Extended X-ray Absorption Fine-Structure Studies of the Internal Aggregate Structure in Lightly Sulfonated Polystyrene. 1. Determination of the Coordination Environment about the Cation

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ABSTRACT: Three lightly sulfonated polystyrenes containing 6.1 mol % sulfonate groups neutralized with Ni^{2+}, Cd^{2+}, and Zn^{2+} were studied with the extended X-ray absorption fine-structure (EXAFS) technique. Using the simulation package FEFF5, it was found that the atomic arrangement which led to the best description of the experimental data was very similar for the nickel- and zinc-neutralized materials. Nickel was octahedrally coordinated to oxygen in the first shell, while zinc was tetrahedrally coordinated to oxygen. In both cases, the second shell was sulfur atoms with a metal–oxygen–sulfur angle of 135–140°. In octahedrally coordinated nickel, nearest-neighbor metal atoms are located along one "magic angle" line and close to, if not on, an orthogonal axis, while for tetrahedrally coordinated zinc, zinc atoms are contained on a single line. Because of the finite domain size, the metal atoms at the boundary between the ionic aggregates and the polymer matrix are probably coordinated to oxygen from water. Based on the experimental error, it is possible that nickel may have two waters of hydration in the immediate coordination structure, although the fit is not as accurate as in the former case. In the cadmium-neutralized material, cadmium cations are also octahedrally coordinated to oxygen. However, simulations of 6-fold sulfonate structure are definitely inferior to those with two oxygen atoms belonging to water molecules and the remaining four oxygens from sulfonate groups. Overall, the structures are well-ordered, and some implications of these results are discussed.

Introduction

Ionomers are polymers with a small mole fraction of ionic groups covalently bonded to the polymer backbone. Because of energetic incompatibility between the nonpolar organic polymer backbone and the polar inorganic ionic groups, the ionic groups will microphase separate into ionic rich domains. Determining the structure inside these domains is extermely important in ionomer research, since this information is necessary to understand the thermodynamics and mechanism of phase separation in these materials.

Unfortunately, methods to probe internal phase structure which have been applied to other microphase-separated systems cannot be successfully utilized on ionomers. Differential scanning calorimetry, which is sensitive to the glass and/or melting temperature of each phase, does not exhibit any features from an ionic phase transition due to the well-known fact that ionic aggregates are thermodynamcially stable to the degradation temperature of the polymer. Wide-angle X-ray scattering curves do not have peaks from crystalline ordering inside the ionic phase because the aggregates are very small; hence, even if the aggregates are crystalline on a local scale, only two or three unit cells can exist in any direction. Dynamic mechanical thermal analysis (DMTA) does have a high-temperature feature which is attributed to the presence of ionic groups, but a recent theory[1] attributes this transition to the motion of immobilized polymer chains rather than ionic groups.

One of the few morphological probes which has been successfully applied to help understand internal aggregate order has been extended X-ray absorption fine strucutre (EXAFS). EXAFS is the measure of oscillations in the absorption coefficient (μ) about its mean value at energies between 50 and 1000 eV above an atomic absorption edge. An absorption edge occurs when the energy of an X-ray is sufficient to cause the ejection of a photoelectron; the K-edge corresponds to the ejection of a 1s electron. Oscillations occur because the outgoing photoelectron wave can be backscattered by neighboring atoms which leads to interference between the outgoing and backscattered waves. Qualitatively, the shape and period of the oscillations will be a function of the absorbing atom as well as the type, distance, and number of atoms around the absorbing atom. Generally, the distance between the central atom and the backscattering atom must be less than 5 Å in order for the interference to be significant.

The simplest correct theoretical description of this phenomenon was originally developed by Stern *et al.*[2] and has been labeled single-electron single-scattering theory. This theory assumes that multiple-scattering events are unimportant and that disorders, both thermal and static, are small. The fundamental equation from this theory assuming a completely isotropic sample is

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} = \sum_j N_j S_0^{\,2}(k) \frac{F_j(k)}{kR_j^{\,2}} e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda_j} \sin[2kR_j + \phi_{ij}(k)] \quad (1)$$

where $\mu(E)$ and $\mu_0(E)$ are the measured and mean absorption coefficients, respectively, at the energy E, N_j is the number of atoms of type j in the jth shell, $S_0^2(k)$ is the amplitude reduction factor which is due to excitations of electrons other than 1s electrons (for a K-edge) in the X-ray absorbing atom, $F_j(k)$ is the backscattering amplitude (called the amplitude function) from the N_j atom, R_j is the root mean square distance between the central atom and the jth atom, σ_j is the Debye–Waller factor which measures the variation in R_j about its mean, λ_i is the

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electron mean free path, and ϕ_{ij} is the phase shift (called the phase function) experienced by the photoelectron, which is a function of both the absorbing i atom and the backscattering atom. The k dependence of the amplitude reduction factor is usually quite small, and for the purposes of this paper, this factor was treated as a constant. k is called the wavevector because $2\pi/k$ is the wavelength of the ejected photoelectron. Through a simple energy balance it can be shown that:

$$k = \left[\frac{2m_e}{h^2}(E - E_0)\right]^{1/2} \qquad (2)$$

where E_0 is the absorption edge energy, m_e is the mass of an electron, and h is Planck's constant divided by 2π. EXAFS has been applied to a number of ionomers, including carboxy-telechelic polyisoprenes,[3] sulfonated and carboxylated polyurethanes,[4,5] ethylene–methacrylic acid copolymers,[6] polyurethane cationomers,[7] perfluorosulfonate ionomers,[8–11] and carboxylated and sulfonated polystyrenes.[12,13] It also should be noted that the amplitude and phase functions in these studies either were those of Teo and Lee[14] or were derived from model compounds.

