(9) Noda, I.; Saito, S.; Fujimoto, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 4048.
(10) Noda, I.; Mizutani, K.; Kato, T. *Macromolecules* **1977**, *10*, 618.
(11) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(12) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(13) Meyerhoff, G. *Makromol. Chem.* **1970**, *134*, 129.
(14) Amber, M. R.; McIntyre, D. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 589.

Small-Angle X-ray Scattering Study of Perfluorinated Ionomer Membranes. 1. Origin of Two Scattering Maxima

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ABSTRACT: Small-angle X-ray scattering (SAXS) from perfluorinated ionomer membranes was studied in order to investigate their internal supermolecular structure. The SAXS curves generally exhibit scattering maxima at $s = (2 \sin \theta)/\lambda$ nearly equal to 0.07 and 0.3 nm^{-1} (θ and λ being one-half the scattering angle and the wavelength of the X-rays, respectively). Simultaneous investigation of wide-angle X-ray scattering indicated that the SAXS maximum at the smaller s is associated with crystallinity (the larger the crystallinity, the more distinct is the SAXS maximum) and is attributed to a long identity period in lamellar crystals. The maximum at the larger s is associated with the existence of ionic clusters whose size is a function of the number of perfluoroether side chains (with pendant sulfonic acid or carboxylic acid groups and their salts) per chain, the nature of the ionic sites (e.g., the electrostatic interaction energy released upon cluster formation), the temperature, and the amount of water absorbed by the membranes.

I. Introduction

The electrochemical behavior of perfluorinated ionomers as ion-exchange membranes[1] as well as their mechanical properties[2,3] should be closely related to their internal structure, especially the spatial distribution of ionic sites, e.g., structure and size of ionic clusters, if these exist. In this series of reports we will analyze the structure of perfluorinated membranes in the absence of any applied external electric field by means of the small-angle X-ray scattering (SAXS) technique.

We studied the molecular organization of Nafion (registered trademark of E. I. du Pont de Nemours and Co., Inc., for its perfluorinated sulfonic acid products) and their salts with Na^+, Cs^+, and propanediamine (SO_2NHR, R = $(CH_2)_3NH_2$) derivatives as well as that of the perfluorinated carboxylic acid and carboxylates which are obtained by chemical modification of the Nafion membranes.[21] The molecular organization of the ionic species as assessed in our studies can be compared with that obtained for other hydrocarbon-based carboxylated ionomer membranes, such as polyethylene, polystyrene, and polybutadiene.[4] Especially, the structure of the carboxylated perfluorinated ionomers should bear a close similarity to that of the ethylene ionomers with the following differences: (i) fluorocarbon chains are replaced by hydrocarbon chains and (ii) the number of carboxylic acid groups of typical perfluorinated ionomers is larger than that of the usual ethylene ionomers.

As in the hydrocarbon-based ionomers, the carboxylated and the sulfonated perfluorinated ionomers show clustering of ionic groups.[4] The ion clusters give rise to a SAXS maximum at $s = (2 \sin \theta)/\lambda$ (λ and 2θ being the wavelength of the X-rays and the scattering angle, respectively) approximately equal to the inverse of the cluster size. We show in this paper that, as in the case of the hydrocarbon-based ionomers, we can interpret this scattering maximum in terms of two models: (1) core–shell models, as proposed by MacKnight, Stein, and co-workers[5,6] (the scattering maximum being attributed to intraparticle interference of the core–shell-type clusters) and (2) a two-phase model proposed by Marx, Caulfield, and Cooper[7] (the maximum being attributed to interparticle interference between the ionic clusters). The origin of this "ionic scattering maximum" will be discussed in detail in a forthcoming paper.[8] In addition to the scattering maximum associated with the ionic clusters, the perfluorinated ionomer membranes generally exhibit another scattering maximum at an even smaller scattering angle. The origin of this maximum is here shown to be due to a regularity of the interlamellar spacing (section III-I).

In a recent publication, Roche et al.[23] reported results on small-angle neutron scattering (SANS) and SAXS from sulfonic acid and sodium sulfonate Nafion membranes having an equivalent weight (EW, i.e., weight of polymer which will neutralize 1 equiv of base) of 1200. They showed that there exist in general two types of small-angle scattering maxima of different origin: (i) the scattering maximum at small angles, which can be assigned to interference between crystalline structures, and (ii) the scattering maximum at larger angles, which can be assigned to the ionic clusters. Their conclusions are generally confirmed and further reinforced by the present studies, which extend the SAXS studies to a series of perfluorinated ionomer membranes having different equivalent weights, different cations (H^+, Na^+, Cs^+, etc.), and different anions (COO^- and SO_3^-) (section V).

II. Experimental Section

1. Chemical Modifications and Test Specimens. A series of Nafion membranes with different equivalent weights (1100, 1150, 1200, 1400, and 1500) are chemically modified to prepare a series of sulfonic acid and carboxylic acid perfluorinated ionomer membranes having equivalent weights corresponding to the original Nafion membranes. For a given equivalent weight (1100), membranes in the form of sulfonic acid, sodium and cesium sulfonates, sulfonyl chloride (SO_2Cl), and sulfonamide (SO_2NHR, R = $(CH_2)_3NH_2$) as well as carboxylic acid and sodium carboxylate were prepared.

