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Absence of Schroeder's Paradox in a Nanostructured Block Copolymer Electrolyte Membrane

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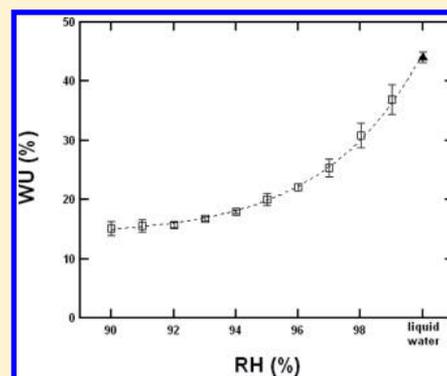
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ABSTRACT: This is a study of morphology, water uptake, and proton conductivity of a sulfonated polystyrene-*block*-polyethylene (PSS-PE) copolymer equilibrated in humid air with controlled relative humidity (RH), and in liquid water. Extrapolation of the domain size, water uptake, and conductivity obtained in humid air to RH = 100% allowed for an accurate comparison between the properties of PSS-PE hydrated in saturated vapor and in liquid water. We demonstrate that extrapolations of domain size and water uptake on samples equilibrated in humid air are consistent with measurements on samples equilibrated in liquid water. Small (5%) differences in proton conductivity were found in samples equilibrated in humid air and liquid water. We argue that differences in transport coefficients in disordered heterogeneous systems, particularly small differences, present no paradox whatsoever. Schroeder's Paradox, wherein properties of polymers measured in saturated water vapor are different from those obtained in liquid water, is thus not observed in the PSS-PE sample.



INTRODUCTION

Polymer electrolyte membranes (PEMs) are composed of nanoscale hydrophilic domains embedded in a hydrophobic matrix. When properly designed PEMs are exposed to either humid air or liquid water, the hydrophilic domains spontaneously absorb water molecules, resulting in the self-assembly of continuous proton-conducting channels in a hydrophobic matrix. The hydrophobic phase provides the membrane with the mechanical properties necessary for operation in the device of interest.

There has been a long-standing debate on the differences in properties of materials in contact with either saturated water vapor or liquid water. The first known report on this debate was published in 1903 by Schroeder who studied the absorption of water in gelatin. He noted that gelatin samples absorbed less water when contacted with saturated water vapor than they did in liquid water.¹ Subsequent studies on this subject have frequently referred to this phenomenon as Schroeder's Paradox.²⁻⁵ The paradox arises because the chemical potential of water in saturated humid air and liquid water is identical, and thus, the water content of equilibrated materials in the two cases should be identical.^{6,7} In related studies, researchers found that the length scale of periodic structures obtained when lipid bilayers are exposed to either saturated water vapor or liquid

water is not identical. This phenomenon is called the Vapor Pressure Paradox.⁸ Regardless of name, the physics that underlies the paradoxes is the same.

There are two logical explanations for the paradox: (1) The materials are not at equilibrium under one of the conditions. In some systems it has been found that equilibration times when samples are contacted with water vapor are much larger than those obtained when the samples are contacted with liquid water.^{4,9} Since the concentration of water molecules at the surface of the sample is larger when it is contacted with liquid water, one expects shorter equilibration times in this case. However, the observation of Schroeder's Paradox may arise because samples in contact with both vapor and liquid water are out of equilibrium. (2) The morphology of the interface between the sample and its surroundings maybe different in the two cases; the presence of air may increase the interfacial concentration of hydrophobic moieties. This effect can only be important in relatively thin samples wherein the free energy of the sample is significantly affected by interfacial effects.

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Many recent studies of Schroeder's Paradox involve nano-structured PEMs, which are of interest for applications such as fuel cells,¹⁰ solar energy conversion devices,^{1,11} and water filtration.¹² PEMs are typically ionomers, which are polymers with a fraction of charged monomers. In the case of a fuel cell, which is an open system, water content is controlled through the use of a humid air feed stream that enters the cell at the cathode. Depending on the application and operating conditions, PEMs in fuel cells are exposed to a variety of environments: air with varying relative humidity due to changes in the properties of air that surrounds the fuel cell or liquid water if the fuel cell is flooded. It is obvious that, in addition to fundamental interest, resolving the Schroeder's Paradox for PEMs is a matter of considerable practical importance.

