Light Scattering Studies of Block Ionomer Aggregation Characteristics in Nonpolar Solvent

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ABSTRACT: Static and dynamic light scattering studies are presented on the aggregation characteristics of a block ionomer in nonpolar solvent. In the dilute solution regime (1-5 mg/mL), the solution behavior of poly(*tert*-butylstyrene)-*b*-lightly sulfonated polystyrene (sodium neutralized with a 2.3 mol % sulfonation content) dissolved in cumene was compared with that of the parent neutral copolymer. For the block ionomer studied, reverse aggregates with the salt groups in the interior were obtained as expected. However, in all cases, as indicated by combining static and dynamic light scattering measurements, a dominating portion of single chains (~83 wt %) and a small amount of reverse aggregates (~17 wt %, each aggregate consisting of, on average, about 10 unimers) coexist in a nearly constant weight ratio. There seems to be no real equilibrium between these two distinctive species. Most likely, the aggregates detected are essentially made up of less soluble, but higher ionic content, copolymer chains, as resulted from the composition heterogeneity in terms of the ionic content among individual block ionomer chains.

Introduction

Ionomers are a class of ion-containing polymers, consisting of nonpolar macromolecular chains, to which a small number of ionic groups (usually in the range of 1-10 mol %) are chemically bound. These salt groups are randomly distributed along the backbone and interact strongly with one another, especially in a nonpolar matrix. Thus, the introduction of ionic groups into a neutral polymer may lead to substantial changes in its physical and mechanical properties, arising from the microphase separation of the salt groups in the bulk state. While many studies have been devoted to ionomers in the solid state, the solution behavior of ionomers started to be investigated actively only in the early 1980s, as stimulated by the availability of sulfonated polystyrene ionomers. It is now recognized that the solution properties of ionomers are largely dependent on the polarity of the solvent.[1,2] 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.

Lundberg and co-workers[3] studied the reduced viscosity-concentration relationship for ionomers in nonpolar solvent in comparison with their precursor in the same solvent. They observed a crossover behavior, i.e., the intersection of the viscosity curves for the ionomer and the precursor at a certain concentration C^*. It has been suggested that for ionomer solutions the enhancement of viscosity at concentrations of $C > C^*$ arises from *interchain* ion pair associations, whereas the *intrachain* aggregation formation predominates in the dilute region ($C < C^*$), thus resulting in smaller viscosities as compared with those of the precursor. It is known that for the purpose of detecting occurrence of association or monitoring a variation in the aggregate size, light scattering possesses considerably higher sensitivity than viscometry. For instance, Pedley et al.[4] studied the xylene solution of a sodium-neutralized sulfonated polystyrene ionomer using light scattering and suggested an equilibrium existing between single coils and aggregates as a function of concentration and obeying the open association model. They claimed that at low concentrations single ionomer chains and dimeric aggregates are dominating. Very recently, Bakeev et al.[5] examined by dynamic light scattering the aggregation behavior of a similar system, but in the zinc form, and found that the crossover concentration obtained from dynamic light scattering, C^*_{LS}, was about 10 times smaller than C^*_η deduced from viscometric measurements. Both single coils and aggregates consisting of 8-10 unimers were found approximately in the concentration region between C^*_{LS} and C^*_η. Above C^*_{LS} the aggregate portion first increased rapidly with increasing concentration and then leveled off with a final weight fraction of about 14%.

Block ionomers consisting of a neutral block and an *ionomer* block constitute an interesting area for polymer research, because they are expected to demonstrate a combination of properties characteristic of block copolymers and ionomers. The selectivity and the polarity of the solvent have strong effects on the solution properties of block ionomers. For block ionomers, in principle, reverse micelles or aggregates are likely formed in a low-polarity solvent and the formation of regular, charged micellar particles may occur in high-polarity solvents. Such *amphiphilic* block ionomers could display a wide range of properties, depending on the relative size and structural characteristics of the ionomer block and the neutral part, the ionic content (e.g., the sulfonation level) of the ionomer part, the polymer concentration, and the solvent quality and temperature.

To date a number of studies[6-10] have dealt with the solution properties of ionic block copolymers that are made up of a neutral block and a *polyelectrolyte* block. But, relatively little is known about the behavior of block ionomers in solution. Although ionic block copolymers and block ionomers are closely related to each other, the latter can be conveniently viewed as a modification or

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extension of the ionomer, whereas the former can be considered as a derivative of the polyelectrolyte. Apparently, it is of importance to investigate block ionomer solutions in order to get a better understanding of, in general, the behavior of weakly charged macromolecules in solution and, specifically, the effect of the presence of a neutral block on the ionomer behavior or vice versa.

