Heterogeneities in Random Ionomers. A Small-Angle X-ray Scattering Investigation of Alkylated Polystyrene-Based Materials

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ABSTRACT: The effects of internal plasticization on the morphology of alkylated poly(styrene-*co*-cesium methacrylate) ionomers are studied using small-angle X-ray scattering. In agreement with previous mechanical studies of these ionomers, moderate levels of alkylation enhance ionic aggregation. However, very high levels of alkylation disrupt ionic aggregation. For intermediate levels of alkylation, the multiplet size remains fairly constant and is comparable to the multiplet size of the nonalkylated ionomer (radius of 3–4 Å). The average distance between these multiplets is constant, regardless of the amount of side chain material attached to the polymer backbone between the ionic groups. As the degree of alkylation increases, the intensity of the small-angle upturn (SAUT) decreases. In light of the recent multiplet-cluster model for random ionomers, it is believed that internal plasticization allows more ion pairs to form multiplets, thus increasing the size of the clusters (i.e., the correlated regions). As these correlated domains become larger, the SAUT shifts to lower angles, resulting in an apparent progressive decrease in intensity in the observable range.

Introduction

It is generally agreed that the morphology of random ionomers is based on the existence of ionic multiplets (i.e., aggregates of tightly packed ion pairs) which are distributed throughout the polymer with a liquid-like order. As the degree of ionic aggregation increases (i.e., as the multiplets increase in number), large regions of closely spaced multiplets are formed, termed clusters. These clusters are large, irregularly shaped regions (>50–100 Å in size) with an average multiplet density slightly larger than that of the surrounding ion-poor regions and strongly affect the mechanical properties of the polymer. According to a recent model,[1] the "ionic" peak maximum in the small-angle X-ray scattering (SAXS) profile of a typical random ionomer is proposed to arise from the most prevalent intermultiplet distance (i.e., center to center) within the clusters. These proposed aspects have been supported by a range of morphological investigations of random ionomers, including a study of systems containing ionic groups at the ends of variable-length side chains.[2]

At very low scattering angles (e.g., $q < 0.1$ Å^{-1}; q is the scattering vector defined as $q = (4\pi/\lambda) \sin \theta$, where λ is the X-ray wavelength and θ is half the scattering angle), typical SAXS profiles also show, in addition to the ionic peak, a strong increase in scattered intensity, termed the small-angle upturn (SAUT). While numerous investigations have been devoted to the elucidation of the origin of the ionic peak,[3–12] the small-angle upturn has received considerably less attention. Recently, however, its importance has been recognized as an inherent consequence of the ionomer structure.[10,13]

Previously, the origin of the small-angle upturn has been attributed to a variety of artifacts including voids, impurities, excess neutralizing agents in the sample, or simply poor background subtractions. However, anomalous small-angle X-ray scattering (ASAXS) investigations of nickel-neutralized sulfonated polystyrene ionomers have shown that both the ionic peak and the small-angle upturn are related to the spatial distributions of the ionic groups throughout the material. Since the dimensions of the heterogeneities in electron density giving rise to the small-angle upturn were found to be much larger than the multiplet dimensions, the small-angle upturn was attributed to an inhomogeneous distribution of isolated ionic groups in the matrix.[13]

It should be noted that an alternative explanation for the origin of the small-angle upturn is an inhomogeneous distribution of multiplets throughout the sample. In the telechelics, in which the multiplets are not clustered, the inhomogeneities are an inherent aspect of the system.[10] This explanation, however, is also consistent with the existence of large clustered and nonclustered domains in the random ionomers. Further evidence for attributing the small-angle upturn to the spatial arrangement of the ionic groups has been reported for room temperature solution-cast sulfonated polystyrene ionomers.[11] By annealing these materials, the intensity of the small-angle upturn was observed to decrease with an increase in the extent of ionic aggregation (i.e., the degree of multiplet formation) and an accompanying growth in the ionic peak.

