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Small-Angle Neutron Scattering from Polypentenamer Sulfonate Ionomers

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ABSTRACT: The physical structure of polypentenamer sulfonate ionomers has been investigated by small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS). For a 17% cesium salt, a SAXS peak is observed in the dry state at a value of the scattering vector $Q = 0.18$, but this ionomer peak is undetectable by SANS. The addition of several water molecules per salt group affords adequate neutron scattering contrast to identify a scattering maximum corresponding to the X-ray peak. SANS maxima are also observed in swollen 5.8% and 12% polypentenamer ionomers as well as in hydrogenated ionomers. Higher water contents appear to effect a physical change in the water-swollen ionomers—the peak position shifts to much lower angles and the peak intensity greatly increases. The SANS results are similar to those obtained from a fluorocarbon sulfonate ionomer and show behavior consistent with a phase-separated morphology.

Introduction

Ionomers are defined as copolymers containing predominantly linear backbones and less than about 10 mol % neutralizable side groups. Over the past decade, considerable research has been focused on determining the structure and state of aggregation of the ionic groups in the bulk. However, this important question has not as yet been fully answered. The literature concerning ionomers has become sizable and a suitable introduction to the subject may be found in two recent books and a review.[1-3] From structural studies employing many different techniques, several models of the structure of ionomers have been suggested, although we shall be concerned in this paper with only one of these, which we believe to be generally applicable.[4] The model envisages the presence of at least two kinds of ionic aggregates, referred to as multiplets and clusters.[5] The multiplets consist of isolated ion pairs, quartets, etc. which are not phase separated from the hydrocarbon matrix. The clusters consist of the order of 100's of ion pairs and have dimensions in the 10–50-Å range. For amorphous polymers this model implies a two-phase structure consisting of dispersed ionic clusters in a continuous matrix of the hydrocarbon chain segments and the isolated multiplets. It is quite remarkable that all ionomers, regardless of backbone type or the chemical nature of the ionic moiety, appear to have similar structure and properties.

The most striking feature of ionomers is a scattering maximum observed at low angles in both small-angle X-ray and small-angle neutron scattering patterns. This scattering maximum or peak corresponds to a Bragg spacing of between 20 and 90 Å, depending upon the exact chemical structure of the ionomer and the presence or absence of polar impurities such as water. The so-called "ionomer peak" was first observed by Wilson et al.[6] and persists in the melt up to the polymer decomposition temperature. In general, this peak is absent from the free acid form of hydrocarbon copolymers but is observed for the sulfonic acid form of fluorocarbon ionomers.[7]

The ionomer peak shifts to smaller scattering angles (larger Bragg distances) in the presence of polar impurities such as water or alcohols.[8] Here, the water molecules are assumed to be preferentially absorbed by the polar ionic clusters. For water-saturated ethylene/carboxylate ionomers, the small-angle peak is no longer observable by small-angle X-ray scattering, but the scattering curve still reveals the presence of particles having dimensions of about 17 Å.[9]

The great majority of ionomer scattering studies have proposed either intracluster interference or intercluster interference to explain the existence of the ionomer peak. The exact nature of the structure of the clusters remains unclear, but experiments suggest a cluster dimension of about 3–13 Å embedded in the hydrocarbon matrix containing randomly dispersed multiplets. A recent deformation study of an ethylene/cesium carboxylate ionomer has shown the X-ray peak position to be azimuthally dependent on sample elongation.[10] This dependence was best fit by a lamellar intracluster scattering model but could also be fit by a spherical intracluster scattering model.

Ionomers based on lightly sulfonated polypentenamer have been synthesized and well characterized by Rahrig et al.[11,12] In both the amorphous elastomeric form and the hydrogenated semicrystalline form, these polymers exhibit the physical, electrical, and mechanical properties commonly observed for ionomers. A preliminary small-angle neutron scattering study of a sulfonated polypentenamer ionomer has revealed a high-intensity small-angle maximum for a water-saturated sample.[9] The results of that study suggest that when saturated, all of the water is present in a separate phase.

