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Characterization of Self-Assembly and Charge Transport in Model Polymer Electrolyte Membranes

By

Keith Morgan Beers

A dissertation submitted in partial satisfaction of the

requirements for the degree in

Doctor of Philosophy

in

Chemical Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in Charge:

Professor Nitash P. Balsara, Chair Professor Rachel A. Segalman Professor Andrew M. Minor

Fall 2012

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Abstract

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University of California, Berkeley

Professor Nitash P. Baslara, Chair

There is broad interest in creating polymer electrolyte membranes (PEMs) that have a charged hydrophilic nanophase, where the size and geometry of the phase can be precisely controlled. The applications for such materials range from portable power generating devices to water purification. There is a need to better characterize the selfassembly, thermodynamics, and performance of both current and future PEMs. To this end a series of chapters is presented, that explore the development of techniques, equipment, methods, and materials to enable further progress in the field.

The interaction of PEMs with external ionic solutions can be used to determine fundamental thermodynamic properties of the ions that reside within the membrane itself. Traditional techniques used to probe ions in PEMs, such as conductivity, can be greatly enhanced by knowing the number of dissociated ions and their activity coefficients. A technique is presented that provides one of the first methods able to quantify such properties in PEMs.

The ionic species in PEMs are believed to reside in nanoscale ionic aggregates. Only recently have researchers begun to focus on the properties of this aggregation in regards to PEM performance. A summary of this phenomenon, as well as speculation on its effect on transport and thermodynamic properties is presented. In addition, evidence that suggests block copolymers offer a method of inhibiting aggregate formation is discussed.

Characterization of PEM morphology is critical to properly understand structurefunction relationships. Due to a lack of proper equipment, the morphological characterization of PEMs has been mostly limited to the dry state. The design and operation of a novel sample stage, used to simultaneously measure morphology and conductivity in humid air as a function of temperature and relative humidity is presented. Precise control over humidity and accurate determination of morphology and conductivity over a wide range of temperatures is shown.

At present there is an incomplete understanding of the thermodynamic interaction between PEMs and water of varying activity. The morphology, water uptake, and proton conductivity of sulfonated polystyrene-*block*-polyethylene (PSS-PE) was studied under controlled relative humidity (RH) and in liquid water. Extrapolation of the domain size, water uptake, and conductivity in humid vapor to RH = 100% allowed for an accurate comparison between the properties of PSS-PE hydrated in saturated vapor and in liquid water. Absent from this system was Schroeder's Paradox, which expects the properties in saturated water vapor to be less than those obtained in liquid water.

Polymers that are semi-crystalline are ubiquitous as commercial polymers because of their mechanical properties. Little is known about the effects of polymer crystallization on PEM structure and performance. The model system, PSS-PE, was synthesized at a variety of molecular weights to probe how crystallization affects performance for a variety of conducting domain sizes. Results are shown that indicate crystallization disrupts the self-assembly of low molecular weight PEMs, resulting in poor water uptake and proton conductivity in small domains. Increasing domain size results in less morphological disruption, leading to an improvement in performance at larger domain sizes.

This work improves upon the ability of researchers to characterize and understand the relationship between the structure and performance of PEMs. The findings presented herein provide further understanding toward the goal of rational design of nanostructured membranes that show improved conductivity in a variety of conditions.

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Chapter 1. Introduction and Outline

This thesis is focused on polymer electrolyte membranes (PEMs) for use in Polymer Electrolyte Fuel Cells (PEFCs). A simplified schematic of a typical PEFC with a PEM is shown in Figure 1.1.



Figure 1.1. Schematic of a Polymer Electrolyte Fuel Cell (PEFC).

In typical PEFC operation, hydrogen gas is fed the anode and reacts to form protons and electrons. The electrons are transported outside of the device to perform work, while the protons travel across the PEM to the cathode. Oxygen enters the cathode and reacts with the electrons and protons to form water. It is because of this, that water is the only by-product, that PEFCs have received so much attention. There are three roles required of PEMs in a PEFC as outlined below.

- (1) Conduct ions (this thesis is focused on protons)
- (2) Absorb water (this facilitates proton transport)
- (3) Remain mechanically stable (Act as a physical barrier between electrodes)

The most important property on this list is (1), without the ability to conduct ions a PEFC cannot generate electricity. Property (2) is related to the fact that PEMs are typically made of ionomers, which are polymers with a fraction of monomers containing bound charges (with protons acting as mobile counterions). To achieve adequate conductivity, ionomers are typically hydrated with water. Finally, the absorption of water can mechanically destabilize PEMs, leading to them falling apart. So while water is essential for PEMs to conduct ions (1), it can simultaneous lead to mechanical problems as well (3).

There is complex interconnection of the essential PEM properties listed above, and there is no current solution to address them all. This thesis is focused on developing new tools to understand current PEMs, and applying them to novel model polymers. The goal of this is to further understand structure-function relationships in PEMs, and allow for rational design of future materials.

An example of a commercial and well-studied ionomer is Nafion, shown in Figure 1.2. Nafion is a random copolymer of hydrophobic tetrafluoroethylene and

hydrophilic perfluoroether side chains that have terminal sulfonic acid groups. At room temperature Nafion conducts protons well and has good mechanical properties. The reasons for this are unclear. To further develop the understanding of the thermodynamics of Nafion, experiments detailing the interaction of Nafion with external HCl solutions were performed. The results of these experiments are discussed in Chapter 2. These experiments are believed to be the first to quantify a phenomenon known as counterion condensation in PEMs. Quantifying counterion condensation is important because it allows one to understand the activity of the ions in PEMs, which is necessary to fully understand proton conductivity.



Figure 1.2. Chemical structure of Nafion.

Another problem with both Nafion and other PEMs is a lack of knowledge of how the ions bound to the polymer chain (sulfonic acid groups for Nafion) self-assemble. Dipole-dipole interactions between the ion pairs along the polymer chain, causes reversible clustering of ion-rich moieties within a non-polar polymer matrix. A summary of this phenomenon and a discussion of its implications on conductivity are discussed in chapter 3.

As discussed above, PEMs require hydration to achieve adequate proton conductivity. To properly understand structure-function relationships in PEMs, it is therefore necessary to be able to characterize the hydrated morphology. Despite this fact, PEMs are typically characterized in the dry state due to a lack of humidity control equipment for experiments like small angle X-ray scattering (SAXS). Chapter 4 details the design and successful operation of an *in situ* humidity control chamber for X-ray scattering.

There has been a long-standing paradox that PEMs absorb less water in saturated water vapor than in liquid water. A likely explanation for this is that experimental limitations have led to inaccurate conclusions. PEMs, such as Nafion, can take as long as 2 months to reach equilibrium. Another type of PEM, one made of a block copolymer, where two polymer chains are covalently bonded to each other, has been shown to equilibrate on the order of hours to days. Through the design and synthesis of a novel block copolymer PEM, along with the development of an alternate experimental method, the paradox is investigated in Chapter 5. No paradox is observed in this model block copolymer system.

Future success of PEFCs will likely require operation above ambient temperatures. Unfortunately, Nafion and many other PEMs lose water at elevated temperatures, leading to decreased proton conductivity. Block copolymers have been shown to remain hydrated at elevated temperatures. Unfortunately this is achieved through the use of very low molecular weight polymers, which are mechanically unstable. As mentioned above, it is important that membranes be mechanically stable. To investigate how to improve the mechanical stability of low molecular weight PEMs, a semi-crystalline block copolymer system was and studied. The effect of crystallization on block copolymer self-assembly is discussed in Chapter 6. It is shown that crystallization disrupts the properties of small channel block copolymers. Alternate approaches to achieving small channel properties in mechanically stable PEMs are discussed.

Chapter 2. Counterion Condensation in Nafion

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Nafion(117) membranes in contact with acidic solutions were characterized by small angle X-ray scattering (SAXS) and by acid solution uptake measurements. The principle of Donnan equilibrium was used to obtain independent estimates of the extent of counterion condensation in the membranes from the three experiments. The surprising conclusion of our study is that a large fraction of the protons in Nafion are in the condensed form when the membrane is immersed in pure water. Estimates of the fraction of condensed protons range from 72 to 98%.

2.1. Introduction

Polymers that conduct protons are currently a subject of considerable interest due to their relevance in a variety of traditional applications such as chlor-alkali cells,^{1,2} and the development of clean energy devices such as hydrogen fuel cells^{3,4} and photoelectrochemical cells.⁵⁻⁷ The most widely studied proton conducting membrane is Nafion, a copolymer with hydrophilic perfluorosulfonic acid moieties located randomly along a hydrophobic backbone.^{1,2} The ion exchange, electrochemical, and morphological properties of Nafion have been extensively studied.^{4,8-18} The ratio moles of sulfonic acid sites per gram of polymer is commonly reported as the ion exchange capacity (IEC). It is generally assumed, either explicitly or implicitly, that proton transport is enabled by the dissociation of all of the acidic protons in the membrane, based on the value of the IEC.¹⁹⁻ To our knowledge, there are two prior studies that have addressed the possibility of

counterion condensation in Nafion: (1) Sondheimer et al.²³ who studied the catalytic activity of Nafion, and (2) Rollet et al.²⁴ who used small angle neutron scattering to determine the locations of the dissociated counterions. No quantitative estimate of the extent of counterion condensation was provided in these papers.

The polymer chains in a Nafion membrane exhibit complex conformations due to their self-assembly into hydrophilic and hydrophobic domains.^{4,13-16,20} A much simpler situation arises when a linear polyelectrolyte chain such as polystyrenesulfonate (PSS) with randomly located sulfonic acid groups is dissolved in excess water. Incomplete dissociation of these chains, even in the limit of infinite dilution, is obtained, due to a phenomenon called counterion condensation.²⁵ The free energy of a completely dissociated chain is higher than that of a partially dissociated chain due to the coulombic repulsion of closely spaced negative charges that are confined to the polymer backbone.^{25,26} The extent of counterion condensation in hydrated dense PSS brushes is higher than that in individual chains due to intra- and inter-chain coulombic repulsion of negative charges confined to the brush.^{27,28} The purpose of this paper is to use a

technique derived from the work of Balastre et al. on counterion condensation in polyelectrolyte brushes²⁸ to evaluate the extent of counterion condensation in Nafion. Our efforts to determine the extent of counterion condensation in Nafion is motivated by the possibility that the mobility of condensed counterions is lower than that of that of dissociated counterions. This in turn could have serious implications on membrane performance.

The present study is based on a hypothesis that combines the Donnan equilibrium principle with the self-assembly of copolymers shown schematically in Figure 2.1, where we show a polymer electrolyte membrane in contact with an aqueous ionic solution. The polymer is microphase separated into hydrophilic and hydrophobic domains. The hydrophilic domains are hydrated due to diffusion of water into the membrane. We assume that a fraction of the positive counterions in the membrane are condensed while the remaining counterions are dissociated, as shown in Figure 2.1. When the chemical potential of the ions in solution is lower than that of the dissociated ions in the membrane, there is no driving force for ions from the solution to enter the membrane as indicated in Figure 2.1a. As the concentration of ions in the solution is increased, the chemical potential of the ions outside will exceed that of the dissociated ions within the membrane and the solution will enter the membrane as indicated in Figure 2.1b. We use the symbol $c_{\rm D}$ to denote the solution concentration at which the ions begin to cross-over and enter the membrane (Donnan concentration). The presence of additional ions in the membrane will result in increased screening of the charges inside the membrane when the solution concentration exceeds $c_{\rm D}$. The size of polymer chains in free solution decreases as screening increases.²⁹ One thus expects a shrinking of the hydrophilic channels when the solution concentration, $c_{\rm o}$ is greater than $c_{\rm D}$, as shown in in Figure 2.1b. It is logical to expect a decrease in the acid solution uptake of the membrane when c becomes greater than $c_{\rm D}$. Measurements of the domain size and acid solution uptake as a function of c can thus be used to estimate $c_{\rm D}$.

The depiction of ion dissociation in Figure 2.1 is clearly an over-simplification. Our coarse-grained approach is based on two states (Figure 2.1): a condensed state wherein the counterion is close to the fixed charge (i.e. the distance between the positive and negative ions is much less than the Bjerrum length), and a dissociated state wherein the counterion is far away from the fixed charge (i.e. the distance between the positive and negative ions is much greater than the Bjerrum length). In reality, there will be a distribution of distances between the fixed charges and the counterions. Additional complexities arise due to the different kinds of solvation shells surrounding the dissociated counterions.³⁰ Our approach does not account for these effects.



Figure 2.1. Schematic of a periodically structured polymer electrolyte membrane in contact with an external electrolyte solution. The hydrophilic microphase (colored blue) contains the ionic species while the hydrophobic microphase (colored gray) is free of ions. (a) When the external electrolyte concentration, c, is below the Donnan concentration, c_D , the external ions cannot enter the membrane because their chemical potential is lower than that of the ions in the membrane. (b) When c is greater than c_D , the external because their chemical potential exceeds that of the ions in the membrane, resulting in a decrease in the length scale of the periodic structure and a decrease in the concentration of water in the membrane.

2.2. Experimental Methods

Sample Preparation. Nafion 117 membranes (178 m reported thickness) with a reported IEC of 0.91 mmol/g were purchased from Sigma-Aldrich. Samples were cut and boiled in 10 weight percent nitric acid solution for one hour. The samples were then soaked in de-ionized water, with the external solution frequently replaced until the pH was neutral. The samples were then boiled in 10 weight percent hydrogen peroxide for one hour, washed and soaked in de-ionized water, followed by drying at room temperature under vacuum for 3 days.

