# Unraveling the Complex Hydration Behavior of lonomers under Thin Film Confinement

Shudipto K. Dishari,<sup>\*,†,§</sup><sup>(b)</sup> Christopher A. Rumble,<sup>‡,||</sup><sup>(b)</sup> Mark Maroncelli,<sup>‡</sup><sup>(b)</sup> Joseph A. Dura,<sup>⊥</sup> and Michael A. Hickner<sup>\*,†</sup><sup>(b)</sup>

<sup>†</sup>Department of Materials Science and Engineering and <sup>‡</sup>Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

<sup>§</sup>Department of Chemical and Biomolecular Engineering, University of Nebraska—Lincoln, Lincoln, Nebraska 68588, United States <sup>II</sup>Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, 1211 Geneve 4, Switzerland <sup>II</sup>NIST-Center for Neutron Research, Gaithersburg, Maryland 20899, United States

**Supporting Information** 

**ABSTRACT:** The mechanical and transport properties of submicron thick ionomer films are crucial in the study and understanding of the ionomer–catalyst interfaces in the porous electrodes of energy conversion and storage devices, such as fuel cells and batteries. Interestingly, ionomers in thin films behave differently from bulk ionomer membranes, and the behavior of these thin films is not well understood. The complex hydration behavior of thin ionomer films in the confined state is described in this work. Here, thin films (~25–250 nm) of sulfonated Radel (S-Radel) were investigated to understand thickness and hydration effects on the density and mechanical properties of these sulfonated thin polymer films. The density values obtained



from quartz crystal microbalance and spectroscopic ellipsometry showed a thickness trend similar to density values obtained from neutron reflectometry with thin films of ~25 nm thickness having lower densities than thicker, ~250 nm films. Thicker films were always more dense and less water-rich at the interface compared to thinner samples. The mechanical properties of nanoscale thick polymer films are challenging to probe with traditional techniques. A fluorescent rotor probe was thus incorporated into the polymer samples to infer the distribution of material stiffness from fluorescence lifetime measurements. The lower density of the thin films as measured by ellipsometry and neutron reflectometry rationalized greater mobility from fluorescence measurements in the thinner films when dry. When the thin sample was hydrated, the film density and interfacial water volume fraction significantly increased. Also, the samples with lower thicknesses antiplasticized, indicating poor water–polymer mobility inside the film. The plasticization properties and water–polymer mobility appeared to be controlled by both film density and competing interfacial phenomena, between the air–polymer and polymer–substrate interfaces, depending on the level of hydration.

# INTRODUCTION

Thin polymer films respond to humidity and uptake water in a distinctly different manner compared to bulk ionic polymer films and membranes.<sup>1-6</sup> When the thickness of a polymer film approaches tens of nanometers, the properties of the films are dominated by the free and confined interfaces. Confinement constrains the mobility of the polymer chains, changes the morphology, induces density gradients, and influences the modulus and hydration behavior of the material.<sup>3,7,8</sup> The relative strength of the interaction between water, the polymer, and the substrate determines the plasticization behavior of a film or membrane.<sup>1,9</sup> Also, the polymer-substrate interaction can lead to changes in ionic domain morphology (e.g., the lamellar phase<sup>10</sup> near the substrate interface in Nafion thin films), accompanied by large changes in water uptake at the interface which has been investigated for a number of cases.<sup>1,9,11-15</sup> It has been observed that the water uptake by polymer thin films does not always lead to the usual additive increase in volume<sup>16</sup> and that strong water–polymer interactions in thin films can lead to antiplasticization.<sup>1,9,16</sup> Modestino et al.<sup>11</sup> showed that the structure of ionic domains and film morphology in hydrated thin films are thickness dependent. Therefore, it is important to measure how thin polymer films behave under hydration as a function of film thickness,<sup>9,17–20</sup> processing,<sup>18,20–22</sup> and substrate composition.<sup>1,12,18,20,23</sup>

Ionomer thin films are an integral part of fuel cells in the porous catalyst layers.<sup>24</sup> Knowledge of hydration-induced swelling trends and mechanical properties of thin ionomer films is crucial in advanced design and understanding of

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Figure 1. (a) Chemical structure of S-Radel. (b) Working principle of fluorescent rotor probe CCVJ with chemical structure.

polymer ( $\sim 2-30$  nm thick)–catalyst interfaces to promote ion conductivity in electrode layers in proton exchange membrane fuel cells (PEMFCs).<sup>1,5,11,25–27</sup> However, our understanding of thin film behavior in this context is still incomplete.<sup>28</sup>

Sulfonated poly(arylene ether)-based ionomers<sup>29,30</sup> have been adopted for PEMFC technology due to their good mechanical properties and low cost.<sup>31</sup> Kreuer<sup>30</sup> showed that these ionomers exhibited significantly different phase segregation compared to Nafion, a well-studied sulfonated perfluoroalkyl-based polymer, in both thin film<sup>1,5,9-11,14,15,32</sup> and membrane<sup>33-35</sup> forms. The differences between sulfonated polysulfone S-Radel (Figure 1a) and Nafion arise from differences in backbone rigidity  $((T_g)_{Nafion} = 120 \text{ °C}; (T_g)_{S-Radel}$ = 220 °C)<sup>31</sup> and ionic group acidity.<sup>30,31,36</sup> S-Radel is wellstudied as a membrane,<sup>37-40</sup> but its performance characteristics as a thin film in fuel cell electrodes are still being pursued.<sup>41-43</sup>