In a recent paper[11] we reported the cooling-down-induced micellization behavior of a diblock copolymer of styrene and *tert*-butylstyrene in a polar, selective solvent, dimethylacetamide (DMA). Standard thermodynamic functions of micellization were determined on the basis of either static or dynamic light scattering results. In another recent paper,[12] light scattering experiments were performed to study the structure and dynamics of block ionomers in the same polar solvent. The block ionomers used were two lightly sulfonated polystyrene/poly(*tert*-butylstyrene) copolymers with sulfonation levels of 5.8 and 12.0 mol %, respectively. In all cases the scattered intensities observed were greatly reduced as compared with that by the parent neutral diblock copolymer. Besides, a bimodal relaxation of the intensity correlation functions was found instead of the single-exponential decay process characteristic of the parent copolymer. The repulsive electrostatic interactions between the ionized groups of block ionomer chains appear to be responsible for these distinctive properties in solution.

In this work we want to extend the scope of our investigation on block ionomers, namely, to study the aggregation characteristics of block ionomers in a nonpolar medium. The solvent employed was cumene which has a low dielectric constant of 2.38 at 25 °C and therefore is a good solvent for both the polystyrene block and the poly(*tert*-butylstyrene) block. Because of the poor solubility of block ionomers with high ionic content in nonpolar solvent, a copolymer sample with a low sulfonation content of 2.3 mol % in the sodium form, obtained from the same parent PS-*b*-P(*t*-BS) as in previous studies,[11,12] was used. By combining static and dynamic light scattering experiments in the dilute solution region (1–5 mg/mL), it is found that in all cases a dominating portion of single chains and a small portion of aggregates coexist in a nearly constant weight ratio. It seems that there is no real equilibrium between these two portions, suggesting that due to the composition heterogeneity in the ionic content among individual block ionomer chains, most likely, aggregates are essentially made up of those chains that show higher sulfonation level, i.e., are less soluble in the solvent.

Experimental Section

Materials and Preparation of Solutions. In the present study we used a sodium-neutralized sulfonated polystyrene-*b*-poly(*tert*-butylstyrene) sample which contained 2.3 mol % sulfonation. The parent diblock copolymer has a molecular weight of 1.85×10^5 and a polydispersity index of 1.1, containing ~700 repeat units for each of the component blocks. The sulfonation of the styrene/*tert*-butylstyrene diblock copolymer and its neutralization were performed under the conditions used to sulfonate polystyrene.[13] 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 cumene solvent was of 99% grade (Aldrich Co.) and used as received.

Block ionomer solutions were prepared from dilutions of a stock solution ($C \simeq 5$ mg/mL) which was obtained by dissolving a known amount of block ionomer in cumene under gentle agitation and then heating it at 60 °C for 8 h to ensure complete dissolution. The parent copolymer was easily dissolved in cumene. The solution clarification procedures (made dust-free by consecutive centrifugation and filtration) were the same as described previously.[11] All the clarified solutions were kept in sealed, cleaned vials.

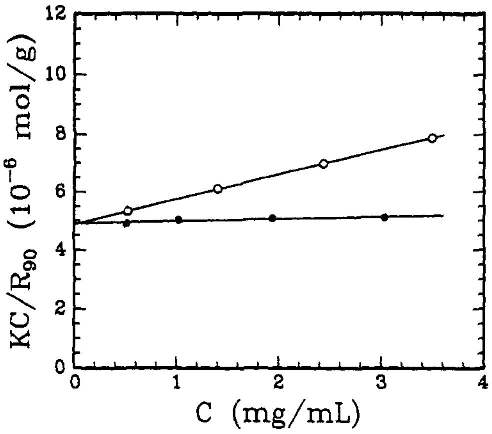

Figure 1. Plots of KC/R_{90} versus concentration for polystyrene-*b*-poly(*tert*-butylstyrene) in cumene at 25 °C (open circles) and in dimethylacetamide at 60 °C (filled circles).