Small-Angle X-ray Scattering (SAXS). The Nafion samples described above were placed in solutions of HCl inside SAXS cells with Kapton windows as shown schematically in Figure 2.2 (inset). The cells contained Teflon washers for sealing the contents. The samples were equilibrated in the HCl solutions for a minimum of 24 hours before measurements were made. The equilibration time was determined from the time required for the acid solution uptake of the membranes to reach time-independent values (approximately 1 hour). The presence of the HCl solution in the path of the X-ray beam does not affect the angular dependence of the SAXS profiles. SAXS experiments were conducted at beam line 1-4 at Stanford Synchrotron Radiation Lightsource (SSRL). The resulting two-dimensional scattering data were averaged azimuthally to obtain intensity versus magnitude of the scattering wave vector q ($q = 4\pi \sin(\theta/2)/\lambda$, where λ is the

wavelength of the X-rays and θ is the scattering angle). The scattering data were corrected for the CCD dark current and the scattering from air and Kapton windows.



Figure 2.2. Plots of SAXS intensity, *I*, versus scattering vector, *q*, of Nafion in contact with HCl solutions of varying concentration. Curves are shifted vertically for clarity. Increasing concentrations are shown in ascending order: 0 M (red), 0.01 M (orange), 0.1 M (light green), 0.4 M (light blue), 1 M (blue). The inset illustrates schematic of SAXS cell used to ensure contact between Nafion and the acidic solution.

Acid Solution Uptake Experiments. Dry Nafion 117 samples were removed from vacuum and weighed using a mass balance. Samples were then placed in HCl solution vials of known concentration and sealed to prevent evaporation. Membranes were removed for measurement using Teflon tweezers and placed on a Kimwipe to blot off excess liquid. Samples were then weighed on a mass balance and returned to the solution vials. Acid solution uptake, *SU*, is defined as the ratio of the weights of the sample after acid solution uptake to that of the dry film weight as shown in equation 2.1.

$$SU = \frac{\text{hydrated film weight} - \text{dry film weight}}{\text{dry film weight}}$$
(2.1)

It is important to note that SU is a measure of the uptake of both acid and water molecules.

Acid Release Experiments. The objective of this experiment is to determine the concentration of dissociated negative ions inside the membrane, c_{m-} , when it is equilibrated in an external acid solution with molar concentration, c. It is obvious that $c_{\rm m}$ is related to the moles of free acid molecules in the membrane. Nation membranes were equilibrated in a vial containing HCl solutions as described above, removed from solution, and blotted dry to remove solution on the surface of the films. The membranes were then placed in a second vial consisting of 7-10 mL of de-ionized water, and allowed to equilibrate for 24 hours. The membranes were then removed and the resulting pH of the solution was measured. Samples were placed in a third vial and the pH of this solution was also measured to ensure complete removal of the absorbed electrolyte. The amount of Nafion used in each experiment was chosen such that the measured pH in the second vial was measurably lower than the pH of de-ionized water. Control measurements were also performed using polystyrene films to ensure that residual acid residing on the surface of the films after our blotting protocol did not affect our measurements. The value of c_{m} is determined from the number of moles of acid removed from the Nafion film and SU.

2.3. Results

SAXS intensity, *I*, from Nafion equilibrated with HCl solutions with varying concentrations, *c*, is plotted as a function of the scattering vector, *q*, in Figure 2.2. The SAXS profiles contain a single broad peak at $q=q_{\text{peak}}=1.2 \text{ nm}^{-1}$. This feature, which is consistent with previous SAXS studies on Nafion, indicates the presence of a periodic structure with a length scale $d=2 / q_{\text{peak}}=5.2 \text{ nm}$. In Figure 2.3a we show the dependence of *d* on *c*. It is evident that *d* is nearly independent of *c* when c < 0.01 M. When c>0.03 M d decreases rapidly with increasing *c*. The lines in Figure 2.3a are error-weighted least squares fits through the low and high concentration data sets. The intersection of these lines, which occurs at $c=c_D=0.07 \pm 0.07 \text{ M}$, provides one estimate of the Donnan solution concentration, based on the hypothesis presented in Figure 2.1.

The dependence of acid solution uptake, SU, of the Nafion membranes on c is shown in Figure 2.3b. It is evident that SU is nearly independent of c when c < 0.01 M. When c>0.03 M, SU decreases rapidly with increasing c. The low concentration data in Figure 2.3b are in agreement with a large body of literature on water-equilibrated Nafion.³¹ The lines in Figure 2.3b are error-weighted least squares fits through the low and high concentration data sets. The intersection of these lines, which occurs at $c=c_D=0.06 \pm 0.04$ M, provides a second estimate of the Donnan solution concentration, based on the hypothesis presented in Figure 2.1.

The macroscopic deswelling of the membrane shown in Figure 2.3b and the microscopic deswelling of the hydrophilic domains seen in Figure 2.3a are remarkably similar. Consequently, it is not surprising that the values of c_D determined from the two

experiments are similar. For simplicity, we use the values of c_D based on the acid solution uptake experiments in the discussion that follows.



Figure 2.3. Response of Nafion to changes in external HCl concentration, c, characterized by (a) domain size, d, measured by SAXS, and (b) acid solution uptake, *SU*. Both figures indicate that deswelling occurs at approximately c=0.06 M HCl, which leads to the conclusion that 98 ± 1 % of the protons in Nafion are in the condensed form.

In the dilute limit where ideal mixing is obtained and the activity coefficients can be approximated to be unity, we expect the concentration of dissociated protons inside the hydrophilic channels of the membrane equilibrated with pure water, c_{m0+} , to be equal to the measured values of c_D .³² Based upon the IEC and pure water uptake of Nafion, the estimated concentration of protons (both dissociated and undissociated) inside the hydrophilic channels of the membrane, c_{IEC} , is 3.2 M. This value is obtained by dividing the IEC by the liquid water uptake, followed by a unit conversion to volumetric concentration using the density of water. The fraction of free counterions in the hydrated membrane under the ideal mixing approximation is thus $c_D/c_{IEC}=0.02 \pm 0.01(=0.06 \text{ M/3.2 M})$. In other words, 98 ± 1 % of the protons are condensed in Nafion equilibrated with pure water.

The standard analysis of Donnan equilibrium relates the concentration of dissociated negative ions inside the membrane, c_{m-} , to the external ionic concentration, c, ignoring contributions due to effects such as chain stretching due to acid solution uptake, microphase separation, and non-ideality of the solutions both inside and outside the membrane. At low values of c, c_{m-} is nearly zero, and positive deviations from zero are expected when c exceeds c_D (Figure 2.1). The relationship between and c_{m-} and c depends on the concentration of negative charges (fixed charges) bound to the membrane, c_b .

$$C_{m-} = \frac{-c_b + \sqrt{c_b^2 + 4c^2}}{2}$$
(2.2)

Figure 2.4 compares the experimentally determined c_{m} versus c dependence with theoretical predictions with $c_b=c_D=0.06$ M and $c_b=c_{\text{IEC}}=3.2$ M which constitute the two limits of interest. It is clear that the experimental data are not in agreement with either prediction. We also use an error-weighted least squares fit to determine a fitted value of the bound ion concentration, c_{Fit} . The fitting leads to $c_b=c_{\text{Fit}}=0.9\pm0.3$ M, and this curve is also shown in Figure 2.4. The value of c_{Fit} indicates that 72 ± 9 % of the protons are in the condensed form. We offer no explanation for the difference in counterion condensation estimated using the Donnan theory and that using SAXS and acid solution uptake except to note that many previous studies on acid solution uptake in ion-exchange resins have reported significant discrepancies between the Donnan theory and experiment.^{34,35}



Figure 2.4. Results of acid release experiments. Squares represent the measured concentration of dissociated negative ions inside the membrane, c_{m-} , as a function of the external acid concentration, *c*. Curves represent theoretical predictions based on Donnan equilibrium [equation (2.2)] the assumed concentration of negative charges bound to the membrane, c_{b} , equal to 0.06 M (solid line), 0.9 M (dashed line), and 3.2 M (dashed and dotted line). This leads to the conclusion that 72 ± 9 % of the protons in Nafion are in the condensed form.

Our assumption of ideal mixing is a reasonable approximation for HCl solutions with c<0.06 M.³⁶ It is conceivable, however, that our assumption of ideal mixing within the membrane is not valid. If all of the protons in the membrane were fully dissociated then the activity coefficient of the ions in the membrane would have to be 0.02 in order to satisfy the chemical potential equality constraint at $c=c_D$. In other words, large negative deviations from ideality for the ionic solutions inside the membrane are needed if the extent of counterion condensation in the membrane is significantly lower than our estimate. We are not aware of any theoretical justification for large negative deviations from ideality for confined ionic solutions. It is important to note that the activity

coefficient of a 3.2 M HCl solution is about 1.3,³⁶ i.e. unconfined acidic solutions exhibit positive deviations from ideality. While *ab initio* computer simulations of ionically functionalized carbon nanotubes show that the distance between fixed charges has a significant impact upon the dissociation,³⁷ generalizations to other kinds of confined systems have not yet been made. We hope that our results will motivate further studies of the effect of confinement on the thermodynamics of ionic solutions.

We conclude this section by reviewing some of the previous studies on Nafion that are directly related to the work presented here. Two groups have used acid solutions to examine the static properties of Nafion.^{20,38} However, neither group used the results to determine the fraction of free ions versus ion-pairs. Measurements of the transference number and electro-osmotic drag coefficient of Nafion in contact with acidic solutions presented in refs.³⁹⁻⁴² can, in principle, be used to determine counterion condensation but we are not aware of a framework that enables this determination. Likewise, proton diffusion measurements such as those of Zawodzinski and coworkers⁴³ may also contain signatures of counterion condensation but these have not yet been identified. As mentioned in the introduction, the works of Sondheimer et al.²³ and Rollet et al.²⁴ represent the only previous studies on the subject of counterion condensation in Nafion.

2.4. Conclusion

In summary, we have conducted SAXS and uptake measurements on Nafion membranes in contact with acidic solutions. The principle of Donnan equilibrium was used to interpret the data. Our experiments indicate that a large fraction of the protons within Nafion in contact with pure water are in the condensed form. Estimates of the fraction of condensed protons range from 72 to 98%; the former value is obtained from the acid release experiments while the latter value is obtained from SAXS and acid solution uptake measurements. Our conclusions are similar to those of Balastre et al.²⁸ who also concluded that 20% of the counterions in hydrated polyelectrolyte brushes were dissociated. These conclusions are based on the ideal mixing assumption inside the membrane. Further work on determining the chemical potential of ions in confined media and the relationship between dissociation constants and transport properties in polymer electrolyte membranes seems warranted.

2.5. Acknowledgement

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2.6. References

1. Banerjee, S.; Curtin, D. E. *Journal of Fluorine Chemistry* **2004**, 125, (8), 1211-1216.

2. Grot, W. Chemistry & Industry 1985, (19), 647-649.

3. Kreuer, K. D., Hydrocarbon membranes. In *Handbook of fuel cells – fundamentals, technology and applications*, Vielstich W, L. A., Gasteiger H,, Ed. John Wiley & Sons Ltd.: Chichester, UK, 2003.

4. Mauritz, K. A.; Moore, R. B. Chemical Reviews 2004, 104, (10), 4535-4585.

5. Park, H.; Choi, W. *Langmuir* **2006**, 22, (6), 2906-2911.

6. Mau, A. W. H.; Huang, C. B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, J. M.; Webber, S. E. *Journal of the American Chemical Society* **1984**, 106, (22), 6537-6542.

7. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y. Solar Energy Materials and Solar Cells **2006**, 90, (5), 549-573.

8. Hsu, W. Y.; Gierke, T. D. Journal of Membrane Science 1983, 13, (3), 307-326.

9. Doyle, M.; Lewittes, M. E.; Roelofs, M. G.; Perusich, S. A.; Lowrey, R. E. *Journal of Membrane Science* **2001**, 184, (2), 257-273.

10. Edmondson, C. A.; Stallworth, P. E.; Chapman, M. E.; Fontanella, J. J.; Wintersgill, M. C.; Chung, S. H.; Greenbaum, S. G. *Solid State Ionics* **2000**, 135, (1-4), 419-423.

11. Silva, R. F.; De Francesco, A.; Pozio, A. *Journal of Power Sources* **2004**, 134, (1), 18-26.

12. Zawodzinski, T. A.; Springer, T. E.; Uribe, F.; Gottesfeld, S. *Solid State Ionics* **1993**, 60, (1-3), 199-211.

13. Haubold, H. G.; Vad, T.; Jungbluth, H.; Hiller, P. *Electrochimica Acta* **2001**, 46, (10-11), 1559-1563.

14. Gebel, G.; Lambard, J. *Macromolecules* **1997**, 30, (25), 7914-7920.

15. Gierke, T. D.; Munn, G. E.; Wilson, F. C. *Journal of Polymer Science Part B-Polymer Physics* **1981**, 19, (11), 1687-1704.

16. Schmidt-Rohr, K.; Chen, Q. *Nature Materials* **2008**, 7, (1), 75-83.

17. Kim, M. H.; Glinka, C. J.; Grot, S. A.; Grot, W. G. *Macromolecules* **2006**, 39, (14), 4775-4787.

18. Yeo, S. C.; Eisenberg, A. *Journal of Applied Polymer Science* **1977**, 21, (4), 875-898.

19. Futerko, P.; Hsing, I. M. Journal of the Electrochemical Society **1999**, 146, (6), 2049-2053.

20. Yeo, R. S. Journal of the Electrochemical Society **1983**, 130, (3), 533-538.

21. Pushpa, K. K.; Nandan, D.; Iyer, R. M. *Journal of the Chemical Society-Faraday Transactions I* **1988**, 84, 2047-2056.

22. Kreuer, K. D. Journal of Membrane Science **2001**, 185, (1), 29-39.

23. Sondheimer, S. J.; Bunce, N. J.; Lemke, M. E.; Fyfe, C. A. *Macromolecules* **1986**, 19, (2), 339-343.

24. Rollet, A. L.; Diat, O.; Gebel, G. *Journal of Physical Chemistry B* **2002**, 106, (12), 3033-3036.

25. Manning, G. S. Journal of Chemical Physics 1969, 51, (3), 924-&.

26. Dobrynin, A. V.; Rubinstein, M. Progress in Polymer Science 2005, 30, 1049-1118.

27. Toomey, R.; Tirrell, M. Annual Review of Physical Chemistry 2008, 59, 493-517.

28. Balastre, M.; Li, F.; Schorr, P.; Yang, J. C.; Mays, J. W.; Tirrell, M. V. *Macromolecules* **2002**, 35, (25), 9480-9486.

29. Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *Macromolecules* **1995**, 28, (6), 1859-1871.

30. Lowry, S. R.; Mauritz, K. A. *Journal of the American Chemical Society* **1980**, 102, (14), 4665-4667.

31. Onishi, L. M.; Prausnitz, J. M.; Newman, J. *Journal of Physical Chemistry B* **2007**, 111, (34), 10166-10173.

32. Newman, J.; Thomas-Alyea, K. E., *Electrochemical Systems*. 3rd Edition ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2004.

33. Hills, G. J., Membrane Electrodes. In *Reference Electrodes*, Ives, D. J. G.; Janz, G. J., Eds. Academic Press: New York, 1961; p 411.

34. Bauman, W. C.; Eichhorn, J. *Journal of the American Chemical Society* **1947**, 69, (11), 2830-2836.

35. Helfferich, F. G., *Ion exchange*. McGraw-Hill: New York, 1962; p 624 p.

36. Lewis, G. N.; Randall, M.; Pitzer, K.; Brewer, D. F., *Thermodynamics*. McGraw-Hill: New York, 1961.

37. Habenicht, B. F.; Paddison, S. J.; Tuckerman, M. E. *Physical Chemistry Chemical Physics* **2010**, 12, (31), 8728-8732.

Verbrugge, M. W.; Hill, R. F. *Journal of Physical Chemistry* **1988**, 92, 6778-6783.
 Fuller, T. F.; Newman, J. *Journal of the Electrochemical Society* **1992**, 139, (5), 1332-1337.

40. Okada, T.; Xie, G.; Gorseth, O.; Kjelstrup, S.; Nakamura, N.; Arimura, T. *Electrochimica Acta* **1998**, 43, (24), 3741-3747.

41. Pak, Y. S.; Xu, G. Solid State Ionics **1993**, 60, (4), 347-350.

42. Pivovar, B. S.; Smyrl, W. H.; Cussler, E. L. *Journal of the Electrochemical Society* **2005**, 152, (1), A53-A60.

43. Zawodzinski, T. A.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *Journal of Physical Chemistry* **1991**, 95, (15), 6040-6044.

Chapter 3. Design of Cluster-free Polymer Electrolyte Membranes and Implications on Proton Conductivity

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Nanoscale ionic aggregates are ubiquitous in copolymers containing charged and uncharged monomers. In most cases, these clusters persist in the hydrated state when ion-conducting channels percolate through the sample. We argue that these clusters impede ion motion due to: (1) the requirement that ions must hop across ion-free regions in the channels as they are transported from one cluster to the next, and (2) increased counterion condensation due to proximity of fixed acid groups in the clusters. Block copolymers wherein the size of the ion-containing microphase is 6 nm or less provides one approach for eliminating the clusters.

3.1. Introduction

Significant research has been conducted on ion containing polymers because of their potential use as polymer electrolyte membranes (PEMs) in fuel cells,^{1,2} batteries,³ actuators,⁴ and solar energy conversion devices.^{5,6} Of particular interest are chains where a fraction of monomers are charged. One charge is bound to the backbone of the polymer chain while the other counterion is mobile. These materials are called single-ion conductors because only one of the ions carries current. An important consequence of this is the absence of concentration gradients during charge transport. This lowers the overpotential needed for operation of fuel cells, batteries, etc. The electrolyte in a fuel cell is an open system, wherein water contained in humid air fed at the cathode enters the membrane. Single-ion conductors are thus essential for fuel cell electrolyte applications because any added salt will eventually be washed out.

Ion containing polymers are also of commercial interest due to their unique mechanical properties. Dipole-dipole interactions between the ion pairs along the polymer chain, causes reversible clustering of ion-rich moieties within a non-polar polymer matrix. These ionomers, which typically contain a heavy metal cation, are robust solids due to the fact that the clusters act as physical cross-links between polymer chains. However, these materials are thermoplastics, i.e. they can be processed at moderate temperatures because the cross-links are reversible.^{7,8}

An interesting common feature in both single-ion conductors and thermoplastic ionomers is the presence of ion clusters. The standard methodology for detecting their presence is small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS). The typical value of the average distance between clusters, d_{cluster} , is 5 nm. In Table 3.1 we show literature data for a wide variety of charged polymers: polymers with both strong and weak acidic groups (e.g. sulfonic vs. carboxylic acid groups), polymers neutralized with metallic counterions such as sodium and zinc, dry and hydrated polymers, crystalline and amorphous polymers, random copolymers and block copolymers.⁹⁻²¹ Also included in Table 3.1 is recent work on the synthesis and characterization of precise ionomers wherein the ionic groups are located periodically along the backbone.^{9,10,18,22} It is remarkable that the values of d_{cluster} obtained from all of the systems listed in Table 3.1 lie between 1.8 and 6.0 nm.

Monomer Chemistry	Abbreviation	Ionomer Type ^a	Acid Group	Counterion	Hydration ^b	Crystallinity ^c	$m{d}_{ m cluster}\left({f nm} ight)^{ m d}$
Ethylene/ Methacrylic Acid, Ethylene/ Acrylic Acid ¹⁴	EMAA, EAA	R	CO ₂	Li ⁺ , Na ⁺ , Cs ⁺	D	С	2.9 ± 0.6
Styrene/ Sulfonated Styrene ²⁰	PSS	R	SO ₃ ⁻	H^+, Na^+, K^+, Zn^{2+}	D	А	3.3 ± 0.8
Tetrafluoroethylene/ Perfluoroether Sulfonic Acid ¹¹	Nafion	R	SO ₃ -	H^+	D	С	5.0 ± 0.6
Ethylene Oxide/Sulfonated Polyester ⁹	PEO/PES	Р	SO ₃ ⁻	Li ⁺	D	С	2.3 ± 0
Ethylene/ Acrylic Acid ^{10,18}	EpAA	Р	CO ₂ -	H^+ , Zn^{2+}	D	С	1.8 ± 0.7
Ethylene/ Geminal Phosphonic Acid ²²	EpgPA	Р	PO_{3}^{2}	H^+	D	С	2.4 ± 0
Sulfonated Styrene/ Ethylene/ Butylene ¹⁵	S-SEBS	В	SO ₃ -	H ⁺ , Na ⁺ , Zn ²⁺	D	А	6.0 ± 0.3
Ethylene/ Methacrylic Acid ¹⁹	EMAA	R	CO ₂ -	Na ⁺	Н	С	2.1 ± 0.3
Styrene/ Sulfonated Styrene ²¹	PSS	R	SO ₃ ⁻	Zn ²⁺	Н	А	4.7 ± 1.6
Tetrafluoroethylene/ Perfluoroether Sulfonic Acid ¹³	Nafion	R	SO ₃ -	H^+	Η	С	4.5 ± 1.0
Sulfonated α-Methylstyrene/ Fluornated Arylene Ether ¹⁶	PMSS-PAE	С	SO ₃ -	H^+	Η	А	3.0 ± 0.4
Sulfonated Styrene/ Vinylidene Difluoride/ Hexafluoropropylene ¹⁷	PSS- PVDFcoHF P	В	SO ₃ -	H ⁺ , TMA ⁺	Н	А	3.7 ± 1.5
Sulfonated Styrene/ Methylbutylene ¹²	PSS-PMB	В	SO ₃ -	H^+	Н	А	3.8 ± 0.8

Table 3.1. Ionomers from select references, of varying composition, are presented with a representative value of d_{cluster} , all of which lie between 1.8 and 6.0 nm.

^aIonomer types: R – random copolymer, P – precise copolymer, B – block copolymer, C – comb copolymer

^bHydration: \vec{D} – dry ionomer, H – hydrated ionomer

^cCrystallinity: A – amorphous, C – semi-crystalline

^dFor references that contained multiple samples, the presented value represents the middle of the range of d_{cluster} values and is followed by the difference between the extremes of that range and the middle value listed.

The purpose of this paper is to explore the effect of clustering on proton transport in PEMs. We propose that proton transport is hindered by the presence of clusters and present an approach for achieving cluster-free PEMs.

The types of polymer chains of interest are shown in Figure 3.1a. The simplest example is sulfonated polystryene (PSS) with randomly functionalized styrene units along an amorphous polystyrene backbone. Also shown in Figure 3.1a is Nafion, a random copolymer of hydrophilic perfluoroether side chains with a terminal sulfonic acid moieties, and hydrophobic tetrafluoroethylene monomers that crystalize. The last example in Figure 3.1a is a block copolymer comprising a PSS block and an uncharged block, polymethylbutylene (PMB). In this case the charged monomers are confined to a portion of the chain, the PSS block.



Figure 3.1. (a) Examples of molecular structures for different types of ionomers, from left to right: a random copolymer Nafion, a random copolymer sulfonated polystyrene (PSS), and a block copolymer sulfonated polystyrene-block-polymethylbutylene (PSS-PMB). Schematics of ion clusters in (b) random ionomers such as PSS and Nafion and (c) a block copolymer. The green spheres represent the ionic clusters that are a distance, d_{cluster} , apart. (d) Proton transport through hydrated ionic clusters a distance d_{cluster} apart,

with a region free of ions between the clusters a distance $d_{\text{ion-free}}$ long, with fixed charges inside the clusters being on average a distance $d_{\text{fixed-ion}}$ apart.

Figures 3.1b and 3.1c each show a schematic of self-assembled structures formed by the random and block copolymers discussed above. Figure 3.1b shows clusters formed in Nafion and PSS that are present throughout the sample. Figure 3.1c shows clusters formed in microphase separated PSS-PMB copolymers wherein clustering is restricted to one of the microphases. Figures 3.1b and 3.1c also contains an illustration of the ionic clusters. The spherical morphology of the ionic clusters was first proposed for PSS by Yarusso and Cooper²⁰ and for Nafion by Hsu and Gierke.¹¹

To achieve adequate proton conductivity in fuel cells, PEMs are operated in the hydrated state. At low water concentrations, the ionic clusters are swollen with water. At sufficiently high water concentration one expects connections between the clusters, as shown schematically in Figure 3.1d. A percolated network of hydrated channels is essential for proton transport though the membrane, and the model we have adopted in Figure 3.1d was originally proposed by Hsu and Gierke.¹¹ In principal the percolated channel could be devoid of clusters. However, SAXS and SANS data in the hydrated state usually contain a scattering peak that is very similar to that seen in the dry state (see Table 3.1). This indicates the presence of clusters in both dry and hydrated states. As indicated in Figure 3.1d, the consequence of the presence of clusters with an average spacing of d_{cluster} is the creation of an ion-free region of length $d_{\text{ion-free}}$; both d_{cluster} and $d_{\text{ion-free}}$ are shown in Figure 3.1d. An additional length scale that is important is the average distance between fixed anions that are covalently bonded to the polymer backbone, $d_{\text{fixed-ion}}$, which depends on the nature of clustering, extent of hydration, and the average number of ionic groups per chain. It is obvious that $d_{\text{fixed-ion}}$ is reduced by clustering, relative to the hypothetical case wherein clustering is absent.

Hsu and Gierke recognized that clustering impedes ion motion.¹¹ One expects the average distance between pairs of dissociated negative and positive ions in hydrated PEMs to be about 0.7 nm, the Bjerrum length of water.²³ The passage of current requires protons to hop from one cluster to the next across regions that are devoid of ions, which is represented in Figure 3.1d by $d_{\text{ion-free}}$. Geometric arguments indicate that $d_{\text{ion-free}} = d_{\text{cluster}} - 2*r$ where r is the radius of the clusters. Since r has not been measured in most PEMs it is difficult to quantify $d_{\text{ion-free}}$. For PEMs with $d_{\text{cluster}} = 5$ nm (the most common value), $d_{\text{ion-free}}$ is estimated to be ~3 nm, assuming $r \sim 1$ nm. Support for the proposed value of r will be presented shortly. It is clear that the hopping distance ($d_{\text{ion-free}}$) is expected to be significantly greater than the Bjerrum length. In such cases, one expects a large activation barrier for inter-cluster hopping. This activation barrier will not exist if clustering were avoided.

The three approaches for studying clusters are rheology, electron microscopy, and scattering. The rheological properties of ionomers are similar to those of chemically cross-linked polymers, indicating the presence of physical cross-links or ionic aggregates.^{7,24} More direct evidence for the presence of clusters should, in principle, come from electron microscopy but this is not the case. Reasons for this include the small size of the clusters, lack of contrast between the clusters and the hydrophobic matrix, and the limited stability of polymers in an electron beam. To our knowledge, the only clear micrograph of acidic clusters in a PEM is contained in the work of Yakovlev et

al.²⁵ Tomographic reconstruction of high angle annular dark field (HAADF) electron micrographs from thin films of PSS-PMB block copolymers revealed that the distribution of cluster sizes in the sample is gaussian with an average cluster diameter of 1.4 nm. Figure 3.2 shows the HAADF image and the cluster distribution results from ref. 25. To date there are no clear images of clusters in hydrated systems.



Cluster diameter, nm

Figure 3.2. Electron micrograph showing acidic clusters in a dry PSS-PMB membrane and cluster size distribution determined from the micrograph. See ref. 25 for details.

There have been numerous attempts to determine the morphology of clusters in hydrated random copolymers, particularly Nafion, using SAXS and SANS. There is still significant disagreement over interpretation of the scattering data because the profiles obtained in the hydrated state also contain a single broad peak. Disparate morphologies such as connected spheres,¹¹ core–shell structures,²⁶ hard spheres,²⁰ bundles of rods,²⁷ parallel cylindrical channels,²⁸ and lamellar channels,²⁹ are all consistent with the observed scattering profiles. A notable exception to this is the work on precise ionomers where higher order scattering peaks, indicating the presence of long range order, are seen.^{10,18,22} Even in this case, the structure of individual clusters (cluster form factor) was inferred from the absence of an expected scattering peak.

