Thin-film mechanical properties were determined by the use of an Instron Model TTD Universal Testing Instrument at Texas Research Institute, Austin, TX.

Preparation of Polyamic Acid 1 from 3,5-DBP, ODA, and PMDA. To a stirred solution of 1.01 g (5.04 mmol) of ODA in 10 mL of DMAc was added 0.962 g (2.63 mmol) of 3,5-DBP at room temperature under an atmosphere of argon. The mixture was stirred at 130 °C for 20 h to give a brown solution of amine-capped trimer. After the reaction mixture cooled to room temperature, 0.583 g (2.67 mmol) of PMDA was added over a period of 6 h. The volume of solvent was adjusted in order to maintain a concentration of ca. 10% solids by weight. After 12 h of stirring, the brown, viscous solution was poured into ca. 400 mL of rapidly stirring water, and the gray precipitate was collected by suction filtration and then washed with water and dried in a vacuum desiccator. Inherent viscosity was 0.73 dL/g (0.245 g/dL in DMAc at 22.0 °C) and the pure yield was 93%. IR (film) 1712, 1605 (C=O), 3279 cm^{-1} (N—H, O—H). Anal. Calcd.: C, 70.70; H, 4.10; N, 5.70. Found: C, 68.32; H, 4.25; N, 5.87.

Preparation of Polyamic Acid 2 from 3,5-DBP, ODA, and 6FDA. A similar procedure to the one described above was followed except 1.05 g (5.24 mmol) of ODA, 0.962 g (2.63 mmol) of 3,5-DBP, and 1.25 g (2.81 mmol) of 6FDA were added to the reaction flask. The pure yield was 3.16 g (97%) of a gray precipitate. Inherent viscosity was 0.96 dL/g (0.264 g/dL in DMAc at 25.3 °C). IR (film) 1700, 1600 (C=O), 3275 cm^{-1} (O—H, N—H); Anal. Calcd.; C, 66.45; H, 3.66; N, 4.63; F, 9.41. Found: C, 64.87; H, 3.41; N, 4.72; F, 8.59.

Preparation of Polyamic Acid 3 from 3,5-DBP, ODA, and BTDA. A similar procedure to the one described above was followed except 1.62 g (8.10 mmol) of ODA, 1.47 g (4.01 mmol) of 3,5-DBP, and 1.33 g (4.13 mmol) of BTDA were added to the reaction flask. An ice bath was used prior to addition of the dianhydride in order to maintain a low temperature during the initial stages of the polymerization. The reaction proceeded readily under the previously stated conditions to give a high yield (97%) of a tan powder. Inherent viscosity was 0.71 dL/g (0.250 g/dL in NMP at 25.3 °C). IR (film) 1708, 1601 (C=O), 3268 cm^{-1} (N—H, O—H).

Thermal Cyclodehydration of Polyamic Acids to Corresponding Copoly(imidine–imides). Copolymer 1 was obtained by heating polyamic acid 1 in the Abderhalden drying apparatus using 1,2,4-trichlorobenzene (bp 214 °C) under vacuum for 68 h to complete dehydration and cyclization. The dehydrated samples were used for elemental and thermal analyses. The yellow product was soluble in *m*-cresol and *o*-chlorophenol. Anal. Calcd.: C, 76.31; H, 3.53; N, 6.14. Found: C, 74.32; H, 3.37; N, 6.29. Copolymer 2 was obtained in the same manner from polyamic acid 2 and was also soluble in *m*-cresol and *o*-chlorophenol. Anal. Calcd.: C, 70.65; H, 3.18; N, 4.92; F, 10.0. Found: C, 69.55; H, 3.07; N, 4.79; F, 9.97. Copolymer 3 was obtained by heating polyamic acid 3 at 200 °C under vacuum for 36 h to complete curing. Anal. Calcd.: C, 76.76; H, 3.57; H, 5.51. Found: C, 75.19; H, 3.62; N, 5.45.