Plasticization may also be used to alter the extent of ionic aggregation in ionomers.[14–20] Internal plasticization (i.e., low molecular weight species ionically or covalently attached to the ionomer chains) is particularly useful because the diluent is not volatile or capable of diffusing away from the chain during thermal treatment. Prior investigations of internally plasticized ionomers have shown that the extent of ionic aggregation is strongly dependent on the level of plasticization.[14,19]

Previous dynamic mechanical studies of alkylated poly(styrene-*co*-sodium methacrylate) ionomers have suggested that low levels of plasticizer enhance multiplet formation, while high levels disrupt multiplet formation.[14] To obtain quantitative evidence for this phenomenon, we have used small-angle X-ray scattering to probe the morphology of a series of alkylated poly(styrene-*co*-cesium methacrylate)

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ionomers with varying levels of alkylation. Of particular interest are the effects of changes in ionic aggregation on the characteristics of both the SAXS ionic peak and the small-angle upturn. The result of this investigation is presented here.

Experimental Section

Materials. Poly(styrene-*co*-methacrylic acid) containing 7 mol % of MAA units was prepared by using a previously described[14] free-radical copolymerization technique. The molecular weight of this copolymer was ca. 10^5. The methacrylic acid content was determined by titrating 0.4-g samples dissolved in a 90:10 (v/v) benzene-methanol solvent with a standard methanolic 0.05 N NaOH solution to the phenolphthalein end point.

A postpolymerization Friedel-Crafts alkylation technique was developed to graft variable amounts of 1-decene (up to ca. 100 mol % based on the styrene units) onto the aromatic styrene rings.[14] Since rearrangement of alkylating species is common in Friedel-Crafts reactions, 1-decene was found to attach to the styrene rings via a secondary carbonium ion mechanism. This postpolymerization reaction produced an alkylated terpolymer having the following structure.
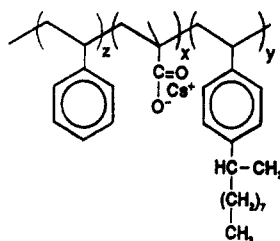
x = 7 mol%

y = 0 - 93 mol%

z = 93 - 0 mol%

The degree of alkylation (i.e., the ratio of alkylated to total styrene units) was determined by titrimetric and ^{1}H NMR spectroscopic methods. The polymers used in this study were found to be 0, 10, 18, 52, 67, 74, and 103 mol % alkylated. The ionomeric forms were prepared by neutralizing quantitatively 1-g samples of the terpolymers with methanolic CsOH. The solvent for the terpolymers was 90:10 benzene-methanol. The ionomer samples were then recovered by precipitation of the concentrated polymer solutions into methanol. The 10 and 18 mol % samples will be referred to as the lightly alkylated ionomers. The 52, 67, and 74 mol % samples will be referred to as the highly alkylated ionomers, and the 103 mol % sample will be referred to as the completely alkylated ionomer.

Prior to molding, the precipitated ionomers were dried for 24 h at 60 °C in a vacuum oven. The SAXS samples were compression molded from ca. 0.1 g of the dried polymers at ca. 30 °C above the temperatures attributed to the respective cluster glass transitions, $T_{g,c}$.[14] The heater was then turned off, and a pressure of ca. 28 MPa was maintained while the samples slowly cooled to room temperature. The samples were all ca. 1 mm thick and were stored in a desiccator until used for the SAXS analysis.

SAXS Instrumentation. The small-angle X-ray scattering experiments were conducted at the D22 station of the LURE-DCI synchrotron radiation source (Orsay, France). The fixed-exit, double-crystal monochromator[21] was turned to provide a beam of 9.5-keV X-rays (λ = 1.30 Å). The size of the beam at the sample was smaller than 1 mm^2 so that no desmearing of the data was necessary. Two beam deflectors and NaI scintillator detectors were positioned before and after the sample chamber to constantly monitor the relative input X-ray intensity and sample absorption. The scattered X-rays were detected with a Xe-CO$_2$ gas-filled, one-dimensional position-sensitive detector having a resolution of 152 μm.

The sample-to-detector distance at 360 mm allowed SAXS data to be obtained in the q range from 0.035 to 0.74 Å^{-1}. The

data are plotted as the relative intensity versus q after correction for parasitic scattering, background scattering (the SAXS profile of pure polystyrene was subtracted from the SAXS profile of each ionomer sample), and sample absorption. All samples were normalized to a thickness of 1 mm.