Studies of the morphology of ion-containing block copolymers in the hydrated state by SAXS and SANS suggest a morphology shown schematically in Figure 3.3a. There are two levels of microphase separation in these systems. At the higher level one obtains hydrated PSS-rich and dry PMB-rich microdomains with a characteristic length scale, d_{block} . Within the PSS-rich phase one obtains a percolated network of ion clusters and hydrated channels as proposed by Hsu and Gierke.¹¹ The morphology of ion containing block copolymers is thus governed by three length scales, d_{block} , $d_{cluster}$, and $d_{cluster}$.



Figure 3.3. Schematic of the hydrated block copolymer ionomer where (a) the block copolymer domain, d_{block} , is sufficiently large that the hydrated ionic phase is equivalent to its bulk structure and (b) d_{block} is on the sample length scale as the ion cluster morphology (i.e. $d_{block}/2 \approx d_{cluster} \approx 5$ nm) resulting in a homogenous ion phase and an increase in distance between fixed charges, $d_{fixed-ion}$.

It is convenient to use SANS to study the morphology of hydrated samples due to the high contrast between D_2O and ordinary hydrogenous polymers.^{16,17} Kim et al. conducted a systematic study of clustering in symmetric PSS-PMB copolymers. In Figure 3.4 we show SANS data from two hydrated samples, PSS-PMB[13-9] and PSS-PMB[5-4]. (Polymers are named according to the block molecular weights. The numbers within square brackets are the molecular weights of the PSS and PMB blocks, respectively, in

kg/mol.) The characteristics of these two polymer samples in the hydrated state are summarized in Table 3.2. The peaks marked by triangles are related to microphase separation between PSS and PMB in the presence of water. The morphology of the polymers was studied by SANS and TEM, and was determined to be hexagonally packed PMB cylinders in a PSS matrix. The most important difference between the scattering curves is the presence of a cluster peak for PSS-PMB[13-9] corresponding to $d_{\text{cluster}} = 3.1$ nm (peak marked by * in Figure 3.4) and the absence of a cluster peak in PSS-PMB[5-4].¹² It is worth noting that the cluster peak was not seen in PSS-PMB[5-4] in both dry and hydrated states. The value of d_{block} of PSS-PMB[13-9] was 22.4 nm while that of PSS-PMB[5-4] was 11.6 nm. It is evident that there is a correlation between higher level morphology and cluster formation. In particular, small values of d_{block} suppress the formation of clusters. This is shown schematically in Figure 3.3b where the ioncontaining microphase is homogeneous. An interesting consequence of this homogenization is the increase in $d_{\text{fixed-ion}}$ as depicted in Figure 3.3b. The second and third columns in Table 3.2 summarize SANS characterization results of samples PSS-PMB[5-4] and PSS-PMB[13-9].



Figure 3.4. *In-situ* SANS scattering intensity of hydrated PSS-PMB block copolymers plotted verses the scattering vector, q, at 60 °C and 95% relative humidity. Data for scattering profiles were obtained from reference 12 and are offset vertically for visual clarity. The position of the primary scattering peak, $q_{\mathbf{v}}$, is denoted by inverted filled triangles (\mathbf{V}) and is related to block copolymer domain size, d_{block} , by the relationship $d_{block} = 2\pi/q_{\mathbf{v}}$. The position of higher order scattering peaks related to the block copolymer morphology are denoted by the inverted open triangles ($\mathbf{\nabla}$). Both samples exhibit a hexagonal morphology, while the size of d_{block} for PSS-PMB[13-9] is larger

than that of PSS-PMB[5-4]. A cluster peak is observed for PSS-PMB[13-9] and is denoted by an asterisk (*), the position of this peak corresponds to a distance between clusters, d_{cluster} , of 3.1 nm. A cluster peak is absent in the scattering profile of PSS-PMB[5-4] and is due to confinement with in a sufficiently small block copolymer domain.

Table 3.2. Summary of morphology properties of polymers PSS-PMB[5-4] and PSS-PMB[13-9] taken from ref. 12: domain sizes of block copolymer, d_{block} , in the hydrated state and the distance between ionic clusters, $d_{cluster}$, in the hydrated state. Ion clustering is absent in PSS-PMB[5-4], and is a result of the small size of d_{block} . The proton conductivity in ref. 37 of PSS-PMB[5-4] is much higher than that of PSS-PMB[13-9] despite the nearly constant water content and is likely a result of the homogeneous PSS microphase.

Name	$d_{ m block} \left({ m nm} ight)^{ m a,12}$	$d_{\text{cluster}} \left(\text{nm} \right)^{\text{a},12}$	σ (S/cm) ^{b,30}	$\lambda^{b,30}$		
PSS-PMB[5-4]	11.6	-	1.6×10^{-1}	22.5		
PSS-PMB[13-9]	22.4	3.1	9.1×10^{-2}	22.0		
^a Obtained at 60 °C and 95 % relative humidity						

^bObtained at 60 °C and 93 % relative humidity

It is intuitively obvious that clustering will be affected by higher level selfassembly when the size of the hydrophilic domains approaches the average distance between clusters. For the case of symmetric block copolymers this occurs when $d_{\text{block}}/2 \approx$ d_{cluster} . One thus expects qualitative differences in clustering when the size of the hydrophilic phase, $d_{block}/2$ approaches 5 nm. One can qualitatively ascribe this to the well-established effect of confinement on phase separation. Liquid-liquid phase separation in the bulk is driven by free energy differences between the homogeneous state and the phase separated states. The energetic penalty associated with the formation of an interface between the phase separated states is irrelevant. However, as the size of the coexisting phases decreases the interfacial energy becomes increasingly important and when the system size decreases beyond a certain critical value, the homogenous phase is stabilized. This was modeled by Nauman and Balsara using the Cahn-Hilliard approach, ignoring wetting interactions between the liquid and the confining medium.³¹ A more refined model that included the effect of wetting was proposed by Liu et al.³² Experiments of Lin et al. showed that confining water/lutidine mixtures within the pores of Vycor glass (pore diameter = 7 nm) resulted in homogenization.³² (Water/lutidine mixtures are phase separated in the bulk.) Our hypothesis is that the homogenization of the ion-containing microphases in PSS-PMB[5-4] is due the confinement of the ionic domains to 6 nm wide PSS-rich domains. We acknowledge that the phase separation of ionic clusters from non-ionic chain segments is much more complicated than that of binary liquid mixtures. More work is thus necessary to confirm our hypothesis.

Incomplete dissociation of highly charged polymers in water, even at infinite dilution, is well-established.^{23,33,34} This is because the free energy of a completely dissociated, highly charged chain is larger than that of a partially dissociated chain due to

the Coulombic repulsion of closely spaced negative charges that are confined to the polymer backbone. This phenomenon, often referred to as counterion condensation, occurs when the average distance between fixed charges along the polymer backbone is less than the Bjerrum length. In the case of hydrated ionomers, sulfonic acid groups are confined to the interface between the hydrophobic matrix and the hydrated channels (see Figure 3.1d). One expects counterion condensation on surfaces to be more significant than in linear chains due to the increased number of neighbors.³⁴⁻³⁶ The clustering of ions results in a small value of $d_{\text{fixed-ion}}$ which in turn increases counterion condensation.^{36,37} We thus propose that counterion condensation in PSS-PMB[5-4] is less than that in PSS-PMB[13-9] due to the larger value of $d_{\text{fixed-ion}}$.

Park et al. found that proton conductivity of hydrated PSS-PMB block copolymers was a strong function of d_{block} .³⁰ Higher conductivity was obtained when d_{block} in the dry state was lower than 12 nm. Block copolymers with such small values of d_{block} are typically difficult to achieve due to small values of Flory-Huggins interaction parameter, χ , between the two blocks. In ionic systems however χ is estimated to be much higher, with estimates of χ between sulfonated polystyrene and polystyrene ranging from 5.6 to 25 (typical values of γ for neutral polymer systems are much less than 1).³⁸⁻⁴⁰ The characterization results for PSS-PMB[5-4] and PSS-PMB[13-9] are shown in Table 3.2, the proton conductivity of PSS-PMB[5-4] is 1.6×10^{-1} S/cm while that of PSS-PMB[13-9] is 9.1×10^{-2} S/cm, water uptake measurements indicate no substantial difference between the samples ($\lambda = 22.5$ vs. 22.0 for PSS-PMB[5-4] and PSS-PMB[13-9], respectively). It was noted in ref. 37 that increased water retention seen in PSS-PMB block copolymers with d_{block} less than 12 nm could be attributed to capillary condensation. While this can certainly affect ion conduction, arguments presented in this paper suggest that homogenization of ion-conducting microphases is an additional factor that affects ion transport when $d_{block} \leq 12$ nm. Homogenization increases conductivity for two reasons: (1) the absence of channels of pure water that the protons must hop across and (2) reduction of counterion condensation. We propose that eliminating clusters is one avenue for improving the conductivity of hydrated polymer electrolyte membranes. While we have focused exclusively on proton transport, similar clusters are obtained in polymeric single-ion conductors with Li⁺ counterions. The relationships between clustering and ion transport that we have discussed here are also applicable to Li^+ transport.

3.2. Acknowledgement

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3.3. References

1. Kreuer, K. D. Journal of Membrane Science 2001, 185, (1), 29-39.

2. Mauritz, K. A.; Moore, R. B. *Chemical Reviews* **2004**, 104, (10), 4535-4585.

3. Thomas, K. E.; Sloop, S. E.; Kerr, J. B.; Newman, J. J. Power Sources **2000**, 89, (2), 132-138.

4. Nemat-Nasser, S. J. Appl. Phys. 2002, 92, (5), 2899-2915.

5. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y. Solar Energy Materials and Solar Cells **2006**, 90, (5), 549-573.

6. Spurgeon, J. M.; Walter, M. G.; Zhou, J.; Kohl, P. A.; Lewis, N. S. *Energy & Environmental Science* **2011**, 4, (5), 1772-1780.

7. Eisenberg, A. *Macromolecules* **1970**, *3*, 147-154.

8. Eisenberg, A.; M., K., Ion Containing Polymers, Physical Properties and Structure. Academic Press: New York, NY, 1977.

9. Wang, W. Q.; Liu, W. J.; Tudryn, G. J.; Colby, R. H.; Winey, K. I. *Macromolecules* **2010**, 43, (9), 4223-4229.

10. Baughman, T. W.; Chan, C. D.; Winey, K. I.; Wagener, K. B. *Macromolecules* **2007**, 40, (18), 6564-6571.

11. Hsu, W. Y.; Gierke, T. D. Journal of Membrane Science 1983, 13, (3), 307-326.

12. Kim, S. Y.; Park, M. J.; Balsara, N. P.; Jackson, A. *Macromolecules* **2010**, 43, (19), 8128-8135.

13. Kusoglu, A.; Modestino, M. A.; Hexemer, A.; Segalman, R. A.; Weber, A. Z. *Acs Macro Letters* **2012**, 1, (1), 33-36.

14. Macknight.Wj; Taggart, W. P.; Stein, R. S. Journal of Polymer Science Part C-Polymer Symposium **1974**, (45), 113-128.

15. Mani, S.; Weiss, R. A.; Williams, C. E.; Hahn, S. F. *Macromolecules* **1999**, 32, (11), 3663-3670.

16. Nieh, M.-P.; Guiver, M. D.; Kim, D. S.; Ding, J.; Norsten, T. *Macromolecules* **2008**, 41, (16), 6176-6182.

17. Rubatat, L.; Shi, Z. Q.; Diat, O.; Holdcroft, S.; Frisken, B. J. *Macromolecules* **2006**, 39, (2), 720-730.

18. Seitz, M. E.; Chan, C. D.; Opper, K. L.; Baughman, T. W.; Wagener, K. B.; Winey, K. I. *Journal of the American Chemical Society* **2010**, 132, (23), 8165-8174.

19. Tsujita, Y.; Yasuda, M.; Kinoshita, T.; Takizawa, A.; Yoshimizu, H.; Davies, G. R. J. Polym. Sci. Pt. B-Polym. Phys. **2002**, 40, (9), 831-839.

- 20. Yarusso, D. J.; Cooper, S. L. Macromolecules 1983, 16, (12), 1871-1880.
- 21. Yarusso, D. J.; Cooper, S. L. Polymer 1985, 26, (3), 371-378.

22. Buitrago, C. F.; Opper, K. L.; Wagener, K. B.; Winey, K. I. Acs Macro Letters **2012**, 1, (1), 71-74.

23. Manning, G. S. Journal of Chemical Physics 1969, 51, (3), 924-&.

24. Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, 23, (18), 4098-4107.

25. Yakovlev, S.; Wang, X.; Ercius, P.; Balsara, N. P.; Downing, K. H. *Journal of the American Chemical Society* **2011**, 133, (51), 20700-20703.

- 26. Fujimura, M.; Hashimoto, T.; Kawai, H. Macromolecules 1982, 15, (1), 136-144.
- 27. Loppinet, B.; Gebel, G. *Langmuir* **1998**, 14, (8), 1977-1983.
- 28. Schmidt-Rohr, K.; Chen, Q. Nature Materials 2008, 7, (1), 75-83.
29. Litt, M. H. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) **1997**, 38, (1), 80-81.

30. Park, M. J.; Downing, K. H.; Jackson, A.; Gomez, E. D.; Minor, A. M.; Cookson, D.; Weber, A. Z.; Balsara, N. P. *Nano Letters* **2007**, *7*, (11), 3547-3552.

31. Nauman, E. B.; Balsara, N. P. Fluid Phase Equilibria 1989, 45, (2-3), 229-250.

32. Liu, A. J.; Durian, D. J.; Herbolzheimer, E.; Safran, S. A. *Physical Review Letters* **1990**, 65, (15), 1897-1900.

33. Dobrynin, A. V.; Rubinstein, M. Progress in Polymer Science 2005, 30, 1049-1118.

34. Toomey, R.; Tirrell, M. Annual Review of Physical Chemistry 2008, 59, 493-517.

35. Balastre, M.; Li, F.; Schorr, P.; Yang, J. C.; Mays, J. W.; Tirrell, M. V. *Macromolecules* **2002**, 35, (25), 9480-9486.