Direct measurement of mechanical properties of thin films is challenging since conventional bulk characterization techniques (used for free-standing membranes) are difficult to employ on fragile, supported nanothin films.<sup>35,44</sup> Moreover, the presence of a substrate can significantly alter the thickness-dependent mechanical properties of a film.<sup>1,9</sup> There are continuing efforts to establish techniques to predict mechanical properties of ionomer thin films on various substrates.<sup>1,8,9,45</sup> Fluorescent rotor probe-based measurements of rigidity of thin Nafion films have been demonstrated by our group using the CCVI fluorophore (Figure 1b) in earlier reports.<sup>1,9</sup> Steady-state fluorescence intensities<sup>46–48</sup> of rotor probes exhibit sensitivity to changes in the viscosity of the local molecular environment. A high local viscosity hinders the deactivating motion of rotor probes such as CCVJ leading to high fluorescence intensity, while low viscosity leads to fluorescence quenching. Steadystate fluorescence captures the collective response of all dye molecules in the sample, and therefore this technique indicates an overall change in the film's mechanical properties and overall mobility of the polymer-water mixture. However, in some cases, nonfluorescent photoproducts may convolute the interpretation of steady-state emission data.<sup>48</sup> Time-resolved measurements eliminate the source of potential ambiguity. In addition, lifetime measurements enable one to infer important information about the distribution of environments in the sample rather than only the average provided by total intensity data. Lifetime measurements of julolidine-based rotor probes have been performed in solutions<sup>48-50</sup> and membranes.<sup>51</sup> However, TCSPC (time correlated single photon counting) of rotor probes has not been reported so far to explore the properties of hydrated thin ionomer films. The intramolecular rotation of the rotor probe is hindered if the probe experiences

an environment where water and ionomer chains also experience confinement in the film. Reduced rotation gives rise to longer lifetimes of the rotor probe (Figure 1b). On the other hand, if the water and ionomer are more mobile, the lifetime of rotor probe is shortened due to increasing twisted intramolecular charge transfer (TICT).

The difference in dye mobility in dry and hydrated films can be sensitive to composition gradients in the sample. The density obtained from quartz crystal microbalance (QCM, mass) and spectroscopic ellipsometry (SE, thickness) measurements is an average density value which can be validated by neutron reflectometry (NR).<sup>52</sup> NR not only probes the bulk density and any gradients present but also gives the volume fractions of water, polymer, and void inside the films.<sup>10,12,14,15,53–55</sup> In one study of Nafion thin films, NR was even able to reveal the phase segregation of sulfonate groups from the fluorocarbon chains within interfacial lamellae.<sup>13</sup> Vogt et al. showed that the water concentration profile is correlated to the polymer film's adhesion to the substrate<sup>54</sup> and the film modulus.<sup>55</sup> Thus, simultaneous measurements of fluorescence lifetime and NR are useful to explain the inherent structure-induced changes in density and mechanical properties of films upon hydration as well as interfacial phenomena.

In the current work, we spin coated films of S-Radel doped with CCVJ and measured the fluorescence lifetime of CCVJ as a function of film thickness and relative humidity. Water mass uptake (QCM, NR) and film thickness measurements (SE, NR) were used to calculate the density of the samples. The density and lifetime data on films of varying thickness are discussed in the context of film composition and the density profile obtained from NR. This work provides a clear picture of the hydration-induced compositional, structural, and mechanical changes in thick and thin S-Radel films.

## METHODS

**Materials.** 9-(2-Carboxy-2-cyanovinyl)julolidine (CCVJ) was purchased from Sigma-Aldrich (St. Louis, MO). Sulfonated Radel (S-Radel) polymer with IEC (2.5 mequiv  $g^{-1}$ ) was synthesized as reported earlier.<sup>56</sup>

Film and Membrane Preparation. S-Radel polymer was dissolved as a 10 wt % solution in dimethylacetamide (DMAc). This stock solution was further diluted with DMAc to obtain 5 and 2 wt % solutions. For time-resolved fluorescence measurements, CCVJ in DMSO (5 mg mL<sup>-1</sup>) was added to 10, 5, and 2 wt % S-Radel solutions to maintain a dye:polymer mass ratio of 0.003. Bare silicon wafers with native oxide were cut into (2 cm  $\times$  2.5 cm) pieces, rinsed with methanol, dried

under flowing air, and UV-ozone treated for 20 min. 10, 5, and 2 wt % S-Radel solutions containing CCVJ were spin-coated at 3000 rpm with target thicknesses of ~250, 90, and 25 nm, respectively. All films were dried under vacuum for 3 h at 42 °C followed by 7 h at 100 °C and then cooled to room temperature for 12 h under vacuum.