Light Scattering Measurements. We used a standard, laboratory-built light scattering spectrometer[14] capable of both time-averaged scattered intensity and photon correlation spectroscopy measurements in an angular range of 15–140°. Intensity correlation function measurements were carried out in the self-beating mode by using a Brookhaven BI 2030AT 136-channel digital correlator. A Spectra-Physics Model 165 argon ion laser operated at 488 nm was employed as the light source. The cumulants[15] and CONTIN[16] methods were used for the data analysis of dynamic light scattering results. Note that, because of the ill-posed nature of the Laplace inversion involved, CONTIN gives the most probable solution among a number of fitted solutions.

Results and Discussion

1. Diblock Copolymer Precursor in Polar and Nonpolar Solvents.

Some prior knowledge on the solution behavior of the neutral copolymer precursor, which can serve as a reference, is often useful to obtain, by comparison of information on the structure and dynamics of its derivative—block ionomer in solution. Therefore, static and dynamic light scattering experiments were made on polystyrene-*b*-poly(*tert*-butylstyrene) in both polar and nonpolar solvents. Figure 1 shows the reduced scattering intensity results of the unmodified diblock copolymer in DMA (at 60 °C) and cumene (at 25 °C) in the dilute solution region. For all the solutions examined, the forward and backward scattering were the same, and thus the excess scattered intensity at the 90° scattering angle was used. The weight-average molecular weight M_w and the second virial coefficient A_2 were obtained by the relation

$$KC/R_{90} = 1/M_w + 2A_2C \qquad (1)$$

where $K(=4\pi n_0^2(\mathrm{d}n/\mathrm{d}C)^2/N_A\lambda_0^4)$ is an optical constant with N_A, n_0, and λ_0 being Avogadro's number, the solvent refractive index, and the wavelength of light in vacuo, respectively. R_{90} is the excess Rayleigh ratio at a scattering angle 90° with vertically polarized incident and scattered beams, C is the concentration in grams per milliliter. Benzene was used as the reference standard. The refractive index increments of copolymer solutions were calculated using the relation

$$\mathrm{d}n/\mathrm{d}C = w_A(\mathrm{d}n/\mathrm{d}C)_A + w_B(\mathrm{d}n/\mathrm{d}C)_B \qquad (2)$$

Table 1. Refractive Index Increments of PS-*b*-P(*t*-BS) in DMA and Cumene[a]

solvent	temp (°C)	$(dn/dC)_{PS}$[b] (cm^3 g^{-1})	$(dn/dC)_{P(t\text{-}BS)}$[c] (cm^3 g^{-1})	dn/dC[d] (cm^3 g^{-1})
DMA	60.0	1.70×10^{-1}	1.29×10^{-1}	1.45×10^{-1}
cumene	25.0	1.14×10^{-1}	7.12×10^{-2}	8.81×10^{-2}

[a] The dn/dC value of the homopolymer solution was calculated by using the Glastone and Dale formula.[20] [b] At 25 and 60 °C, $n_{PS} = 1.61$ and 1.593 and $d_{PS} = 1.05$ and 1.02 g/cm^3 were taken, respectively. [c] At 25 and 60 °C, $n_{P(t\text{-}BS)} = 1.563$ and 1.547 and $d_{P(t\text{-}BS)} = 1.026$ and 0.997 g/cm^3 were taken, respectively. [d] Calculated by eq 2 in the text.

Table 2. Static and Dynamic Properties of PS-*b*-P(*t*-BS) in Polar and Nonpolar Solvents

	cumene (25 °C) ($\epsilon = 2.38$)	dimethylacetamide (60 °C) ($\epsilon = 37.8$)
M_w	2.02×10^5	2.04×10^5
A_2 (cm^3 mol g^{-2})	4.3×10^{-4}	3.7×10^{-5}
D_0 (cm^2 s^{-1})	2.48×10^{-7}	4.01×10^{-7}
R_h (nm)	11.9	10.0
k_D (cm^3 g^{-1})	43.9	-10.7

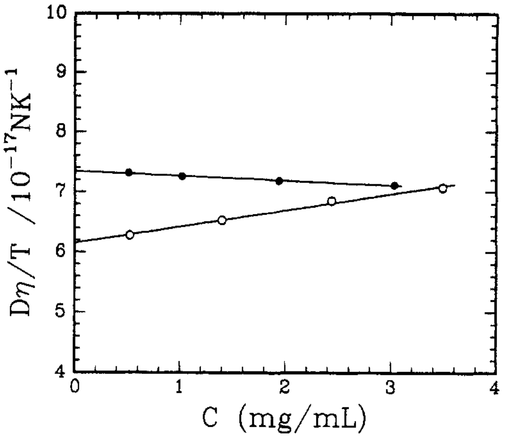

Figure 2. Plots of reduced diffusion coefficient ($D\eta/T$) versus concentration for the same systems with the same symbols as in Figure 1. The intercept is a measure of the particle size of interest.

