Block Copolymer Ionomers: Solution Behavior of Lightly Sulfonated Polystyrene-*b*-Poly(*tert*-butylstyrene) in Polar Solvent

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ABSTRACT: Light scattering experiments were performed to study the structure and dynamics of block copolymer ionomers in polar solvent. Two lightly sulfonated polystyrene-*b*-poly(*tert*-butylstyrene) copolymers in the sodium form with a sulfonation level of 5.8 and 12.0 mol % dissolved in *N*,*N*-dimethylacetamide were studied at 25, 45, and 60 °C in the dilute-solution regime. A polyelectrolyte-like solution behavior was observed. Due to the repulsive electrostatic interactions between like charges, the scattered intensities monitored were greatly reduced as compared with those of the unmodified diblock copolymer. In particular, a characteristic bimodal relaxation mode was observed on block ionomer solutions in strong contrast to the single-exponential decay found for the parent (neutral) copolymer solutions. Both the free-particle diffusion coefficient and the macroscopic self-diffusion coefficient as a function of temperature and concentration were determined and discussed. It seems that at 45 and 60 °C charged monomolecular micelles are formed, whereas charged polymolecular aggregates would exist at room temperature arising from the delicate balance between the aggregation tendency and the solvent affinity.

Introduction

It is well established that, in analogy to conventional surfactants, block copolymers exhibiting amphiphilic nature can self-assemble into organized structures in various selective solvents.[1,2] For a given polymer the solvent quality can often be altered by changing the temperature when using a single solvent or by adjusting the solvent composition when using a mixed solvent. Thus, in many cases the dynamic equilibrium between the polymeric micelles and the molecularly dispersed chains, the aggregation number, and the micellar size can be manipulated by means of temperature control. For example, in recent years a number of studies[3–6] have been concentrated on the temperature-induced micelle formation in dilute solution as well as the temperature-induced gelation behavior in concentrated systems for block copolymers of the poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene) (PEO–PPO–PEO) type in aqueous solution. In addition, for this class of block copolymers water-induced association into polymeric reverse micelles has lately been reported.[7]

Ionomers are a class of ion-containing polymers, consisting of linear hydrocarbon chains, to which a small number of ionic groups (usually up to 10 mol %) are chemically bound. These salt groups are randomly distributed along the backbone and interact strongly with one another. Their solution properties are greatly dependent on the polarity of the solvent.[8–11] In solvents of high polarity, due to the dissociation of ionic groups a solution behavior characteristic of polyelectrolytes is observed. In nonpolar solvents the salt groups exist as contact ion pairs, resulting in associating polymer behavior.

As a part of our fundamental work on block copolymers, we have chosen diblock copolymers of styrene and *tert*-butylstyrene as model systems to investigate their reversible aggregation behavior in both the solution state and the bulk state. The reasons for making such a choice are as follows: (1) polystyrene-*b*-poly(*tert*-butylstyrene) (PS-*b*-P(*t*-BS)) samples with well-defined composition and controlled block length are available on a laboratory scale and are nearly monodisperse, (2) the two polymer components are similar to each other in their chemical structure, and more importantly, (3) the copolymer properties can be modified by introducing some functional groups to meet the specific purposes. For instance, block ionomers, i.e., ion-containing block copolymers of low ionic content, can be prepared, say, by controlled sulfonation. In this case, lightly sulfonated polystyrene constitutes the ionic block and poly(*tert*-butylstyrene) is the neutral block. Such *amphiphilic* block copolymers are of interest, as they could display a variety of properties, depending on the solvent polarity and quality, the temperature as well as the relative size, and structural characteristics of the component blocks. Apparently, a prior knowledge on the copolymer precursor behavior as a reference state should be useful for a proper understanding of the solution behavior of the modified copolymer.

