Electron Spin Resonance Study of Polymer Self-Assembling: Cationic Spin Probes in Aqueous Solutions of Poly(ethylene-*co*-methacrylic acid) (EMAA) Ionomers

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ABSTRACT: Aqueous solutions of the ionomer poly(ethylene-*co*-methacrylic acid) (EMAA) in the concentration range 0.5−23 wt % were studied by the electron spin resonance (ESR) spin probe method. The spin probes selected for this study were 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl iodides (CAT*n*) with different alkyl groups: methyl (CAT1), octyl (CAT8), and hexadecyl (CAT16). The main objective of this study was to compare the ESR spectra of the CAT*n* probes as a function of temperature and ionomer content in order to deduce details on the structure and dynamics of EMAA micelles and on the interface region between the aggregates and the solvent. ESR spectra were recorded in the temperature range 120−360 K, and the line shape variations and the ^{14}N hyperfine splittings, a_N, were key parameters for the interpretation of the results in terms of the spin probe mobility, and its location in and bonding to the polymeric aggregates. The detection of two spectral components in the ESR spectra of the probes provided evidence for the existence of an equilibrium between large multichain aggregates and unimeric micelles, in accord with previous ESR (based on doxylstearic acid spin probes) and fluorescence (based on pyrene as the luminophore) studies. The results indicated that most spin probe molecules are bound to large intermolecular micelles; the long alkyl chains of CAT8 and CAT16 penetrate into the interior of the aggregates but exhibit different dynamics, suggesting that the longer alkyl chain of CAT16 penetrates deeper, into the more viscous regions of the micelle, compared to CAT8. This conclusion implies that the cationic probes with different alkyl substituents can be used to map the local viscosity and the viscosity gradient. In the EMAA solutions an isotropic triplet was also detected, as a minor spectral component. Its contribution depends on the type of probe and on ionomer concentration and ranges from ≈1% for CAT16 in the 23 wt % EMAA solution to ≈10−15% (depending on probe concentration) for CAT8 in the 0.5 wt % EMAA solution at 300 K. This component was assigned to spin probes bound to unimeric (intramolecular) micelles. Analysis of the ^{14}N hyperfine splittings indicated the formation of an ionic bond between the carboxylic group of the ionomer and the cation of the probes.

Introduction

The amphiphilic polymers known as ionomers, which consist of a nonpolar polymer backbone and a small fraction of pendant or terminal ionic groups (≤15 mol %), self-assemble in the bulk, in the presence of a swelling solvent, and in aqueous solutions.[1,2] The driving force toward self-assembling is the incompatibility between the two components of the polymer chains and, in the presence of solvents, the additional and different *specific* interactions between the solvents, and the polar and nonpolar chain components. In the case of perfluorinated systems, the increased backbone hydrophobicity, compared to protiated analogues, provides an additional impetus for the formation of structures such as micelles, reverse micelles, and lamellar phases, depending on the type of solvent and on polymer content.[3] Electron spin resonance (ESR) spectroscopy based on paramagnetic probes that intercalate in the various regions of the self-assembled system has emerged as an important technique for the study of the structure and dynamics of protiated and perfluorinated ionomers as swollen membranes and in solutions.[4−6] In particular, using amphiphilic spin probes based on doxylstearic acid with the doxyl group attached to carbon atoms at different positions relative to the headgroup (*n*DSA), information has been obtained on the local polarity, the molecular packing, and the degree of order in the system. Such studies have been performed in our laboratory on Nafion, the perfluorinated ionomer containing pendant chains terminated by sulfonic groups,[4,5] and more recently on the protiated ionomer poly(ethylene-*co*-methacrylic acid) (EMAA, Chart 1).[6] A common axiom in spin probe studies is that the use of nitroxide radicals chemically *bonded* to the polymer ("spin labels") leads to more detailed information on the morphology and dynamics of the system compared to spin probes, which are physically *mixed* in the system. The study of EMAA ionomers based on ESR spectra of *n*DSA spin probes has demonstrated, however, that by judicious choice of the polarity, size, and chemical structure of the probe, it becomes possible to insert it in specific regions of the self-assembled system, thus bypassing the often difficult synthetic step of spin labeling.[6] The spin probe ESR method has also been

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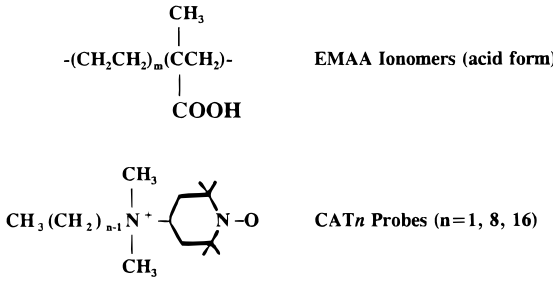
Chart 1: Poly(ethylene-*co*-methacrylic acid) (EMAA) Ionomers and CAT*n* Spin Probes



used to advantage in other ionomeric systems, to characterize the ionic aggregates in poly[styrene-*co*-(sodium methacrylate)] random ionomers,[7] in polymers end-functionalized with ionic groups (*telechelic* ionomers),[8] and in ionically capped diblock copolymers.[9]

While ESR methods have been used to study the dynamics and the local polarity in ionomers, the size of aggregates is usually deduced from small-angle X-ray and neutron scattering studies (SAXS and SANS, respectively).[10−13] For aqueous solutions of EMAA, the results of SANS experiments together with simulations of the scattering curves have convincingly indicated the presence of large colloidal aggregates shaped as cylinders or ellipsoids with short semiaxes in the range 55−135 Å, and a particle length that increases dramatically for low ionic contents; the small dimensions were found to be proportional to the average distance between the ionized groups.[14] An ESR study of doxyl-type spin probes in EMAA ionomers as swollen membranes and in aqueous solutions, together with the SANS data, led to a structural model of EMAA micelles.[6] According to this model, the aggregates 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. Fluorescence studies using pyrene as the probe have provided support for this model: The analysis of the fluorescence emission of pyrene as a function of ionomer concentration has indicated a low polarity of the micellar core (similar to that of *n*-hexane); the core viscosity, estimated from the intensity ratio of the monomer to excimer emissions of 1,3-bis(1-pyrene)propane (P3P), is very high (≥230 cP).[15]