First we describe a procedure to prepare the carboxylic acid form (designated as Nf-COOH for convenience). The Nafion membrane was first treated with 2 N HCl for 3 h at 80 °C to prepare the sulfonic acid form, Nf-SO_3H. In this way we obtained a series of sulfonic acid forms. The membrane was then washed with water for 3 h, followed by reaction with 5% NH_4OH for 16 h at room temperature to obtain Nf-SO_2NH_4. The membrane was again washed with water for 4.5 h, dried under vacuum, and

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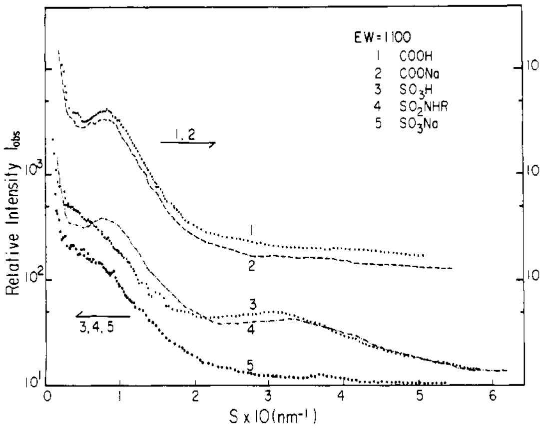

Figure 1. Typical SAXS curves for various perfluorinated ionomer membranes with EW = 1100 in the room-temperature dry state. $s = (2 \sin \theta)/\lambda$, θ being half of the scattering angle.

refluxed with 1:4 (v/v) $PCl_5/POCl_3$ for 70 h to obtain Nf-SO_2Cl. The membrane was then refluxed with CCl_4 for 18.5 h and dried under vacuum. A part of this membrane was then used for X-ray measurements. The Nf-SO_2Cl membrane was further reacted with HI at about 80 °C for 115 h to obtain the carboxylic acid form, Nf-COOH, and washed with methanol for 8 h. The membrane was then refluxed with a 10% methanol solution of sodium hydroxide for 15 h to prepare the sodium carboxylate form, Nf-COONa. The membrane was then washed with water for 6 h and reacted with 2 N HCl at about 80 °C for 16 h, followed by washing with water for 3 h and drying under vacuum at 130–140 °C for 18.5 h to prepare the carboxylic acid form, Nf′-COOH, for X-ray measurements. The residual amount of sulfonate groups was quantitatively estimated to be minute by using fluorescent X-ray spectroscopy to analyze for sulfur before and after the chemical modification. The sulfonates and carboxylates were also prepared by a standard method. The Nf-SO_2Cl membrane was reacted with a methanol solution of propanediamine for 3–4 weeks to obtain Nf-SO_2NHR.

2. X-ray Measurements. The X-ray measurements were performed on dry specimens and on specimens swollen by water. Some of the measurements were carried out at the so-called "standard state": the standard swollen state is obtained after boiling the membrane in water for 0.5 h and the standard dry state is obtained after drying the specimen at 107 °C for 18 h in a vacuum oven. Hereafter the standard states are simply designated as the "dry" or "swollen" states. Some measurements were carried out under nonstandard conditions: the specimens were dried at room temperature, designated as "room-temperature dry" specimens, and were soaked in water for a few days, designated as "soaked" specimens.[22]

The SAXS and wide-angle X-ray scattering (WAXS) profiles were taken with a one-dimensional position-sensitive proportional counter or a conventional scintillation counter mounted on a goniometer with a step-scanning device. Cu Kα radiation (λ 1.54 Å), monochromatized by a graphite crystal, was used for the incident X-ray beam. A pulse height analyzer in the detector electronics eliminated the higher order harmonics of white X-rays. The X-ray beam is generated by a 12-kW rotating-anode X-ray generator (RU-z or RU-a, Rigaku-Denki). The scattering curves were corrected for absorption, background scattering, slit-length and slit-width smearings, and so on, as described in detail in our previous papers.[9-11]

The details of the apparatus utilizing the position-sensitive detector[10] and associated correction factors[11] are also described elsewhere.

III. Results

Figures 1 and 2 present typical SAXS curves for various ionomer membranes having an equivalent weight of 1100. The results in Figure 1 are obtained in the "room-temperature dry" state, while those in Figure 2 are obtained in a "standard dry" state. All curves are corrected for both slit-length and slit-width smearing effects. Obviously there exist two types of scattering maxima, one at $s \cong 0.07$ nm^{-1} and one at $s \cong 0.3$ nm^{-1}, as first observed by Gierke.[16b] We suggest below that the small-angle scattering maximum originates from a long identity period of crystallites, possibly of lamellar platelets, and that the wide-angle scattering maximum originates from ionic clusters.

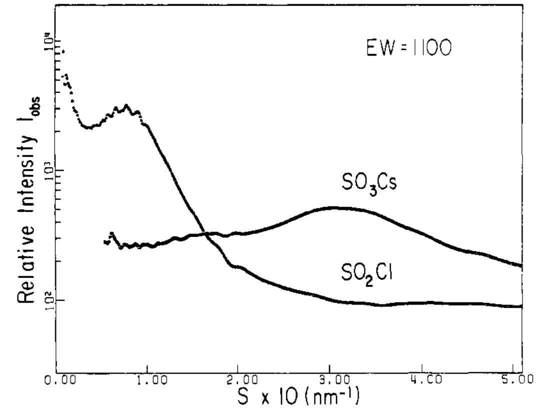

Figure 2. SAXS curves for perfluorinated ionomer membranes with EW = 1100 in the dry state.