In a previous paper[12] we reported the temperature-induced associating behavior of the PS-*b*-P(*t*-BS) copolymer (molar ratio 1:1) in *N*,*N*-dimethylacetamide (DMA) which is a good solvent for the PS block but a nonsolvent at room temperature for the P(*t*-BS) part. Both the time-averaged scattered intensity and photon correlation measurements clearly demonstrated that, upon cooling from 65 °C down to room temperature, three temperature regions of unimer, transition, and micellar particles appeared sequentially. The molecular weight and the hydrodynamic radius of the polymeric micelles formed at 25 °C were found to be 1×10^7 g mol^{-1} and 50 nm, respectively, whereas those of unimers examined at 60 °C were 2×10^5 g mol^{-1} and 10 nm. Importantly, a narrow size distribution was found for both the unimer and micelle species. The concentration-dependent transition temperature region where micelles are in equilibrium with single polymer chains is reasonably sharp (4–5 °C). For this system the enthalpy factor is the driving force for

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micellization, which is in strong contrast to the PEO–PPO–PEO/water system where the entropy contribution is responsible for the micelle formation.

A number of studies[13–17] have been reported on the solution properties of ionic block copolymers, including a review paper.[18] Among them few papers have been devoted to the behavior of block ionomers.[17] However, it is of importance to investigate the block ionomers in solution because, in the sense of carrying ionic groups, they represent the intermediate situation between, on the one side, the neutral parent copolymers and, on the other side, the classical random ionomers, the ionic block copolymers, and finally the polyelectrolytes. To be specific, we want to know what the main effects are on the solution properties when introducing only a small number of ionic groups on the polystyrene block, by using both static and dynamic light scattering techniques. Thus, in the present study, two lightly sulfonated block ionomers with a sulfonate content of 5.8 and 12.0 mol %, respectively, obtained on the basis of the same diblock copolymer PS-*b*-P(*t*-BS) as in the previous work,[12] were used in the sodium salt form and dissolved in the same solvent, i.e., *N*,*N*-dimethylacetamide. Static and dynamic light scattering measurements were made in the dilute-solution regime (1–5 mg mL^{-1}) at three differing temperatures (25, 45, and 60 °C). These three temperatures were chosen to correspond to the micelle, transition, and unimer regions of the copolymer precursor, respectively. In all cases the scattered intensities observed were greatly reduced as compared to those measured on the unmodified diblock copolymer under the same conditions. Moreover, instead of the single-exponential decay nature for the parent copolymer in its intensity correlation functions, bimodal relaxation processes were found to be characteristic of the block ionomer solutions studied. Accordingly, the Coulombic interactions between sulfonate groups which dissociate in DMA are one of the major factors determining the solution behavior. At room temperature, however, the strong micellization tendency of the poly(*tert*-butylstyrene) part should become very important.

Experimental Section

Materials and Preparation of Solutions. For our investigations we used two sodium-neutralized sulfonated polystyrene-*b*-poly(*tert*-butylstyrene) samples which contained 5.8 and 12.0 mol % sulfonation, respectively. The parent diblock copolymer has a molecular weight of 1.85 × 10^5 g mol^{-1} and a polydispersity index of 1.1, containing ~700 repeat units for each of the component blocks. The sulfonation of styrene/*tert*-butylstyrene diblock copolymers and their neutralization were performed under the conditions used to sulfonate polystyrene.[19] The sulfonated diblock copolymer was isolated through steam stripping and dried in a vacuum oven at 80 °C for 24 h. The sulfonation level was determined by means of the Dietert sulfur analysis, and the calculated sulfonate content was based on the polystyrene content of the copolymer precursor. The *N*,*N*-dimethylacetamide solvent used was of HPLC grade (Aldrich Co.) and used as received.

Block ionomer solutions were prepared from dilutions of a stock solution ($C \simeq 5$ mg mL^{-1}). The solution preparation and clarification (made dust-free) procedures were the same as described elsewhere.[12] All the clarified solutions were kept in sealed, cleaned vials. It should be emphasized that, in contrast to the unmodified copolymer, it took *several months* for these block ionomer solutions to reach equilibrium in their solution properties, in particular, for low concentration solutions at room temperature. Therefore, one should be patient in dealing with block ionomer solutions. Peiffer et al.[20] also reported the time effect in the viscosity behavior of sulfonated ionomer solutions, but in a nonpolar solvent.