A number of different cations were tested in a series of carboxy-telechelic polyisoprenes including Ca^{2+}, Sr^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}.[3] In all cases, the analysis indicated either one or two coordination shells, where the first shell was due to oxygen and the second shell was due to a cation. Because no carbon shell was found, the authors concluded that water was contained in the aggregate. Carboxylated and sulfonated polyurethanes[4,5] showed only small differences in the local environment around the cation, even though the geometries of the planar carboxylate anion and the tetrahedral sulfonate ion are quite different. For the sulfonated polyurethanes, only one shell was found for Ca^{2+}, Zn^{2+}, Cd^{2+}, Eu^{2+}, and Sr^{2+} sulfonated polyurethanes with poly(tetramethylene oxide) soft segments and toluene diisocyanate hard segments. Two or three shells were visible for the nickel-neutralized ionomer. The nickel-neutralized material was unique in that the sample preparation method and soft segment type did not seem to affect the local environment significantly, while both of these factors changed the radial structure function (RSF) in Cd^{2+}- and Sr^{2+}-neutralized materials.

Quite detailed studies have been performed on perfluorosulfonate ionomers. In the iron-neutralized ionomer with two obvious coordination shells,[9] the authors found that the first shell was fit better by two sets of oxygen atoms at different distances, while the second shell was fit with 1.5 iron atoms. However, the agreement factor for a single shell was within an acceptable range, and the introduction of a second distance provides two additional fitting parameters. The authors also tested sulfur and oxygen individually for the second shell and found that neither atom gave physically reasonable parameters. A bridged oxo strucutre was postulated similar to that found in other iron compounds.[15] A bridged hydroxy strucutre has also been postulated for this material dried under vacuum at 150 °C.[11] Studies of nickel-neutralized membranes also concluded that the second shell was due to nickel because individual sulfur and oxygen fits were not satisfactory.[8] Finally, a study of the zinc-neutralized material concluded that the second shell was due to sulfur. This conclusion was based not on the quality of fit to EXAFS data but rather on the fact that dehydration studies indicated that insufficient water molecules were present to provide four oxygen atoms for the tetrahedrally coordinated zinc. The second-shell peak was very small and corresponded to only 1.5 sulfur atoms, much smaller than four which would be necessary for tetrahedrally coordinated zinc.

Lightly sulfonated polystyrenes (SPS) neutralized with zinc[12] and nickel[13] have been previously investigated. In the zinc-neutralized material, two shells were found. The first was attributed to tetrahedral coordination of oxyen with a metal–oxygen distance of 1.97 Å. If the second shell was due to only sulfur, then based on this EXAFS data the shell would have contained approximately one sulfur at 3.15 Å. Hence, the coordination structure about zinc would have consisted of three water molecules with one sulfonate group. As the authors recognized, this probably was incorrect since local charge neutrality would not be maintained in the structure. The authors realized that the nature of the amplitude and phase functions meant that an oxygen atom coordinated at approximately the same distance as sulfur can destructively interfere with sulfur backscattering, and hence less sulfur atoms than are actually present will appear in the EXAFS signal. An excellent fit to the data was obtained if this shell consisted of four oxygen atoms and four sulfur atoms at 3.15 Å. Based on this postulate, two structures were presented which both satisfactorily explained the data. Because these structures are central to the work presented in this paper, further discussion of these arrangements appears later in this paper.

For nickel sulfonated polystyrene, three shells were found: the first shell was attributed to octahedral coordination of oxygen from waters of hydration at a distance of 2.04 Å, while the second and third shells were attributed to oxygen and sulfur from the sulfonate group at distances of 3.08 and 3.88 Å from the nickel atom, respectively. The second- and third-shell assignments were incorrect since the sulfonate groups cannot be this close to the water molecules due to prohibitive overlap between the water molecule and oxygen from the sulfonate group. The authors claim this structure is similar to zinc benzenesulfonate hexahydrate; however, the second-shell metal–oxygen distance in the hexahydrate is approximately 4.25 Å, while the third-shell metal–sulfur distance is approximately 5 Å.[16] The data to be presented shortly is very similar to the data presented previously, which is certainly reassuring. However, a structure will be presented consistent with the EXAFS pattern and with molecular packing requirements. Even more remarkable, this structure is very similar to the structure postulated for ZnSPS, which is tetrahedrally coordinated to oxygen.

The determination of the structures presented in this paper would not have been possible without the software package FEFF5.[17] This package performs *ab initio* calculations of EXAFS patterns based on user-supplied coordinates of the atomic structure and includes single- and multiple-scattering curved wave paths. Two questions should be asked about this software package: how accurate are the simulations and can different structures produce the same EXAFS patterns? To answer the first question, the EXAFS patterns were collected for a number of different inorganic compounds with a known crystal structure. These particular compounds were chosen because their structure is similar to the internal aggregate structure. The crystal structure was used to determine the information necessary to simulate EXAFS patterns with FEFF5, and comparisons between experimental and simulated patterns will be presented in this paper. Generally, the simulations were quite accurate for the first two shells, and in one case the accuracy extended to the fourth shell. Each coordination shell has one adjustable parameter, and the overall pattern has one other adjustable scaling parameter which was determined almost entirely by the first shell.

Although it is certainly possible to create the same EXAFS pattern with different structures, the known bond distances coupled with the absolute necessity to prevent overlap between atoms (whose atomic radii can be fixed within a fairly narrow range) greatly reduce the number of possible structures. The software program MATHCAD was used to solve systems of equations to determine atomic coordinates. Criteria used to develop these equations include known or EXAFS generated bond distances, oxygen–metal–oxygen bond angles, sulfonate group geometry, and third-shell symmetry in the appropriate structures. Space-filling constraints were also satisfied (i.e., two atoms cannot have overlapping atomic radii). For some structures, if the actual interatomic distances and angles were exactly known, then the atomic structure and coordinates would be unique, since the structure eliminates all rotational degrees of freedom. For other structures, packing requirements are less severe and some bond rotations are allowed. The differences between these two types of structures will be highlighted in the text.

