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Spin Probe ESR Study of Cation Effects on Methanol and DMMP Solvation in Sulfonated Poly(styrene−isobutylene−styrene) Triblock Copolymers at High Ion-Exchange Capacities

Jamie S. Lawton and David E. Budil*

Northeastern University Center for Renewable Energy Technology (NUCRET) Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, 02115

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ABSTRACT: The solvent uptake properties of sulfonated poly(styrene−isobutylene−styrene) (sSIBS) triblock copolymers exchanged with Mg^{2+}, Al^{3+}, Ba^{2+}, and Cs^{+} ions are investigated using the electron spin resonance (ESR) spin probe method with the nitroxide probes 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (TEMPONE) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPOL). sSIBS membranes were equilibrated with varying amounts of methanol, dimethyl methyl phosphonate (DMMP), both as pure solvents and as solvent−water mixtures. As a standard for comparison, Li^{+} ion exchanged Nafion 117 membranes were also characterized using the same spin probes and solvent combinations. Solvent uptake trends were measured for each of the membrane-solvent combinations. Some membranes, particularly those exchanged with Cs^{+}, preferentially uptake water in the presence of organic solvent. sSIBS membranes containing pure methanol or DMMP exhibit two phases which were assigned to the sulfonated styrene block of the polymer, and to the hydrophobic isobutylene block. Whereas methanol enhances the phase separation, DMMP penetrates the less mobile hydrophobic phase at a concentration that depends upon the identity of the exchange ion, which increases in the order $Cs^{+} > Ba^{2+} \sim Al^{3+} > Mg^{2+}$. Thus, cations appear to disrupt the lamellar structure of the polymer, making the nonpolar phase more susceptible to permeation by the solvent. This disruption correlates with the free volume contribution to the rotational diffusion of the probe in both phases, suggesting that the cations affect the solvation of the different phases of sSIBS mainly through their influence on the ordering of the solvent. No clear correlation of this effect with either ionic radius or charge could be identified.

Introduction

Ionomer membranes have been investigated for a variety of uses, including fuel cells, permselective materials for chemical reactions, sensors, actuators, and water treatment, and as a barrier in textiles that selectively block the permeation of organic molecules such as toxins or warfare agents.[1−5] Recently, particular interest has been directed toward aromatic hydrocarbon ionomers as a less expensive, more environmentally friendly replacement for Nafion in fuel cell applications.[6] Another important possible application of permeable membranes is as protective clothing against nerve agents such as Sarin. For this application, the membrane must be breathable, i.e., have high water permeability, but protective, i.e., exhibit low permeability of the chemical agent.[7] A common model compound used to simulate Sarin is dimethyl methylphosphonate (DMMP) which is a dipolar, aprotic molecule.[1]

While Nafion performs well at 80−90 °C,[8] exhibits good mechanical, thermal, and chemical stability, and has good proton conductivity at high relative humidity, its proton conductivity suffers at low hydration and high temperature, and it exhibits high methanol crossover.[9] These attributes are commonly used to compare ionomer membranes for fuel cell applications.

Sulfonated block copolymers offer a degree of control over the phase morphology of a membrane. Block copolymers show a microphase domain segregation that depends on the miscibility and the number of monomers of the differing constituents.[10] A sulfonated block copolymer includes a sulfonic acid group on one of the comonomers, which can lead to additional nanoscale segregation in the polymer morphology. In principle, such polymers may exhibit a three-phase morphology, consisting of a hydrocarbon domain and an ionic domain, which is further segregated by electrostatic interactions among the ion pairs. Small angle X-ray scattering (SAXS) studies by Weiss et al.[11] have observed such a three-phase structure in sulfonated poly(styrene-*b*-(ethylene-*r*-butylene)-*b*-styrene) (SEBS), which exhibited spacings of 3−4 nm domains from aggregation within the sulfonated moiety and 20−30 nm in the block copolymer texture.

The connectivity and morphology of the hydrophilic domain are important factors in determining the proton conductivity, water uptake and permeability of the membrane. In a comparative study of a random copolymer, an alternating polymer and a multiblock copolymer, all based on sulfonated poly(arylene ether sulfone), it was determined that the random copolymer had small hydrophilic domains with good connectivity, the alternating polymer had large domains but low connectivity and the multiblock copolymer had large domains with good connectivity. As a result, the multiblock copolymer was found to have higher proton conductivity with less dependence on relative humidity.[12]

The phase behavior of block copolymer membranes is therefore important for both fuel cell and protective clothing applications. Although each application requires different traits, it is important to understand the morphology of the hydrophilic

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*To whom correspondence should be addressed. E-mail: d.budil@neu.edu. Fax: 617-373-3697.

phase and how it changes with different variables so that the polymers can be tailored to maximize their usefulness for the necessary application. One block copolymer that has recently been studied for such applications is sulfonated poly(styrene−isobutylene−styrene (sSIBS)[13−18] Previous studies of sSIBS have focused on fuel cell and protective clothing applications, investigating the effects of sulfonation levels,[5,14] ion exchange[16,19] and polymer architecture.[17] SIBS is also used as a biomaterial for drug delivery to arterial walls when coated on a coronary stent.[20]

Because of their large water uptake, at high sulfonation levels, sSIBS form an elastic hydrogel composed of two hydrophilic, ionic blocks (A) and one hydrophobic, elastic block (B) in the arrangement A−B−A. Such membranes swell considerably in water, but maintain complete immiscibility. Similar sulfonated homopolymers, i.e., sulfonated polystyrene, dissolve at analogous sulfonation levels. Proton conductivity, which has been shown to increase with water uptake, is higher than that of Nafion in sSIBS with ion exchange capacity of 2 mequiv/g, where water uptake is very high. Unfortunately, because of the mechanical instability of the elastic hydrogel, fully hydrated sSIBS at higher sulfonation levels may not be suitable for use in fuel cells; however, it could be used in a hydrogen fuel cell at low humidity levels.[5,14] Exchange of cations into the membrane has been shown to alter the characteristics of sSIBS, and has been studied as a means of controlling the permeability of the membrane for use in protective clothing. The presence of metal cations in the membrane has also been observed to reduce the diffusion coefficient of water due to alterations in the membrane architecture, since multivalent ions form cross-linking ionic bonds with neighboring sulfonic acid groups.[18]

These considerations motivate our present effort to apply new methods to study highly sulfonated SIBS equilibrated with water, methanol, and DMMP and exchanged with monovalent, divalent and trivalent cations. Electron spin resonance (ESR) of nitroxide spin probes has been used previously to observe the effects of water, methanol and ion exchange on Nafion.[21,22] In particular, this method reveals changes in the local polarity and microscopic viscosity of the membrane phase occupied by the probe. Schlick and co-workers have applied the ESR spin probe method to study the block copolymers poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)[23] and poly(dimethylsiloxane)-*b*-poly(methacrylic acid)[24] in aqueous media. In both cases they observed multiple component spectra which they could resolve on the basis of local polarity and motion, which enabled a description of the phase structure of the polymer. Similar findings have been reported for block copolymers incorporating dimethylsiloxane[25,26] and polystyrene[27,28] in nonaqueous media.

As described below, we also find two distinct phases in sSIBS block copolymer membranes solvated with an organic solvent, and show that additional information can be obtained by detailed analysis of the ESR line shapes from the individual phases.[29] In particular, we demonstrate that the phases can be characterized individually and quantitatively in terms of their polarity and local viscosity. We assign the more mobile phase to the subdomains of the styrene blocks of the polymer into which the sulfonated groups are segregated, whereas the more viscous nonpolar phase most likely corresponds to the blocks consisting of polyisobutylene hydrocarbon linkers.

