and thus reported the value of the first transition in their diagram). One should recognize that a whole family of plots with higher $T_{c\to n}$ are possible for "blocky" or "alternating ordered" systems.

Conclusions

Poly(HNA) has been characterized and shown to display crystal morphologies and thermal transitions almost identical with those reported for poly(HBA). This represents the second example of formation of single-crystal polymer morphologies starting with solution polycondensation. In analogy to poly(HBA), the first transition at 338 °C can be described as a plastic crystal or highly ordered smectic transition.[17,19] The argument in support of a highly ordered smectic structure requires a symmetry which permits retention of single-crystal morphology on cooling.[17] Since we have been unable to identify examples where any smectics (polymer or nonpolymeric) display this kind of behavior, we lean toward the concept of a one-dimensional plastic crystal where the naphthylene units have rotational freedom and the ester units, while having some motional freedom, still provide a three-dimensional framework.

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Single-Chain Dimensions in Semidilute Ionomer Solutions: Small-Angle Neutron Scattering Study

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ABSTRACT: Small-angle neutron scattering has been used to measure individual chain dimensions in aggregates in ionomer solutions. Lightly sulfonated polystyrene was studied over a range of ionic substitutions and polymer concentrations in tetrahydrofuran. The molecular dimensions are compared with macroscopic solution viscosity measurements. Despite clear evidence in the viscosity data of interchain aggregation occurring at higher concentrations, the individual polymer chains preserve relatively constant dimension over the whole concentration range. In the free acid ionomer the interactions are not sufficiently strong to cause intermolecular aggregation and the individual chain dimensions are simply proportional to ionic content. These results clarify the role of interaction strength in associating polymer systems.

Introduction

Associating polymer systems are known to assemble into aggregates at relatively low concentrations in appropriate solvents. When this assembly is driven by strong interactions between randomly located sites along the chain, as in the case of ionomer solutions, the resulting aggregate can be thought of as a microgel particle. Within such a particle, the polymer concentrations is locally semidilute and so the chain conformation must be governed by a balance between screening effects and strong site-specific interactions. It is therefore clearly of interest to determine the individual chain conformation within ionomer solutions over a range of compositions and concentrations.

Ionomers are a class of mainly linear hydrocarbon polymers containing up to 10 mol % salt groups which are usually randomly distributed along the chains. They have

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attracted considerable attention in recent years, mainly because their physical properties differ markedly from those of similar unmodified hydrocarbon polymers. Their applications in the bulk—for example, as selective membranes—are the subject of extensive literature.[1-3] In solution the main application has been as viscosity modifiers. Their unusual viscosity behavior arises from interactions of the ionic groups and hence is very dependent on the polarity of the solvent.[4-7] In a nonionizing solvent such as tetrahydrofuran (THF), the observed reduced viscosity lies below that of the parent polymer for solution concentrations up to a concentration c', which is of the order of a few grams per deciliter and subsequently increases very sharply (c' depends markedly on the level of ionic substitution). This phenomenon had been interpreted on the basis of interactions between ion pairs. Above c', intermolecular interactions were thought to dominate, leading to gel formation, while below c' intramolecular interactions were proposed to cause chain collapse. However, at any given concentration, a balance between these two effects would be anticipated. The coexistence of inter- and intrachain interactions is supported by recent light-scattering[8,9] and small-angle neutron-scattering (SANS)[10] experiments which demonstrate the existence of large aggregates even at concentrations well below c'. SANS is a particularly useful tool for such studies because it allows investigation of both the aggregate dimensions and the single-chain conformation within an aggregate. The retrieval of single-chain information from a locally semidilute environment is made possible by exploiting the difference in coherent neutron scattering lengths of hydrogen and deuterium. This neutron scattering length determines the contrast between different regions of the sample in the same way as refractive index does in light scattering. Thus a deuterated molecule surrounded by hydrogenous ones is visible to the neutron experiment. In the experiments reported here, a mixture of deuterated and hydrogenous ionomers was prepared in a solvent (THF) which was also an h–d mixture. In the solvent the ratio of hydrogen to deuterium was chosen such that the *average* scattering length density in the solvent matched the *average* scattering length density among the polymers. There was thus no contrast between whole aggregates and the solvent and they were "invisible" to the experiment. On the other hand, there was contrast between hydrogenous and deuterated polymer molecules within the aggregates, so that a signal characteristic of their shape and size was obtained.