In the work reported in this paper, we have investigated by small-angle X-ray and small-angle neutron scattering the morphological structure of sulfonated polypentenamer films. Samples covering a range of sulfonate contents and having both unsaturated, amorphous backbones and saturated, semicrystalline backbones have been studied. To examine the effect of water on the ionomer morphology, we have employed water contents ranging from zero to saturation. Ionic scattering peaks were observed with Bragg spacings between 30 and 90 Å, depending on the ionic content and the amount of water absorbed.

Experimental Section

The sulfonated polypentenamers were prepared by the method of Rahrig et al.[11] The starting polypentenamer was obtained from Dr. N. Calderon of the Goodyear Tire and Rubber Co. and is the same as that previously used. The sulfonation reaction was conducted in dilute chloroform solution using a 1:1 complex of sulfur trioxide to triethyl phosphate. Polymer isolated in the sulfonic acid form was found to be unstable; therefore the reaction solution was precipitated into dilute aqueous base to convert the product directly to the sodium or cesium salt. Because of the 5 carbon repeat units for polypentenamers, the ionic group content per 100 carbon atoms equals the mole percent divided by 5. The

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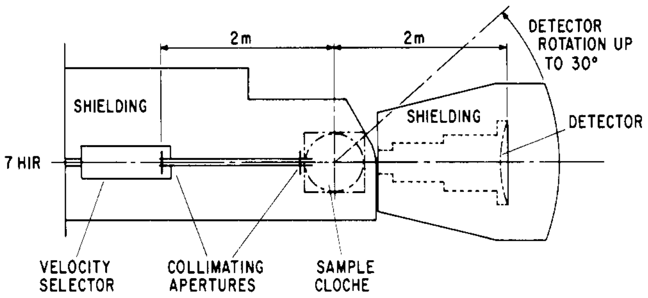

Figure 1. Schematic representation of the small-angle scattering apparatus at AERE, Harwell.

sulfonated ionomers were subsequently stabilized with antioxidant, and films were compression molded at 403 K with slow cooling under pressure. Hydrogenation of the residual unsaturation in the sulfonated ionomers was accomplished by using toluenesulfonohyrazide as the homogeneous catalyst source according to the method of Lenz.[13]

Water absorption was achieved by two methods. The first was by immersion of films at room temperature for various periods of time followed by sealing the soaked film in a dry glass ampule to ensure equilibration. For the lower levels of water uptake, dried films were suspended over measured volumes of water in sealed ampules and allowed to absorb water vapor at room temperature. Water-containing films were prepared at least 1 week before the scattering experiments to allow for equilibration.

The SANS experiments were carried out with the D-11 spectrometer[14] at the Institut Laue-Langevin (ILL), Grenoble, France, and with the small-angle scattering apparatus (SAS) at AERE Harwell, Berkshire, U.K. A schematic of the SAS is presented in Figure 1. The sample-to-detector distance is fixed at 2.0 m so that the range of scattering vectors, $\tilde{Q}$, is varied by changing the speeds of the rotating wavelength selector.

At a wavelength of 6 Å, the neutron flux obtained from the Harwell PLUTO reactor is 2.8×10^4 n compared to 4×10^6 n for the D-11 in Grenoble. Typical counting times for D-11 experiments were about 20 min while times were 2–6 h on the SAS.

The sample chamber of the SAS is under vacuum, so to prevent loss of water the ionomer films were sealed between quartz windows with a rubber O-ring gasket in a specially designed sample cell. In both experiments, detector normalization was carried out by using the incoherent scattering from a pure water sample held in a linear quartz cell under identical experimental conditions. Several wavelengths between 4.2 and 6.1 Å were used.

Small-angle X-ray scattering experiments were conducted at Queen Elizabeth College (University of London) with a Kratky camera. Copper radiation ($K\alpha$) was used in conjunction with a nickel filter. The sample-to-detector distance was 25.3 cm and a stepping motor controlled counter was used to scan the small-angle range.

Contrast Factors

The normalized coherent scattering intensity for SANS can be represented by[9]

$$I = K^* \langle F^2(Q) \rangle \qquad (1)$$

where the structure factor F is

$$F = \int_0^\infty S(\tilde{x}) \exp[-2\pi i(\tilde{Q}\cdot\tilde{x})]\, d\tilde{v}_x \qquad (2)$$

where $S(\tilde{x})$ is the shape factor, $d\tilde{v}_x$ is a differential volume element, and $\tilde{Q}$ is the scattering vector ($|\tilde{Q}| = (4\pi/\lambda) \sin(\theta/2)$, where λ is the wavelength of the neutrons and θ is the scattering angle). The factor K^* is directly proportional to the contrast factor

$$K = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \qquad (3)$$

b_1 and b_2 are the scattering lengths per molecular unit in phases 1 and 2, and v_1 and v_2 are the molar volumes of these molecular units.

