Self-Assembling of Ethylene−Methacrylic Acid Ionomers in Aqueous Solutions and as Swollen Membranes, from ESR Spectra of Amphiphilic Spin Probes. 1. Structure of Aggregates and Effect of Ionomer Concentration

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ABSTRACT: The nitroxide spin probe ESR method was applied to the study of chain aggregation in aqueous solutions of poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers. The probes selected differed in their hydrophilicity and in the position of the nitroxide group with respect to the head group. Two spectral sites were detected for the more hydrophilic probes and were assigned respectively to probes with restricted mobility incorporated in large aggregates and to probes with high mobility dispersed in the water phase and/or in the proximity of single-chain micelles (unimers); only the site with restricted mobility was detected in the more hydrophobic probes. The spectral parameters for the site associated with the aggregates suggest that the probes are located in different regions of the aggregates and are faithful reporters on the local hydration and polarity. On the basis of analysis of ESR spectra for six spin probes, we suggest that the aggregates present in aqueous solutions consist of three main regions: a hydrophobic core, an intermediate layer that contains both ionomer chains and some ions, and a hydrophilic region where most of the ions are located. The results for the solutions were compared with results obtained for ionomer membranes equilibrated with water. This study has revealed important structural differences between the aggregates in EMAA ionomers, and in the perfluorinated ionomers (PFI) that were studied previously by the method used in this study. The most important difference is the gradual increase in hydration of the EMAA aggregates from the hydrophobic core to the solvent−ionomer interface, compared to the complete phase separation into ionic and nonpolar domains in the PFI.

Introduction

Ionomers are polymers that consist of a hydrophobic backbone and a small amount (usually <15 mol %) of pendant or terminal ionic groups. Numerous studies have established that neat and solvent-swollen ionomers have a microphase-separated morphology consisting of the hydrophobic polymer matrix and ionic regions.[1,2] In neat ionomers, this structure results in excellent physical properties, such as glasslike high clarity (because of low crystallinity) and modulus superior to the corresponding host polymers.[1−4] The potential to design optimal properties of bulk ionomers has motivated extensive research efforts intended to elucidate the structure−property−function relationships in ionomers containing a variety of ionic groups and neutralizing ions.

The self-organization of ionomers *in the presence of a third component* such as water or organic solvents has been explored recently, and the results have suggested that the structures obtained are sensitive to the nature and concentration of the solvents.[5−9] Although ionomer solutions are of great practical importance, for instance as stabilizers for paint solutions and as coating materials, only very few fundamental studies have focused on the aggregation behavior of *random* ionomers in solution.[10] Such studies have been performed on perfluorinated ionomers (PFI) with long (Nafion) and short (Dow ionomers) pendant chains terminated by sulfonic acid groups: Small-angle X-ray and neutron scattering, SAXS and SANS, respectively, have indicated that PFI form rodlike micelles with a diameter of 40−60 Å in water and in many nonaqueous solvents.[5] ESR studies of aqueous Nafion solutions doped with amphiphilic spin probes have suggested that the probes are associated with large aggregates, that the motion of the probes inside the aggregates is highly restricted and anisotropic, and that the order parameter derived from an analysis of the ESR anisotropy increases toward the aggregate interior.[6−9] The scattering and spectroscopic studies of PFI solutions are complementary, because SAXS and SANS measurements provide data on the *average* size and shape of the aggregates, whereas ESR studies lead to information on the *local* structure and the dynamic properties inside the aggregates.

The poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers, Chart 1a, were one of the first ionomers to be studied,[3,4,11−19] and the term "ionomer" was used in this system for the first time.[3,4] SAXS studies in partially or fully neutralized EMAA ionomers have revealed a new peak that became known as the "ionic peak" and is still considered diagnostic for microphase separation in ionomers. The ionic peak has been assigned to scattering from ordered hydrocarbon chains between the ionic aggregates.[11] The model of ion aggregation has been significantly refined recently to explain results for other ionomers,[12] and additional data on the EMAA ionomers have been obtained by mechanical, dielectric, ESR, infrared, and conductivity measurements.[13]

Because EMAA ionomers are insoluble in water or the usual organic solvents, most studies have been performed on neat or solvent-swollen membranes. A procedure for the dissolution of the EMAA ionomers in water in an autoclave has however been developed,[20a] thus making possible the study of the solution structure and comparison with results obtained for the mem-

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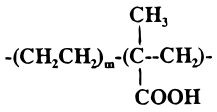
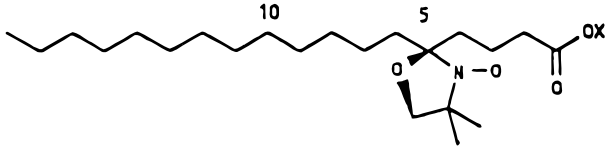
Chart 1

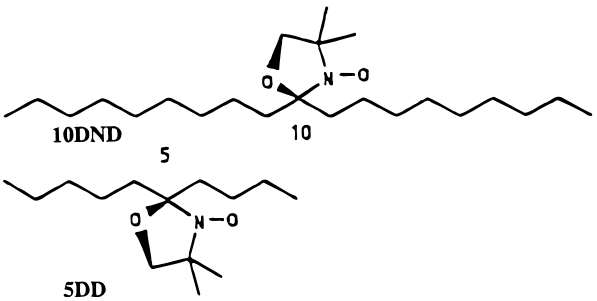
a. EMAA Ionomer, Acid Form



b. Nitroxide Spin Probes



5DSK: $n=5$, **X=K** (*n*: doxyl position)
5DSA: $n=5$, **X=H**
10DSA: $n=10$, **X=H**
10DSE: $n=10$, **X=CH$_3$**



branes and other ionomer solutions such as PFI. A recent study of aqueous (D_2O) solutions by SANS[21] has centered on five aqueous solutions of EMAA ionomers varying in the amount of MAA (5.4 and 7.5 mol %). These measurements have suggested that large colloidal particles exist in the solutions. The short semiaxis of the particles varies in the range 59−124 Å, depending on the type of counterion and the degree of neutralization. Two systems have been investigated in greater detail by SANS: The results for one aqueous solution (5.4 mol % MAA, 60% neutralization by Na^+) have suggested the presence of ellipsoidal particles with long and short semiaxes of 355 and 124 Å, respectively. For a second solution (7.5 mol % MAA, 90% neutralization by K^+), the corresponding dimensions are greatly reduced, to 105 and 59 Å, respectively. In general, the dimensions of the aggregates vary linearly with the average distance between the ionic groups.[21]