Film Casting. An appropriate amount of the polyamic acid sample was dissolved in DMAc or NMP so that the solution was about 10–15% solids by weight. This polymer solution (dope) was used for film casting and subsequent imidization. The dope was pipeted onto a clean, dry glass plate and spread evenly using a disposable pipet or a doctor knife. The plate was then placed in an oven at 80 °C under a positive flow of argon for several hours. After the initial drying, the temperature was increased to 200 °C and the sample was heated under vacuum for 16 h. Upon cooling, the copolymer film was removed from the glass plate by soaking in distilled water.

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Long-Range Inhomogeneities in Sulfonated Polystyrene Ionomers

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Small-angle X-ray scattering (SAX) has been used extensively for morphological studies of ionomers.[1] Their scattering profiles generally exhibits a broad, so-called "ionic peak" and an "upturn" at very small scattering an-

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gles. Many models have been proposed to explain the ionic peak with the main ones being either an inter-aggregates interference model[2] or an intra-aggregate interference model.[3,4] Relatively less attention has been paid to the scattered intensity upturn at small scattering angles. MacKnight et al.[3] attempted to use the Guinier approximation to analyze the small-angle upturn and obtained an average radius of gyration for the ion aggregates. In most cases, such upturns were simply ignored when fitting the data with the various models.

For a dilute solution of macromolecules, the Guinier approximation can be used to analyze the SAXS curves in the small-angle limit. The apparent radius of gyration $R_g(C)$ at concentration C is obtained by using the following equation:

$$I(q,C) = I(0,C) \exp\left(-\frac{q^2 R_g^2(C)}{3}\right) \qquad (1)$$

where $q = (4\pi/\lambda) \sin (\theta/2)$, with λ and θ being the X-ray wavelength and the scattering angle, respectively, and $I(0,C)$ is the extrapolated scattered intensity at $q = 0$ for a given finite C. The radius of gyration $R_g(0)$ can be obtained by an extrapolation of $R_g(C)$ to zero concentration. Equation 1 may be applicable to ionomers if the ionic aggregates exist as individual particles and if the interparticle interference effect is negligible.

Debye and co-workers[5] have shown that for a system with a random distribution of inhomogeneities in electron density ($\eta(\mathbf{r})$), the electron density correlation function $\gamma(r)$ has the form

$$\gamma(r) \equiv \langle \eta(\mathbf{r}_1)\eta(\mathbf{r}_2)\rangle / \langle \eta^2 \rangle = \exp\left(-\frac{r}{a}\right) \qquad (2)$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and a is a correlation length characterizing the inhomogeneity of the system. The corresponding scattered intensity $I(q)$ in q-space is represented by

$$I(q) = \frac{A}{(1 + q^2a^2)^2} \qquad (3)$$

where A is a constant, independent of q. We propose to use the Debye approach (eq 2 and 3) as a reasonable way to explain the small-angle upturn in the SAXS curve of ionomers. Such an approach has been used to study the inhomogeneity of glasses by light scattering (LS),[5] of an ion-exchange resin by SAXS,[6] and of concentrated polymer solutions by small-angle neutron scattering (SANS) and LS.[7] Recently Clough et al. applied the Debye–Bueche theory to SANS of ampholytic styrene ionomer films; a correlation length of ~30 nm was reported.[8] It should be noted that the correlation function concept is quite general and we are not restricted in its application by means of only eq 2 and 3, which are valid for random two-phase inhomogeneities. We do not claim that the scattering data support the Debye–Bueche model. We only use it to provide a measure of the long-range inhomogeneities in the spatial arrangement of the metal ions.

The net SAXS curves of sulfonated polystyrene ionomers clearly showed a broad ionic peak with its maximum at $q \sim 1.7$ nm^{-1} and a very strong small-angle upturn.[9] In this paper, the small-angle upturn is analyzed in terms of both the Guinier approximation and the Debye approach. The results suggest that the correlation function could be a viable approach to depict the spatial arrangement of ionic aggregates in ionomers.