Investigations into Schroeder's Paradox in PEMs have focused primarily on a commercial polymer membrane, Nafion, as summarized in by Onishi et al.⁴ Investigations into Nafion are difficult because of the long "equilibration" times. Onishi et al. found that timescales on the order of months were necessary to equilibrate Nafion after step changes in temperature.⁴ Semicrystalline polymers such as tetrafluorethylene, the hydrophobic backbone of Nafion, comprise coexisting crystalline and amorphous domains that are, by definition, out of equilibrium. Long equilibration times in Nafion may be due to rearrangement of the crystalline and amorphous domains. The hydrophilic perfluoroether side chains with terminal sulfonic acid groups in Nafion are arranged randomly along the hydrophobic backbone. This randomness is also expected to result in long equilibration times.¹³ In addition to long equilibration times, the random copolymer structure leads to ill-defined morphologies that are still not fully characterized.¹⁴ Researchers have attributed the existence of Schroeder's Paradox in Nafion to both morphological and thermodynamic factors.^{2,3,5,9} Schroeder's Paradox has also been observed in other ionomers such as cross-linked sulfonated polystyrene.²

This paper is part of a series on model PEMs based on diblock copolymers of sulfonated polystyrene and polyolefins.^{15–19} This study is based on a sulfonated polystyrene-block-polyethylene (PSS-PE) with a PSS volume fraction 0.17. This particular polymer equilibrates relatively rapidly in response to changes in the water vapor content of the surrounding air and is stable in liquid water. We present data on the morphology, water uptake, and proton conductivity of this material equilibrated in both humid air and liquid water.

The relative humidity of the air in our experiments is limited to 99% and below. We did not attempt experiments at 100% relative humidity because of the potential for condensing water on our samples due to minor uncontrolled temperature fluctuations. It was noted by Katsaras²⁰ that the Vapor Pressure Paradox in lipid bilayers was due to uncontrolled fluctuations in relative humidity. The extent to which such problems affect measurements related to Schroeder's Paradox in PEMs is not clear. Our decision to limit relative humidity to 99% was made to avoid these problems. A limitation of this approach is that the vapor phase data must be extrapolated to 100% relative humidity before comparisons with water-equilibrated samples can be made.

MATERIALS AND METHODS

Sample Synthesis and Characterization. A poly(styrene-*block*-ethylene) (PS-PE) copolymer was synthesized by sequential anionic polymerization of styrene and butadiene, followed by selective hydrogenation of the polydiene as

described previously.²¹ Anionic polymerization was performed in benzene resulting in 78% of 1,4 additions of the butadiene monomers. Hydrogenation was followed by sulfonation of the PS block, as described by Park et al.,¹⁷ to yield a sulfonated polystyrene-*block*-polyethylene (PSS-PE) *block* copolymer, the structure of which is shown in Figure 1. PSS-PE was not soluble

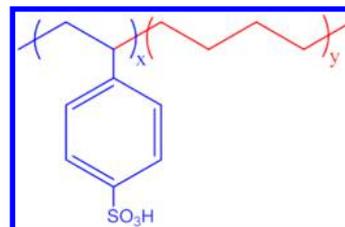


Figure 1. Chemical structure of sulfonated polystyrene-*block*-polyethylene (PSS-PE).

in dichloroethane at the reaction conditions used by Park et al.,¹⁷ so the PS-PE precursor was mechanically agitated under solvent reflux conditions at the boiling point of dichloroethane to produce a uniform dispersion of PS-PE micelles which was then sulfonated under the same conditions described by Park et al.¹⁷ While the extent of sulfonation was controlled, the locations of the sulfonic acid groups were not. The sulfonic acid groups are thus expected to be randomly distributed within the PSS block. The fraction of sulfonated styrene units, *SL*, as defined in eq 1, was determined using an ion-exchange capacity measurement (IEC) which is quantified in eq 2 as the moles of sulfonic acid groups per gram of polymer (millimole/gram).