The two solvents investigated have very different effects on the sSIBS membranes. Whereas methanol appears to enhance the phase separation for all exchange ions studied, DMMP apparently penetrates the linker region and disrupts the phase structure, leading to a transition of the viscous domains of the membrane from a nonpolar to a polar environment. This transition is strongly dependent on the identity of the cation, and correlates with the rate at which the probe's rotational mobility increases with increasing solvent content. We interpret these effects qualitatively in terms of a free volume model for rotational diffusion that has previously been applied to spin probe rotation in Nafion.

Table 1. Samples Used in this Work

membrane	counter ion	ionic radius (Å)	sulfonation level (%)
S-Sibs-84-Mg	Mg^{2+}	0.72	84
S-Sibs-84-H	H^+	a	84
S-Sibs-84-Al	Al^{3+}	0.54	84
S-Sibs-84-Cs	Cs^+	1.88	84
S-Sibs-84-Ba	Ba^{2+}	1.61	84
Li Nafion 117	Li^+	0.76	b

[a] Relevant radius is that of the hydrated ion for H^+. [b] One sulfonate per 1100 molecular weight of the polymer.

Experimental Section

Ion exchanged sSIBS membranes were provided by the U.S. Army Research Lab, Aberdeen Proving Ground, MD, and used as received. All membranes were made from sulfonated SIBSTAR-073T polystyrene-polyisobutylene-polystyrene and contain 30% styrene by weight. Table 1 lists the samples used, including sulfonation level and counterion, as well as literature values for the radius of the counterion.[30,31] Nafion 117 membranes (Ion Power, Inc., New Castle, DE), used as a point of comparison, were treated and ion exchanged with $LiClO_4$ (Sigma-Aldrich, St. Louis, MO) as previously described.[21]

Samples were equilibrated in dimethyl methylphosphonate (DMMP) (Fluka Analytical), methanol (Sigma-Aldrich), and deionized water as well as 20%, 40%, 60%, and 80% mixtures by volume of methanol/water and DMMP/water all with 0.25 mM of either 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (TEMPONE) spin probe or 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPOL). These were chosen for their stability, similar shape and different polarities.

Solution uptake was measured gravimetrically using a Cahn C-33 microbalance by determining the mass of the equilibrated sample and the mass after thorough drying at 40 °C and 635 mm Hg in a Fisher Scientific Isotemp vacuum oven, model 280A. Uptake values are reported in grams of solvent per grams of dried membrane. While this does not reflect the concentration of methanol/water or DMMP/water at intermediate solvent compositions, it provides a basis for comparing the membranes in order to observe changes that depend upon the total concentration of solvents.

All samples were deoxygenated in a glove bag by bubbling with ultra high purity argon that had been passed through an oxygen/moisture trap (model OT-4-SS, Agilent). The deoxygenated samples were placed in a sealed Teflon sample tube, and ESR spectra obtained on an X band Bruker EMX spectrometer. For each spectrum, three scans of 2048 points were averaged using magnetic field modulation of 0.02 mT at 100 kHz; a time constant of 20.48 ms and conversion time of 81.92 ms.

The fitting method utilized a MATLAB (MathWorks) based version of EPRLL, the slow-motional line shape program of Freed and co-workers,[32,33] which can include the microscopic order, macroscopic disorder (MOMD) model. The parameters that were varied during the fitting procedure included isotropic Gaussian inhomogeneous broadening, the A_{zz} tensor component, and the orienting potential parameter c_{20}. The A_{zz} tensor component was then used to determine values for g_{xx} and g_{yy}, as described previously.[21] Several groups have observed that the relation between the isotropic *g*-value, g_{iso}, and a_N (or that between g_{xx} and A_{zz}) is approximately linear.[34−37] This relationship was used to scale g_{xx} and g_{yy} with respect to A_{zz} since the only tensor components that are appreciably affected by the local electric field are g_{xx}, g_{yy}, and A_{zz}.[38] Reported slopes of g_0 vs a_N in protic solvents[34−37] range from -3.2×10^{-4} to -4.0×10^{-4} G^{-1}. We then make the approximation that $\Delta g_x = (g_x - g_z)$ is linearly

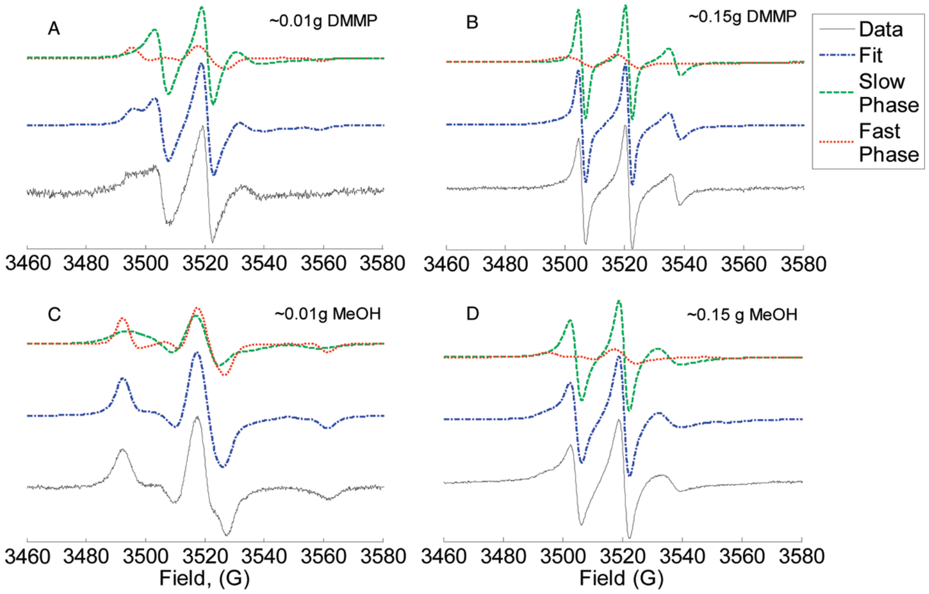

Figure 1. Illustration of the resolution of two components from least-squares fits to the ESR spectra of the TEMPOL spin probe in Mg^{2+}-exchanged sSIBS at solvation levels of 0.01 and 0.15 g of solvent per gram of polymer for DMMP (A, B) and methanol (C, D). Each plot shows the data (solid line, bottom), the calculated fit (middle line, dot−dash) and the individually resolved fast (top, dashed), and slow (top, dotted) components. A range of cases is shown including slow motion in both phases (C) and fast motion in both phases (B).