Sodium and zinc salts of sulfonated polystyrene ($M_w = 1.15 \times 10^5$ g/mol, $M_w/M_n = 1.04$, ~4.5 mol % of sulfur, 100% neutralized) were studied by means of SAXS using a modified Kratky block collimation system[10] at X21A, State University of New York (SUNY) Beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). With $\lambda = 0.154$ nm, a small-angle limit of 0.75 mrad corresponding to a $q \sim 0.03$ nm^{-1} or a Bragg spacing ~200 nm was achieved. The net scattered intensity profiles, originated from ions, ion pairs, or ion aggregates in the ionomers, were obtained by subtracting the scattering profile of the polystyrene or that of the ionomer in acid form from the ones containing the salt groups. In the absence of anomalous small-angle X-ray scattering (ASAXS) where the scattered X-ray intensity of selected metal ions can be changed by using X-ray energies near and away from the K (or L) absorption edge, our approach of comparing the net SAXS curves using the polystyrene backbone and the acid form of the same ionomer before neutralization probably represents a reasonable approximation to achieve the net scattered intensity due to ions alone. By subtracting the PS backbone intensity from the sodium (or zinc) form of ionomer scattered intensities, we have obtained the net scattered intensity due to the salt groups, provided that the PS backbone conformation remains unchanged. This assumption cannot be valid exactly because ionomers consist of PS chains with interacting pendant salt groups. However, if the scattering power of the ionomer is much greater than that of the uncharged PS backbone, we may consider the net scattered intensity as mainly due to the salt groups. By subtracting the acid form of the ionomer from the sodium (or zinc) form of the ionomer, we obtain the net scattered intensity due mainly to the metal ions. Here we have assumed that PS chains with pendant acid sulfonate groups or the corresponding salt forms have the same chain conformations (or morphology). This assumption is partially supported by a weak ionic peak for the acid-form ionomer occurring at about the same position as that for the sodium (or zinc) salt of the ionomer with the same mole percent sulfur and the same PS molecular weight. In fact, we have also ignored the scattering due to the hydrogen in the acid form of S-PS. Again, if the acid scattering is weak enough and if the results by using the two different methods of subtraction agree, we have confidence in claiming that the strong upturn in the small-angle region in sodium and zinc salts of S-PS is due to the metal ions.

The ionomer samples of the salts and of the acid form together with polystyrene were molded to films (~1 mm thick) and very well annealed under the same conditions in order to minimize possible errors in the scattered intensity subtraction procedure. All SAXS profiles, cumulated for 600 s at room temperature, were corrected for the nonlinearity of the linear position sensitive detector, the X-ray source intensity fluctuation, the sample absorption, and the parasitic (background) scattering and were normalized to 1-mm sample thickness and 1-s experiment duration.

Figure 1 shows four typical SAXS curves in the small-angle region for the sodium salt of sulfonated polystyrene (4.5 mol % sulfur), from top to bottom: (1) an original curve without background subtraction, I; (2) a curve with background subtraction, $I - I_{BK}$; (3) an excess scattering curve over polystyrene, $(I - I_{BK}) - (I_{PS} - I_{BK})$; (4) an excess scattering curve over the acid form of sulfonated polystyrene, $(I - I_{BK}) - (I_H - I_{BK})$. The background scattering (I_{BK}) at small scattering angles was fairly weak, ensuring a reliable background correction.

