Self-Assembling of Ethylene−Methacrylic Acid Ionomers in Aqueous Solutions and as Swollen Membranes from ESR Spectra of Amphiphilic Spin Probes. 2. Dynamics in Aggregates and Correlation with Thermal Transitions

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ABSTRACT: Electron spin resonance (ESR) spectroscopy based on nitroxide spin probes was applied to the study of self-assembling in poly(ethylene-*co*-methacrylic acid) ionomers in aqueous solutions and in the corresponding membranes swollen by water. The probes selected for study were based on the stearic acid backbone, differed in their hydrophobicity and in the position of the nitroxide group with respect to the head group, and are known to intercalate in the chain aggregates and to report on the hydration level at various depths from the ionomer−solvent surface. The dynamic properties of the aggregates were deduced from ESR spectra measured in the temperature range 120−360 K for the solutions and 120−410 K for the swollen and dry membranes and from thermal transitions measured by DSC. ESR results for the *solutions* indicate that a clear aggregate−solvent interface exists even at 360 K; inside the aggregate, however, the local mobility is fast on the time scale of the ESR experiment, and the correlation times of the probes are $\sim 10^{-9}$ s/rad. Restricted mobility was detected in a layer of thickness of ~10 Å from the aggregate−solvent interface and was attributed to constraints arising from the presence of proximal ionic groups. In the case of *membranes* swollen by water, the ESR spectra of the spin probe located near the water pools changed dramatically near 335 K, and two components differing in their local mobility were detected. Possible reasons for this behavior were discussed. Taken together, the results obtained in this study demonstrate that the amphiphilic spin probes behave as "dipsticks" for the dynamics in the aggregates and provide details on the specific and separate effects on dynamics of the polar domains, the chain characteristics (glass transition of amorphous polyethylene and melting transition of crystalline domains), and the solvent.

Introduction

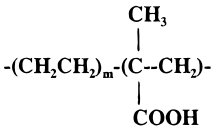
Self-organization of the poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers shown in Chart 1a has been investigated by spectroscopic, scattering, and relaxation methods for more than thirty years.[1−4] At ambient temperature, the ionomers are insoluble in water and organic solvents, due to the cross-links formed by crystallization of the polyethylene component. For this reason, most studies to date have been performed on bulk or solvent-swollen membranes.[5−12] Small-angle X-ray scattering (SAXS) of EMAA ionomers[5−8] has clearly indicated that the water molecules sorbed are preferentially located in ionic regions. As a result, the *ionic peak*, which originates from the presence of the ionic regions, shifts to lower angles and becomes broader when the amount of solvent increases. Infrared (IR) spectra of EMAA as sodium salts[8] have suggested that three water molecules per sodium ion form the primary hydration shell; excess water is outside the primary hydration layer and forms the "water pool", where the water molecules are strongly hydrogen bonded. Dielectric experiments[9] on fully hydrated ionomers have detected the "water peak", attributable to a reorientation of the hydroxy groups of the water molecules, with a very high dielectric increment of ~200 at 250 K, due to interfacial polarization; these experiments also have suggested the presence of water pools.

A method for the dissolution of EMAA ionomers in water in an autoclave[13] has opened the possibility of studying the solution structure and comparing the results for the *protiated* EMAA system with those obtained for *perfluorinated* ionomers (PFI).[14−18] Small-angle neutron scattering (SANS) studies of EMAA ionomers dissolved in D_2O have suggested the presence of ellipsoidal *or* cylindrical aggregates with a short semiaxis of 59−124 Å, depending on the amount of MAA groups, the type of counterion, and the degree of neutralization.[19]

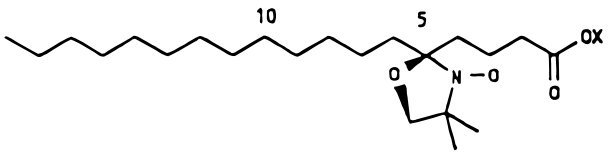
We have initiated spin probe electron spin resonance (ESR) studies of EMAA ionomers, with the following three main objectives: (a) to obtain details on the local environment of the probes associated with ionomer aggregates, (b) to assess the dynamic properties of the aggregates, and (c) to compare the behavior of *protiated* and *perfluorinated* ionomer systems. The spin probes selected are based on stearic acid and differ in their

Chart 1

a. EMAA Ionomer, Acid Form



b. Doxyl Stearic Acid Spin Probes



5DSA: $n=5$, X=H (n: doxyl position)
10DSA: $n=10$, X=H
10DSE: $n=10$, X=CH_3

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polarity and in the position of the nitroxide group with respect to the head group (carboxylic acid or methyl ester group), as shown in Chart 1b. The same probes have been used to extract structural and dynamical details on the PFI systems.[14−17]

In the preceding paper,[20] our attention was focused on the aggregate structure of EMAA ionomers in water solutions and as membranes swollen by water and on the effect of ionomer concentration on the degree of aggregation. For the more polar probes in EMAA solutions, the ESR spectra consist of two sites, which were attributed to probe molecules with restricted mobility incorporated in large aggregates and to probes in the motionally narrowed regime, respectively. The *motionally narrowed* component is similar to that of the corresponding probe in neat water at ambient temperature and has been assigned to probe molecules dispersed in the aqueous phase, or in the vicinity of single-chain micelles ("unimers"). From the analysis of the ^{14}N hyperfine splittings for the *slow motional* site, we have proposed that the aggregates in aqueous solutions of EMAA ionomers consist of three main regions: a hydrophobic core, an intermediate layer, and a hydrophilic region (at the water−aggregate interface) where most of the ions are located. The presence of the intermediate layer has been interpreted as evidence that the boundary between the ionic groups and the hydrophobic regions is gradual, and that some ionic groups, accompanied by a small number of water molecules, are present inside this region of the aggregate.

