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Immobile Light Water and Proton−Deuterium Exchange in Polyelectrolyte Multilayers

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ABSTRACT: To describe the swelling of polyelectrolyte multilayers (PEMs) on a molecular scale, the PEM architecture is varied. The polyanion is poly(styrenesulfonate) (PSS) and the polycation poly(allylamine hydrochloride) (PAH). PEM either consists of 10 protonated polyelectrolyte bilayers (p_{10}), 10 deuterated bilayers (d_{10}), or two different blocks, p_5d_5 or d_5p_5. Prior to the exposure to 100% relative humidity (RH) D_2O or H_2O, the PEM is immersed in liquid D_2O or H_2O, respectively. The obtained scattering length density profiles provide insight into the exchange rates of the constituent molecules: The data indicate that three mobile protons of each PAH monomer are replaced by deuterium ions, yet most of the H_2O molecules found in PEM at 0% RH remain bound at 100% RH D_2O. This is in consistency with the fact that the core of PEM is in a glassy state. At 0% RH, the amount of bound water in the deuterated layers does not depend on the film architecture, whereas in the protonated layers it does.

Introduction

In materials science, polyelectrolyte multilayers (PEMs) are widely used as coatings or membranes. The basic principle of PEM formation is the sequential adsorption of positively and negatively charged polyelelectrolytes.[1−3] Ideal PEMs consist of stratified layers which were grown step-by-step into the third dimension. While the principle is clear and the technical applications are broad, many questions concerning the molecular scale remain open. Especially the inter- and intramolecular interactions, which are relevant for the multilayer formation, are still poorly understood. Systematic investigations are necessary to identify and describe those interactions beyond simple electrostatics. In this paper we investigate water/polymer interaction.

We focus on poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) prepared from a NaCl solution as a well-characterized model system[1] to probe the contribution of secondary intramolecular forces effective during multilayer buildup. We found that it is necessary to decrease both the range and the amplitude of the electrostatic force by using an ion concentration of at least 0.1 mol/L in the solution.[4] Under these conditions the thickness of a deposited polycation/polyanion bilayer pair increases due to heating the deposition solution.[5,6] Above a limiting temperature T_{limit} PEM preparation is no longer possible.[7] This finding is attributed to the hydrophobic effect: In cold water (near room temperature), the water molecules surrounding the nonpolar solute (i.e., the polyelectrolyte backbone and some of the functional groups) form good hydrogen bonds (low enthalpy) in structured cages (low entropy). The molecules surrounding the hydrophobic groups are called the first shell water. With rising preparation temperatures more first shell water configurations are accessible (higher entropy). However, some configurations have weaker or unformed hydrogen bonds and/or van der Waals interactions (higher enthalpy), which allows the hydrophobic chains to get closer to each other.[4,7] In turn this leads to an increase of the polyelectrolyte coverage and interpenetration at each single deposition step.

The heating experiments on capsules prepared from PEMs are also intriguing.[8,9] Heating the capsules in an autoclave eventually leads to an irreversible expulsion of all water and a decrease of the capsule surface area as well as a thickening of the capsule wall.[10] At room temperature, the capsules are swollen in an aqueous solution, and thus contain more water than the tightly bound water observed in flat PEMs at 0% RH. For flat PEMs immersed in water or exposed to 100% RH the thickness increases by about 30%, while the water content is basically the same.[11,12] The water uptake or loss is described as almost sudden. However, to the best of our knowledge it has not been possible before to obtain equilibrium neutron reflectivity curves in 100% RH D_2O, since the exchange of heavy and light water is slower than a day.[3]

PEMs are often described by a three-zone model, with the precursor zone next to the support and the final deposited layers in the outer zone. The second zone, the core of PEM, is elastic or glassy, while the zone next to the substrate is softer.[13−15] The elastic modulus of the PAH/PSS multilayer was studied in dry and wet states, and it decreased from 5.8 ± 0.4 GPa to 590 ± 90 MPa after it had been soaked in deionized water.[16,17] This suggests that swelling reduces the elastic constant.

To improve the contrast in neutron reflectivity experiments, selectively deuterated polyanion layers are used in PEMs. With this labeling technique it is possible to monitor the roughness of the internal interfaces, the internal order of the multilayers (superlattice structure by partial deuteration), and the water content, although the deuteration may affect structural and transport properties. In some neutron reflectivity studies, more bound water has been observed in deuterated polyanion layers sandwiched between some protonated polycation/polyanion bilayers,[1,3] but the quantitative data vary by about a factor of 3. An increased attractive enthalpy of D_2O molecules leads to an increase of both the melting and the boiling point of heavy

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water compared to normal water. Because it is not clear, whether this increased enthalpy is important for the formation of first hydration shell, or rather for the interaction of PEMs with loosely bound water, we compare the swelling in 100% RH H_2O and D_2O.

For a better understanding of the secondary intermolecular forces, the amount of bound water has to be quantified. It has to be determined how intact the first water shell of the adsorbing polyelectrolyte is. For flat PEMs, the amount of bound water is determined by investigating PEMs at 0% RH, with neutron reflectivity.[4] Another way to measure the amount of bound water is to make use of the immobility of tightly bound water. Even if PEM is immersed in D_2O for 90 min, bound H_2O molecules with an exchange rate well above seconds should remain within PEM without exchanging with D_2O. However, according to protein NMR, the proton−deuterium exchange of an amino group with three protons is fast on the NMR time scale (below 0.5 ms, assuming a frequency of 2 kHz).[18]

Here we report data on the water uptake of selectively deuterated polyelectrolyte multilayers (PEM) consisting of PSS, deuterated PSS (PSSd), and PAH with an amino group providing the positive charge. Established preparation conditions are chosen, both the thickness per polycation/polyanion bilayer and its water content at 0% RH are known for PEMs consisting of protonated layers. The film architecture is selected to obtain as many independent parameters as possible. The broad variation of the water content in deuterated layers found in the literature may partly be due to ambiguous data analysis.[1−3,19] For instance, if the thickness of the deuterated layer is lower than half of the roughness characterizing the interface between the protonated and the deuterated layer, the parameters “scattering length density of the deuterated layer” and “internal roughness” are coupled.[7] In the scattering length density profile, the thin deuterated layer looks almost Gaussian. It is possible to obtain almost the same scattering length density profile if both the intensity and the roughness of the Gaussian are increased, and the fits to the reflectivity curves do not change. Thick deuterated blocks allow to independently determine the roughness and the scattering length density, and it is possible to determine the amount of water bound to deuterated layers.