Table I
Scattering Lengths ($\bar{b}$) and Contrast Factors (K) for Chemical Units in Ionomers[a]

chemical unit	$\bar{b} \times 10^{12}$, cm	$K \times 10^{28}$, cm^{-2}
$(CH_2)_3CH{=}CH$	0.0041	1.54
$(CH_2)_3CH{=}C(SO_3^-Cs^+)–$	0.0165	
$(CH_2)_3CH{=}CH$	0.0041	84
D_2O	0.096	
CH_2CH_2	−0.0071	106
D_2O	0.096	

[a] Contrast factors are calculated assuming equal densities.

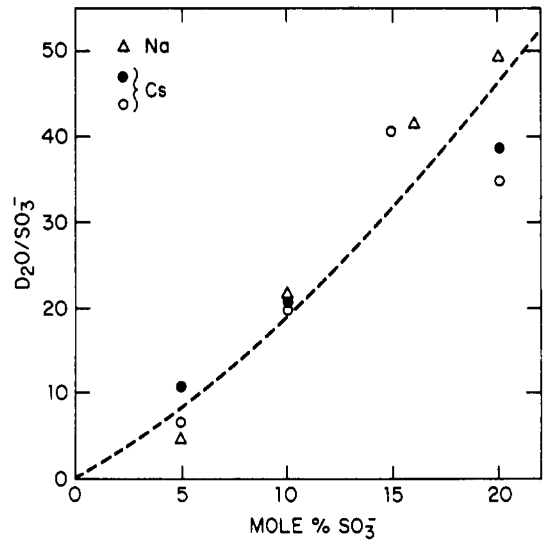

Figure 2. Ratio of D_2O to sulfonate groups as a function of sulfonate ion content.

Table I contains scattering lengths for the various chemical units used in this study along with contrast factors between the hydrocarbon and ionic phases. This table shows the neutron contrast between polypentenamer chains and the cesium sulfonate groups is small. However, the contrast between D_2O and either the polypentenamer or hydrogenated polyethylene-like backbone chains is substantial. For reference, the neutron contrast between undeuterated polystyrene and perdeuterated polystyrene is 53×10^{-28} cm^{-2}.

Results and Discussion

The amount of water uptake at equilibrium saturation was determined over the range of sulfonation levels examined. Figure 2 shows that as the amount of ionic material increases, the greater is the film's ability to absorb water. The water molecules must be preferentially absorbed by the ionic phase, and as shown by Roche et al.,[9] for a 20 mol % cesium salt of a sulfonated polypentenamer containing 47% water, essentially all the water is present in a separate phase from the hydrocarbon portion of the polymer. These results also indicate that at higher degrees of sulfonation these ionomers may become water soluble.

The small-angle X-ray scattering curve for the dry 17% Cs salt is shown in Figure 3. Here, a peak is evident near a scattering vector of $Q = 0.18$; $Q = (4\pi/\lambda) \sin(\theta/2)$. This peak position corresponds to a Bragg spacing of 32 Å. As discussed in the Introduction, this "ionomer peak" has been taken as evidence for structural regularity within the

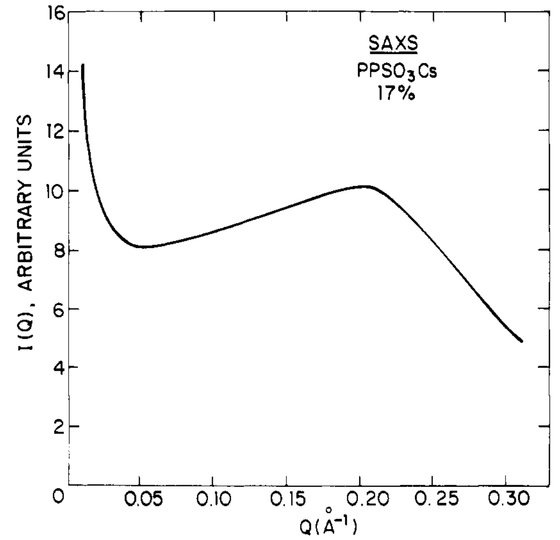

Figure 3. Smeared X-ray scattered intensity vs. scattering vector, Q, for the dry 17% cesium ionomer.