Experimental Section

Sulfonated polystyrene with 6.1% sulfonate groups stoichiometrically neutralized with Na^+ was kindly supplied by R. D. Lundberg of the Exxon Chemical Co. In order to convert the cation to nickel, zinc, or cadmium, NaSPS dissolved in tetrahydrofuran (THF) was first passed through a column containing Amberlyst 15 resin (Aldrich Chemical Co.) to convert the SPS to the acid form. Samples were filtered and dried at room temperature in air until the samples were dry to the touch. The sample was split into three different portions at this point for further treatment. The appropriate metal salt was created by neutralizing a 10% solution in THF with a stoichiometric amount of zinc acetate dihydrate, nickel hydroxide, or cadmium acetate hydrate (all from Aldrich Chemical Co.). Salts were premixed in THF before addition to the polymer solution; if necessary a small amount of water was added to the salt solution to promote solubility. In all cases no visible powder was found after filtration of the neutralized polymer and elemental analysis (Galbraith Labs) confirmed that neutralization was within 10% of the stoichiometric amount for all samples. After drying in air to remove the bulk of the solvent, the samples were dried for 1 week at 70 °C under vacuum to remove the residual solvent. Samples were compression molded into 4 × 1 cm bars at 220 °C using 90 000 N in a platen press such that $\mu t \approx 2$ (±20%) at 100 eV above the K-edge of the neutralizing cation. t is the sample thickness. Then, samples were heated to 185 °C and quickly quenched to room temperature for reasons described in the following paper of this series.[18]

One cannot state with any certainty whether the drying conditions removed all of the residual solvent. As is argued later in the paper, the cations require a minimum number of coordinating molecules and it is probably difficult, if not impossible, to remove these molecules by any set of drying conditions. The results of this paper suggest that drying was at least close to complete since the EXAFS patterns clearly indicate that the cations are primarily coordinated to sulfonate groups, which suggests that large amounts of solvent molecules are not contained inside the aggregates.

K-edge EXAFS spectra were collected at the Cornell High Energy Synchrotron Source (CHESS). The sulfonated polystyrene spectra were collected during recent trips to CHESS. Spectra of metal oxide standards were collected by previous members of our research group at CHESS and have been presented previously.[3] Details of the sample preparation method, etc., appear in this previous publication. However, the original raw data were reanalyzed by the authors of this paper to eliminate any difference between the standards and the current SPS samples due to the data analysis procedure. Also, the signal to noise ratio of the data was much lower in these previous data sets.

For the SPS samples, 5-eV steps were used in the preedge region and the EXAFS region, while 2-eV steps were employed from 20 eV below the edge to 60 eV above the edge. Entrance slits of 0.5 mm were used to obtain high-energy resolution. Energy calibration was performed with the pure metal foil. A 15-cm ionization chamber filled with N_2 and a 30-cm ionization chamber filled with Ar, both at 1 atm, were used to monitor the incoming and outgoing intensities of X-rays respectively for the nickel and zinc edges. Because of the higher energy, both ionization chambers were filled with Ar gas for the Cd edge. A total of 12 scans (each scan lasted approximately 10 min) were collected, and these scans were added after E_0 determination before further data analysis to improve the signal to noise ratio.

After isolation of the EXAFS oscillations, the data were Fourier transformed which gave a result termed the radial structure function (RSF). The radial structure function is similar to a radial distribution function because peaks in the RSF usually correspond to distinct coordination shells. The abscissa of the RSF has units of angstroms, but the location of the peaks is shifted from the real distances as indicated in eq 1; hence, a subscript F will be used to distinguish this distance from the actual interatomic distance R. BAN, a commercial software package available from Tolmar Instruments, was used for conversion of the measured μt vs E curve to $k^2\chi(k)$ vs k, subsequent Fourier transformation, isolation of each shell, backtransformation, and application of the ratio method. All simulations were also weighted by k^2 in order to facilitate direct comparison between the simulated and experimental curves.

Many of the parameters appearing in eq 1 were determined by FEFF5 directly. For the standards, the only free parameters in eq 1 were the Debye–Waller factor for each shell and the amplitude reduction factor; all other terms either were determined by FEFF5 or were obtained from the known crystal structure. For the sulfonated polystyrenes, the metal–oxygen distance and the number of oxygen atoms in the first shell were determined by the ratio method. The ratio method[19] calculates N/N_{ref}, $E_0 - E_{0,\text{ref}}$, $\sigma^2 - \sigma_{\text{ref}}^2$, and $R - R_{\text{ref}}$ where the subscript ref represents the value for the metal oxide reference. Although E_0 can be identified from a μt vs E plot, generally E_0 should be allowed to vary when applying the ratio method to correct for errors in energy calibration and phase transferability.[20] The amplitude reduction factor was assumed to be identical for the two samples when the ratio method was applied. For the remainder of the unknown SPS structure, a model for the structure was developed using MATHCAD, and then the structure was simulated using FEFF5 and compared to the experimental spectra using the best-fit Debye–Waller factors and amplitude reduction factor.

All structures presented in this paper assume an S–O bond distance of 1.42 Å and tetrahedral geometry about sulfur. The basis for the former number comes from the S–O bond distances in Na_2SO_3,[21] zinc benzene sulfonate hexahydrate,[16] and the normal single-bond S–O bond distance.[22] The error in this number is approximately ±0.03 Å. The second assumption was the most accurate when the structure had all three sulfonate oxygen atoms coordinated to the metal cation, since the S–C single bond is expected to have some double-bond character, with important resonance structures being available with the unsaturated benzene ring. Certainly in some cases, the SO_3^- may be more planar than tetrahedral. The inability to know these parameters exactly inhibits somewhat the capability of distinguishing between different proposed structures.