SAXS Data Analysis. The SAXS intensity profiles were treated as arising from a system of isolated multiplets in a polystyrene matrix which occupy a negligible volume fraction of the total sample (e.g., the volume fraction of multiplets in the ionomers of this study were typically <0.007). The SAXS peak is assumed to be related to a correlation between multiplets within the clusters. The Bragg spacing obtained from the ionic peak maximum ($d_{Bragg} = 2\pi/q_{max}$) is thus believed to yield an estimate of the average center-to-center intermultiplet distance.

Using standard scattering theories,[22,23] characteristic lengths pertaining to the morphology of the samples were obtained by combining the asymptotic form of the scattered intensity and the scattering invariant, Q, such that

$$\frac{\lim_{q\to\infty} I(q)q^4}{\int_0^\infty I(q)q^2 \, dq} = \frac{K_P}{Q} = \frac{S}{\pi V} \quad (1)$$

where K_P is the Porod constant and S/V is the specific interfacial area. The lower limit of the Porod region (i.e., $q > q_{max}$) was chosen such that the statistical errors (95% confidence) in the slope and intercept of a plot of $I(q)q^4$ versus q^4 were minimized. For each sample, the Porod region, used to calculate K_P, contained ca. 200 data points. The slope provided an evaluation of the background which had to be subtracted prior to calculating the scattering invariant.

Equation 1 does not require absolute intensity measurements and provides a direct determination of the surface/volume ratio of the scattering particles. Assuming a spherical shape of the multiplets,[24] the S/V ratio was used to calculate an approximate multiplet radius, R_m. The error limits reported with the R_m and V_m data were determined by the propagation of error from the Porod analysis (above). It is important to note that these error limits only reflect the precision in the data analysis and not the total experimental error.

The number of ion pairs per multiplet, n_i (i.e., the aggregation number), was estimated by dividing the multiplet volume (eq 1) by the molecular volume of a model ionic compound. In this investigation, cesium oxalate was used as the model ionic compound. Cesium oxalate has a molecular weight of 353.8 and a density of 3.28 g/cm^3, which yields a molecular volume of 182 Å^3. The aggregation numbers calculated using this method will be denoted as $n_{i,o}$. It should be noted that this method of calculating n_i is very dependent on the molecular parameters (e.g., the density) of the model ionic compound and should only be used as an estimate.[2]

Simple space-filling calculations were also used to calculate n_i. These calculations are based on the assumptions that all of the ion pairs are in multiplets and that the SAXS peak is related to a characteristic center-to-center distance between ionic multiplets distributed on a simple cubic lattice. The Bragg spacings were obtained from the peak maxima ($d_{Bragg} = 2\pi/q_{max}$) for each of the ionomer samples and related to n_i by

$$n_i = \frac{\rho N_A (d_{Bragg})^3}{EW} \quad (2)$$

where ρ is the polymer density (g/Å^3), N_A is Avogadro's number, and EW is the ionomer equivalent weight. The aggregation numbers calculated using this method will be denoted as $n_{i,s}$. Since it is likely that a fraction of the ion pairs in random ionomers exist as lone ion pairs in the matrix,[9] these space-filling calculations should be considered as yielding an upper limit for n_i.

