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Communications to the Editor

State of Water in Disulfonated Poly(arylene ether sulfone) Copolymers and a Perfluorosulfonic Acid Copolymer (Nafion) and Its Effect on Physical and Electrochemical Properties

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Introduction. There has been great interest in proton-conducting sulfonated copolymers and their application in polymeric electrolyte membrane fuel cells (PEMFC).[1] In the operation of a PEMFC, membrane hydration is critical to the fuel cell performance and influences proton conductivity,[2] methanol permeability,[3] and electro-osmotic drag.[4] However, the degree of water absorption on a mass basis does not correlate well with those properties, especially when comparisons are made between different macromolecular systems. It is proposed in this paper that the state of water[5] as it is confined in the membrane plays a more significant role in determining the membrane transport properties than previously suggested. The state of water in polymers has been extensively studied,[5] but mainly in the context of hydrogels. It has been generally defined as follows: (1) *nonfreezing water*, water that is strongly bound to the polymer chain and has a role in effective glass transition reduction (plasticization); (2) *freezable loosely bound water*, water that is weakly bound to the polymer chain or interacts weakly with nonfreezing water and displays relatively broad melting endotherms; and (3) *free water*, water that is not intimately bound to the polymer chain and behaves like bulk water, i.e., a sharp melting point at 0 °C. This picture of three states of water as defined primarily by their differential scanning calorimetry transitions has been adopted to describe the phenomena observed in this work.

The aim of this Communication is to show the effect of the behavior of the absorbed water or the distribution of the “states of water” on important physical and electrochemical properties of well-known, sulfonated copolymers. Thus, it has been of interest to investigate directly copolymerized sulfonated poly(arylene ether sulfone) copolymers[6] and the standard perfluorinated copolymer, Nafion. The state of water in the copolymers was quantified by both pressure differential scanning calorimetry (DSC) and ^{1}H pulse NMR techniques. These two characterization techniques are complementary since DSC measurement can show the depression of the glass transition temperature, T_g, caused by the nonfreezing strongly bound water, while the spin−spin relaxation time, T_2, measurement by ^{1}H pulsed NMR allows one to calculate the distribution of each state of water in the copolymers. In addition to DSC and NMR results, methanol permeation and electro-osmotic drag data are presented as additional examples of properties that are shown to be directly affected by the state of water.

Experimental Section. a. Copolymer Synthesis. Biphenol-based wholly aromatic sulfonated poly(arylene ether sulfone) statistical copolymers (BPSH-*XX*; *XX*: mole percent of disulfonated monomer) were successfully synthesized via nucleophilic aromatic substitution polycondensation of 4,4′-biphenol, 4,4′-dichlorodiphenyl sulfone, and 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone, as previously reported.[6] The intrinsic viscosity (NMP, 25 °C) was 0.9 dL/g or higher, corresponding to an M_n of >40K g/mol. Membranes were prepared by solution casting from *N*,*N*′-dimethylacetamide (10% w/v). The 40% disulfonated copolymer membranes in their sodium salt form were then converted to the corresponding acid form by immersion in 0.5 M boiling sulfuric acid solution for 2 h, followed by immersion in boiling deionized water for 2 h.[7] The Nafion membrane with an equivalent weight of 1100 and ion-exchange

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capacity (IEC) of 0.91 mequiv/g (N1135, Du Pont) was acidified via the same procedures described above.

b. Differential Scanning Calorimetry (DSC). DSC measurements were performed on a TA DSC equipped with liquid nitrogen cooling accessories for subambient operation. To hydrate the membranes, about 5−10 mg of the previously dried samples was placed either in a humidity chamber at 30−50 °C for about 24 h or in deionized water for 24 h followed by blotting to remove surface water. The samples then were transferred immediately to sealed aluminum pans capable of enduring at least 10 atm. DSC data were collected during the first run for temperatures scanned at 10 °C/min from −60 up to 200 °C. For the well-dried sample, a hermetic aluminum pan was used which covered a temperature range from −60 to 300 °C.

c. ^{1}H NMR T_2 Measurements. The proton spin−spin relaxation times, T_2, were measured with a Bruker MSL 300 spectrometer using a 90° pulse of 6.5 μs at room temperature. The Carr−Purcell−Meiboom−Gill pulse sequence was used to determine the relaxation times for the copolymers. A total of 64 decay points were collected over 4 ms, and the signal-to-noise ratio was enhanced by coadding 32 scans. The samples were equilibrated in distilled water at room temperature until they had reached their equilibrium mass uptake of water. Then, just prior to the NMR measurements, they were removed from the water and placed in the NMR probe.