36. Beers, K. M.; Hallinan, D. T., Jr.; Wang, X.; Pople, J. A.; Balsara, N. P. *Macromolecules* **2011**, 44, (22), 8866-8870.

37. Rollet, A. L.; Diat, O.; Gebel, G. *Journal of Physical Chemistry B* **2002**, 106, (12), 3033-3036.

38. Park, M. J.; Balsara, N. P. *Macromolecules* **2008**, 41, (10), 3678-3687.

39. Tan, N. C. B.; Liu, X.; Briber, R. M.; Peiffer, D. G. *Polymer* **1995**, 36, (10), 1969-1973.

40. Zhou, N. C.; Xu, C.; Burghardt, W. R.; Composto, R. J.; Winey, K. I. *Macromolecules* **2006**, 39, (6), 2373-2379.

Chapter 4. Design of a Humidity Controlled Sample Stage for Simultaneous Conductivity and Synchrotron X-ray Scattering Measurements

We report on the design and operation of a novel sample stage, used to simultaneously measure morphology and conductivity of a polymer electrolyte membrane (PEM) surrounded by humid air as a function of temperature and relative humidity. We present data obtained at the Advanced Light Source (ALS) and Stanford Synchrotron Radiation Laboratory (SSRL). We demonstrate precise humidity control and accurate determination of morphology and conductivity over a wide range of temperatures. The sample stage is used to study structure-property relationships of a semi-crystalline block copolymer PEM, sulfonated polystyrene-*block*-polythethylene (PSS-PE).

4.1. Introduction

Synchrotron radiation is a valuable tool for characterizing the morphology of nanostructured materials.¹⁻³ Materials that are receiving increasing attention are polymer electrolyte membranes (PEMs) for applications such as fuel cells,^{4,5} batteries,⁶ actuators,⁷ and solar energy conversion devices.^{8,9} This paper focuses on ionomers where a fraction of the monomers contain charged species. One charge is bound to the backbone of the polymer chain while the other ion is mobile. Examples of such PEMs are Nafion, a random copolymer of hydrophilic perfluoroether side chains with terminal sulfonic acid groups and hydrophobic tetrafluoroethylene, and sulfonated polystyrene (PSS) with randomly functionalized styrene units along a polystyrene backbone. Block copolymers comprising a PSS block and an uncharged block such as polymethylebutylene (PMB) can also serve as PEMs.¹⁰ These materials self-assemble into nanoscale hydrophilic and hydrophobic domains. Rapid ion transport is generally obtained when the membranes are hydrated. Understanding the relationship between morphology and charge transport in these systems is challenging due to the multicomponent nature of hydrated PEMs. Additional problems arise due to slow kinetics of equilibration. Equilibration of Nafion requires time scales on the order of months.¹¹ Even model systems such as PSS-PMB block copolymers require several days for equilibration.¹² Thus in many cases the transport properties of PEMs depend not only on state of the system at the time of measurement but on thermal and hydration history. Simultaneous measurement of morphology and conductivity is thus crucial for PEM characterization. Such measurements also shed light on the dynamical properties of PEMs as they function in inherently unsteady devices such as fuel cells and solar energy conversion devices.

In this manuscript, we report on the design and operation of a novel sample stage, used to simultaneously measure morphology and conductivity of a PEM surrounded by humid air as a function of temperature and relative humidity. We present data obtained at the Advanced Light Source (ALS) and Stanford Synchrotron Radiation Laboratory (SSRL). We demonstrate precise humidity control over a wide range of temperatures. The sample stage is used to study structure-property relationships of a semi-crystalline block copolymer, sulfonated polystyrene-*block*-polythethylene (PSS-PE).

Our sample stage contains a water-well inside a sealed chamber with Kapton windows for transmitting X-rays. The transfer of water between the well and the air in the chamber is affected by a Peltier device that is in thermal contact with the well. A humidity sensor provides input for a feedback controller that controls the Peltier device.

Our approach is derived from the humidity chamber designed for neutron scattering experiments at the National Center for Neutron Research at the National Institute for Standards and Technology (NIST).^{13,14} Similar methods were used to construct chambers capable of fixed 100 % relative humidity.^{15,16} In a recent paper Salas-de la Cruz et al reported on the design of a humidity-controlled sample stage for X-ray scattering, wherein two air streams, one dry and one saturated with water vapor, are mixed in a separate location and fed into the sample stage.¹⁷ The water content of the air flowing past the sample is controlled by controlling the ratio of the flow rates of the two streams. The limitation of this approach is the presence of gradients that must accompany mass transfer from the air to the sample (boundary layers). The precision with which humidity can be controlled in such a stage is inherently lower than the NIST design. However, many applications require the flow of air past the membrane.¹⁸ Data obtained from the sample stage described in ref 17 is directly relevant to such applications.

4.2. Sample Stage Design

Overall description

The sample stage features a specimen chamber, a sample holder, heating rods, thermocouples and humidity sensors, a water-well at the bottom of the specimen chamber, a Peltier device, and a heat sink. A schematic of the sample stage is presented in Figure 4.1, and details of the sample stage specifications are listed in Table 4.1. The temperature of the sample is controlled by heating rods are located within the chamber walls. The power to the heating rods is controlled by a Watlow temperature controller. Feedback to the controller is provided by a thermocouple located inside the chamber. Water is either removed from or condensed into the well at the base of the chamber. The well is thermally isolated from the walls of the chamber and a Peltier device is used to heat or cool the water-well. The Peltier device is controlled by an Eurotherm X26 controller which uses a Honeywell HC-610 sensor to provide feedback using a PID control system. Heat generated by the Peltier device during cooling of the water-well is removed using a heat sink which is maintained at constant temperature by a recirculating water bath. The chamber control can be operated either manually using the Watlow and Eurotherm controllers, or custom Labview programs. Temperature and relative humidity was logged using the Labview program.



Figure 4.1. Picture and schematic of *in situ* humidity chamber.

Property	Description
Radiation type	Synchrotron X-rays
Geometry	Transmission
Exit Angle	± 35 °
Temperature range	25 - 85 °C
Temperature precision	0.2 °C
Temperature gradient	< 1 °C
Relative humidity range	20 - 95 %
Relative humidity precision	0.1 %

Table 4.1: Humidity chamber specifications

Specimen chamber and temperature control

The chamber is comprised a single aluminum block with wall 5.7 mm thick with an internal chamber measuring $31.7 \times 63.5 \times 61.5$ mm (w x l x h) in size. This chamber is housed in a polyether ether ketone (PEEK) insulation that is 12.8 mm thick. Windows 12.5 mm in diameter are drilled through the PEEK and aluminum to enable X-ray scattering. The windows are sealed with Kapton tape. The lid of the chamber is a piece of aluminum with two screws, and a recessed rubber gasket to allow for a tight seal when closed. The lid features one large hole for inserting the temperature and humidity sensors, and four small holes for measuring sample conductivity using a four-point-probe. The lid has a corresponding PEEK insulating cover, with a center hole to allow for wires to pass through. The PEEK lid fits snugly into place and requires no screws. In the simplest implementation the sample is fixed to either a washer or Kapton tape and hung by copper

wires fixed to the lid. Sample temperature control is indirect through equilibration with the copper wires attached to the lid, and with the temperature of the ambient air. Active control of the sample temperature would be simple to implement in this current design.

The bottom of the specimen chamber has a 14.3 by 46.0 mm rectangular hole in which the water-well is placed. The water well measures 12.73 by 44.43 and 14.24 mm deep. The well has a 1.46 mm thick PEEK sleeve to insulate it from the chamber walls.

The sample chamber is heated by two heating rods in the walls of the chamber. These rods are connected to a Watlow controller and thermocouple located directly above the sample provides feedback to the controller. The heating rods are grounded to the side of the aluminum chamber wall through a screw that is inserted through the PEEK insulation. The chamber is held together by screws through the PEEK walls, with the aluminum interior chamber sliding snuggly into place. The PEEK housing is screwed through its base into the heat sink and into a metal clip. Motors used to translate the sample stage are connected to the stage by the metal clip.

Humidity control

The water vapor content of the air in the specimen chamber is achieved through control of heat flow in and out of the water-well in the specimen chamber. The Peltier device controlled by a Kepco bipolar operational power supply controller below the well is used to supply or remove heat. The magnitude and polarity of the current are determined by a Eurotherm X26 controller. A Honeywell HC-610 humidity sensor located in the sample chamber provides feedback to the Eurotherm controller. Heat produced by the Peltier device is removed by a heat sink. The heat sink is a large aluminum block with channels bored out and thermal contact between the heat sink and the Peltier device is improved through the use of thermal grease. The flow of water through the channels of the heat sink is affected by the water recirculating bath that is maintained at a fixed temperature (20 °C).

Accurate calibration of the humidity sensors used in these studies is important. While the Honeywell sensors come with a general manufacturer calibration, we have found unpredictable differences between individual sensors. A temperature dependent calibration curve of each sensor was obtained by placing the chamber lid with the sensor and thermocouple into an ESPEC humidity chamber which utilizes an analogue wet-bulb style humidity control strategy. Examples of calibrations are presented in Figure 4.2. It should be noted that the operating limits for humidity and temperature for this systems is dependent upon the sensor itself with reported stability up to T = 85 °C and RH = 95%. We only present data at temperatures, T, between T= 25 and 85 °C, and relative humidity, RH, values between RH = 20 and 95%. Temperatures above 85 °C cause irreversible damage to the sensors. Relative humidity values greater than 95% cause sensor output to drift. Whilst this paper is limited to water / air mixtures, solvents other than water and gases other than air could, in principle, be used if appropriate sensors are obtained.



RH Reading (%)

Figure 4.2. Calibration data obtained for the humidity sensor based on the real and set point humidity value calibrated using an commercial humidity chamber for T = 25, 60, and 85 °C. The dashed line is an example of a linear fit through T = 60 °C data.

Chamber performance

The sealed sample stage design enables excellent temperature and humidity control. Chamber temperature fluctuations were less than ± 0.2 °C of the set point and the difference between the base of the chamber and the sample is less than 1 °C. Relative humidity fluctuations were less than $\pm 0.1\%$ of the set point value. The responses of the sample stage to changes in RH set points at constant T are presented in Figure 4.3. Figure 4.3a shows RH as a function of time and Figure 4.3b shows T as a function of time. Stable control around the set-point with no overshoot is seen in Figure 4.3. It does, however, take several minutes for the sample stage to equilibrate. In this regard, vapor flow chambers are better suited for studying fast kinetics in PEMs.



Figure 4.3. Performance of humidity chamber for step changes in humidity at fixed T = 80 °C with (a) relative humidity, RH, as a function of time and (b) temperature, T as a function of time.

Conductivity measurements

A PEEK sample holder was constructed to allow for the *in situ* measurement of conductivity and X-ray scattering under humidity control as shown in Figure 4.4. The sample holder comprising four platinum electrodes is fixed to the aluminum lid by two screws. The platinum electrodes extend out of the chamber and Teflon sleeves are used to insulate the electrodes from the chamber lid. A Gamry potentiostat was used to determine the in-plane conductivity of the humid membranes using the standard four-point-probe configuration. Films of PEMs 200-400 microns in thickness were melted on top of the four electrodes. X-rays pass through a rectangular window in the middle of the sample as shown in Figure 4.4. Kapton tape is used to cover the window to prevent deformation of the sample.



Figure 4.4. Schematic of the conductivity cell used for *in situ* AC impedance spectroscopy measurements. Electrodes are platinum wires inlayed into a PEEK holder. A window is located between the two center electrodes for the X-ray beam to pass through.

X-ray Scattering

SAXS and WAXS experiments were performed at beamline 7.3.3 at the Advanced Light Source at Lawrence Berkeley National Laboratories and 1-4 at Stanford Synchrotron Radiation Lightsource (SSRL). A silver behenate sample was used as a standard, and data were reduced using the Nika program for Igor Pro available from Jan Ilavsky at the Advanced Photon Source. The azimuthally averaged scattering intensity, *I*, is reported as a function of the scattering vector q ($q = 4\pi \sin(\theta/2)/\lambda$), where θ is the scattering angle and λ is the wavelength of the incident beam). The scattering data were corrected for the detector dark current and the scattering from air and Kapton windows. The window sizes were such that scattering angles up to 35 degrees were available.

It is important to evaluate the effect of humid vapor scattering from windows on measured X-ray scattering data. Figure 4.5 shows the effects of changing RH on X-ray transmission at T = 25 and 85 °C. The cell transmission coefficient under humid conditions, t_h , is normalized by that obtained in the dry state, t_d , and the ratio t_h/t_d is plotted on the ordinate in Figure 4.5. The ratio of t_h/t_d is always above 0.93.



Figure 4.5. Transmission data plotted as a function of relative humidity at T = 25 and 85 °C. The cell transmission coefficient under humid conditions, t_h , is normalized by that obtained in the dry state, t_d . The ratio t_h/t_d is always above 0.93.

The chemical structure of PSS-PE is shown in Figure 4.6. The polymer was obtained by first synthesizing a poly(styrene-*block*-ethylene) copolymer (PS-PE) as described in ref 19,¹⁹ followed by sulfonation of the polystyrene block as described in ref $10.^{10}$ The molecular weights of the PS and PE blocks were 600 and 800 g/mol, respectively, and the mole percent of PS monomers functionalized with sulfonic acid groups was 61%. The melting of the crystalline PE block, as determined differential scanning calorimetry (DSC), occurs between T= 60 and 80 °C.



Figure 4.6. Chemical structure of the model PEM, sulfonated polystyrene-*block*-polyethylene (PSS-PE).