Light Scattering Measurements. A standard, laboratory-built light scattering setup was used as described in detail previously.[3] A Spectra-Physics Model 165 argon ion laser operated at 488 nm was employed as the light source. Static light scattering measurements were performed at angles between 20° and 140°. Photon correlation measurements were carried out, in most cases at scattering angle $\theta = 45°$, in the self-beating mode by using a Brookhaven BI 2030AT 128-channel digital correlator. The cumulants method[21] was used for the analysis of the dynamic data. The temperature constancy in scattering measurements was controlled to within ±0.03 °C. The values of the refractive index (n) of the solvent at $\lambda_0 = 488$ nm were taken to be 1.4356, 1.4265, and 1.4197 at 25, 45, and 65 °C, respectively (see ref 22), in order to compute the magnitude of scattering vector q. q is defined as $(4\pi n/\lambda_0)\sin(\theta/2)$.

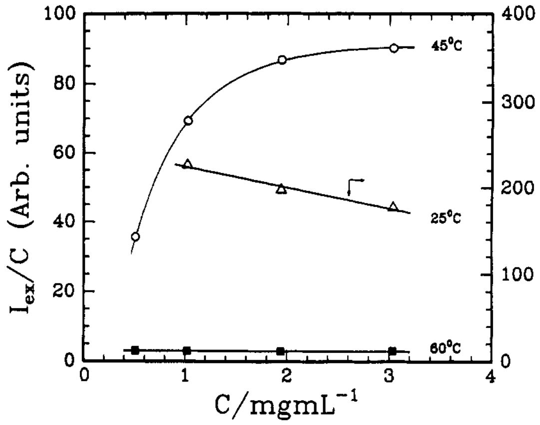

Figure 1. Plots of the reduced scattered intensity I_{ex}/C (in arbitrary units) versus concentration at different temperatures for the unmodified diblock copolymer in *N*,*N*-dimethylacetamide (DMA).

Results and Discussion

As noted in ref 27, polyelectrolyte solutions without added salt represent one of the most mysterious states of condensed matter. In this connection, no satisfactory theoretical treatment is available. It is well-known that, for an ion-containing polymer in a salt-free ionizing solvent, both the light-scattering and viscosity behavior are "unusual", arising from the fact that the polyions are increasingly extended in dimension with dilution. Thus, the interpretation of experimental results is not straightforward. A frequently used approach to suppress or eliminate such anomalous behavior is the addition of salt to screen off the ionic charges in solution. However, the salt added may also function as "perturbance"; e.g., the presence of salt may inevitably change the conformation of the ion-containing polymer chains and, in some cases, may even alter the solvent quality.[18] Nevertheless, an alternative but safe way which we would prefer is to take the neutral copolymer precursor in solution as a reference and thereby to obtain information on the conformation of block ionomers in the same selective polar solvent and in the absence of salt.

Static Light Scattering. Figure 1 shows the scattered intensity results of the unmodified diblock copolymer as a function of concentration at three different temperatures. Figure 2 shows the results for block ionomer solutions with a sulfonation level of 5.8 and 12.0 mol %, respectively. For convenience in comparison, the reduced scattered intensity (I_{ex}/C) was used, where I_{ex} is the excess scattered intensity expressed as $(I_{solution} - I_{solvent})/I_{benzene}$. As shown from Figure 1, at 60 °C where single polymer chains[12] (M_w = 2 × 10^5 g mol^{-1} and R_h = 10 nm) exist, low scattered intensities ($I_{ex}/C \simeq 3.0$) were found. In contrast, much stronger scattering was detected at room temperature (25 °C) as indicated by the large I_{ex}/C values of about 200, which correspond to the polymeric micelles,[12] with M_w