Results

ZnSPS. The RSF for ZnO is shown in Figure 1 along with the result of FEFF5 simulations. Zinc oxide has a pseudohexagonal zincite unit cell,[23] and Table 1 gives the positions of each atom relative to the zinc atom origin. The atoms which are grouped together have the same chemical environment for the purposes of FEFF5 simulations. This table demonstrates the precise detail which is necessary to use FEFF5. As Figure 1 shows, the simulation predicts the position of the peaks in the RSF for the first four coordination shells, a remarkable achievement given that this fit has only five adjustable parameters. Indeed, the peak shapes and heights were described very well for the first two shells. On the basis of simulations reported here and elsewhere,[7,24] FEFF5 quantitatively predicts features due to the first two

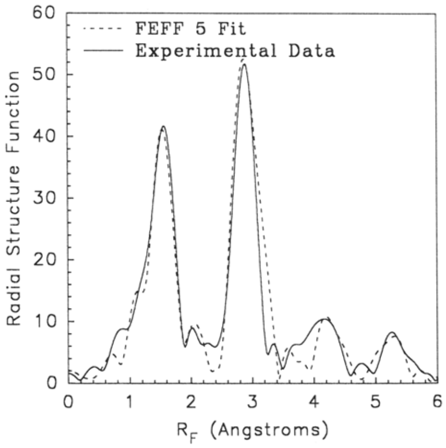

Figure 1. RSF for zinc oxide and FEFF5 simulations. The Debye–Waller factors for shells 1 and 2 = 0.001 Å^2, for shell 3 = 0.004 Å^2, for shell 4 = 0.007 Å^2, and for shell 6 = 0.005 Å^2. All other scattering paths were arbitrarily given a Debye–Waller factor of 0.006 Å^2. The amplitude reduction factor for the simulation was 0.66.

Table 1. Atomic Coordinates for Zinc Oxide

X (Å)	*Y* (Å)	*Z* (Å)	atom
0	0	0	Zn
0	0	1.99148	O(1)
-0.93802	-1.62475	-0.61177	O(2)
-0.93802	1.62475	-0.61177	
1.87604	0	-0.61177	
-0.93802	-1.62475	-2.60325	Zn(3)
-0.93802	1.62475	-2.60325	
-0.93802	-1.62475	2.60325	
1.87604	0	-2.60325	
-0.93802	1.62475	2.60325	
1.87604	0	2.60325	
0	3.24950	0	Zn(3)
0	3.24950	0	
-2.81415	1.62475	0	
2.81415	1.62475	0	
-2.81415	-1.62475	0	
2.81415	-1.62475	0	
-3.75209	0	-2.60325	Zn(4)
-3.75209	0	2.60325	
1.87604	3.24950	-2.60325	
1.87604	3.24950	2.60325	
1.87604	-3.24950	2.60325	
1.87604	-3.24950	-2.60325	
0	0	-5.20650	Zn(5)
0	0	5.20650	
-3.75209	-3.2495	2.60325	Zn(6)
-3.75209	3.2495	2.60325	
-0.93802	-4.87425	2.60325	
-0.93802	4.87425	2.60325	
4.69011	-1.62475	2.60325	
4.69011	1.62475	2.60325	

coordination shells accurately, but at higher distances the results are not as accurate.

The RSF for ZnSPS shown in Figure 2 has only one major peak near R_F = 1.5 Å, which is due to four oxygen atoms at 1.954 ± 0.010 Å. The distance is consistent with both FEFF5 simulations and application of the ratio method using ZnO as a reference. The error is 2 standard deviations and was calculated from the data presented in the second paper of this series.[18] The zinc–oxygen distance is consistent with the work presented in an earlier study.[12] As also noted in this previous study, the Zn–O first-shell coordination number and the interatomic distance are interrelated in inorganic compounds, and the values presented here are consistent with this relationship.

The single peak of Figure 2 is markedly asymmetric, and there appears to be a number of small peaks between R_F = 2 and 3.5 Å causing this asymmetry. This RSF is quite different than the RSF presented in Figure 2 of ref 12, since the second-shell peak was much more resolved in this previous study. Some of the difference might be attributed to k^3 rather than k^2 weighting; however, k^3 weighting of our data did not significantly improve the peak separation. The effect could also be due to improper background subtraction by the former authors as an inspection of Figure 1 in ref 12 would suggest. This conclusion is based on the presence of a peak at low R_F; generally such peaks are due to improper background subtraction. Another possibility was that the ZnSPS samples in this earlier study contained more water in the zinc coordination environment, which could cause an increase in the second-shell peak height as discussed more fully below.

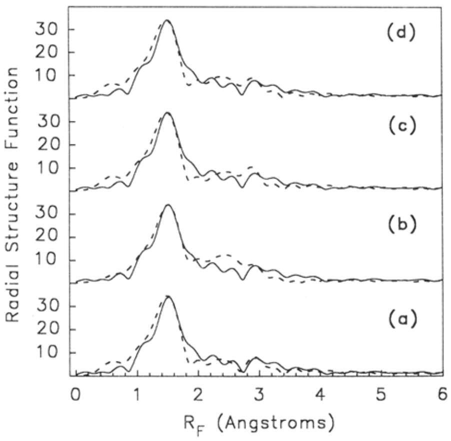

Figure 2. RSF for ZnSPS, with the solid line representing the experimental data (same for all the plots) and the dashed line representing the FEFF5 simulation. The dashed line in part a is the simulation for the structure shown in Figure 3. The dashed line in part b represents the simulation of Figure 3 with the third-shell oxygen atoms omitted from the structure. The dashed line in part c is the simulation with arbitrarily shifted third-shell oxygen atoms as indicated in the text, while in part d two of the sulfonate groups shown in Figure 3 have been replaced by water molecules. The fitting parameters for all the simulations were a Debye–Waller factor for all shells of 0.006 Å^2 and an S_0^2 of 0.786.