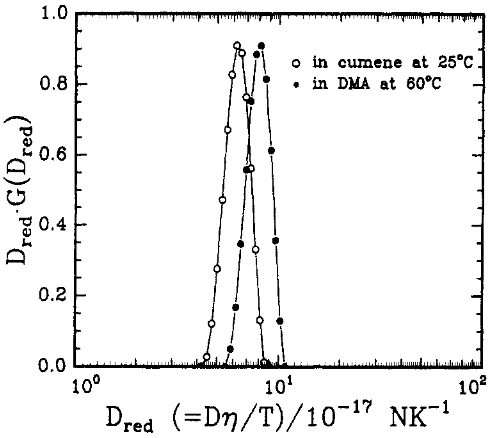

Figure 3. Relaxation rate distributions obtained by the CONTIN analysis of the intensity correlation functions of the 0.52 mg/mL diblock copolymer solutions. The reduced diffusion coefficient ($D\eta/T$) was used to compare directly the peak positions in the two different solvents at different temperatures.

where w is the weight fraction and the subscripts A and B denote the PS and P(*t*-BS) blocks, respectively. All the dn/dC values estimated for the copolymer and the two homopolymers are listed in Table 1. For block copolymers which are heterogeneous in both molecular weight and composition, eq 1 yields an apparent molecular weight ($M_{w,app}$) which differs from the true one, M_w. Correspondingly, a correction should be made (see ref 17) to get the true molecular weight. In our case, the variation in the molecular weight introduced by this correction was about 1%.

The M_w and A_2 values obtained are summarized in Table 2. It is seen that the M_w values determined in cumene and DMA are nearly identical and in agreement with the nominal value 1.85×10^5. Thus, the diblock copolymer precursors are molecularly dispersed in solution when dissolved in both cumene at 25 °C and DMA at 60 °C. Note that there are some uncertainties associated with the calculated dn/dC values, but they do not prevent us from reaching this conclusion.

For the PS-*b*-P(*t*-BS)/cumene system, the physical quantity A_2, as a measure of polymer–solvent interactions, has a value of 4.3×10^{-4} cm^3 mol g^{-2} which is comparable in magnitude to the value of 4.8×10^{-4} for polystyrene in xylene.[4] This means that at room temperature cumene is a good solvent for the neutral diblock copolymer. On the contrary, for the copolymer in dimethylacetamide, A_2 becomes much smaller by a factor of ~12, implying that, even at an elevated temperature (60 °C), DMA behaves almost like a Θ solvent. It also explains why the diblock copolymer under study exhibits enhanced association tendency in DMA when the temperature is reduced.[11]

Figure 2 shows the dynamic light scattering results in DMA and cumene. The relaxation rates measured displayed a q^2-dependence, with q being the magnitude of the scattering vector ($q = (4\pi n/\lambda_0)\sin(\theta/2)$), indicating that the diffusive mode was monitored. The concentration dependence plots given in Figure 2 were obtained based on the cumulants analysis. Here the reduced diffusion coefficient D_{red} ($=D\eta/T$) is used to allow for the difference in the temperature and viscosity terms between the two solvents when the Einstein–Stokes relation is put into use,

$$D = kT/6\pi\eta R_h \tag{3}$$

The advantage is that the reciprocal intercept in Figure 2 is a direct measure of the particle size of interest. As seen from Table 2, the relevant hydrodynamic radius (R_h) in cumene is about 20% larger than that in DMA, reflecting that in the former case the single copolymer coils are more expanded due to the stronger polymer–solvent interactions. In addition, the diffusion second virial coefficient k_D derived from the concentration dependence

$$D = D_0(1 + k_D C) \tag{4}$$

shows a large positive value in cumene but a small negative one in DMA, as given in Table 2. Such an observation on the difference in k_D between the two solvents is in accordance with their relevant A_2 values.