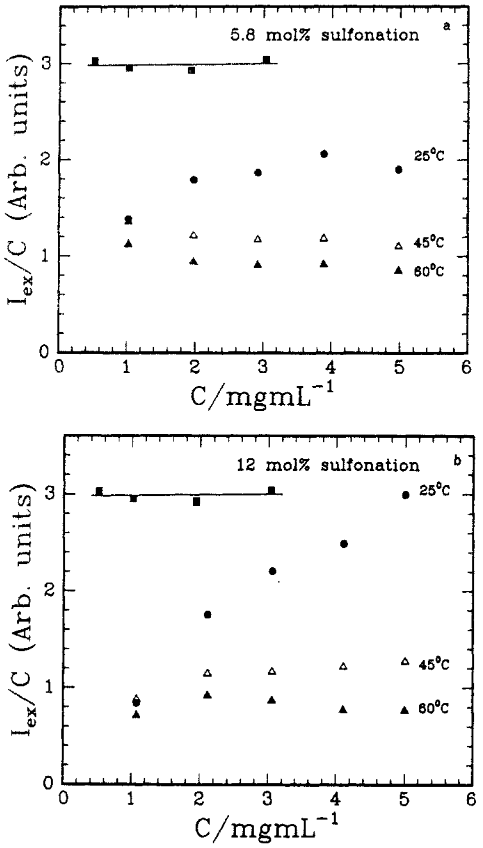

Figure 2. Plots of reduced scattered intensity as a function of concentration for block ionomer solutions at $q = 1.4 \times 10^{-2}$ nm^{-1}: (a) 5.8 mol % sulfonation; (b) 12.0 mol % sulfonation. The top line represents the same data points as the bottom line in Figure 1.

and R_h being 1×10^7 g mol^{-1} and 50 nm, respectively. The temperature of 45 °C led to an intermediate situation. Intermediate level but strongly concentration-dependent scattered intensities ($I_{ex}/C \simeq 35$–90) were observed, meaning that an equilibrium mixture of micelles and unimers exists and the equilibrium is shifted toward micelles with increasing copolymer concentration.

As seen from Figure 2, the scattered intensities measured on block ionomer solutions at a small q value of 1.4×10^{-2} nm^{-1} ($\theta = 45°$) are much weaker than those of the copolymer precursor obtained under the same temperature and concentration conditions. There are two main points characteristic of their scattering behavior. First, the top horizontal line given in parts a and b of Figure 2 represents the scattering power (in arbitrary units) of single polymer chains at unit weight concentration for the parent copolymer and therefore roughly defines the lower boundary value of reduced scattered intensity for block ionomers in the absence of interparticle interactions. Here we have implicitly assumed that the presence of a small amount of sulfonate groups has little influence on the optical properties. In almost all cases the scattered intensities examined were considerably less than this limiting value. Even those ionomer solutions which showed the strongest scattering among the solutions under test still gave a scattering close to this boundary value. It is known that both the diblock copolymer precursor and its ionomer counterpart are chemically stable, thus excluding the possibility that degradation may occur either in the sulfonation process or by the solution preparation. It is also known that, in an ionizing solvent such as dimethylformamide (DMF), sulfonate-based ionomers with a low ionic content show polyelectrolyte-like behavior.[8,9] Note that DMA and DMF are similar in solvent polarity since their dielectric constants (=37.8 and 36.7, respectively) are very close to each other. Therefore, it is naturally concluded that the electrostatic interactions (repulsive in our case) resulting in more or less ordered structures in solution account for the very weak scattered intensities in the small q region, as shown in Figure 2. A similar behavior of weak light scattering has been reported on dilute solutions of salt-free random ionomers[9] and of salt-free polyelectrolytes.[23] Second, in view of the concentration dependence of scattering, there exist two temperature regions. In the higher temperature region (45 and 60 °C) the reduced scattered intensities, observed for the 5.8 and 12.0 mol % sulfonation ionomers, are weakly dependent on concentration and have low values, roughly about one-third of the minimum scattering mentioned above. Accordingly, it seems that, on the one hand, the component block of the lightly sulfonated polystyrene behaves like a polyelectrolyte and likes the surrounding DMA molecules more than the neutral polystyrene does; on the other hand, the poly(*tert*-butylstyrene) part has poor affinity to DMA and shows a tendency of forming a separated microdomain, because DMA may serve as a Θ solvent at 60 °C and the solvent quality becomes poorer at 45 °C. On the basis of this argument, we may expect that, in order to be energetically favorable, in this temperature region the block ionomer chains would exist in the form of monomolecular micelles, which consist of a P(t-BS) core and an outer swollen corona of charged polymer chain surrounded by a certain number of counterions. As will be described later, by dynamic light scattering measurements and by correction for the repulsive interparticle interactions, the hydrodynamic radius for the 12.0 mol % sulfonation block ionomer in solution at 45 and 60 °C is estimated to be about 15 and 17 nm, respectively. When compared with $R_h = 10$ nm for single chains of the diblock copolymer precursor, these values seem quite reasonable, because the salt groups on the polystyrene block are ionized, resulting in repulsion of like charges and thereby chain expansion. The situation is different at room temperature (25 °C). As seen from Figure 2, the light scattering intensity per unit concentration becomes larger with increasing concentration, the concentration dependence being more appreciable for the block ionomer of higher ionic content. Such an enhancement in scattering with concentration could be understood, if we consider the strong self-assembly tendency into polymolecular aggregates for the poly(*tert*-butylstyrene) part at room temperature.[12] In other words, in the low-temperature region, most likely, charged polymolecular aggregates would exist instead.