Table 2. Solvent Uptake Measurements of the Membrane Samples Equilibrated in Pure Solvents

	water/g of polymer		DMMP/g of polymer		MeOH/g of polymer	
membrane	g	mmol	g	mmol	g	mmol
S-Sibs-84-Ba	0.31 ± 0.03	1.8	0.11 ± 0.05	0.09	0.071 ± 0.02	0.22
S-Sibs-84-Al	1.1 ± 0.7	5.9	0.30 ± 0.07	0.24	0.26 ± 0.04	0.83
S-Sibs-84-Mg	1.8 ± 0.4	9.8	0.52 ± 0.05	0.42	0.27 ± 0.03	0.86
S-Sibs-84-Cs	6.7 ± 0.4	37	0.13 ± 0.07	0.11	0.086 ± 0.027	0.27
S-Sibs-84-H	9.4 ± 1.5	52	6.1 ± 0.8	4.9	2.9 ± 0.2	8.9
Li Nafion 117	0.35 ± 0.15	1.9	1.14 ± 0.01	0.92	1.04 ± 0.07	3.3

related to $\Delta g_y = (g_y - g_z)$. This linear relationship is evident from the extensive data tabulation of Lebedev for different nitroxide spin probes,[39] for which a linear fit gives $\Delta g_y \cong 0.20\ \Delta g_x$. The remaining parameters were fixed at the values $g_{zz} = 2.0023$, $A_{xx}/\gamma e = 5.0$ G, and $A_{yy}/\gamma e = 5.5$ G. Also varied in the least-squares fitting procedure was the isotropic rotational diffusion constant R, which is related to the rotational correlation time by $\tau_c = 1/(6R)$. In many cases, two components were clearly evident in the spectra, and could be characterized in terms of the magnetic parameters and rotational correlation times of each component, as well as the relative intensities of the two components. Examples of two-component fits are shown in Figure 1 for spectra of TEMPOL in Mg^{2+}-exchanged sSIBS at different solvation levels. The spectra shown cover the full range of cases from broad slow-motional spectra in both phases (Figure 1C) to narrow three-line spectra reflecting faster motion in both phases (Figure 1B).

Solvent sorption in membranes equilibrated in pure DMMP and pure methanol were accomplished by taking ESR measurements while monitoring the weight change using a Cahn C-33 microbalance as the membrane dried. This could not be done with the protonated sample, which was too fragile.

Results and Discussion

Solvent Uptake. Table 2 shows the liquid uptake values for membranes equilibrated with pure solvents. Many investigations of Nafion exchanged with mono- and di- valent ions have concluded that ion radius plays a large part in determining the water uptake of the Nafion membrane.[40,41] The order of increasing radius for the ions used here is as follows: $H^+ < Al^{3+} < Mg^{2+} < Ba^{2+} < Cs^+$. In comparison, the order of water uptake is: $H^+ > Cs^+ > Mg^{2+} > Al^{3+} > Ba^{2+}$, which correlates with ionic radius except for Al^{3+} and Cs^+. The anomalous solvent uptake in the presence of exchanged Al^{3+} has also been observed in previous investigations of Al^{3+}-exchanged Nafion. This was explained in terms of the stronger electrostatic interactions of Al^{3+} with the anion groups in the membrane, which constrain the size of the hydrophilic membrane phase more than those of lower-valence ions. A similar effect could explain the reduced uptake in Al^{3+}-exchanged sSIBS in comparison to the uptake in the presence of some of the larger ions.

On the other hand, Cs^+-exchanged sSIBS uptakes significantly more solvent than Al^{3+}, Ba^{2+}, and Mg^{2+}, all of which have smaller ionic radii. In contrast, Cs^+ has been shown to dramatically reduce water sorption in Nafion,[42−44] consistent with predictions based on its large ionic radius.[2] A similar but somewhat smaller reduction of solvent absorption by Cs^+ exchange has been observed in other aromatic membranes as well, including polystyrene-divinylbenzene-sulfonate[43] and a sulfonated triblock copolymer with a midblock of styrene and hydrogenated butadiene[2] (Dais Analytical Corp.) This latter membrane also exhibited deviations from the trend in solvent sorption with ionic radius; for example, Cs^+-exchanged Dais membranes take up more water than those exchanged with the smaller Ca^{2+} ion.

Parts A and B of Figure 2 shows trends in the solvent sorption of the membrane samples as a function of liquid compositions for mixtures of water with DMMP and methanol. The protonated sSIBS, not shown, had the highest sorption levels at all concentrations, particularly in water−methanol mixtures. Uncertainties in the measurement of solvent uptake in the protonated sSIBS was high since the consistency of the highly swollen membrane made it difficult to manipulate and measure. The uptake levels for Cs^+-exchanged sSIBS were also high in pure water and mixed solvents with high water content, but dropped off significantly with increased levels of methanol or DMMP. Figure 2B shows a detail of the low uptake region. Unlike

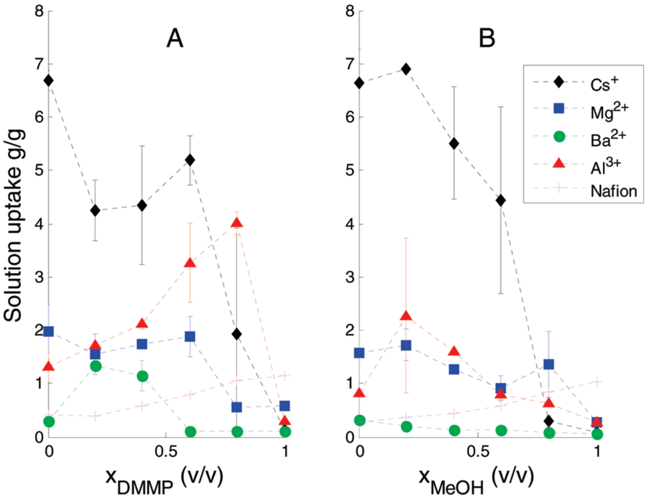

Figure 2. Uptake of DMMP/water (A) and methanol/water (B) mixtures as a function of composition for sSIBS membranes exchanged with Cs^+ (◆), Mg^{2+} (■), Ba^{2+}(●), and Al^{3+}(▲) and Nafion exchanged with Li^+ (+).

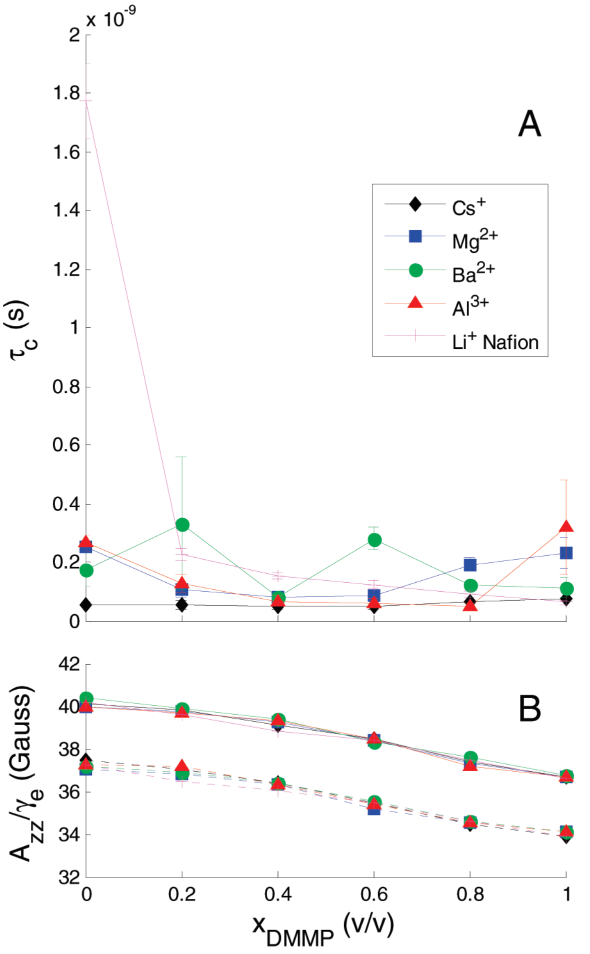

Figure 3. (A) Average rotational correlation times τ_c and (B) hyperfine splitting A_{zz} of the TEMPOL and TEMPONE spin probes for different compositions of DMMP/water mixtures equilibrated with sSIBS membranes exchanged with Cs^+ (◆), Mg^{2+} (■), Ba^{2+}(●), and Al^{3+}(▲) and Nafion exchanged with Li^+ (+). The τ_c values for the two probes are similar; symbols in (A) show the average values with the differences indicated by error bars. In (B), open and filled symbols represent TEMPOL and TEMPONE, respectively.