The relaxation rate distributions at the given temperatures were obtained by the CONTIN analysis, and the typical distribution patterns, for example, for a 0.52 mg/mL solution, are shown in Figure 3. Again, the reduced diffusion coefficient is employed to directly compare the peak locations in the two different solvents. $D_{red}G(D_{red})$ is expressed in arbitrary units but normalized to the highest value to facilitate comparisons. As seen from Figure 3, provided that the copolymer chains are molecularly dispersed, the relaxation rate distributions in different solvents indeed reveal a common profile which is characteristic of the copolymer sample concerned but is regardless of the solvent used. The only difference is that the peak position in cumene has been shifted to a smaller D_{red} value as expected. In both solvents, a small variance $\mu_2/\bar{\Gamma}^2$ of about 0.02–0.025 was found, where μ_2 is the second central moment of the distribution and $\bar{\Gamma}$ is the mean characteristic line width (or relaxation rate), indicating

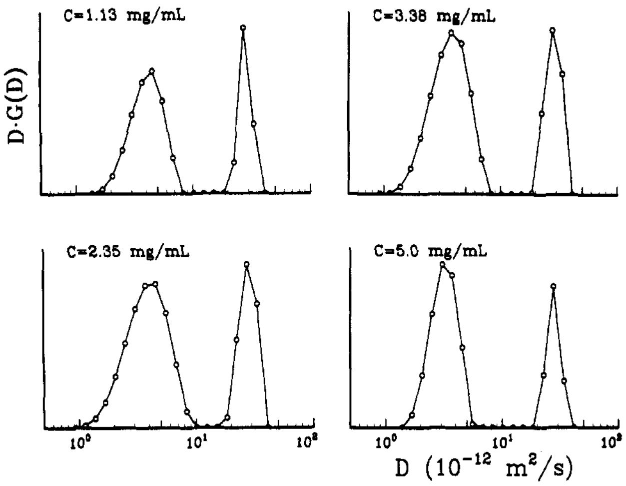

Figure 4. Relaxation rate distributions obtained at 25 °C for the block ionomer (2.3 mol % solfonation for the polystyrene block) solutions at the four indicated concentrations. The fast peak represents the single coils, and the slow peak corresponds to the contribution by the aggregates.

that the parent diblock copolymer under study is essentially homogeneous in molecular weight. Furthermore, on the basis of the relation $\mu_2/\bar{\Gamma}^2 = (1/4)(M_z/M_w - 1)$,[18] a M_z/M_w value of 1.08–1.10 is obtained in good agreement with the polydispersity index (=1.1) of the copolymer material studied.

2. Block Ionomer in Nonpolar Solvent. Dynamic Light Scattering. Photon correlation spectroscopy measurements were performed on the block ionomer sample in cumene at 25 °C. A scattering angle 30° was selected to meet the requirements that the relation $qR_g < 1$ essentially holds for all the structures possibly existing in solution. In so doing, the internal motion contributions, if any, can be neglected in the data analysis. Four solutions were examined in the concentration range 1.1–5.0 mg/mL. All the intensity correlation function curves measured showed a bimodal relaxation behavior in contrast to the single-exponential decay characteristics of the copolymer precursor in cumene. Figure 4 shows the bimodal distribution results obtained by the CONTIN analysis on block ionomer solutions, the two relaxation processes concerned being well separated. The fast relaxation peak seems to represent the single coils of the block ionomer, since the hydrodynamic radius calculated from the peak position is, to some extent, smaller than that of the parent copolymer, as discussed below. The slow peak can be considered as the contribution by the aggregates or associated structures arising from the attractive interactions between the salt groups in a nonpolar solvent. Interestingly, the area ratio of these two peaks, i.e., the intensity ratio of aggregate to unimer is almost a constant (2.0:1), being essentially independent of the solution concentration for the concentration range covered. The meaning of this constancy will be discussed later. Furthermore, to eliminate the interparticle interactions, a linear extrapolation was made for each of these two peaks to obtain an average diffusion coefficient at infinite dilution, as shown in Figure 5. The D_0 and R_h values thus obtained for the unimers and the aggregates in cumene are listed in Table 3.

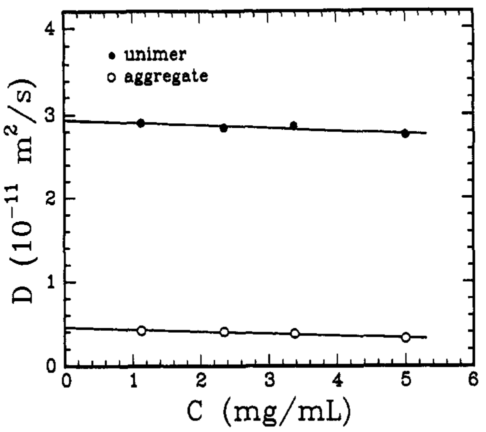

Figure 5. Concentration dependence plots of average diffusion coefficients in cumene at 25 °C for unimer peaks and aggregate peaks shown in Figure 4.