In this paper, we will describe the dynamic behavior of the aggregates, based on the ESR spectra of the spin probes in the temperature range 120−410 K and will correlate the spectral changes with the thermal transitions detected by differential scanning calorimetry (DSC).

Experimental Section

The starting ionomer material was a random copolymer of ethylene and methacrylic acid, with 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 %, meaning that the average number of backbone carbons between the ionic groups is 26. This material was neutralized (90%) in the melt by K_2CO_3 in an extruder;[21] the notation we use for the neat ionomer is EMAA-0.9K. The corresponding aqueous solution was prepared in an autoclave as described.[13,20] The solution containing 25.5% (w/w) ionomer and the dry membrane EMAA-0.9K were a gift from Du Pont-Mitsui Polychemicals Co. Ltd, Chiba, Japan. The ionomer content of the aqueous solution was determined from the weight loss of the samples after drying in vacuum at ∼440 K for 20 min. The water content (15 ± 1% w/w) in the membranes swollen by water was determined from the weight increase during swelling.

The spin probes 5DSA and 10DSA from Aldrich and 10DSE from Molecular Probes, Eugene, OR, were used without further purification. All the samples for ESR measurements were prepared as described in previous papers.[14,20] The spin probe concentration in the ionomer solutions was ∼1 mM, which corresponds to the ratio $[COO^-]/[\text{spin probe}] \approx 500$ in the most concentrated ionomer solution (25.5% w/w). The corresponding ratio in the water-swollen membranes was estimated to be ∼1000 from the integrated intensity and the weight of membrane.[20] For comparison, dry membranes doped with spin probes were also prepared, by vacuum-drying the water-swollen membranes at ∼413 K for 20 min. The notation of the ESR samples is probe/S and probe/M, where S and M stand for ionomer solutions and swollen ionomer membranes, respectively.

ESR spectra were measured in the temperature range 120−410 K with a Bruker X-band spectrometer Model ESC106, equipped with the ESP 3240 data system for acquisition and manipulation and with the ER4111 VT variable-temperature unit. After the desired temperature was reached all samples were allowed to equilibrate for 10 min (if $T < 300$ K) or 5 min (if $T > 300$ K). The overall heating rate in the temperature range 300−410 K was 16 ± 4 K/h. In the ESR measurements of probe/M, the sample tube was sealed after adding a drop of water to carry out the temperature variation at a relative humidity of 100%. Additional experimental details have been described in the preceding paper.[20]

Thermal transitions in the range 230−430 K were measured with a Du Pont 9900 series differential scanning calorimeter at a heating rate of 10 K/min, under nitrogen flow. The instrument was calibrated with indium (mp 429.75 K, ΔH 28.4 J/g).

Results

ESR of Probes in EMAA Solutions. In Figure 1 we present selected X-band ESR spectra of the probes in EMAA aqueous solutions containing 25.5% (w/w) ionomer in the temperature range 120−360 K, for 5DSA/S (a), 10DSA/S (b), and 10DSE/S (c). The spectra were measured on increasing temperature, after rapid quenching of the samples from ambient temperature to 120 K. The average values of the extreme separation at 120 K are 71.3 (5DSA), 69.3 (10DSA), and 68.0 G (10DSE) and are, within experimental error, the same as the values of the extreme separation in the rigid limit, $2A_{zz}$, measured at 77 K. The gradual decrease of $2A_{zz}$ from 5DSA to 10DSA and 10DSE was assigned to a polarity gradient in the chain aggregates, from the region near the polar interface where 5DSA is located, to the aggregate interior where the most hydrophobic probe 10DSE is located.[20] No significant spectral changes were detected up to 200 K, except a progressive increase in resolution. At and above 200 K, the extreme separation between the two outer peaks ($2A'_{zz}$) and the line widths decrease, due to motional averaging. The total spectral intensity decreases in the interval 260−275 K, most likely due to melting of the frozen solution and the corresponding change in density.

For 5DSA/S (Figure 1a) above 300 K, the signals become sharper with increasing temperature, but the slow motional component, which is associated with the large-chain aggregates,[20] is the only signal detected in the entire temperature range. The extreme separation at 360 K is 47.7 G, an exceptionally large value for a doxyl spin probe at this temperature.[14−16] The absence of dynamical averaging is a clear indication of the immobilization of the probe and suggests that the water−aggregate interface still exists at 360 K. The isotropic ^{14}N hyperfine splitting A_{iso}, estimated from the positions of the well-resolved extreme features that define the A_{max} and A_{min} values,[14,15] is 15.2 G at 360 K.