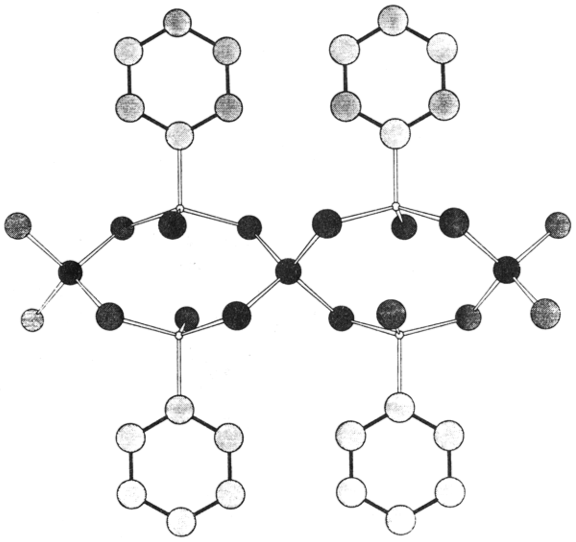

Figure 3. Possible structure for ZnSPS. The small filled cirlces represent zinc atoms, the larger filled circles represent sulfur atoms, and the largest unfilled circles represent oxygen atoms.

The results of the best-fit simulation for ZnSPS are shown as the dashed line in part a of Figure 2, while the structure used to generate the atomic coordinates is shown in Figure 3. Because of the lack of features after the first peak in this study, the second-shell zinc–sulfur distance was assumed to be the same as found in ref 12. As discussed in the Introduction, these authors of ref 12 made a very insightful observation. They realized that the amplitude and phase functions of sulfur and oxygen were such that the EXAFS signals could partially cancel if the distances of the two atoms to the central atom were about equal. This observation was based on the wavefunctions of Teo and Lee[14] and also by comparison of experimental data from first-shell backscattering in ZnO and ZnS. The dashed curve in part b of Figure 2 shows the FEFF5-simulated RSF if the four approximately equidistant oxygen atoms were not included in the simulation. As is apparent by comparing parts a and b of Figure 2, the second-shell peak height due to sulfur is much larger in the latter case.

Even without considering water, another possibility besides Figure 3 still exists for the local coordination strucutre about zinc. It is possible that the four sulfonate groups which have oxygen atoms coordinated to one zinc atom also have oxygen atoms coordinated to four zinc atoms rather than only two. If the ionic aggregates were large, one would expect the latter to dominate since this is a more efficient packing method. More importantly, if four sulfonate groups were bonded to four different zinc atoms, a rotational degree of freedom would allow the metal–oxygen third-shell distance to vary. The dashed line in part c of Figure 2 shows the results of a simulation using the same parameters employed in part a of Figure 2; however, the oxygen atoms have been arbitrarily displaced by ±0.05 and ±0.10 Å about the value used previously. As is clear, even these extremely small displacements cause a significant increase in the higher order peak heights, indicating that the cancellation is much less effective. Hence, only structures which force the oxygen atoms into a fixed position will have a significant cancellation effect. The only structure which does this is the linear structure shown in Figure 3.

If water was present in the coordination environment about zinc, then the symmetric structure could not exist and one would expect the remaining sulfonate groups to be bonded to different zinc atoms. The dashed curve in part d of Figure 2 shows the result if two of the sulfonate groups are replaced by water and all other atomic coordinates remain the same as in Figure 3. Again, however, the position of the oxygen atoms on the remaining sulfonate groups would vary and the fit would not be as precise as indicated by this curve since the two remaining sulfonate oxygens were fixed in the positions shown in Figure 3. Perhaps the linear coordination structure shown in Figure 3 might terminate at the aggregate/matrix interface with two water molecules.

NiSPS. Nickel oxide has a simple cubic crystal structure with $a = 4.1768$ Å.[21] Except for the first coordination shell, oxygen atoms were not included in the atomic coordinates for FEFF5 since simulations indicated that the third coordination shell oxygen atoms contributed very little to the RSF. Figure 4 compares the results between the measured RSF and the simulated RSF. The simulation underpredicts the first ($R_F \approx 1.6$ Å) and overpredicts the third ($R_F \approx 3.8$ Å) shell peak heights relative to the second ($R_F \approx 2.5$ Å) Ni–Ni peak height and does not predict the higher order peaks. However, the location of these first three peaks matched very well with the experimental data.

The experimental RSF for NiSPS is shown as the solid curves in Figure 5. In agreement with the previous paper,[13] the first shell was composed of six oxygen atoms at a distance of 2.04 ± 0.01 Å. Sulfur atoms at a distance of 3.24 ± 0.01 Å from the central nickel atom comprise the second shell. R was calculated for the second shell from FEFF5 simulations. As mentioned previously, the error is from calculations given in the second paper of this series.[18] The Ni–O–S angle is 135–140°C, identical to the Zn–O–S angle in ZnSPS. Based strictly on peak heights without any interfering oxygen atoms, this result indicates that approximately three sulfur atoms are located at 3.24 Å. Once again, however, nearby sulfonate oxygen atoms significantly lowered the peak intensity of the second shell.

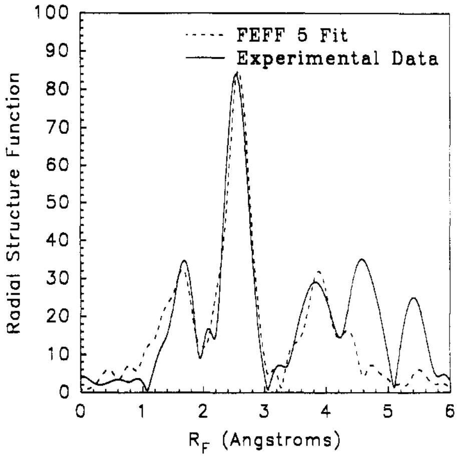

Figure 4. RSF for NiO and FEFF5 simulation. The Debye–Waller factor for the first shell was 0.0076 Å^2, the Debye–Waller factor for the second shell was 0.0046 Å^2, and the value of all the other shells was 0.006 Å^2, S_0^2 was 0.64.