An important finding of the ESR experiments was the detection of small intramolecular aggregates formed within one unimer, in equilibrium with the large aggregates. ESR evidence for the existence of such unimeric micelles has been obtained for aqueous solutions of Nafion and of EMAA ionomers. The conclusions for the EMAA system are in agreement with recent evidence obtained by fluorescence probe spectroscopy.[15] The presence of two spectral components differing in line widths (and thus in the dynamics) has been also detected in ^{19}F NMR studies of Nafion solutions.[16] Unimeric micelles have not been detected in small-angle scattering experiments, most likely because of the limited contribution to scattering from a small amount of small aggregates.

The present paper describes the study of aqueous solutions of EMAA based on ESR spectra of the cationic nitroxide spin probes 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl iodides (CAT*n*) with different alkyl groups: methyl (CAT1), octyl (CAT8), and hexadecyl (CAT16), as shown in Chart 1. The main objectives were to compare the ESR spectra of CAT*n* probes with $n = 1$, 8, and 16 in order to deduce details on the interface between the aggregates and the solvent, and on the structure and dynamics of EMAA micelles, and to revisit the contribution of probes associated with unimeric micelles to the ESR signal. CAT1 in Nafion solutions in different solvents has been studied in our laboratory in the temperature range 260−300 K. The results have suggested the presence of strong ionic interactions between the spin probe and the SO_3^- group of the ionomer in water;[17] similar conclusions were deduced for CAT1 in Nafion membranes swollen by water and in perfluoropolyethers.[3] It was therefore expected that CAT*n* probes provide information on polar domains close to the micellar surface.

Experimental Section

The starting material poly(ethylene-*co*-methacrylic acid) (EMAA) 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 by K_2CO_3 in an extruder at 180−260 °C. Aqueous solutions were prepared from EMAA pellets suspended in deionized water in the presence of KOH in an autoclave at 150 °C for 30 min. After dissolution, the autoclave was cooled to 25 °C in 90 min while stirring. The ionomer content of the solution, 23 wt %, was determined from the weight loss of the samples after drying to constant weight at 390 K. This aqueous solution was prepared in the laboratories of DuPont-Mitsui Polychemicals Co. Ltd. in Chiba, Japan. Less concentrated solutions were prepared by diluting the original solution with doubly distilled water and stirring overnight. Additional details have been published.[6,18] The solutions examined in this as well as in the previous study[6] were slightly turbid. The turbidity is due to unsoluble residuals (≈3 wt % of the total polymer content) that were removed by filtration with filters of pore diameter 0.45 μm (SFCA Nalge Nunc International, from VWR Scientific). Control experiments with filtered samples indicated, however, that the presence of the suspended particles has no effect on the ESR spectra of the CAT*n* spin probes.

The spin probes 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl iodides were obtained from Molecular Probes, Eugene, OR, and used without further purification. The proper amounts of the stock solution of the spin probe in ethanol were evaporated in sample vials with a stream of nitrogen to obtain films that were then dissolved in neat water or in the ionomer solutions. To facilitate the solubilization of the probe, the samples were sonicated for 20 min (Branson bath sonicator) and stirred with magnet bars at ≈40 °C. In most experiments the spin probe concentration was ≤0.5 mM. The molar ratio $[-COO^-]/[CATn]$ in the EMAA solutions was in the range ≈1000 (in 0.5 mM CAT*n*/23 wt % EMAA systems) to ≈20 (in 0.5 mM CAT*n*/0.5 wt % EMAA systems). Some experiments were performed with a *constant* probe-to-ionomer ratio (vide infra). The solutions were prepared in a glovebox, in an oxygen-free atmosphere. The neat water and the original ionomer solution were bubbled with nitrogen for 20 min at least; the nitrogen used for deaeration of the ionomer solutions was presaturated with water. The solutions were transferred, also in the glovebox, to capillaries made of disposable pipets that were sealed first with Parafilm and finally flame-sealed before the ESR measurements.

ESR spectra at the X-band were measured with a Bruker ECS106 spectrometer equipped with the ESP 3240 data system for acquisition and manipulation, and with the ER4111 VT variable temperature unit. The following parameters were used for spectral acquisition: magnetic field modulation, 100 kHz; microwave power, 2 mW; modulation amplitude, 0.3−1 G depending on line width and signal intensity; time constant, 20 ms; conversion time, 41 ms; number of points, 2048; number

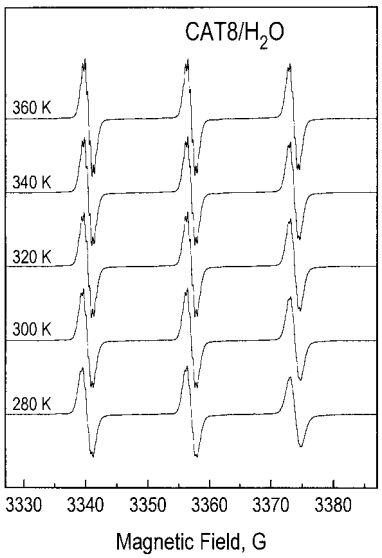


Figure 1. X-band ESR spectra of aqueous CAT8 (probe concentration 0.23 mM) at the indicated temperatures. Modulation amplitude in all spectra: 0.3 G.

of accumulated scans, 10−20; temperature, 120−360 K for the ionomer solutions and 275−360 K for the neat water solutions of the CAT*n* probes. When ESR spectra were measured as a function of temperature, the ionomer samples were quenched in liquid nitrogen to ensure that the micellar structure was retained[19] and transferred to the ESR cavity while at 120 K.