For 10DSA/S, a trace of the isotropic component appears at ∼275 K, but does not grow with increasing temperature, and is masked by the major change of the slow motional component above 330 K; the isotropic component is attributed to mobile probe molecules outside the large aggregates, as mentioned in the Introduction. The evolution of the spectra for 10DSA/S and 10DSE/S above 330 K is similar: The extreme separation of the slow motional component associated with the large aggregates gradually decreases, and the corresponding spectra of 360 K are typical of a motionally averaged triplet, with A_{iso} values of 14.6 G for 10DSA/S and 14.1 G for 10DSE/E. The gradual variation of A_{iso}, from 15.2 (5DSA) to 14.6 (10DSA) and to 14.1 G (10DSE) mirrors the trend in the values of $2A'_{zz}$ and provides additional support for the picture based

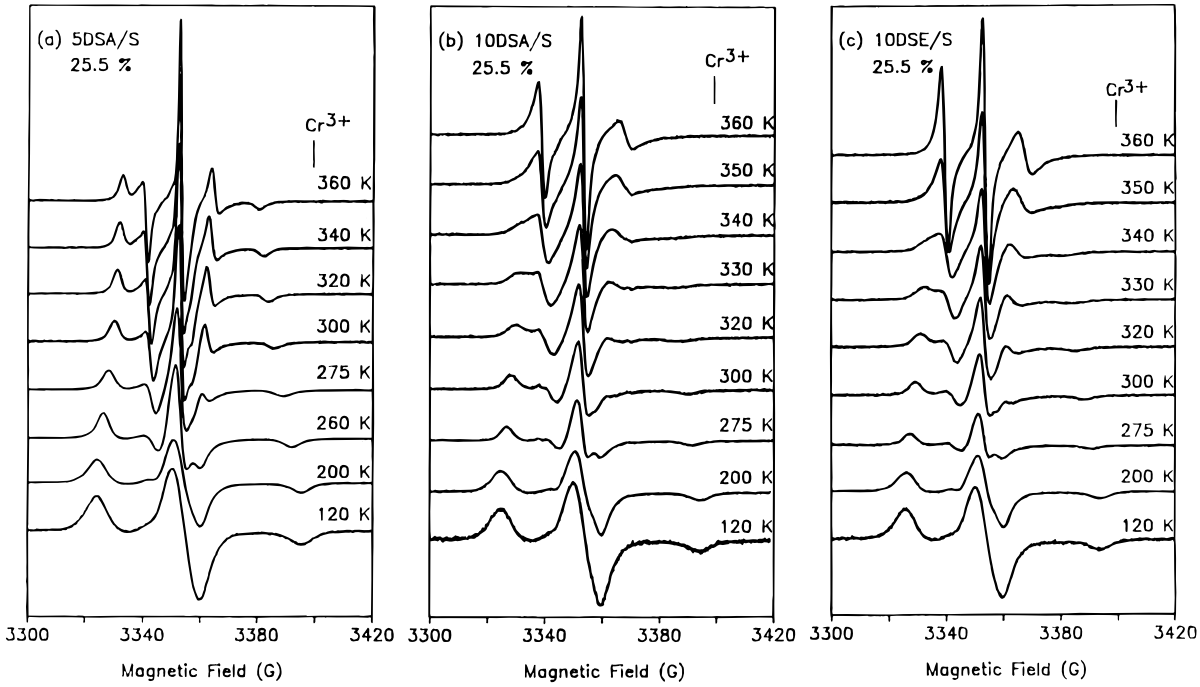

Figure 1. X-band ESR spectra of the probes in ionomer solutions (25.5% w/w ionomer) as a function of temperature in the range of 120−360 K: 5DSA/S in (a), 10DSA/S in (b), and 10DSE/S in (c). The modulation amplitude is 2.0 G in the range 120−297 K; in the range 300−360 K, the modulation amplitude was 0.5 G for 5DSA/S and 1.0 G for both 10DSA/S and 10DSE/S.

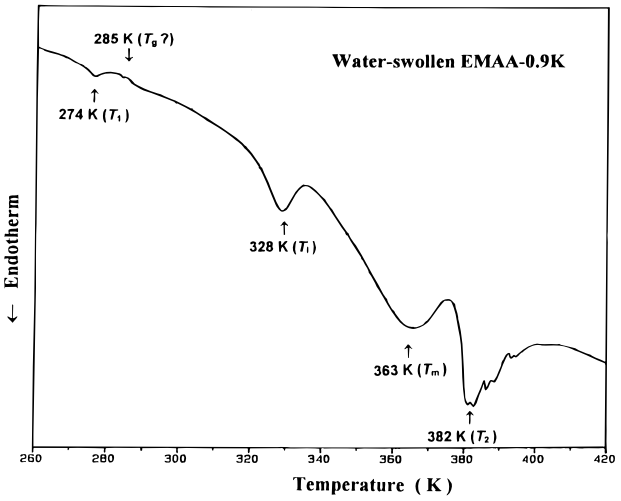

Figure 2. DSC thermogram of the EMAA-0.9K membrane fully swollen by water in the temperature range 260−420 K.

on a polarity gradient in the chain aggregates. The head groups of 5DSA and 10DSA are expected to be anchored at the aggregate−solvent interface. The markedly different line shapes of the spectra at 360 K for 5DSA/S and 10DSA reflect therefore the difference in the local dynamics for nitroxide groups at the C5 and C10 positions, respectively, from the end groups: the probe located deeper in the aggregate, 10DSA, rotates much more freely at 360 K, compared to 5DSA.