Figure 2 shows typical net SAXS profiles for sodium and zinc salts of sulfonated polystyrene (S-PS) as well as S-PS

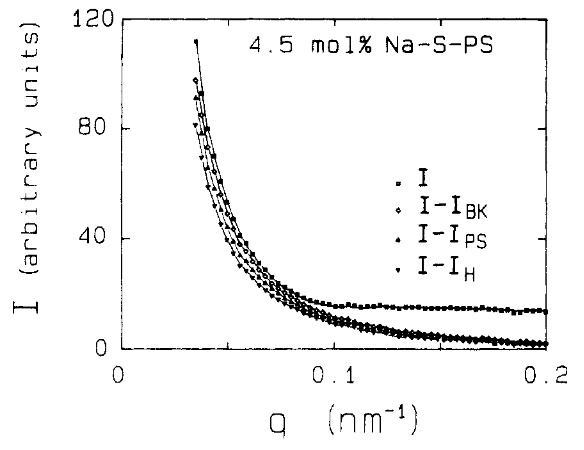

Figure 1. SAXS profiles for the sodium salt: original curve without any subtractions (squares), with background subtracted (diamonds), with the SAXS from PS subtracted (triangles), and with the SAXS from the acid form of S-PS subtracted (reverse triangles).

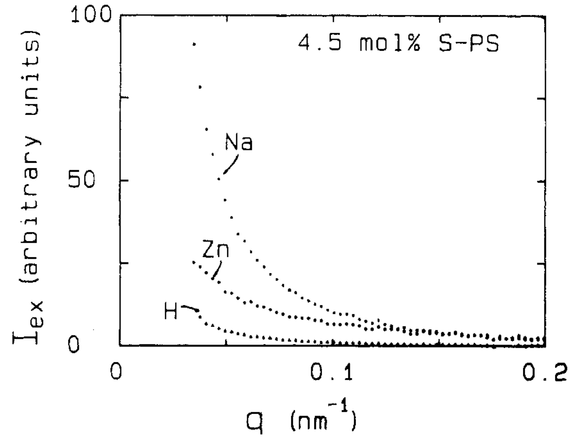

Figure 2. Excess SAXS profiles of salt groups for the sodium (Na) and the zinc (Zn) salts of narrow molecular weight distribution sulfonated polystyrene (M_w = 1.15 × 10^5 g/mol, M_w/M_n = 1.04, 4.5 mol % sulfur, 100% neutralized) with the SAXS from the PS backbone already subtracted. H denotes the excess SAXS profile from the acid form of S-PS.

in the acid form, after subtraction by the SAXS profile of polystyrene. It is noted that the S-PS with sodium salt yields a more intense scattered intensity at small scattering angles than the S-PS with zinc salt. This behavior is in contrast to the ionic peaks where the S-PS with zinc salt shows a higher ionic peak than the S-PS with sodium salt.[9]

Figure 3 shows plots of log $I_{ex}(q)$ versus q^2 for the sodium and the zinc salts of S-PS where $I_{ex}(q)$ is the excess scattered intensity of the ionomers over that of polystyrene. According to eq 1, the slope in the small angles determines the apparent radius of gyration R_g of the ionic aggregates. For the sodium salt and the zinc salt of S-PS, R_g = 39 and 30 nm, respectively. Similar plots using the acid form as the background yield R_g = 39 and 25 nm respectively for Na S-PS and Zn S-PS. However, based on available evidence, the radius of ionic aggregates for most ionomers is smaller than 5 nm. Thus it appears that the Guinier approximation is not valid. Unfortunately, the interparticle interference model does not predict the small-angle upturn either.[2]

Figure 4 shows plots of $I_{ex}^{-1/2}$ versus q^2 according to eq 2 where polystyrene is used as the background. The square root of the ratio of the slope to the intercept in the small-angle limit yields the correlation length a. For the sodium and the zinc salts of S-PS, a = 23 and 15 nm, respectively. If we use the acid form as the background, a = 23 and 12 nm, respectively. The net small-angle upturn results imply the existence of long-range inhomogeneities of metal ions in the ionomers. The two different procedures have not significantly changed the correlation length a, because the ionomer in acid form scatters only slightly more than the polystyrene backbone. The sodium salt shows a higher small-angle scattered intensity and a large correlation length than the zinc salt in our sulfonated polystyrene ionomers.

