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# Swelling Behavior of Polyelectrolyte Multilayers in Saturated Water Vapor

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ABSTRACT: The swelling behavior of layer-by-layer assemblies of poly(styrenesulfonate) sodium salt (PSS) and poly(allylamine hydrochloride) (PAH) with various number of layers were investigated. The data presented in this paper suggest that swelling and deswelling are completely reversible and reproducible. At 99% relative humidity, a pronounced "odd−even effect" in the swollen thickness is observed depending on the type of polyelectrolyte in the *outermost* layer. Contact angle measurements confirmed that the PSS surface is more hydrophilic than the PAH surface. The "odd−even effect" indicates that water has to be pressed out of the multilayer when PAH is adsorbed onto the PSS surface of the multilayer and that again more water penetrates into the multilayer on adsorption of the next PSS layer. It was also found that the relative amount of swelling with respect to the total film thickness decreases with increasing number of layers. This is an indication that the loosely packed *outer layers* are more sensitive to environmental humidity and consequently swell in a significantly more pronounced way than the inner ones closer to the substrate.

## Introduction

Driven by the development and miniaturization of electronic and optical devices with new properties, the modification of surfaces by the adsorption of ultrathin films has become increasingly important. During the past decades a new kind of polymer films formed by the alternate physisorption of polyanions and polycations from aqueous solutions raised tremendous scientific interests.[1] With this layer-by-layer technique, ultrathin films can be constructed with angstrom precision with no constraints on the shape of the templates.

Polyelectrolyte multilayer assemblies (e.g., planar films or walls of hollow capsules) are well-known to be sensitive to external parameters such as ionic strength and pH,[2−5] temperature,[6] or humidity. These features make them particularly attractive for technical applications like sensors and containers for drugs. Few publications[7−14] deal with the swelling behavior and hydration of polyelectrolyte multilayers. The typical amount of water uptake in high humidity environment or water varies between 30 vol % for the poly(styrenesulfonate)/poly(allylamine hydrochloride) (PSS/PAH) system[7,9] and 300 vol % in the case of the poly(acrylamide)/poly(diallyamine hydrochloride) (PAA/PDADMAC) system.[2]

The question arises whether (1) the film swells homogeneously or do certain parts of the multilayer swell more than others and (2) the surface charge has an effect on the swelling properties. Recently, NMR techniques[12−14] have been used to probe the hydration of various systems, showing that the amount of immobilized water depends on the type of polyelectrolyte in the outermost layer. However, it is not clear how the amount of immobilized water is related to the volume fraction of water within the swollen film.

The present paper focuses on swelling properties of planar multilayers composed of a weak (PAH) and a strong polyelectrolyte (PSS). The swelling behavior of the multilayers was quantitatively followed by measuring in situ the changes in the film thickness between low (3%) and high (99%) relative humidity (rh) using ellipsometry and contact angle measurement. To avoid confusion, note that "outermost layer" is used to describe the last layer adsorbed while "outer layers" describe an ensemble of layers close to the multilayer/air interface.

## Experimental Section

**Materials.** Poly(styrenesulfonate) sodium salt ($M_w = 70000$) (PSS) and Poly(allylamine hydrochloride) ($M_w = 65000$) (PAH) were purchased from Aldrich (Steinheim, Germany) and were used without further purification. Polyelectrolyte dipping solutions were made from 0.25 M NaCl in 18 MΩ cm Millipore water.

**Multilayer Preparation.** The multilayers were prepared according to the layer-by-layer method suggested by Decher.[1] As substrate, silicon wafers were used, provided by Wacker Siltronic AG, Burghausen, Germany. The wafers were cleaned for 30 min in a 1:1 mixture of $H_2O_2/H_2SO_4$, then rinsed thoroughly with deionized water and finally with Millipore water. The silicon wafers were alternatively immersed in aqueous solutions containing $10^{-2}$ monoM (concentration based on monomer unit) of the respective polyelectrolyte. Between each adsorption step, the silicon wafers were rinsed three times for 1 min in Millipore water. The films were dried once in a smooth stream of purified air *after* completion of the multilayer assembly. The first layer is always PAH so that an *odd layer* number indicates that the outermost layer is PAH while an *even layer* number coincides with the PSS outermost layer. Wafers were coated with thin films of 1−12 layers. In addition, some thicker samples (26 layers) were prepared as a reference sample.