DSC Measurements. In Figure 2 we present the DSC thermograms (first heating) from 260 to 420 K of EMAA-0.9K membranes fully swollen by water. Four endothermic transitions, with peak temperatures at 274, 328, 363, and 382 K, and a glass transition at 285 K (T_g) are detected. The DSC curve in Figure 2 is similar to that previously obtained for hydrated sodium salts of EMAA (MAA content 5.4 mol %).[8] The four endotherms were assigned to[8,22] melting of freezable water (T_1), a structural transition of the ionic aggregates (T_i), melting of the crystalline polyethylene (T_m), and release of sorbed water (T_2). For clarity of reference to previous studies, we maintain the same notation of the endothermic peaks. Dielectric measurements for hydrated sodium salts of EMAA with the MAA content of 5.4 mol % (for example EMAA-0.6Na-1.49H_2O,[9] where 0.6Na and 1.49H_2O indicate 60% neutralization and 1.49 water molecules/Na^+ ion, respectively) have detected a weak shoulder at ∼290 K, which was attributed to the glass transition of amorphous polyethylene. Similarly, we assign the glass transition-like step at 285 K to the same origin. Itoh et al.[22] have investigated the DSC curves of EMAA-0.6Na (MAA content 5.4 mol %) containing various amounts of water; on the basis of enthalpy change at the T_2 transition, they reported that 7% of the sorbed water is freezable in membranes containing 10% (w/w) water. In water-swollen EMAA-0.9K, where the MAA content is 7.5 mol %, we estimated the amount of freezable water, using the method described in ref 22, at 2% only. This difference suggests that the number of water pools in the swollen EMAA-0.9K is larger, but the average water pool size is smaller, compared to the EMAA ionomer containing 5.4 mol % MAA.

ESR of Probes in EMAA Membranes. In Figure 3 we present selected X-band ESR spectra in the temperature range 120−410 K for 5DSA/M (a), 10DSA/M (b), and 10DSE/M (c); the water content in the membranes was 15 ± 1% (w/w) in all samples. At and below 300 K, the spectra for all probes consist of one component typical of a slow motional component.[20] The $2A'_{zz}$ values at 120 K are 71.4 (5DSA), 69.1 (10DSA), and 67.2 G (10DSE); as in the probe/S systems, the spectra gradually evolve as the temperature is raised to 300 K. The $2A'_{zz}$ values at 300 K are 60.9, 61.9, and 60.1 G for the above probes, respectively. The spectra for 5DSA/M and 10DSA/M also contain a negligible amount of the isotropic component at ∼290 K, probably from probes dispersed in small water droplets on the sample surface.

As for the EMAA solutions, the evolution of the ESR spectra of 5DSA/M is significantly different compared

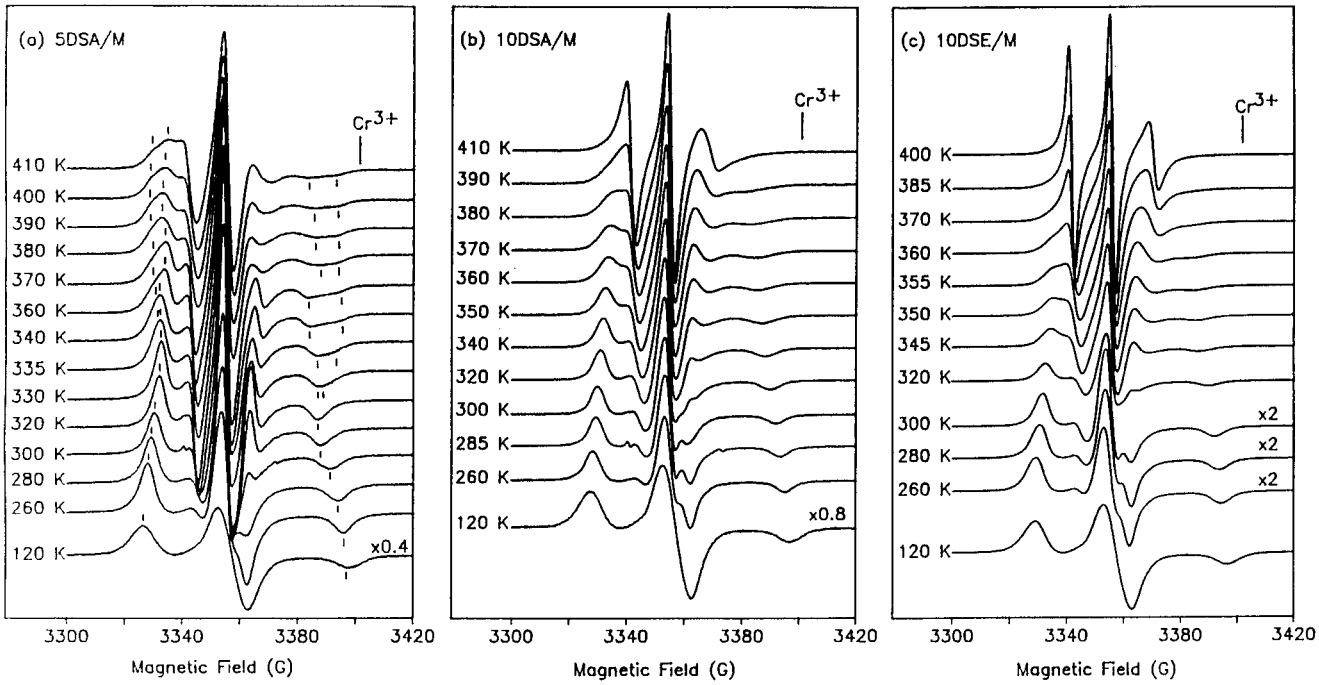

Figure 3. X-band ESR spectra of the probes in fully swollen EMAA membranes as a function of temperature in the range of 120−410 K: 5DSA/M in (a), 10DSA/M in (b), and 10DSE/M in (c). The modulation amplitude was 0.5 G at all temperatures.