S-Radel membrane was cast from 8 wt % polymer solution in DMAc and dried overnight in a convection oven at 80 °C. The cast membrane was stored in 0.5 M HCl solution to maintain the material in acid form. The membrane was removed from the acid solution prior to use, immersed in water for 12 h, and dried under vacuum at 42 °C for 12 h. The membranes were then immersed in CCVJ solutions ([CCVJ] = 0.018 wt % in 1:1 mass  $C_2H_5OH$ : water solution) for 18 h, rinsed, dried for 1 day under vacuum at 42 °C followed by 7 h at 100 °C, and then cooled to room temperature.

Water Uptake. Water uptake of thin films was measured using a quartz crystal microbalance (QCM) (MAXTEK, Inficon, NY) and Sauerbrey analysis. Thermally evaporated SiO<sub>2</sub>-coated 6 MHz crystals (Tangidyne, SC) were employed as QCM substrates. Water uptake of membranes was studied via thermogravimetric analysis (TGA) (see Supporting Information). The % mass of water uptake was calculated as follows:

% mass of water uptake  
= 
$$\frac{\text{mass of water}}{\text{mass of dry film (or membrane})} \times 100\%$$

. 1

Thickness. The thicknesses of all the polymer films were measured using variable angle spectroscopic ellipsometry (SE) (M-2000, V.A.S.E., J.A. Woollam Co., Inc., Lincoln, NE) with a spectral range of 0.7-5 eV at ambient conditions. The angle of incidence was 75°. The RH-dependent thickness measurements were performed using a liquid cell (J. A. Woollam Co., Inc., Lincoln, NE). A bare QCM crystal with a thermally evaporated oxide layer and a bare silicon wafer with a native oxide layer were used as substrate models for polymer film measurements as appropriate. The psi ( $\psi$ , amplitude ratio) and delta ( $\Delta$ , phase difference between p- and s-polarized light waves) curves were fitted with a Sellmeier model The dry state (0% RH) thickness values of the films were used to denote the films in the entire discussion unless otherwise stated. Swelling (%) of the samples was calculated as follows:

% swelling = 
$$\frac{(\text{film thickness})_{\text{RH}} - (\text{film thickness})_{\text{dry}}}{(\text{film thickness})_{\text{dry}}}$$

× 100%

The density  $((mass)_{QCM}/((thickness)_{SE} \cdot area))$  values were estimated from the water uptake and thickness data for films on SiO<sub>2</sub> crystals using  $1.23 \text{ cm}^2$  as the active area.

Time-Resolved Fluorescence. Fluorescence lifetimes of CCVJ in films were measured using a custom-built timecorrelated single photon counting (TCSPC) setup.<sup>57</sup> The excitation source (440 nm) was the doubled output of a cavitydumped Ti:sapphire laser (Coherent Mira 900F + APE PulseSwitch) operating at a repetition rate of 3 MHz. Fluorescence data were collected at the magic angle with respect to the excitation polarization through a monochromator (ISA H10) with an emission bandpass of 4 nm. The instrumental response of this setup was 25-30 ps (fwhm). Significant nonexponentiality was observed in the fluorescence decay which was attributed to a distributed population of CCVJ

environments. Therefore, the decays were fitted to a stretched exponential function,  $I(t) = I_0 \exp\{-(t/\tau)^{\beta}\}^{58,59}$  where  $I_0$  is the intensity at t = 0,  $\tau$  is the time constant, and  $\beta$  is the stretching parameter ( $0 \le \beta \le 1$ ). The average decay times at each RH were calculated as  $\tau_{\rm RH} = (\tau/\beta)\Gamma(1/\beta)$  with  $\Gamma$  being the gamma function.

RH-dependent lifetime measurements were performed by connecting a custom-built RH control system (as described in next section) to the fluorometer sample cell to produce a sample environment with specific water activities.

Humidification. Air at dew point was produced by a sparging system. The humidified air was mixed with a stream of dry air and the flow rates of the wet and dry streams were varied to achieve the desired relative humidity. An RH probe (Omega HX15-W) was connected to the gas outlet of the humidity chamber for in situ monitoring of the relative humidity of the sample environment. It is to be noted that each sample was dried for 2 h inside the humidity chamber by purging dry air to remove any moisture adsorbed during sample exchange from the drying oven to the humidity chamber prior to increasing the RH.

Neutron Reflectometry (NR). NR data were obtained using the MAGIK (multiple angle grazing incidence K (vector)) off-specular neutron reflectometer (NG-D) at the National Institute of Standards and Technology (NIST) Center for Neutron Research which is similar to an instrument described in the literature.<sup>60</sup> NR measures variations in reflected intensity of a collimated monochromatic beam of neutrons as a function of the grazing angle of incidence,  $\theta$ . Fitting the data determines the scattering length density (Nb) as a function of depth, z, with sub-Angstrom accuracy for features as small as typically 0.5-2 nm determined approximately by  $2\pi/Q_z$  (maximum), where  $Q_z$  is momentum transfer vector in the *z*-direction and  $\lambda$  is the neutron wavelength (5 Å):

$$Q_z = \frac{4\pi \sin \theta}{\lambda}$$

 $Q_z$  (maximum) is the largest  $Q_z$  for data with features above the noise. At a given  $z_i$ , the scattering length density (Nb) is the sum over all isotopes of the bound coherent scattering length of that isotope  $b_{c,i}$  times the number density of the isotope  $N_i(z)$ :