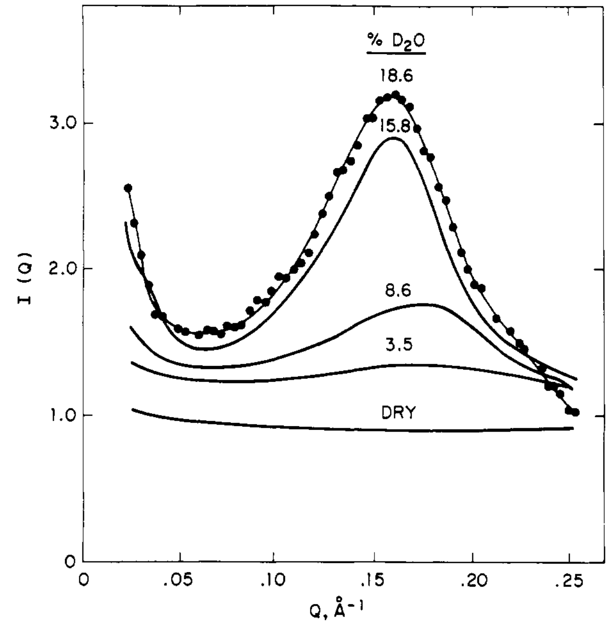

Figure 4. Neutron scattered intensity vs. scattering vector, Q, for the 17% cesium ionomer. Numbers above each curve indicate weight percent D_2O.

clustered ionic phase. The X-ray scattering contrast is due to the high electron density cesium atoms.

SANS results for this same 17% cesium salt are displayed in Figures 4 and 5. For the dry film, there is no evidence of a scattering maximum. Reference to Table I reveals that the neutron scattering contrast factor is very small for the dry sample. However, as small amounts of D_2O are added to the ionomer, the SANS peak becomes detectable. As the amount of water increases, the neutron scattering contrast between the deuterium atoms and the hydrocarbon matrix increases. In effect, D_2O molecules are "tagging" the location of the cesium sulfonate groups. At very high D_2O contents (Figure 5), the peak moves considerably to smaller Q values.

Similar scattering curves are obtained for the 5.8% and 12% ionomers, and the results are summarized in Table II. With no water present, there is no SANS peak observed. But when small amounts of D_2O are absorbed by the ionomer, the ionomer peak is apparent.

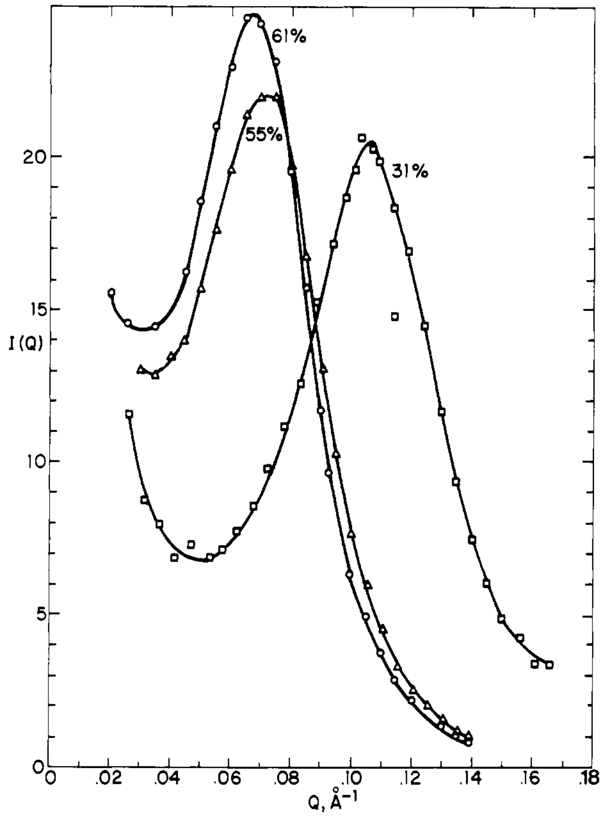

Figure 5. Neutron scattered intensity vs. scattering vector, Q, for the 17% cesium ionomer. Numbers above each curve indicate weight percent D_2O.