For random ionomers in a polar solvent, usually the reciprocal reduced scattered intensity first increases markedly with concentration and then levels off at higher concentrations.[9a] A similar but weaker tendency on the concentration dependence of the light scattering intensity can be seen for the block ionomer with 5.8 mol % sulfonation at 45 and 60 °C as shown in Figure 2a. However, this characteristic behavior becomes ambiguous with the 12 mol % sulfonated block ionomer, especially at concentrations ≤2 mg mL^{-1}. An important reason could be that the block ionomer solutions used in the present work were not dilute enough, having a number density of about 10^{15}–10^{16} cm^{-3}, whereas a much smaller concentration of 5×10^{12} cm^{-3} was employed in ref 9a, where the above distinct behavior was observed.

In general, the Debye–Huckel screening length (κ^{-1}) is an important parameter when discussing the behavior of polyelectrolytes in solution and of charged colloidal particles in dispersion, because it determines the range of the electrostatic interactions between particles. κ is defined by the relation

$$\kappa^2 = e^2\sum z_i^2 n_i/(\epsilon kT) \qquad (1)$$

where ϵ is the permittivity of the medium, e the charge of an electron, z_i the valence, and n_i the number of ions of type i per unit volume. For the present system without added salt, the κ^{-1} value is estimated to be 25–100 nm, depending on the sulfonation level and the solution concentration. Note that the above value is underestimated if the salt groups are only partially dissociated.

According to Vrij and Overbeek,[24] the fluctuation theory of scattering applies to polyelectrolyte solutions if the following relation is satisfied:

$$2\sin(\theta/2)/(\kappa\lambda) \ll 1 \qquad (2)$$

This criterion explains why it is not feasible to determine the molecular weight and the second virial coefficient for *salt-free* polyelectrolyte solutions where electrostatic interactions are of long range and the conventional scattering theory breaks down. Accordingly, one should be cautious when dealing with the light scattering data of ion-containing polymers in an ionizing solvent.

The existence of a broad maximum in the angular dependence of the scattered intensity is also characteristic of ion-containing polymers and charged colloids, as confirmed by neutron scattering experiments[25-27] at relatively large q values between 0.1 and 2.0 $\mathrm{nm^{-1}}$ for salt-free semidilute polyelectrolyte solutions. The neutron scattering curves[8c] obtained on ionomers in polar solvent showed that the peak shifted to smaller angles with increasing ionomer molecular weight. For highly dilute, salt-free aqueous polyelectrolyte solutions[22] or deionized aqueous suspensions of charged polystyrene spheres,[28,29] both with a number concentration of 10^{12}–10^{13} $\mathrm{cm^{-3}}$, the peak positions of light scattering were found at much smaller q values of 10^{-2} $\mathrm{nm^{-1}}$. The existence of a maximum in the scattered intensity can be attributed to the short-range ordering of the polyions or the charged colloidal particles due to repulsive shielded electrostatic interactions. The peak location $q_{\max}$ is a measure of the interparticle spacing d

$$d = 2\pi/q_{\max} \qquad (3)$$

As described above, at 45 and 60 °C the block ionomer chains in solution can be approximately considered as charged monomolecular micelles. The solution concentrations used in the present study correspond to a number density range of 3×10^{15}–1.5×10^{16} $\mathrm{cm^{-3}}$. Thus, the scattering maximum, if it exists, would be beyond the q range accessible to the light scattering technique. Therefore, weak scattered intensities were detected at small q values which are far away from $q_{\max}$. However, at 25 °C the number concentration is reduced as caused by the formation of charged polymolecular aggregates. Accordingly, the peak position is expected to move to lower q. Figure 3 shows the scattered intensity by an ionomer solution (5.8 mol % sulfonation; C = 2.92 mg $\mathrm{mL^{-1}}$) at three temperatures. As can be expected, all scattering curves go upward, more or less noticeably, with increasing q. This tendency becomes more appreciable at 25 °C, thus supporting the concept that polymolecular aggregates are formed at lower temperatures.