$$Nb = \sum_{i} b_{c,i} N_i(z)$$

Sensitivity to certain elements with large isotopic differences in scattering length can be optimized by choice of the isotope, for example H (or water) and Li.  $D_2O$  (Nb = 6.36 × 10<sup>-6</sup>) is therefore used herein since it gives a larger contrast than H<sub>2</sub>O  $(Nb = -5.59 \times 10^{-7})$  to dry S-Radel  $(Nb = 2.18 \times 10^{-6})$  and also can be distinguished from voids (Nb = 0). The volume fractions of two components of a film with known scattering length density (determined experimentally or by known composition and density) can be determined from Nb(z)using the lever rule. While NR measures the entire depth profile of the SLD, in order to compare the results from NR to other techniques that average over the entire film, the average (or overall) film density was calculated from the densities of the water and polymer phases, weighted by both the layer thickness and volume fractions within each layer. Modeling and data fitting were performed using the Parratt formalism and reflpak software.<sup>61</sup> The thickness of the films can also be measured from the difference between two maxima or minima of subsequent fringes in reflectivity fits using the equation



**Figure 2.** Time-resolved fluorescence of rotor probe CCVJ in S-Radel thin films on a silicon wafer. Fluorescence decay constants  $(\tau_{RH} / \tau_0)$  (b), and stretching exponent ( $\beta$ ) (c) of S-Radel thin films ( $\blacksquare$ , 241 nm;  $\bullet$ , 88 nm;  $\blacktriangle$ , 26 nm) as functions of relative humidity.



Figure 3. Hydration behaviors of S-Radel thin films: (a) mass % change (uncorrected: empty symbols; corrected: filled symbols) and (b) % swelling (with error bars) of S-Radel thin films upon moisture sorption.

$$Q_z = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}$$

where d is the film thickness.

The 3 in. diameter silicon wafers with a native oxide layer (EL-CAT Inc., Ridgefield Park, NJ) were used as NR substrates. The substrate cleaning and film preparation procedures were the same as those used to make samples for other measurements. The samples were inserted into a temperature and humidity controlled chamber and equilibrated at certain RH values with humidified argon gas for NR measurement as described elsewhere.<sup>13</sup> The sample temperature was maintained at 31  $\pm$  0.2 °C, and the dew point was controlled by a humidity generator with argon as the carrier gas. The temperature of the entire gas-handling system was maintained above the dew point to avoid condensation. The relative humidity was recorded during data acquisition; however, for greater accuracy the reported RH values were determined from the sample temperature and dew point.

#### RESULTS AND DISCUSSION

In this work, we used spun-cast s-Radel thin films on silicon wafers to obtain polymer films of thickness ~250, 90, and 25 nm from 10, 5, and 2 wt % S-Radel solutions in DMAC, respectively. For the fluorescence lifetime experiments, rotor probe CCVJ was added to the polymer solution (dye:polymer mass ratio = 0.003). The annealed samples were placed in an enclosed chamber with a continuous supply of air with controlled humidity (0–95% RH). The details of sample preparation, heat treatment, and humidification procedure are described in the Methods section. The emission lifetimes of annealed S-Radel samples of varying thickness were measured

(Figure 2a–c). The decay constant,  $\tau_{RH}$ , of CCVJ in the dry 26 nm thick film (Figure 2a) was ~1010 ps, which was significantly lower than the  $\tau_{\rm RH}$  of ~1300–1450 ps for the dry 88 and 241 nm thick films. When the mobility of a rotor probe increases (typically in a less viscous and/or less confined environment), the twisting becomes more facile and charge transfer thereby leads to quenching of the fluorescence and lower  $\tau_{\rm RH}$  (Figure 1b). The shorter lifetime observed in the thinner 26 nm film is thus attributed to the less viscous, more mobile, and less rigid nature of the thinner film in the dry state. We also found that the rigidity of the dry films decreased (or mobility of polymer chain increased) as the density of the films decreased (density measurements shown later). Figure 2b shows the ratio of fluorescence decay constants at a given RH  $(\tau_{\rm RH})$  to that in the dry state  $(\tau_0)$ .  $\tau_{\rm RH}/\tau_0$  for the 26 nm thick film increased from 1 to 1.06 when the humidity increased from 0% to 25% RH and remained relatively flat with a further increase in RH. This trend indicates confinement of the thin film upon hydration and antiplasticization or a stiffening of the material with exposure to water vapor. On the contrary, hydration of thicker films (88 or 241 nm samples) did not show confinement effects. The lack of confinement in the thicker samples led to plasticization and a viscosity decrease when water was added, and the  $\tau_{\rm RH}/\tau_0$  ratio declined. Also, the lifetime of CCVJ at 94% RH shortened significantly in the 241 nm sample (40% decrease) as opposed to 26 nm sample (10% decrease) compared to the dry state. This is an indication of a larger increase in water-polymer mobility within the thicker films upon hydration. The observed trends in hydrationinduced changes in fluorescence properties of CCVJ in confined and bulk polymer films have also been observed for Nafion samples from steady-state measuremens<sup>1,9</sup> and correlated to interfacial ionomer confinement triggered by hydrogen bonding with water.<sup>16,62</sup>

The term  $\beta$  (Figure 2c) quantified the distribution of CCVJ fluorescent lifetimes in the samples. The higher the value of  $\beta$  (from 0 to 1), the more the lifetime of the dye in the film approaches an ideal exponential decay. A  $\beta$  of 1 is observed in homogeneous liquids;<sup>58</sup> thus,  $\beta$  values for these experiments can serve as a measure of the distribution of environments occupied by the dye. Dry films of all thicknesses showed high values of  $\beta$  (~0.72–0.76) and the  $\beta$  values declined with increasing RH, which indicates that the films became more heterogeneous during hydration. The range of  $\beta$  values in the 26 nm thick film was less than the range observed for the thicker films indicating a more homogeneous environment within the thin film as the RH was increased.