$$SL = \frac{\text{mol SSA}}{\text{mol S} + \text{mol SSA}} \quad (1)$$

$$\begin{aligned} IEC &= \frac{\text{concentration of } H^+ \text{ in solution}}{\text{mass of dry polymer}} \\ &= \frac{1000 \times \text{mol SSA}}{MW_{\text{SSA}} \times \text{mol SSA} + MW_{\text{S}} \times \text{mol S} + MW_{\text{E}} \times \text{mol E}} \end{aligned} \quad (2)$$

where SSA is styrene sulfonic acid, S is styrene, E is ethylene, and MW is molecular weight of the SSA, S, and E monomers in gram/mol. The procedure for IEC measurement was taken from Zou et al.²² Dried polymer of known mass was placed into a 0.1 M NaCl solution for 48 h to allow for the exchange of acidic protons on the PSS with sodium ions in solution. The concentration of protons was then determined by measuring the pH of the solution with a pH meter (Orion, Thermo Scientific). The IEC (millimolar equivalent/gram) was then determined using eq 3:

$$IEC = \frac{10^{-\text{pH}} \times V_{\text{NaCl}}}{m_0} \times 1000 \quad (3)$$

where V_{NaCl} (L) is the volume of NaCl solution used and m_0 (killigram) is the dry weight of the film. *SL* and IEC measurements were made at 25 °C. The PE block is semicrystalline at this temperature.

Important properties of the polymer used in this study are summarized in Table 1. The volume fraction of the PSS phase reported in Table 1 was obtained using pure component densities (of polystyrene (PS), polyethylene (PE), and sulfonated polystyrene (PSS) melts at 140 °C, assuming no

Table 1. Properties of the Sulfonated Polystyrene-*block*-polyethylene (PSS-PE) Sample Studied

sample name	PS precursor molecular weight (kg/mol)	PE molecular weight (kg/mol)	PSS volume fraction (%)	IEC (mmequiv/g)	sulfonation level (calculated) (%)
PSS-PE	15.0	67.6	17.0	0.932	78.7

volume change on mixing: 0.97 (PS),²¹ 0.78 (PE),²³ and 1.44 (PSS) g/cm³.¹⁶

In Situ Small-Angle X-ray Scattering. Samples for synchrotron small-angle X-ray scattering (SAXS) measurement were prepared by hot pressing at a temperature, $T = 120$ °C, to a thickness of 10 μm . SAXS was performed at beamline 7.3.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.²³ Humidity-controlled SAXS was performed using a custom designed humidity stage as reported previously.²⁴ Samples were equilibrated for 2 h at each relative humidity of interest before measurements were made. The original two-dimensional scattering images were azimuthally averaged to generate one-dimensional scattering intensity profiles, $I(q)$, where the magnitude of the scattering wave vector $q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of the incident beam.

Transmission Electron Microscopy. Transmission electron micrographs (TEMs) of dry and water-equilibrated sample were obtained from cryomicrotomed samples. In the water equilibrated case, samples were plunged rapidly into the liquid ethane and stored under liquid nitrogen. Sections of the polymer were cut on a cryomicrotome (LiecaEMFC6) at $T = -120$ °C. The thickness of the sections was set to 75 nm. Sections were sandwiched between two sides of oyster TEM grids with a lacy carbon support film. Sections were stored under liquid nitrogen and transferred into the microscope using a cryo-transfer stage (Gatan). Dry samples were dried under vacuum and then prepared in the same manner as the hydrated samples. No metal stain was used for the dry and hydrated samples. Electron micrographs were obtained on a Phillips CM 200 FEG transmission electron microscope using 200 keV acceleration voltage at $T = -170$ °C.