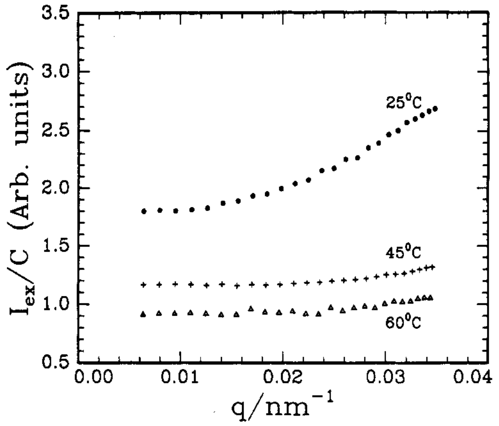

Figure 3. Plots of the reduced scattered intensity as a function of scattering vector q for a block ionomer solution (5.8 mol % sulfonation, C = 2.92 mg $\mathrm{mL^{-1}}$) at different temperatures.

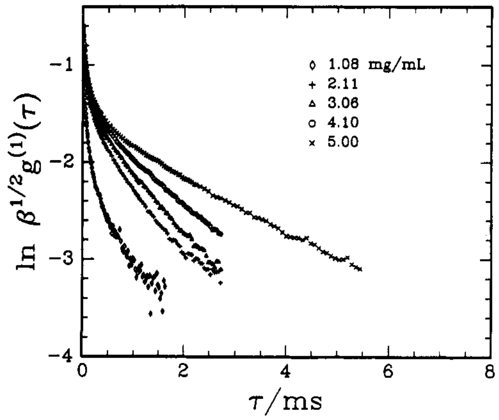

Figure 4. Plots of the logarithmic electric field correlation function against delay time for block ionomer solutions (12.0 mol % sulfonation) of different concentrations at $q = 1.4 \times 10^{-2}$ $\mathrm{nm^{-1}}$ and 45 °C.

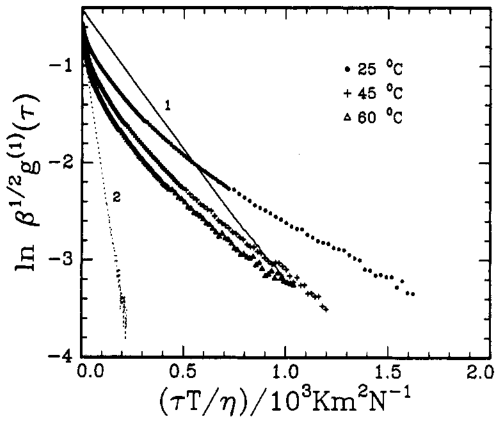

Figure 5. Plots of the logarithmic electric field correlation function against delay time for a block ionomer solution (5.8 mol % sulfonation, C = 4.98 mg $\mathrm{mL^{-1}}$) at three different temperatures. $q = 1.4 \times 10^{-2}$ $\mathrm{nm^{-1}}$. For comparison, the single-exponential decay plots for the copolymer precursor are also given: 1, 25 °C; 2, 60 °C.