We present a study of self-assembling of EMAA ionomers as swollen membranes and in aqueous solutions. This study was initiated with three main objectives: (a) to obtain details on the local environment of the probes associated with the ionomer aggregates in solutions and in swollen membranes and to compare with current models for the swollen membranes;[22,23] (b) to assess the dynamic properties of the aggregates; (c) to compare the behavior of *protiated* and *perfluorinated* ionomer systems. In this paper, we will include the analysis of ESR spectra for spin probes that differ in their hydrophilicity and that are associated with the ionomer aggregates formed in aqueous solutions, as a function of ionomer concentration. The following paper[24] will focus on the dynamic nature of the aggregates in aqueous solutions and in swollen membranes and will present the results obtained from an analysis of the temperature variation of ESR spectra. Selected preliminary results have been presented.[25]

Experimental Section

The starting material, poly(ethylene-*co*-methacrylic acid), had a melt index of 60 g/10 min, $M_n = 20\,500$ and $M_w = 84\,900$; the content of methacrylic acid was 7.5 mol %, and thus the average number of backbone carbons between carboxylic groups was 26. The copolymer was neutralized (90%) in the melt[26] by K_2CO_3 in an extruder at 180−260 °C;[27] the notation for the neat ionomer is EMAA-0.9K. Aqueous solutions were prepared from EMAA pellets (25 kg) suspended in deionized water (75 L) in the presence of KOH (2940 g) in an autoclave (inner volume, 100 L) at 150 °C for ∼30 min; the rotation rate was 71 rpm. After dissolution, the autoclave was cooled to 25 °C in 90 min while stirring.[20b] The ionomer content of the solution, 25.5% (w/w), was determined from the weight loss of the samples after drying in vacuum at ∼440 K for 20 min. The 25.5% (w/w) aqueous solution and the dry membrane EMAA-0.9K were prepared in the laboratories of Du Pont-Mitsui Polychemicals Co. Ltd., Chiba, Japan. Less concentrated solutions, in the range 0.5−17% (w/w), were prepared by diluting the original solution with distilled water and stirring overnight.

Six nitroxide spin probes were selected for this study (Chart 1b), for the following reasons: 5- and 10-doxylstearic acid, 5DSA and 10DSA, respectively, have the COOH group in common with the EMAA ionomers and differ in the position of the doxyl group; these probes are expected to report on the local environment at different distances from the head group and, thus, at different distances from the COO^- side group of the ionomers. The most hydrophilic probe is 5-doxylstearic potassium salt (5DSK), and the spin probe 10-doxylstearic methyl ester (10DSE) is the most hydrophobic of the probes based on stearic acid. Most conclusions from the present study are based on the ESR spectra of these spin probes. The most hydrophobic probes, 5-doxyldecane (5DD) and 10-doxylnonadecane (10DND), were studied in order to verify the conclusions deduced from the other four probes. The six probes chosen are therefore expected to be reporters at sites with different polarities and degree of hydration in the ionomer aggregates.

The probes 10DSE, 5DD, and 10DND were from Molecular Probes, Eugene, OR, and the others were from Aldrich; all were used with further purification. The stock solution of 5DSK in water was obtained by neutralizing 5DSA with 0.1 M aqueous KOH (Fisher Scientific) and dilution with distilled water. Stock solutions were prepared in cyclohexane (5DD), chloroform (10DND), and ethanol (the other probes). All stock solutions were divided into several vials, as described previously for the PFI systems.[7] After evaporation of the solvent, the ionomer solution was added to the dry spin probe; the solution was then shaken by hand for several minutes, sonicated for 20 min, kept in a glovebox in an oxygen-free atmosphere for at least 20 min, transferred to capillaries made from disposable pipets, and flame-sealed for the ESR measurements. The spin probe concentration in the ionomer solutions was 0.7−1 mM, which corresponds in the ionomer system to the ratio $[COO^-]/[\text{spin probe}] = 40-500$ at ionomer concentrations of ≥ 2% (w/w) and ∼20 at ionomer concentrations of 0.5 and 1% (w/w).

The doped membranes were prepared by soaking dry films of EMAA-0.9K of thickness 0.3 mm and dimensions 25 mm × 8 mm in $\sim 10^{-4}$ M aqueous solutions of the spin probes at room temperature for 18 days until a swelling equilibrium was established, as verified by a constant weight gain of the membranes. The doped membranes were then rinsed with distilled water, sonicated in distilled water at room temperature for 10 min, dry-blotted with Kimwipes, cut into 3 mm × 10 mm pieces, inserted in 4 mm o.d. quartz tubes, and sealed in air with parafilm. The water content in the membranes was 15 ± 1% (w/w) from the weight increase during swelling and did not vary with the type of spin probe. The ratio $[COO^-]/[\text{spin probe}]$, ∼1000, was estimated by comparing the integrated intensity of a known membrane weight with that of a solution of the spin probe similarly positioned in the ESR