Figure 3a shows the % mass uptake of water for S-Radel films on SiO<sub>2</sub>-coated QCM crystals as a function of film thickness and RH. The water mass uptake data were corrected since prior studies showed evidence of water accumulation within the porous structure of the QCM crystals.<sup>63–65</sup> We used the data of Kushner and Hickner<sup>65</sup> to calculate the mass of water sorbed within the SiO<sub>2</sub> layer of the porous QCM crystal. We subtracted that amount of water (sorbed by QCM crystal) from the water mass sorbed by our S-Radel films which yielded corrected mass of water sorbed only inside the polymer films. The spectroscopic ellipsometry data were not corrected as the ellipsometry data were taken with regular silicon wafer with a native oxide which is not porous. The mass % of water sorbed increased as the film became thinner. This thickness trend in water uptake was consistent with that of Nafion thin films.<sup>1,9</sup> For Nafion, the larger water uptake of thinner films (Figure S1) was attributed to interfacial water-rich regions<sup>1,9,10,12-14</sup> which became the predominant volume fraction of the entire film as the film became thinner. The mass % of water sorption for the membrane (25  $\mu$ m, Figure S2 in Supporting Information) at 94% RH was 43% and was close to that of the thickest (240 nm) film studied (32%, Figure 3a). This observation proves that bulk films and membranes behave in a very different manner as compared to supported thin films.

The swelling behavior of both thick and thin films is shown in Figure 3b. Most interestingly, thinner films swelled more than thicker films. These results were in agreement with Vogt's observation<sup>53</sup> of enhanced swelling in thinner films. The swelling and water uptake both increased as the dry state S-Radel film thickness decreases. However, swelling was insignificant up to 50% RH at a given film thickness while water uptake was not. Benziger et al.<sup>66</sup> showed that the volume of mixing of water and polymer is negative ( $\sim -0.05 \text{ cm}^3/\text{cm}^3$ ) in a similar aromatic polymer, sulfonated poly(ether ether ketone) (SPEEK), while nonaromatic Nafion ionomer showed a positive volume of mixing. This insight supports the low swelling of S-Radel films up to 50% RH despite significant water uptake. Beyond 75% RH, an abrupt increase in swelling was observed for the 25 nm thick film, as commonly observed in thin films of other polymers.<sup>54,67–69</sup> Such a high swelling was accompanied by a small decrease in  $\tau_{\rm RH}/\tau_0$  (Figure 2b) when the RH increased from 75% to 95% RH which indicates a strong water-polymer interaction preventing mechanical plasticization of the film.

The density values (Figure 4) were calculated from the mass (QCM) and thickness (SE) of dry and hydrated S-Radel films as shown in Figure 3. The densities obtained using QCM/SE



Figure 4. Density of S-Radel thin films as a function of water activity (■, 230 nm; ●, 80 nm; ▲, 23 nm).

were closer to what reported by NR (1.28 g/cm<sup>3</sup> (NR) and 1.15 g/cm<sup>3</sup> (QCM/SE) for 27 nm thick film at 25% RH) as shown in Table 1. The density of the dry films decreased as the samples became thinner, which is in agreement with the trends in fluorescence lifetime  $(\tau_{\rm RH})$  with thickness (Figure 2a) and indicates the possible presence of higher void fractions and lower densities in thinner films. Dry state refractive indices (Figure S3) and density both followed a similar thickness trend. While the 23 nm thick film showed the lowest density in the dry state, it showed the highest density change when water was absorbed in the film. The same film showed the largest antiplasticization (increased  $\tau_{\rm RH}/\tau_0$  from dry state) of all films at intermediate (30%) RH. Additionally, while the  $\tau_{\rm RH}/\tau_0$  ratio decreased significantly at higher RH (e.g., 95% RH) in the 240 nm thick film, the density did not. This indicates that there are factors other than density which dominate the water-polymer mobility, especially under humid conditions.  $T_g$  suppression, an indication of increased segmental motion of polymer chains, has been observed for other supported polymeric systems when dry with decreasing film thickness. Such a phenomenon has been prominent within 20 nm (comparable to the thickness of our thinnest film studied ~23 nm) from the free surface of supported polymer thin films.<sup>70</sup> It is to be noted that the polymer-substrate interaction, if attractive, can lead to increase in  $T_{\sigma}$  and decrease in mobility as seen in polymer-inorganic nanoparticle composite systems and films.<sup>70,7</sup>