Water Uptake. Polymer films with thicknesses of about 200 μm were prepared by hot pressing at $T = 120$ °C. The films were dried in a vacuum oven at room temperature until the weight of the film was constant. The dry sample weights were measured immediately after they were removed from the vacuum oven. The dry film was placed in a quartz pan that was hooked on the end of a quartz spring (Deerslayer) in a humidity-controlled oven (SH-241, Espec. Corp). The spring and pan was held in a glass tube with an open end to avoid rotation and breakage due to the air flow. The spring extension was measured through an open window in the oven by a cathetometer equipped with an optical zoom telescope located outside the oven. Care was taken to minimize the time when the window was opened (typically 15 s). The spring was calibrated with standard masses at experimental temperatures and relative humidity in the chamber before use (spring constant was about 0.0049 N/m). Water uptake, WU , is defined as the ratio of the weights of the sample after water uptake to that of the dry film weight, as shown in eq 4.

$$WU = \frac{\text{hydrated film weight} - \text{dry film weight}}{\text{dry film weight}} \times 100\% \quad (4)$$

Conductivity. Free-standing films of PSS-PE with dimension 2 cm \times 1 cm \times 200 μm were prepared for conductivity measurements by hot pressing at $T = 120$ °C and then cutting to the appropriate shape using a razor blade. The thickness of sample films was measured using a micrometer. In-plane proton conductivity of hydrated membranes was measured by ac impedance spectroscopy using platinum electrodes in the standard four-probe configuration using a BekkTech sample clamp. Data were collected over a frequency range from 100 Hz to 100 kHz in a humidity- and temperature-controlled oven (SH-241, Espec. Corp). Conductivity, σ , is given by

$$\sigma = \frac{l}{A \times R} \quad (5)$$

where A is the cross-sectional area of sample film, R is the touchdown of the Nyquist semicircle on the real axis, and l is the distance between the inner platinum electrodes.

RESULTS AND DISCUSSION

Since equilibration is an important issue, we begin by describing the time dependence of water uptake, WU , after a dry PSS-PE membrane is placed in liquid water (Figure 2). We

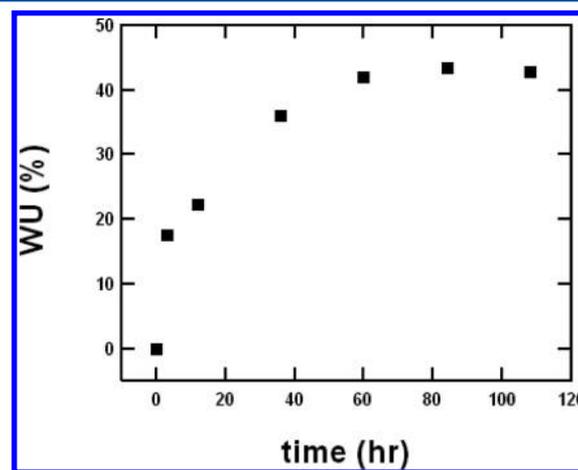


Figure 2. Water uptake, WU , of a PSS-PE sample in liquid water (■) at $T = 25$ °C as a function of time. The estimated uncertainty in the equilibrated value of WU , based on repetitions on different samples, is about 1%.

find that WU increases monotonically over a time scale of 40–60 h, approaching the equilibrium WU value of $44 \pm 1\%$. While the observation of a time-independent value of WU is a necessary condition for equilibrium, it is not sufficient. It is impossible to prove that a sample is at equilibrium from a finite set of experiments because, in principle, one must explore all of the available initial states. Figure 3 presents the transient response in σ as a function of time when a particular dry PSS-PE sample was immersed in liquid water. Upon hydration, there is a rapid increase in σ during the first 3 h, followed by a gradual decrease, eventually reaching a plateau value of $\sigma = 0.014$ S/cm. Repeated measurements of equilibrated conductivity of samples in a given hydrated state led to a standard deviation of about 0.001 S/cm. We do not address systematic errors in this study; since we use the same instrument to compare samples

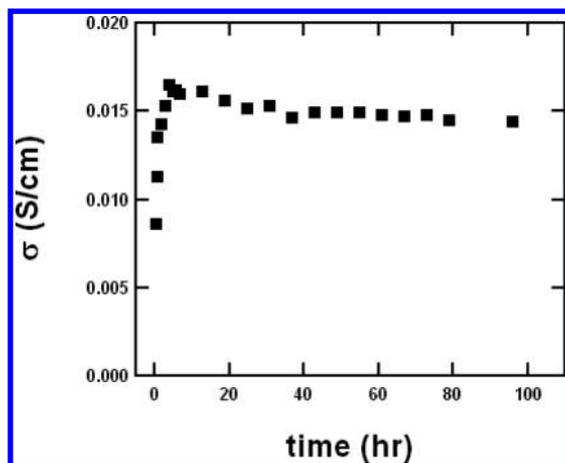


Figure 3. Proton conductivity, σ , of a PSS-PE sample in liquid water (■), at $T = 25$ °C as a function of time. The estimated uncertainty in the equilibrated value of WU , based on repetitions on different samples, is about 0.001 S/cm.