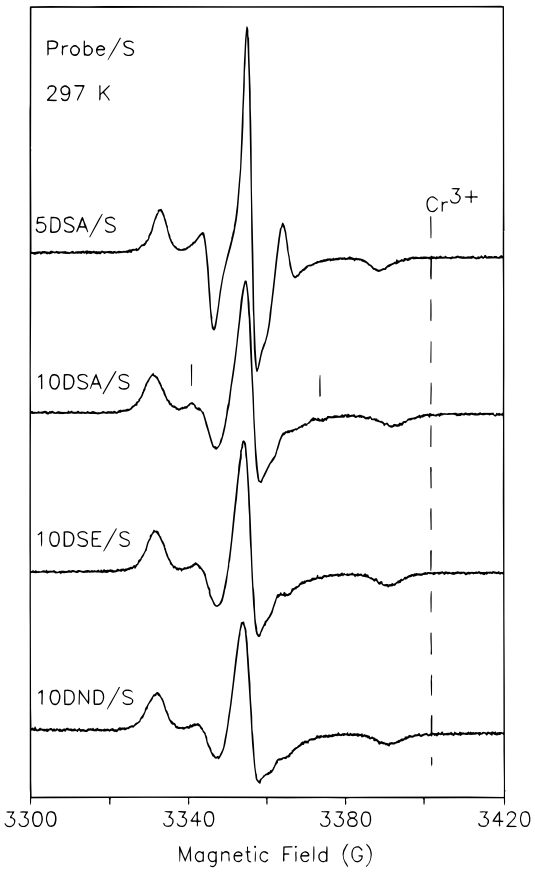


Figure 1. X-band ESR spectra at 297 K for the indicated spin probes in EMAA aqueous solutions (ionomer concentration, 25.5% w/w). Spectra are normalized in terms of total intensity and microwave frequency. Vertical bars for 10DSA/S indicate two of the three lines of the motionally averaged component (see text). The position of the *g* standard (Cr^{3+}, $g = 1.9796$) is also shown. Microwave power, 2 mW; modulation amplitude, 2 G.

cavity. The notation used for the samples is probe/S and probe/M, where S and M stand for ionomer solution and swollen ionomer membrane, respectively.

ESR spectra at X band were measured with a Bruker ECS106 spectrometer at 9.7 GHz (empty cavity at ambient temperature) and 100 kHz modulation, equipped with the ESP 3240 data system for acquisition and manipulation. The microwave frequency was measured with the Hewlett-Packard 5342A microwave frequency counter. A Cr^{3+} marker ($g = 1.9796$ [28]) was used for field calibration. Spectra at 120 K were measured with the ER4111 VT variable-temperature controller and at 77 K in the liquid nitrogen finger dewar inserted in the cavity. The spectral titration method, which involves normalization of spectra, subtraction, and integration, was performed with the Bruker software mentioned above.

Results and Discussion

1. Location of Probes. In Figure 1 we present ESR spectra of the doxylstearic probes and of 10DND in the most concentrated ionomer solution (25.5% w/w), at 297 K. All the spectra consist of a slow motional component, which is assigned to probes with restricted mobility incorporated in large aggregates.[7] The possibility that the probes induce the formation of the polymer aggregates was considered but can be ruled out: Such an effect is expected to be more important at lower ionomer concentrations, when the ratio probe molecules/ionic groups is larger, but no such behavior was observed. In addition, the solubility of the probes in the ionomer solutions is larger when the ionomer concentration is larger; in the case of the hydrophobic 10DSE probe, we have shown for the PFI systems that the probe is solubilized by the ionomer,[7] due to intercalation in the aggregates. A similar result was observed in the EMAA solutions (*vide infra*).

A very weak triplet (relative intensity, ≤1%) is indicated by vertical bars for 10DSA and will be discussed in the next section. The signals from 5DSA are narrower compared to the other probes, a result that can be explained by additional motional averaging, a more clearly defined site for 5DSA in the aggregates, or a combination of these two effects: spectral simulations are expected to clarify this issue and will be reported separately in the near future. The extreme separations of the outer peaks ($2A'_{zz}$) at 55.7, 61.2, and 59.7 G for 5DSA, 10DSA, and 10DSE, respectively. Because the probes have similar magnetic parameters in the same environment, these values suggest in a qualitative way that the site of 5DSA is more defined compared to the other two probes, in accord with the narrower signals.

In order to separate dynamical and polarity effects on the extreme separation, we have measured the values of $2A_{zz}$ in the rigid limit at 77 K for the doxyl stearic probes in the 25.5% (w/w) solution (Table 1); these values are expected to reflect the local polarity.[29−31] The $2A_{zz}$ values are 71.1, 69.3, and 67.3 G for 5DSA, 10DSA, and 10DSE, respectively, suggesting a polarity gradient in the aggregates, with the highest polarity corresponding to the location of 5DSA. To confirm this conclusion, we also measured the spectra of 10-doxylnonadecane (10DND) at 297 K (the lowest spectrum in Figure 1) and at 77 K, because 10DND is more hydrophobic than the DSA and DSE probes; the values are $2A'_{zz} = 59.1$ G and $2A_{zz} = 66.6$ G, respectively. As only very slight differences in *g* and ^{14}N hyperfine values are expected for 10DND compared to the doxylstearic probes, the results for 10DND clearly support the above conclusion: The hydrophobic 10DSE and 10DND spin probes are located in the hydrophobic core of the aggregates, while the hydrophilic 5DSA probe is in the polar domain at the ionomer aggregate−solvent interface; and 10DSA is located in an intermediate region.