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**Ellipsometry under Controlled Humidity.** To determine changes in thickness and refractive index during swelling and deswelling, in situ ellipsometric measurements were performed with a PCSA (polarizer−compensator−sample−analyzer) ellipsometer (Plasmos GmbH Prozesstechnik, München, Germany). The experiments were carried out at a constant wavelength of 632.8 nm and a fixed angle of incidence of 70° (near the Brewster angle of the Si/air interface).

The relative atmospheric humidity was precisely controlled by a self-made humidity chamber[15] and could be adjusted between 3% and 99% by a constant flow of a mixture of dry air (dried with molecular sieve and active charcoal filters) and water vapor. The samples were at least 15 min in the respective humidity, after which time thermodynamic equilibrium was reached. Ellipsometric measurements were carried out within days of preparation of the samples, but verification after several months on the same samples showed no effect of aging on the swelling/shrinking behavior.

The total Fresnel reflection coefficients parallel and perpendicular to the plane of incidence, $R_p$ and $R_s$, are related to the ellipsometric data $\Delta$ and $\Psi$ by[16]

$$R_p/R_s = \tan \Psi \exp(-i\Delta)$$

From the measured $\Delta$ and $\Psi$ angles, the thickness and/or the refractive index can be determined with a least-squares fit using a box model with four layers: (i) air, (ii) polymer, (iii) $SiO_x$, and (iv) Si. For the refractive indices, $n = 3.868 - i0.024$ for bulk silicon and $n = 1.46$ for silicon oxide were used, respectively. Since it is not possible to fit *d and n* for very thin layers (below 100 Å) simultaneously, the effective refractive index was obtained from a thick multilayer system with well-defined dry film thickness $d_o$. This value was used as the refractive index of the other dry films with fewer layer numbers. To take the change in the refractive index due to the water uptake into account, the Garnet equation[15,17] was used to calculate $n_F$ and $d_{swollen}$ of the multilayers in the swollen state in a self-consistent manner:

$$n_F = n_M \sqrt{1 + \frac{3\Phi}{\left(\frac{n_0^2 + 2n_M^2}{n_0^2 - n_M^2}\right) - \Phi}}$$

where $n_M$ is the refractive index of pure water and $\Phi$ the volume fraction of the polyelectrolyte within the multilayer, which is related to the layer thickness $d_{swollen}$ by $\Phi = d_0/d_{swollen}$.

The effective refractive index $n_0$ of the dry polyelectrolyte multilayer was obtained from a reference multilayer of 26 single layers at 3% rh. For this film, a refractive index of 1.477 and a thickness of 265 Å were determined. In the case of polyelectrolyte multilayers, this refractive index is an average of the index of the individual layers weighted with their individual thickness. The value of $n_0 = 1.477$ is in good agreement with the refractive indices of individual PAH (1.468) and PSS (1.484) layers as determined by Ruths et al.[18] Under the assumption that the refractive index $n_0$ of the *dry* multilayer is independent of the thickness, the same value of $n_0 = 1.477$ was also used to calculate the thickness $d_0$ of the other dry films with fewer layer numbers (5−12 single layers). So, the unknown variables in the Garnett equation, $n_F$ and $d_{swollen}$ can be obtained by an iterative fitting starting from $n_F = n_0$ and $d_{swollen} = d_0$. For example, a thickness of 342 Å and a refractive index of 1.438 were determined for the swollen 26 single layers.

**Contact Angle Measurements.** The optical contact angle measurements were carried out with an OCA 20 from Dataphysics (Filderstadt). A drop of water was placed on the multilayer-coated Si wafer which was itself mounted on a glass support (Pillenglas) inside a glass box containing water to reduce evaporation, and the contact angle of the sessile drop in the humid atmosphere is determined by an image analysis program.