In the earlier work[10] it was found that there was very little perturbation of the ionomer molecular dimensions from those of the unmodified parent polymer in the same solvent. The data were available only for one level of substitution and for one counterion (sodium). We now report a more systematic investigation of the effect of the degree of substitution and of the cation type.

As in the previous study the samples are lightly sulfonated polystyrenes of about 100 000 molecular weight. These serve as a good model for associating systems and, being based on polystyrene, are available with well-controlled molecular weights and microstructures.

Experimental Section

Materials. Anionically polymerized polystyrene was purchased from Polymer Laboratories Ltd. The molecular weight of the polymer was 105 300 g mol^{-1} for the hydrogenated polymer and 108 000 g mol^{-1} for the perdeuterio polystyrene component as determined by gel permeation chromatography. A typical preparation of the free acid sulfonated polystyrene (H-SPS) is given below. Polystyrene (15 g: 12.0 g of polystyrene, H-PS, and 3.0 g of perdeutero polystyrene, D-PS) was dissolved in 150 mL of 1,2-dichloroethane (1,2-DCE) at 25 °C, giving a polymer concentration of 10.0 g/dL. The solution was then heated to 50 °C and the appropriate amount of acetyl sulfate was added, in this instance 0.40 mL of acetic anhydride and 0.30 mL of concentrated sulfuric acid. The solution was continuously stirred for 60 min at 50 °C and the reaction terminated with the addition of a mixture of 10.0 mL of methanol and 0.8 mL of water. It is noted that the free acid copolymer is completely soluble in 1,2-DCE. The polymer was subsequently filtered and the acid copolymer isolated by steam stripping, typically after 1 h had elapsed. The steam stripping procedure lasts 60 min. The sulfonated polymer was vacuum-dried for 24–48 h at 100 °C. Sulfur content was determined by Dietert sulfur analysis and was used to calculate the sulfonation level. In this specific procedure the sulfonate content was 1.0 mol % (0.31 wt % sulfur).

Table I
Scattering Lengths and Densities

material	density, g/cm^3	scattering length per monomer, fm	scattering length density, nm^{-2}
H-PS	1.07	23.3	0.144×10^{-3}
D-PS	1.15	106.6	0.659×10^{-3}
THF	1.07	2.48	0.022×10^{-3}
D-THF	1.19	85.8	0.768×10^{-3}
THF/D-THF (2:1 by vol)	1.10		0.271×10^{-3}
H-PS/D-PS (8:2 by wt)	1.09		0.232×10^{-3}

A portion of the free acid powder was subsequently neutralized to form the sodium and zinc sulfonate salts. This procedure was utilized in order to ensure that the sulfonation level remained invariant and only the counterion structure was varied. A typical neutralization scheme is described below. Sulfonated free acid, 5 g, was dissolved in 95 mL of 1,2-DCE at 25 °C, giving a polymer concentration of 5.3 g/dL. The solution was continuously stirred for 60 min at 50 °C and the neutralization accomplished with the addition of 0.5 g of sodium acetate dissolved in a mixture of 5.0 mL of methanol and 1.0 mL of water. Again the polymer was filtered and the sodium-neutralized polymer isolated by steam stripping as previously described.

THF solutions containing these ionomers were prepared at room temperature with a conventional magnetic stirring apparatus. In all instances clear solutions were obtained in 15–60 min, depending on the sulfonation level. The specific solvent compositions are presented in Table I. The solvent was a mixture of deuterated and protonated THF chosen to match the average neutron-scattering length of the mixture of the protonated and deuterated polymer. Solutions in the concentration range 0.5–3.0 g/dL were prepared from ionomers of 1.0–4.0 mol % S as well as the unmodified polystyrene. The acid, sodium and zinc forms of the ionomers were studied.