Table II
Scattering Peak Positions for 5.8%, 12%, and 17% Polypentenamer Sulfonate Ionomers with Various Water Contents

% Cs salt	wt % D_2O	machine	λ, Å	$Q_{\max}$, Å^{-1}
5.8	7	D-11	4.54	0.95
5.8	12	D-11	4.54	0.86
12	8.3	H-SAS	4.20	0.14
12	15.1	H-SAS	4.20	0.12
12	31.0	D-11	4.54	0.077
12	32.0	D-11	4.54	0.078
17	(dry)	X-ray	1.54	0.2
17	3.5	H-SAS	4.20	0.18
17	8.6	H-SAS	4.20	0.17
17	15.8	H-SAS	4.20	0.16
17	31.0	H-SAS	6.06	0.11
17	55.0	D-11	4.54	0.072
17	61.0	D-11	4.54	0.066

The SANS results for a water-saturated, hydrogenated ionomer are shown in Figure 6. This sample is the hydrogenated 17% cesium salt and shows a similar high-intensity, low-angle peak when compared to the unsaturated 17% ionomer. Several points of interest should be noted when analyzing the scattering from this sample. This hydrogenated polypentenamer ionomer resembles linear polyethylene containing pendant sulfonate groups, and even though it is semicrystalline, it absorbs more water than the amorphous ionomer. For cesium methacrylate/ethylene ionomers, the SANS peak is observed to disappear upon water saturation.[9] But for this cesium sulfonate/ethylene ionomer, the peak remains with a high intensity. The disappearance of the ethylene/carboxylate ionomer peak when water saturated has been attributed to a breakup of cluster order,[8,9] although the ionic material remains in a separate phase. For the ethylene/sulfonate ionomers, the apparent retention of cluster order may be a result of sulfonic acid being a much stronger acid than carboxylic acid.

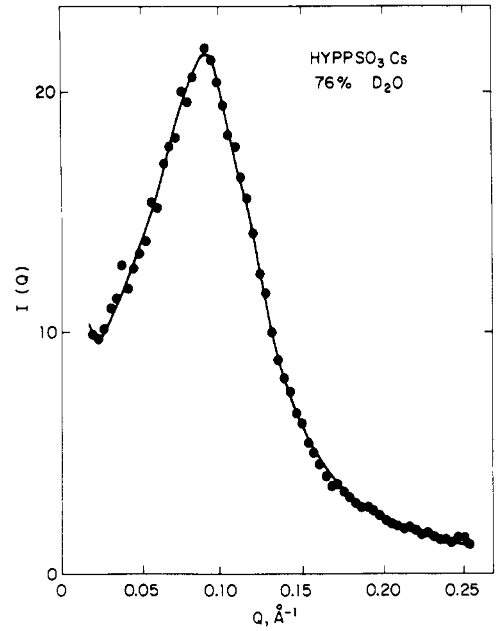

Figure 6. Neutron scattered intensity vs. scattering vector, Q, for the hydrogenated 17% cesium ionomer containing 72 wt % D_2O.