## Results and Discussion

Figure 1a shows plots of $\Delta$ and $\Psi$ as a function of relative humidity for two systems each with a different polyelectrolyte in the outermost layer, and Figure 1b shows corresponding plots of the film thickness and the refractive index of the swollen polyelectrolyte multilayers as a function of relative humidity. Both systems show that swelling and deswelling is completely reversible (no hysteresis observed) and reproducible (independent of the history of the samples). For clarity and visual guide for the eyes, the film thickness at dry relative humidity (3%) on deswelling is shown in Figure 1, parts a and b.

Figure 2 shows the thickness of films at low (3%) and high (99%) relative humidity as a function of the number of layers. The thickness of the swollen film, $d_{swollen}$, has been calculated from the ellipsometric data of $\Delta$ and $\Psi$, using the respective $d_0$ which was calculated with $n_0 = 1.477$ and $n_M = 1.33$. While in the dry state one can observe an almost continuous increase in film thickness with increasing number of layers, this is no longer the case at high relative humidity. At 99% rh a pronounced "odd−even effect" in the swollen thickness is observed, depending on the type of polyelectrolyte in the outermost layer. The results show that multilayers with PSS in the outermost layer (even) swell in a more pronounced way than multilayers with PAH (odd) in the outermost layer. This is in agreement with neutron reflectometry data which show that PSS attracts twice more water per volume than PAH does.[7] Owing to poor contrast, it is not possible to get reasonable results for the thickness of films with less than six layers.

The "odd−even effect" implies that the nature of the outermost layer determines the swelling behavior of the whole film. On that basis, one can expect the surface wettability of PSS to be different from that of PAH. This was investigated and confirmed by the distinct difference between the contact angles obtained every time an additional layer of PSS or PAH was added. Figure 3 shows the change in the water contact angles as a function of the number of adsorbed layers. Although it is not a symmetrical zigzag while switching from one layer to the other, the trend is clear that multilayers with PSS as the outermost layer have a lower contact angle than multilayers with PAH as the outermost layer; i.e. the PSS surface is more hydrophilic than the PAH surface. McCarthy[19] reported similar findings on PAH/PSS system deposited on various substrates. This hydrophilicity impaired to PSS is quite intriguing since PSS, by its very chemical structure, possesses a more hydrophobic backbone due to the presence of benzene rings and this leads to a stronger adsorption of PSS at the air/water interface than in the case of other polyelectrolytes.[20] But PSS being a strong polyelectrolyte could have a higher charge density at the surface than PAH (which is a weak polyelectrolyte). Its charge density could be reduced at/near a charged surface, which in turn could make PAH less hydrophilic than PSS. Another reason for the "odd−even effect" could be explained by the results of simulations on the formation of multilayers performed by Holm.[21] They showed that the positively charged polyelectrolyte adsorbs quite flat on the substrate, while the following negatively charged polyelectrolyte form complexes with the underlying positively charged polyelectrolyte which results in the coiling of both layers. The next positively charged polyelectrolyte layer adsorbs again in a flatter confor-