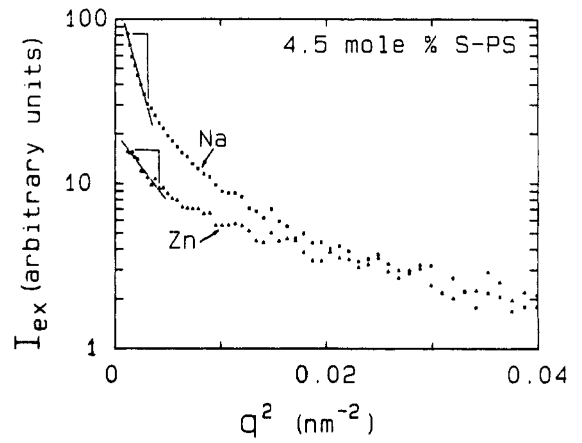

Figure 3. Plots of the excess SAXS profiles (Figure 2) in log I_{ex} versus q^2 (nm^{-2}) for the sodium and the zinc salts of S-PS. Apparent radius of gyration R_g = 39 nm for the sodium salt and 30 nm for the zinc salt, if we follow the Guinier approximation.

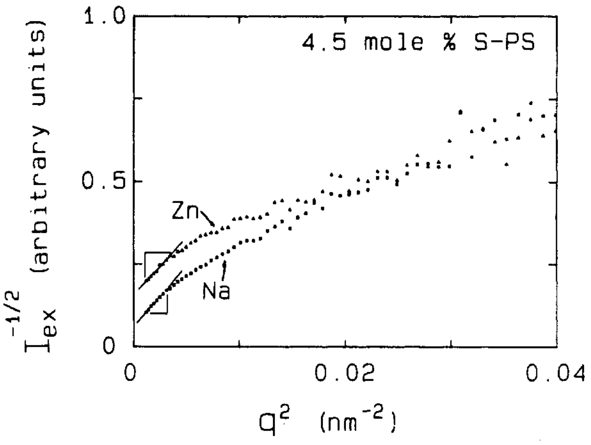

Figure 4. Plots of $I_{ex}^{-1/2}$ versus q^2 for the sodium and the zinc salts of S-PS (Figure 2). Correlation length a = 23 nm for the sodium salt and 15 nm for the zinc salt.

Galambos et al. reported a kinetic SAXS study of solvent-casted sulfonated polystyrene ionomers that did not show an initial ionic peak. After heating the sample above T_g, a growth of the ionic peak and a change in the small-angle upturn were observed. Although the authors did not compute a correlation length for the long-range inhomogeneities, they did mention that the small-angle upturn could be associated with the spatial arrangement of the ions. Recently, by using anomalous small-angle X-ray scattering (ASAXS), Cooper[12] also showed that the small-angle upturn was due to metal ions.

The long-range inhomogeneity could be added to an intraparticle structure factor so that a product of an interference term and the original structure term[3,4] might be used to explain the small-angle upturn as well as the ionic peak. On the other hand, the "interparticle interference model",[2] which assigns the ionic peak to the interparticle interference of the ionic aggregates, cannot explain the strong long-range inhomogeneity. However, lack of structure in the ionic peak prevents a definitive conclusion in distinguishing a simple ionic core from a core–shell ionic aggregate. Therefore the origin of the ionic peak must be determined by considering the entire SAXS profile, in addition to information from other techniques.

Conclusions

The excess scattered intensity due to ions at very small scattering angles can be measured for the sulfonated polystyrene ionomers of sodium and zinc salts by subtracting the scattered intensity of either the corresponding polystyrene backbone or the ionomer in acid form from the scattered intensity of the ionomer salt. This approach simulates ASAXS,[12] because the metal ions dominate the SAXS curve. The Guinier approximation failed to yield a reasonable R_g value for the ionic aggregates. Both "intra" and "inter" models failed to explain the strong small-angle upturn. The correlation function approach, which was also used by Williams et al.[13] to explain their small-angle data in a study of telechelic ionomers, resulted in correlation lengths of 23 and ~15 nm respectively for the sodium and the zinc salts of S-PS. The small-angle upturn could therefore be attributed to the long-range inhomogeneity of the ions. Studies of SAXS profiles with changes in ion content, polstyrene polydispersity, and experimental temperature are under way.