Table 3. Static and Dynamic Properties of Block Ionomer in Cumene in a Dilute Region

	single coil	aggregate
M_w	2.04×10^5 [a]	2.1×10^6
wt-ave aggregation number	1	~10
weight fraction	0.83	0.17
D_0 (cm^2 s^{-1})	2.94×10^{-7}	4.57×10^{-8}
R_h (nm)	10.0	64.6
scattered intensity ratio[b]	1:2.14	

[a] Obtained by adding the sulfonate group contribution to the molar mass value 2.02×10^5 given in Table 2. [b] Obtained by extrapolation to zero scattering angle, using the measured scattered intensity data.

As seen from Table 3, the R_h value of 10.0 nm obtained for the unimer species at infinite dilution is about 16% smaller than the value 11.9 nm for the neutral copolymer precursor in the same solvent. Similar contraction behavior has lately been observed on the zinc salt of a sulfonated polystyrene ionomer in xylene in the dilute regime.[5] This contraction of the single-chain dimension of the block ionomer can be attributed to the intramolecular ion pair attractions in a nonpolar solvent. In principle, for block ionomers, such a contraction in dimension due to the intrachain association should be less profound as compared to the random ionomers with the same ionic content in dilute solution, because in the former case the neutral block makes no contribution but a "negative" influence on the contraction of the *overall* size of the macromolecular chain. This argument is justified according to the observation by Pedley et al.[4] that a contraction of about 25% was found for a sodium sulfonated polystyrene ionomer of less ionic content (1.39 mol %) in xylene ($\epsilon = 2.2$, very close to $\epsilon = 2.4$ for cumene) in comparison with the unmodified polystyrene. Figure 4 also shows that, while the single coils (unimers) of the block ionomer exhibit a narrow polydispersity in size as expected, the aggregates having an average hydrodynamic radius of ~65 nm (Table 3) are relatively polydisperse with $\mu_2/\bar{\Gamma}^2 \simeq 0.12$, which is likely due to the polydispersity of the sulfonation content among individual block ionomer chains. It should be noted that, in contrast to the large positive k_D value of ~44 cm^3/g for the neutral diblock copolymer in cumene, negative k_D values of −11 and −55 cm^3/g were obtained for the ionic unimers and aggregates, respectively, implying that here the polymer–polymer interactions become important, in particular for the aggregates.

Static Light Scattering. For block ionomer solutions an angular dependence of the time-averaged scattered intensity was observed. A typical plot of the q^2-dependence of the reciprocal excess scattered intensity obtained on a 5.0 mg/mL solution at 25 °C is given in Figure 6. The variation of the slope of the plot at low and high q values strongly suggests the coexistence of, most likely, two kinds of structures with different sizes, as verified by the above-mentioned CONTIN analysis on the dynamic data. From the initial slope and the intercept an apparent z-averaged

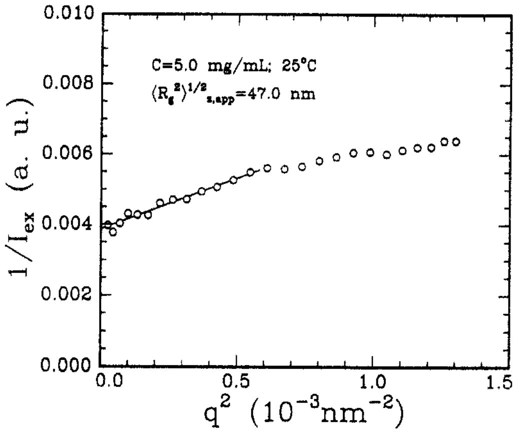

Figure 6. Plot of reciprocal excess scattered intensity versus squared scattering vector for the 5.0 mg/mL block ionomer solution at 25 °C. $\langle R_g^2\rangle^{1/2}{}_{z,app}$ = 47.0 nm as deduced from the limiting slope and intercept.