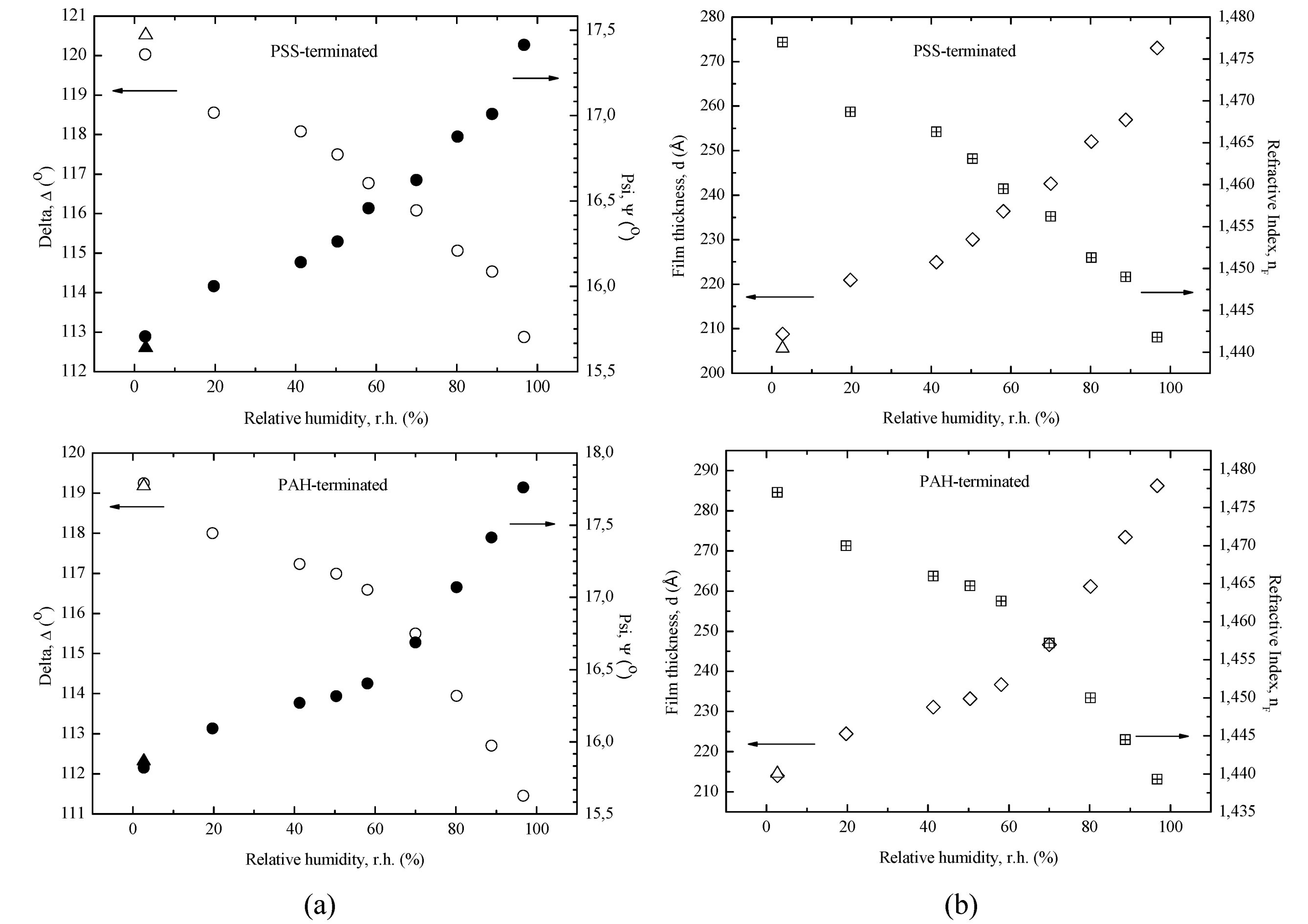


**Figure 1.** Variation of (a) Δ and Ψ from raw ellipsometric data, and (b) film thickness and refractive index, when an 18-layer (PSS as outermost layer) and 19-layer (PAH as outermost layer) film is exposed to increasing relative humidities (swelling). Deswelling (with decreasing humidity) is reversible, and for clarity, only one data point (triangular symbols) at 3% is shown in each plot.

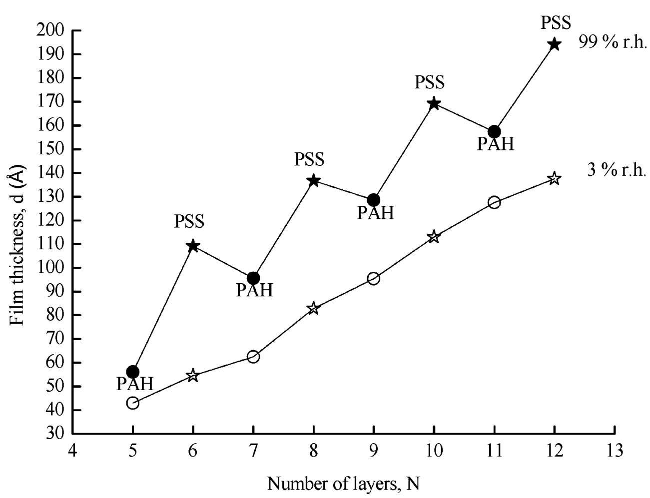


**Figure 2.** Ellipsometric data of multilayers of PAH/PSS prepared from 0.25 M NaCl polyelectrolyte solutions at 3% (dry state) and 99% (swollen state) rh.