The ESR spectra at 297 K of the indicated spin probes in the membranes swollen to equilibrium by water are shown in Figure 2. Only the slow motional component is detected, and the spectral shapes differ in the central portion. The $2A'_{zz}$ values are 62.2, 62.2, and 60.5 G for 5DSA/M, 10DSA/M, and 10DSE/M, respectively. The corresponding $2A_{zz}$ values at 77 K in the rigid limit show a clear trend: 71.1, 68.6, and 66.6 G for 5DSA/M, 10DSA/M, and 10DSE/M, respectively. These values are similar to, and show the same trend as, the corresponding values for probe/S, indicating that for a given probe the local polarities in solution and in the swollen membrane are similar.

2. Effect of Ionomer Concentration. The extreme separations at 297, 120, and 77 K (rigid limit) for the spin probes in the solutions as a function of ionomer concentration are summarized in Table 1. The standard deviations (from at least two, usually more, separate preparations) are also shown, as a measure of the experimental error. Although the extreme separations at 120 and 77 K are not significantly different, we will consider the value of $2A_{zz}$ at 77 K as the rigid limit value, if measured. The isotropic ^{14}N splittings in water, in the absence of ionomer are $A_{iso} = 15.81$ (5DSA) and 15.85 G (10DSA), both ±0.05 G.

Table 1. Extreme Separation ($2A_{max}$, in G) of ESR Spectra at 297, 120, and 77 K[a]

EMAA-0.9K	5DSK	5DSA			10DSA			10DSE			10DND		
(% w/w)	297 K	297 K	120 K	77 K	297 K	120 K	77K	297 K	120 K	77 K	297 K	120 K	77 K
0.5	56.0	55.5	69.5		61.9	68.4		60.6	nd[b]		60.2		
1	55.9	55.9	71.4		62.5	68.6		60.6	67.6				
2		56.0	71.7										
4.5	55.4	55.7	71.2		61.9	68.0		60.3	67.0		59.8		
10	55.7	55.8	70.7	71.4	61.3	68.5	69.5	60.4	67.8	67.3			
17					61.2	68.1							
25.5		55.7	71.3	70.7	61.2	69.3	69.1	59.7	68.0	67.3	59.1	67.8	66.6
average	55.8	55.8	71.0	71.1	61.7	68.5	69.3	60.3	67.6	67.3	59.1	67.8	66.6
85		62.2	71.4	71.1	62.2	69.1	68.6	60.5	67.2	66.6			

[a] The experimental uncertainty in the determination of the extreme separations is ±0.3 G. [b] Not determined.

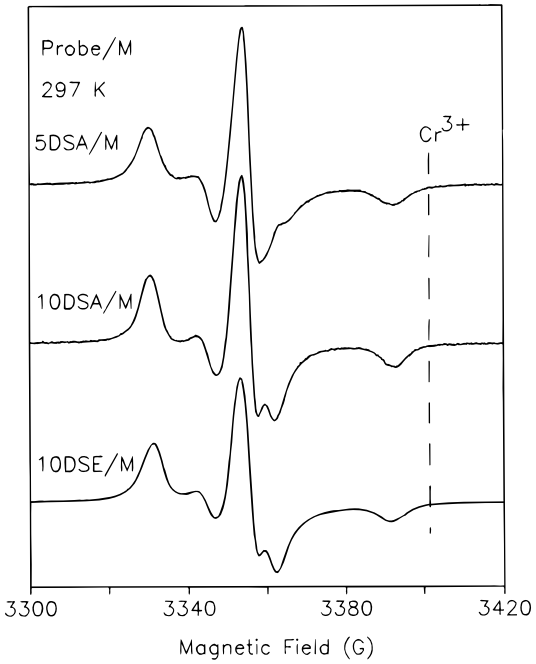


Figure 2. X-band ESR spectra at 297 K for 5DSA/M, 10DSA/M, and 10DSE/M. Spectra are normalized in terms of total intensity and microwave frequency. Microwave power, 2 mW; modulation amplitude, 0.5 G.

In Figure 3a we present ESR spectra of 5DSA/S at 297 K in aqueous solutions of EMAA-0.9K for the indicated ionomer concentrations. As mentioned above, the spectrum at the highest concentration (25.5% w/w) consists of the slow-motional component only. As the concentration decreases, a sharp motionally averaged triplet appears and gradually grows with decreasing polymer content; spectra at concentrations of ≤10% (w/w) consist of two components. The variation of the extreme separation $2A'_{zz}$ of the slow-motional component with concentration is within the experimental error, as indicated in Table 1. The narrow triplet is identical to that obtained for the probe in neat water at 297 K and can therefore be assigned to spin probes free of ionomer chains. The water phase in the polymer solutions may contain a small number of polymer chains; therefore it is probable that the probe molecules are in the vicinity of the chains. The triplet could represent probes associated with smaller aggregates, where the probe molecules rotate freely and isotropically. In Nafion, it was tentatively proposed that such aggregates consist of single chains, or "unimers".[7] A rough estimate of the radius r_u of the single-chain aggregate can be obtained from the ionomer density ($d \approx 1$ [32]) and molecular weight (20 500), by assuming that the aggregate contains no water; the result is $r_u \approx 20$ Å. Consequently, there are two possibilities for assigning the triplet signal, to probes in the solvent or associated with unimers; more data are needed to select one of these two options.

ESR spectra of 10DSA/S as a function of ionomer concentration are presented in Figure 4a. The overall trend is similar to that mentioned above for 5DSA: The relative ratio of the slow motional component gradually decreases and the ratio of the isotropic component increases, as the ionomer concentration decreases. However, the probes 5DSA/S and 10DSA/S are different in two important ways: First, the spectrum of 10DSA contains a (small) contribution from the isotropic component even at the highest ionomer concentration, as indicated in Figure 1 by vertical bars; second, the relative intensity of the motionally averaged triplet for 10DSA/S is clearly larger than that for 5DSA/S at a given (low) ionomer concentration. To emphasize the quantitative difference between 5DSA/S and 10DSA/S, we used the spectral titration method, as described previously,[7,29] to deconvolute the spectra at the lower ionomer contents into the two components. The slow motional component obtained after subtraction of the narrow triplet is shown in Figures 3b (for 5DSA/S) and 4b (for 10DSA/S).