Results

In this section we will present and interpret the experimental ESR spectra of CAT*n* spin probes in terms of line shapes and a_N values. The general, the theory of ESR spectra from nitroxide radicals has been summarized in numerous reviews, and in three comprehensive volumes.[20]

All ESR spectra presented in stack plots were normalized to the same integrated intensity and, if necessary, expanded or reduced vertically by the factor indicated to the right of the spectrum.

CAT*n* Probes in Aqueous Solutions. ESR spectra of the probes were measured in the temperature range 275−360 K, for probe concentrations of 0.23 mM. Typical spectra are shown in Figure 1, for CAT8 in neat water; similar spectra were obtained for CAT1 and CAT16. In all cases, motionally averaged signals were observed, consisting of the three lines due to the interaction of the unpaired electron, which is localized mainly on the −NO fragment, with the ^{14}N nucleus ($I = 1$). These lines exhibit a well-resolved superhyperfine (shf) structure due to the additional small interaction of the unpaired electron with the protons of the piperidinyl ring. As seen in Figure 1, the spectral resolution increases with temperature. From measurements of numerous ESR spectra we also concluded that the resolution is more pronounced at lower concentrations of the probe, and less pronounced in samples that were not deoxygenated by bubbling with nitrogen.

The critical micelle concentration (cmc) for CAT16 as the bromide salt, 0.46 mM, was determined by ESR, from the appearance of a broad singlet due to the aggregation of probe molecules;[21] for the corresponding iodide salt the cmc, 0.25 mM, was determined from surface tension measurements.[22] The cmc for CAT8 is expected to be higher than that of CAT16, because of the lower hydrophobicity. The probe concentration in the aqueous solutions studied, 0.23 mM, was therefore below the critical micelle concentration, cmc, of the probes. The narrow lines seen in the ESR spectra such as those shown in Figure 1, and the absence of the broad line due to probe aggregation, indicated that this was the case.

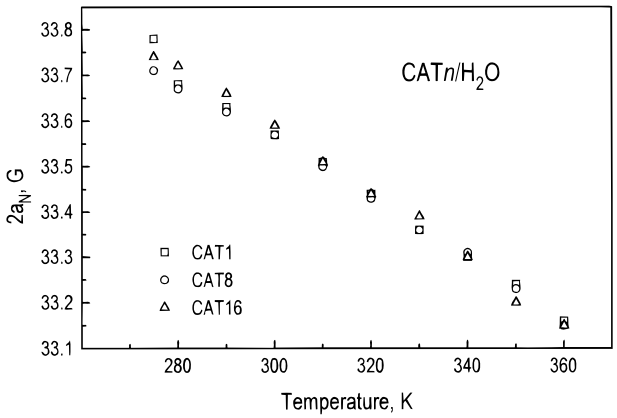


Figure 2. Dependence of total spectral separation $2a_N$ on the temperature for the CAT*n* spin probes in neat water.

The a_N values determined from the ESR spectra are the same for all the examined CAT*n* spin probes (within the uncertainty ≤0.05 G) and decrease with temperature, as shown in Figure 2, where the total spectral separation $2a_N$ is plotted. The average a_N values are 16.79 G at 300 K and 16.58 G at 360 K. Data measured at 300 K are in reasonable agreement with those reported in the literature: 16.8 G for CAT1, and 16.9 G for CAT9, CAT12, and CAT16 (as bromide salts) at 298 K.[23] Furthermore, the a_N value we reported earlier for CAT4 at 320 K (16.75 G)[24] is identical to the present values at this temperature (average of 16.72 G for CAT1, CAT8, and CAT16). Increasing the pH of the solutions to 10, which is characteristic for the EMAA solutions, had no effect on the spectra, as checked for CAT8 and CAT16 in the range 275−300 K.

The decrease of a_N for CAT4, CAT8, and CAT16 with temperature is relatively small and can be related to the lowering of the dielectric constant, ϵ, of the solvent: from $\epsilon \approx 85$ at 280 K to $\epsilon \approx 59$ at 360 K.[25] This temperature effect was not observed for *n*DSA spin probes: the a_N value of 15.80 ± 0.03 G was deduced at 300 K as well as at 360 K.[4−6] Thus the CAT*n* probes appear to be more sensitive than the *n*DSA probes to changes of the local polarity. To the best of our knowledge this temperature effect in neat water solutions of CAT*n* probes is presented here for the first time.

The ESR spectra of the aqueous solutions of the CAT*n* probes will be taken as reference when interpreting the spectra of the probes in solutions containing EMAA ionomers.

CAT*n* Probes at 300 K in Aqueous Solutions of EMAA. X-band ESR spectra of CAT*n* probes at 300 K as a function of EMAA concentration in aqueous solutions are presented in Figures 3 (CAT1), 4 (CAT8), and 5 (CAT16). The spectra of CAT1 are motionally narrowed, as in neat water; the presence of EMAA, however, leads to an increase of the line width and to a gradual decrease of a_N with an increase in EMAA content: $a_N = 16.62 \pm 0.03$ G for the ionomer content of 23 wt %. In contrast to CAT1, two components are clearly seen in the ESR spectra of CAT8 and CAT16. The motionally averaged "fast" signal (triplet whose outermost lines are indicated by downward arrows in

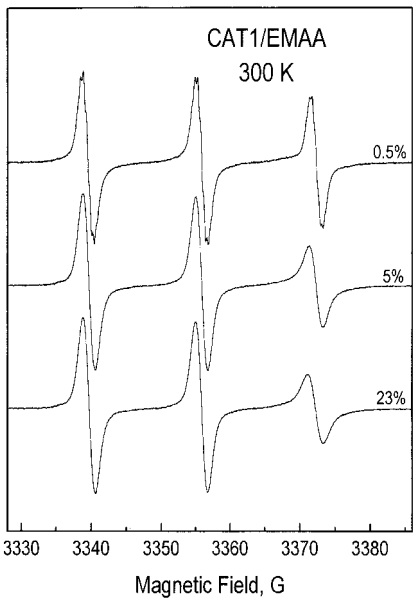


Figure 3. X-band ESR spectra of CAT1 (concentration 0.35 mM) in EMAA solutions for the indicated ionomer concentrations (in wt %) at 300 K. Modulation amplitude: 0.3 G.