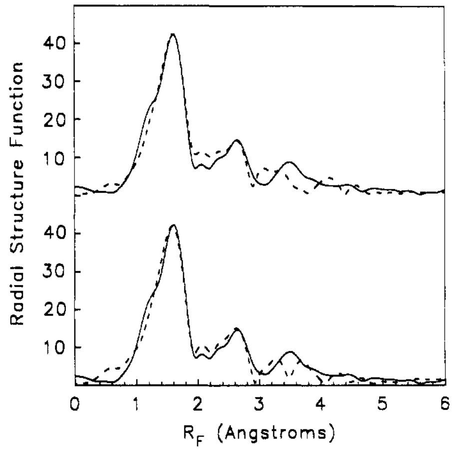

Figure 5. RSF for NiSPS simulation, with the solid line representing the experimental data (same for both plots) and the dashed lines representing the FEFF5 simulation. The bottom dashed curve represents the simulation for the structure shown in Figure 6. The Debye–Waller factor for the first shell was 0.0075 Å^2, for the second 0.0085 Å^2, for the third 0.005 Å^2, and for all remaining shells 0.007 Å^2. S_0^2 was 0.93. The top dashed curve is the simulation for the structure shown in Figure 7a. The Debye–Waller factor for the first shell was 0.0075 Å^2, for the second 0.0046 Å^2, and for all remaining shells 0.007 Å^2. S_0^2 was 0.865 for this simulation.

A large number of atomic arrangements were considered as possibilities for the local structure about nickel in NiSPS. The best-fit structure is shown in Figure 6 and produced the RSF shown as the bottom dashed curve in Figure 5. In this example, three sulfonate groups are coordinated to two nickel atoms, while the third remaining oxygen for these sulfonate groups is coordinated to a nickel atom located close to (if not on, depending on bond distances and angles) an orthogonal axis. Therefore, the nickel atoms lie on the "magic angle" line and also very possibly on the orthogonal axis, which makes for a very simple unit cell. The magic angle line represents the line where the magnitudes of the x, y, and z coordinates are identical. In fact, the authors were not able to produce a structure which had all six oxygens belonging to sulfonate groups and did not have this nickel atom sharing without

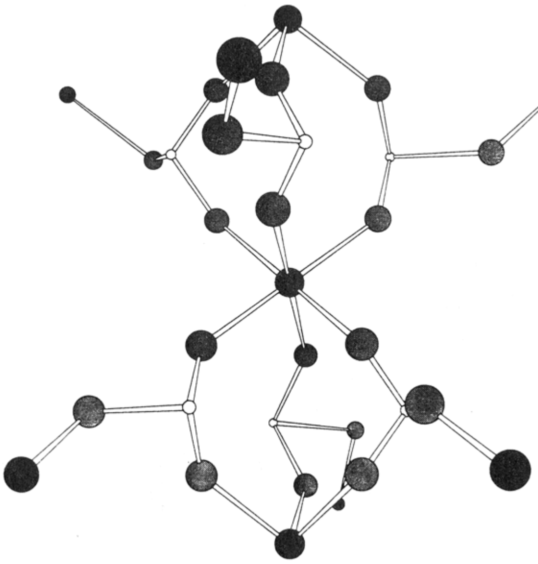

Figure 6. Structure of the local environment about nickel used to create the RSF in Figure 5. In this structure, all oxygens in the first coordination shell come from sulfonate groups and two oxygens from three sulfonate groups share two nickel atoms. Symbols as in Figure 3.

significant prohibitive interatomic overlap. The third peak in the RSF is not fit very well by this model structure however. This failure is not due to artifact in this particular data set since RSFs of stretched samples also show the third feature at this position.[18]

Although no other basic structure is possible without introducing water, a number of structures with water can reproduce the RSF reasonably well, although not as well as the structure without water. Two different structures with four sulfonate groups and two waters of hydration are shown in Figure 7. In one case, sulfonate groups share a nickel atom, while in the other example, each sulfonate group is linked to a different nickel atom. In the latter case, a rotational degree of freedom would allow the third-shell oxygen distances to vary widely and hence the cancellation would not be as efficient. The top dashed curve of Figure 5 shows the FEFF5 simulation for the structure of Figure 7; the fit in the second and third shells is not as good as found in the bottom curve. However, on the basis of the accuracy of the fit to model compounds, the authors do not believe that a sufficient difference between the sets of curves shown in Figure 5 exists to conclude that Figure 6 presents a better picture of the local environment about nickel than Figure 7. Further, the 6-fold structure cannot propagate throughout the entire aggregate, since near the edges of the aggregate this structure cannot persist. Therefore, some nickel atoms must have a local structure more like Figure 7a although the best-fit local structure sill remains the 6-fold sulfonate coordinated nickel.

CdSPS. FEFF5 simulations and experimental data for the simple cubic compund CdO ($a = 4.6954$ Å) are shown in Figure 8. In this case, the peak positions are not correctly predicted by FEFF5; the Cd–O first ($R_F \approx 1.6$ Å) shell is approximately 0.04 Å closer than the simulation predicts, while the Cd–Cd second ($R_F \approx 3.1$ Å) shell is approximately 0.04 Å further than the prediction. The peak heights and shapes are very accurate; even the two small peaks between the major coordination peaks are predicted by FEFF5. Once again, the simulation does not agree with the experimental data for higher coordination shells.

Cadmium in CdSPS is also octahedrally coordinated to oxygen in the first shell, and the Cd–O distance is 2.340 ± 0.011 Å based on the ratio method with CdO as the reference compound. No obvious second peak is present in the RSF of Figure 9; however, the marked asymmetry of the peak toward higher R_F suggests significant back-scattering by other atoms. Assuming a Cd–O–S angle of 138° and the structure shown in Figure 6, the simulated RSF is shown by the bottom dashed line of Figure 9. The atomic coordinates of the first-shell oxygen have been adjusted to 2.30 Å to reflect the mismatch between the experimental and theoretical RSF for CdO. A significant disagreement between the experimental and theoretical curves exists for the 6-fold model, while the top dashed cuve, which is based on the structure shown in Figure 7a, fits the data much better. As the reader might infer from these figures, cancellation of sulfur backscattering by oxygen is much less important in CdSPS because of the amplitude and phase functions in combination with the greater Cd–S and Cd–O distances, which makes it simpler to distinguish between different proposed structures since features from the second-shell sulfur atoms are more prominent. A simulation with four oxygen atoms from water and only two sulfonate oxygen atoms (not shown)