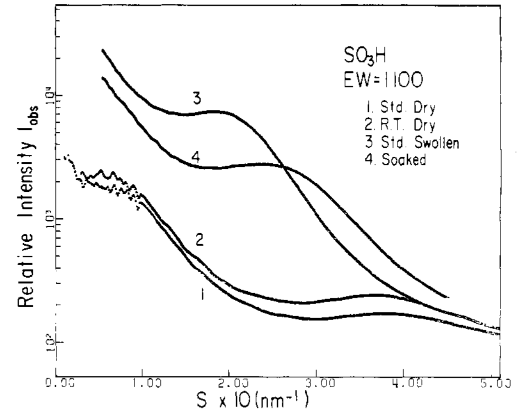

Figure 3. Comparison of the scattering curves obtained in the standard dry (curve 1) and swollen (curve 3) states and the nonstandard dry (i.e., room-temperature dry, curve 2) and swollen (i.e., soaked state, curve 4) states for the sulfonic acid form of the membrane with EW = 1100.

Figure 3 presents a comparison of the results obtained in the standard and nonstandard states for the ionomer membranes having sulfonic acid groups, EW = 1100. In comparison with the scattering curves obtained from the standard-state dry specimens, the room-temperature dry specimens exhibit a more distinct scattering maximum at large s due to the ionic clusters, having an enhanced peak intensity and being slightly shifted toward smaller angles. As discussed later, the general trend can be well interpreted in terms of a difference in water uptake in the two states, the water uptake in the room-temperature dry specimens being naturally higher than that in the standard-state dry specimens. Similarly, the difference between the two curves obtained in the standard swollen state and in the "soaked" state can be interpreted in terms of a difference in water uptake in the two states, the water uptake in the standard-state swollen specimens being greater than that in the soaked specimen.

Although some results in this paper are obtained from measurements in nonstandard states, our conclusions would not be affected by these measuring conditions.

1. Scattering from a Long Identity Period (Scattering Maximum at Small *s*). It is shown from Figures 1 and 2 that membranes having COOH, COONa, SO_2NHR, and SO_2Cl groups exhibit a more distinct

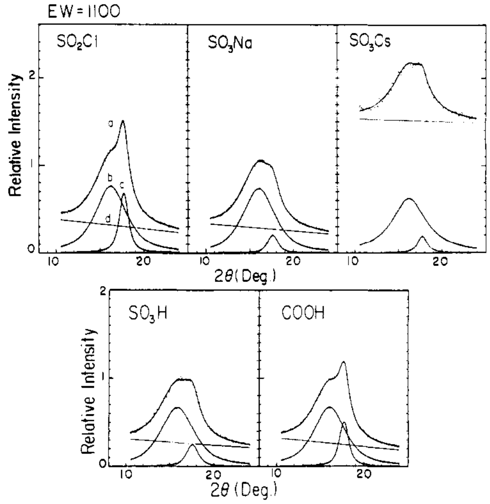

Figure 4. Wide-angle X-ray diffraction profiles of the membranes with a fixed value of EW (1100) and various functional groups (SO_2Cl, SO_3Na, SO_3Cs, SO_3H, and COOH). The measured profiles are shown by dots, while curves b–d correspond to the decomposed profiles and curve a corresponds to the profile reconstructed from curves b–d.

small-angle scattering maximum at $s \cong 0.07$ nm^{-1} than those with sulfonic acids and sulfonates. In order to understand the origin of the maximum at small s, we study below the relationship between the SAXS maximum and the crystallinity as observed by WAXS.

Figure 4 shows typical WAXS profiles for (standard state) "dry" ionomer membranes with various functional groups having EW = 1100, where the measured profiles are shown by dots, curves b–d are decomposed profiles, and curve a is the curve reconstructed from curves b–d. The measured profiles were decomposed into the fundamental profiles b–d, where decomposition was achieved by a least-squares fit of the measured profile with the calculated (or reconstructed) curve a by a superposition of the three fundamental profiles b–d. In attaining the least-squares fit, we assumed each fundamental profile to be Gaussian, Lorentzian, a linear combination of Gaussian and Lorentzian, or a linear polynomial (for the background scattering profile d), with its peak position, peak height, peak width, the relative abundance of Gaussian and Lorentzian (for the linear combination of the two), and the parameters of the polynomial as variables. The measured curves are decomposed into a broad peak at $2\theta = 16.1°$ with a full width at half-maximum (fwhm) of 4° and a sharp peak at $2\theta = 17.7°$ with a (fwhm) of 1.2°.

It is tempting to ascribe the broad and narrow maxima to diffraction from the noncrystalline and crystalline regions, respectively. The results shown in Figure 5 confirm this assignment, where the WAXS is plotted as a function of temperature for the membrane containing sulfonic acid with EW = 1100. When the specimen was heated to 275 °C the sharp peak disappeared but the broad peak was enhanced. When the specimen was cooled from 275 °C to room temperature, the sharp peak appeared again. These results are apparently associated with melting and crystallization, the melting point, however, being much depressed in comparison to the melting temperature of poly(tetrafluoroethylene) due to the existence of the impurity (perfluoroether side chains).[12] Thus we ascribe the sharp and broad peaks to the crystalline and noncrystalline regions, respectively, and estimate weight-average crystallinity, W_{cr}, from the decomposed profiles

$$W_{cr} = \int_0^\infty I_{cr}(s)s^2\,ds \Big/ \int_0^\infty [I_{cr}(s) + I_{am}(s)]s^2\,ds$$

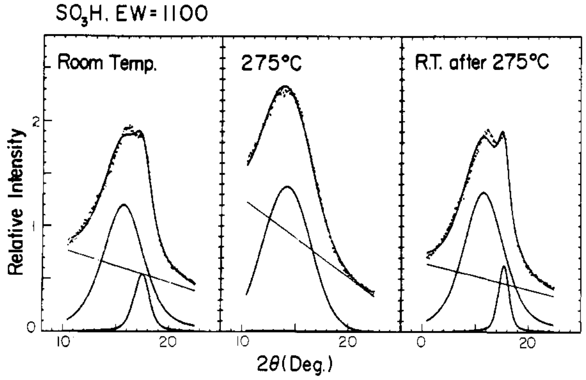

Figure 5. Temperature dependence of the wide-angle X-ray scattering profiles of the sulfonic acid membranes with EW = 1100: (left) measured at room temperature; (middle) measured at 275 °C; (right) measured at room temperature for specimens heated once at 275 °C.