to the other two probes, and two major spectral changes are clearly seen (Figure 3a) in the temperature range 300−410 K: the first change occurs between 330 and 335 K, and the second between 370 and 380 K. At and above 335 K, the extreme low-field and high-field signals broaden significantly. The splitting detected for the high-field peak is evidence for two sites for the probe. Above 380 K, the broadening of the spectral pattern becomes more prominent, and the shoulder that becomes visible near 3335 G in the low-field region, in addition to the splitting of high-field peak, further emphasizes the presence of **two** spectral components. Vertical bars in Figure 3a point to the splitting of the high- and low-field extreme peaks. The spectral changes for 5DSA/M in the temperature range ∼330−370 K appear to be gradual and to correspond to the temperature interval defined by the two endotherms T_1 and T_2, as seen in the DSC curve, Figure 2.

The origin of the spectral changes for 5DSA/M can be assessed in view of the spectra presented in Figure 4: the ESR spectrum of 5DSA/M at 380 K (a) is almost identical with that of a *dry* EMAA-0.9K doped with 5DSA at the same temperature (b). This similarity in spectral shape is also seen between the spectrum measured at 297 K immediately after heating the swollen membrane to 410 K and quenching to 297 K (c) and the spectrum at 297 K for dry EMAA-0.9K doped with 5DSA (d). These results support the idea that the T_2 DSC peak and the spectral changes clearly detected for 5DSA/M at ∼380 K are due to the loss of the sorbed water from the sample, in accordance with previous results.[8] Comparison of spectra given in parts a and c of Figure 4 also indicate that the environment in the dry membranes is more rigid than that in the swollen membranes.

The X-band spectra of 10DSA/M and 10DSE/M as a function of temperature, Figure 3b and c, consist of one component only in the entire temperature range, the slow motional component assigned to probes in the hydrophobic regions of the chain aggregate.[20] The variation of the spectral pattern with increasing temperature is gradual and no distinct changes are observed below 355 K, in contrast to the results for 5DSA/M mentioned above. The most prominent change is seen at ∼390 K for 10DSA/M and at ∼360 K for 10DSE/M, and the spectra become typical of incipient motional averaging. The presence of the averaged triplet pattern for 10DSE/M may be due to the melting of polyethylene crystalline region at ∼363 K (T_m in Figure 2). In amorphous polymers, the $2A'_{zz}$ value decreases around the glass transition temperature, and the temperature at which $2A'_{zz} = 50$ G, T_{50G}, correlates with T_g. In semicrystalline polymers such as polyethylene, however, $2A'_{zz}$ decreases *gradually* above T_g, because of a cross-linking effect of the crystalline regions on the motion of the backbone chains, and *rapidly* around the melting temperature of crystalline region.[23] The ESR results obtained for 10DSE/M provide additional support for this interpretation.

The higher temperature for the appearance of the triplet in the case of 10DSA/M[24] compared to 10DSE/M (390 vs 360 K) suggests that the carboxylic groups anchored at the interface between the ionic groups and the water pool play an important role in restricting the motion of the nitroxide group at the C10 position. Another source for motional restriction could arise from the few ionic groups that were assumed to reside in the intermediate region of the aggregates.[20]

In order to compare and emphasize the effect of temperature on the ESR spectra of the three probes, we present in Figure 5 the $2A'_{zz}$ values (in G) vs temperature. For 5DSA/M, the larger of the two $2A'_{zz}$ values above 335 K contains a larger experimental error (∼±1 G), compared with the other data points (∼±0.2 G), because the corresponding signals are not well resolved.

Discussion

In this section we will discuss separately the specific effects of the ionic groups, the polymer matrix, and the solvent on the dynamics in the aggregates, will compare