In the absence of water (dry state),  $au_{\rm RH}$  and density trends with thickness are in agreement as the free-surface effect (polymer-air interface) and film density dominate the dye mobility. That is why a less dense thin film, where film thickness approaches the thickness of a typical free-surface effect region, showed higher dye mobility (shorter  $\tau$ ) in the dry state than a dense, thick film. On the contrary, in the hydrated state, a larger degree of stiffening was observed in a less dense (in the dry state) 23 nm thick film. At hydrated state, the polymer-substrate interface can start to dominate over free surface in a film if water accumulates near substrate interface, and a strong hydrogen-bonding interaction among water, polymer (-SO<sub>3</sub>H group in S-Radel), and substrate (-SiOH group on native  $SiO_2$  surface) is present at the substrate interface. Sufficiently strong interfacial bonding initiated by water molecules can stiffen a wet film even if the film is less dense. These indicate that  $\tau_{\rm RH}$  depends not only on film density but also on competing effects of free and substrate interfaces (Scheme 1).

Figure 5 illustrates the fits of neutron reflectivity data as a function of momentum transfer vector,  $Q_z$ . S-Radel films on native SiO<sub>2</sub> with thickness of 26 nm (Figure 5a) and 258 nm

Table 1. Densities	$(\rho)$ , Hydration 1	Numbers $(\lambda)$ , and V	Volume Fractions ( $oldsymbol{\phi}$	) of Solid Polymer,	Void, and Water	Phases in S-Radel
Films						

sample thickness (nm)	RH (%)	$(\phi)_{ m solid\ polymer,NR}$	$(\phi)_{ m void,NR}$	$(\phi)_{ m D_2O,NR}$	$( ho)_{\mathrm{film,NR}}^{a}$	$( ho)_{\mathrm{film},\mathrm{QCM/SE}}{}^a$	$(\lambda)_{\text{film,NR}}^{a}$	$(\lambda)_{\text{film,QCM}}^{a}$		
27	0	0.81	0.19	0	1.14	0.96	0	0		
	50	0.81	0	0.19	1.28	1.15	4.05	6.86		
	94	0.67	0	0.33	1.27	1.05	8.24	20.28		
258	0	0.85	0.15	0	1.20	1.36	0	0		
	50	0.82	0	0.18	1.31	1.40	3.63	2.50		
	94	0.64	0	0.36	1.29	1.31	8.55	7.05		
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The subscripts NR, QCM, and QCM/SE symbolize the techniques used to obtain those parameters.

Scheme 1. Factors Impacting Mechanical Properties and Mobility of Thin S-Radel Films<sup>a</sup>



"Green oval-shaped symbols represent dye CCVJ, while red chains in yellow matrix represent polymer chains in film. The light blue layers near substrate indicate the water accumulation.

(Figure 5b) were equilibrated at 0%, 50%, and 94% RH. Models consisting of 1-3 polymer layers were used as required to fit the data. No systematic density gradient was observed in any of the samples. With the increase in hydration, the Kiessig fringe spacing became narrower, indicating swelling of the film. The water volume fraction was assumed to be zero in the film samples at 0% RH. The solid polymer density (without void) in the dry state was assumed to be  $\sim 1.4 \text{ g/cm}^3$ , as reported for dense membranes of this material.<sup>72</sup> The dry state density of each layer of a sample was determined from the known composition and scattering length density of a layer at 0% RH. The void fraction in each layer was calculated using a solid polymer density (without void) of 1.4 g/cm<sup>3</sup>. It was assumed that in the hydrated state the films consisted of two phasespolymer and water-where polymer and water were phase segregated into separate domains and there were no voids in water-equilibrated films. The bulk density of deuterated water  $(D_2O)$  was used as 1.11 g/cm<sup>3</sup> throughout the films. In addition, the solid polymer density was assumed to be the same in all the layers in a sample at a given RH (>0%). The volume fraction of solid polymer, D<sub>2</sub>O, and void for dry and hydrated films are calculated and presented in Table 1 and Table S1.

For dry samples, the density of the 27 nm thick film (1.14 g/ cm<sup>3</sup>, Table 1, S1) was 81.4% of the bulk polymer density of 1.4  $g/cm^3$ , while the density of the top (1.14  $g/cm^3$ , Table S1) and bottom layer (1.20 g/cm<sup>3</sup>, Table S1) of the 258 nm thick film was 81.7% and 85.6% of bulk density, respectively (Table S1).