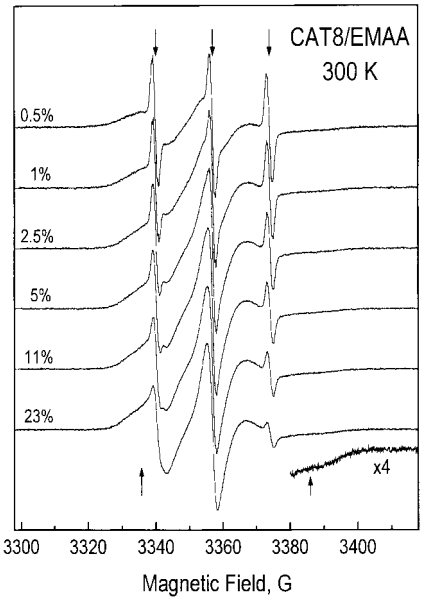


Figure 4. X-band ESR spectra of CAT8 (concentration 0.5 mM) in EMAA solutions for the indicated ionomer concentrations (in wt %) at 300 K. Modulation amplitude: 0.5 G. Downward arrows point to the fast spectral component. Upward arrows indicate the extreme spectral features.

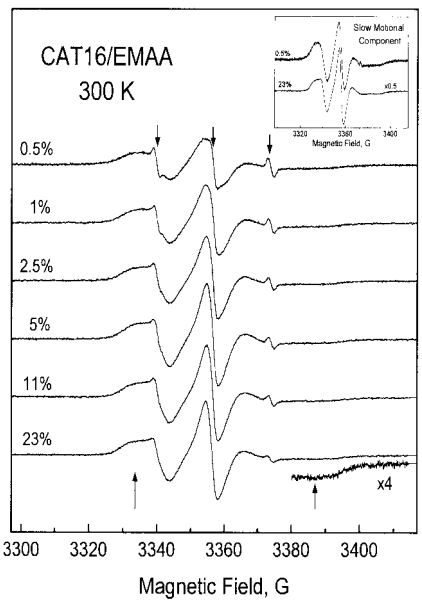


Figure 5. X-band ESR spectra of CAT16 (concentration 0.5 mM) in EMAA solutions for the indicated ionomer concentrations at 300 K. Modulation amplitude: 0.5 G. Arrows are as in Figure 4. The inset shows the slow-motional component obtained by spectral titration for two ionomer concentrations.

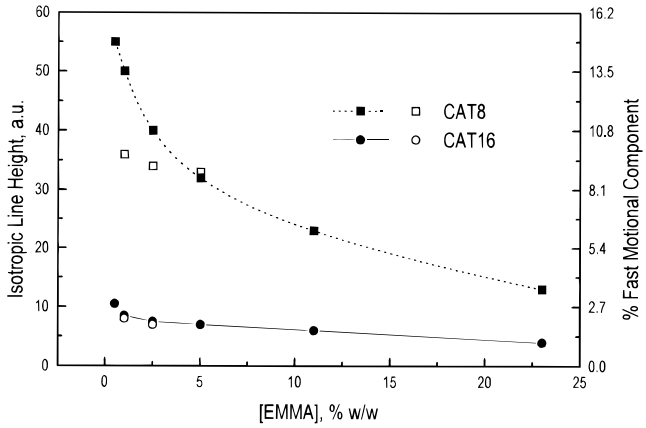


Figure 6. Dependence of the intensity of the fast motional component of CAT8 (- - -) and CAT16 (—) at 300 K on EMAA concentration: ■ and ●, constant probe concentration, [CAT*n*] = 0.5 mM; □ and ○, constant ratio $[COO^-]/[CATn] \approx 500$.

Figures 4 and 5) is a minor component and is superimposed on the signal typical for slow-tumbling spin probes. The maximum ("extreme") separation, indicated in Figures 4 and 5 by upward arrows, is independent of EMAA concentration and is 54 ± 1 G for CAT16. In the case of CAT8 the outermost peaks are not as well resolved, but it is quite evident that the maximum separation is lower, only ≈50 G.

The fast component in CAT8/EMAA and CAT16/EMAA spectra differs from the corresponding signal in neat water in terms of line widths and a_N values: In the EMAA systems the ^{14}N hyperfine splitting is higher: $2a_N = 34.07 \pm 0.05$ G for CAT8, and $2a_N = 33.97 \pm 0.07$ for CAT16, as determined for the lower ionomer concentrations where the low field lines are well resolved. Furthermore, the lines are broader by 0.1−0.3 G (measured peak-to-peak), depending on EMMA concentration. For these reasons it was not possible to deconvolute precisely the two spectral components by spectral titration[5,6] using the corresponding CAT*n*/H_2O signal as a titrant. The contribution of the fast component was estimated, however, by comparing the amplitude of the high field line ($m_I = -1$) of the triplet in spectra normalized to the same integrated intensity. The results are plotted in Figure 6, where the solid symbols represent the results for a constant probe concentration, [CAT*n*] = 0.5 mM (as for spectra presented in Figures 4 and 5), and the open symbols those for a constant ratio $[COO^-]/[CAT] \approx 500$, a value identical to that in the 0.5 mM CAT*n*/11 wt % EMAA solutions. Although the amplitudes are not strictly proportional to the intensity of the fast component (due to line width variations), it is clear from Figure 6 that the contribution of the fast component decreases with the EMAA content and is higher for CAT8 than for CAT16, especially at lower EMAA concentrations. For