The Lego approach is the most clear-cut method to interpret the data. Four different film architectures are investigated: 10 protonated polyelectrolyte bilayers (p_{10}), 10 deuterated bilayers (d_{10}), or alternate blocks of 5 protonated and 5 deuterated bilayers (p_5d_5 and d_5p_5).

Materials and Methods

The polished surface of the Si (100) wafers (Matthias Schmehl, Rostock, Germany) serve as negatively charged substrates. Branched polycation poly(ethylene imine) (PEI; M_w = 75 kDa; Sigma-Aldrich, Germany) is an efficient first layer, and polycation PAH (M_w = 56−70 kDa; Sigma-Aldrich, Germany) is used for all subsequent layers. As polyanions, protonated PSS (M_w = 77.4 kDa; PSS) and deuterated PSSd (M_w = 83.7 kDa; PSS, Polymer Standard Service, Mainz) are used. Ultrapure water is from Millipore (Milli-Q).

All deposition solutions contain a polyelectrolyte concentration of 3 mmol/L (with respect to the monomer) and 1 M NaCl (Merck, Darmstadt, Germany). Before use, the Si substrates are cleaned in a standard RCA procedure (immersed in a boiling $H_2O-NH_4OH-H_2O_2$ mixture (5:1:1) for 15 min and then rinsed extensively with deionized water). The cleaned substrates are immersed in the respective polyelectrolyte solutions alternately (30 min for each adsorption step) and then washed in ultrapure water for 3 min. PEMs are prepared by a robot (Riegler & Kirstein, Berlin, Germany). All solutions are kept at the same temperature, which is adjusted externally by a thermostat (Haake, Germany). Four different film architectures are employed: PEI/PSS(PAH/PSS)$_9$ (p_{10}), PEI/PSSd(PAH/PSSd)$_9$ (d_{10}), PEI/PSS(PAH/PSS)$_4$(PAH/PSSd)$_5$ (p_5d_5), and PEI/PSSd(PAH/PSSd)$_4$(PAH/PSS)$_5$ (d_5p_5). If not indicated otherwise, the films are prepared from 15 °C solutions.

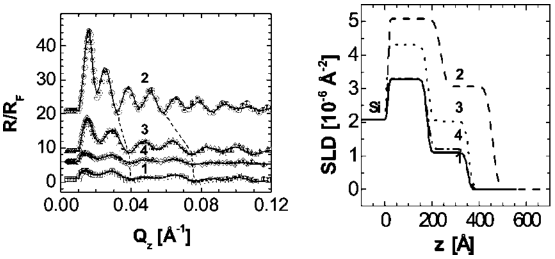

Figure 1. Left: normalized neutron reflectivity curves of d_5p_5 PEM. It consists of five deuterated and five protonated bilayers and is prepared at 15 °C from an aqueous solution containing 1 mol/L NaCl. The sequence of the experiments is 0% RH (after 1−2 h of drying, curve 1) ⟹ 100% RH D_2O (after immersing the film for half an hour in D_2O, curve 2) ⟹ 0% RH (after 20 h of drying, curve 3) ⟹ 0% RH (after immersion for 6 h in H_2O and 20 h of drying, curve 4). Straight lines are fits; dashed lines connect interference minima of the same order. To guarantee for an equilibrium, the measurement at 100% RH D_2O is repeated (cf. Supporting Information). Right: the corresponding scattering length density profiles.

To control the relative humidity (RH), the film is placed into a gastight enclosure. Additionally, the enclosure contains a Petri dish filled with salt or solution (P_2O_5 for 0% RH, H_2O or D_2O for 100% RH). P_2O_5 is purchased from Merck (Darmstadt, Germany) and D_2O from Sigma-Aldrich (Germany).

The films are first examined by X-ray reflectometry and then by neutron reflectometry, not later than 2 weeks after preparation. The measurement of a neutron reflectivity curve takes about 6−8 h. X-ray reflectometry experiments are performed with a Seifert XRD 3003 TT diffractometer (Seifert, Germany) using Cu Kα radiation (wavelength λ = 1.54 Å). The neutron measurement are carried out at instrument V6 at the Hahn-Meitner Institut, Berlin, Germany (λ = 4.66 Å).[20] In these reflectivity experiments, the deviation $\delta = 1 - n$ of the refraction index n of 1 depends linearly on material constants, which are directly related to the constituting molecules. For X-rays, the important material constant is the electron density ρ ($\delta = \lambda^2 \rho r_0 / 2\pi$ with Thomson radius r_0). Similarly, for neutrons the scattering length density $\mathrm{SLD} = \sum_i n_i b_i / \sum_i n_i V_i$ is the relevant parameter, with SLD being the ratio of the sum of the scattering lengths b_i and the volumes V_i of the atoms and molecular groups of the system ($\delta = \lambda^2 \mathrm{SLD}/2\pi$).