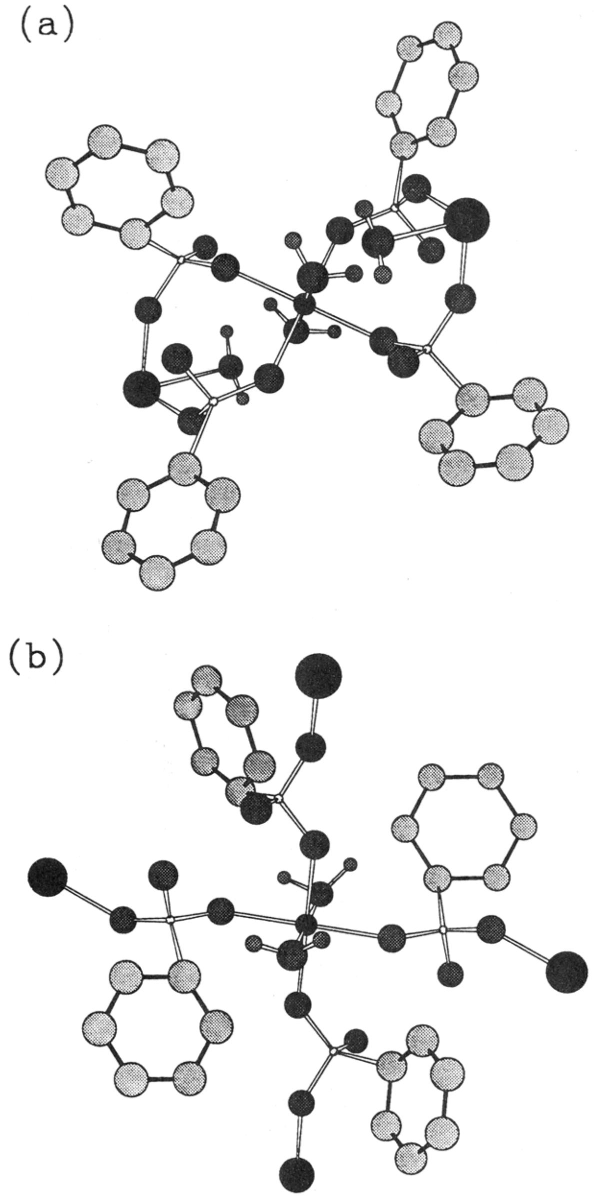

Figure 7. Structure of the local environment around nickel which contains two waters of hydration. (a) Two sulfonate groups share two zinc atoms. (b) Each sulfonate group which has one oxygen coordinated to a nickel atom has a different nickel atom for the other coordinating oxygen atom. Symbols as in Figure 3.

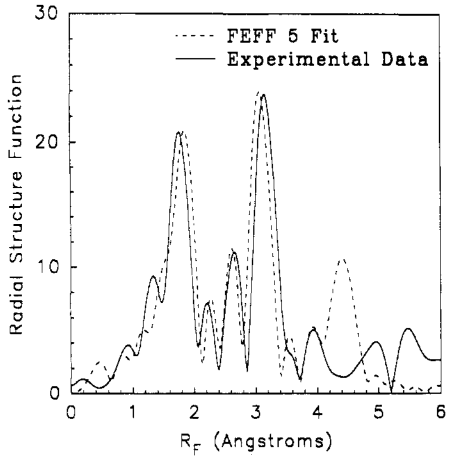

Figure 8. RSF for CdO and FEFF5 simulation. The Debye–Waller factor for the first shell was 0.005 Å^2, the Debye–Waller factor for the second shell was 0.006 Å^2, and the value for all other paths were 0.006 Å^2, $S_0{}^2$ was 0.45.

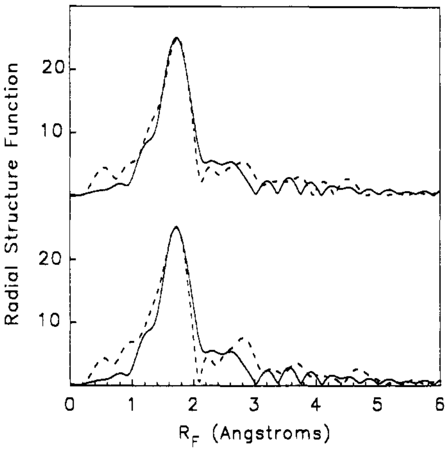

Figure 9. RSF for CdSPS simulation, with the solid line representing the experimental data (same for both plots) and the dashed line representing the FEFF5 simulation. The bottom dashed curve represents the simulation for the structure shown in Figure 6. The Debye–Waller factor for all shells was 0.0075 Å^2, and $S_0{}^2$ was 0.93. The top dashed curve is the simulation for the structure shown in Figure 7a. The Debye–Waller factor for the first shell was 0.005 Å^2 and for all the other shells was 0.006 Å^2. $S_0{}^2$ was 0.82.

could not adequately reproduce the experimental RSF since the second-shell features were too small.

Discussion

Many of the previous EXAFS studies of ionomers have attributed second-shell peaks to cation–cation coordination[3,5,9,11] rather than a combination of sulfur and oxygen atoms as is proposed in this paper. Generally, cation–cation distances on the order of 3 Å are proposed for this coordination. It is difficult to understand in many cases how this can be possible, given the presence of at least four, if not six, first-shell coordinated oxygen atoms at a distance of approximately 2 Å.

As originally argued for the perfluorosulfonate ionomers,[9,11] one way to relieve this space-filling problem is to have bridging oxygen atoms or hydroxyl groups. An atom or functional group is bridging when it resides in the coordination spheres of two different metal cations. With the exception of iron and copper, this sort of bridging is extremely rare. Also, there are only a handful of examples of bridging in compounds which contain sulfonate groups. Finally, when such bridging occurs in small-molecule compounds, there are generally two discrete metal–oxygen bond distances and two distances have not been noticed in many previous studies.