Results

Effect of Alkylation on the SAXS Intensity Profiles. Figure 1 shows the SAXS data for pure poly(styrene-*co*-cesium methacrylate) and the 10 and 18 mol % alkylated ionomers. The SAXS profile for the nonal-
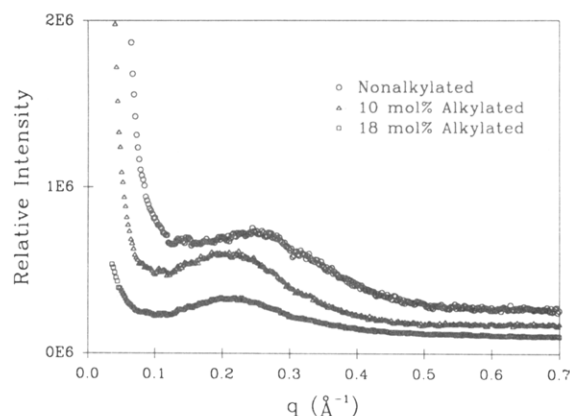
Figure 1. SAXS data for the 0 (O), 10 (△), and 18 mol % (□) alkylated ionomers. All samples were dry and converted to the Cs⁺ form.
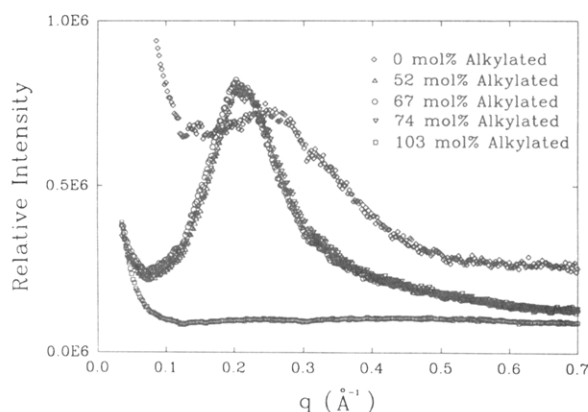

Figure 2. SAXS data for the 0 (◇), 52 (△), 67 (O), 74 (▽), and 103 mol % (□) alkylated ionomers. All samples were dry and converted to the Cs⁺ form.

Table I
SAXS Relative Intensity Data for the Alkylated Ionomers

sample	I_{peak}[a] (at q_{max})	I_{SAUT}[a] (at $q = 0.035$)	I_{peak}/I_{SAUT}
0% alkylated	304	5112	0.06
10% alkylated	241	1311	0.18
18% alkylated	116	220	0.52
52% alkylated	248	85	2.90
67% alkylated	232	88	2.63
74% alkylated	216	85	2.54
103% alkylated		81	

[a] The relative intensity data have been normalized for the change in ionic concentration.

Table II
Characteristic Dimensions of the Alkylated Ionomers

sample	EW[a]	q_{max}	d_{Bragg} (Å)	R_m (Å)[b]
0% alkylated	1600	0.255	25	3.2 ● 0.2
10% alkylated	1800	0.194	32	4.5 ● 0.4
18% alkylated	1965	0.214	29	3.1 ± 0.1
52% alkylated	2637	0.216	29	2.9 ± 0.1
67% alkylated	2945	0.210	30	3.4 ± 0.2
74% alkylated	3085	0.216	29	3.4 ± 0.2
103% alkylated	3659			

[a] EW is the ionomer equivalent weight, equal to the grams of polymer per equivalent of ionic groups. [b] Error limits signify the statistical precision of the data analysis (see Experimental Section).

kylated ionomer shows a weak and very broad ionic peak at ca. $q = 0.26$ Å⁻¹ and a strong upturn in intensity as q approaches zero. The general features of this profile are typical of carboxylate ionomers.[25] The peak appears skewed because of the strong contribution of the SAUT. For the alkylated ionomers, both the broad ionic peak and the strong small-angle upturn are also observed. Furthermore, as the extent of alkylation is varied from 0 to 18 mol %, these data show a trend of decreasing intensity of both the ionic peak and the small-angle upturn with increasing alkylation. It should be noted, however, that most of the variation in peak heights and positions is, most likely, due to variations in SAUT contributions.

The SAXS profiles for the highly alkylated ionomers are shown in Figure 2. Comparison of these profiles with those of Figure 1 show that the ionic peak maxima for the highly alkylated ionomers are more intense and somewhat narrower than the peaks observed with the lightly alkylated ionomers. Between 52 and 74 mol %, the SAXS profiles are superimposable and became insensitive to changes in the degree of alkylation. However, when the polystyrene backbone is completely alkylated (i.e., the 103 mol % sample), the ionic peak is no longer observed.