Spectroscopic studies<sup>73</sup> on similar materials suggest that this lower density is the result of increased free volume in the thin films. The void fraction was calculated as 18.6 vol % for the 27 nm thick film, while 18.3 and 14.4 vol % were calculated for the top and bottom layer (overall void fraction of 15 vol %) for the 258 nm thick film, respectively. The overall film densities of the 27 and 258 nm thick films, obtained by fitting the NR data, are also shown in Table 1 and compared with the values obtained from QCM/SE. At 0% RH, the 258 nm thick S-Radel film had a density  $(1.20 \text{ g/cm}^3)$  higher than the 27 nm thick sample (1.14) $g/cm^3$ ) which corresponds with the density trends derived from QCM/SE data (1.36 and 0.96 g/cm<sup>3</sup> for 258 and 27 nm thick samples, respectively). The higher overall void fraction (and low density) in the thinner film also rationalizes the higher mobility in the thinner sample in the dry state as seen in Figure 2a. The less dense structure of the thinner films originated from the film preparation procedure used in this work. The thickness of the spin-coated films was controlled by varying the polymer concentration in solution. The 10 and 2 wt % polymer solutions were spun on the substrate to obtain  ${\sim}258$  and  ${\sim}27$ nm thick polymer films, respectively. The thicker (258 nm) film was moderately dense due to a relatively viscous polymer solution used to make the film. On the contrary, a dilute polymer solution will have lower viscosity and less chain entanglement<sup>74</sup> as compared to a concentrated solution. The less entangled chains,<sup>74</sup> when spin coated, vitrified during solvent removal at room temperature and resulted in a lower



Figure 5. Neutron reflectivity of S-Radel films. NR data (symbols) and best model fits (lines in red) for S-Radel films with dry thickness of 27 nm (a) and 258 nm (b) at 0% (black), 50% (blue), and 94% (green) RH are shown. Error bars and uncertainties indicate one standard error throughout this paper.



Figure 6. Nb profiles of S-Radel films. Films with dry thickness of 27 nm (a) and 258 nm (b) were studied at at 0% (black), 50% (red), and 94% (blue) RH. Inset shows zoomed view of the profile near the interface.

density in the thinner films. Usually the lower density can be eliminated by annealing as thermal treatment relaxes the polymer chains. However, S-Radel films could not be annealed above  $T_g$  (250 °C)<sup>75</sup> since annealing at such a high temperature decomposes the sulfonic acid groups of the polymer.<sup>76</sup> Thus, the heat treatment of the films at 100 °C (used in this study) could not effectively eliminate the voids in thinner 27 nm films.

The density of the films increased initially when they absorbed water. Also, thinner (27 nm) films showed higher RH induced densification as compared to the thicker (258 nm) sample at 50% RH. This data is in agreement with the observed increase in rigidity of the film at 50% RH compared to the dry state (Figure 2b). In the 27 nm thick film, the void fraction when dry (18.6%) was similar to the measured water volume fraction (19%) at 50% RH (Table 1). This observation possibly indicated that the voids filled with water at 50% RH in

minimally swollen (7% thickness increase) samples. A further increase in RH from 50% to 94% caused swelling of the film, and thus the water volume fraction increased. Also, a decrease in density of the films was observed when RH increased from 50% to 94% RH, indicating plasticization of the films as seen in fluorescence lifetime measurements (Figure 2a,b). The trend in density values (with RH and film thickness) obtained from NR and QCM/SE complemented each other (Table 1). However, the density values obtained from NR and QCM/SE did not agree perfectly (Table 1). Also, the % swelling and hydration number ( $\lambda$ ) of films obtained from NR (Table S1) did not change with thickness. It is to be noted that QCM, SE, and fluorescence lifetime measurements were performed within a day of the sample preparation, and the films thus may have not relaxed due to physical aging of the thin films. On the contrary, a strong thickness effect was not observed in the NR data,

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possibly due to the relaxation of the thinner films during the lengthy NR measurement (which took about a week from the day of sample preparation). Prior evidence from the literature shows that thinner dry films can relax faster than bulk films.<sup>70</sup> Moreover, some of our prior experiments with mobility sensitive dye CCVI in freshly made and 1 week old Nafion films have also shown that the antiplasticization can drastically change in thinner (<100 nm) films upon aging (results to be reported) and become closer to the behavior of thicker films. On the other hand, the antiplasticization behavior of thicker films was not very sensitive to aging. The relaxation process occurred within 200 min in submicrometer thick films in other work." Such relaxation and reorganization of polymer chains (in the dry state) may lead to chain packing/conformation not favorable for water uptake (leading to % swelling insensitive to thickness).<sup>78</sup> Abuin et al. showed that the hydration number  $(\lambda)$  of Nafion nanothin films aged up to 2 days can be higher (up to 2  $\lambda$  units greater) than the same films aged between 10 and 30 days. The large decrease in water sorption (calculated as mass of water/mass of dry Nafion) between 0 and 40 days was attributed to slow relaxation and change in microstructure of the Nafion films.<sup>79</sup> The roughness and thickness of the silicon oxide layer on the QCM crystals (~10 nm RMS roughness, 200 nm thick thermally evaporated oxide) and wafers used for NR (~0 nm RMS roughness, 0.53 nm thick native oxide) were very different, which may be another contributing factor causing such differences in density values.<sup>63</sup>