The relative intensities of the slow motional component (in %) versus ionomer concentration for these two spin probes, together with the data for 5DSK, the fully neutralized potassium salt of 5DSA, are shown in Figure 5. The results for 5DSA and 5DSK are considered within the experimental error. We note that in a spectral titration procedure the isotropic component subtracted from the composite signals was the spectrum of the corresponding probe in neat water at 297 K; careful examination of the integrated spectrum indicated the presence of a broad line, which contributed ∼10−20% to the total intensity; this signal is assigned to the aggregation of the probes. Although it was hard to avoid the contribution of the broad signal in the more intense signals, we confirmed that the errors from this origin were always smaller than the scattering of data from multiple preparations that are shown by error bars in Figure 5. From Figure 5, it is clear that the intensity decrease of the slow motional component with decreasing concentration is more significant for 10DSA/S than for 5DSA/S: At 0.5% (w/w) ionomer, the relative intensity is 75 ± 3% for 10DSA/S and 95.4 ± 0.7% w/w for 5DSA/S. This means that, even at 0.5% (w/w), almost all 5DSA molecules reside in large ionomer aggregates, compared to 75% only for 10DSA. A similar behavior has also been observed for these spin probes in Nafion. It is possible that the intercalation of 5DSA in the aggregates is facilitated by the larger amount of water

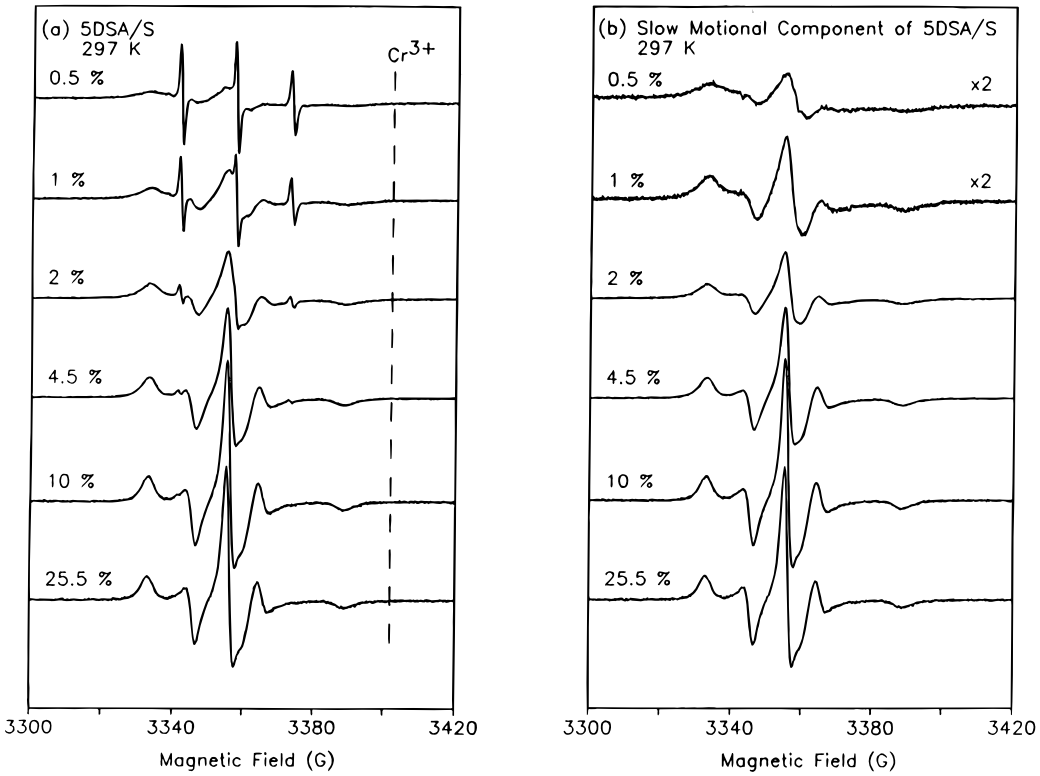


Figure 3. (a) X-band ESR spectra at 297 K for 5DSA/S as a function of ionomer concentration (in % w/w). Spectra are normalized in terms of total intensity and microwave frequency. Microwave power, 2 mW; modulation amplitude, 0.5 G. (b) Slow motional component deduced by spectral titration for 5DSA/S at 297 K as a function of ionomer concentration (in % w/w). Spectra are normalized in terms of total intensity and microwave frequency and then expanded vertically by the factor given on the right.