In both cases n only deviates by $\approx 10^{-5}$ from 1. Thus, approximations are possible, and the measured reflectivity R can be described as the Fresnel reflectivity R_F of an infinitely sharp interface modulated by interference effects from the thin surface layer.[21] Above about two critical angles of total external reflection ($\alpha_c = \sqrt{2\delta}$) the reflectivity is given by the kinematic approximation

$$\frac{R}{R_F} = \left| \frac{1}{\rho_{\mathrm{sub}}} \int \rho'(z) e^{iQ_z z} \, dz \right|^2 \qquad (1)$$

Here, ρ_{sub} is the electron density (or SLD) of the bulk phase, $\rho'(z)$ the gradient of the electron density (scattering length density) along the surface normal, and Q_z the wave vector transfer normal to the surface. The electron density profiles (scattering length density profiles) are first calculated by an indirect Fourier transform of the master formula.[22,23] Then the exact matrix formalism is used.[24]

The surface layer is parametrized as consisting of different slabs (each slab is described by a density and a thickness; each interface is characterized by a roughness parameter). In all cases the simulated reflectivity is convoluted with the angular divergence of the respective spectrometer (X-rays: 0.012°; neutrons: 0.017°).

Results

Figure 1 shows the neutron reflectivity curve of the d_5p_5 film at 0% RH. Two superimposed interference patterns can be

Table 1. Parameters of the d_5p_5 Film, Deduced from the Measurements and Fits Shown in Figures 1 and 2[a]

d_5p_5	0% RH	100% RH (D_2O) for PAD_3	back to 0% RH without H_2O contact for PAD_2H	back to 0% RH after H_2O contact for PAH_3
protonated block				
l_p [Å]	173.2	$218.4 = 1.29 \times 173$	174.6	170.0
SLD_p [10^{-6} Å^{-2}]	1.02	3.06	2.01	1.14
$d_{BL,p}$ [Å]	34.6	43.7	34.9	34.0
$n_{water,swell}$	3.4	6.9	3.5	3.1
m_{H_2O}	3.4	2.7	2.6	3.1
m_{D_2O}	0	4.2	0.9	0.0
deuterated block				
l_d [Å]	165.2	$224.2 = 1.36 \times 165$	172.2	167.0
SLD_d [10^{-6} Å^{-2}]	3.30	5.08	5.35	3.33
$d_{BL,d}$ [Å]	33.04	44.84	34.44	33.4
$n_{water,swell}$	1.9	6.0	2.4	2.0
m_{H_2O}	1.9	1.1	1.2	1.9
m_{D_2O}	0	4.9	1.2	0.1
σ_{sub} [Å]	5	5	5	5
$\sigma_{air} = \sigma_{int}$ [Å]	10.93	18.75	14.30	15.06

[a] For the fit five free parameters are necessary (the respective scattering length densities SLD_p and SLD_d, the thickness of the respective slab l_p and l_d, and the roughness at the film/air interface σ_{air}). For each slab, additionally the thickness of a bilayer d_{BL} is given as well as the change in thickness occurring at high relative humidity.

observed. The long period is about 0.037 Å^{-1} and the short one half as much, i.e., 0.0185 Å^{-1}. The interference with the shortest periodicity is caused by the largest distance in the sample, which corresponds to the thickness of the whole film. Accordingly, the longer periodicities can be attributed to slabs which are about half as thick as the film, and they are due to a superposition of the reflectivities of the protonated and deuterated blocks.

In a next step, the film is immersed in D_2O for 30 min, and the changes of the thickness and scattering length density are measured by neutron reflectivity at 100% RH D_2O (cf. Figure 1). To make sure that an equilibrium is obtained, the experiment is repeated immediately. The neutron reflectivity curves are identical, and the second curve is shown in the Supporting Information. Compared to the initial measurement at 0% RH, the contrast is an order of magnitude larger, which suggests an incorporation of D_2O or deuterium ions. However, the interferometric pattern is essentially the same and shows two periods, one twice as big as the other. Nevertheless, both periods are shorter, indicating increased film thickness.

If the film is dried its thickness decreases again (cf. Figure 1), while the periods are identical to those obtained for the freshly prepared, dried film; i.e., the same amount of water is incorporated in the film as at the beginning of the experiment. However, the contrast is larger than for freshly prepared film. The original reflectivity curve can be obtained by immersing the sample in H_2O for 6 h and by drying the film afterward (cf. Figure 1). This suggests that dipping the dried film into light water causes a deuterium−proton exchange.

Swelling experiments in 100% RH D_2O performed with films dried in a vacuum show that one proton of each allylamine hydrochloride monomer changes position with one deuterium ion.[25] Since the film shown in Figure 1 is not only exposed to 100% RH D_2O, but first immersed in liquid heavy water, one can imagine that not only one, but three of the protons of the allylamine hydrocholoride monomers are replaced by deuterium ions, as suggested by NMR experiments of proteins in D_2O.

To quantify the results, the measurements are fitted with a model consisting of two slabs: one for the deuterated and one for the protonated block. The roughness at the film/substrate interface is set to 5 Å, a value obtained from X-ray reflectivity measurements. The scattering length densities of the substrate (Si) and air are known. Thus, the reflectivity curves, the respective thickness of the deuterated and protonated slabs (l_d, l_p), the corresponding scattering length densities (SLD_d, SLD_p), and the roughness at the film/air interface σ_{air} are described by five free parameters. The first fits included an additional, sixth parameter: the internal roughness σ_{int} between the protonated and the deuterated block. Yet, σ_{int} is within 10% identical to σ_{air}. Therefore, $\sigma_{int} = \sigma_{air}$ guarantees for no loss of information or quality of the fits. Table 1 contains all parameters obtained under the different conditions.

For the freshly prepared film at 0% RH the parameters for the protonated block are in almost perfect agreement with the values reported previously for identical preparation conditions: The thickness per polycation/polyanion bilayer is $d_{BL} = 34.6$ Å, and the number of water molecules for a pair of monomers is $n_{H_2O,dry} = 3.4$ (expected: $d_{BL} = 35 \pm 1$ Å and $n_{H_2O,dry} = 3.5$).[4] The thickness of the deuterated block is slightly smaller ($d_{BL} = 33$ Å), and the water content is decreased by a factor of 2 ($n_{H_2O,dry} = 1.9$).