The most striking feature of Figures 1 and 2 is the effect of the degree of alkylation on the intensities of the small-angle upturn relative to the intensities of the upturn. Table I lists the intensity of the small-angle upturn, I_{SAUT} (i.e., the relative intensity measured at $q = 0.035$ Å⁻¹ for all samples), the intensity of the ionic peak maximum, I_{peak}, and the ratio of I_{peak} to I_{SAUT} for each of the ionomer samples. For the nonalkylated ionomer, the intensity of the small-angle upturn is well over one order of magnitude

greater than the intensity of the ionic peak ($I_{SAUT}/I_{peak} \sim$ 17). Furthermore, it is of interest to note that the upturn for the nonalkylated ionomer begins at a large q value (i.e., near $q = 0.1$ Å⁻¹), similar to that observed for other carboxylated polystyrene-based ionomers,[25] and is the dominant feature of the SAXS profile.

As the degree of alkylation increases, the intensity of the small-angle upturn decreases relative to the ionic peak. At high degrees of alkylation (i.e., greater than ca. 50 mol %), the intensity of the small-angle upturn is greatly diminished, such that the ionic peak becomes the dominant feature of the SAXS profile. Even though an ionic peak is not observed with the 103 mol % sample, it is interesting to note that a substantial small-angle upturn is clearly present in the SAXS profile.

Effect of Alkylation on the Characteristic Dimensions of the Ionomer Heterogeneities. Table II lists the ionomer equivalent weight, EW (i.e., the grams of polymer per equivalent of ionic groups), the q_{max}, the Bragg spacing, d_{Bragg}, and the radius of the ionic multiplets, R_m, for each of the samples shown in Figures 1 and 2. While a slight increase in d_{Bragg} is apparent between the pure poly(styrene-co-cesium methacrylate) and the alkylated ionomers, it is important to note that the exact position of the ionic peak may be convoluted by the large upturn intensity. If the SAUT contribution is subtracted (recognizing that this is a very qualitative procedure), then somewhat smaller values for d_{Bragg} are obtained. This suggests that while the 0% sample does, indeed, show a smaller distance, those for the other samples are essentially the same. This, naturally, has an influence on R_m and the calculated aggregation numbers. For the complete series of alkylated ionomers, the Bragg spacing remains remarkably constant ($d_{Bragg} = 29.8 \pm 2.6$ Å) with increasing alkylation, despite a 100% increase in the ionomer equivalent weight.

For the nonalkylated ionomer, the average radius of the ionic multiplets is determined to be approximately 3.2 Å, the lower size limit accessible by this technique. Interestingly, this value is in agreement with the multiplet radius for 7 mol % poly(styrene-co-cesium methacrylate) ionomers extrapolated from a recently reported side chain
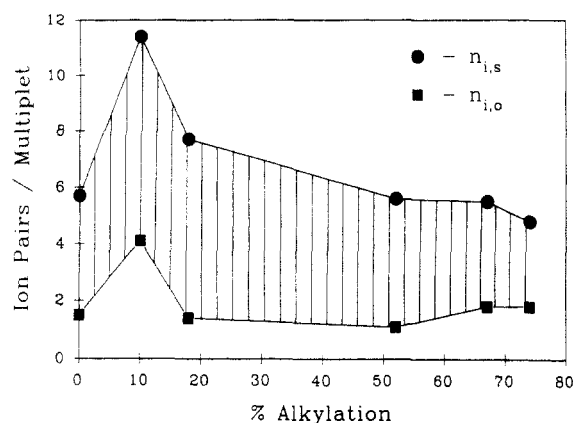
Figure 3. Plot of the number of ion pairs per multiplet versus the mole percent alkylation. The shaded area refers to the range between the upper limit ($n_{i,s}$, ●) and the lower limit ($n_{i,o}$, ■).

length correlation.[2] The uncorrected R_m for the lightly alkylated, 10 mol % ionomer appears surprisingly large relative to the other ionomer samples but this should be regarded with caution, as pointed out above. Between 18 and 74 mol % alkylation, the multiplet radii are quite comparable to R_m for the nonalkylated ionomer and are apparently insensitive to changes in the degree of alkylation.

Figure 3 shows the effect of alkylation on the number of ion pairs per multiplet. Both $n_{i,s}$ (calculated from simple space-filling arguments) and $n_{i,o}$ (calculated from the multiplet volume and the molecular volume of cesium oxalate) are plotted as a function of the mole percent alkylation. In both sets of data, there is an increase in the aggregation number at 10 mol % alkylation. However, as was pointed out above, this observed increase in aggregation number may be artificial since it depends strongly on the peak position. Beyond 10 mol % alkylation, the aggregation numbers appear to be insensitive to the degree of alkylation and are approximately equal to the respective aggregation numbers of the nonalkylated ionomer.