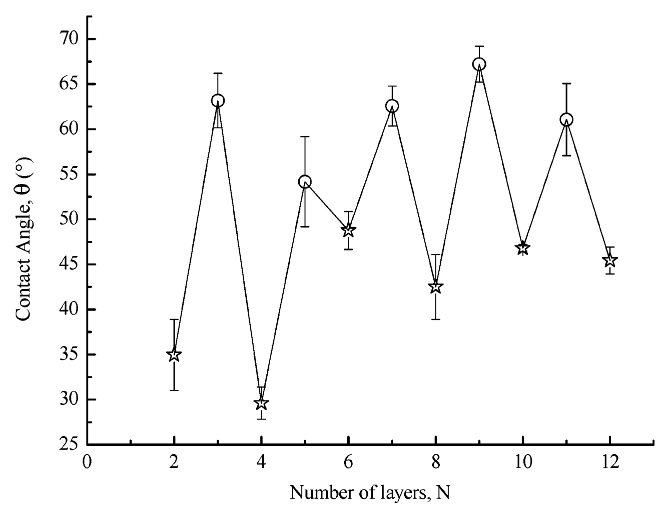


**Figure 3.** Change in the water contact angle measurements of the films as the outermost layer is alternately changed from PAH (circle) to PSS (star).

mation. According to the stronger swelling of the multilayers with (negatively charged) PSS as the outermost layer, this would mean that the rougher surface swells in a more pronounced way than the smoother surface. Bulk PSS is, by nature, more hygroscopic than bulk PAH. This, couple with the fact that PSS-terminated surface is more hydrophilic, it is not surprising that multilayers with PSS as the outermost layer swell more than those with PAH as the outermost layer.

Figure 4a shows a plot of the percentage of water in the swollen film[22] as a function of the number of layers in the film. The "odd−even effect" is still omnipresent, but it is reduced with increasing number of layers. In addition, the relative amount of water is effectively reduced from 50% in a 6-layer film to about 30% in a 12-layer film (and 23% in a 26-layer film). The "odd−even effect" in thickness is consistent with changes in

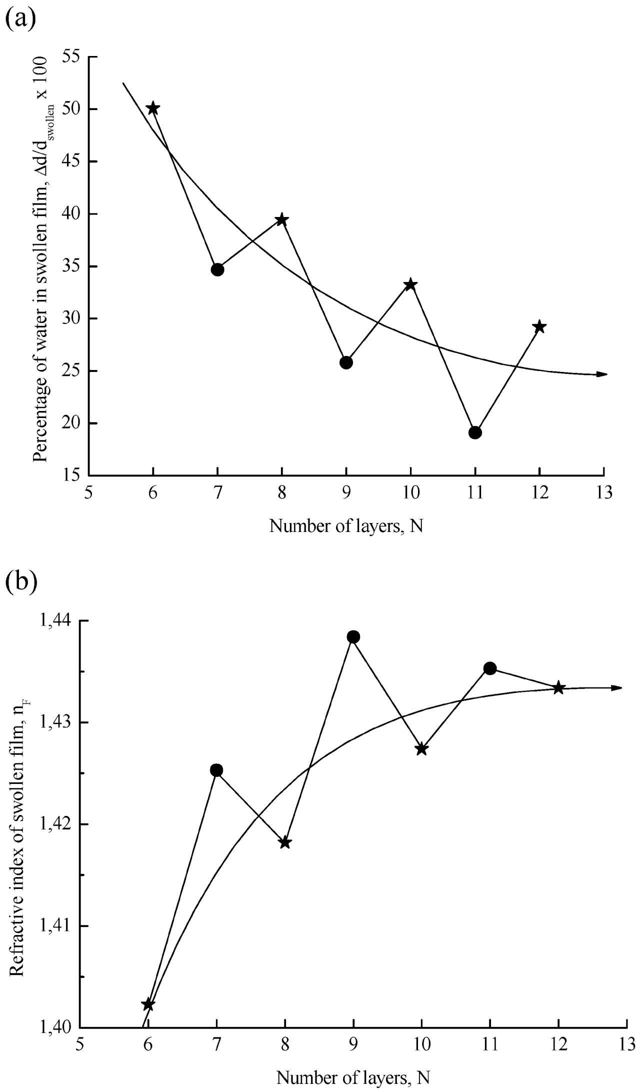


**Figure 4.** Plot of the (a) percentage of water content within the swollen film and the (b) refractive index of the swollen film, as a function of the number of layers.