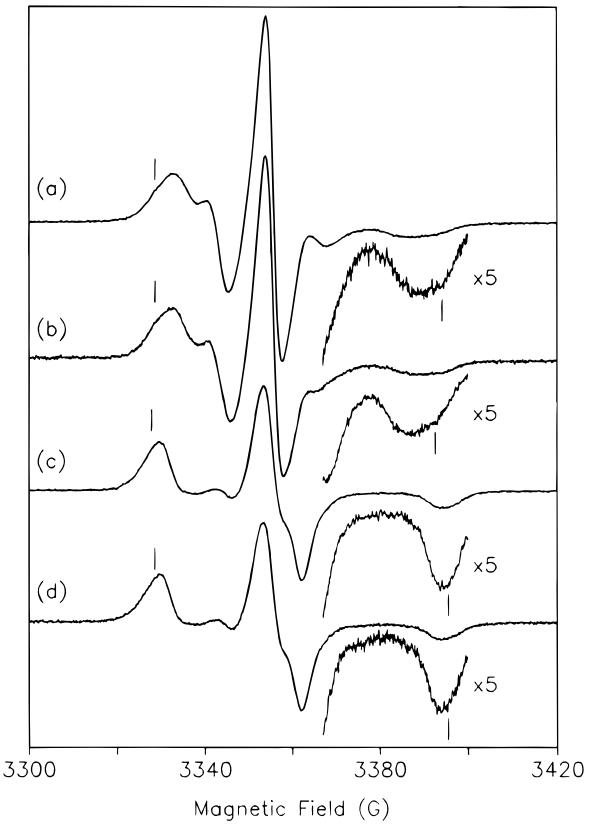

Figure 4. X-band ESR spectra of (a) 5DSA/M (*initially* containing 15% (w/w) water at ambient temperature) at 380 K, (b) dry EMAA-0.9K membrane doped with 5DSA at 380 K, (c) 5DSA/M (*initially* containing 15% w/w water) at 297 K immediately after quenching from 410 K, and (d) dry EMAA-0.9K membrane doped with 5DSA at 297 K. In order to compare the four spectra, spectra in (c) and (d) have been normalized to the same integrated intensity, and the intensity ratio between (a) and (b) is identical to the ratio between (c) and (d). Modulation amplitude: 0.5 G in (a) and (c) and 1.0 G in (b) and (d). Vertical bars show the extreme separation of the spectral component with the larger $2A'_{zz}$ value. The vertically expanded high field portion of the spectra is also shown.

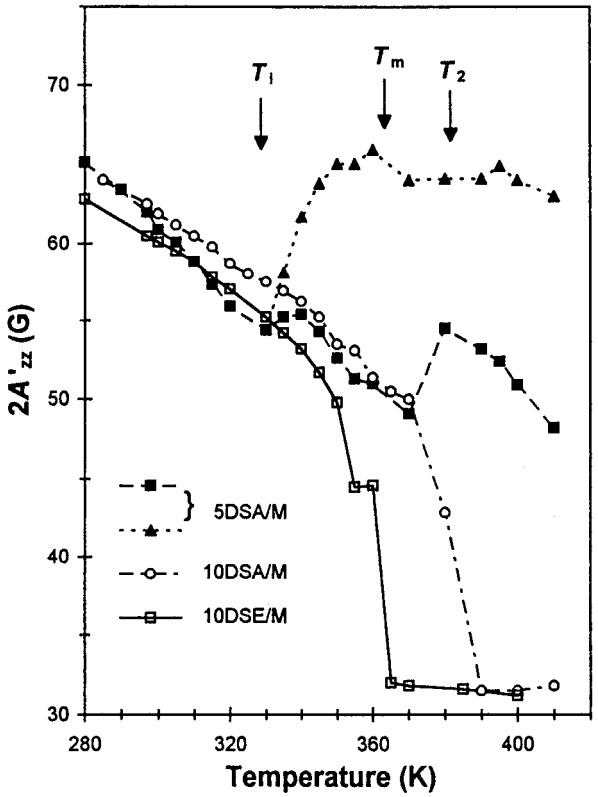

Figure 5. Plots of $2A'_{zz}$ vs temperature for 5DSA/M (■, ▲) (see text), 10DSA/M (○), and 10DSE/M (□). Arrows on the top horizontal scale point to the thermal transitions measured by DSC and presented in Figure 2.

the conclusions from this study with those in related ionomer systems, and will address the meaning of the spin probe vs spin label concept, as applied to the EMAA ionomers.

Effect of Ionic Groups on Dynamics in the Aggregates. The results presented in Figures 1 and 3 for the probes in the EMAA solutions and in the swollen membranes clearly indicate that the probe anchored at the ionomer−solvent interface, 5DSA, reflects a part of the aggregate where the mobility of the ionomer chains is greatly restricted. This conclusion is derived from the highly rigid and anisotropic ESR spectra measured for this probe in the ionomer solution even at 360 K (Figure 1a), and in the swollen membranes even at 410 K, especially by comparison with the spectra at the same temperatures obtained for the probes that are known to intercalate deeper into the aggregates,[20] 10DSA and 10DSE (Figure 1b and c, respectively). Moreover, the temperature variation of the spectra presented in Figures 1 and 3 suggests that the mobility of the ionomer chains in the solutions and the swollen membranes *in similar locations of the aggregates* (interior vs interface) is about the same. This conclusion becomes obvious by considering the similarity of the spectra for a given probe at the same temperature in the solutions (Figure 1) and in the membranes (Figure 3). Therefore, the major result from this study is the detection of gradual variations in the mobility of the probes, depending on their locations. These variations reflect a *gradient* of dynamics for the ionomer chains in the aggregates: from restricted mobility near the ionomer−solvent interface, to a much higher mobility toward the less polar regions of the aggregates, in both ionomer solutions and swollen membranes.

The spatial resolution in the determination of the gradient in the dynamics of the chain aggregates can be deduced from the position of the nitroxide group relative to the polar head: the NO group is at ∼8 Å from the head group in 5DSA and at ∼14 Å from the head group in 10DSA.[20] The data shown in Figures 1 and 3 highlight the large difference in the dynamics at sites occupied by these probes. Therefore, the layer thickness L whose motion is restricted by the ionic groups is 8 Å $< L <$ 14 Å, or $L \approx$ 10 Å. This result implies a very high spatial sensitivity of the probes to their local environment, leading to a good resolution of the estimation of L, ±1 Å. To the best of our knowledge, the only other direct spectroscopic evidence for the existence of a shell of constrained polymer near the ionic groups has been obtained in high-resolution solid-state ^{13}C NMR cross-polarization studies of telechelic ionomers containing selectively deuteriated segments (500 Da in length) at the two chain ends.[25,26] The picture of a "skin" of ionomer constrained by the ionic groups is at the crux of a model proposed recently by Eisenberg et al.,[27,28] who formulated their model to explain the thermal transitions of dry ionomers and the effect of nonpolar, polar, and amphiphilic plasticizers. This study provides support for the validity of this approach also for the case of swollen membranes and aggregates in aqueous media.