Results and Discussion. Figure 1 provides the DSC thermograms of BPSH-40 and Nafion-1135 as a function of water content. Both systems show that the T_g initially decreases with increasing water content. The T_g depression is assigned to the effective plasticization by water which is strongly bound to the sulfonic acid groups or associated with the polymer backbone. Figure 1 also shows that the samples with high water content had two overlapping endotherm peaks which consisted of the broad melting peak range from −30 to 10 °C, assigned to the weakly bound water and the sharp melting peak at 0 °C due to the free water.

Figure 2 shows the variation of measured T_g with water content along with values predicted from the Kelley−Bueche copolymer equation[9] (eq 1):

$$T_g = \frac{R\phi_1 T_{g1} + \phi_2 T_{g2}}{R\phi_1 + \phi_2} \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of the component 1 (BPSH-40, T_{g1} = 270 °C) and component 2 (water, T_{g2} = −139 °C),[10] respectively. T_{gi} are the pure component glass transition temperatures, and $R \equiv \alpha_1/\alpha_2$, with α_i being the difference in thermal expansivity between liquid and glass for component i. These values have generally been taken to be $\alpha_2 = 4.8 \times 10^{-4}$ and $\alpha_1 = 10^{-3}$, leading to the value[10] of $R = 2.1$.

The experimental data indicate that the T_g of BPSH-40 decreased from 267 °C for a completely dry sample to about 126°C as the water content increased to approximately 20 vol %, then leveled off, and thereafter deviated from eq 1. These observations are only partially predicted by eq 1, which predicts a sustained monotonic decrease in T_g. For hydrated Nafion-1135, the deviation between the experimental data and theory was more significant since the T_g depression followed the predicted value to only about 5 vol % water and then became somewhat insensitive to additional water. The appearance of the melting endotherm peak of the freezable water correlated well with the deviation from the theoretical prediction for T_g (see Figure 1). These results indicate that only nonfreezing strongly bound water acts as a plasticizer while freezable water molecules do not have much influence on T_g. Furthermore, these results suggest that Nafion-1135 has much higher freezable water content than BPSH-40 under fully hydrated conditions, even though the total water content of Nafion is lower.

