensity cannot be discussed in this paper.

The whole set of experimental data (d_{Bragg} dependence on concentration and sample preparation) reported in this paper has been tentatively rationalized by a simple model for polystyrene chains terminated with a barium sulfonate group. The $^1/_3$ exponent in the general dilution law indicates an isotropic phase morphology, since the swelling ratio is independent of direction. A $^1/_2$ exponent would have been expected in the case of a two-dimensional swelling (e.g., organization of the ion pairs in a rodlike structure). Finally, a lamellar morphology would give rise to a one-dimensional swelling with a characteristic exponent α close to 1.[29] From the $^1/_3$ exponent, it also comes out that the mean number of chains per multiplet must be independent of both the polymer concentration and molecular weight. Indeed, an increase in the size of the multiplets with concentration should result in an exponent becoming smaller than $^1/_3$.[23] Conversely, an exponent larger than $^1/_3$ could indicate an increase of the mean number of chains per multiplet upon decreasing concentration. The experimental observations are thus in complete agreement with a liquid-like arrangement of stable multiplets, as has been proposed previously for randomly sulfonated polystyrene.[6,26] On that basis, the effect of the sample preparation on the SAXS profiles could be explained as follows. Sulfonic acid terminated chains are neutralized in solution initially containing polar compounds, such as methanol and acetic acid, which limit the average aggregation degree to a few ion pairs. As the neutralization proceeds, these compounds are removed by the azeotropic distillation of the solvent and larger multiplets are formed, the size distribution of which is expected to be large. The ionic peak is accordingly broad and the small-angle intensity upturn important. Since the multiplets are stable, there is no opportunity for a significant ion pair redistribution versus time. This situation prevails when solutions are prepared by the "concentration" method. In contrast, in the "swelling" method, the solvent is completely removed and the neutralized polymer is annealed at 160 °C under vacuum. This thermal treatment 60 °C above T_g of polystyrene might allow an association–dissociation equilibrium to take place, together with a more homogeneous size distribution. On rapid cooling, the phase structure is frozen in, and it might be stable enough to persist in toluene at 25 °C. Nevertheless, for the 1-week equilibration time in solution, some changes in the composition and space arrangement of the multiplets might occur. Some isolated ion pairs, which did not associate during the fast cooling step, would have the opportunity to be incorporated into multiplets. Furthermore, traces of water in non previously dried toluene (analytical grade) might facilitate the ion pair redistribution between multiplets and lead to a more homogeneous solution as supported by a better resolution of the ionic peak.

Estimated values of the average size of the multiplets (see Experimental Section) are given in Figure 8, where the mean number of chains per multiplet has been plotted versus concentration of ω- and α,ω-barium sulfonato polystyrenes of various molecular weights in toluene. Figure 8 shows that the size of the multiplets is essentially independent of the solution concentration (at least in the investigated range) for each analyzed polymer. When ω- and α,ω-barium sulfonato polystyrenes of the same molecular weight are compared (6K and 7K di; 13K and 14K di), the end functionality of polystyrene chains clearly has no effect on the ion pair association. Finally, no clear-cut relationship emerges as far as chain length is concerned.

The main difference between ω- and α,ω-metal sulfonato polystyrenes is the independence of the intermultiplet distance on concentration exhibited by the difunctional chains in the dilute regime (Figure 3). This could be accounted for by a continous decrease of the multiplet size upon dilution, which would keep constant the average distance between neighbor multiplets (characteristic ex-

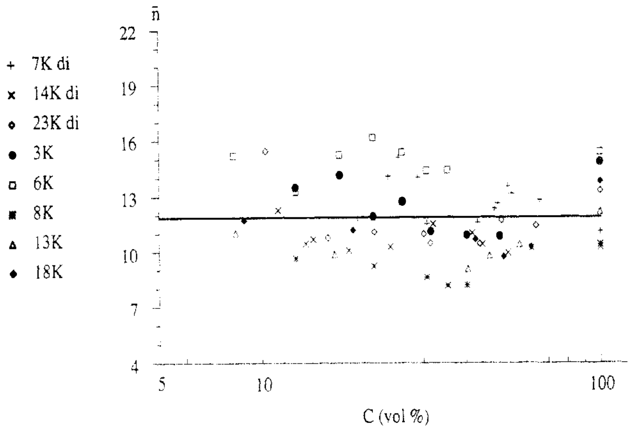

Figure 8. Mean number of chains per multiplet as a function of concentration for ω- and α,ω-barium sulfonato polystyrene in toluene (molecular weight is reported in thousands, and "di" refers to α,ω-functional polymers).

ponent $\alpha = 0$).[23] This explanation assumes that when the chains reach a critical extension in the gel state, multiplets are unable to withstand the mechanical strength associated with an upper swelling ratio. An alternate explanation might be that, beyond this critical swelling ratio, spinodal decomposition occurs, leading to a toluene-rich phase separated from a gel phase whose characteristic features would remain constant. However, the former explanation is more realistic, since a homogeneous solution of the α,ω-barium sulfonato polystyrene (no supernatant toluene) is formed in the highly dilute state (i.e., upon addition of analytical grade toluene). Whatever the explanation, the critical polymer concentration below which the plateau regime is observed (Figure 3) should correspond to a critical swelling ratio of the subchains interconnecting multiplets, as is supported by the comparison of the plateau distance with the theoretical average unperturbed end-to-end distance of the polystyrene chains.[33] For both 7K and 14K difunctional samples, a critical swelling ratio $\alpha = 1.5$ can be calculated in the plateau region. Of course, this problem is not relevant for monofunctional polymers, since the ion pair association does not engage the polystyrene chains in a tridimensional polymer network.

Depending on the authors, the small-angle intensity upturn has been attributed to either large-scale heterogeneities in the multiplet distribution[13,32] or isolated ion pairs distributed throughout the polymeric matrix.[7] If the second hypothesis is correct, the loose chain ends should be mobile enough in solution to be incorporated into existing multiplets. Since the small-angle upturn does not decrease markedly upon increasing equilibration time, it more likely originates from large-scale heterogeneities associated with the multiplet space distribution.

Conclusions

SAXS studies of solutions of ω- and α,ω-barium sulfonato polystyrenes in toluene have concluded that ion pairs associate into stable multiplets participating in an isotropic multiphase system. There is no structural discontinuity from the bulk state to solution. The same conclusion holds when mono- and difunctional samples are compared. The nature of the cation has no significant effect on the SAXS profile. As long as the intermultiplet distance increases upon dilution, the average number of chains per multiplet appears to be constant. A general law has been derived for the average intermultiplet distance as a function of the polymer concentration, molecular weight, and functionality. This relationship is not valid for α,ω-functional chains beyond the dilution at which the swelling ratio reaches a critical value of 1.5; partial multiplet dissociation would then occur upon further dilution and account for a constant intermultiplet distance.

The small-angle upturn in the scattered intensity has been attributed to large-scale heterogeneities in the space distribution of multiplets throughout the solution. This characteristic feature in combination with the stability of the metal sulfonate multiplets allows understanding of the dependence of the SAXS profile on the solution preparation mode and the thermal history of the sulfonato-telechelic polymer.

The formation of approximately isotropic multiplets by metal sulfonate ion pairs is in sharp contrast to the results published by Duplessix and Jalal, consistent with the association of metal carboxylates into rodlike structures.[29]

A more complete characterization of solutions of monofunctional sulfonated polystyrene by viscosimetry and light scattering is in progress and will be reported in a forthcoming paper.

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