Nafion, which imbibes more methanol and DMMP than water, all of the sSIBS membranes take up much less liquid in pure methanol and DMMP than in water. Many of the sSIBS samples exhibit a maximum in their uptake levels at intermediate solvent compositions, although the composition of fluid in the membrane relative to that of the bulk solution was not determined. In Cs^+ and Mg^{2+}-exchanged sSIBS in DMMP/water mixtures the solvent uptake levels remain fairly constant until the solvent concentration reaches 60%, where it decreases dramatically. This indicates that sSIBS membranes exchanged with these ions minimize absorption of solvent mixtures with low water content, a potentially beneficial characteristic for materials with protective properties against solvent penetration.

Water/DMMP Mixtures. Part A and B of Figure 3 depict the changes in hyperfine splitting (A_{zz}) and rotational correlation time (τ_c) of the TEMPOL and TEMPONE probes for different concentrations of DMMP and water in the soaking solution equilibrated with the membrane. The τ_c values in Figure 3 represent an average of measurements for both spin probes in the membrane samples, since the probes did not differ significantly in their mobility. The error bars represent the standard deviation of the measurements. For comparison Table 3 shows the magnetic parameters for each of the two spin probes in the different pure solvents used in this paper.[45]

Significantly, although the τ_c of the spin probes in pure DMMP is higher than that in water due to the higher viscosity of DMMP (cf. Table 3), most of the membranes exhibit a *decrease* in τ_c (i.e., an increase in mobility) upon the addition of DMMP. This effect is particularly pronounced in Nafion, where both probes undergo an order-of-magnitude reduction in τ_c upon going from pure water to about 20% (v/v) DMMP. However, Figure 3 highlights a major difference between the sSIBS triblock polymers and Nafion: whereas τ_c decreases monotonically with DMMP concentration in Nafion, most of the sSIBS membranes exhibit a minimum in τ_c around 40−60% DMMP. The minimum in τ_c generally correlates with the maximum observed in solvent uptake for these samples (cf. Figure 2). One exception to this trend is the Cs^+ exchanged sSIBS, for which τ_c remains relatively small despite the large decrease in solvent uptake at high methanol and DMMP concentrations.

Table 3. Magnetic Parameters of the Tempone and Tempol Spin Probes in the Pure Solvents Water, Methanol, and DMMP

		TEMPOL		TEMPONE	
solvent	viscosity (mPa s)	τ_c (s)	A_{zz}/γ_e (G)	τ_c (s)	A_{zz}/γ_e (G)
water	0.890	1.4×10^{-11}	40.44	1.8×10^{-11}	37.55
methanol	0.544	0.10×10^{-11}	37.73	0.80×10^{-11}	34.98
DMMP	1.75	3.1×10^{-11}	36.46	2.2×10^{-11}	33.70

Figure 3B shows that A_{zz} decreases with increasing DMMP concentration in a manner that closely follows that observed for Nafion in water/methanol mixtures. This indicates that the effective polarity of the solution phase of the membrane reflected by A_{zz} decreases monotonically as the DMMP content increases. The dependence of polarity on liquid composition for all the sSIBS membranes studied is nearly identical to that of Nafion (Figure 3B). Also similar to previous observations with Nafion,[21] the apparent polarity inside membranes equilibrated with pure DMMP is higher than that of the pure solvent for both spin probes, although the difference is small in the case of DMMP.

DMMP Solvation. Figure 4 shows the changes in A_{zz} and rotational diffusion rate $R = 1/6\tau_c$ with increasing content

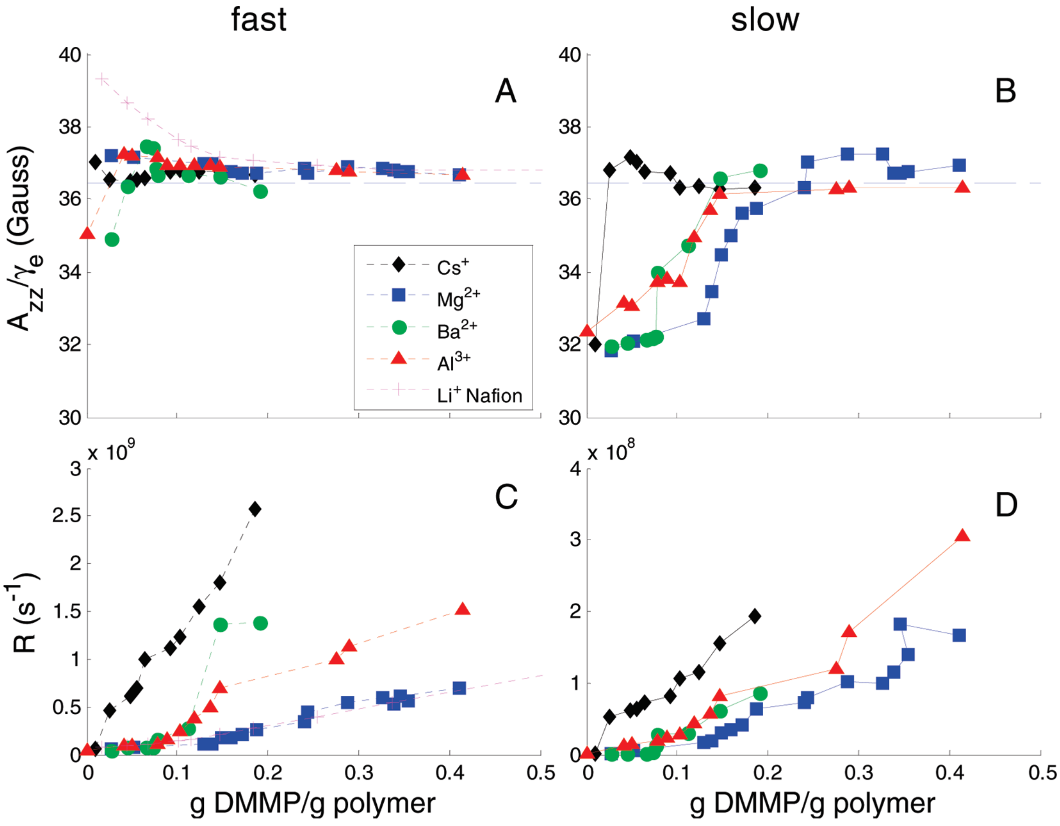

Figure 4. Hyperfine splitting (A, B) and rotational rate (C, D) data for the TEMPOL spin probe as a function of DMMP solvation in two phases of sSIBS membranes exchanged with Cs$^+$ (◆), Mg^{2+} (■), Ba^{2+}(●), and Al^{3+}(▲). In sSIBS, TEMPOL partitions into two phases in which it exhibits fast motion (open markers, panels A and C) and slow motion (solid markers, panels B and D). For reference, measurements are shown for Li$^+$-exchanged Nafion (+), which only exhibited a fast phase.

of pure DMMP for the TEMPOL spin probe in sSIBS membranes exchanged with different cations. As the solvent content decreases, a second, slower and less polar phase becomes evident in the spectra for each of the metal ions studied, which may be separately characterized by line shape analysis (cf. Figure 1). The A_{zz} and R values for the slow component are plotted in Figure 4, parts B and D. Those for the faster, more polar phase are shown in Figure 4, parts A and C. For comparison, a DMMP solvation study for Li$^+$-exchanged Nafion is also shown; in contrast to the sSIBS membranes, this sample exhibited only a fast, polar phase.