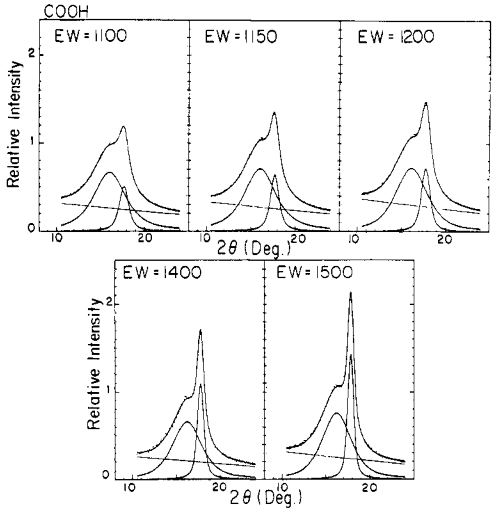

Figure 6. Dependence of the wide-angle X-ray diffraction profiles on equivalent weight for carboxylic acid membranes.

where I_{cr} and I_{am} are the relative scattered intensities of the sharp and broad peaks, respectively. The estimated crystallinities for the series of membranes having EW = 1100 are as follows: 0.23, 0.18, and 0.14 for Nf-SO_2Cl, Nf-COOH, and Nf-COONa, respectively, all of which exhibit distinct SAXS maxima at small s; 0.12, 0.08, and 0.03 for Nf-SO_3H, Nf-SO_3Na, and Nf-SO_3Cs, respectively, all of which exhibit less distinct maxima at small s. Thus the SAXS maxima at small s (in Figures 1 and 2) are apparently related to crystallinity and ascribed to a long identity period of crystallites. This conclusion is further confirmed by observing the SAXS and WAXS as a function of equivalent weight for a given functional group, e.g., for Nf-COOH.

Figure 6 shows a series of measured and decomposed WAXS profiles for Nf-COOH having different equivalent weights. The weight-average crystallinity at room temperature increases with increasing equivalent weight (i.e., with decreasing fraction of the functional group), 12, 19, 20, and 22 wt % for EW = 1100, 1200, 1400, and 1500, respectively. Corresponding SAXS profiles at small s are shown in Figure 7. It is clearly shown that, with increasing X-ray crystallinity, the peak intensity increases and the peak position shifts toward smaller s. The intensity change may be interpreted in terms of the change of the mean-square electron density, $\langle\eta^2\rangle$, which may be approximated by

$$\langle\eta^2\rangle = \phi_{cr}(1 - \phi_{cr})(\rho_{cr} - \rho_{am})^2$$

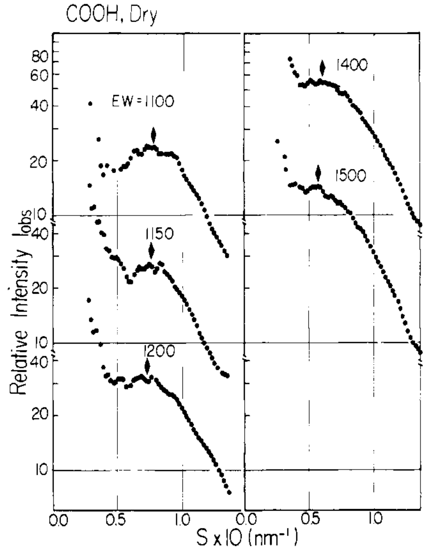

Figure 7. Dependence of the SAXS at small s on equivalent weight for carboxylic acid membranes.

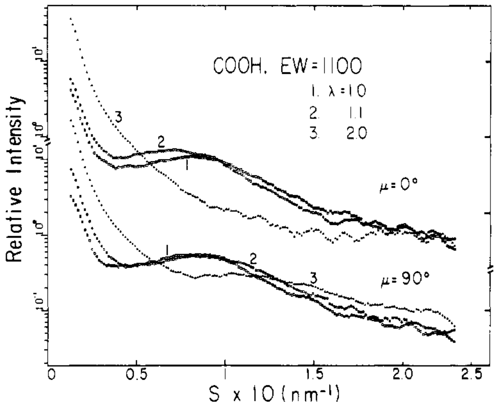

Figure 8. Change of SAXS profiles at small s with uniaxial stretching of the carboxylic acid membranes with EW = 1100. λ is the elongation ratio, and $\mu = 0$ and 90° designate the profiles at the meridian (i.e., in the direction parallel to the stretching direction) and the equator, respectively.

where ϕ_{cr} is the volume fraction of the crystalline phase and ρ_{cr} and ρ_{am} are the electron densities of the crystalline and amorphous phases, respectively. Thus, increased intensity with increasing crystallinity is due to the increased ϕ_{cr}. The shift of the peak position with increasing crystallinity is attributed to increased interlamellar spacing, which, in turn, may be attributed to a thickening of lamellar platelets. The existence of crystal lamellae for the ionomer membranes is not self-evident and requires further investigation. However, by demonstrating that the change of the SAXS maximum at small s upon stretching the ionomer membranes bears close resemblance to that observed with polyethylene films, we show that the existence of a lamellar structure in the membranes is quite possible.