CAT8 the effect of EMAA content is less pronounced if the ratio [COO^-]/[CAT] remains not lower than ≈500. Spectral deconvolution of selected CAT*n*/EMAA systems at 300 K was done by subtracting from the composite spectrum the signal of the CAT*n*/H_2O solution at 280 K, in which the line separation has been numerically increased to match the value observed in the presence of EMAA. The slow-motional component for CAT16 at two ionomer concentrations is shown in the inset of Figure 5. The lines are broader in the more diluted EMAA solution, most probably due to enhanced spin−spin interactions as the concentration of the micelles decreases and more probe molecules become bound to one aggregate. The contribution of the fast component obtained by the spectral titration followed by integration was 15.5 ± 2.0%, 2.6 ± 0.4%, and 0.9 ± 0.2% for CAT8/0.5 wt % EMAA, CAT16/0.5 wt % EMAA, and CAT16/23 wt % EMAA, respectively. On the basis of these results, we have rescaled in Figure 6 the line heights into the units of percentage of fast component, as indicated on the right-hand axis.

It is evident from the above results that in EMAA solutions the CAT*n* spin probes are bound to the ionomer: their ESR spectra are different than those in neat water, in terms of the line shapes and a_N values. The slow motional component detected for CAT8 and CAT16 has not been observed at all in neat water solutions of the probes at 300 K; and the fast component for these probes has a higher a_N value compared to that in neat water. The broader lines and lower a_N values observed for the CAT1/EMAA system indicate that the rotational diffusion of the probe is slower and its microenvironment is less polar than in water, suggesting a solubilization site in EMAA micelles; the magnetic parameters for CAT1 will be discussed in greater detail in the Results.

The probe mobility is greatly affected by the presence of the ionomer in the case of CAT8 and CAT16. The major slow motional component of their spectra is assigned to species embedded in the large aggregates that consist of a number of EMAA chains. The minor 3-line component is assigned to spin probes bound to intramolecular micelles formed within one chain. Such micelles are expected to have an internal molecular packing looser than the large aggregates, and also, because they are small, the rotation of the aggregate as a whole may be possible on the time scale of the ESR experiment. Consequently, the probe signal becomes motionally averaged.

It is important to mention that the CAT*n* concentration in samples that contained EMAA was 0.5 mM, above the cmc in neat water. Because the majority of the probe molecules are associated with and solubilized by the ionomer (as seen in Figure 6), probe aggregation is not expected and was not detected in these systems.

Temperature Effects on ESR Spectra of CAT*n* Probes in EMAA Solutions. The evolution of the ESR spectra as a function of temperature has been followed for CAT1 in the aqueous solution containing 23 wt % EMAA, and for the other two probes at six EMAA concentrations in the range 0.5−23 wt %. The results are illustrated in Figures 7−9 for the three probes. At the lowest examined temperature, 120 K, typical rigid limit spectra were detected from which the parallel component, A_{zz}, of the hyperfine splitting tensor for ^{14}N was determined. The values of A_{zz} and a_N reflect the local polarity sensed by the nitroxide group.[20] The

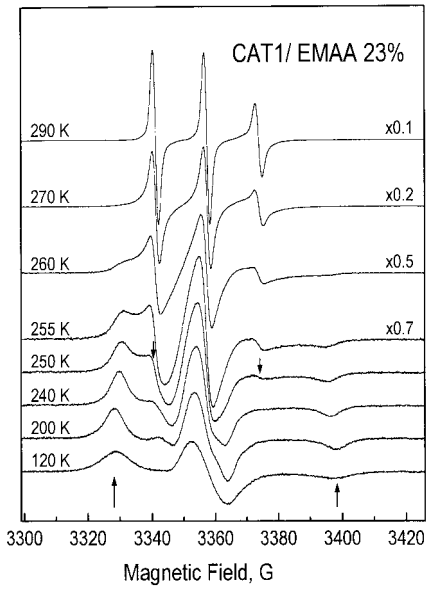


Figure 7. Selected X-band ESR spectra as a function of temperature of CAT1 (concentration 0.34 mM) in EMAA solutions containing 23 wt % ionomer. Modulation amplitude: 1 G.

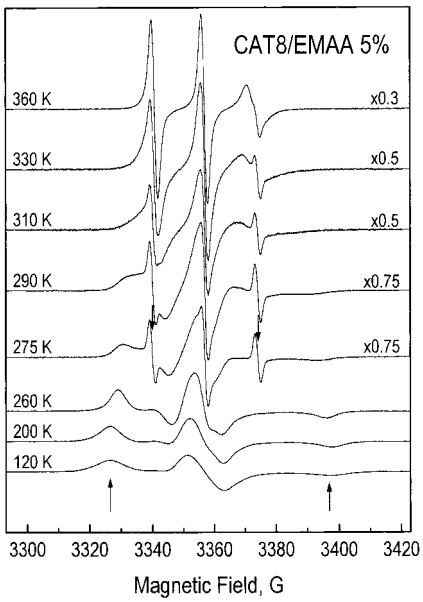


Figure 8. Selected X-band ESR spectra as a function of temperature of CAT8 (concentration 0.5 mM) in EMAA solutions containing 5 wt % ionomer. Modulation amplitude: 1 G.