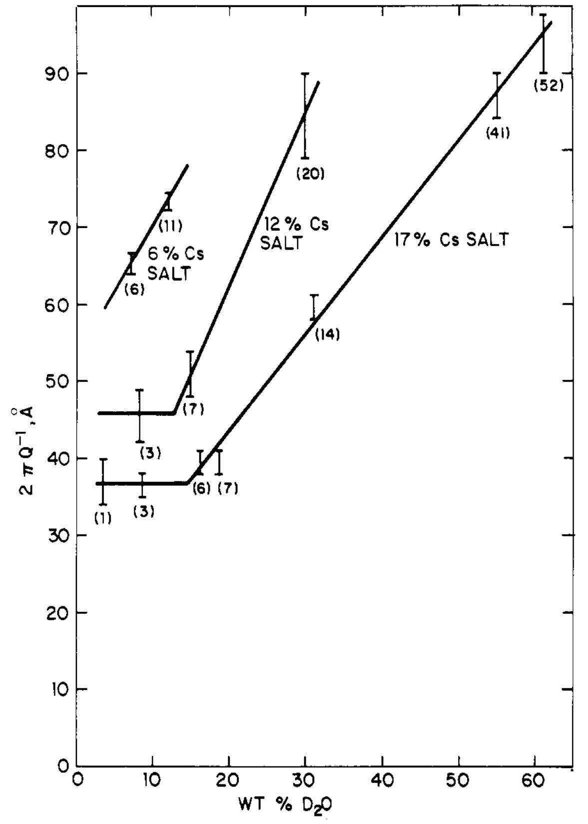

Figure 7. Bragg spacing of the SANS peak for the 5.8%, 12%, and 17% ionomers as a function of weight percent water. The figures in parentheses refer to H_2O/SO_3^- ratios.

As noted in Table II, the scattering peak observed by SAXS for the dry 17% ionomer occurs at almost exactly the same Bragg spacing as for the SANS peaks at low water concentrations. The scattering contrast in the two experimental techniques results from different chemical entities and we therefore should not expect identical results. However, their similarity indicates that the origin of the order giving rise to the maximum in both experiments is the same.

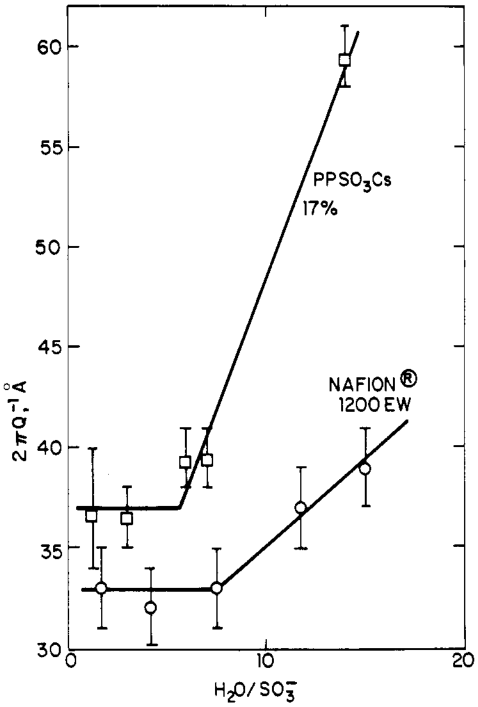

Figure 8. Bragg spacing of the SANS peak vs. waters per sulfonate groups for the 17% polypentenamer sulfonate ionomer and a 1200 equivalent weight Nafion membrane. The Nafion results are data from Roche et al.,[16] used with permission.

Figure 7 displays the change in the Bragg spacing as a function of water content for the three cesium ionomers investigated. The weight percent water is calculated based on the total sample plus water weight. As well as the abrupt shift in peak position near 30% water for the 12% and 17% ionomers, these two samples both exhibit a concurrent large increase in peak intensity. These changes in scattering behavior occur at a water-to-sulfonate group ratio of about 6. At the lowest water concentrations investigated, the 5.8% ionomer already contained more than 6 molecules of water per ionic group.

The primary hydration shell formed around a metal sulfonate group is composed of up to 6 water molecules.[15] Evidence for the existence of similar hydration shells around sulfonate groups in perfluorosulfonate ionomers has been presented by numerous workers.[16-18] These workers have observed changes in the infrared spectrum, the ^{23}Na NMR chemical shift, and the neutron scattering behavior of Nafion ionomer membranes when the water content reaches about 4–6 molecules per sulfonate group. Figure 8 compares the present neutron scattering results with those obtained by Roche et al.[16] using 1200 equivalent weight Nafion. This fluoropolymer ionomer contains about 5 sulfonate groups per 100 backbone carbon atoms while the 17% sulfonated polypentenamer contains about 3.4 sulfonate groups per 100 backbone carbons. The observed behavior is surprisingly similar. Up to about 4–6 waters per sulfonate, the scattering peak position remains constant, but at higher water contents there appears to be a large increase in the calculated Bragg spacing with increasing water content.