The resolution of two components with distinct polarities and mobilities in the ESR spectrum clearly reflects the presence of two phases in the block copolymer membrane. At low DMMP concentrations, the two phases differ significantly both in their polarity (compare Figure 4, parts A and B) and local viscosity (note the difference in vertical scales between parts C and D of Figure 4). The polarity of the less viscous (fast) phase quickly approaches that of DMMP solvent (shown by dashed lines in Figure 4, parts A and B) as the DMMP concentration increases. In contrast, the more viscous (slow) phase is quite nonpolar at low DMMP concentrations as reflected by the smaller A_{zz} values, but increases significantly with increasing DMMP content for all the cation-exchanged membranes, eventually reaching a polarity comparable to that of the DMMP solvent. The transition from a nonpolar to a polar environment is fairly sharp in each case. The DMMP concentration at which the transition occurs depends on the identity of the exchanged ion. For Cs$^+$, the transition occurs at very low DMMP levels (0.01 g DMMP/g sSIBS). The transition occurs at increasingly higher levels of DMMP for Ba^{2+}, Al^{3+}, and Mg^{2+}.

The rotational rate, R, of the TEMPOL spin probe increases substantially with increasing DMMP content for both the polar and nonpolar phases. The rate at which R increases with DMMP depends upon the identity of the exchange ion. Interestingly, this rate decreases in the order Cs$^+$ > Ba^{2+} ~ Al^{3+} > Mg^{2+}, which is exactly the same order in which the nonpolar-to-polar transitions occurs in the slow phase (cf. Figure 4B). The rotation rates of the probe in the fast phase also increase with increasing DMMP content again in the order Cs$^+$ > Ba^{2+} ~ Al^{3+} > Mg^{2+}. The dependence of R on DMMP solvation for the Mg^{2+}-exchanged sSIBS membrane was nearly identical to that of Nafion, (+ symbols in Figure 4C); all of the other exchanged sSIBS membranes exhibited significantly higher probe mobility in the fast, polar phase compared with Nafion.

The DMMP solvation studies discussed above for the TEMPOL spin probe were also carried out with the TEMPONE probe to check whether the different polarity of the spin probe would lead to different partitioning between the phases of the sSIBS membrane. The results are shown in Figure 5. In general, TEMPONE exhibits similar trends in mobility with DMMP concentration for both the slow and fast phases, although the rate at which R increases follows the order Cs$^+$ > Ba^{2+} > Al^{3+} ~ Mg^{2+}. In terms of the polarity, TEMPONE exhibits consistency similar to that of TEMPOL in the fast phase but much more moderate changes with DMMP content in the slower phase. In contrast to TEMPOL, the polarity reflected by the A_{zz} of TEMPONE does not approach the value for pure DMMP at high DMMP concentrations (dashed lines, Figure 5, parts A and B). In addition, the range of A_{zz} values as well as and the apparent differences in the polarities of the fast and slow

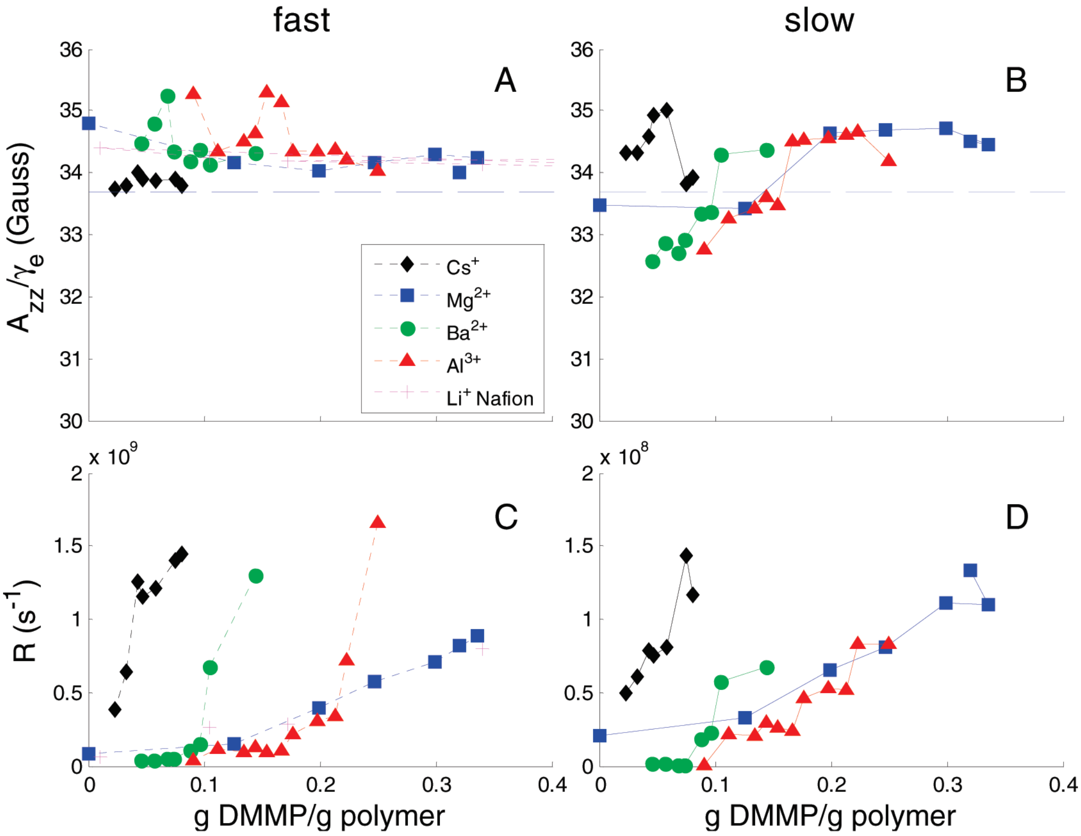

Figure 5. Hyperfine splitting (A, B) and rotational rate (C, D) for the TEMPONE spin probe as a function of DMMP solvation in two phases of sSIBS membranes exchanged with Cs$^+$ (◆), Mg^{2+} (■), Ba^{2+}(●), and Al^{3+}(▲). In sSIBS, TEMPONE partitions into two phases in which it exhibits fast motion (open markers, panels A and C) and slow motion (solid markers, panels B and D). For reference, measurements are shown for Li$^+$-exchanged Nafion (+), which only exhibited a fast phase.

component phases are much smaller for the TEMPONE spin probe. These results combine to suggest that the TEMPONE probe may be undergoing more rapid exchange between the two phases than TEMPOL, so that its measured parameters reflect a more highly averaged local environment.