Figure 8 shows the change of the SAXS at small s upon stretching the membranes in the form of carboxylic acid with EW = 1100.[25] Upon stretching, the equatorial scattering maximum (i.e., the maximum at $\mu = 90°$) shifts toward higher angles, while the meridional scattering maximum shifts toward the smaller angles. Upon further stretching, the meridional scattering maximum loses its intensity and finally disappears. This tendency is identical with that observed upon stretching spherulitic polyethylene films; interlamellar spacing tends to be compressed and expanded in the polar and equatorial parts of the deformed spherulites, respectively. Moreover, as shown in Figure 9 the membrane turns out to have a spherulitic structure, as indicated by four-leaf clover type depolarized light scattering patterns.[15] Therefore the change of the SAXS maximum at small s upon stretching the membranes may be best interpreted to arise from a change of the interlamellar spacing in the spherulitic texture.

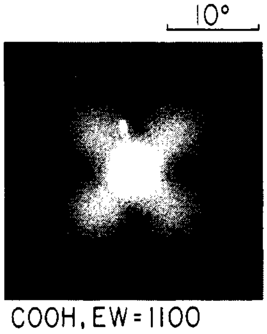

Figure 9. Depolarized small-angle light scattering pattern from the carboxylic acid membranes with EW = 1100.

2. Scattering from Ionic Clusters. "Ionic Scattering" Maximum at Large s. We consider the origin of the ionic scattering maximum at large s ($\simeq 0.3$ nm^{-1}). From Figures 1 and 2 it is seen that membranes having un-ionized or only weakly ionized groups (Nf-SO_2Cl and Nf-COOH) do not exhibit an ionic scattering maximum but that membranes having ionized groups, such as Nf-SO_3H, Nf-SO_2NHR, and Nf-SO_3Cs, do. Consequently, the scattering maximum is clearly associated with the ionic sites, their spatial distribution, and their organization.

A problem to be solved first is that membranes having ionized groups, such as Nf-COONa and Nf-SO_3Na, do *not* exhibit the scattering maximum. As in the case of hydrocarbon-based carboxylated ionomers (e.g., polyethylene, polystyrene, and polybutadiene ionomers),[4-7] we assume that the ionic sites of Nafion-based ionomers form ionic clusters which are essentially ion-rich regions containing some fluorocarbon chains. The clusters are stabilized by dipole–dipole interactions between ion-dipolar complexes[16a] such as $-SO_3^{-}\cdots H^{+}$. The electrostatic energy released upon cluster formation should be counterbalanced by the elastic free energy associated with deformation of fluorocarbon chains, giving rise to an optimum size for the clusters.[17]

In order to interpret this ionic scattering maximum for the perfluorinated ionomer membranes, we consider here the two basic models which have been proposed for the hydrocarbon-based carboxylated ionomers (Figure 10): (i) the two-phase model (Figure 10a), in which the ionic clusters are dispersed in a matrix composed of fluorocarbon chains and nonclustered ions, i.e., multiplets,[19] as proposed by Cooper et al. for hydrocarbon-based carboxylated ionomers[7,24] (the ionic scattering maximum is then attributed to an intercluster interference, and Debye hard-sphere type scattering[18] may be the simplest possible model for describing the scattering maximum) and (ii) the core–shell model proposed by MacKnight, Stein, and co-workers[5,6] (Figure 10b), in which an ionic cluster (ion-rich core) is surrounded by a shell, rich in fluorocarbon chains (the core–shell particles are dispersed in a matrix of fluorocarbon chains and nonclustered ions and multiplets; the short-range order distance in the core–shell particle gives rise to the ionic scattering maximum). It is not our purpose to distinguish the models in this paper but to show qualitatively that both models describe the scattering maximum. Some attempts to distinguish the models, and

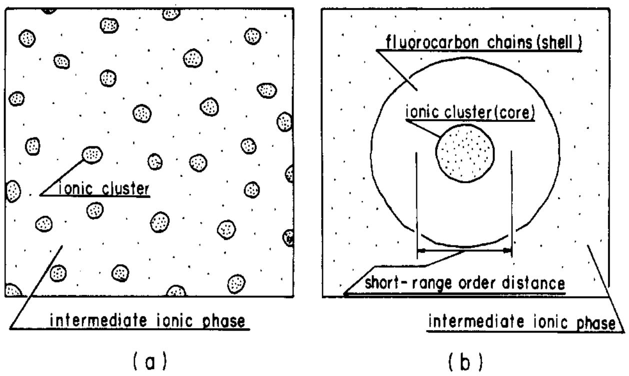

Figure 10. Two models for the spatial organization of the ionic sites. (a) Two-phase model composed of ionic clusters (ion-rich region) dispersed in a matrix of the intermediate ionic phase, i.e., the phase composed of fluorocarbon chains and nonclustered ions. (b) Core–shell model in which the ion-rich core is surrounded by the ion-poor shell composed mostly of perfluorocarbon chains, the core–shell particles being dispersed in the intermediate ionic phase. Note that the crystalline region is not drawn in the model for the sake of simplification and that the shape of the core–shell particle may not neccessarily be spherical.