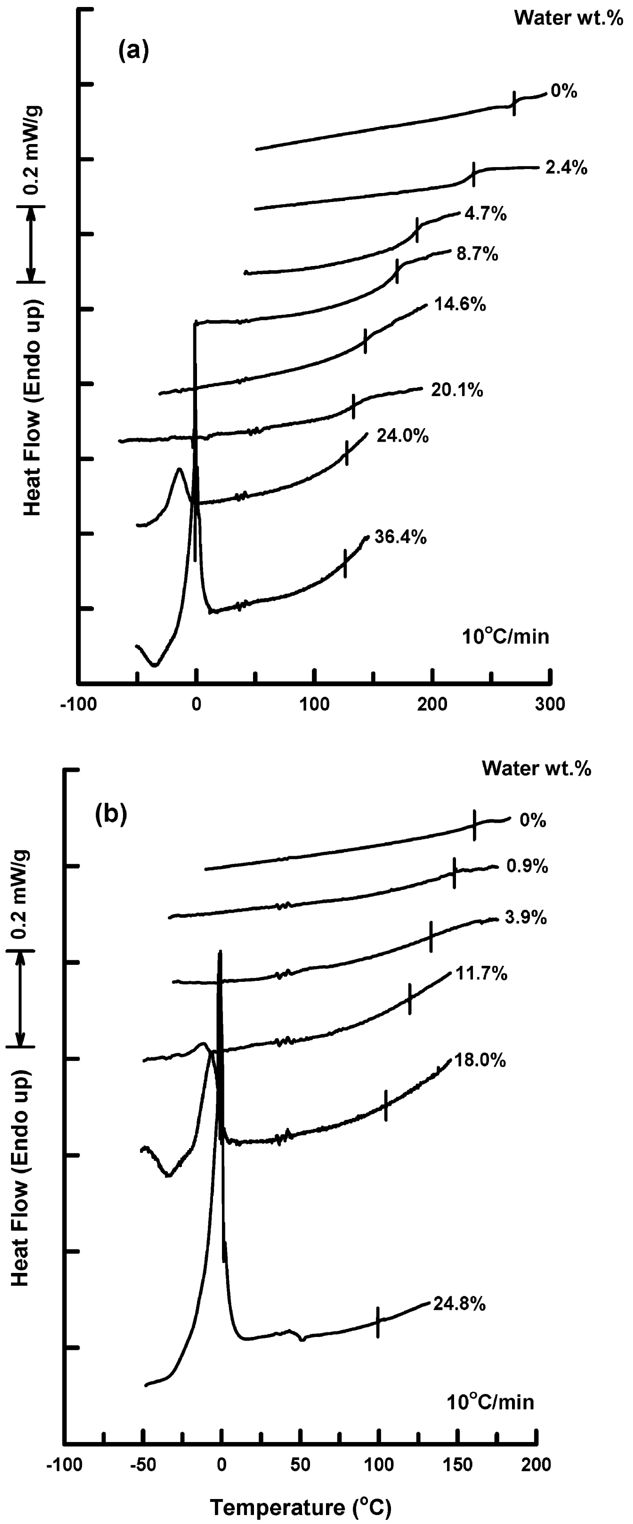

Figure 1. Pressure DSC thermograms for (a) BPSH-40 and (b) Nafion-1135 as a function of water content.

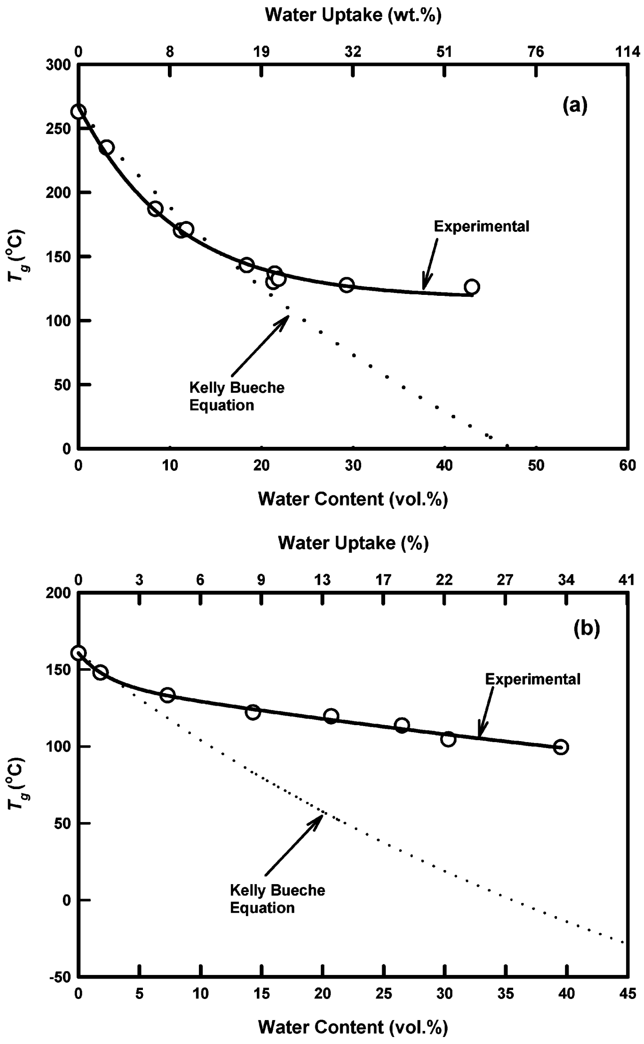

Figure 2. T_g depression of (a) BPSH-40 and (b) Nafion-1135 as a function of water content. The dotted line is predicted by eq 1.

Quantification of each state of water by DSC is obviously of great interest but is difficult not only because of the two overlapping melting peaks but also because the heat of fusion of the absorbed water is not constant in these systems and varies with the strength of interaction between the water and copolymer.[11] Only the nonfreezing water content can be computed by the maximum water content where no endothermic melting peak is observed in the DSC thermogram.