Water/Methanol Mixtures. Studies of A_{zz} and R as a function of liquid composition were also carried out for membranes equilibrated with methanol/water mixtures using both spin probes, as shown in Figure 6. As was the case for DMMP, the mobilities of the two probes in a given membrane were quite similar at all compositions, so only the average τ_c value is shown in Figure 6A. For Nafion, the effect of increasing methanol concentration is qualitatively similar to that for DMMP; τ_c decreases monotonically with increasing organic solvent concentration in both cases, although the decrease is not as steep for methanol. In contrast, for the sSIBS membranes the effect of methanol is quite different from that of DMMP. Whereas τ_c exhibited a minimum at intermediate DMMP concentrations for most of the sSIBS membranes, it increases monotonically with added methanol for all the membranes studied. This trend is opposite to that observed in Nafion and is most pronounced in the Cs$^+$ sSIBS, which also shows the largest decrease in solvent uptake at high methanol and DMMP concentrations (cf. Figure 2). Another notable case is Ba^{2+}-exchanged sSIBS, which has the lowest solvent uptake at all solvent compositions, yet exhibits a dramatic monotonic increase in τ_c across the entire range of methanol concentrations.

As Figure 6B shows, the dependence of A_{zz} on solvent compositions is qualitatively similar to that previously observed in Nafion,[21]and is nearly identical for most of the sSIBS membranes. The single exception is the Cs$^+$-exchanged sSIBS, which exhibits slightly higher A_{zz} values below about 70% methanol, and slightly lower A_{zz} values above this composition. This switch correlates with the substantial jump in τ_c value for Cs$^+$-exchanged sSIBS, as well as with a decrease in the fluid uptake at this methanol concentration (cf. Figure 2). These results further suggest that Cs$^+$-exchanged membranes preferentially uptake water from the equilibrating solution at methanol concentrations of 60% and below.

Methanol Solvation. Solvation studies of A_{zz} and R were carried out for methanol using both spin probes. As in the DMMP solvation studies, a second, slower and less polar phase became evident in the spectra as solvent was removed. Also similar to the DMMP studies, the TEMPOL spin probe exhibited larger and more clearly resolved differences between the two phases, suggesting that TEMPONE may be exchanging relatively rapidly between phases. We therefore restrict our discussion of methanol solvation to the TEMPOL results shown in Figure 7 (results for TEMPONE are given in the Supporting Information). Parameters obtained from fits to the fast component are shown in Figure 7, parts A and C, and those for the slow component in Figure 7, parts B and D.

As a comparison of Figure 7A and Figure 4A shows, the effects of DMMP and methanol solvation are qualitatively quite similar in Nafion. (A more direct comparison of the Nafion samples is given in the Supporting Information.) Only one, mobile phase is observed with very comparable probe rotational rates at low solvent concentrations and similar, monotonic decreases in polarity as solvent is added.

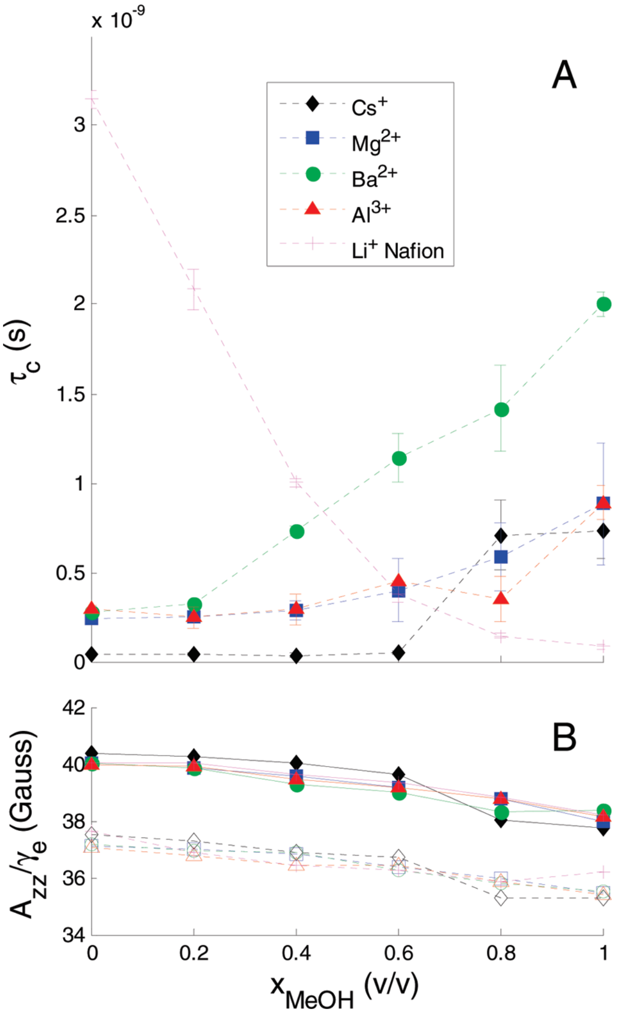

Figure 6. (A) Average rotational correlation times τ_c and (B) hyperfine splitting A_{zz} of the TEMPOL (closed symbols) and TEMPONE (open symbols) spin probes for different compositions of methanol/water mixtures equilibrated with sSIBS membranes exchanged with Cs^+ (◆), Mg^{2+} (■), Ba^{2+}(●) and Al^{3+}(▲) and Nafion exchanged with Li^+ (+). In part A, symbols show the average of the similar τ_c values values for the two probes, with the differences indicated by error bars.

The major difference between the two solvents is that the apparent polarity of the membrane mobile phase is less than that of bulk solvent (dashed line in Figure 7A) in the case of methanol.

In contrast, Figure 7 reveals a number of important differences between the effects of methanol and DMMP in sSIBS membranes. In the lower-viscosity (fast) phase, the polarity is much lower than that of pure solvent at low solvent concentrations, and the change in polarity with added solvent is much larger in the case of methanol. Whereas A_{zz} in the mobile phase is essentially independent of both the solvent content and the identity of the exchange ion in the presence of DMMP (Figure 4A), it increases significantly with increasing methanol content, reflecting a conversion to a phase that is somewhat more polar than bulk methanol. The solvent content at which this transition occurs depends slightly upon the exchange ion, increasing according to the order $Cs^+ < Ba^{2+} < Mg^{2+} < Al^{3+}$ although the dependence is less pronounced than in the membranes swollen with DMMP.

There are also strong contrasts between methanol and DMMP in the slow phase: the changes in the polarity of this phase are much smaller in the case of methanol, and there is no evidence for a sharp transition from a nonpolar to a polar environment as was observed for DMMP (Figure 4B). Instead, the slow phase remains significantly less polar than the bulk solvent (dashed line in Figure 7B), and its polarity actually decreases with added solvent. The composition at which this decrease occurs again depends on the exchange ion, increasing according to the order $Cs^+ < Ba^{2+} < Mg^{2+} < Al^{3+}$, which parallels the accompanying rise in polarity of the fast phase. Interestingly, the Mg^{2+}- and Al^{3+}-exchanged sSIBS membranes exhibit a maximum in the polarity of the fast phase and a corresponding minimum in the slow phase at about 0.1−0.2 g of methanol/g of sSIBS. As has been noted previously, the Cs^+ and Ba^{2+}-exchanged membranes do not absorb much organic solvent in the absence of water, so that data could not be obtained at high enough methanol concentrations to observe a minimum or maximum in these cases. The polarity data from the two phases combine to suggest that methanol at low concentrations has the effect of polarizing the phases of sSIBS.