Measurements. Neutron-scattering experiments were carried out using the D17 small-angle spectrometer at the ILL, Grenoble, which is equipped with a two-dimensional position-sensitive detector.[11] A sample–detector distance of 3.46 m and wavelength of 15 Å were used to give a range of scattering vectors between 0.006 and 0.08 Å^{-1}. The samples were measured in 1-mm path length quartz cells at a temperature of 25 °C. After radial averaging, the data were corrected for background scattering of cells and solvent, normalized for detector efficiency and converted to absolute units with the scattering from a 1-mm water sample as a reference.[12] The resulting data represent the coherent scattered intensity from single polymer molecules in the semidilute solution of protonated and deuterated polymer molecules and solvent, together with a small component due to the incoherent scattering of the polymer, which is essentially flat.

SANS measurements were made on the 4 mol % Na and Zn ionomers, on the 1 mol % Zn ionomer, and on polystyrene all at four concentrations between 0.5 and 3 g/dL. Selected measurements were made on the free acid and other ionomers at 1 and 3.4 mol % sulfonation.

Solution viscosities were measured with a standard Ubbelohde capillary viscometer in a temperature-controlled water bath at 25 °C. The solutions were temperature equilibrated for approximately 20 min prior to viscosity measurement. The measurements were repeated to ensure reproducible flow times. The data are presented as reduced viscosity $\eta_{red} = (\eta - \eta_0)/(\eta_0 c)$, where η_0 is the solvent viscosity and η is the viscosity of a solution with concentration c.

Data Analysis. The intensity $I(\mathbf{q})$ due to the coherent scattering from a solution containing both deuterated and hydrogenous polymer molecules can be written as

$$I(\mathbf{q}) = KMcN_A/m_0^2[(b_H - b_D)^2(1 - x)S_s(\mathbf{q}) + (b_p - b_s^*)^2S_t(\mathbf{q})] \quad (1)$$

where the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$. Here λ is the incident neutron wavelength and θ is the angle of scatter. In the above expression N_A is Avogadro's number, c is the total polymer concentration in g/mL, M is the polymer molecular weight, and m_0 is the molecular weight of the polymer. The constant K can be calculated from the intensity of scattering from a water sample and the known water scattering cross section. $S_s(\mathbf{q})$ and $S_t(\mathbf{q})$ are the single chain and total scattering functions, related by the following relationship:

$$S_t(\mathbf{q}) = S_s(\mathbf{q}) + S_p(\mathbf{q}) \quad (2)$$

where $S_p(\mathbf{q})$ is the pair scattering function. The scattering lengths b_H and b_D refer to the hydrogenous and deuterated monomers, b_s^* is the scattering from the solvent corrected for the difference between the volume of a solvent molecule and the volume of a monomer unit in the polymer, and b_p is the average scattering length of the polymer. The mole fraction of deuterated polymer is denoted by x.

In previous experiments[10] two different h/d ratios at identical polymer concentrations were measured in deuterated THF, giving two expressions for eq 1, which could be solved to give the single-chain scattering $S_s(\mathbf{q})$. In this paper we have taken a simpler approach by arranging that $b_p = b_s^*$ by using an appropriate mixture of deuterated and hydrogenous THF. These mixed-labeling techniques are applicable to a wide range of polymer solutions and concentrations and corrections necessary for model fitting can be found in papers by Ullman et al.[13,14]

The single-chain scattering from a Gaussian polymer chain is given by the Debye function[15]

$$S_s(\mathbf{q}) = 2/u^2[\exp(-u) - 1 + u] \quad (3)$$

where $u = q^2R_g^2$ and R_g is the radius of gyration of the scattering molecule.