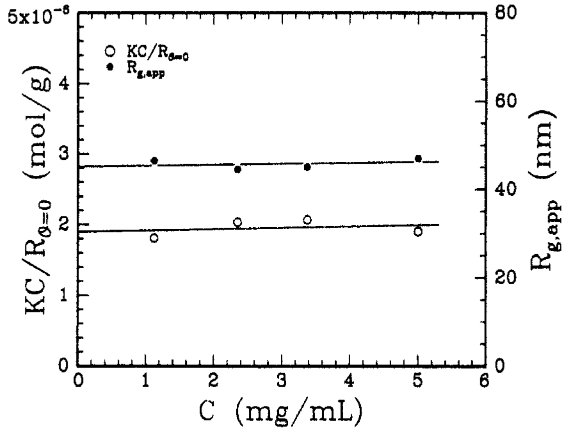

Figure 7. Concentration dependence plots of $KC/R_{\theta=0}$ and $\langle R_g^2\rangle^{1/2}{}_{z,app}$ for the block ionomer in cumene at 25 °C.

squared radius of gyration $\langle R_g^2\rangle_{z,app}$ can be deduced for the block ionomer solution studied by using the relation

$$\langle R_g^2\rangle_{z,app} = 3(\text{slope/intercept}) \qquad (5)$$

Correspondingly, the excess Rayleigh ratios of xylene solutions extrapolated to zero scattering angle were used instead of R_{90} in putting eq 1 into use. Figure 7 shows the concentration dependence plots of $KC/R_{\theta=0}$ and $\langle R_g^2\rangle_{z,app}$. According to Pedley et al.,[4] the refractive index increment of lightly sulfonated polystyrene in xylene is about 11% larger than that of the polystyrene homopolymer in the same solvent, the experimentally measured values being 0.120 and 0.108 cm^3/g at 488 nm, respectively. By taking this difference caused by the presence of a small amount of sulfonate groups into account, we estimated the dn/dC of the ionomer block (2.3 mol % sulfonated polystyrene) in cumene to be 0.127 cm^3/g. Thus, for the block ionomer sample dissolved in cumene to form a mixture of unimers and aggregates, the overall weight-average molar mass M_w was found to be 5.3 × 10^5. Moreover, $\langle R_g^2\rangle^{1/2}{}_{z,app}$ extrapolated to infinite dilution has a value of 45.1 nm. With a small number of sulfonate groups present on the nonpolar macromolecular backbone, the second virial coefficient A_2 in nonpolar solvent becomes, as seen from Figure 7, considerably smaller (~1 × 10^{-5} cm^3 mol g^{-2}). This behavior is well consistent with the observations on ionomers by other research groups.[2a,4]

Estimation of Aggregation Number and Weight Fraction of Aggregates. A combination of the results obtained by static light scattering with those from dynamic light scattering experiments can further provide information on the aggregation number as well as the weight fraction of the aggregates in solution. To a first approximation, we may assume that the dn/dC is approximately the same for both single-coil and aggregate species. Consequently, the intensity ratio of aggregate to unimer as deduced by the CONTIN analysis and given in Table 3 (extrapolated to zero scattering angle by taking into account the particle scattering function for the aggregates at a finite scattering angle 30°) can be related to the weight fraction and molar mass of each species in the mixture by the expression

$$\text{lim intensity ratio} = (1 - x)M_{agg}/(xM_u) \qquad (6)$$

where x is the weight fraction of the unimer, and M_u and M_{agg} are the weight-average molar masses of unimers and aggregates, respectively. The overall weight-average molar mass (=5.3 × 10^5) obtained at infinite dilution has contributions from both unimers and aggregates and therefore follows the relation

$$\text{overall } M_w = xM_u + (1 - x)M_{agg} \qquad (7)$$

By combining eqs 6 and 7, we have

$$x = 0.83$$

and

$$n_{agg}\ (=M_{agg}/M_u) \simeq 10$$

Thus, the aggregates formed are composed of, on average, about 10 single chains with the salt groups located in the interior and the poly(*tert*-butylstyrene) block extending into the nonpolar medium in order to meet the minimum free energy principle. There are two approximate approaches to estimate the average radius of gyration of the aggregates $R_{g,agg}$. On the basis of the relation $\langle R_g^2\rangle_z = [xM_uR_{g,u}^2 + (1 - x)M_{agg}R_{g,agg}^2]/[xM_u + (1 - x)M_{agg}]$ and assuming $R_{g,u} \approx 6$ nm, we estimated $R_{g,agg}$ to be 55 nm. Alternatively, by using the intensity ratio value given in Table 3, we can subtract the flat background scattering of single coils and thus obtain the angle-dependent scattering solely due to the aggregates. In this way we estimated $R_{g,agg}$ to be ~64 nm. The ratio R_g/R_h has a value of 0.85–0.99, suggesting that the aggregates have loose structures.