The ^{1}H pulse NMR experiments, on the other hand, should be able to measure the state of water quantitatively.[12] According to the BPP theory,[13] the spin−spin relaxation time, T_2, decreases continuously as the correction time, τ_c, in molecular motion increases. Figure 3 shows the ^{1}H T_2 decay curves for three different samples. The poly(arylene ether sulfone) control (BPSH-00) shows a single-exponential decay, which indicates there is only one polymer phase, and very little absorbed water can be observed. For the 10% disulfonated copolymer, the decay of the transverse magnetization was found to be a double exponential. This was demonstrated using a least-squares data fitting program (SigmaPlot). The short component of T_2 (T_{2s}) for BPSH-10 is close to that of the control. The proportion of water molecules relaxing with a time constant of T_{2s} expressed as a weight fraction of the total absorbed water for BPSH-10 is 40 wt %. This relatively small value of T_{2s} suggests that the water molecules contributing to this component have short diffusive path lengths. This can be correlated to water that is strongly interacting with the copolymer chains, and the most likely interaction is through hydrogen bonding. The second component of the decay shows relatively long T_2 values (T_{2l}), which suggests that the water molecules contributing to this component are relatively loosely bound to the copolymer. The water uptake and T_2 data suggested that each sulfonic acid group in the BPSH-10 sample is surrounded by a glassy hydrophobic matrix, and it absorbs eight water molecules, in which approximately three have strong interaction with the sulfonic acid group, whereas the other five are loosely bound with the sulfonic acid group. The water uptake increases with the concentration of the disulfonic acid groups. The now rubbery hydrophilic domains contain water molecules, sulfonic acid groups, and some of the copolymer chain. For example, Figure 3c shows the T_2 decay for a BPSH-40 sample. In addition to T_{2s} and T_{2l}, another component with an even longer relaxation time can be observed. It is suggested that this component corresponds to water that is highly mobile and is assigned to the free water molecules. The T_2 for pure water at 307 K is 1.0 s, and the T_2 component of the free water molecules in BPSH-40 sample is nearly constant, at the experimental time scale of 4 ms. The free water molecules are likely aggregated in the hydrophilic domains, together with the tightly and loosely bound water molecules, the sulfonic acid groups, and, by calculation from the water uptake and T_2 data, approximately 19% of the BPSH-40 copolymer chains. In this case, it is proposed that

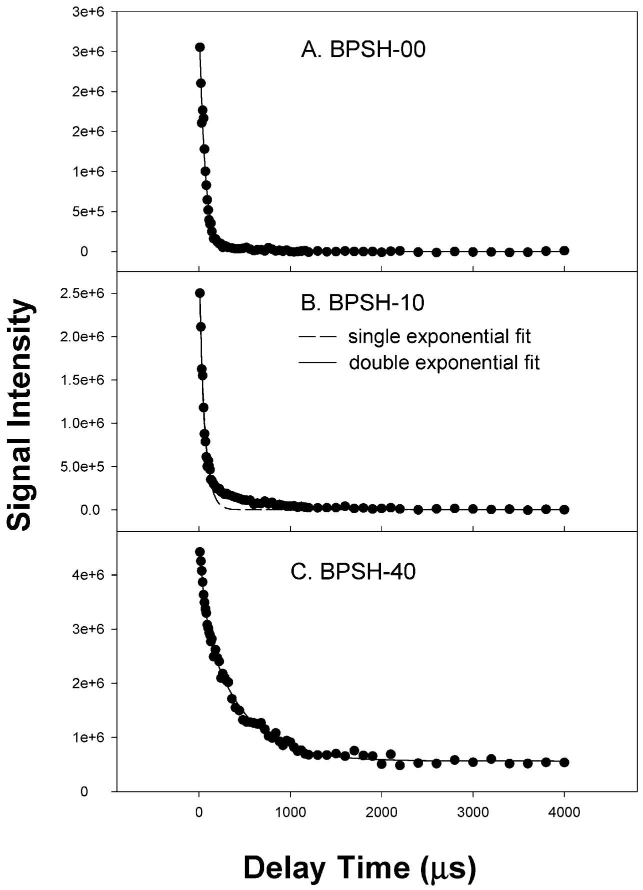

Figure 3. Influence of disulfonic acid concentration on ^{1}H T_2 decays for the control BPSH-00, BPSH-10, and BPSH-40 copolymers.

Table 1. Characterization of Ion-Exchange Capacity (IEC), Water Uptake, Composition of Each State of Water, T_g, Upper Limit Use Temperature, Electro-osmotic Drag, and Methanol Permeability of BPSH Copolymers and Nafion

			no. of water per sulfonic acid group, λ								
copolymer	IEC (mequiv/g)	water uptake (%)	total water	non-freezing water	loosely bound water	free water	T_g of dried sample (°C)	T_g of fully hydrated sample (°C)	upper limit use temp[a] (°C)	electro-osmotic drag coeff[b]	methanol permeability[c] (10^{-8} cm^2/s)
BPSH-0	0	0	0	0	0	0	223				2.4
BPSH-10	0.5	7	8.1	3.2	4.9	0	232				
BPSH-20	0.9	18	10.8	3.6	7.2	0	246				22
BPSH-30	1.3	29	12.0	4.1	7.9	0	257	136	140	1	36
BPSH-40	1.7	56	18.0	5.1	10.8	2.2	267	126	120	1.5	81
BPSH-50	2.0	124	33.1	4.9	24.5	3.7	272	98	100	2.5	151
Nafion-1135	0.9	33	20.2	2.2	13.1	4.9	160	99	100	3.3	167

[a] Data obtained from ref 8. [b] Data obtained from ref 14. [c] Data obtained from ref 15.

tightly and loosely bound water molecules are all located in the hydrophilic domains. The T_2 data cannot distinguish them from each other, but a combination of DSC and NMR experiments allows the state of water in these copolymers to be analyzed, as shown in Table 1.