For $qR_g < 1$ this may be reduced to

$$S_s(\mathbf{q}) = 1/(1 + q^2R_g^2/3) \quad (4)$$

Therefore for contrast-matched solutions in which $b_p = b_s^*$, eq 1 becomes

$$AKc/I(q) = 1/M[1 + q^2R_g^2/3] \quad (5)$$

This equation is often termed the Zimm expression where the virial coefficient term ($2A_2c$) has been truncated. This term would usually have arisen from the pair scattering function $S_p(\mathbf{q})$, which is removed by the contrast-match condition. For $qR_g > 1$, eq 5 can still be used to determine the molecular weight and radius of gyration with appropriate correction factors calculated by Ullman.[16]

Results

The results of a series of solution viscosity measurements are shown in Figure 1. Upon comparison of the unmodified polystyrene with the various ionomer materials, it is seen that the sodium and zinc salts act as associating species. Aggregation is evidenced by the rapid increase in viscosity with concentration. By contrast, the free acid and unmodified polystyrene do not exhibit unusual viscosity concentration profiles. This implies that, as anticipated, the parent polystyrene does not aggregate under these conditions. These solution viscosity results are in complete agreement with earlier measurements.[8,9]

Contrast-matched solutions of these ionomers have been measured by SANS throughout the same concentration range. Additional materials with different numbers and species of ions have been measured as well. Typical Zimm plots and the resulting molecular parameters are shown in Figures 2–5 and Table II. In each case, linear plots were obtained and the process of ref 16 was used to correct for the appropriate limited angular range. For comparison, we have also fitted the Debye function[15] to the data. This Fourier transform of a Gaussian segment density distribution has the form of eq 3 and is heavily influenced by uncertainty at low q. As a consequence, the lowest concentrations (0.5 g/dL) were not analyzed in this way. At all other concentrations, the statistics of the low-q data were sufficient to use the Debye function and comparisons are made with the corrected Zimm analyses. A typical Debye fit is shown in Figure 6.

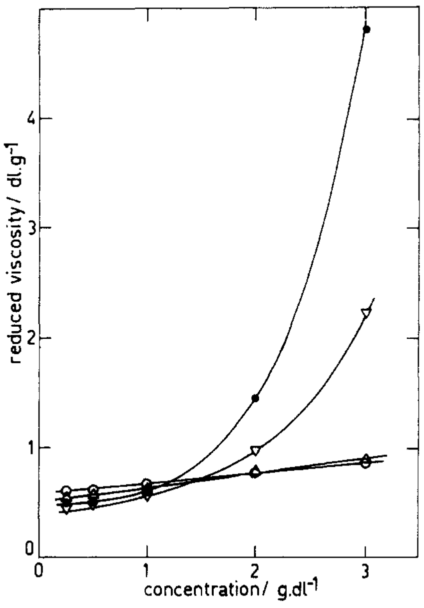

Figure 1. Concentration dependence of the reduced viscosity of polystyrene and sulfonated polystyrene (4.0 mol % S) in THF: (○) PS; (△) acid; (●) Na; (▽) Zn.

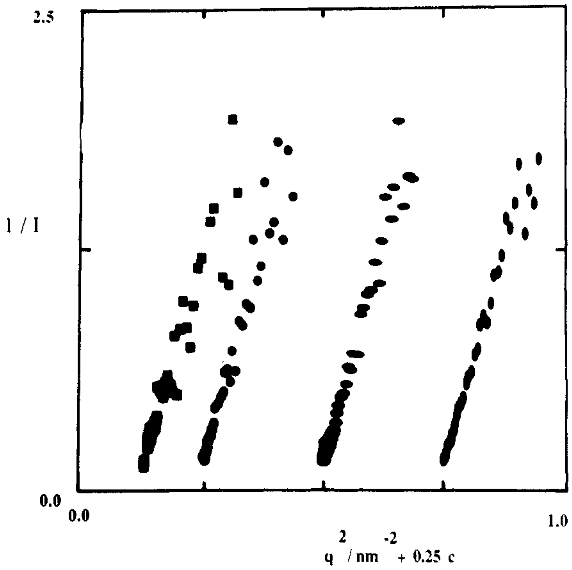

Figure 2. Zimm plot for the mixture of the protonated/deuterated (80:20) PS in a mixture of protonated/deuterated (2:1) THF. T = 25 °C, the concentrations used are (■) 0.5, (●) 1.0, (●) 2.0, and (●) 3.0 g/dL.