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^{23}Na NMR Study of Competitive Binding of Ions to Polyelectrolytes in Mixed Counterion Systems

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Introduction

Significant specificities in the interactions between polyions and counterions in solution have been known to exist for more than 2 decades.[1] Most of the studies on counterion-selective binding were carried out at high ionic strength by various experimental techniques. Thus, for example, Hen and Strauss[2] investigated the interactions of poly(vinylsulfonate) with hydrogen, silver, and selected alkali and alkaline-earth metal ions by dilatometry, dialysis equilibrium, and viscosity methods and found that the preference of this polyanion follows the order $Ag^+ > K^+ > Na^+ > H^+ \approx Li^+$ for the univalent cations and $Ba^{2+} > Mg^{2+}$ for the divalent cations. More recently, Mattai and Kwak[3] made use of a dye spectrophotometric method[4] to investigate polyion–counterion interactions in the mixed counterion system $M^{2+}/M^+/Cl^-$/polyion ($M^{2+} = Mg^{2+}$, Ca^{2+}; $M^+ = Na^+$, K^+; polyion = poly(styrenesulfonate), poly(galacturonate), and (carboxymethyl)cellulose). Their experiments were carried out in the presence of excess salt, and the results were compared with the prediction of Manning's two-variable theory.[5] This theory is applicable in the presence of excess salt and is formulated in terms of the dimensionless charge–density parameter, ξ, defined by

$$\xi = \frac{e^2}{4\pi k T l \epsilon_0 \epsilon_r} \tag{1}$$

where e is the elementary charge, l the projection of the intercharge distance when polyelectrolyte is considered as a cylinder, k Boltzmann's constant, T the Kelvin temperature, ϵ_0 permittivity in vacuum, and ϵ_r the dielectric constant of the solvent. These authors found that their results were in agreement with the two-variable theory in the case of sulfonated or sulfated polyions, but were in disagreement with the theoretical predictions in the case of carboxylated polyions.

According to Manning's model,[6] the charge fraction of the polyion—that is, the charge per ionic group of the polyelectrolyte—equals the constant value of $(z\xi)^{-1}$, z being the valence (without sign) of a given counterion. Thus, the number of counterions associated with or "atmospherically condensed" onto the polyanion per unit charge, P_b, is given by

$$P_b = 1 - (z\xi)^{-1} \tag{2}$$

and is independent of concentration, excess salt, and radial dimension of the polyelectrolyte.

Although considerable experimental evidence[7] supports the validity of eq 2 in concentrated solutions and in the presence of salts, it is no longer valid at low concentrations and in the absence of excess salts. This was clearly demonstrated by the ^{23}Na NMR studies of sodium poly(galacturonate), poly(mannuronate), and poly(galuronate) in aqueous solutions by Grasdalen and Kvam.[8] These authors extracted the correlation times, τ_c, from the spectral line shapes which become distinctly non-Lorentzian for τ_c exceeding 0.5 ns. Using the concentration dependence of τ_c, they showed that the data were consistent with the Poisson–Boltzmann (PB) model[9] and a theory developed by Halle et al.[10] for the quadrupolar relaxation of counterions, as testified by the relative constancy of the ^{23}Na quadrupolar coupling constant at different polyelectrolyte concentrations, the latter being calculated from the mathematical formulation of this model. It occurred to us that the study of competitive binding of counterions in the absence of salts using ^{23}Na NMR would be of interest for several reasons. In the absence of salts, a direct and simple method for studying competitive binding is available, and such a study would compliment other studies in the presence of salts. As will be shown below, our results indicate that some polyanions behave "ideally" with respect

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