At the beginning of the experiment, the definition of the scattering length density (SLD) of each block is used to calculate n_{H_2O}, i.e., the amount of H_2O molecules per PAH/PSS monomer pair:

$$\mathrm{SLD} = \frac{b_{PAH} + b_{PSS} + n_{H_2O} b_{H_2O}}{V_{PAH} + V_{PSS} + n_{H_2O} V_{H_2O}} \tag{2a}$$

(The numerical values are[26] $b_{PAH} = -0.614 \times 10^{-5}$ Å, $b_{PSS} = 47.203 \times 10^{-5}$ Å, $b_{PSSd} = 120.07 \times 10^{-5}$ Å, $b_{H_2O} = -1.675 \times 10^{-5}$ Å, $b_{D_2O} = 19.145 \times 10^{-5}$ Å, $V_{PAH} = 97$ Å^3, $V_{PSS} = V_{PSSd} = 200$ Å^3, $V_{H_2O} = V_{D_2O} = 30$ Å^3.)

$$n_{H_2O} = \frac{b_{PAH} + b_{PSS} - \mathrm{SLD}(V_{PAH} + V_{PSS})}{\mathrm{SLD} V_{H_2O} - b_{H_2O}} \tag{2b}$$

With these formulas the water content can be calculated at 0% RH at the beginning of the experiment, $n_{H_2O} = n_{H_2O,dry}$ (cf. Table 1).

In a next step we assume that the water incorporation caused by the exposure to 100% RH can be quantified by the increase in thickness

$$\frac{V_{PAH} + V_{PSS} + V_{H_2\mathbf{O}} n_{water,swell}}{V_{PAH} + V_{PSS} + V_{H_2O} n_{H_2O,dry}} = \frac{l_{swell}}{l_{dry}} \tag{3a}$$

The thickness of the dry and the swollen slab are denominated by l_{dry} and l_{swell}. The amount of water per PAH/PSS monomer pair ($n_{water,swell}$) is then given by

$$n_{water,swell} = \frac{1}{V_{H_2O}} \left(\frac{l_{swell}}{l_{dry}} (n_{H_2\mathbf{O},dry} V_{H_2O} + V_{PSS} + V_{PAH}) - (V_{PSS} + V_{PAH}) \right) \tag{3b}$$

The reflectivity curves in 100% RH D_2O show very large intensities due to the high SLD of deuterium. The deuterium incorporation has to be understood on a molecular basis. The number of water molecules per PAH/PSS monomer pair, $n_{water,swell}$, is determined by the increase in thickness. Even if we assume that all incorporated molecules are D_2O the reflected intensity is too low. The "fits" do not show each maximum, and every second maximum is akin to a shoulder; especially the scattering length density of the deuterated block SLD_d is too small. To explain the magnitude of SLD_d, a certain number of protons and deuteriums are required, which are distributed

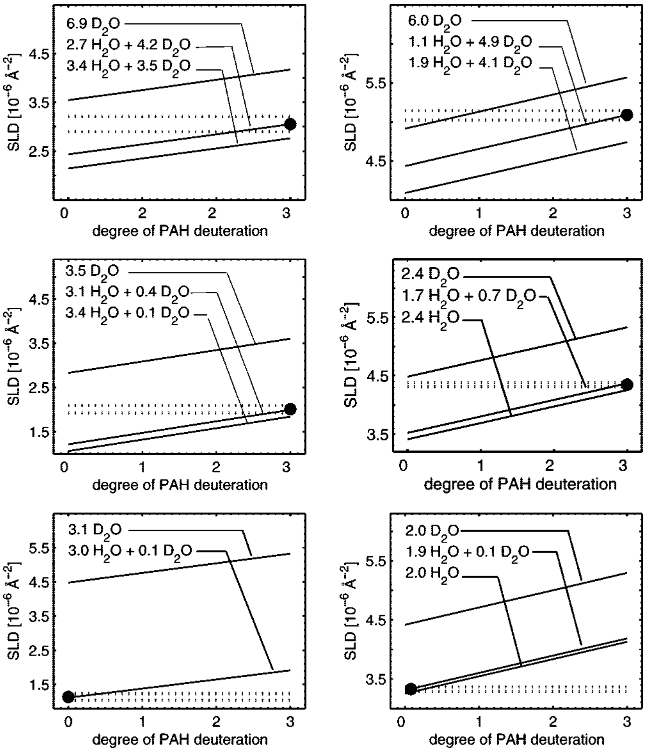

Figure 2. Calculation of the composition of the scattering length densities SLD_p (left column) and SLD_d (right column) for the d_5p_5 PEM shown in Figure 1. Top: 100% RH D_2O; center: 0% RH. Bottom: 0% RH after immersion in H_2O. The x-axis gives the degree of PAH deuteration ($PAH_{3-i}D_i$, with $0 \leq i \leq 3$); the dotted lines show the confidential region of SLD (±10% χ^2 variation) determined by the fits. The straight lines are calculated for different values of m_{H_2O} using the constraint $n_{\text{water,swell}} = m_{H_2O} + m_{D_2O}$. $n_{\text{water,swell}}$ is known from the thickness change of the film.