Figure 6 shows the scattering length density (Nb) profiles of S-Radel films at 0%, 50%, and 94% RH. For a given composition, the Nb values are proportional to the density  $(\rho)$  of the material. At 0% RH, the 27 nm thick film consisted of single layer with an Nb value of  $2.07 \times 10^{-06}$  (Figure 6a) which was equivalent to a density of 1.14 g/cm<sup>3</sup> (Table 1 and Table S1). In the dry state, the 258 nm thick sample consisted mostly of a thick bulklike layer (~252.8 nm thick, Figure 6b and Table S1). Despite the differences in measured data between NR and QCM/SE, the fitting of NR data yielded water-rich layers near substrate interface for both 27 and 258 nm thick films upon humidification, and a 27 nm thick film was more water rich than a 258 nm thick film near substrate interface. The water volume fraction in the polymer layer adjacent to the substrate was ~49% in 27 nm thick film at 50% RH, while it was only ~18% in 258 nm thick film at the same RH (Table S1). This supports the stronger RH-induced antiplasticization of the thinner film (as seen in lifetime studies) originating from the constraints to the motion of water and polymer chains imposed by the stronger hydrogen-bonding interaction at the substrate (native SiO<sub>2</sub>) interface. The waterrich layer in 27 nm thick film evolved into an ~1.05 nm thick pure water layer (Nb =  $6.36 \times 10^{-6}$  for D<sub>2</sub>O) at the native SiO<sub>2</sub> interface at 94% RH. Such a high water accumulation near the interface is likely to be facilitated by the less dense nature of the thinner films and leads to plasticization of the 27 nm thick film. A similar interfacial water segregation was seen in Nafion films coated on porous hydrophilic substrates.<sup>12</sup>

On the contrary, the interfacial water-rich layer was thicker (~2.45 nm) in the 258 nm thick film (as compared to the 27 nm thick film) at 94% RH, but the water volume fraction (~89%) was lower. The other two layers (top layer in contact with air and the bulk middle layer) of the 258 nm thick films were less water rich ( $\varphi_{D_2O} \sim 34-43\%$ ) at 94% RH. In both the dry and 50% RH cases, the fits included a very thin surface layer

of nearly the same Nb value as the bulk, which may be interpreted as the effects of surface roughness.

In short, thicker (~258 nm thick) and denser films had a lower vol % of interfacial water (substrate interface) at all RHs with smaller change in overall density (Table 1 and Table S1). NR also provided evidence of densification  $((\rho)_{\text{film,NR}} \text{ Table 1})$ of the 27 nm thick film when the voids were filled with water (at 50% RH) as well as when water segregates near substrate interface (50%–94% RH range).  $\tau_{\rm RH}/\tau_0$  (Figure 2b) increased (0%-50% RH range) and slightly decreased (50%-94% RH range) for the same film. All these observations indicate a high affinity of water for the silica surface<sup>80,81</sup> and a strong interaction of water near the substrate interface causing rigidity and poor water mobility in hydrated thinner films. Unlike perfluorinated NAFION thin films on hydrophilic surfaces including native SiO<sub>2</sub> studies with NR, the Nb profile did not show any evidence of water-polymer lamellar multilayer interfacial structure in the hydrated aromatic S-Radel thin films on native SiO<sub>2</sub> (no significant layering in the Nb close to substrate interface) for any thickness or humidity values. Such observations (water accumulation, but no water-polymer alternate lamella formation near substrate) are consistent with other aromatic ionomers in thin films.<sup>82</sup> This lack of order in S-Radel thin films in the thickness direction is likely due to the difference between Nafion's ability to self-assemble and S-Radel's previously measured disordered hydrophilic/hydrophobic nanophase morphology in membranes.<sup>83</sup> In NAFION, the sulfonic acid is attached via extended side chains, allowing greater segregation between the sulfonic acid and fluorocarbon backbone compared to S-Radel where sulfonic acid is closely attached to a more rigid backbone thus inhibiting self-assembly.

#### CONCLUSIONS

A thorough investigation of S-Radel nanoscale thin films was performed as a function of RH and thickness using fluorescence lifetime, QCM, SE, and NR measurements. Film densities and compositions obtained from QCM/SE and NR were analyzed to develop a deeper understanding of the role of hydration on the physical and mechanical properties of the thin polymer films. An  $\sim$ 27 nm thick S-Radel film had a lower density and lower stiffness compared to a thicker ~258 nm film under dry conditions. The sorption of water into the samples densified the thinner 27 nm film more than the 258 nm thick film at 50% RH. Strong water-polymer-substrate interactions were evident as water filled the voids and accumulated near the substrate interface and the fluorescence lifetime of the CCVI rotor probe increased (water-polymer mobility decreased). A further increase in RH to 94% plasticized the thicker 258 nm film (as evidenced by a large decrease in  $au_{
m RH}/ au_0$ ) with an insignificant change in density which indicates that mechanical properties of and water mobility within thinner films are complex functions of density and polymer-air and polymersubstrate interfacial phenomena. Combining the information from lifetime with water distribution and density data from NR and SE enabled a reliable interpretation of thin film hydrationinduced changes in density and mechanical properties of these samples.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11888.

Details of NR data, refractive index, and water uptake of polymer thin films (PDF)

## AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail hickner@matse.psu.edu, Tel 814-933-2204, Fax 814-865-2917 (M.A.H.).

\*E-mail sdishari2@unl.edu, Tel 402-472-7537, Fax 402-472-6989 (S.K.D.).

#### ORCID 0

Shudipto K. Dishari: 0000-0003-1679-2332 Christopher A. Rumble: 0000-0003-1757-8960 Mark Maroncelli: 0000-0003-1633-1472 Michael A. Hickner: 0000-0002-2252-7626

## Notes

The authors declare no competing financial interest.

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