Dynamic Light Scattering. Figure 4 shows the logarithmic first-order electric field correlation function, measured at 45 °C and $q = 1.4 \times 10^{-2}$ $\mathrm{nm^{-1}}$, as a function of delay time τ for solutions of a block ionomer with 12.0 mol % sulfonation. Five solutions were examined in the concentration range 1–5 mg $\mathrm{mL^{-1}}$, i.e., in the dilute-solution regime. Here β is a constant depending on the scattering geometry and has a value of ~0.32 for the present light scattering setup. Figure 5 shows the results obtained at three differing temperatures for a 5 mg $\mathrm{mL^{-1}}$ solution of the lower ionic content block ionomer. For comparison, the results for the unmodified diblock copolymer at 25 and 60 °C are also given. In order to compare conveniently the relaxation behavior at different temperatures, reduced delay time ($=\tau T/\eta$) was used for the plotting given in Figure 5. The solvent viscosity η was taken to be 0.927, 0.722, and 0.610 mPa s at 25, 45, and 60 °C, respectively (see ref 22). Obviously, all the curves in Figures 4 and 5 (except for curves 1 and 2 in Figure 5) show a characteristic bimodal relaxation behavior. The decay rates monitored at short times largely differ from those at longer times. Note that such bimodal decay behavior is typical of all the block ionomer solutions examined. As reported elsewhere,[12] DMA solutions of the diblock copolymer precursor, in which the electrostatic interactions are absent, exhibit single-exponential decay for their intensity correlation functions in both the unimer and micelle regions (see curves 1 and 2 in Figure 5). Thus, the effect of electrostatic interactions on the dynamic properties is striking. As shown later, some valuable information can be obtained from the initial and final slopes of the time correlation functions. It should be noted that both the initial and final slopes increase linearly with q^2, as we have checked on some of the block ionomer solutions at 45 °C over an angular range of 30–90°.

For salt-free polyelectrolyte solutions the intensity correlation function curves are fitted by the sum of two exponentials. The deviations from the single-exponential behavior are largest at low concentrations,[23a] and the nature of the slow mode is not well understood. Dynamic light scattering study[9c] of ionomer solutions in a polar solvent also reported a discrepancy from the single-exponential decay behavior, but no statement on the existence of two relaxation modes was given.

Regarding the short-time dynamics, an effective diffusion coefficient D_{eff} can be derived from the initial slope. Taking into account the effect of the interparticle interactions, D_{eff} can be related to the free-particle diffusion coefficient D_0 by the expression

$$D_{\mathrm{eff}} = D_0/S(q) \qquad (4)$$

where $S(q)$ is the static structure factor which reflects the correlations in particle positions, and D_0 is given by the Einstein–Stokes expression.

For dilute systems where strong interparticle interactions are present, a small degree of particle polydispersity can have profound effects[30-32] on dynamic properties, resulting in a slow decay mode in the low-q limit for the intensity correlation function when measured on a long-time scale. Such a slow mode in the relaxation behavior for $q \ll q_{\mathrm{max}}$ has been experimentally observed[33,34] on dilute aqueous suspensions of charged polystyrene latex particles. From the long-time slope associated with slow decay mode (single-exponential nature), the macroscopic self-diffusion coefficient can be deduced. As seen from Figures 4 and 5, it is indeed the case for the block ionomers studied, because they meet both the strong interaction and the polydispersity requirements. As mentioned above, the diblock copolymer precursor, used to prepare the sulfonated block ionomer samples, has a polydispersity index of 1.1. In addition, the sulfonation process may cause a new polydispersity in composition and in spatial distribution of the ionic groups in the polymer chain, since the added salt groups, most likely, are not evenly distributed among different polymer chains.

The reduced scattered intensity from the neutral parent copolymer solution at 60 °C has its origins from the single copolymer chains in the absence of electrostatic interactions. When q is given, to a first approximation, the ratio of the reduced scattered intensity for a block ionomer solution to this quantity gives the value of the static structure factor $S(q)$. This approach of determining $S(q)$ is applicable at two temperatures, 45 and 60 °C, because the molecular weight value for both the charged and uncharged species should be essentially the same. The presence of a small fraction of sulfonate groups as well as the difference in the chain conformation between charged monomolecular micelles and single neutral copolymer chains may have some influence on the optical properties, but they are of minor importance when compared with the major contribution made by the molecular weight factor.