The state of water in the sulfonated copolymers clearly has a critical influence on the electrochemical properties of the membranes, which may be very important in PEM fuel cells. For example, the tightly bound water results in a T_g depression of the sulfonated copolymers. The T_g depression of the sulfonated copolymers under hydrated conditions indirectly affects the proton conductivity by influencing the temperature of viscoelastic induced morphological relaxation. Previously, we reported the proton conductivity of fully hydrated BPSH and Nafion under pressure at 100% relative humidity in the temperature range from 70 to 140 °C.[8] Generally, the proton conductivity of those copolymers first increased with temperature, to a certain upper limit use temperature, and then decreased. Table 1 shows the comparison of the upper limit temperature with the T_g of fully hydrated BPSH of varying disulfonic acid concentrations and Nafion copolymer control. One concludes that the upper limit use temperature of the copolymers is close to the T_g of the fully hydrated samples, indicating that the morphological relaxation occurs at or near the glass transition temperature. This result indicated that the concept of a hydrated membrane T_g can be an important barometer for predicting the upper limit use temperature of a PEMFCs.

The transport of water across the proton-exchange membrane by electro-osmotic drag is known to have a critical role in the water management of both the catalyst layers on a local scale and the overall system. Large electro-osmotic drag coefficients are undesirable due to catalyst flooding/drying and system recycle or replenishment. Protons are conducted across a water-absorbing sulfonated polymeric membrane likely by a combination of both hopping and vehicle mechanisms.[16] The mechanism of proton transport for any well-hydrated sulfonic acid-based membrane has been suggested to be a similar distribution of the two mechanisms. However, electro-osmotic drag coefficients are found to be as high as 3.3 H_2O/H^+ for Nafion and as low as 1.0 H_2O/H^+ for BPSH-30 (Table 1). This difference, even for macromolecules with similar water content, is suggested to be a function of the increased local viscosity of the water in the BPSH copolymers because of the larger fraction of tightly bound water as compared to the case of Nafion. Even BPSH-40 and BPSH-50 copolymers, with equivalent or greater λ (20.0 and 36.5, respectively) and much higher overall water uptake by weight (56% and 124%), have lower electro-osmotic drag coefficients (1.5 and 2.5) than Nafion. Clearly, there is less viscous drag of the water by proton movement in the BPSH series. These experimental results support the hypothesis that the concentration of loosely bound and free water plays a more important role in transport across the membrane than merely the total water uptake.

Methanol permeability is another important membrane property related to the state of water contained in a sulfonated copolymer. For direct methanol fuel cell (DMFC) technology, membranes with low methanol permeability are required because methanol crossover from the anode to the cathode leads to lower cell voltage and decreased fuel efficiency. In general, it has been recognized that perfluorinated copolymers such as Nafion have undesirably high methanol permeability compared to that of hydrocarbon-based copolymers, even though the fluorinated copolymer has lower water uptake. On the basis of the results described herein, it is suggested that an important reason for the higher methanol permeability for Nafion is its higher fraction of loosely bound and free water compared to that of the poly(arylene ether)-based copolymers, as shown in Table 1.

It has been previously established[6] by tapping mode AFM that both Nafion and BPSH copolymers nanophase separate into ion-rich and ion-poor domains due to the hydrophilic and hydrophobic units along the copolymer chain. While the phase separation behaviors are qualitatively similar, the domain structures of each copolymer are certainly quantitatively different as evidenced by the length scales estimated from AFM measurements and the experimental data presented in this paper. The quantitative differences in the domain structure of the copolymers can be explained by considering the distribution of states of water within each copolymer as measured by DSC and ^{1}H NMR relaxations.

In conclusion, the state of absorbed water within the polymer rather than the total water content may be a stronger indicator of the water and methanol membrane transport properties. In this work it is has been convenient to adopt the three states of the water model that has been proposed for hydrophilic media. The DSC and ^{1}H NMR relaxation measurements correspond well to this idealized three-state picture. However, one must realize that there is most likely a distribution of states for absorbed water that varies continuously between the two extremes of tightly bound water and free water. The experimental data lends itself to partitioning the water into three identifiable states for discussion purposes. This Communication has outlined three important properties—glass transition temperature, electro-osmotic drag coefficient, and methanol permeability—that are related to the state of water in the membrane rather than bulk water uptake.

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