equilibrated in vapor and liquid environments, these errors do not affect our conclusion. One might expect the time dependence of σ to be similar to that of WU as increasing water concentration generally leads to an increasing conductivity in PEMs. Figures 2 and 3 show that this is not the case. The time-dependence of WU and σ are very different, demonstrating that conductivity is governed by factors other than the average water concentration in the membrane. In the discussion below, we show values of WU and σ obtained after steady values were obtained. The times required to obtain these values varied from 24 to 60 h (lower annealing times were adequate for small step changes in RH). Only 2 h of annealing time was used for the SAXS experiments due to limited access to the SAXS beamline; however, this decrease in annealing time is believed to be offset by the approximately factor of 20 decrease in sample thickness.

Figure 4 shows SAXS profiles for the PSS-PE sample in the dry state and in liquid water. A single broad peak with a maximum at $q = q^*$, is evident in both profiles. While this peak does not enable evaluation of the geometry of the microphase

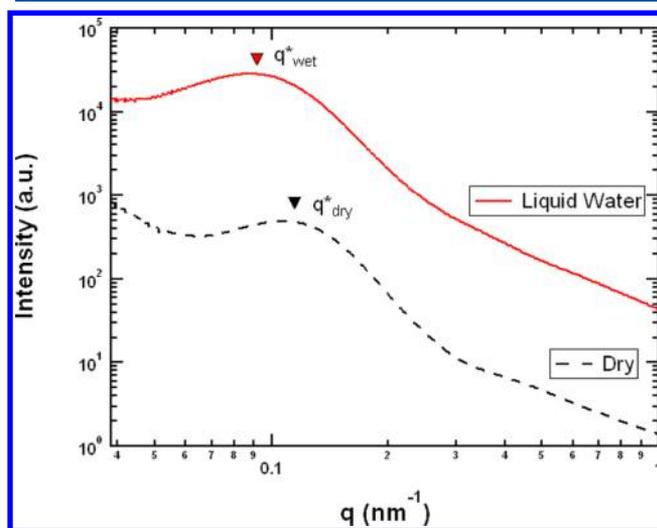


Figure 4. SAXS profiles of a PSS-PE sample in the dry state and after equilibration in liquid water at $T = 25$ °C.

separated PSS-PE sample, we can assert that the sample has a periodic structure with a characteristic domain size, $d = 2\pi/q^*$. Figure 5a shows a TEM image for a dry PSS-PE sample. The