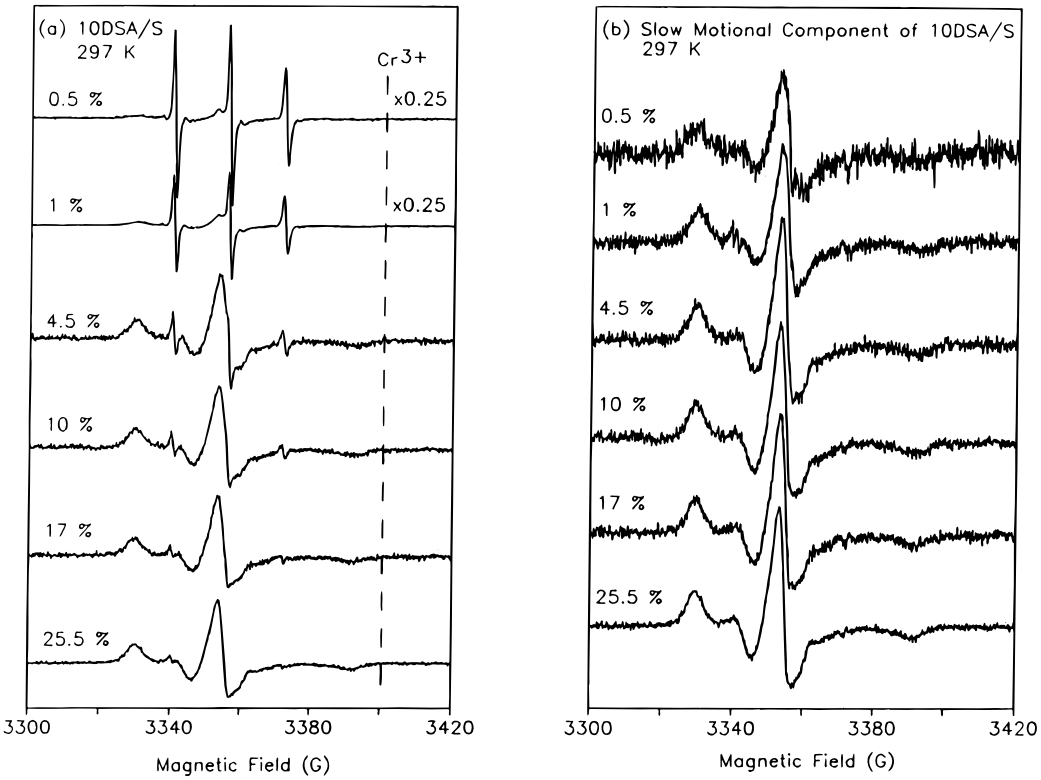


Figure 4. (a) X-band ESR spectra at 297 K for 10DSA/S as a function of ionomer concentration (in % w/w). Spectra are normalized in terms of total intensity and microwave frequency and then expanded vertically by the factor given on the right. Microwave power, 2 mW; modulation amplitude, 0.5 G. (b) Slow motional component deduced by spectral titration for 10DSA/S at 297 K as a function of ionomer concentration (in % w/w). Spectra are normalized in terms of total intensity and microwave frequency.

near the aggregate−solvent interface, whose effect is expected to be solubilization of nitroxide group in the 5-doxyl ring. If this rationale is correct, the data deduced from the 5DSA/S samples are more representative of the actual degree of aggregation than those deduced from the 10DSA/S samples.

The line shapes of the slow motional components are also affected by ionomer concentration, as seen in

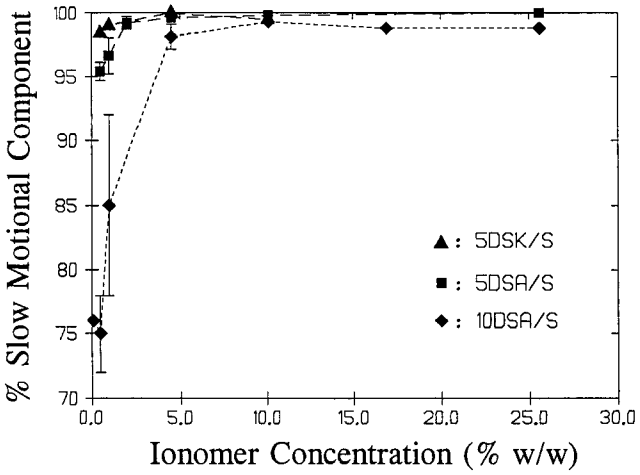


Figure 5. Relative intensity (%) of the slow-motional component for 5DSK/S (▲), 5DSA/S (●), and 10DSA/S (◆) as a function of ionomer concentration (in % w/w).

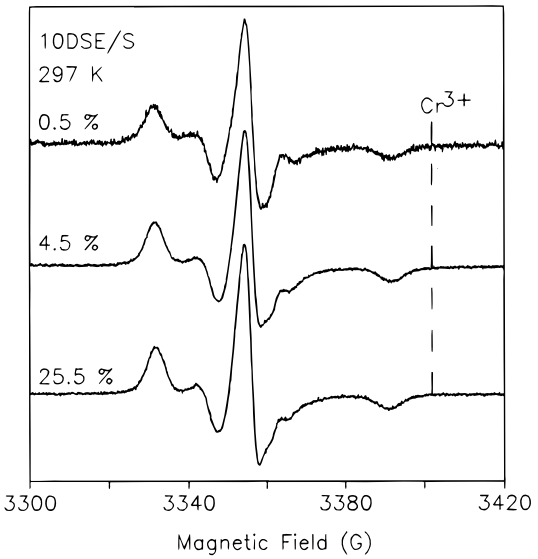


Figure 6. X-band ESR spectra at 297 K for 10DSE/S for the indicated ionomer concentrations. Spectra are normalized in terms of total intensity and microwave frequency. Microwave power, 2 mW; modulation amplitude, 2 G.

Figures 3b and 4b, for 5DSA and 10DSA, respectively. For 5DSA/S, the signals gradually broaden with decreasing ionomer concentration, whereas those of 10DSA/S show no change for ionomer contents in the range 25.5−4.5% (w/w) and only a slight broadening below 4.5% (w/w). To interpret these results quantitatively, spectral simulation is required and will be reported; qualitatively, it is possible that the broader signals at lower ionomer contents be due to a distribution of sizes of the polymeric micelles, spin−spin interactions, or a combination of these two effects.