maximum line separation, $2A_{zz}$, within ≈0.3 G, is constant with temperature up to 200 K for CAT1 and CAT8 and up to 220 K for CAT16; the only effect is line narrowing. The average values of $2A_{zz}$ are summarized in Table 1. For all probes the values are essentially the same at a given ionomer concentration. In the EMAA solution containing 23 wt % ionomer $2A_{zz} = 70.9 \pm 0.3$ G, a value somewhat lower than those deduced from simulations of the spectra of different CAT*n* probes in neat water (71.4 or 72.4 G).[23] The results for CAT8 and CAT16 suggest that the $2A_{zz}$ values increase with dilution of the ionomer system; the largest difference between the $2A_{zz}$ values is ≈1 G, significantly larger than the experimental error. Changes of $2A_{zz}$ with EMAA content parallel those of the fast ESR component, for which a_N is higher than in neat water solutions.

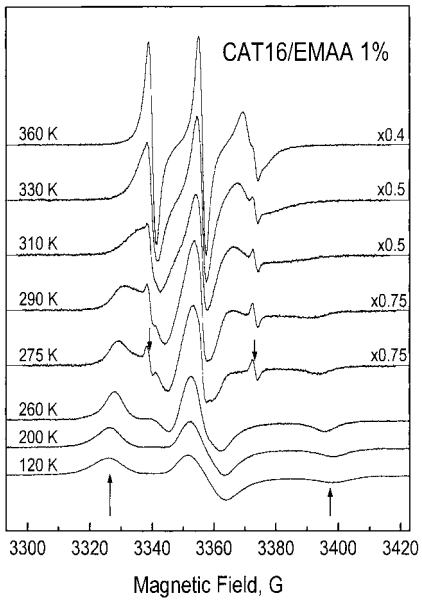


Figure 9. Selected X-band ESR spectra as a function of temperature of CAT16 (concentration 0.5 mM) in EMAA solutions containing 1 wt % ionomer. Modulation amplitude: 1 G in the range 120−290 K and 0.5 G in the range 300−360 K.

Table 1. Extreme Separation, $2A_{zz}$, of CAT*n* Spin Probes in EMAA Solutions[a]

[EMAA], wt %	CAT1	CAT8	CAT16
0.5		72.4	72.2
1.0		72.3	72.0
2.5		71.5	71.7
5.0		71.0	71.4
11.0		70.8	71.1
23.0	70.8	70.7	71.2

[a] The data are average values for the temperature ranges 120−200 K (CAT1 and CAT8) and 120−220 K (CAT16); standard deviation ≤0.3 G.

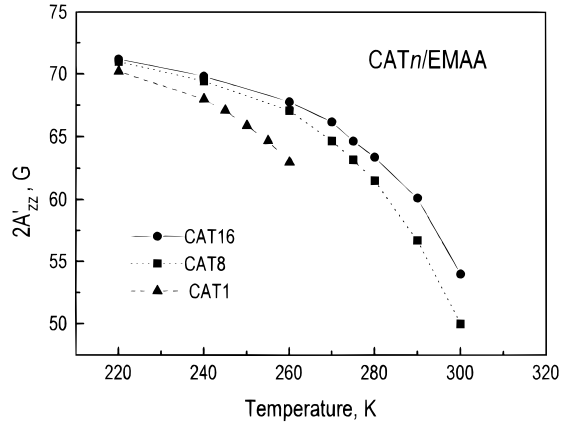


Figure 10. Dependence of the extreme separation in slow motional spectra of CAT*n* spin probes in EMAA solutions, $2A'_{zz}$, on temperature. See text for details.

Above ≈200 K the maximum line separation decreases due to the enhanced mobility of the spin probes, and the corresponding values, denoted as $2A'_{zz}$, do not depend on the ionomer concentration within ±0.3 G. The $2A'_{zz}$ data are plotted vs temperature in Figure 10. Data for CAT8 at all temperatures and for CAT16 above ≥240 K are average values for the entire range of EMAA concentrations; data for CAT1 are for EMAA solutions containing 23 wt % ionomer. From Figure 10 it is clear

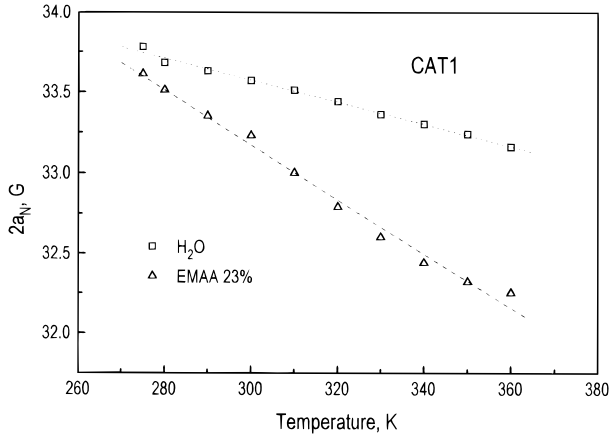


Figure 11. Temperature dependence of $2a_N$ for CAT1 in 23 wt % EMAA solutions (△) and in neat water (□). Modulation amplitude: 0.3 G.

that for a given temperature the $2A'_{zz}$ values decrease in the order CAT16 > CAT8 > CAT1; this comparison shows that the probe mobility increases with decreasing chain length of the alkyl substituent of the probe and implies different sites within the polymeric aggregates.

At 250 K for CAT1, and at ≈270 K for CAT8 and CAT16, the additional, motionally-narrowed, component appears in the ESR spectra, as indicated by downward arrows in Figures 7−9. For CAT1 the two components merge into a three-line spectrum at 270 K, and on further temperature increase the lines become narrower and the a_N value decreases; we propose that this effect is a direct result of averaging the signals from the CAT1 probes bonded to large aggregates with the signals from probes bonded to unimeric micelles. This effect is clearly seen in Figure 11, where the $2a_N$ values for CAT1 in EMAA solutions are plotted as a function of temperature and compared with the corresponding $2a_N$ values in neat water. The decrease of a_N with temperature that was described above is more pronounced in the presence of the ionomer, because of the lower polarity of the EMAA aggregates.