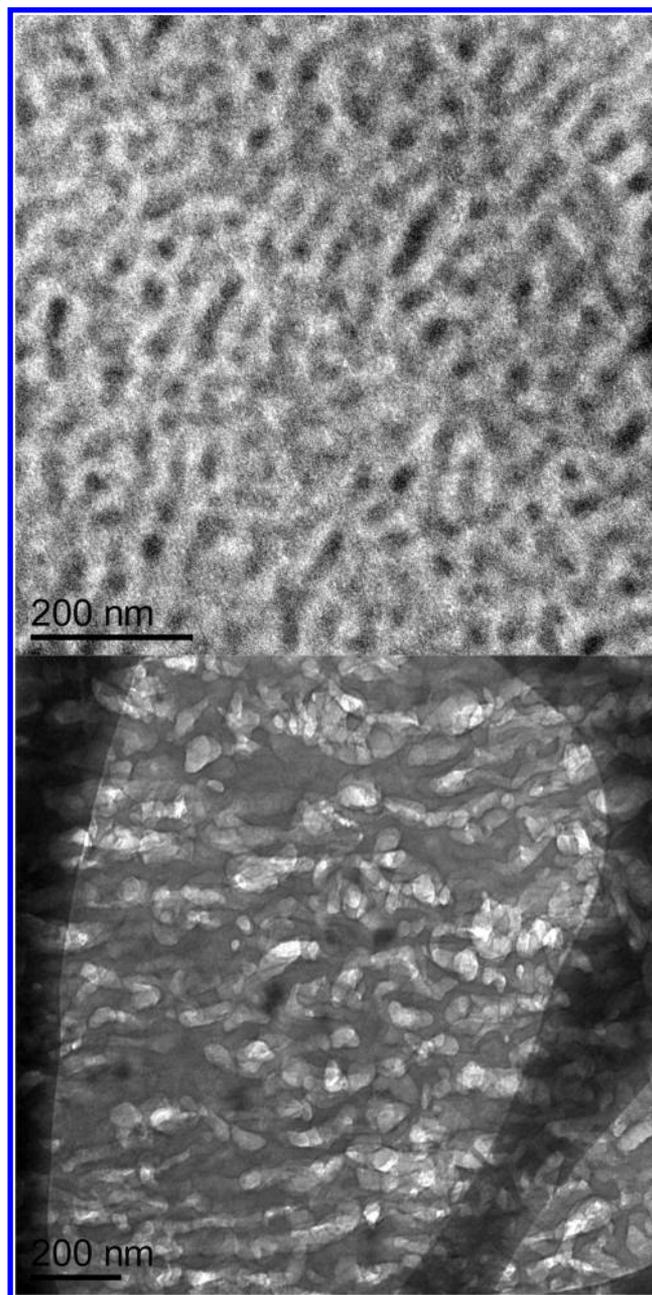


Figure 5. Transmission electron microscopy (TEM) images for (a) dry PSS-PE membrane and (b) hydrated PSS-PE quenched after equilibration in liquid water at $T = 25$ °C. In the dry sample, the PSS phase is dark. In the hydrated sample, the water-swollen PSS phase appears bright. Both samples (unstained) appear to have a disordered cylindrical morphology, although the cylinders in the hydrated membrane appear to be more extended.

minor PSS phase appears dark due to its higher density and the presence of higher atomic number atoms such as oxygen and sulfur. A lack of long-range order is observed and is consistent with a lack of higher order peaks in SAXS. The dark PSS phase appears wormlike and highly disordered. It is not clear if the spherical PSS domains seen in Figure 5a are spheres or slices through wormlike structures oriented perpendicular to the

plane of the section. Figure 5b shows a TEM image of a PSS-PE sample equilibrated in liquid water. The presence of a large amount of amorphous water in the PSS phase causes a change in contrast for the system, with the water-rich PSS phase appearing bright, while the PE matrix now appears dark. Hydration causes a dramatic change in the observed morphology with the hydrophilic phase assuming an extended geometry that is much more cylinderlike. These cylinders, however, do not appear to be located on a hexagonal lattice, as is seen in neat block copolymers. Most of the hydrated cylinders appear to be horizontal. This orientation may be due to sample preparation (melt-pressing the sample may have resulted in preferential orientation).

In Figure 6, we show values of d obtained in humid air at RH values of 90, 95, and 96%, in addition to that obtained in liquid

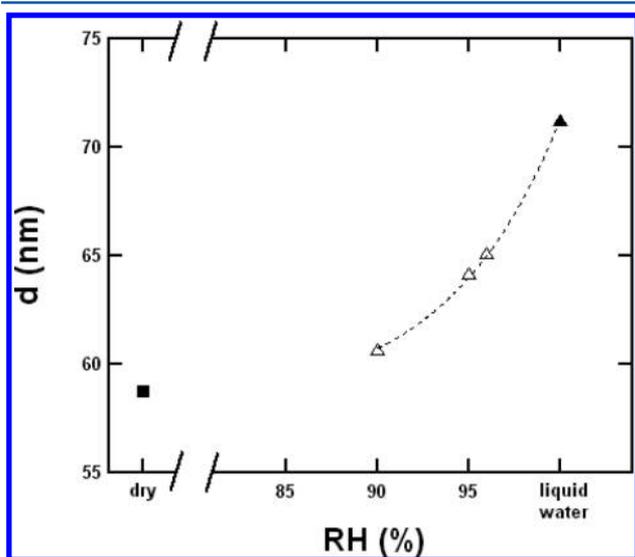


Figure 6. Domain size, d , of a PSS-PE sample hydrated in humid vapor (Δ) plotted as a function of relative humidity, RH, at $T = 25$ °C. The domain size in the dry (\blacksquare) and liquid-water-equilibrated states (\blacktriangle) are also presented. This data is from a single experiment, experimental error of d , based on repeated measurements on similar samples, is expected to be less than 1 nm.