The spin probes used in this study reflect different dynamics not only between the chains in the vicinity of

the ions and the other chains but also between chain segments in different parts of the *interior* of the aggregated chains: the similar and nearly motionally averaged spectra of 10DSA/S and 10DSE/S at 360 K suggest similar dynamic environments on first approximation only. More subtle differences are revealed by calculating the rotational correlation time τ_c at 360 K using eq 1,[23,29] where $h(1)$, $h(0)$, and $h(-1)$ are the

$$\tau_c\,(\mathrm{s/rad}) = 1.0238 \times 10^{-6}\Delta H(0)\{[h(0)/h(1)]^{1/2} + [h(0)/h(-1)]^{1/2} - 2\}/[g_{iso}(A_{||} - A_{\perp})^2] \quad (1)$$

peak heights of the $m_I = 1$, 0, and -1 transitions, respectively, and $\Delta H(0)$ is the line width of the central line (in G). The constant on the right-hand side of eq 1 is in s/(rad·G). The magnetic parameters for the probes are $g_{xx} = 2.0088$, $g_{yy} = 2.0061$, $g_{zz} = 2.0027$, $A_{xx} = 6.6$ G, $A_{yy} = 6.0$ G, and $A_{zz} = 34.9$ G; this choice of parameters is discussed in detail elsewhere.[16] The intensity ratios of the three lines, $h(1):h(0):h(-1)$, is 0.50:1:0.13 for 10DSA/S and 0.70:1:0.17 for 10DSE/S. The $\Delta H(0)$ values at 360 K are 1.85 G for 10DSA and 1.97 G for 10DSE. The τ_c values obtained are 2.9×10^{-9} and 2.5×10^{-9} s/rad for 10DSA/S, and 10DSE/S, respectively, at 360 K; the correlation time for the inner section of the aggregates is therefore shorter than in the intermediate section where the probe 10DSA resides; we propose that this effect is connected to the presence of some ions in the latter domains, as discussed in the previous paper.[20] The effect of the ions on the local dynamics in the intermediate region of the aggregates is also reflected in the line widths of the ESR spectra of the probes in the swollen membranes: at 400 K the peak-to-peak line width of the central peak ($\Delta H(0)$) is 2.7 G for 10DSA/M and only 2.0 G for 10DSE/M.

Effect of Polymer Matrix on Dynamics in the Swollen Membranes. This effect can be assessed from the temperature dependence of the $2A'_{zz}$ values for 10DSA/M and 10DSE/M shown in Figure 5. As the temperature is increased, the $2A'_{zz}$ value for 10DSE/M decreases moderately up to at 310 K, and more rapidly around 350 K, in the vicinity of T_m; the extreme separation is 31 G at 365 K. These effects are clearly due to the onset of crystallite melting at 310 K and to the melting of polyethylene crystallites at 363 K. The behavior of 10DSA/M is similar: The $2A'_{zz}$ values decrease almost linearly with increasing temperature, with two slightly steeper decreases at 320 and 360 K. The rapid drop for the extreme separation in the case of 10DSA/M is at a higher temperature compared to 10DSE/M; we assign this behavior to the presence of some ions in the intermediate regions of the aggregates. It is quite natural that the presence of ions prevent the formation of crystalline domains in the intermediate layers.

Taken together, the results shown in Figure 5 for 10DSA/M and 10DSE/M suggest the existence of crystalline regions in the nonpolar regions removed from the water pools in the swollen membranes.

Effect of Solvent on Dynamics in the Swollen Membranes. For 5DSA/M, an important change in the local environment occurs at 335 K, resulting in the appearance of two spectral components. Above this temperature, the $2A'_{zz}$ value for the site with more restricted motion increases with increasing temperature and reaches an almost constant value of 64 ± 1 G above 350 K. The corresponding value for the *more mobile* probes decreases almost linearly with increasing temperature (after a small jump at 335 K), increases near 380 K, and then decreases gradually. The jump near 380 K is assigned to the release of sorbed water,[8] a process that is expected to impede the mobility of the ionic groups.

The appearance of two signals corresponds to a change in the environment of 5DSA probes that occurs at ~335 K. We can only speculate on the reason for the detection of two spectral components for 5DSA/M in the range 330−410 K. The simplest explanation is to assume that the water content gradually decreases as the temperature increases; therefore, some of the 5DSA probes in the aggregates, near the ionic domains, are further immobilized. In support of this idea is the similarity of the spectra for 5DSA in the dry and swollen membranes (Figure 4). It is quite possible that the loss of water is a gradual process, depending on the type of water: bound or free. An alternative scenario could involve deformation of the water pools due to melting of thin and imperfect crystals that are expected to activate translational motions of the backbone and to perturb the ionic domains. Further investigation, possibly with ionic nitroxide spin probes, is needed in order to elucidate the nature of the spectral changes that occur for 5DSA/M above 330 K.