Discussion

First we consider the results for the unmodified polystyrene listed in Table II. As is immediately apparent, a constant molecular weight is obtained at all concentrations.

Table II
Single-Chain Parameters for Sulfonated PS Ionomers in THF[a]

sample	concn, g/dL	molec wt, g/mol	R_g, nm (Zimm)	R_g, nm (Zimm, corr)	R_g, nm (Debye)
PS	0.5	107000	13.9 ± 1.7	11.3	
	1.0	104000	13.7 ± 0.7	11.1	11.6
	2.0	105000	13.8 ± 0.5	11.2	11.4
	3.0	102000	13.0 ± 0.4	10.6	10.8
sodium salts					
1 mol %	3.0	100000	14.8 ± 0.5	12.0	11.3
3.4 mol %	2.0	100000	14.4 ± 0.6	11.7	11.4
	3.0	96000	13.3 ± 0.3	10.8	10.8
4 mol %	0.5	100000	13.1 ± 1.0	10.7	
	1.0	100000	12.6 ± 0.4	10.2	11.8
	2.0	107000	13.3 ± 0.4	10.8	11.0
	3.0	107000	13.4 ± 0.4	10.9	10.7
zinc salts					
1 mol %	0.5	100000	14.3 ± 1.2	11.6	
	1.0	107000	17.0 ± 2.1	13.8	10.9
	2.0	88000	13.1 ± 1.7	10.7	11.6
	3.0	100000	15.1 ± 0.7	12.3	11.6
3.4 mol %	2.0	97000	13.8 ± 1.6	11.2	10.9
	3.0	102000	13.6 ± 2.0	11.1	10.7
4 mol %	0.5	76000	13.9 ± 1.7	11.3	
	1.0	85000	14.9 ± 1.0	12.1	13.8
	2.0	141000	15.4 ± 0.6	12.5	11.1
	3.0	107000	14.7 ± 0.4	12.0	11.0
free acid					
1 mol %	3.0	105000	14.2 ± 0.4	11.5	11.6
3.4 mol %	3.0	105000	15.2 ± 0.4	12.4	11.8
4 mol %	3.0	105000	15.6 ± 0.6	12.7	12.6

[a] Zimm fits are done typically in the range $1 < qR_g < 3$; for Debye fits $0.13 < q < 0.45$ nm^{-1}. Errors on the Debye values and molecular weights are estimated to be ±10%.

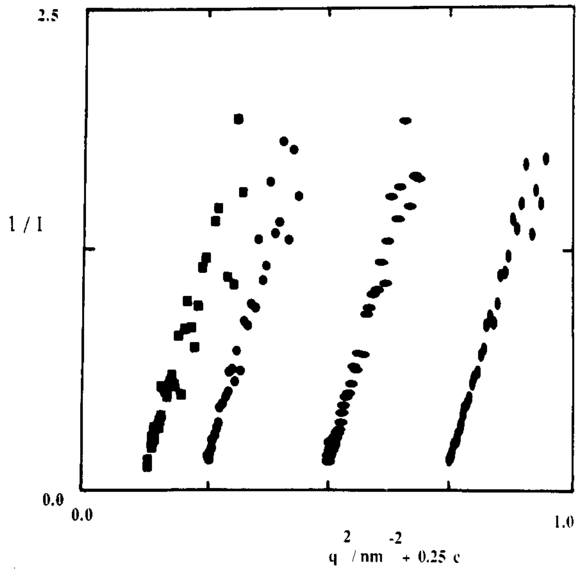

Figure 3. Zimm plot for the contrast-matched sodium sulfonated PS with 4 mol % degree of sulfonation. The proton/deuterium ratios for the polymer and solvent and concentrations are as in Figure 1.