It should be pointed out that the ion pair density estimates, used to calculate the $n_{i,o}$ data, yield aggregation numbers which are too low for a sufficient scattering contrast. Therefore, it is reasonable to expect that the "true" aggregation numbers for these ionomers lie in the shaded area between the upper limit (i.e., the $n_{i,s}$ values) and the lower limit (i.e., the $n_{i,o}$ values).

Discussion

Effect of the Matrix Glass Transition Temperature on Ionic Aggregation. For the series of ionomers listed in Table I, the matrix T_g decreases from ca. 133 °C for the nonalkylated ionomer to ca. 33 °C for the completely alkylated ionomer.[14] This decrease in T_g with increasing alkylation increases the ionomer backbone mobility which consequently increases the ability of the ion pairs to pack efficiently into organized multiplets and clusters. Moreover, since ionic aggregation involves a balance between opposing electrostatic and elastic forces and the extent of ionic aggregation is enhanced as the T_g decreases,[20] the overall morphology of these materials is strongly influenced by the magnitude of the glass transition temperature.

At low levels of plasticization, the ionomer chains experience a slight increase in mobility; however, the overall morphology (i.e., the distribution and concentration of multiplets) remains similar to that of the nonalkylated ionomer. If the 10 mol % alkylated ionomer indeed contains larger multiplets, then the slight increase in mobility of the ionomer chains is apparently sufficient to

allow for multiplets to form in regions too hindered to do so in the absence of plasticizer.

The previously measured rheological properties[14] show maxima in apparent cross-link density at low plasticization levels, in that the 10 and 18 mol % samples give higher values than those below or above those concentrations. An inspection of Figure 3 shows that the $n_{i,s}$ values for the 10 and 18 mol % sample also appear higher than the others. The uncertainty (due to the SAUT contribution in the ionic peak range) is high for the $n_{i,s}$ values for the 10 mol % sample, and a rough correction gives similar values for the 10 and 18 mol % estimates for $n_{i,s}$. Therefore, it is worth noting that both mechanical and SAXS data show some differences between these two samples and the others, although admittedly with a large uncertainty. It is worthwhile to recall that in some unclustered systems, low levels of plasticization were found to induce clustering.[19]

For higher alkylation levels, as kT at T_g drops, more and more ion pairs will be able to get incorporated into multiplets, since elastic forces which oppose multiplet formation decrease while electrostatic interactions do not. Thus, the observed enhancement in the tendency to form multiplets with increasing plasticizer content is not unexpected. It should be noted, however, that these arguments, while involving balances of forces, should not be taken as implying that equilibrium multiplet sizes are encountered.

Effect of Steric Constraints on Ionic Aggregation. Since the alkyl chains are attached on the para position of a neighboring styrene unit and are highly mobile, alkylation levels between 18 and 74 mol % apparently do not influence the ion pair packing efficiency. In a manner similar to that observed with the halato-telechelic ionomers, the maximum size of these tight multiplets would be governed by the cross-sectional area of the polymer chains relative to the size of the ionic groups.[10,24] Therefore, since the ionic group in the alkylated ionomers are attached directly to the polymer backbone, the multiplet size is governed by the same steric factors which influence sizes in unalkylated styrene ionomers. For the 103 mol % alkylated sample, however, the large quantity of bulky alkyl chains in the polymer clearly has a disruptive effect on ionic aggregation. This reduced ionic aggregation in the completely alkylated ionomer is again in agreement with the previous mechanical studies of these ionomers.[14]

Effect of Alkylation on the Large-Scale Ionomer Heterogeneities. As has been stated by many investigators the small-angle upturn is related to the presence of large-scale heterogeneities in ionomers.[10,13] These large-scale heterogeneities have been attributed to uneven distributions of ion pairs[13] or multiplets.[10] For clustered systems, the recently proposed multiplet-cluster model[1] is consistent with the latter suggestion because large-scale heterogeneities in electron density are an inherent component of the model (i.e., clusters are large-scale regions of closely spaced, electron-rich multiplets). Thus, we ascribe the SAUT to distances which are characteristic of the dimensions of the electron-rich clustered regions, where the multiplets are highly correlated and also give rise to the well-known "ionomer" peak via that correlation.