water using SAXS. (For reference we also show the value of d obtained in the dry state.) The dashed curve in Figure 6 is power-law fit through the humid air data and liquid water data [$d = k(\text{RH})^m + n$ where $k = 3.80 \times 10^{-32}$ nm, $m = 16.3$, $n = 58.4$ nm]. At this juncture, we do not ascribe any physical significance to the power law fit parameters: they provide a simple and consistent approach for analyzing data obtained from vapor- and liquid-equilibrated samples. The large magnitude of the exponent m is indicative of the fact that d is a sensitive function of RH in the high humidity limit. The fact that data obtained in humid air and liquid water lie on the same relatively simple curve (within experimental error) is consistent with the notion that the Vapor Pressure Paradox is not observed in our PSS-PE sample.

In Figure 7, we show water uptake values, WU , obtained in humid air and liquid water. The dashed curve in Figure 7 represents a power-law fit through all of the data [$WU = k(\text{RH})^m + n$, where $k = 5.46 \times 10^{-63}$, $m = 32.1$, and $n = 14.0$]. The fact that data obtained in humid air and liquid water lie on the same curve (within experimental error) is consistent with

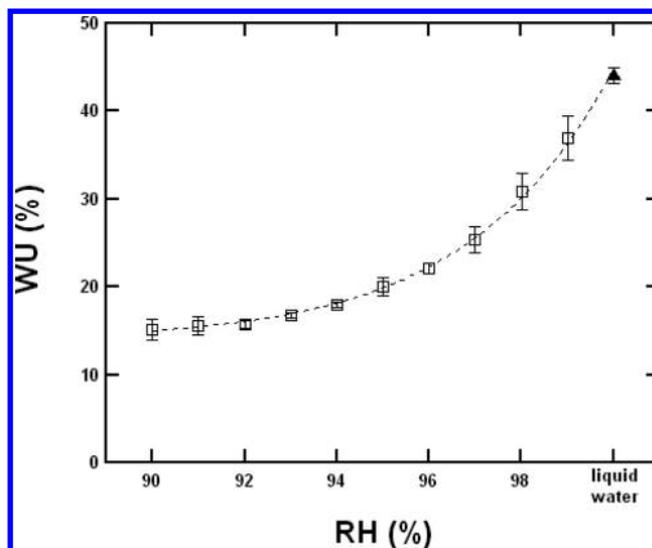


Figure 7. Water uptake, WU , of PSS-PE in humid vapor (\square) and in liquid water (\blacktriangle) plotted as a function of relative humidity, RH, at $T = 25$ °C. The dashed curve represents a power-law fit through the humid vapor data.

the notion that Schroeder's Paradox is not observed in water uptake data of our PSS-PE sample.

In Figure 8, we show proton conductivity values obtained in humid air and liquid water. This experiment comprised three

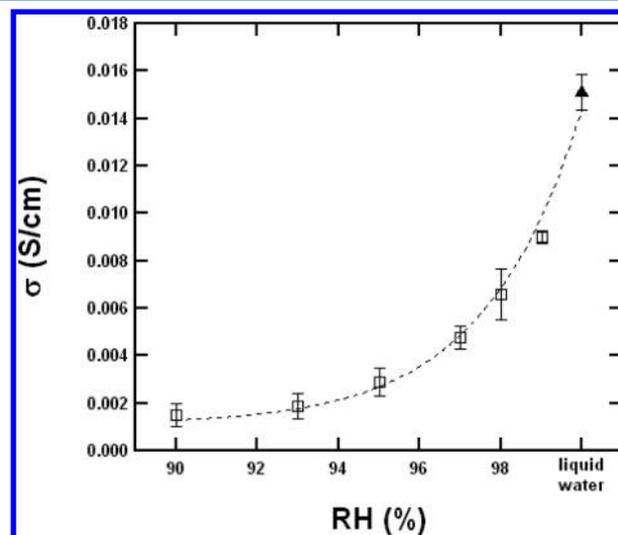


Figure 8. Proton conductivity, σ , of PSS-PE in humid vapor (\square) and liquid water (\blacktriangle) plotted as a function of relative humidity, RH, at $T = 25$ °C. Humid vapor data were obtained after equilibration in liquid water. The dashed curve represents a power-law fit through the humid vapor data.