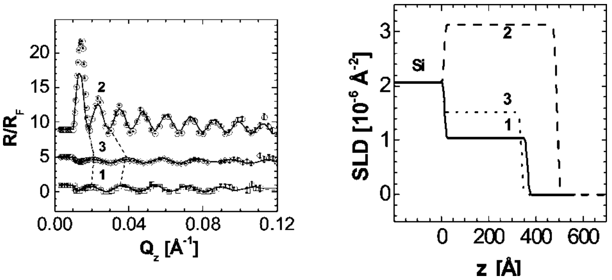

Figure 3. Left: normalized neutron reflectivity curves of the p_{10} PEM. It consists of 10 protonated bilayers prepared from 1 mol/L NaCl at 15 °C. The sequence of the experiments is 0% RH (curve 1) ⟹ 100% RH D_2O (after immersing the film for half an hour into D_2O, curve 2) ⟹ 0% RH (after immersion for 34 h in H_2O and 86 h of drying, curve 3). Straight lines are fits; dashed lines connect interference extrema of the same order. Note that at 100% RH D_2O a contrast inversion at the substrate/film interface occurs, causing a 180° shift in the reflected intensity. Therefore, minima of curve 2 are connected with maxima of curves 1 and 3. To ensure reversibility, the measurement at 100% RH D_2O is repeated three times; curve 3 is also repeated once (cf. Supporting Information). Right: the corresponding scattering length density profiles.

Table 2. Parameters of the p_{10} Film Deduced from the Measurements and Fits Shown in Figure 3

p_{10}	0% RH	100% RH (D_2O)	back to 0% RH
l_p [Å]	351.3	475.2 = 1.35 × 351	329.8
SLD_p [10^{-6} Å^{-2}]	1.04	3.10	1.52
$n_{\text{water,swell}}$	3.2	7.9	2.5
m_{H_2O}	3.2	3.0 for PAD_3	2.0 for PAH_3
m_{D_2O}	0	4.9 for PAD_3	0.5 for PAH_3
$d_{BL,p}$ [Å]	35.1	47.5	33
σ_{sub} [Å]	5	5	5
σ_{air} [Å]	6.0	13.4	6.7

between the water molecules and the amino groups of the polycation. For the deuterated block at 100% RH D_2O the numbers are 12.8 D and 2.2 H (cf. Figure 2, top right). Because of the fast proton−deuterium exchange found for protein NMR, we suggest that three D are bound to each amino group and call the polycation PAD_3. A fixed amount of water ($n_{\text{water,swell}}$) is composed of H_2O and D_2O:

$$n_{\text{water,swell}} = m_{H_2O} + m_{D_2O} \tag{4}$$

The six water molecules per monomer pair as derived from the increase of thickness consist of 4.9 D_2O and 1.1 H_2O molecules per monomer pair. This results in $m_{H_2O} = 1.1 \leq n_{H_2O,\text{dry}} = 1.3$ and $m_{D_2O} = 4.9$ and is consistent with $n_{\text{water,swell}} = 6$.

After the sample has been dried, the periodicity increases and the height of the peak decreases (cf. Figure 1). This observation suggests that loosely bound water, i.e. D_2O, is evaporated. Thus, what remains are basically the tightly bound water molecules which are not exchanged during exposure to liquid D_2O, and we expect an identical or slightly decreased value for m_{H_2O} for the dried film compared to the value obtained at 100% RH D_2O. Assuming the polycations in the dried film consist of PAD_3, we obtain $m_{H_2O} = 1.7$, which is higher than the value observed at 100% RH D_2O ($m_{H_2O} = 1.1$). This deviation is presumably within error.

Finally, the thin film is immersed in H_2O and dried. The thickness of the pristine film is found again, and the deuterium ions and the heavy water molecules are removed. In summary, this experiment is reversible in terms of proton−deuterium exchange and swelling. The results are consistent with a complete replacement of three H^+ in the polycation monomers by three D^+ after submerging the film for half an hour in liquid D_2O. Most of the tightly bound water molecules found at the beginning of the experiment remain in the film. To find out whether this behavior is general, we have to study the swelling behavior of the other block architectures.

At 0% RH the parameters of a p_{10} film (cf. Figure 3) are in the expected range of a film built at 15 °C from an aqueous solution containing 1 mol/L NaCl. The thickness of the bilayer is $d_{BL} = 35.1$ Å and $n_{H_2O,\text{dry}} = 3.2$ (expected: $d_{BL} = 35 \pm 1$ Å and $n_{H_2O,\text{dry}} = 3.5$).[4]

The same experimental procedure is used to determine the swelling of the film in 100% RH D_2O after having dipped it into liquid D_2O for half an hour. The water uptake is very interesting. The increase in thickness results in $n_{\text{water,swell}} = 7.9$. Again the protons are exchanged, and the data are consistent with PAD_3. In this case 4.9 D_2O molecules are incorporated, and almost all tightly bound H_2O molecules remain in the film (cf. Table 2).

Then the film is immersed in H_2O for half an hour and dried. After 86 h of drying the water removal was more thorough than in a freshly prepared film, which was dried for 1 or 2 h only. This experiment also shows that the removal of deuterium is less complete than originally assumed (0.5 tightly bound D_2O molecules per PAH/PSS monomer are found). A possible interpretation is a deuterium migration from PAD_3 to the tightly bound almost immobile H_2O molecules.

A film architecture complementary to the one shown in Figure 1 is $p_5d_{5,35\,°C}$ (cf. Figure 4). The initial PEI layer was adsorbed at room temperature, the other polyelectrolyte layers at 35 °C. This film is used to confirm the emerging picture (substitution of all protons of the polycation by deuterium ions on immersion into heavy water, most of the tightly bound water found in the films at 0% RH remains in the film and is not replaced by D_2O molecules) and to address some related questions such as (1)