On the basis of these arguments as well as the results presented in this paper, we believe that the cation–cation second-shell coordination proposed in these previous papers was incorrect in some cases and the second shell was actually due to sulfur atoms (or carbon in carboxylate ionomers). Because the RSF was distorted due to nearby oxygen atoms, fits with only sulfur or carbon yielded physically unreasonable parameters which led the authors to reject these structures. The structures shown in this paper also have the added benefit that the negative charge is close to the metal cation, unlike structures which postulate a water first shell and cation second shell. To determine the characteristics of the second shell of any ionomer, one must consider possible interference effects, since the exact shape of this second-shell peak in the RSF can be highly dependent on any nearby atoms. Finally, one must only consider structures which fulfill a series of equations which preserve space-filling arguments as well as geometrical constraints. On the basis of the similarity of the RSFs for a given cation in different sulfonate ionomers found in the literature to the ones presented in this paper, the authors suggest that the local environment is essentially only a function of the metal cation and the ionic plasticizer content. Further comparisons are not really possible because the raw data were not collected or analyzed in the same way.

Electron spin resonance studies (ESR) of hydrated perfluorosulfonate ionomers have found that a Cu^{2+} cation can exist in two environments: one in which the cations are separated by more than 10 Å and another where the cation–cation separation distance is 5.0 ± 0.2 Å.[25] The latter was thought to correspond to a Cu^{2+}–Cu^{2+} dimer with a structure very similar to the ones presented in this paper, except that only two cations were involved with just three of the six oxygens from sulfonate groups. It was not apparent from this paper and others by the same author[26–28] whether structures such as the ones presented in this current paper would be inconsistent with ESR results, plus water contents in the perfluorosulfonate samples were certainly much higher than in the present study. Clearly, however, this distance is inconsistent with the bridging hypothesis and consistent with the types of structures presented in this paper.

An important factor when considering the internal aggregate structure is the overall shape and form of the aggregate. SAXS modeling results[29] indicate that the aggregates are on the order of approximatley 1–2 nm. When one considers the size of the structures presented in this paper, it becomes clear that these aggregates can only contain a few metal cations. The real purpose of water or other polar solvents in ionomers may be to provide a coordination site for the metal cations located on the edges of the aggregates. Hence, the finite aggregate size may explain the high resistance to dehydration found in most ionomers.

Small-molecule compounds which have an analogous structure to the ionic groups would greatly improve the ability to absolutely determine the structure of the aggregates. In our opinion, the best model compounds for SPS with water in the first coordination shell are the benzene and toluene sulfonate hexahydrates. In these compounds, the second coordination shell is oxygen over 4 Å away from the metal cation. The RSFs of SPS ionomers in this present study clearly have features from a coordination shell closer than 4 Å which strongly suggests that cations are not surrounded completely by water, a hypothesis which has been advanced in other EXAFS studies. However, as was pointed out earlier, some water is probably present because aggregates have finite size. Unfortunately, the authors are not aware of any published crystal structures for these compounds with lower water contents.

The water content of ZnSPS with 7.3 mol % of the benzene rings para-substituted with sulfonate groups was discussed in a recent paper by MacKnight et al.[30] These authors reported that drying under vacuum at 70 °C for 1 day produced a material with approximately two water molecules for every zinc cation, which based on the results presented here would suggest tetrahedral coordination with two sulfonate oxygens and two water oxygens. The drying conditions in this study were identical to those in the previous study except the drying time was 1 week rather than 1 day. Also it was not clear from this paper how precise the ratio of water to zinc was; for example, a reasonable aggregate size coupled with the model presented in Figure 4 assuming two terminal water molecules would suggest that the ratio of water to zinc atoms is approximately 1. It was also claimed that drying at 100 °C for 1 day under vacuum removed all of the residual water. This latter claim is very hard to justify because the aggregate finite size strongly suggests that some water must be present to fill the coordination environment of the cations located at the edges of the aggregate. The other possibilities are that the cation local environment remains unfilled (extremely unlikely because of the high energies involved) or that some other atom fulfills the coordination sphere of zinc; however, there are no likely candidates. Finally, based on the similarity of the FTIR spectra, the authors found that the fully hydrated ZnSPS had a local cation environment very similar to zinc toluenesulfonate hexahydrate. Hence, since zinc was 4-fold rather than 6-fold coordinated to oxygen, clearly zinc was not surrounded by water molecules in this current study.

If the ionic groups were isolated in the matrix, one would expect at most two coordinating sulfonate groups, with the remainder of the coordination environment consisting of waters of hydration. Based on FEFF5 simulations presented in this paper, there are more than two sulfonate groups surrounding the metal cation. This indicates that the vast majority of the ionic groups in a sulfonated polystyrene containing 6.1 mol % sulfonate groups are contained within aggregates. ^{23}Na NMR studies of this same ionomer neutralized with sodium also show that an extremely small number of ionic groups are isolated in the polymer matrix.[31]

Conclusions

Three different sulfonated polystyrenes, each with 6.1 mol % sulfonate groups, were studied by EXAFS, and a number of different internal aggregate structures were simulated by the software package FEFF5 and compared with experimental data. Simulations indicate that zinc atoms in ZnSPS were all contained on one line in a very efficient linear structure. The best-fit structure for NiSPS had a very analogous arrangement to ZnSPS, except nickel was octahedrally rather than tetrahedrally coordinated. The best-fit structure for CdSPS had two waters of hydration surrounding the cadmium along with four other oxygens from sulfonate groups. These studies illustrate the importance of incorporating interference of phase and amplitude functions when simulating EXAFS patterns. Finally, the finite size of aggregates suggests that water or some other small coordinating molecule must be present in order to satisfy the coordination needs of the metal cation at the aggregate boundaries where the repeat structure terminates.

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