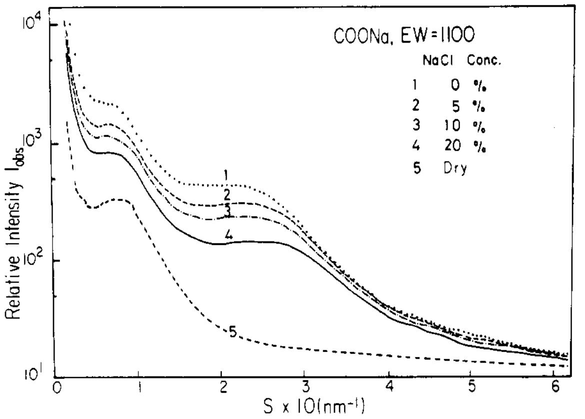

Figure 11. Change of SAXS curves upon swelling the sodium sulfonate membranes having EW = 1100 with aqueous solutions of sodium chloride.

computer simulation of the scattering maximum based on the models, will be discussed in a forthcoming paper.[8]

Now we return to the first problem of why the Nf-COONa and Nf-SO_3Na membranes do not exhibit the ionic scattering maximum. We propose that this is not due to the absence of clusters but rather simply to the small electron density difference between the clusters and the surrounding medium in the case of sodium carboxylate and sulfonate. Upon replacement of sodium by hydrogen, i.e., by changing SO_3Na into SO_3H, the electron density of the clusters becomes lower than that of the surroundings, thus giving rise to an ionic scattering maximum, as shown in Figure 1. Upon replacement of sodium by cesium, the electron density of the clusters becomes higher than that of the surroundings, thus again giving rise to the ionic scattering maximum, as shown in Figure 2. Thus we may conclude that ionic clusters exist in the dry state for membranes having ionic groups. This conclusion can be further confirmed by the results shown in Figures 11 and 12.

Figure 11 shows the change of the SAXS at large s upon soaking the sodium sulfonate membranes with EW = 1100 in an aqueous solution of sodium chloride, its concentration being varied from 0 to 20 wt %. Water is preferentially taken up by the ionic clusters to result in increased cluster size, thus giving rise to a shift of the ionic scattering maximum toward smaller s. The water uptake also decreases the electron density of the clusters relative to the surrounding, producing an enhancement of the scattering intensity. The water uptake increases with decreasing concentration of sodium chloride, giving rise to increased scattered intensity and a greater shift of the scattering maximum toward smaller s.

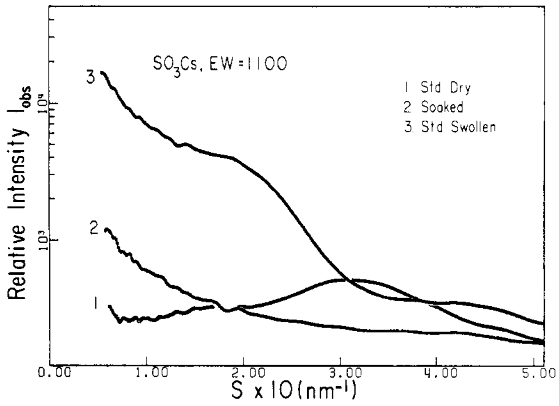

Figure 12. Change of SAXS curves upon swelling the cesium sulfonate membranes having EW = 1100 with pure water.

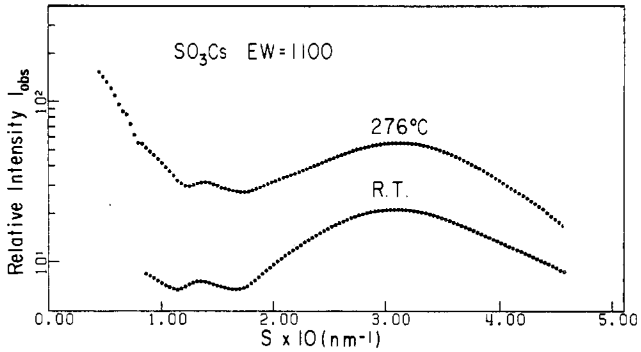

Figure 13. Change of SAXS curves with temperature for the cesium sulfonate membranes with EW = 1100.

Figure 12 shows the SAXS at large s for the cesium sulfonate membrane with EW = 1100 in the dry state (curve 1) and soaked (curve 2) and swollen (curve 3) states with pure water. Water taken up by the clusters decreases their electron density. This results in a smaller electron density difference between the clusters and their surrounding medium and hence in disappearance of the ionic scattering maximum (see curve 2). As more water is taken up by the clusters (as in the standard swollen membranes), the electron density of the clusters becomes lower than that of the medium and the clusters grow in size, resulting in the reappearance of the scattering maximum with its maximum position shifted toward smaller s ($\simeq 0.2$ nm^{-1}) (see curve 3).

IV. Nature of the Ionic Clusters

1. Swelling Behavior. Upon swelling the membranes with water or aqueous solutions of sodium chloride, we estimated the change of the Bragg spacing associated with the ionic scattering maximum as well as the change in macroscopic dimensions. As discussed in section III-2, the Bragg spacing is associated with either an intercluster distance or an intracluster distance. In either case, in our qualitative discussion throughout sections IV and V we can assume that the increase of the spacing reflects an increase of cluster size. The results indicate that the microscopic degree of swelling as observed by SAXS is much greater than the macroscopic degree of swelling, suggesting that the core–shell model may be more probable than the two-phase model in this respect. This point is further

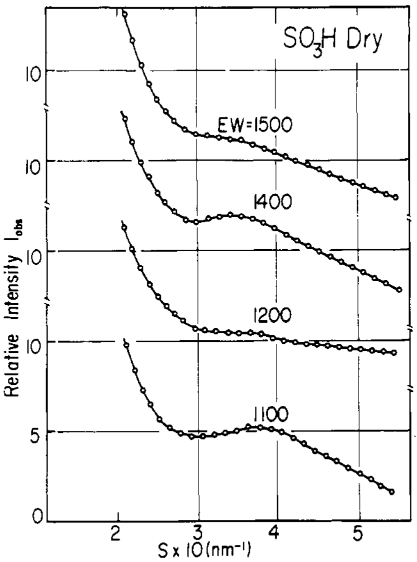

Figure 14. SAXS curves at large *s* as a function of equivalent weight for the sulfonic acid membranes.

studied in a forthcoming paper.[8]