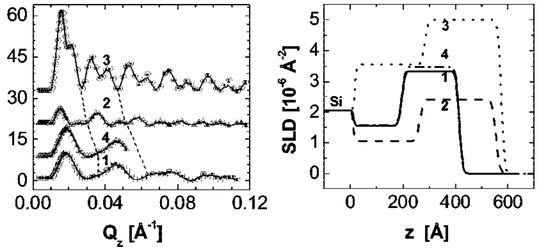

Figure 4. Left: normalized neutron reflectivity curves of a $p_5d_{5,35\,°C}$ PEM. It consists of five protonated followed by five deuterated bilayers and is prepared from 1 mol/L NaCl solution at 35 °C. The sequence of the experiments is 0% RH (curve 1) ⟹ 100% RH H_2O (after immersion for 30 min in H_2O, curve 2) ⟹ 100% RH D_2O (after immersion for 30 min in D_2O, curve 3) ⟹ 0% RH (after reimmersion in H_2O for 8 h and 8 h of drying, curve 4). Straight lines are fits; dashed lines connect interference extrema of the same order. Note that at 0% RH the substrate and the protonated block have almost the same scattering length density; thus, contrast is reduced. At 100% RH D_2O the contrast is inversed at this interface (interference minima and maxima of the same order are connected with dotted lines). To ensure reversibility, the measurements at 100% RH H_2O and D_2O were repeated; they are shown in the Supporting Information. Right: the corresponding scattering length density profiles.

how sound is our assumption that we can calculate the water incorporation from the thickness change only and (2) does heavy water induce more swelling than light water.

There is hardly any water in the protonated layer adjacent to the substrate ($n_{H_2O,dry} = 0.1$ instead of $n_{H_2O,dry} = 3.5$). Furthermore, the thickness per polyelectrolyte bilayer in the protonated block is lower than expected for PEMs prepared at this elevated temperature ($d_{BL} = 36.7$ Å instead of the expected 44 ± 1 Å[4]). If the standard value of bound water is assumed, the thickness of bilayer is larger than described in literature ($n_{H_2O,dry} = 3.5$ leads to a bilayer thickness of $d_{BL} = 49.7$ Å instead of the expected 44 ± 1 Å[4]). Thus, the polymer coverage in precursor layers exceeds the coverage in the center of the film, and the water is bound less tightly.

The thickness of the bilayer in the deuterated block ($d_{BL} = 44$ Å) is consistent with the expected value of 44 ± 1 Å, although the water content is smaller ($n_{H_2O,dry} = 1.7$ instead of 3.5). Exposed to 100% RH H_2O the same amount of water is incorporated in both layers $n_{water,swell} - n_{H_2O},dry = 3.8$, as indicated by the changes of the thickness and the decrease in scattering length density.

With the swelling experiment of $p_5d_{5,35°C}$ at 100% RH H_2O we can also cross-check the validity of our approach to calculate the swelling both from the change in scattering length density (eq 2a) and from the increase of the thickness (eq 3a). Since we do not incorporate additional deuterium ions, we have two equations and one parameter, $n_{water,swell}$, for both the protonated and the deuterated layer; $n_{water,swell}$ differs by 0.1 water molecule per PAH/PSS monomer pair depending on the equation used.

At 100% RH D_2O (after dipping the film in heavy water for half an hour) the thickness of the protonated block increases (at 100% RH D_2O $n_{water,swell} = 4.6$ instead of 3.8 at 100% RH H_2O) while the thickness of the deuterated block remains almost unchanged. As expected, the scattering length densities increase dramatically. At the substrate/film interface there is a contrast inversion—the scattering length density of the film is now larger than that of the substrate. Note that the interpretation of the scattering length density is rather unambiguous (cf. Table 3): the scattering length density of the protonated block is so large that two or three protons per polycation monomer have to be replaced by deuterium ions; otherwise, m_{H_2O} would be negative. It is possible to return to the original film composition, yet in the deuterated block a fraction of D_2O molecules remains ($m_{D_2O} = 0.2$ with $n_{H_2O,dry} = 1.7$).

Table 3. Parameters of the $p_5d_{5,35\,°C}$ Film Deduced from the Measurements and Fits Shown in Figure 4

$p_5d_{5,35\,°C}$	0% RH	100% RH	100% RH (D_2O)	back to 0% RH
		protonated block		
l_p [Å]	183.5	254 = 1.38 × 184	266.6 = 1.45 × 184	184.3
SLD_p [10^{-6} Å^{-2}]	1.55	1.04	3.54	1.59
$d_{BL,p}$ [Å]	36.7	50.8	53.3	36.9
$n_{water,swell}$	0.1	3.9	4.6	0.1
m_{H_2O}	0.1	3.9	0.6 for PAD_3	0.1 for PAH_3
m_{D_2O}	0	0	4.0 for PAD_3	0.0 for PAH_3
		deuterated block		
l_d [Å]	219.3	290.2 = 1.32 × 219	291.7 = 1.33 × 219	219.4
SLD_d [10^{-6} Å^{-2}]	3.34	1.59	5.00	3.47
$d_{BL,d}$ [Å]	43.9	58.0	58.3	43.9
n_{water}	1.7	5.5	5.6	1.7
m_{H_2O}	1.7	5.5	1.2 for PAD_3	1.5 for PAH_3
m_{D_2O}	0	0	4.4 for PAD_3	0.2 for PAH_3
σ_{sub} [Å]	5	5	5	5
$\sigma_{air} = \sigma_{int}$ [Å]	10.5	12.0	10.3	10.3

To confirm the unexpected observation that there is no tightly bound water in the protonated block next to the substrate, another film with p_5d_5 architecture was investigated. The expected bilayer thickness is lower than for the film shown in Figure 4 because this film is prepared at 15 °C and not at 35 °C, while the expected water content is the same (expected:[4] $d_{BL} = 35 \pm 1$ Å with $n_{H_2O,dry} = 3.5$). The measurements and fits are shown in the Supporting Information.

The freshly prepared p_5d_5 film shows a similar water content as the $p_5d_{5,35\,°C}$ film ($n_{H_2O,dry} = 0$ for the protonated and $n_{H_2O,dry} = 1.1$ for the deuterated block). Again, the bilayer thickness within the protonated block is lower than expected, yet the deuterated block is in agreement with the literature ($d_{BL} = 31.2$ and 34.9 Å, respectively). Assuming 3.5 water molecules incorporated bilayers of the protonated block, the thickness of the bilayer is again larger than expected ($n_{H_2O} = 3.5$ would lead to a bilayer thickness of $d_{BL} = 42.2$ Å, which exceeds the expected 35 ± 1 Å). Thus, we conclude that the precursor layers next to the substrate show increased polymer coverage and less bound water.