The data indicate that the first several absorbed water molecules per salt group form a primary hydration shell around each ion pair and that this hydration shell probably does not greatly affect the internal cluster structure. In the neutron scattering experiments, the hydration of the salt groups by several D_2O molecules in effect allows the position of the metal ions to be "seen" by the neutrons, and hence we observe an ionic peak originating from the

Table III
Peak Intensity and Contrast Factor Dependences on D_2O Content

D_2O/SO_3	% D_2O	peak intensity	intensity at minimum	K_2/K_1
0	0	0.95	0.95	1.00
1	3.5	1.34	1.20	2.04
3	8.6	1.78	1.33	4.57
6	15.8	2.90	1.46	8.60
7	18.6	3.20	1.56	9.90
14	31	21	7	17.7
41	55	23	13	33.4
52	61	26	14	36.6

intracluster structure that is also responsible for the dry X-ray peak.

At higher water concentrations, the large shift in scattering peak position is most probably a result of rearrangement of the ionic phase. For samples containing 30% or more of water, the scattering peak could be simply a result of the interference scattering from randomly packed spheres of water, with the Bragg spacing being related to the size of the spheres.[19] However, this interpretation cannot be used for the 5.8% ionomer, where there is less than 12% water present.

In order to obtain more quantitative information from the scattering experiments, we can first assume a two-phase system where ionic groups are all phase separated and the scattered intensity depends on contrast between cesium sulfonate groups and the amorphous polypentenamer backbone. As the contrast factors from Table I indicate, very little contrast exists between these groups, which agrees with the observed flat curve for the dry samples. At low water contents, we assume each sulfonate group associates with the number of water molecules calculated by mass balance. The water molecules will then increase the total scattering length per gram of D_2O. If the water molecules affect contrast between the ionic phase and the hydrocarbon matrix, the expected scattered intensity, $I_2(Q)$, is related to the dry intensity, $I_1(Q)$, by the equation

$$I_2(Q)/I_1(Q) = K_2/K_1 \qquad (4)$$

where K_2 and K_1 are the contrast factors calculated for the polypentenamer backbone and sulfonate groups associated with water molecules and between dry sulfonate groups and the polypentenamer backbone, respectively.

Because the scattering peak shape as well as the position of the maximum changes with water content, the scattering maximum and the minimum between Q = 0.02 and 0.08 were chosen for comparison of intensities. Table III shows that at low water contents the contrast factors, K, increase 3–5 times faster than the observed intensity increases. This result would indicate that our assumption of a two-phase system at low water levels is not valid. The measured low-intensity values could be accounted for by a significant fraction of the water molecules being present in the matrix as well as in the ionic phase. This situation would than be envisaged as a two-phase system of an ionic-rich phase and a hydrocarbon matrix containing some ionic groups and water molecules, thereby reducing the contrast between the phases.

However, among the three highest water contents, relative ratios of scattered intensity and contrast factors are nearly identical for the minimum near Q = 0.05 as shown in Figure 9. This trend is evidence that at high water contents, the assumption of a two-phase system is a valid one. The two phases would be a hydrocarbon polypentenamer matrix and a polar phase containing essentially all the water and sulfonate ionic groups. The data do not preclude that some of the sulfonate plus water groups are located within the matrix but indicate that the scattering power of the matrix remains constant at high water levels. So while the intensity differences at high water content can be accounted for by the two-phase model, the shift in peak position indicates that the size or other structural features of the phases change with increasing water content.

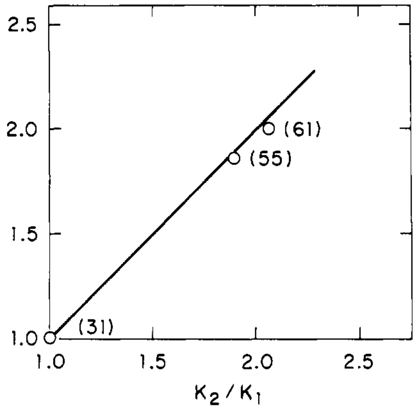

Figure 9. Ratio of scattering minima at Q = 0.05 compared to ratio of calculated contrast factors for high water content samples. Numbers in parentheses are weight percent D_2O in the sample.

A similar argument for two-phase behavior at high water contents has been made by Roche et al.[9] by using isotopic replacement of H_2O and D_2O in water-saturated polypentenamer sulfonate salts. Also, recent SANS and SAXS results from Nafion ionomers[15] show that at high water contents intensity differences can be predicted by a two-phase system but that at low water contents the two-phase model for the structure of ionomers is less valid. Results from the present work confirm the same trends for the sulfonated polypentenamers.