Figure 4.7a shows SAXS profiles of the PSS-PE polymer at T = 25 °C in the crystalline state at RH = 30 and 90 %. The broad primary scattering peak at $q = q^*$ in both profiles is due to microphase separation between PSS-rich and PE-rich domains. The center to center distance between adjacent PSS lamellae, $d = 2\pi/q^*$. Increasing RH from 30 to 90 % results in an increase in *d* from 8.1 to 8.5 nm (5% change). While it is well known that PE is crystalline in the dry state (RH = 30%), the effect of humidity on crystal structure within block copolymer microphases remains unresolved. It is thus not clear if the change in *d* is due to hydration or a change in the crystalline properties of the PE microphase. Figure 4.7b shows WAXS results for the same polymer and conditions shown in Figure 4.7a. The dominant scattering peak at $q_c = 14.2 \text{ nm}^{-1}$ corresponds to scattering from the PE crystallites. This peak is seen in both RH = 30 and 95 % data. It is clear that increasing the humidity of the surrounding air at T = 25 °C has no effect on PE crystallites. The weak shoulder at $q=q_a=13 \text{ nm}^{-1}$ is attributed to the amorphous halo seen in PE.²⁰ This halo is also not affected by humidity.



Figure 4.7. Scattering intensity, *I*, plotted as a function of scattering vector, *q*, at T = 25 °C in the crystalline state under controlled humidity for (a) the effects of hydration on the block copolymer structure showing a change in domain size, $d(d=2/q^*)$ upon hydration despite the presence of crystalline polyethylene (PE) and (b) the negligible change in the crystalline PE as evidenced the negligible change in the crystalline scattering peak, $q_{\rm C}$. The amorphous halo at $q_{\rm A}$, due to the semi-crystalline nature of PE is also unchanged.

Figure 4.8 shows SAXS data for PSS-PE at T = 85 °C at RH = 48 and 85 %. The broad scattering peak observed at RH = 48 % is characteristic of disordered block copolymers. In contrast the sharp primary peak located at $q^*=1.01 \text{ nm}^{-1}$, and the second order scattering peak at $2q^*$ indicate the formation of a lamellar phase. The dramatic sharpening of the primary peak and appearance of the higher order peak indicates that the sample experiences a humidity induced disorder-to-order transition (DOT). This effect is reversible as the disordered state is obtained upon dehydration at RH = 48 % (data not shown for brevity).



Figure 4.8. Scattering profiles of PSS-PE plotted as a function of intensity *I*, plotted as a function of scattering vector, *q*, at T = 85 °C in the melt state. Peak positions are marked by inverted triangles ($\mathbf{\nabla}$). At low RH the polymer is disordered and upon hydration the polymer undergoes a disorder-to-order transition to an ordered lamellar state.

Figure 4.9 shows the result of simultaneous SAXS and conductivity, σ , measurements on the PSS-PE sample at T = 80 °C. The RH of the surrounding air was increased step-wise from 25 to 50 % in steps of 1%. After each step the relative humidity of the surrounding air was kept constant until stable values of *d* and σ were obtained. It is clear that the increase in d with hydration is accompanied by an increase in σ . The process can also be performed with the *in situ* conductivity cell shown in Figure 4.4, allowing for simultaneous determination of the morphology as a function of the polymer morphology and domain size. Data typical of this approach is summarized in Figure 4.9. For the PSS-PE sample in the ordered phase Figure 4.9 shows the effect of changing RH on *d* and proton conductivity, σ . To our knowledge this represents the first simultaneous measurement of nanoscale morphology and ionic conductivity in a hydrated PEM.



RH (%)

Figure 4.9. Effect of RH on domain size, *d*, and proton conductivity, σ , at T = 80 °C. Increasing RH causes an increase in both variables, with qualitatively similar trends in both variables suggesting a strong coupling between structure and transport.

4.3. Conclusion

We have reported on the design of a humidity controlled sample stage for simultaneous conductivity and synchrotron X-ray scattering measurements. Successful operation at the Advanced Light Source (ALS) and Stanford Synchrotron Radiation Laboratory (SSRL), demonstrated precise humidity control over a wide range of temperature. Data obtained from a model polymer electrolyte membrane (PSS-PE) in different states of hydration provided data on the relationship between morphology and ion transport rates. To our knowledge, this is the first report on simultaneous measurement of morphology and conductivity under humidity control.

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4.5. References

1. Hamley, I. W.; Castelletto, V. Prog. Polym. Sci. 2004, 29, (9), 909-948.

2. Putnam, C. D.; Hammel, M.; Hura, G. L.; Tainer, J. A. *Quarterly Reviews of Biophysics* **2007**, 40, (3), 191-285.

3. Schmidt, P. W. Journal of Applied Crystallography **1991**, 24, 414-435.

4. Kreuer, K. D. J. Membr. Sci. 2001, 185, (1), 29-39.

5. Mauritz, K. A.; Moore, R. B. *Chemical Reviews* **2004**, 104, (10), 4535-4585.

6. Singh, M.; Odusanya, O.; Wilmes, G. M.; Eitouni, H. B.; Gomez, E. D.; Patel, A.

J.; Chen, V. L.; Park, M. J.; Fragouli, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D.; Balsara, N. P. *Macromolecules* **2007**, 40, (13), 4578-4585.

7. Nemat-Nasser, S. J. Appl. Phys. 2002, 92, (5), 2899-2915.

8. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y. Solar Energy Materials and Solar Cells **2006**, 90, (5), 549-573.

9. Spurgeon, J. M.; Walter, M. G.; Zhou, J.; Kohl, P. A.; Lewis, N. S. *Energy & Environmental Science* **2011**, 4, (5), 1772-1780.

10. Park, M. J.; Downing, K. H.; Jackson, A.; Gomez, E. D.; Minor, A. M.; Cookson, D.; Weber, A. Z.; Balsara, N. P. *Nano Letters* **2007**, *7*, (11), 3547-3552.

11. Onishi, L. M.; Prausnitz, J. M.; Newman, J. Journal of Physical Chemistry B 2007, 111, (34), 10166-10173.

12. Wang, X.; Yakovlev, S.; Beers, K. M.; Park, M. J.; Mullin, S. A.; Downing, K. H.; Balsara, N. N. *Macromolecules* **2010**, 43, (12), 5306-5314.

13. Lai, D.; Liu, W. H.; Wang, W. C.; Glinka, C. J.; Worcester, D. L.; Lin, Y.; Huang, H. W. *Langmuir* **2004**, 20, (21), 9262-9269.

14. Yang, L.; Weiss, T. M.; Lehrer, R. I.; Huang, H. W. *Biophysical Journal* **2000**, 79, (4), 2002-2009.

15. Caracciolo, G.; Petruccetti, M.; Caminiti, R. *Chemical Physics Letters* **2005**, 414, (4-6), 456-460.

16. Katsaras, J.; Watson, M. J. Rev. Sci. Instrum. 2000, 71, (4), 1737-1739.

17. Salas-de la Cruz, D.; Denis, J. G.; Griffith, M. D.; King, D. R.; Heiney, P. A.; Winey, K. I. *Rev. Sci. Instrum.* **2012**, 83, (2).

18. Kusoglu, A.; Modestino, M. A.; Hexemer, A.; Segalman, R. A.; Weber, A. Z. Acs *Macro Letters* **2012**, 1, (1), 33-36.

19. Wong, D. T.; Mullin, S. A.; Battaglia, V. S.; Balsara, N. P. J. Membr. Sci. 2012, 394, 175-183.

20. Rangarajan, P.; Register, R. A.; Fetters, L. J. *Macromolecules* **1993**, 26, (17), 4640-4645.

Chapter 5. Absence of Schroeder's in a Block Copolymer Electrolyte Membrane

The morphology, water uptake, and proton conductivity of sulfonated polystyrene-*block*-polyethylene (PSS-PE) was studied under controlled relative humidity (RH) and in liquid water. Extrapolation of the domain size, water uptake, and conductivity in humid vapor to RH = 100% allowed for an accurate comparison between the properties of PSS-PE hydrated in saturated vapor and in liquid water. Absent from this system was Schroeder's Paradox, which expects the properties in saturated water vapor to be less than those obtained in liquid water. We speculate that the reason previous reports have noted the presence of such a paradox is likely due polymer membranes not reaching equilibrium and faulty attempts to achieve saturated water vapor.

5.1. Introduction

There has been a long standing debate on the differences in properties of hydrophilic 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 molecules in saturated water vapor 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 randox.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.

Many studies of Schroeder's Paradox are based on polymer electrolyte membranes (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. To facilitate charge transport, PEMs are typically hydrated with water. 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 membrane at the cathode. Depending on the exact application and operating conditions,

devices with PEMs can be expected to be exposed to water of varying relative humidity or liquid water as is the case in a flooded fuel cell. It is obvious that resolving the Schroeder's Paradox for PEMs is a matter of practical importance.

Investigations into Schroeder's Paradox in PEMs have focused primarily on a commercial polymer membrane, Nafion, as summarized in ref⁴. Investigations into Nafion are difficult because of the long "equilibration" times. Onishi et al found that timescales on the order of months was necessary to equilibrate Nafion after step changes in temperature.⁴ Semi-crystalline polymers such as tetrfluoroethylene, 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 amporphous 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 or thermodynamic factors.^{2,3,5,9} It should be noted that Schroeder's Paradox has also been observed in other ionomers such as crosslinked 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 0.15 (xx). 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 minor temperature fluctuations. It was noted in ref²⁰ 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.

5.2. 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 to reduce the crystallinity of the PE block. Polymerization in benzene resulted in xx % of 1,4 additions of the butadiene monomers. Hydrogenation was followed by sulfonation of the PS block, as described in ref ¹⁷, to yield a sulfonated polystyrene-block-polyethylene (PSS-PE) block copolymer, the structure of which is shown in Figure 5.1. PSS-PE was not soluble in dichloroethane at the reaction conditions used in ref ¹⁷, so

the PS-PE precursor was mechanically agitated and refluxed in the solvent to produce a uniform dispersion of PS-PE micelles which was then sulfated under the same conditions described in ref 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 more or less randomly distributed within the PSS block. The fraction of sulfonated styrene units, SL, as defined in equation 5.1, was determined using ¹H NMR as described previously, with the polymer dispersed in a d_3 -methanol solution. Ion exchange capacity (IEC) in eq 4 quantified as the moles of sulfonic acid group per gram of polymer (mmol/g) was calculated from SL and the molecular weight of the copolymer. Sample properties are summarized in Table 5.1.

where SSA is styrenesulfonic acid, S is styrene, E is ethylene, and MW is molecular weight of the SSA, S, and E monomers in g/mol. All measurements were made at 25 °C. The PE block is semi-crystalline at this temperature.



Figure 5.1. Chemical structure of sulfonated polystyrene-*block*-polyethylene (PSS-PE).

Table 5.1.	Properties	of the	sulfonated	polystyrene	-block-po	lyethylene	(PSS-PE)	sample
studied.								

Sample	PS Precursor	PS Volume	IEC
Name	Molecular	Fraction	(calculated)
	Weight	(%)	(mmequiv/g)
	(kg/mol)		
PSS-PE	15	15	0.46

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 microns. SAXS was performed at beamline 7.3.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Humidity controlled SAXS was performed using a home built humidity stage as reported previously in Chapter XX. Samples were equilibrated for 2 hours 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 scattering angle and λ is the wavelength of the incident beam.

Transmission Electron Microscopy

Transmission electron micrographs (TEMs) of dry and a water-equilibrated sample were obtained from crymicrotomed 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 the 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 μ m thick polymer films 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 Deerslayer quartz spring 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 0.5 mgforce/mm). 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 5.3.

$$WU = \frac{\text{hydrated film weight} - \text{dry film weight}}{\text{dry film weight}} \times 100\%$$
(5.3)

The degree of hydration, λ , defined as the moles of water per mole of sulfonic acid groups in the membrane, is calculated using eq 5.4

$$\lambda = \frac{[H_2 O]}{[SO_3^-]} = \frac{WU(\%) \times 10}{MW_{H_2O} \times IEC(\frac{mmol}{g})}$$
(5.4)

Where $MW_{\rm H2O}$ is 18.02 g/mol.

Conductivity

Free-standing films of PSS-PE with dimension 2 cm x 1 cm x 200 μ m 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 of 100 Hz-100 kHz in a humidity- and temperature-controlled oven (SH-241, Espec. Corp). Conductivity, σ , is given by:

$$\sigma = \frac{l}{A \times R} \tag{5.5}$$

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.

5.3. 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 5.2). We find that WU increases monotonically over a time scale of 40-60 h, approaching the equilibrium WU value of 44 %. (While the observation of a timeindependent 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 5.3 presents the transient response in σ as a function of time when a dry PSS-PE sample is immersed in liquid water. Upon hydration, there is a rapid increase in σ during the first three hours, followed by a gradual decrease, eventually reaching a plateau value of $\sigma =$ 0.014 S/cm. 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 5.2 and 5.3 show that this is not the case. This demonstrates the complex interdependence of conductivity on the distribution of water within the membrane. In all data below, we show values of parameters obtained after steady values were observed. The times required to obtain these values varied from 24 to 60 hours (lower annealing times were adequate for small step changes in RH).



Figure 5.2. Water uptake, WU, of PSS-PE in liquid water (\blacksquare) at T = 25 °C as a function of time.



Figure 5.3. Proton conductivity, σ , of PSS-PE in liquid water (**•**), at T = 25 °C as a function of time.

Figure 5.4 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 enable evaluation of the geometry of the microphase separated PSS-

PE sample, we can assert that the sample has a periodic structure with a characteristic domain size, $d = 2\pi/q^*$. Figure 5.5a shows a TEM image for a dry PSS-PE sample. The 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 5.5a are spheres of slices through worm-like structures oriented perpendicular to the plane of the section. Figure 5.5b 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 light, 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 cylinder-like. 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).



Figure 5.4. SAXS profiles of hydrated PSS-PE presented dry and hydrated in liquid water at $T = 25 \text{ }^{\circ}\text{C}$.



Figure 5.5. 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. The dry sample shows a coexistence of a spherical and cylindrical morphology. The hydrated sample shows a disordered cylindrical morphology.