In terms of the present work, we believe that an increase in the alkyl side chain content makes it easier for unassociated "lone" ion pairs to be included in multiplets. This occurs because, as the T_g drops, kT_g becomes smaller relative to the strengths of the dipolar (electrostatic) interactions. This increase in the number of multiplets (at the expense of the number of free pairs) leads to an

increase in the dimensions of the correlated regions (i.e., the clusters). The increase in cluster dimensions consequently shifts the scattering which gives rise to the SAUT toward lower angles and thus shifts progressively larger fractions of the SAUT behind the beam stop. Viewed at a constant low angle (e.g., I_{SAUT} measured at a value of q = 0.035 Å^{-1}), this progression of the small-angle scattering toward lower angles would appear as a decrease in the intensity of the SAUT. Because of these considerations, as well as the inherent polydispersity in cluster sizes, calculations of a characteristic size, e.g., via Debye–Bueche analysis,[26] are not meaningful. In addition, since the ionomer peak position is attributed to an average interparticle distance between multiplets in a cluster, these large-scale heterogeneity arguments are also consistent with the observation of a constant ionomer peak position, as well as a constant multiplet size as a function of the degree of alkylation.

Since the 103 mol % alkylated ionomer does not contain ionic clusters, the existence of a small-angle upturn for this sample (Figure 2) suggests that the origin of the heterogeneous electron density distribution is different from that of the clustered ionomers. It is important to note that a strong small-angle upturn without evidence of an ionic peak has also been observed in solution-cast sulfonated polystyrene ionomers.[11] Because of the large degree of steric interaction in the completely alkylated ionomer, apparently even significant multiplet formation is suppressed. Therefore, a possible explanation for the observed large-scale heterogeneity in electron density may be that this completely alkylated ionomer contains an inhomogeneous distribution of lone ion pairs.[13] Clearly, further studies focusing on the highly alkylated materials are required to fully explain the dramatic changes in the SAXS profiles between the 74 and 103 mol % samples.

Conclusions

Typical random ionomers such as poly(styrene-*co*-cesium methacrylate) contain both small- and large-scale heterogeneities. The small-scale heterogeneities are formed by the aggregation of fixed ionic groups into multiplets. The spatial arrangement of these small-scale heterogeneities gives rise to the ionomer peak in small-angle scattering experiments. The large-scale heterogeneities arise from an inhomogeneous distribution of electron density throughout the sample. A possible origin of these heterogeneities, which yield intense scattering at very low angles, may be large regions containing a high density of multiplets (i.e., clusters).

In this investigation, internal plasticization (i.e., alkylation of the polystyrene rings) is shown to influence the dimensions of both the small- and large-scale heterogeneities. In agreement with previous mechanical studies of these materials,[14] the results of this study suggest that internal plasticization increases ionic aggregation while complete alkylation disrupts ionic aggregation. For intermediate levels of alkylation, the multiplet sizes and the spacings between the multiplets in clusters remain constant with increasing alkylation, despite a 100% increase in the ionomer equivalent weight.

The intensity of the small-angle upturn, as measured at a constant low scattering angle, relative to the intensity of the ionic peak decreases as the degree of alkylation

increases. At high degrees of alkylation, the small-angle upturn is no longer the dominant feature of the SAXS profile. This phenomenon is attributed to an increase in the large-scale dimensions of the clustered regions which shift the scattering profile toward lower angles with increasing alkylation. This shift makes visible progressively smaller portions of the scattering profile beyond the beam stop, which consequently appears as a decrease in the intensity of the SAUT. For the completely alkylated ionomer, clustering and even multiplet formation are suppressed; however, a significant small-angle upturn is still observed in the SAXS profile. Thus, the origin of this large-scale heterogeneity may be attributed to an inhomogeneous distribution of a large concentration of lone ion pairs.

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