The ESR spectra of 10DSE/S as a function of ionomer concentration are presented in Figure 6. In contrast to the results for 5DSA/S and 10DSA/S, only the slow motional component was detected for 10DSE/S in the entire concentration range studied, and the spectral pattern showed no detectable changes with ionomer concentration. As clearly seen from the increasing signal-to-noise ratio with increasing ionomer concentration, the 10DSE probe is solubilized in the water solution by the presence of the ionomer. When the same concentration of the probe per volume of solution is used, the increase in signal intensity is by a factor of

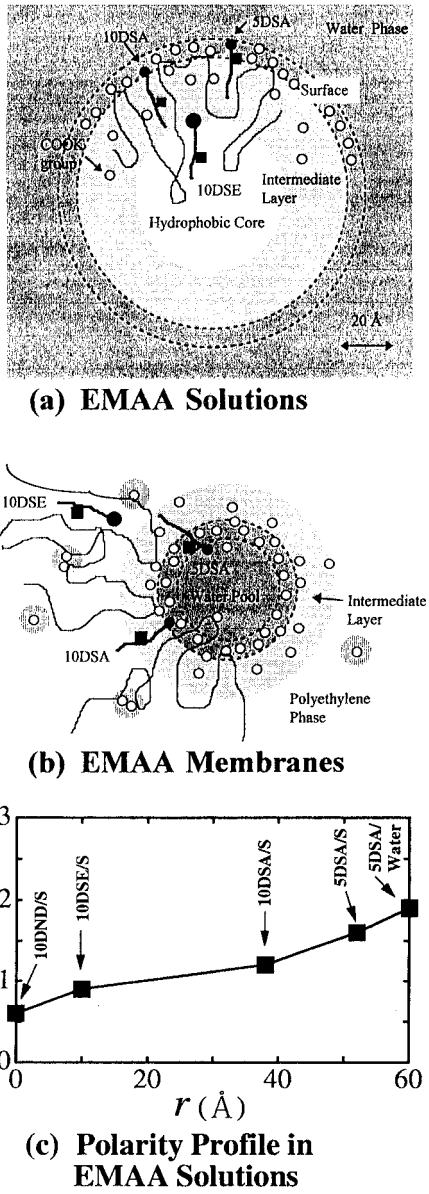


Figure 7. Suggested models for (a) aggregates in aqueous solutions of EMAA ionomers and (b) aggregates in EMAA ionomer membranes swollen by water. The locations of 5DSA, 10DSA, and 10DSE probes in the aggregates are based on the analysis of the ESR results; the carboxylate groups of the ionomer (○) and the acid groups (•), the methyl ester group (●), and the nitroxide groups (■) of the probes are also indicated. Dark shaded, thinly shaded, and white regions represent, respectively, the water phase (hydrophilic phase including a small amount of hydrocarbon chain), the intermediate layer, and the hydrophobic phase. (c) The polarity profile in the aggregates in aqueous solutions of EMAA ionomers along the shorter axis, as derived from this ESR study. The distance (in Å) from the center of the aggregate is *r*.

∼2.6 when going from 0.5 to 4.5% (w/w) ionomer; no noticeable change was observed with further increase in concentration, up to 25.5% (w/w).

3. Structure of Polymer Aggregates in Solutions and in Swollen Membranes. The ESR spectra of 5DSA, 10DSA, and 10DSE indicate locations in regions of decreasing polarity. Based on the results presented above, we propose the locations of the probes and the models for the aggregates in the ionomer solutions and in the swollen membrane given in Figure 7a and b, respectively. We suggest therefore that the aggregates in the aqueous solutions consist of three main regions:

a hydrophobic core (white region), an intermediate layer (thinly shaded region), and a hydrophilic region (thickly shaded region) where most of ions are located. The scale (in Å) is estimated as follows. The maximum length of the three probes in the extended form, l_{max}, and the distance of the nitroxide reporter from the head group, can be calculated from eq 1, where n is the number of

$$l_{max} = 1.5 + 1.265n \quad (1)$$

carbon atoms in the chain[33] ($n = 18$ for the stearic-based probes). We obtain $l_{max} = 24$ Å; the distances to the head group for the C5 and C10 atoms are 8 and 14 Å, respectively. In Figure 7a we have placed the nitroxide group of 5DSA in the hydrophilic region. The NO group in 10DSA was placed in the center of the intermediate region, and the head group at the interface between the intermediate and the hydrophilic region. The location of 10DSE was selected so that the head group is at the interface between the core and the intermediate region, and the C18 atom is near the core center. The length of the short semiaxis deduced from these assumptions is ~60 Å, similar to that deduced in the preliminary SANS experiments, which have been interpreted in terms of an ellipsoidal particle with the shorter semiaxis equal to 59 Å.[21]

In Figure 7b we propose a model for the locations of the three probes in the swollen ionic aggregates. The central shaded region is the "water pool", and its presence in swollen EMAA ionomers has been confirmed by several physical techniques, including SAXS, dilatometry, IR, and dielectric measurements.[22,23] The $2A_{zz}$ values at 77 K (in the rigid limit) vary gradually from 71.1 (5DSA), to 68.6 (10DSA), and to 66.6 G (10DSE) (Table 1), clearly indicating a gradual change in polarity (and hydration) between the hydrophilic and the hydrocarbon regions; this intermediate region is shown as a thinly shaded region in Figure 7b; the nitroxide groups of 10DSA are located in this region. We have no way of estimating the size of the water pool from the data presented in this study. We are currently using cationic probes based on alkylammonium nitroxide probes with different lengths of the alkyl groups (CAT1, CAT8, and CAT16)[34] in order to characterize the polar domains in EMAA solutions and swollen membranes. Plans for the future include characterization of the polar regions with paramagnetic transition metal cations such as VO^{2+} and Cu^{2+}, as we used in the past for reverse micellar systems[35] and for PFI.[6]

In order to visualize the extent of microphase separation, we attempted to deduce the polarity profile of the aggregates in the aqueous solutions, by plotting the difference ΔA_0 (in G) between the isotropic ^{14}N splitting constant of the probes in the aggregates A_0(agg) and the corresponding value in a nonpolar medium A_0(np), which was taken as 13.9 G for the nDSA probes;[31] for 10DND we measured at 297 K an ^{14}N isotropic splitting of 14.0 G in cyclohexane as a prototype for a nonpolar solvent. The polarity profile is expressed via the polarity index ΔA_0, with $\Delta A_0(G) = A_0(agg) - A_0(np)$.