Conclusions

When small amounts of heavy water are added to give sufficient contrast, a SANS ionic peak is observed, corresponding to the SAXS peak in dry samples. At low levels of water, the peak position is relatively constant. The peak position moves markedly to lower angles above a water-to-salt ratio of about 6. The SANS behavior of the polypentenamer sulfonate ionomers is similar to that observed from perfluoro sulfonate ionomers and is consistent with a phase-separated model where absorbed water is incorporated into the ionic phase, which remains separate from the matrix even at high water contents.

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Small-Angle Neutron Scattering from Elastomeric Networks. Application to Labeled Chains Containing Several Cross-Links[†]

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ABSTRACT: The scattering law for polymer chains in rubber networks has been calculated for the case where the labeled chains contain multiple cross-links. Emphasis is placed on changes in molecular dimensions induced by stretching or swelling. The results differ appreciably from the scattering of end-linked chains in polymer networks in two important ways. First, the chains with multiple cross-links exhibit the anisotropy of macroscopic deformation to a greater extent than end-linked chains. Second, junction fluctuations have a profound influence on chain shape in end-linked chains and are of much less importance in the multilinked case. Since anisotropy in chain deformation is higher in multilinked labeled chains that deform affinely in the mean coordinates, it is relatively easy to determine whether the affine model is valid in real materials. Comparison of the calculation with the one published experiment indicates that deformation on the molecular scale is less than would be expected.

I. Introduction

The molecular dimensions of polymer molecules in bulk can be determined by small-angle neutron scattering (SANS).[1,2] This is achieved by replacing some of the polymer by deuterium-labeled chains.

The SANS method has been exploited in following the changes in molecular dimensions upon stretching or swelling of elastomers as well.[3-8] All these experiments except those of Clough et al.[5] were performed with networks composed of end-linked polymer molecules, and the theory of SANS for rubbers has been developed for these materials.[9-11]

As model rubbers, the end-linked networks are, in principle, more easily characterized and because chain lengths may be kept uniform, more regular in their structure. In general, they are more troublesome to prepare than randomly cross-linked networks. Incomplete cross-linking changes the elastic properties of a network substantially and can lead to incorrect interpretation of otherwise carefully performed experiments. The errors thus induced are greater for end-linked networks and also more serious if the network is trifunctional.

Networks constructed with multiple cross-links on a labeled chain tend to be irregular with variable distances between cross-links and variable numbers of cross-link junctions per chain. The influence of defects is not serious if the number of cross-links per original polymer molecule is sufficiently large.

Deuterated polymer chains incorporated in a network by end-linking are randomly arranged, and therefore the scattering from such an assembly is the sum of the contributions from each molecule, with no contribution from interactions between different molecules. Labeled polymer molecules incorporated into a network with multiple cross-links are also randomly arranged, but the various submolecules between cross-links originating from the same prepolymer molecule are coherently arranged, and contributions from pairs of monomer units on different submolecules must be included in the scattering formulas.

As will be seen, the scattering from multiply-linked elastomers is very different from that of end-linked elastomers, and this difference can be extremely useful in assessing the reliability of models of rubber elasticity.

II. Scattering Theory for Multiply-Linked Elastomers

The excess coherent elastic neutron scattering from D-labeled polymer chains in an H matrix is given by

$$I(\mathbf{q}) = A(b_{\mathrm{D}} - b_{\mathrm{H}})^2 McS(\mathbf{q}) \tag{1}$$

In this equation, $I(\mathbf{q})$ is the scattering intensity at a wave vector $\mathbf{q}$, $\mathbf{q} = (2\pi/\lambda)(\mathbf{k} - \mathbf{k}_0)$ (where $\mathbf{k}_0$ and $\mathbf{k}$ are unit vectors in the directions of incident and scattered rays), λ is the wavelength of the neutrons, and the magnitude of $\mathbf{q}$ equals $(4\pi/\lambda)\sin(\theta/2)$ (where θ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$). A is a lumped constant containing machine parameters and some physical constants, b_{H} and b_{D} are scattering lengths of H and D monomer units, M is the molecular weight of the polymer, and c is the concentration in grams per milliliter. $S(\mathbf{q})$, the scattering law or particle

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