This verifies the separation of purely single-chain information and the absence of second virial coefficient effects. By use of materials of narrow molecular weight distribution, the results are free of any complications due to polydispersity. The measured radius of gyration for polystyrene is found to decrease very slightly with increasing concentration, in agreement with King et al.[13]

The constancy of single-chain molecular weight is observed also for the ionomers. If we consider for example the sodium salt of 4.0 mol % sulfonated polystyrene, a constant radius of gyration is observed over the concentration range 0.5–3.0 g/dL. This is an excellent agreement with earlier SANS measurements.[10] At any given concentration, the measured single-chain radius of gyration will represent the average dimension of all the species present in the solution. Presumably, a larger population of chains will be intramolecularly associated at low concentrations and intermolecularly associated at higher concentrations. The results indicate that either the transition from predominantly intramolecular association to predominantly intermolecular association is not accompanied by large changes in the average radius of gyration or at these concentrations very little intramolecular association occurs. As shown previously,[10] the average single-chain dimensions remain relatively constant during the aggregation process in this system over the concentration range studied.

It should be recalled that the radius of gyration is not, a priori, a measure of the effective hydrodynamic radius of a polymer molecule. Presumably, a single intramolecularly associated ionomer coil will have significantly different draining properties than a single unmodified polystyrene coil, yet the two radii of gyration need not be different. It is therefore not inconsistent to obtain comparable values of R_g for the two species at 0.5 g/dL even though they exhibit significantly different solution viscosities at this concentration.

Interestingly, a comparable radius of gyration is found for both sodium and zinc salts. Both the Na and Zn ionomers show a remarkable constancy of single chain R_g over the full range of sulfonation level and concentrations studied. This is perhaps remarkable in that the zinc ionomer shows a great deal of aggregation even to the extent of solutions appearing turbid. There is some signal from the aggregates seen in the scattering pattern (Figure 6). The excess scattering above the Debye model observed at small angles can be explained (if aggregates are present) by the slight deviation from contrast match. In Figure 6a a fit in a q range 0.08–0.4 nm^{-1} shows systematic deviations from the simple Debye functions. When fits are constrained to the range 0.13–0.45 nm^{-1}, a good fit is obtained except for the smallest angles at high concentrations. For this reason all fits of the Debye model were made only at

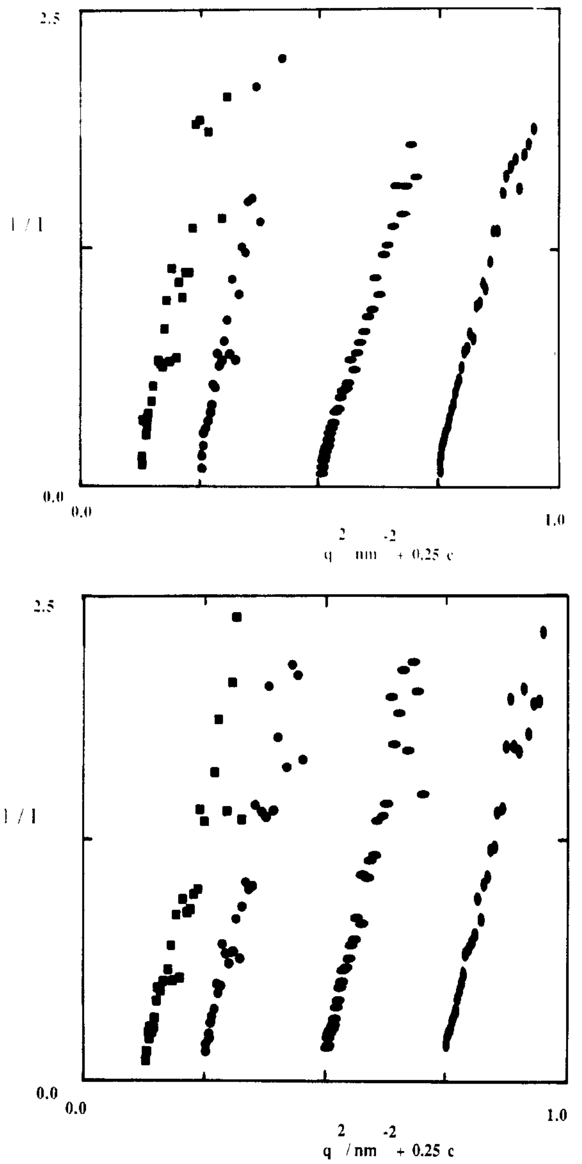

Figure 4. Zimm plot for (top) 4 mol % and (bottom) 1 mol % sulfonated zinc ionomer. All parameters are as in previous figures.