In Figure 5.6 we show values of *d* obtained in humid air at RH values of 90, 95, and 96%, in addition to that obtained in liquid water using SAXS. (For reference we also show the value of *d* obtained in the dry state.) The dashed curve in Figure 5.6 is power-law fit through the humid air data and liquid water data $[d=k(RH)^m]$. 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.



Figure 5.6. Domain size, *d*, of PSS-PE 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 immersed in liquid water (\blacktriangle) are also presented.

In Figure 5.7 we show water uptake values, WU, obtained in humid air and liquid water. The dashed curve in Figure 5.7 represents a power-law fit through all of the data $[WU = k(RH)^m + n]$. The fact that data obtained in humid air and liquid water lie on the same curve (within experimental error) is consistent with the notion that the Schroeder's Paradox is not observed in water uptake data of our PSS-PE sample.



Figure 5.7. Water uptake, WU, of PSS-PE in humid vapor (\Box) 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 data.

In Figure 5.8 we show proton conductivity values obtained in humid air and liquid water. This experiment comprised three 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 equilibrated values of σ . Conductivity values obtained from run 1 were higher than the equilibrated values, consistent with our previous studies on model PSS containing block copolymer PEMs due to nonequilibrium effects.¹⁹ We thus use data obtained from run 2 in our analysis. The dashed curve in Figure 5.8 represents a power-law fit through all of the data $[\sigma = k(RH)^m + n]$. 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 and outside experimental uncertainty. One may argue that strictly speaking, σ , is a transport parameter and thus deviations observed in Figure 5.8 are not paradoxical. However, transport coefficients through equilibrated materials should have well-defined values that depend only on the equilibration conditions and we thus expect to observe similar consistency in the dependencies of d, WU, and σ .



Figure 5.8. Proton conductivity, σ , of PSS-PE in humid vapor (\Box) and liquid water (\blacktriangle) plotted as a function of relative humidity, RH, at T = 25 °C. Humid vapor data is obtained after equilibration in liquid water. The dashed curve represents a power-law fit through the data.

In Figure 5.9 we plot σ as a function of WU for our sample by combining the data presented in Figures 5.7 and 5.8. The dashed curve in Figure 5.9 represents a power-law fit through all of the data [$\sigma = k(WU)^m + n$]. The fact that data obtained in humid air and liquid water lie on the same curve (within experimental error) is consistent with the notion that the Schroeder's Paradox is not observed in the conductivity data obtained from our PSS-PE sample. The lack of quantitative agreement seen in Figure 5.8 is thus attributed to the fact that the dependence of σ on *RH* cannot be explained by a simple power law.



Figure 5.9: Plot of conductivity, σ , in humid vapor (\Box) and liquid water (\blacktriangle) as a function of water uptake, *WU*, demonstrating that the large increase in σ in liquid water is in fact due the amount of water absorbed due to the absence of Schroeder's Paradox. The dashed curve represents a power-law fit through the data.

5.4. Conclusions

The combination of SAXS, TEM, water uptake, and conductivity allowed us to make the following conclusions:

- (1) PSS-PE membranes can be equilibrated in time scales ranging from 10-60 h making them ideal candidates for studying effects such as the Schroeder's Paradox.
- (2) Approaches to equilibrium of seemingly related quantities such as proton conductivity and water uptake can be very different. Measurement of equilibrated values of different parameters may thus require different experimental protocols in spite of the obvious fact that strictly speaking equilibration of a sample occurs on a single, well-defined time scale.
- (3) PSS-PE membranes exhibit Vapor Pressure Paradox. The characteristic size and arrangement of the hydrophilic domains obtained in humid air and liquid water are consistent with each other.
- (4) Schroeder's paradox is absent in this system. Water uptake measurements in humid air and liquid water are consistent with each other.
- (5) Proton conductivity of PSS-PE membranes does not display paradoxical behavior.
- (6)

5.5. Acknowledgements

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5.6. References

1. Schroeder, P. Z. Phys. Chem 1903, 45, 75-117.

2. Bass, M.; Berman, A.; Singh, A.; Konovalov, O.; Freger, V. *Journal of Physical Chemistry B* **2010**, 114, (11), 3784-3790.

3. Choi, P. H.; Datta, R. Journal of the Electrochemical Society 2003, 150, (12), E601-E607.

4. Onishi, L. M.; Prausnitz, J. M.; Newman, J. *Journal of Physical Chemistry B* **2007**, 111, (34), 10166-10173.

5. Weber, A. Z.; Newman, J. *Journal of the Electrochemical Society* **2004**, 151, (2), A311-A325.

6. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1973.

7. Maurer, G.; Prausnitz, J. M. *Fluid Phase Equilibria* **1996**, 115, (1-2), 113-133.

8. Nagle, J. F.; Tristram-Nagle, S. *Biochimica et biophysica acta* **2000**, 1469, (3), 159-95.

9. Kusoglu, A.; Modestino, M. A.; Hexemer, A.; Segalman, R. A.; Weber, A. Z. *Acs Macro Letters* **2012**, 1, (1), 33-36.

10. Kreuer, K. D. Journal of Membrane Science 2001, 185, (1), 29-39.

11. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y. Solar Energy Materials and Solar Cells **2006**, 90, (5), 549-573.

12. Geise, G. M.; Freeman, B. D.; Paul, D. R. *Polymer* **2010**, *5*1, (24), 5815-5822.

13. Eitouni, H. B.; Rappl, T. J.; Gomez, E. D.; Balsara, N. P.; Qi, S.; Chakraborty, A.

K.; Frechet, J. M. J.; Pople, J. A. Macromolecules 2004, 37, (23), 8487-8490.

14. Beers, K. M.; Balsara, N. P. ACS Macro Letters 2012, 1155-1160.

15. Park, M. J.; Balsara, N. P. *Macromolecules* **2008**, 41, (10), 3678-3687.

16. Park, M. J.; Balsara, N. P.; Jackson, A. *Macromolecules* **2009**, 42, (17), 6808-6815.

17. Park, M. J.; Downing, K. H.; Jackson, A.; Gomez, E. D.; Minor, A. M.; Cookson, D.; Weber, A. Z.; Balsara, N. P. *Nano Letters* **2007**, *7*, (11), 3547-3552.

18. Park, M. J.; Nedoma, A. J.; Geissler, P. L.; Balsara, N. P.; Jackson, A.; Cookson, D. *Macromolecules* **2008**, 41, (6), 2271-2277.

19. Wang, X.; Yakovlev, S.; Beers, K. M.; Park, M. J.; Mullin, S. A.; Downing, K. H.; Balsara, N. N. *Macromolecules* **2010**, 43, (12), 5306-5314.

20. Katsaras, J. *Biophysical Journal* **1998**, 75, (5), 2157-2162.

21. Wong, D. T.; Mullin, S. A.; Battaglia, V. S.; Balsara, N. P. *Journal of Membrane Science* **2012**, 394, 175-183.

Chapter 6. The Effect of Crystallization on Proton Transport in Model Polymer Electrolyte Membranes

The effects of incorporating a semi-crystalline structural block on the self-assembly, water uptake, and proton conductivity of a model block copolymer electrolyte are investigated. A novel model system of sulfonated polystyrene-*block*-polyethylene (PSS-PE), is synthesized at a variety of molecular weights to probe how crystallization affects performance for a variety of conducting domain sizes. In block copolymer systems with an amorphous structural block, one expects small domains to perform better, but crystallization is known to disrupt the self-assembly of small block copolymers. We found that crystallization will in fact disrupt the self-assembly of this system resulting in poor water uptake and proton conductivity in small domains. Increasing domain size results in less morphological disruption, leading to an improvement in performance at larger domain sizes.

6.1. Introduction

Many high-volume commercial polymers such as polyethylene and polypropylene are semi-crystalline. The crystalline regions in polymers act as physical crosslinks. Unlike chemical crosslinking which is permanent, physical crosslinks are reversible and therefore melt-processable by heating above the melting point of the crystallites. This paper is concerned with the characteristics of polymer electrolyte membranes (PEMs) used in applications such as fuel cells,¹ solar energy conversion devices,^{2,3} and water filtration.⁴ PEMs are polymers where a fraction of monomers are charged. One charge is bound to the backbone while the other counterion is mobile. PEMs used for hydrogen fuel cells contain protons that are mobile in the hydrated state, and serve to transport protons from anode to cathode. It is, perhaps, not surprising that the most commercially successful PEM, Nafion, is a semi-crystalline polymer. Nafion is a random copolymer of hydrophobic tetrafluoroethylene and hydrophilic perfluoroether side chains that have terminal sulfonic acid groups. The excellent mechanical properties of Nafion, are due to the semi-crystalline nature of the hydrophobic backbone. The hydrophilic domains in materials like Nafion are thus impeded in semi-crystalline matrices. To our knowledge there is limited understanding of the interplay between the semi-crystalline matrices and ion transport. The purpose of this paper is to present a model block copolymer PEM that enables a study of the relationship between polymer crystallization and ion transport.

This paper is part of a series on model PEMs based on diblock copolymers of sulfonated polystyrene and polyolefins.⁵⁻⁹ The membranes used in this study contain nanometer sized domains with well-defined geometry that are charged and hydrophilic. Structural integrity of these membranes in the hydrated state is governed by the polyolefin block (also referred to as the structural block). Previous work is based on polystyrene-*block*-polymethylbutylene (PSS-PMB) copolymers. sulfonated The hydrophobic PMB block is amorphous. Park et al. found that decreasing the size of the conducting domains below 6 nm led to remarkable increases in proton conductivity and water uptake. To achieve PEMs with small conducting domains, very low molecular weight PSS-PMB copolymers were required, and because PMB is a soft rubber, the resulting membranes were mechanical unstable. One approach for improving the mechanical properties of such membranes is by crystallization of the hydrophobic block. In this manuscript we focus on sulfonated polystyrene-*block*-polyethylene (PSS-PE) copolymers. These polymers are chemically similar to PSS-PMB. The only difference is the absence of the pendant methyl group in PE that makes the polymer semi-crystalline. If the crystallites are confined within the PE domains then one expects similar behavior from PSS-PMB and PSS-PE.

Confinement of crystalline domains within diblock copolymers wherein one of the blocks is amorphous (which we shall refer to as A-C block copolymer) has been studied extensively. A framework has been established to predict the self-assembly of copolymers with one non-conducting crystallizable block and one amorphous block.¹⁰⁻¹⁹ The morphology obtained in these systems is dictated by the chemical incompatibility of the two blocks (χ , Flory-Huggins interaction parameter) and the glass transition temperature of the amorphous block.¹⁰⁻¹⁹ When the amorphous block is glassy, the morphology of the melt-state is retained and the crystallization of the second block is confined within the nanoscale domains.^{12,14,17,20,21} However our non-crystalline block must be rubbery to enable proton transport and thus this mechanism of confinement is unimportant. When the amorphous block is rubbery, the morphology in the crystallinestate depends on both segregation strength (χN , where N is the number of monomers per chain) between the blocks.^{10,12,14,16} The melt-state morphology is retained only in strongly segregated systems when the product χN exceeds a certain critical value.¹⁴⁻¹⁶ In weakly segregated systems, the crystalline phase "breaks out" of the confining block copolymer domain.^{10-12,16,18,19} The morphology of the crystalline phase is often lamellar as this geometry is commensurate with that of chain folded crystals.^{10,12,19,22,23} This was first anticipated by theorists^{22,23} and subsequently observed experimentally.^{10,12,19} The thermodynamic properties of our P3EHT-*b*-PEO block copolymer are consistent with this general framework. It was shown by Loo et al that as the product of the Flory-Huggins chi parameter and polymer chain length, χN , is increased so too is the ability to confine the crystallization process. In addition, as the glass transition temperature, T_{σ} , of the amorphous chain is increased, so is the ability to confine crystallization.

The desired trends in molecular weight for PEM performance and crystallization confinement are in direct conflict with each other. Our work on polymers with amorphous structural blocks indicates that conductivity is enhanced at low molecular weights while literature indicates that confined crystallization is only expected in high molecular weight samples. The purpose of this paper is to elucidate this conflict.

6.2. 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.²⁴ Anionic polymerization was performed in cyclohexane to maximize the crystallinity of the PE block, on average resulted in 93 % 1,4 additions of the butadiene monomers. Hydrogenation was followed by sulfonation of the PS block, as described in ref⁷, to yield a sulfonated polystyrene-block-polyethylene (PSS-PE) block copolymer, the structure of which is shown in Figure 6.1. PSS-PE was not soluble in dichloroethane at the reaction conditions used in ref⁷, so the PS-PE precursor was mechanically agitated and refluxed in the solvent to produce a uniform

dispersion of PS-PE micelles which was then sulfated under the same conditions described in ref⁷. 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 more or less randomly distributed within the PSS block. The fraction of sulfonated styrene units, SL, as defined in equation 6.1, was determined using ¹H NMR as described previously, with the polymer dispersed in a d_3 -methanol solution. Ion exchange capacity (IEC) in eq 6.2 quantified as the moles of sulfonic acid group per gram of polymer (mmol/g) was calculated from SL and the molecular weight of the copolymer. Sample properties are summarized in Table 6.1.

where SSA is styrenesulfonic acid, S is styrene, E is ethylene, and MW is molecular weight of the SSA, S, and E monomers in g/mol. All measurements were made at 25 °C. The PE block is semi-crystalline at this temperature.



Figure 6.1. Chemical structure of sulfonated polystyrene-block-polyethylene (PSS-PE).

		1 2 2		
Sample ID ^a	PS MW	ϕ_{PS}^{b}	IEC	
	(kg/mol) ^b		(mmol/g) ^c	
p1	1.2	.45	2.6	
p3	2.5	.48	2.8	
p5	4.5	.48	2.9	
p9	9.0	.45	2.9	
p18	18.2	.47	2.8	

Table 6.1. Characteristics of polymers used in this study.

^aSamples are labeled according to the nominal molecular weight of the nonsulfonated PS block. Sample p1, for example, is the PSS-PE block copolymer with a 1.2 kg/mol PS block .

^bProperties are of the PS-PE precursor.