At 100% RH H_2O the additional amount of incorporated water is similar for both blocks. The deuterated block includes more water because it had more water in the dried state ($n_{water,swell} = 3.8$ for the protonated and $n_{water,swell} = 5.0$ for the deuterated block). Exposed to 100% RH D_2O, the swelling is slightly increased for both blocks ($n_{water,swell} = 4.5$ for the protonated and $n_{water,swell} = 5.4$ for the deuterated block).

The common finding with the p_5d_5 and $p_5d_{5,35\,°C}$ films is that the thickness increases in 100% RH D_2O slightly more than in 100% RH H_2O. Averaging over all blocks there is an increase of 4%.

Finally, a d_{10} film is investigated (cf. Figure 5 and Table 4). Here we find very little water in the dry state ($n_{H_2O},dry = 1.3$), and the thickness of the bilayer is very much in the expected range ($d_{BL} = 34.4$ Å, expected $d_{BL} = 35 \pm 1$ Å). The 0.6 H_2O molecules remain bound after swelling in 100% RH D_2O and assuming the formation of PAD_3. Since both PAD_1H_2 and PAD_0H_3 would lead to a negative water content, it has to be that two or three protons per PAH monomer are exchanged by deuterium ions.

Summary of common findings that have not been discussed before: Most measurements show an increased roughness at the film/air interface upon exposure to 100% RH. After drying, the roughness decreases somewhat but does not necessarily reach

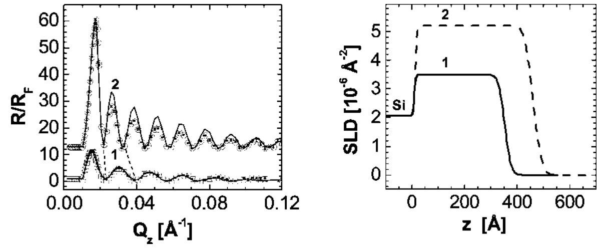

Figure 5. Left: normalized neutron reflectivity curves of a d_{10} PEM prepared from 1 mol/L NaCl solution at 15 °C. The sequence of the experiments is 0% RH (curve 1) ⟹ 100% RH D_2O (after immersion for 30 min in D_2O, curve 2). Straight lines are fits; dashed lines connect interference minima of the same order. To ensure reversibility, the measurement at 100% RH D_2O is repeated (cf. Supporting Information). Right: the corresponding scattering length density profiles.

Table 4. Parameters of the d_{10} Film Deduced from the Measurements and Fits Shown in Figure 5

d_{10}	0% RH	100% RH (D_2O)
l_d [Å]	343.6	451.3 = 1.31 × 344
SLD_d [10^{-6} Å^{-2}]	3.50	5.23
$n_{water,swell}$	1.3	4.8
m_{H_2O}	1.3	0.6 for PAD_3
m_{D_2O}	0	4.2 for PAD_3
$d_{BL,d}$ [Å]	34.4	45.1
σ_{sub} [Å]	5	5
σ_{air} [Å]	19.1	19.0

the original value (cf. Tables 1−4). The results obtained on the immobile water molecules are shown in Figure 6. The number of protons attributed to tightly bound water molecules (per monomer pair) is shown for all films investigated under different environmental conditions. All protons found after applying eqs 2a and 3a are shown for 100% RH D_2O and 0% RH D_2O. To verify the hypothesis that the amount of tightly bound water molecules within a film is fairly constant for 0% RH H_2O three protons of an amino group in a polycation monomer are subtracted. All deuterated blocks show a very similar behavior with 2.8 ± 0.8 protons (or 1.4 ± 0.4 water molecules) bound. Two different kinds of protonated blocks exist: The core and/or outer zone with about 6.2 protons per monomer pair (p_{10} and d_5p_5), which is in agreement with the values[7] found in the literature. The proton block in the precursor zone contains about 0 protons (or no water) (p_5d_5 and $p_5d_{5,35\,°C}$). There are deviations from a straight line, and a few data points suggest that two, not three, protons are exchanged by deuterium ions per polycation monomer pair.

We do not show some experimental points obtained at the end of the experiment at 0% RH H_2O when we were not sure to have obtained an equilibrium. It is well-known that the water uptake is almost immediate, while apparently the water release has a longer time scale for the protonated blocks: After 86 h of drying the p_{10} block has only 2.4 water molecules (instead of the original 3.2 obtained after 30 min of drying), and the protonated block of p_5d_5 does not come back to 0.1 water molecules, but still has 1.4 water molecules after 6 h of drying.

Discussion

In summary the experiments on p_{10}, d_{10}, p_5d_5, $p_5d_{5,35\,°C}$, and d_5p_5 are all consistent with the following features:

(i) After immersion in D_2O all PEM data indicate that three protons in the amino group of each polycation monomer are exchanged by deuterium.

(ii) The majority of the tightly bound water molecules found in the freshly prepared, dried films remains in the film and is not replaced by D_2O molecules.