Because the A_0(agg) values for the spin probes cannot be measured directly, we estimated them using the correlation diagram between A_0 and A_{zz} for various solvents given in the literature.[31] The polarity profile shown in Figure 7c was drawn with the additional assumption that the nitroxide group of 10DND is at the center of the aggregates. The positions of the other spin probes follow from the probe locations shown in Figure 7a. Figure 7c suggests a gradual increase in the local polarity from the center to ~40 Å, followed by a more significant increase to the solvent interface. We note that, in the case of microsomal lipid bilayers,[31] the polarity index ΔA_0 in the hydrophobic region is 0.5, similar to that for 10DND in the core of the EMAA aggregates in solution.

4. Comparison of EMAA and PFI Systems. In this subsection we will compare the results obtained for aqueous EMAA ionomers with those for the perfluorinated ionomers (Nafion), and will list the similarities first, followed by the differences.

Similarities. In both systems, two spectral sites were detected for the 5DSA and 10DSA spin probes in aqueous solutions of the ionomers, and the relative intensity of the slow motional component decreased with decreasing ionomer content. Moreover, deconvolution of the spectra for 5DSA/S suggested that the relative amount of ionomer present as aggregates is substantial in both systems, even at very low ionomer concentrations, <1% (w/w). The deconvolution based on 10DSA results in slightly lower percentages of probes associated with aggregated chains at a given ionomer content, a result that was explained in this study by assuming that the solubilization of the nitroxide group in the doxyl ring, and therefore the intercalation of 5DSA in the aggregates, is facilitated by the larger amount of water at the periphery of the aggregates.

The location suggested for the stearic acid-type probes is similar in the two systems, with 5DSA at the interface, and 10DSA and 10DSE progressively deeper inside the aggregates. In both Nafion and EMAA ionomers, the spin probe 10DSE is soluble in water only in the presence of the ionomer, and the degree of solubilization increases with ionomer content.[7] In the water-swollen membranes, only the slow motional component is detected in both systems.

Differences. The $2A'_{zz}$ values at 300 K for 5DSA in aqueous solutions of Nafion increase with ionomer content; on the basis of this result, we have suggested a gradual increase of aggregate size with ionomer concentration. The $2A'_{zz}$ in the membranes swollen by water are significantly higher. The corresponding $2A'_{zz}$ values in EMAA solutions and swollen membranes are constant within experimental error; such behavior can be justified by assuming that the degree of aggregation is very high in the EMAA system even at low ionomer content.

The most important difference between the two systems is evident from the $2A_{zz}$ values in the rigid limit at 77 K. In the EMAA system, the values for 5DSA, 10DSA, and 10DSE, ~71, 69, and 67 G, respectively, reflect the decreasing local polarity from the ionomer−solvent interface to the core of the aggregate. This result is in contrast with that obtained for Nafion, where the $2A_{zz}$ values were larger (73−74 G) and almost the same for 5DSA, 10DSA, and 10DSE.[7] The results in Nafion were interpreted by assuming that the probes localized in the hydrophobic regions *drag* part of their hydration shell into the aggregates. Clearly, this different behavior is driven by the lower compatibility of the protiated probes with the perfluorinated environment in Nafion, compared with the EMAA ionomers. In this respect, the amphiphilic probes chosen are more faithful reporters of the local structure in the EMAA ionomers than in Nafion.

The similarities and differences described above can be understood in a qualitative way by considering the

structure of the ionomer chains, and especially the position of the ionic groups in the chain. The ionic groups of the EMAA ionomers are directly attached to the backbone chains, and the average distance between the ionic groups along the chain is ∼33 Å, much less than the size of aggregates (semiaxes of 60−100 Å from SANS studies), suggesting that some ionic groups must reside in the aggregates; the phase separation between the ionic groups and the hydrophobic backbone chains is therefore expected to be incomplete. In Nafion, the average repeat distance of the ionic groups along the chain is ∼20 Å[7] and the ionic groups are connected to the backbone through a spacer with the length of ∼7 Å. The presence of ionic groups at the end of flexible pendant chains allows more extensive phase separation, with the ionic groups located at the water−polymer interface.

Simulations of the ESR spectra for the EMAA systems will allow a quantitative comparison of the dynamics, degree of motional anisotropy, and order parameter in the aggregates.[36]

Conclusions

Two components have been detected in the ESR spectra of doxyl spin probes in aqueous EMAA solutions and, as in Nafion, have been assigned to nitroxide sites with restricted mobility incorporated in large aggregates and to sites experiencing fast and isotropic motion, respectively. The latter probes are isolated, dispersed in water phase, and/or accompanied by a single chain (*unimer*).

The spectral parameters obtained for probes associated with aggregates suggest that probes with different polarities are located in different regions of the aggregates and report on each environment. From this result, it was suggested that the aggregates consist of three regions: a hydrophobic core, an intermediate layer, and a hydrophilic region where most of the ions are located. The presence of the intermediate layer indicates that the boundary between ionic groups and hydrophobic backbone chains is gradual and that some ionic groups are located inside the aggregates.

Taken together, all the results presented here suggest some water penetration into the aggregates. In perfluorinated systems, however, more complete separation into ionic and nonpolar domains has been suggested from similar spin probe studies. This difference can be understood from the position of the ionic groups in the ionomer chain: close to the backbone in EMAA systems and on relatively long pendant chains in the perfluorinated ionomers.

The protiated probes used in this study are more faithful reporters of the aggregation in a protiated system such as EMAA, compared to a perfluorinated system such as Nafion.

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