separate runs. In run 1, dry samples were first exposed to humid air with RH increasing from 90 to 99% and then immersed in liquid water. Following this, in run 2, the liquid equilibrated sample was taken back into the humidity chamber and exposed to humid air with RH decreasing from 99 to 90%. In run 3, a liquid equilibrated sample was placed in the humidity chamber at RH = 90% and studied as a function of increasing RH. Data obtained from runs 2 and 3 were within experimental error and thus take them to be equilibrated values of σ . Conductivity values obtained from run 1 were higher than the equilibrated

values by factors between two and three. This is consistent with our previous studies on model PSS containing block copolymer PEMs,¹⁹ and we propose that this is due to nonequilibrium effects. For consistency, we use data obtained from run 2 in our analysis. The dashed curve in Figure 8 represents a power-law fit through all of the data [$\sigma = k(\text{RH})^m + n$, where $k = 5.46 \times 10^{-86}$ S/cm, $m = 41.7$, and $n = 0.00113$ S/cm]. In this case, the fitted value of σ at RH = 100%, 0.0144 S/cm, is below the experimentally determined value in equilibrated water of 0.0151 S/cm. We assert that the 5% difference in the values of σ obtained in saturated vapor and liquid is not paradoxical in any way. We offer three potential reasons for the observed difference: (1) the tortuosity of the hydrated nanoscale channels obtained in liquid water is slightly lower than that of the channels obtained in humid air. (2) The simple power law function used to describe the relationship between σ at RH is inadequate. (3) The true uncertainty of our measurements is slightly larger than our estimate. In homogeneous systems, transport parameters such as the diffusion coefficient or ionic conductivity, measured in systems that are not significantly perturbed from equilibrium, must be governed entirely by the thermodynamic constraints imposed on the system (e.g., temperature, pressure, and water activity). In disordered heterogeneous systems such as hydrated PEMs, factors such as tortuosity of the conducting channels are not governed only by thermodynamic parameters. Unless efforts are made to control these factors independently (e.g., by creating perfect "single crystals"), differences in transport coefficients, particularly small differences, are not paradoxical.

CONCLUSIONS

We have studied morphology, water uptake, and proton conductivity of a nanostructured PSS-PE electrolyte membrane under controlled relative humidity (RH) and in liquid water to investigate Schroeder's Paradox. PSS-PE membranes can be equilibrated in timescales as low as 10–60 h making them ideal candidates for studying effects such as the Schroeder's Paradox. A unique feature of this study is that the morphology of the PEM in both dry and hydrated conditions can be readily characterized by both X-ray scattering and cryogenic electron microscopy. It was shown that approaches to equilibrium of seemingly related quantities such as proton conductivity and water uptake can be very different, the underlying physics of which is not currently understood. Thus, despite the fact that equilibration should occur on a single, well-defined timescale, measurement of equilibrated values of different properties may require different experimental protocols.

It was determined that the Vapor Pressure Paradox is absent in this system. With the use of SAXS, it was shown that the characteristic size and arrangement of the hydrophilic domains obtained in humid air and liquid water are consistent with each other. It was determined that Schroeder's Paradox is absent in this system. Water uptake measurements in humid air and liquid water are consistent with each other. We argue that the small differences in proton conductivity measured in humid air and liquid water are not paradoxical. Our approach avoids experimental difficulties related to creating a humid air environment with RH = 100% and ensuring the absence of condensation in the sample environment during the duration of the experiment. Assuming the absence of experimental artifacts, it is likely that previous reports of such paradoxes related to morphology, water uptake, and conductivity are due to the fact

that at least one of the samples "equilibrated" in different environments were out of equilibrium.

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Notes

The authors declare no competing financial interest.

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