2. Temperature Dependence. Figure 13 shows the temperature dependence of the SAXS at large *s* for cesium sulfonate membranes with EW = 1100, in which 276 °C is slightly above the melting temperature of the membranes. As the temperature is raised, the ionic scattering maximum shifts toward larger *s*, indicating that the intercluster distance or the short-range order distance decreases with temperature. In any case the decrease of the characteristic distance is essentially due to decreased cluster size. The decreased cluster size with temperature may be rationalized by increased thermodynamic work for determination of polymer coils to form the cluster.[20]

3. Equivalent-Weight Dependence. Figure 14 shows the SAXS at large *s* for sulfonic acid membranes in the dry state as a function of equivalent weight. The ionic scattering maximum is clearly seen to shift to smaller scattering angles with increasing equivalent weight, i.e., decreasing number of functional groups, indicating essentially that the cluster size increases with increasing equivalent weight. This again may be interpreted in terms of the counterbalancing forces which control the equilibrium cluster size.[17] The electrostatic energy per ion released upon cluster collapsed should essentially remain constant with equivalent weight. On the other hand, the thermodynamic work required for elastic deformation of coils to form the clusters should decrease with increasing equivalent weight, i.e., with increasing molecular weight of the chain molecule between ionic sites, which results in increased cluster size with equivalent weight. One should bear in mind, of course, that the work for the elastic deformation of coils is modified by crystallinity, which is also a function of equivalent weight. This factor may complicate our interpretation.

4. Effect of Cations and Anions. From Figures 1 and 2 the spacing of the ionic clusters in the dry state increases in the order Nf-SO_3H, Nf-SO_3Na, and Nf-SO_3Cs (i.e., 2.7, 3.1, 3.2 nm, respectively) for the sulfonated ionomer membranes with EW = 1100. The spacing of Nf-SO_3Na was estimated by extrapolating the spacing observed in the swollen state with sodium chloride aqueous solutions to the dry state (cf. Figure 11).

For a given cation the spacing of the ionic scattering maximum for sulfonates is greater than that for the carboxylates. These differences in spacings may be interpreted in terms of differences in the electrostatic energy released per ion site by the ionic cluster formation through ion-dipolar interactions.[16a] That is, the ion-dipolar interactions of sulfonates may be stronger than those of carboxylates, resulting in a greater energy released per ion site and hence a larger cluster size for the sulfonates than for the carboxylates.

V. Concluding Remarks. Some Comparisons with Ethylene Ionomers

We briefly compare the results with those for polyethylene ionomers (ethylene–methacrylic acid random copolymers and their salts).[4-6] As in the case of ethylene ionomers, the carboxylic acid forms of the perfluorinated ionomer membranes do not exhibit the ionic scattering maximum, at least in the dry state. The electrostatic interaction may be too weak to form ionic clusters.

The ionized forms of the perfluorinated ionomer membranes form ionic clusters, giving rise to the ionic scattering maximum at $s \cong 0.3$ nm^{-1}, as in the case for ethylene ionomers. The size of the cluster or the value of *s* of the scattering maximum for the two types of membrane is about the same and depends on the cations, the size increasing in the order H^+, Na^+, and Cs^+. The size also depends on the number of functional groups per chain: the greater the number, the smaller the size for the two types of membrane.

The clusters in the two types of membrane exist even at temperatures above the crystalline melting point. In the case of perfluorinated ionomer membranes, the size of the clusters is experimentally found to decrease with temperature. This observation may be rationalized by the increased thermodynamic work of elastic deformation of coils (with temperature) required for the cluster formation.[20] The general trend as found in our experiments seems to be understandable in terms of the theory of ionic clusters as proposed by Eisenberg.[17]

As in the case of ethylene ionomers, the ionic scattering changes with deformation, which will be discussed in detail in a forthcoming paper.[8]

The observations described above are commonly found for the two types of ionomer membrane. A marked difference between the two membranes exists in the swelling behavior with water. In the case of ethylene ionomers water solvates the ions and weakens their attraction to the point where the cluster would fall apart. Thus the ionic scattering maximum for the ethylene ionomers is destroyed upon saturating the samples with water.[6] On the other hand, the clusters of the perfluorinated ionomer membranes never fall apart, and the ionic peak is preserved with water saturation. Water present in small quantities in the ethylene ionomers tends to be absorbed into the ionic phase and enhances the ionic peak,[4] the tendency of which is identical with that of the perfluorinated ionomer membranes.

The SAXS peaks at small *s* for the two types of membrane are commonly associated with crystallinity and may be attributed to the interlamellar spacing.

It will be worthwhile to compare the results obtained in this study with those reported by Roche et al.[23] from SAXS and SANS studies on sulfonic acid and sodium sulfonate Nafion membranes having an equivalent weight of 1200. They found the same two types of small-angle scattering maxima as found in the present study. Their conclusions are confirmed and further reinforced by the present studies on the sulfonic acid ionomer membranes having equivalent weights other than 1200 and on cesium sulfonate membranes as well as sodium sulfonate membranes. These conclusions are applicable also to carboxylic acid and carboxylated perfluorinated ionomer membranes.