Significant differences between methanol and DMMP also appear in the probe mobility in both phases. The major contrast is in the slow phase: whereas the mobility increases dramatically with DMMP concentration in an exchange ion-dependent way, the slow phase mobility is much lower in the presence of methanol, is independent of the exchange ion, and does not increase significantly with solvent content for most of the membranes. The notable exception is Mg^{2+}-exchanged sSIBS, which exhibits a dramatic, sharp increase in mobility above about 0.1 g of methanol/g of sSIBS.

Probe mobility in the fast phase is qualitatively more similar to that observed for DMMP, and does increase with methanol concentration at a rate that depends upon the exchange ion. The rate of increase follows the order $Cs^+ > Ba^{2+} > Mg^{2+} > Al^{3+}$ (Figure 7C) which mirrors the order in which the polarity changes in the two phases depend upon exchange ion. However, there are important differences in the fast phase as well: the rotational rates for the probes in DMMP are higher in both phases than in methanol at comparable solvent contents; in fact, with DMMP the mobile phases of the sSIBS membranes are all faster than that of Nafion (Figure 4C) whereas with methanol they are all significantly slower (Figure 7C). The differences in the rotational rates of the probes in the slow phase and the fast phases are more pronounced in methanol-swollen membranes, supporting the conclusion that the different phases are more distinct in this system.

Phase Behavior of sSIBS. A key finding of the present study is the observation of two distinct phases of sSIBS triblock copolymer membranes when they are solvated with an organic solvent. The present study demonstrates that these phases can be characterized individually and quantitatively in terms of their polarity and local viscosity. Both methanol and DMMP exhibit a polar, lower-viscosity phase and a nonpolar, higher-viscosity phase into which the spin probes partition. It is worth noting that even the lower-viscosity phase exhibits probe motion comparable to that of a viscous liquid; i.e., the probe is not immobilized as would be the case for a solid phase polymer. On the basis of these observations, we assign the more mobile phase to the subdomains of the styrene (A) blocks of the polymer into which the sulfonated groups are segregated, whereas the nonpolar more viscous phase most likely corresponds to the (B) blocks consisting of polyisobutylene hydrocarbon linkers.

The morphology of these phases has been demonstrated to depend strongly on the degree of sulfonation. Small angle X-ray scattering experiments by Elabd et al.[5] have indicated

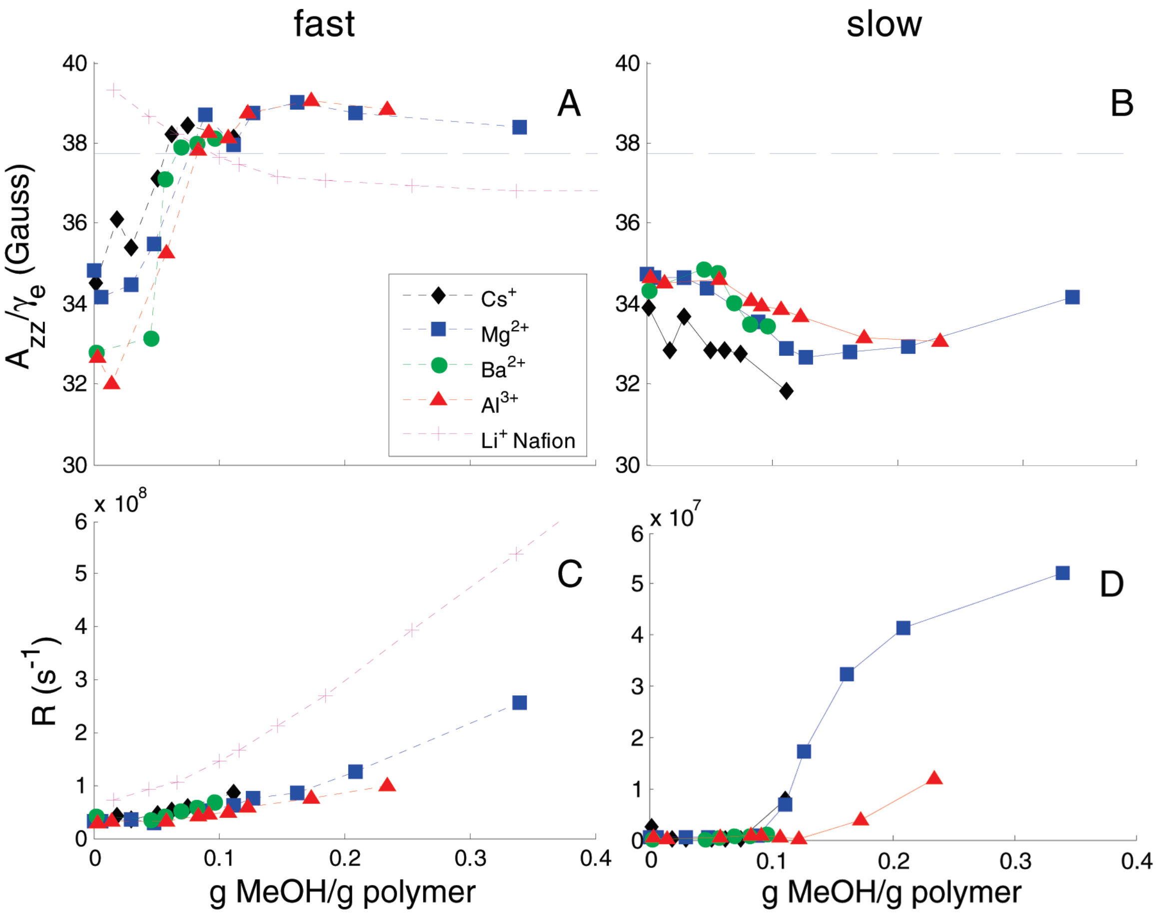

Figure 7. Hyperfine splitting (A,B) and rotational rate (C,D) for the TEMPOL spin probe as a function of DMMP solvation in two phases of sSIBS membranes exchanged with Cs$^+$ (♦), Mg^{2+} (■), Ba^{2+}(●) and Al^{3+}(▲). In sSIBS, TEMPOL partitions into two phases in which it exhibits fast motion (open markers, panels A and C) and slow motion (solid markers, panels B and D). For reference the same quantities are shown for Li$^+$-exchanged Nafion (+), which only exhibited a fast phase.

an isotropic cocontinuous phase morphology at high sulfonation levels comparable to those used in this study.

Addition of DMMP apparently disrupts the phase structure of the block copolymer, leading to a transition of the viscous domains of the membrane from a nonpolar to a polar environment as DMMP penetrates these regions. This finding is consistent with molecular dynamics simulations that have shown that DMMP swells the hydrophobic membrane backbone.[4] However, the concentration at which DMMP penetrates into these regions depends strongly on the identity of the exchange ion.

Although DMMP increases the mobility of both the fast and the slow component more than does methanol, there is a significantly greater difference between the rotational rates of slow and fast components with methanol. This result, combined with the polarity measurements, suggests that methanol enhances the phase separation in sSIBS for all exchange ions studied. In contrast, DMMP exhibits a threshold concentration of solvent at which a dramatic transition from a nonpolar to a polar environment occurs in the slow phase that depends upon the identity of the exchange ion. Thus, DMMP weakens the distinction between hydrophilic and hydrophobic phases as it penetrates deeper into the hydrophobic polymer phase.