large values of the scattering vector where the scattering from aggregates is small and gives good agreement with the simple Zimm fits. The results for sodium confirm the previous work.[10] Our measurements on zinc are new and noteworthy in that no large change in the molecular dimensions are seen despite intermolecular interactions causing aggregation.

If we consider the remainder of the sodium salt solutions in Table II, it can be seen that the average single-chain dimensions are insensitive to ionic content throughout the reported range. Surprisingly, the same behavior is also observed for the zinc salt even though zinc is quite different from sodium. Given that the ionic interactions are sufficiently strong and site specific, the single-chain dimensions appear to be largely determined by the volume swept out by the hydrocarbon sections between interacting sites. This is sensitive to solvent quality but relatively insensitive to the geometry and valency of the ionic sites. The free acid provides an interesting contrast. In this case, the interactions are not sufficiently strong to cause microgel formation. This is evident from Figure 1 where there is no upturn in solution viscosity with increasing concentration. Rather than strong dipole–dipole interactions, the acid is anticipated to exhibit extensive hydrogen bonding to the solvent.[17] As a result, a gradual increase in single-chain dimension would be expected with increasing ionic content simply as a result of steric exclusion of the bulky pendant acid–solvent structures. This is precisely what is observed in the R_g values reported in Table II and is seen in Figure 5. When comparisons are made between solutions of fixed polymer concentration but increasing acid content, a gradual increase in R_g occurs, which is directly proportional to the chain sulfonation.

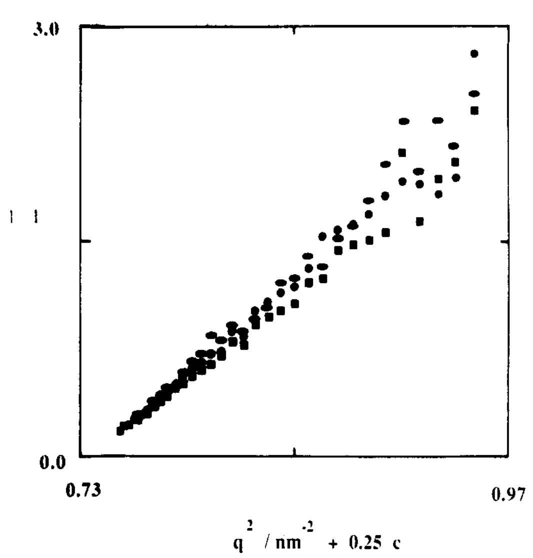

Figure 5. I^{-1} versus q^2 plot for a series of free acid samples with (■) 1, (●) 3.4, and (●) 4 mol % degree of sulfonation. All samples in a mixture of protonated/deuterated (2:1) THF at concentration of 3 g/dL.

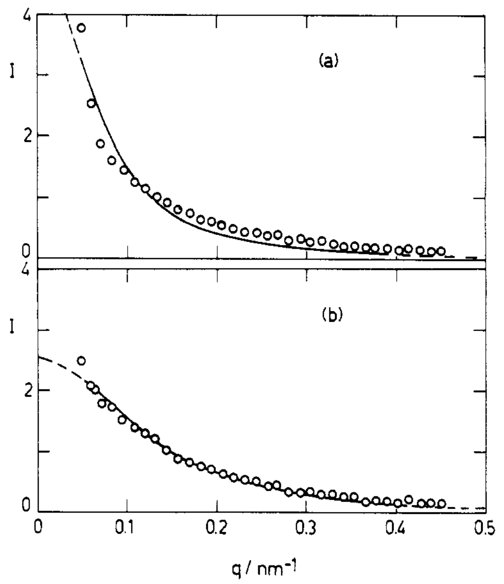

Figure 6. Comparison of experimental data and Debye predictions for (a) zinc sulfonate (4.0 mol % S) polystyrene in tetrahydrofuran and (b) sodium sulfonate (4.0 mol % S) polystyrene in THF. Both concentrations are 3.0 g/dL.