Comparison with Related Systems. Recently, the chain mobility in bulk poly(styrene-*co*-sodium methacrylate) ionomers has been investigated by the spin probe ESR technique.[30] This ionomer system is amorphous. Some conclusions in this study have been deduced by comparing the T_{50G} values of the probes with the glass transition temperatures of the system. The T_{50G} value of the spin probe 4-hydroxy-TEMPO benzoate (hTb) is similar to T_g for the polystyrene matrix, whereas T_{50G} of sodium TEMPO carboxylate, which is expected to be anchored to the ionic aggregates, is higher than the T_{50G} of hTb, and close to the temperature of ion hopping, which is the onset temperature of the glass transition for the cluster phase. In the morphological model of Eisenberg et al.,[27,28] the cluster phase is a region where the chain mobility is strongly restricted by ionic aggregates and can exhibit a distinct glass transition. By using both hTb as a spin probe and a polystyrene oligomer as a preferential plasticizer for the matrix (compared to the cluster regions), two T_{50G} values have been observed, corresponding to the glass transition temperatures of the matrix and of the cluster regions. These results were considered as evidence and support for the model described in ref 27.

The ion-hopping temperature T_i is similar to our assignment of T_i in the EMAA system, in that both T_i temperatures are due to changes in the ionic domains. The origin of this phenomenon in the two systems (EMAA and the polystyrene copolymer) is slightly different. The system studied by Tsagaropoulos et al.[30] has two well-defined glass transitions: that of the polymer matrix and of the ionic clusters, and the latter is the origin of the ion-hopping that begins at T_i. In the EMAA ionomers, an important trigger of the T_i transition can be the melting of thin and imperfect crystalline lamellae; in the swollen ionomers, the T_i transition is expected to be accompanied by the deformation of the water pools in the ionic domains. This difference is a direct effect of the different morphology of the polymer backbone: amorphous in the polystyrene copolymers and semicrystalline in the EMAA ionomers.

Spin Probes vs Spin Labels. A common axiom in the study of polymer dynamics by ESR methods is that

spin *labels*, which are chemically attached to the polymer chain, are sensitive to chain dynamics, whereas spin *probes*, which are only mixed with the polymer, are not.[31] This is usually true and has been explained by assuming that the spin probes find a suitable location in terms of free volume and usually relocate to other sites in the polymer matrix when the temperature is varied; therefore, the spectral variations with temperature do not reflect the *local* chain dynamics.

The hydrophilic spin probes used in this study, 5DSA and 10DSA, are "spin probes" in the sense that they are not covalently bonded to the ionomer chains. Their location in the self-assembled system is, however, fixed, because the probes are anchored to the ionic aggregates through ionic interactions; in this sense they are "spin labels". The more hydrophobic spin probe, 10DSE, avoids the regions that contain ions and selects a site within the aggregate core in aqueous solutions, or a site in the polyethylene amorphous regions in the water-swollen membranes, thus also behaving as a spin label. For these reasons the ESR spectra of the three probes have provided crucial information on the temperature variation of the ionic groups in swollen EMAA ionomers, the type of information that is deduced in most polymeric systems only by spin labels.

Concluding Remarks

The spin probe ESR method was applied to the study of aqueous solutions and water-swollen membranes of EMAA ionomers in the temperature range 120−410 K, in order to assess the dynamic nature of the chain aggregates. The probes chosen for study are amphiphilic and are known[20] to intercalate in the ionomer aggregates and to faithfully report on the local environment in the aggregates.

The results indicate that the water−aggregate interface exists in the ionomer **solutions** even at 360 K; inside the aggregate, however, the motion of the chain segments is fast, and the correlation times of the probes are $\sim 10^{-9}$ s/rad. Restricted mobility of the chains was detected in a thickness of ~10 Å from the ionomer−solvent interface and was attributed to constraints arising from the presence of ionic groups in close proximity.

The dynamics of the chains far from the water pools in the swollen *membranes* is similar to that in the aggregates present in the solutions; ESR spectra of the spin probe located at the solvent−ionomer interface change dramatically at ~330 K, and two components differing in their local mobility are detected in the temperature range 330−410 K. We propose that this effect is due to progressive loss of water, or to a restructuring of the water pools, possibly brought about by the activated thermal motion of the backbone chains.

In the present study, the more polar spin probes 5DSA and 10DSA are tightly anchored to ionic aggregates, acting effectively as "spin labels" in the polar regions of the aggregates. The more hydrophobic probe 10DSE avoids regions in the aggregates that contain ions and also behaves as a spin label.

Taken together, the results obtained in this study demonstrate that the amphiphilic spin probes behave as "dipsticks" of the dynamics in the aggregates and reflect the specific and separate effects of the polar domains, the solvent, and the chain characteristics (glass transition of amorphous polyethylene and melting transition of crystalline domains) on the dynamics in the aggregates.

Note Added in Proof: After this paper had been accepted for publication, further evidence for the existence of a "skin" of restricted chain mobility in a layer near the ionomer−solvent interface came from the SANS studies of the EMAA solutions.[19b] The positive deviation from a constant value in a Porod representation (Figure 6 in ref 19b) has been assigned to a layer at the particle−solvent interface that has a higher scattering length compared to the particle core.

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