For CAT8 and CAT16 the two components can be distinguished even at 360 K. The spectra at 360 K were deconvoluted by spectral titration using the aqueous signal at a lower temperature as a titrant; the results are shown in Figure 12 for the solution 0.5 wt % EMAA. At this temperature the ESR spectra of CAT8 and CAT16 are essentially the same in terms of the line width (thus mobility) and splitting (thus polarity); $2a_N = 31.8 \pm 0.1$ G, less than for CAT1 (32.25 G). A small difference in the intensities (and thus widths) of the ESR lines between the two probes seems to be within the limit of error of the titration procedure.

Discussion

In this section we will discuss the results obtained for the CAT*n* probes in aqueous solutions of EMAA and their interpretation in terms of unimeric and multichain ionomer aggregates, we will consider the results in the perspective of other studies based on these probes, and we will comment on the specific features and advantages of the CAT*n* probes in reporting on polymeric assemblies.

Unimeric Micelles in EMAA Solutions. The two-component ESR spectra observed in this work for the three CAT*n* spin probes provide clear evidence for the conclusion that an equilibrium exists between large

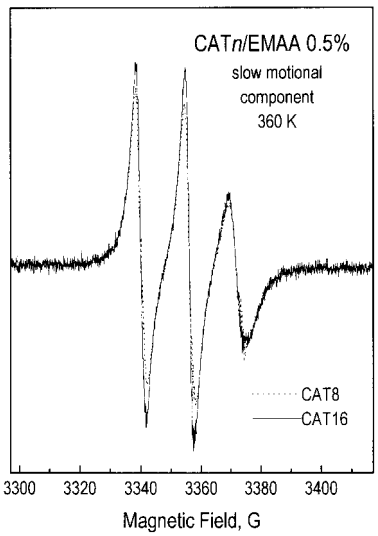


Figure 12. ESR spectra of CAT8 and CAT16 in EMAA solutions containing 0.5 wt % ionomer at 360 K, after subtraction of the fast component. Modulation amplitude: 0.3 G.

ionomer aggregates that have been characterized by SANS[14] and small unimeric micelles in aqueous solutions of EMAA ionomers. The unimeric micelles are represented by the minor spectral component, the motionally averaged triplet. Its contribution at a given EMAA concentration depends on the type of probe; the more hydrophobic CAT16 is preferentially bound to large aggregates compared to the less hydrophobic CAT8, as seen from the intensity of the fast motional component for these probes (Figure 6). In the study of EMAA ionomers with the 5DSA and 10DSA spin probes, the fast spectral component was similar (though not identical) to that observed for the probes in neat water,[6] and skeptics could have argued that it was due to free *n*DSA molecules in the aqueous phase. The key result was, however, the detection of *two* spectral components for 5DSE (5-doxylstearic methyl ester), which is insoluble in water.[15]

In the CAT8/EMAA and CAT16/EMAA systems the motionally averaged ESR component has different parameters (line width and a_N value), compared to the respective aqueous solution spectrum, so there is no doubt that the signal is due to probes bound to the ionomer. The a_N values indicate that in unimeric micelles the nitroxide group is located in a site of high polarity (higher than that in pure water), which can be identified as the micellar Stern layer where the ionic concentration is high. Addition of salt to an aqueous solution of CAT16 does not increase the hyperfine splitting to the value observed for the fast component in EMAA solutions; for the saturated KCl solution we have obtained $2a_N = 33.85 \pm 0.05$ G at 300 K. We thus conclude that the primary effect leading to the hyperfine splitting as high as $2a_N \approx 34.0$ G (determined for the fast component) is the formation of an ionic bond between CAT*n* and the ionized carboxylic group of the ionomer. The effect of charge neutralization has been recently evaluated theoretically and measured experimentally by Schwartz et al.[26] for both cationic and anionic spin probes. An interesting, and extremely relevant to the present study, conclusion is that a_N values for anionic and cationic spin probes behave differently when the probe charge is neutralized: a_N of anionic probes decreases, and a_N of cationic probes increases. This conclusion is in agreement with the increase of a_N to ≈17 G due to the formation of the ionic bond between the probes and the COO^- groups of the ionomer.

Independent support for the existence of unimeric micelles in EMAA solutions was provided by fluorescence probe studies using pyrene as an indicator of the micropolarity in the micellar core.[15] Taken together, the fluorescence and ESR data suggest that there is a critical ionomer concentration for the formation of large aggregates, and above this concentration the two types of aggregates are in equilibrium. Current studies of the salt effect in EMAA solutions provide additional support for this conclusion.[27]

Multichain Micelles in EMAA Solutions. The maximum ("rigid limit") ^{14}N hyperfine splitting (A_{zz}) suggests that all the CAT*n* probes have their nitroxide groups located in a similar environment, which is less polar than an aqueous environment. The values of a_N measured for the three CAT*n* probes up to 360 K confirm the polarity decrease on transfer of the probes from water to the aggregates and reveal that the micellar site of the nitroxide moiety is significantly less polar for CAT8 and CAT16, compared to CAT1.