Roche et al. found that the scattering maximum at small *s* is crystalline in origin by demonstrating that the quenched amorphous sodium salt does not show the scattering maxima. In the present study, this conclusion was quantitatively confirmed by simultaneous measurements of the crystallinity of the membranes by means of the WAXS technique (section III-1). The greater the X-ray crystallinity of the membrane, the more distinct is its SAXS maximum. That is, for a given equivalent weight or mole fraction of functional group, the membranes having sulfonyl chloride, carboxylic acid, or sodium carboxylate groups have higher crystallinity than those having sodium sulfonate or cesium sulfonate groups, and therefore the former types of membrane have a more distinct SAXS maximum at small *s* than the latter types (Figures 1, 2, 4, and 12). In fact, the cesium sulfonate membranes having a very small degree of crystallinity show no small-angle scattering maximum and have only a weak intensity level at small *s* (Figures 2 and 12). For a given functional group (e.g., COOH), the crystallinity increases with increasing equivalent weight, which results in an increased peak intensity of the small-angle scattering (section III-1, Figures 6 and 7). In the present study, we further propose that the small-angle scattering maximum reflects an average spacing between crystalline lamellar platelets from its dependence on crystallinity as discussed above and also from the fact that the change of the scattering maximum upon stretching the membranes bears a close resemblance to that observed for polyethylene films (section III-1, Figures 8 and 9).

Roche et al.[23] found ionic scattering maxima for soaked and boiled membranes. They showed that with increasing water uptake the ionic scattering maximum increases and shifts toward smaller angles, the tendency of which is again in agreement with the present study for the same types of membrane having different equivalent weights and also for the sodium carboxylated membranes. However, we have shown that the cesium sulfonate membranes exhibit a quite different behavior in that the scattering intensity first decreases and then increases with increasing water, which can be predicted from the specific change of the contrast with water as discussed in section III-2 (Figure 12). Roche et al. found that the sodium salt in the dry state (at 23 and 200 °C) shows only a weak or no ionic scattering maximum, which is proposed to be due to a lack of contrast between the clusters and matrix, in agreement with our conclusion. Moreover, we have shown experimental evidence to prove this (section III-2, Figures 2, 3, 12, and 13); that is, the replacement of sodium ions by protons or cesium ions enhances the contrast, and thus the ionic scattering maximum appears in the standard-state dry membranes and membranes heated at 276 °C.

Finally Roche et al. proposed the origin of the ionic scattering maximum to be attributed to (i) an intraparticle interference effect, which may be associated with a short-range order distance of the core–shell structure (Figure 10b), or (ii) an interparticle interference effect reflecting a paracrystalline spatial order of the clusters, with a remark that the former origin may be more probable than the latter. We also tend to support the former origin, i.e., that the ionic maximum arises from the short-range order distance of the core–shell structure, from experimental evidence that the microscopic degree of swelling as observed by SAXS is much larger than the macroscopic degree of swelling (section IV-1).

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References and Notes

(1) See, for example: "Perfluorocarbon Ion Exchange Membrane", presented at the 152nd National Meeting of the Electrochemical Society, Atlanta, Ga., Oct 10–14, 1977.

(2) Yeo, S. C.; Eisenberg, A. *J. Appl. Polym. Sci.* **1977**, *21*, 875.

(3) Hodge, I. M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 289.

(4) Eisenberg, A.; King, M. "Ion-Containing Polymers"; Academic Press: New York, 1977.

(5) Kao, J.; Stein, R. S.; MacKnight, W. J.; Taggart, W. P.; Cargill, G. S. *Macromolecules* **1974**, *7*, 95.

(6) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Part C* **1974**, *45*, 113.

(7) Marx, C. L.; Caulfield, D. F.; Cooper, S. L. *Macromolecules* **1973**, *6*, 344.

(8) Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules*, part 2 of this series (to be submitted for publication).

(9) Todo, A.; Hashimoto, T.; Kawai, H. *J. Appl. Crystallogr.* **1978**, *11*, 558.

(10) Hashimoto, T.; Suehiro, S.; Shibayama, M.; Saijo, K.; Kawai, H. *Polym. J.* **1981**, *13*, 501.

(11) Fujimura, M.; Hashimoto, T.; Kawai, H. *Memoirs Fac. Eng., Kyoto Univ.* **1981**, *43* (2), 224.

(12) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.

(13) Peterlin, A. *Kolloid Z. Z. Polym.* **1969**, *233*, 857.

(14) Gerasimov, V. I.; Genin, Ya. V.; Tsvankin, D. Ya. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2035.

(15) The results on light scattering behavior will be described in detail elsewhere: Hashimoto, T.; Fujimura, M.; Kawai, H., to be published in *ACS Symp. Ser.*, "Perfluorinated Ionomer Membranes ("Nafion" and Others)"; Eisenberg, A., Yeager, H. L., Eds.

(16) (a) Hopfinger, A. J.; Mauritz, K. A.; Hora, C. J. In "Perfluorocarbon Ion Exchange Membrane", presented at the 152nd National Meeting of the Electrochemical Society, Atlanta, Ga., Oct 10–14, 1977. (b) Gierke, T. D. *Ibid.*

(17) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

(18) Debye, P. *Phys. Z.* **1927**, *28*, 135.

(19) The multiplets are defined to be composed only of ionic groups[4] (the fluorocarbon chain being excluded in the multiplets).

(20) It should be noted that the thermal expansion tends to make the cluster bigger. However, this effect may be outweighed by the thermodynamic factor which makes the clusters smaller.

(21) Opened Japanese Patent, 552 24176 (Asahikasei Co.).

(22) During the X-ray measurements the samples were enclosed in a chamber to prevent loss or gain of water.

(23) Roche, E. J.; Pineri, M.; Duplessix, R.; Levelut, A. M. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1.

(24) In the model proposed by Cooper et al.,[7] the clusters do not contain fluorocarbon chains but are composed only of ionic groups, thus corresponding to the multiplets. We can, however, consider here a modified two-phase model in which the clusters, containing some fluorocarbon chains and corresponding to an ion-rich region, are embedded in the intermediate ionic phase.

(25) The intensity distributions were measured by a point collimation.[8]