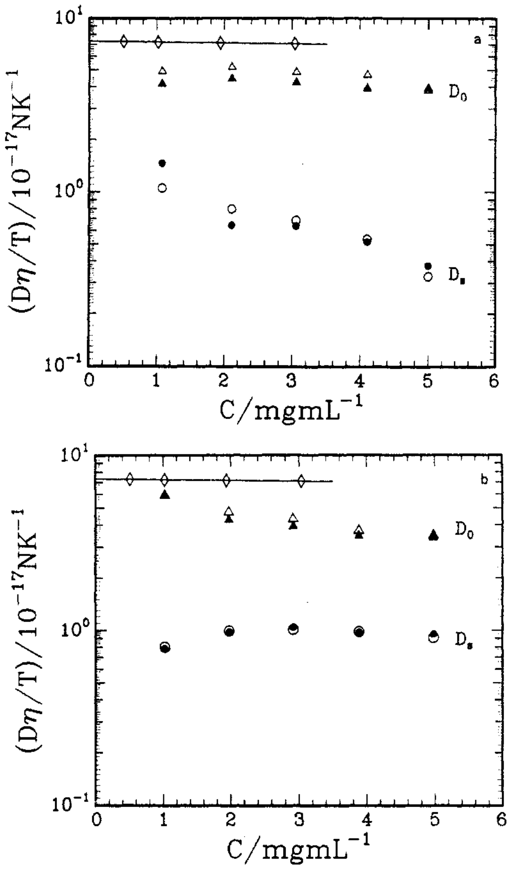

Figure 6. Free-particle diffusion coefficient D_0 and macroscopic self-diffusion coefficient D_s as a function of concentration for block ionomer solutions: (a) 12.0 mol % sulfonation; (b) 5.8 mol % sulfonation. The open symbols denote 45 °C. The filled symbols denote 60 °C. The open diamonds denote the results for the unmodified diblock copolymer, deduced from the single-exponential decay behavior.

The results of the free-particle diffusion coefficient D_0 and the long-time self-diffusion coefficient D_s deduced from the dynamic light-scattering experiments, measured at $q = 1.4 \times 10^{-2}$ nm^{-1} and at 45 and 60 °C, are shown in parts a and b of Figure 6 for the block ionomers of 12.0 and 5.8 mol % sulfonation, respectively. The reduced diffusion coefficient ($D_{\mathrm{red}} = D\eta/T$) values are given so that a comparison can be made easily for these two temperatures. The values for the copolymer precursor at 60 °C are also given as a reference.

As seen from Figure 6a, for the block ionomer with a higher ionic content, and at 45 and 60 °C, D_0 is always smaller than that of the parent copolymer, meaning that the chain expansion indeed occurs because of the repulsion of like charges. The D_{red} value at 45 °C is a little bit larger than that at 60 °C as expected, since the solvent quality becomes worse with decreasing temperature. Importantly, at both temperatures D_0 is independent of concentration, suggesting that, most likely, intramolecular repulsive interactions are responsible for the chain expansion. The D_s values obtained are 4–10 times smaller than D_0 and become smaller with increasing concentration. This is, probably, due to the increasing retarding effect of the slowly varying repulsive interparticle forces from the neighbors.

The dynamic properties of block ionomer solutions with a lower sulfonation level (5.8 mol %), in some aspects, are different from those observed with a higher ionic content. They are mainly as follows: (1) Although not significantly, D_0 becomes larger with increasing dilution. For example, the D_0 value is about 70% larger for the 1 mg mL^{-1} solution than for the 5 mg mL^{-1} solution. The reason for such unexpected behavior remains to be clarified. (2) The macroscopic self-diffusion coefficient is 4–8 times smaller than D_0 as expected but is essentially independent of concentration in the concentration range studied. It is not clear why the concentration effect of the macroscopic self-diffusion coefficient behaves so differently for the two block ionomers studied. Nevertheless, both the D_0 and D_s values obtained are reasonable in magnitude. Interestingly, after correction for the temperature and viscosity variation, the reduced values of either D_0 or D_s are almost identical at both 45 and 60 °C, strongly indicating that essentially the identical structures would exist at these two temperatures.

Conclusions

In contrast to the unmodified neutral diblock copolymer which shows relatively simple micellization behavior in a selective polar solvent, *N*,*N*-dimethylacetamide, the lightly sulfonated block ionomers, when dissolved in the same solvent, exhibit complicated solution properties even in the dilute-solution regime. Two major contributions are responsible for the solution behavior: (1) repulsive electrostatic interactions between the ionized groups are associated with the lightly sulfonated polystyrene part which has an affinity to DMA, and (2) a strong aggregation tendency into separated microdomains which is temperature dependent is characteristic of the poly(*tert*-butylstyrene) part. As a delicate balance between these two forces, charged monomolecular micelles are found at higher temperatures, whereas at lower temperatures the charged polymolecular aggregates would exist. To date no theoretical models are available for charged block ionomers in solution. Certainly, more experimental and theoretical works are needed to explore and understand this interesting field.

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