The effects of DMMP are quite dramatic in comparison to methanol, especially considering the relative molar masses of these two solvents. Although changes in the ESR spectra are observed at comparable solvent to polymer mass ratios, the molar mass of DMMP is nearly 4 times that of methanol. Thus, only a small number of molecules of DMMP are required to drastically alter the local viscosity of both membrane phases.

Molecular Interpretation. An interesting feature of the experimental results is the strong correlation of (1) the solvent concentration at which the slow phase undergoes a transition from a nonpolar to a polar environment, (2) the rate at which the rotational mobility of the probe increases with increasing solvent content, and (3) the identity of the exchange ion. The change in polarity of the viscous phase reflects penetration of the polar solvent molecules into the hydrophobic chain block of the polymer. This penetration most likely results from disruption of the cocontinuous lamellar structure by the solvent. The differences between the two solvents investigated suggest that some degree of solvation of both phases is required to reduce the enthalpic interactions that lead to phase segregation. Thus, the more polar methanol may preferentially solvate the sulfonated regions of the membrane, leading to a better definition between the polar and nonpolar phases. In contrast, the ability of the less polar DMMP to interact with both phases reduces the definition between the two blocks.

The correlation between the change in viscous phase polarity and the rate at which the probe rotational mobility increases with solvent content may also be explained on the molecular level. The most straightforward interpretation is in terms of a free volume model, most often used to describe translational diffusion, but also applicable to rotational diffusion of either solvent or probe molecules. Although the most commonly accepted free volume models apply rigorously only to two-phase systems, they do offer a point of departure for a qualitative description of the interactions between solvent and each of the individual phases of the block copolymer. To a first approximation, the rate at which the rotational diffusion constant R increases with solvent content in a given polymer phase depends upon the relative contributions of that phase and the solvent to the total free volume. Thus, a higher free volume fraction in both membrane phases correlates with disruption of the lamellar structure. This correlation suggests that the major influence of the solvent is its effect on the local molecular ordering in each of the phases, such that greater disorder produced a higher fraction of free volume available for probe rotation.

A molecular level explanation for the correlation of effects (1) and (2) with the identity of the cation is less clear from the available data. These effects do not correlate completely with either ionic size or charge within the limited set of metal ions investigated. The relative free volume contribution decreases according to the order $Cs^+ > Ba^{2+} \sim Al^{3+} > Mg^{2+}$. in DMMP-containing membranes and $Cs^+ > Ba^{2+} \sim Mg^{2+} > Al^{3+}$ in methanol. The combined influence of ion and solvent suggests that the net effect is most likely a complicated function of the strength of the ion's electrostatic interaction with the sulfonate groups in competition with solvation of the ion, both of which may be expected to modulate interactions among the different phases of the coblock polymer. Such interactions should also depend upon the block size and degree of sulfonation, suggesting ways in which this correlation may be tested experimentally.

The case of Cs^+ exchanged sSIBS stands out particularly, since Cs^+ appears to promote the absorption of DMMP into the hydrophobic phase of the membrane at very low DMMP concentrations. This contrasts with Nafion, where Cs^+ has been shown to decrease the uptake of solvents, including water, quite significantly. In Nafion, this reduction has been attributed to the larger radius and small hydration shell of Cs^+, which leads to stronger anion–cation interactions and restricts the volume of the polar phase that is accessible to solvent.[41] This is apparently not the case in the sSIBS membrane examined here, or in membranes with an ionic block similar to sSIBS (Dais Analytical Corp.), where Cs^+ has been observed to increase water uptake relative to other metal ions.[2] This comparison suggests that the influence of ionic radius may be smaller in membranes that lack the well-separated phase structure of Nafion.

Comparison with Nafion. Nafion is frequently used as a standard for comparison of new proton exchange and permselective membranes, and offers a useful reference for discussing the properties of sSIBS. Nafion exhibits only a single phase, which corresponds to the fast phase observed in the sSIBS copolymer. DMMP and methanol behave very similarly in Nafion, in contrast to the sSIBS membranes. Previous comparisons of Nafion and aromatic alternatives have shown that the sulfonic groups on the Nafion fluoroether side chains are more electronegative and thus have a lower pK_a than those on aromatic hydrocarbon rings.[46] In addition, the long side chains of Nafion increase the mobility of the ion groups in comparison to the aromatic sulfonic groups. These differences combine to weaken the definition between the hydrophobic and hydrophilic phases in the aromatic systems and reduce the size of the channels for fluid transport.

Methanol is known to diffuse into the fluoroether side chain region of the Nafion membrane,[47,48] which is often invoked to account for the high methanol crossover observed in Nafion in comparison with other membranes. Even in fully sulfonated sSIBS membranes, methanol permeability has been measured to be much smaller than that in Nafion.[49] A major dissimilarity between sSIBS and Nafion that could account both for the differences in methanol permeation and for the extent of methanol uptake is the absence of long side chains in the hydrophilic block of sSIBS. Because the sulfonate groups in the sSIBS ionic block are linked directly to the aromatic backbone, the region of methanol permeation may be limited in this type of polymer. This is the region of the polymer corresponding to the low-mobility, low-polarity fraction observed in the sSIBS membranes in which spin probes are immobilized close to the hydrophobic polymer backbone. These considerations may therefore account for the relative insensitivity of A_{zz} in the slow phase to the methanol content and also explain why methanol primarily affects the apparent polarity of the faster phase.

Conclusion

The ESR spin probe method has been applied in conjunction with quantitative ESR line shape analysis to characterize the effects of solvents on the morphology of sulfonated SIBS block copolymers exchanged with different metal cations. ESR spectra of DMMP/water mixtures, methanol/water mixtures, and methanol and DMMP swelling of ion-exchanged sSIBS membranes show very different trends compared with previous measurements on Nafion membranes.

Correlations between solvent uptake, probe mobility, and local polarity as a function of composition in solvent/water mixtures indicate that some of the sSIBS membranes, particularly those exchanged with Cs^+, preferentially uptake water. sSIBS membranes containing methanol or DMMP exhibit two phases, including a more mobile, polar phase that was attributed to the fluid region solvating the ions in the sulfonated styrene block of the polymer, and a less polar, less mobile phase assigned to the hydrophobic isobutylene block of the polymer. Whereas methanol appears to strengthen the separation between these phases, DMMP can access both phases, and the concentration at which DMMP penetrates the less mobile phase depends strongly upon the identity of the exchange ion.

The selection of cations for this initial study was somewhat limited by sample availability, and was chosen to cover a range of valences and ion sizes in order to test whether these characteristics have any effect on the probe spectra in this pilot study. Given the extent to which we have found the cation actually does influence both of the observed membrane phases, more systematic studies of exchange ion effects are warranted. The influences of charge and size could be resolved to some degree by studying different series of ions within a family on the periodic table. In light of recent reports of the stabilizing influence of Ce^{3+} ions on perfluorinated membranes,[50] it would be particularly interesting to see whether this ion affects sSIBS membrane structure to the same degree as the similarly charged Al^{3+} ion characterized here.

The results clearly establish the sensitivity of spin probe ESR parameters to the local morphology of sSIBS membranes under different conditions. A more complete picture of phase morphology in such membranes will follow from quantitative measurements of spin probe parameters as a function of block size and sulfonation level in this type of membrane.

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Supporting Information Available: Figures showing additional studies of the TEMPONE spin probe in sSIBS membranes equilibrated with methanol and a comparison of the TEMPOL and TEMPONE spin probes in Nafion. This material is available free of charge via the Internet at http://pubs.acs.org.

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