Summary and Conclusions

The reported measurements provide data on the single-chain conformation of ionomers in semidilute solutions of tetrahydrofuran; sulfonated polystyrene ionomers are known to assemble as aggregates due to the strong interaction between the ionic sites that are located randomly along the chain. Our technique of adjusting the average contrast of the solvent to that of the mixture of deuterated and protonated polymer allows us to observe the scattering only from single chains although these can be assembled as aggregates. The constancy of the molecular weight values that are presented in Table II establishes the validity of the contrast-matching technique and verifies the earlier similar measurements on sodium salts.[10]

The most significant feature of the results is that the radius of gyration is remarkably constant. Only small variation in comparison to the statistical error is observed over the entire range of degree of sulfonation, concentration, and counterion that has been studied in these experiments. This may be contrasted with the knowledge that neutron and light scattering shows these ionomers to form aggregates in this range of concentration and that the viscosity data in Figure 1 show a clear change from depression of viscosity of augmented viscosity that has hitherto been associated with the transition from a collapsed intramolecular association of ionic groups at low concentrations to intermolecular association at higher concentrations.

The free acid ionomer does not associate strongly in tetrahydrofuran; a small but significant trend of expansion with increasing ionic strength is observed in these measurements. This systematic variation is perhaps best attributed to steric effects of solvated acid groups and is consistent with the results of preliminary light-scattering experiments.

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Effects of Internal Plasticization on Ion Aggregation in a Styrene Ionomer

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ABSTRACT: A copolymer of styrene with 7 mol % methacrylic acid was alkylated with 1-decene in a Friedel–Crafts-type reaction. Both glass transition temperatures associated with the matrix and with the clusters were shifted to lower temperatures with increasing alkylation, and the modulus at the rubberlike inflection point dropped by over an order of magnitude. It was shown that ion clustering was enhanced at alkylation levels of up to ca. 20 mol %, compared with the parent ionomer. At higher degrees of alkylation, however, the alkyl chains strongly disrupted the ionic association. Even though some clustering effects were still observed in the loss tangent–temperature curves, the large drop in the rubberlike modulus showed that the influence of the clusters on the rheological properties of the polymer was not significant.

Introduction

For over 2 decades, the field of ion-containing polymers has been an area of growing interest. This is demonstrated by a number of books,[1,2] reviews,[3] and recent symposia[4] on the topic, as well as by the increasing number of ionomers available commercially, with their many current and potential applications.[5] The interest in these materials is justified by the sometimes drastic changes observed in the bulk properties of the polymers, as a consequence of the introduction of low concentrations (up to ca. 15 mol %) of ionic units. The modifications in the properties of anionic materials may be explained on the basis of phase separation,[6] whereby the ions tend to aggregate to form ion-rich regions in the polymer matrix. The existence of two types of aggregates, namely multiplets and clusters, has been proposed.[7]

The behavior of cationomers, however, is very different from that of anionic materials: previous studies on polystyrene-based *N*-alkyl-4-vinylpyridinium halide systems have shown no evidence of clustering;[8] nevertheless, earlier studies on polybutadiene-based cationomers do show some characteristics of clustered systems at comparable ionic concentrations.[9] Butyl acrylate and plasticized ethyl acrylate cationomers also show similar effects.[10]

The differences observed in anionic systems compared with cationic systems of similar structure illustrate one of the many structural factors known to affect ion aggregation, namely, in this case, the type of ion used. Some of the other factors involved are the placement of the ions

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