It is reasonable to assume that the alkyl chains of CAT8 and CAT16 extend into the interior of the aggregates. This assumption is consistent with the observed difference in dynamics of these probes. As seen in the temperature dependence of the extreme separation (Figure 10), CAT16 is significantly less mobile than CAT8 in the temperature range 270−300 K; the dynamics of the nitroxide group reflects the dynamics of the ionomer aggregate. This effect is not observed in neat water and in Nafion solutions;[27] we conclude that we observe the high viscosity of the intermediate region of EMAA micelles, where the amphiphilic CAT*n* are located, in accord with the proposed structural model.[6] Data also indicate that the terminal segments of CAT16 are immersed in more viscous regions, compared to CAT8, which is interpreted to mean that the local viscosity increases from the surface to the interior of the aggregates. CAT1, located close to the micellar surface, undergoes much faster rotational diffusion, as indicated by lower $2A'_{zz}$ values at low temperatures (Figure 10) and narrower lines at high temperatures; these effects can be related to the nonamphiphilic character of the probe, as well as to the lower microviscosity at its solubilization site.

A high viscosity of the micellar core, $\eta \geq 230$ cP, deduced from the fluorescence probe studies[15] would be in line with the postulated viscosity gradient in the ionomer aggregates. The deductions for 10DSA and 10DSE in EMAA lead, however, to an opposite conclusion concerning intramicellar viscosity: From the ESR spectra of the two probes at 360 K it was inferred that the viscosity is higher in the intermediate layer than in the micellar core, and the effect was connected to the presence of some ions in the former region.[6b] A way to reconcile all the results is to assume that the viscosity changes with temperature are more profound in the core than in the intermediate layer, so that the viscosity gradient observed at lower temperatures is reversed at 360 K. In support of this conclusion we note that the melting point of the polyethylene crystallites is ≈360 K and that these crystallites are expected to be present only in the micelle core.[28] The present results for 360 K indicate that at this temperature the viscosity of the intermediate layer is low enough that mobilities of

CAT16 and CAT8 are similar. It is possible that the core viscosity is slightly lower, so that the 10DSE spin probe (in the core) is slightly more mobile than 10DSA (in the intermediate layer), leading to the ≈16% difference in the rotational correlation times.[6b]

These results for the amphiphilic CAT*n* probes indicate that they may be considered as viscosity probes of aggregated systems; this use of CAT16 has been described in a recent study of a mesoporous material.[29]

Comparison with Other Studies of CAT*n* Probes in Aqueous Systems. CAT*n* probes have been important reporters for aggregation in perfluorinated surfactants and perfluoropolyethers,[3,23] in the cationic surfactants such as trimethylammonium dodecyl bromide (DTAB) and trimethylammonium hexadecyl bromide (CTAB),[22c] in the study of the interactions between anionic dendrimers and cationic surfactants,[22a,c] and in Nafion ionomers.[17] In most of these studies the spectra of all CAT*n* probes consisted of the fast component only, and the emphasis was on the effect of probe *concentration*; in some cases, the spectral component assigned to aggregated CAT16 probes (one line with a line width of ≈9 G) was also observed. The site proposed for the nonaggregated CAT*n* probes was an aqueous site, although the a_N values were less than those measured in neat water.

In the present study we detected for the first time slow motional spectra from CAT*n* probes with $n = 8$ and 16 even at ambient temperature, and for CAT16 even above 300 K. Given that the magnetic parameters for the CAT*n* probes (g and ^{14}N hyperfine tensors) in aggregated systems have been deduced from relatively featureless isotropic spectra,[22,23] we expect that in the future it will be possible to better define the parameters by simulation of the highly anisotropic spectra observed for CAT8 and CAT16 in the present study (for instance, those shown in Figures 8 and 9). Also detected for the first time are the *higher* a_N values compared to those published so far, typically 17 G. These values appear to be in agreement with the theoretical approach published recently.[26]

Advantages of CAT*n* Probes as Reporters in Organized Media. At the onset of this study we expected that the CAT*n* probes report on the polar regions in the EMAA solutions and on the interface between the aggregates and the solvent. This expectation was realized, as the results have demonstrated the formation of an ionic bond between the probe and the ionic groups of the ionomer (from the high a_N value of the fast spectral component).

Additional results were deduced from the variation of the alkyl group length, together with the variation of temperature and ionomer concentration, and by comparison with the ESR spectra of the probes in neat water. An important conclusion is that the cationic probes with $n = 8$ and 16 behave as amphiphilic probes, and although the cation site and the nitroxide groups are located at or near the ionomer−solvent interface, the long alkyl penetrates into the aggregate interior and the probes are useful as reporters for the local viscosity.

The ESR spectra of the cationic probes in neat water indicated that the probes are more sensitive reporters of the local polarity compared with the *n*DSA probes.

Conclusions

Aqueous solutions of EMAA ionomers were studied with the cationic nitroxide spin probes 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl iodides (CAT*n*) with $n = 1$, 8, and 16. The main objective was to compare the ESR spectra of CAT*n* probes as a function of temperature and ionomer content in order to deduce details on the interface between the aggregates and the solvent and on the structure and dynamics of EMAA micelles.

The ^{14}N hyperfine splittings, a_N, of the probes in neat water are identical within experimental error for the three probes and decrease with increasing temperature in the range 280−360 K; this effect was attributed to the decrease of the dielectric constant of water from $\epsilon = 85$ at 280 K to $\epsilon = 59$ at 360 K.

The detection of two spectral components for the probes from the temperature variation of the ESR spectra of the probes provided evidence for the existence of an equilibrium between large multichain aggregates and unimeric micelles, in accord with previous ESR (based on doxylstearic acid probes) and fluorescence studies.

Analysis of the ^{14}N hyperfine splittings indicated the formation of an ionic bond between the carboxylic group of the ionomer and the cation of the probe.

Analysis of the probe dynamics as a function of temperature and the alkyl group length in the probes suggested intercalation of the alkyl group into the multichain aggregates at a depth that depends on the length of the alkyl group. This conclusion implies that the cationic probes are reporters of the viscosity gradient in micellar aggregates.

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