Regarding the aggregation behavior observed, two interesting points need to be stressed: (1) As the number density is counted, the number ratio of aggregates to single coils is low, having a value of about 1:49. (2) As mentioned above, the weight fraction of aggregates remains essentially constant in the concentration range studied. From our experiments we know that another block ionomer sample with a 5.8 mol % sulfonation content does not dissolve in cumene after standing at 60 °C even for a few months. By lowering the ionic content, for example, having a 2.3 mol % sulfonation in our case, it turns out that only a minor portion of aggregates exists in solution. Such an abrupt change in the dissolution/aggregation properties with a moderate variation in the ionic content seems to suggest the aggregation process in solution, most likely, to be associated with the composition heterogeneity of the block ionomer concerned. If there were a real dynamic equilibrium between the single coils and aggregates, the equilibrium would shift toward the formation of more aggregates when the concentration is increased. But, as described above, it is not the case. In the sulfonation process, on the one hand, the sulfonate groups introduced are randomly distributed along the same ionomer block, meaning that the salt groups may not be equally spaced. On the other hand, the number of sulfonate groups added to the individual copolymer chains may fluctuate within a certain range (2.3 mol % is the average value), thus leading to a small portion of block ionomer chains with a relatively higher ionic content. In our case, most likely, the aggregates detected by the highly sensitive light scattering technique in a small but nearly constant relative proportion are composed of those block ionomer chains that are more sulfonated and therefore show large aggregation tendency in a nonpolar solvent. On the basis of the same mechanism of composition polydispersity, the aggregates formed are expected to have larger polydispersity in size as compared to the unimer species, as indicated by the results shown in Figure 4. Unfortunately, we have not yet been able to physically separate the aggregates from the unimers to ascertain this supposition.

In some aspects block ionomers and ionic block copolymers are similar to each other, the difference being that the former has a limited number of ionic groups but the latter contains an ionic group on each segment in the block. Therefore, it is not surprising that the above arguments are well consistent with the observations on ionic block copolymers. Recently Eisenberg and co-workers[9] studied the formation of reverse micelles for polystyrene-*b*-poly(sodium or cesium methacrylate) in solvents which are selectively good for the polystyrene block, by using size-exclusion chromatography and dynamic light scattering. For their systems they observed the coexistence of single chains and reverse micelles and found that the relative proportion of the micelles was determined by the length of the polyelectrolyte block. On the basis of their careful studies, they reached the conclusion that there was no dynamic equilibrium between the single chains and micelles, at least, within the time scale of a few days. Importantly, the single chains were found to have a significantly lower ionic content than that of the micelles. In fact, in their earlier studies on amphiphilic ionic block copolymers in solution, Selb and Gallot[19] already pointed out the possibility that the multimerization of copolymer chains may be a nonequilibrium process, i.e., not necessarily an equilibrium process.

Conclusions

It is well recognized that the addition of a small number of salt groups to neutral polymers can lead to significant changes in their physical properties in the solid state. However, when compared with the polymer or copolymer precursors, random ionomers, ionic block copolymers, and block ionomers are often less well-defined in composition homogeneity, which may cause complex states of aggregation in solution. For example, the composition polydispersity may arise from the variation of the sulfonation degree among different copolymer chains, when the sulfonation process is carried out. In the present work, an aggregation process of nonequilibrium nature has been observed in solution for the lightly sulfonated polystyrene-*b*-poly(*tert*-butylstyrene)/cumene system. It manifests itself by the coexistence of a dominating portion of single chains with a small number of aggregates in a nearly constant weight ratio over the concentration range studied. Because of the sulfonation polydispersity, the single chains having a lower ionic content constitute the majority, while the aggregates containing the less soluble chains with a higher content of salt groups are limited in number. Such aggregation characteristics might be universal for block ionomers in nonpolar solvent and can be detected by combining the static and dynamic light scattering techniques. At the present moment, however, we cannot entirely exclude the possibility that, based on the same mechanism of composition polydispersity, the "aggregates" detected in solution might be due to the incomplete dissolution of the ionic copolymer material used. Certainly, more experimental and theoretical works are needed to explore and understand this interesting field.

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