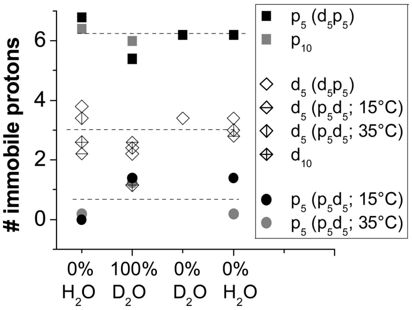

Figure 6. Amount of protons attributed to tightly bound water molecules per monomer pair measured at different environmental conditions and calculated from eqs 2a and 3a. The RH given in the *x*-axis follows the sequence of the experiments. For each measurement performed in a H_2O atmosphere, three protons are subtracted since they are bound to the amino group. Dotted lines are a guide to the eye and indicate three different sorts of layers containing different amount of tightly bound water molecules. We distinguish deuterated layers (≈3 protons or 1.5 H_2O molecules), protonated precursor (≈0 protons), and protonated core and/or outer layers (≈6.2 protons or 3.1 H_2O molecules per monomer pair). For most measurements, the symbols exceed the size of the error bars. For those protonated layers with many protons (≈6.2 protons per monomer pair), the error from the fits shown in the preceding figures is larger and amounts to ±0.6 protons.

(iii) The thickness of deuterated polycation/polyanion bilayers in deuterated PEM or in deuterated blocks is in accordance with previously published results for PEMs consisting of protonated layers. However, there is consistently less bound water in the films ($n_{H_2O,dry}$ = 1.1−1.9 instead of $n_{H_2O,dry}$ = 3.5), which indicates a larger polymer coverage.

(iv) The thickness and water content of the bilayers in protonated PEM and the protonated blocks adjacent to the air side are consistent with previously reported values with respect to thickness of the bilayer as well as the water content. However, protonated layers adjacent to the substrate do not contain any tightly bound water while the polyelectrolyte coverage is slightly higher.

(v) The internal roughness and the film/air roughness are identical, even though it can increase by a factor of 2 if the film is swollen.

Each of the above statements is supported by measurements on at least two different PEMs.

The scattering length density of the deuterated blocks is higher than almost all values published for the selectively deuterated layers in PEMs.[3,4,12,19] For selectively deuterated layers the thickness of the deuterated slab is at best three times the roughness of the internal interfaces above and below the deuterated slab. Therefore, the maximum in the scattering length density profile (which is well described by a Gaussian) is by default smaller than the nominal scattering length density of the deuterated layer. The obtained values are thus an estimate: with an increased scattering length density and increased roughness the same scattering length density profile is obtained. In this context it is helpful to consider that in our experiments the roughness of the internal interface between the protonated and the deuterated block has the same value as the film/air roughness. This may reduce the number of free parameters. However, more detailed experiments will be required to fully explore this issue.

As described previously, we found that almost all films and isolated blocks swell by 30−35%. However, the two p_5d_5 layers behave differently. In 100% RH D_2O the thickness of the protonated layer increases by 45% (cf. Table 3). At 100% RH H_2O the protonated block incorporates just as much water as any protonated PEM ($n_{water,swell} - n_{dry} \approx 3.9$), although the original water content was lower ($n_{H_2O,dry} \approx 0.1$ instead of $n_{H_2O,dry} \approx 3.5$), and therefore the relative change of thickness is higher. It appears that about the same amount of water is incorporated, independently of the number of tightly bound water molecules. The slightly increased swelling in 100% RH D_2O compared to 100% RH H_2O can be explained by the larger enthalpy between the heavy water molecules.

According to the zone model,[13,14] the multilayer consists of a hard core and a softer precursor layer. The p_5d_5 films obviously have a film architecture with a clearly observable precursor zone. The low amount of bound water at 0% RH suggests that the water is mobile and the layer is softer and not in the glassy state like in the central zone of the multilayer.[14] We presume that the p_{10} and d_{10} films also contain less bound water in the layers closest to the substrate, but it is difficult to resolve. Less water in the layers adjacent to the substrate improves the fits, but the assignment of parameter is ambiguous.

At increasing temperatures[4] less water in the films allows for higher polymer coverage. Without a tightly bound hydration shell the polymer chains can get closer to each other, and thus the segment/segment attraction increases and more polymer is adsorbed. This applies to the protonated precursor layer next to the substrate in the p_5d_5 films as well as to the deuterated blocks or films. Both contain less tightly bound water molecules and show higher polymer coverage. Apparently, it is more difficult to form hydration shells around deuterated nonpolar groups.

Finally, our results indicate that proton−deuterium exchange always occurs in the amino groups. We conclude that two or three protons are exchanged by deuterium ions. Furthermore, the water molecules found at 0% RH remains in the film even if the film is stored in D_2O. This is due to the fast exchange rate of the protons and the slow exchange rate of hydration water. There is less conclusive evidence of slow proton−deuterium exchange in the tightly bound water molecules. Drying after immersion in light water does not always lead to a complete removal of the deuterium; a small percentage is retained, and the deuterium ions obviously move into the tightly bound hydration water.

Conclusion

The PEMs investigated either consist of 10 protonated polyelectrolyte bilayers (p_{10}), 10 deuterated bilayers (d_{10}), or of two different blocks, p_5d_5 or d_5p_5. The variation of the PEM architecture leads to a broad variation in the obtained neutron reflectivity curves. If a protonated layer is next to the substrate, contrast inversion occurs after deuterium has been incorporated. If block architecture is used, we observe two different periodicities in the measurement: one from the film thickness, superimposed by the beats from the thinner blocks. The very different results can be explained by the same model which thus provides a robust description of the system.

Prior to the exposure to 100% RH D_2O or H_2O, PEM is immersed in liquid D_2O or H_2O for at least half an hour. The obtained scattering length density profiles provide insight into the exchange rates of the constituent molecules: Two or three mobile protons of each PAH monomer are replaced by deuterium ions, although most of the H_2O molecules found in PEM at 0% RH remain bound at 100% RH D_2O. However, in a p_5 precursor block adjacent to the substrate no tightly bound water is found, which indicates a soft layer as it was suggested by the zone model. Tightly bound water molecules are only found in the PEM core zone. In contrast, in the deuterated layer the amount of tightly bound water molecules is constant and independent of the film architecture.

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Supporting Information Available: Identical neutron reflectivity measurements demonstrating reproducibility and parameter plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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