^cProperties are of the PSS-PE sample studied

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 microns. SAXS was performed at beamline 7.3.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Humidity controlled SAXS was performed using a home built humidity stage as reported previously in Chapter 4. Samples were equilibrated for 2 hours 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 scattering angle and λ is the wavelength of the incident beam.

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$$WU = \frac{\text{hydrated film weight} - \text{dry film weight}}{\text{dry film weight}} \times 100\%$$
(6.3)

The degree of hydration, λ , defined as the moles of water per mole of sulfonic acid groups in the membrane, is calculated using eq 6.4

$$\lambda = \frac{[H_2 O]}{[SO_3^-]} = \frac{WU(\%) \times 10}{MW_{H_2 O} \times IEC(\frac{mmol}{g})}$$
(6.4)

Where $MW_{\rm H2O}$ is 18.02 g/mol.

Conductivity

Free-standing films of PSS-PE with dimension 2 cm x 1 cm x 200 μ m 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 of 100 Hz-100 kHz in a humidity- and temperature-controlled oven (SH-241, Espec. Corp). Conductivity, σ , is given by:

$$\sigma = \frac{l}{A \times R} \tag{6.5}$$

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.

6.3. Results and Discussion

Figure 6.2 shows SAXS profiles for p1 in the solid state at T = 25 °C and in the melt at T = 120 °C. The primary scattering peak in the melt, q_m^* , and in the crystalline state, $q_{\rm c}^{*}$, are indicated on the figure. It is immediately obvious that the positions of $q_{\rm m}^{*}$ and q_c^* are approximately 20% different in size, indicating that for p1 crystallization does affect the block copolymer self-assembly. While it is immediately obvious that crystallization causes a change in the self-assembly, it is necessary to have a quantitative measure of disruption to compare samples. As discussed in ref²¹, when the crystalline chain is PE in A-C block copolymers the stems of the PE chains will want to align roughly parallel to the interface of the two bock copolymer phases when confined, while unconfined PE stems will want to lay orthogonal to the interface of the block copolymer interface. The parallel orientation will cause negligible changes in the interfacial area per chain, while the perpendicular orientation will cause a decrease in interfacial area per chain. Changes in the interfacial area per chain will result in a corresponding change in the domain size, d. As a result, when breakout occurs the domain size in the crystalline state, $d_c = 2\pi/q_c^*$, is larger than the domain size in the melt, $d_m = 2\pi/q_m^*$, while d_c is approximately equal to $d_{\rm m}$ when crystallization is confined.



Figure 6.2. SAXS profiles of p1 in the crystalline state at T = 25 °C (bottom) and in the melt at T = 120 °C in the melt (top). The primary scattering peak in the crystalline state, q_c^* , is much smaller than primary scattering peak in the melt, q_M^* , indicating crystillazation increases the domain size, $d=2\pi/q$, due to breakout of the PE crystallites.

In Figure 6.3, we show the results of the analysis of dry SAXS data for polymers in Table 6.1. Crystallization induced disruption, as measured by the ratio of d_m and d_c , plotted as a function of MW_{PS} shows that the two smallest samples (p1 and p3), experience roughly comparable levels of disruption due to crystallization while the largest samples (p5, p9, and p18) experience no measurable level of disruption.



Figure 6.3. The effects of crystalline breakout on the domain size, d of PSS-PE, as measured by the ratio of the domain size in the melt, $d_{\rm m}$, and the domain size in the crystalline state, $d_{\rm c}$.

Figure 6.4a shows in situ SAXS profiles of p1 for a variety of temperatures at RH = 95%. We focus on the position of the primary peak, q_c^* , of p1 which is relatively unchanging with increasing temperature, indicating the size of the hydrated channel, $d_w = 2\pi/q_c^*$, is relatively unchanging with changing temperature. A summary of in situ SAXS data for all samples in presented in Figure 6.4b. Dashed lines indicated the average of the values, which is effectively constant for all samples studied.



Figure 6.4. Small angle X-ray scattering (SAXS) results for (a) p1 profiles at RH = 95 % and T = 25, 40, 60, 80, and 85 °C (curves are vertically shifted with increasing T for visual clarity) and (b) hydrated domain sizes obtained from *in situ* SAXS as a function of hydrated domain size, d_w .

It has been shown previously that the effects of annealing in humid vapor can have an impact on PEM performance, specifically proton conductivity, σ . This is particularly relevant for this system since the bench mark for crystalline systems is Nafion which is extremely history dependent, and it is unclear to what degree this is due to its random structure, semi-crystalline backbone, and its high molecular weight. Figure 6.5 presents the results of two sequential heating scans for three samples of p1 for a range of temperatures, T = 25 to 90 °C, and under constant controlled relative humidity, RH = 98 %. The first scan of all three samples is significantly different and highly irreproducible, while the subsequent heating scans for all three are very similar. In Figure 6.6 we show the water uptake, WU, for a single p1 sample is shown under similar heating protocol. The WU is unchanging between the two scans, and was confirmed to be true for all other samples. Data presented hereafter will be after having annealed at T = 90 °C and RH = 98 % for a minimum of two days to ensure reproducible data.



Figure 6.5. Effects of annealing on proton conductivity, σ , as a function of temperature, T, for 3 samples undergoing two sequential heating runs. Open symbols represent the first heating scan data ($\circ \Box \Delta$), and closed symbols represent heating scan 2 (••• Δ).



Figure 6.6. Effects of annealing on water uptake, WU, as a function of temperature, T. Open symbol represent the first heating scan (Δ), and closed symbol represent second heating scan (Δ).
The effect of temperature on σ of PSS-PE is presented in Figure 6.7a. All samples showed Arrhenius-like behavior in σ , with values ranging from 2.8 x 10⁻² to 5.6 x 10⁻² S/cm at T = 25 °C and RH = 98 %, and from 8.1 x 10⁻² to 1.4 x 10⁻¹ S/cm at T = 90 °C and RH = 98 %. Figure 6.7b shows the WU as a function of T. Similar to the trend in d_w , WU is nearly constant water content over the range of temperatures studied, with values of WU = 53 to 78 % at T = 25 °C and RH = 98 %.



Figure 6.7. Temperature effects on (a) proton conductivity, σ , and (b) water uptake, WU.

In Figure 6.8, we plot that value of the activation energy for proton transport, E_a , the obtained from Arrhenius fits of the temperature dependence of conductivity as a function of size of the hydrophilic domains, d_{PSS} . The values of E_a show no trend, other than fluctuating around an average value of 14.5 kJ/mol. It is worth noting that this value is within error equal to the value observed in Nafion of 15 kJ/mol and larger than the expected value for the Grotthuss mechanism of 11 kJ/mol indicating that proton transport is likely via a vehicle-like mechanism.²⁵



Figure 6.8. Activation energy, E_A , of proton transport as a function of PSS domain size, d_{PSS} .

In Figure 6.9a we show the effects of changing d_{PSS} on σ at T = 25 and 90 °C and RH = 95%. The dashed lines are power-law fits ($\sigma = kd_{PSS}^{m}$) through the data. Conductivity is found to increase with increasing domain size, and reaching a plateau for samples p9 and p18. This trend is similar to that observed for d_m/d_c in Figure 6.2 and is consistent with the notion that disruption of the morphology due to crystallization has a negative impact on proton transport in PEMs. A similar effect is seen in Figure 6.9b for WU plotted as a function of d_{pss} . Data presented is at T = 25 and 90 °C, and RH = 95%. Dashed lines represent similar power-function fits ($\sigma = kWU^m$). The trend in WU is less dramatic but still shows lower values of WU for samples p1 and p3 when compared to the plateau in values observed for p5, p9, and p18. Breakout crystallization clearly has a negative impact on a PEMs ability to transport protons and absorb water.



Figure 6.9. Effect of PSS domain size, d_{PSS} , on (a) proton conductivity, σ , at T = 25 (**I**) and 90 (**A**) °C and (b) water uptake, WU, at T = 25 (**I**) and 90 (**A**) °C.

In Figure 6.10 we compare the effects of d_{PSS} on σ for the crystalline polymers of this study with the amorphous PSS-PMB samples in ref⁷. Data is presented for T = 25 °C and RH = 98% for brevity. Dashed lines represent power-law fits through the data. PSS-PMB with its amorphous structural block shows a decrease in σ with increasing d_{PSS} while PSS-PE with its semi-crystalline structural block shows an increase in σ with d_{PSS} . Despite their slight differences, these two systems converge to a nearly similar value of σ

at high molecular weight. We attribute this to the suppression of breakout crystallization in PE phase. In Figure 6.10b we show the analogous WU data. As with the conductivity the trends in WU are opposite directions of each other for the two systems. We speculate that the larger WU in PSS-PE samples at high molecular weight is due to structural differences between the two polymers rather than effects due to the crystalline structural block.



Figure 6.10. Comparison of amorphous and crystalline PSS block copolymers as a function of dry hydrophilic channel size at T = 25 °C for (a) proton conductivity and (b) water uptake.

6.4. Conclusion

We have presented hydrated SAXS, water uptake, and proton conductivity data for a series of symmetric PSS-PE copolymers with varying molecular weights. The presence the semi-crystalline PE block is found to perturb the self-assembly of the lowest molecular weight samples studied. This perturbation was found to correlate with an observed decrease in both water uptake and proton conductivity for the lowest molecular weight samples. The observed trend in water uptake and conductivity is opposite of that observed in PSS-PMB which contains an amorphous structural block. This study has shown that incorporation of a semi-crystalline structural block is not an effective method for achieving mechanical stability in low molecular weight PEMs. While this conclusion may not apply to all PEMs of interest, it certainly applies to PEMs composed of low molecular weight diblock copolymers. We speculate that further investigations further investigations into chemical crosslinking as in ref ²⁶, and more complex molecular architectures such as in ref ²⁷, are necessary to further understand how to achieve PEMs with all of the desired functionalities.

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6.6. References

1. Kreuer, K. D. Journal of Membrane Science 2001, 185, (1), 29-39.

2. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y. Solar Energy Materials and Solar Cells **2006**, 90, (5), 549-573.

- 3. Schroeder, P. Z. Phys. Chem 1903, 45, 75-117.
- 4. Geise, G. M.; Freeman, B. D.; Paul, D. R. *Polymer* **2010**, *5*1, (24), 5815-5822.

5. Park, M. J.; Balsara, N. P. *Macromolecules* **2008**, 41, (10), 3678-3687.

6. Park, M. J.; Balsara, N. P.; Jackson, A. *Macromolecules* **2009**, 42, (17), 6808-6815.

7. Park, M. J.; Downing, K. H.; Jackson, A.; Gomez, E. D.; Minor, A. M.; Cookson, D.; Weber, A. Z.; Balsara, N. P. *Nano Letters* **2007**, *7*, (11), 3547-3552.

8. Park, M. J.; Nedoma, A. J.; Geissler, P. L.; Balsara, N. P.; Jackson, A.; Cookson, D. *Macromolecules* **2008**, 41, (6), 2271-2277.

9. Wang, X.; Yakovlev, S.; Beers, K. M.; Park, M. J.; Mullin, S. A.; Downing, K. H.; Balsara, N. N. *Macromolecules* **2010**, 43, (12), 5306-5314.

10. Rangarajan, P.; Register, R. A.; Fetters, L. J.; Bras, W.; Naylor, S.; Ryan, A. J. *Macromolecules* **1995**, 28, (14), 4932-4938.

11. Ryan, A. J.; Hamley, I. W.; Bras, W.; Bates, F. S. *Macromolecules* **1995**, 28, (11), 3860-3868.

12. Quiram, D. J.; Register, R. A.; Marchand, G. R. *Macromolecules* **1997**, 30, (16), 4551-4558.

13. Hamley, I. W. Adv Polym Sci 1999, 148, 113-137.

14. Loo, Y. L.; Register, R. A.; Ryan, A. J. *Phys Rev Lett* **2000**, 84, (18), 4120-4123.

15. Loo, Y. L.; Register, R. A.; Ryan, A. J.; Dee, G. T. *Macromolecules* **2001**, 34, (26), 8968-8977.

16. Loo, Y. L.; Register, R. A.; Ryan, A. J. Macromolecules 2002, 35, (6), 2365-2374.

17. Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *Polymer* **2001**, 42, (13), 5829-5839.

18. Xu, J. T.; Fairclough, J. P. A.; Mai, S. M.; Chaibundit, C.; Mingvanish, M.; Booth, C.; Ryan, A. J. *Polymer* **2003**, 44, (22), 6843-6850.

19. Mai, S. M.; Fairclough, J. P. A.; Viras, K.; Gorry, P. A.; Hamley, I. W.; Ryan, A. J.; Booth, C. *Macromolecules* **1997**, 30, (26), 8392-8400.

20. Loo, Y. L.; Register, R.; Ryan, A. Abstr Pap Am Chem S 1999, 218, U672-U672.

21. Hamley, I. W.; Fairclough, J. P. A.; Bates, F. S.; Ryan, A. J. *Polymer* **1998**, 39, (6-7), 1429-1437.

22. Dimarzio, E. A.; Guttman, C. M.; Hoffman, J. D. *Macromolecules* **1980**, 13, (5), 1194-1198.

23. Whitmore, M. D.; Noolandi, J. *Macromolecules* **1988**, 21, (5), 1482-1496.

24. Wong, D. T.; Mullin, S. A.; Battaglia, V. S.; Balsara, N. P. Journal of Membrane Science **2012**, 394, 175-183.

25. Weber, A. Z.; Newman, J. *Journal of the Electrochemical Society* **2004**, 151, (2), A311-A325.

26. Chen, L.; Hallinan, D. T., Jr.; Elabd, Y. A.; Hillmyer, M. A. *Macromolecules* **2009**, 42, (16), 6075-6085.

27. Chen, Y. B.; Thorn, M.; Christensen, S.; Versek, C.; Poe, A.; Hayward, R. C.; Tuominen, M. T.; Thayumanavan, S. *Nature Chemistry* **2010**, *2*, (6), 503-508.