the refractive index. Figure 4b shows a plot of the refractive index of the swollen film as a function of the number of layers in the film. The water-swollen film with PSS as the outermost layer has a lower *n* (i.e., a higher amount of water) than that with PAH as the outermost layer. As the water content in the swollen film decreases, the refractive index increases with increasing number of layers. The “odd−even effect” is reduced with increasing number of layers to reach a plateau around $n = 1.43$ − as obtained for a 26-layer film. The “odd−even effect” indicates that water has to be pressed out of the multilayer when PAH is adsorbed onto the PSS surface of the multilayer and that again more water diffuses into the multilayer on adsorption of the next PSS layer.

NMR studies[12] revealed a decrease of the water immobilization after the adsorption of a PSS layer, and from these data, it was concluded that multilayers with PAH as the outermost layer swell more than those with PSS as the outermost layer. However, the results of the present paper indicate that PSS associates more water than PAH. To correlate this with the NMR measurements, that could mean that not all the water in the film is immobilized and that there is some mobile water which is not detected by NMR measurements. The swelling after PSS adsorption could remobilize the water within the multilayer. An important fact to bear in mind is the high interdigitation of chains in the dry *as well as* in the swollen films. However, due to the swollen structure after the adsorption of PSS there could be “voids” for mobile water. After the adsorption of a PAH layer, the multilayer structure is more compressed, whereby part of the water can be expelled and part of the mobile water can be immobilized.

The relative amount of swelling with respect to the total film thickness decreases with increasing number of layers (Figures 2 and 3). This means that the effect of the outermost layer on the swelling process is reduced with increasing thickness of the multilayers, which is intuitive. This is also confirmed by the change in the refractive index which becomes less pronounced with increasing number of layers. Furthermore, the relative amount of water is reduced with increasing number of layers which indicates that the outer layers swell in a significantly more pronounced way than the inner ones closer to the substrate. A higher amount of water in the outer layer (∼ 60%) than in the inner part (∼ 40%) has also been observed by neutron reflectometry, where two boxes of different scattering length density were needed to fit the reflectometry curve.[9] The higher amount of water within the multilayers[9] in comparison to the presented results can be explained by the fact that neutron reflectivity experiments were carried out against liquid water. Recent experiments indicates that the multilayers swell more strongly in liquid water than in water vapor.[23] The *dry* multilayer could be fitted with one box of a homogeneous scattering length density. Permeability measurements showed that the diffusion coefficient of small additives (dyes or electron spin-labels) is higher in the outer layers than in the inner ones.[24] In both kinds of experiments the thickness of the more swollen outer layers is on the order of 100 Å. These findings are in good agreement with the three-layer model proposed by Ladam et al. where the two inner parts swell less than the outer part.[25] Figure 5 is a schematic representation of the swelling behavior of a thinner multilayer ($d$ < 100 Å in the swollen state) and of a thicker multilayer ($d$ > 100 Å) to explain the experimental data. It is assumed that for relatively thin multilayers, the whole multilayer swells, resulting in large $\Delta d/d_{swollen}$ values.

## Conclusion

The present paper shows that the swelling behavior of layer-by-layer assembly of PAH/PSS films could be quantitatively investigated under controlled humidity by ellipsometry. Two interesting effects have been found: (1) An “odd−even effect” in the swelling behavior with increasing number of layers in the PAH/PSS system is observed, showing clearly that the amount of water absorbed is dependent on the type of polyelectrolyte in the outermost layer. In the present case, multilayers with PSS as the outermost layer swell more than those with PAH as the outermost layer. This is related to a higher hydrophilicity of PSS-terminated surface as confirmed by a smaller contact angle than that obtained for PAH-terminated surface. The higher refractive index of multilayers with PAH as the outermost layer indicates that water has to be pressed out of the film following the adsorption of PAH, which leads to a decrease in the multilayer thickness. (2) The (average) volume percentage of water in the swollen film de-

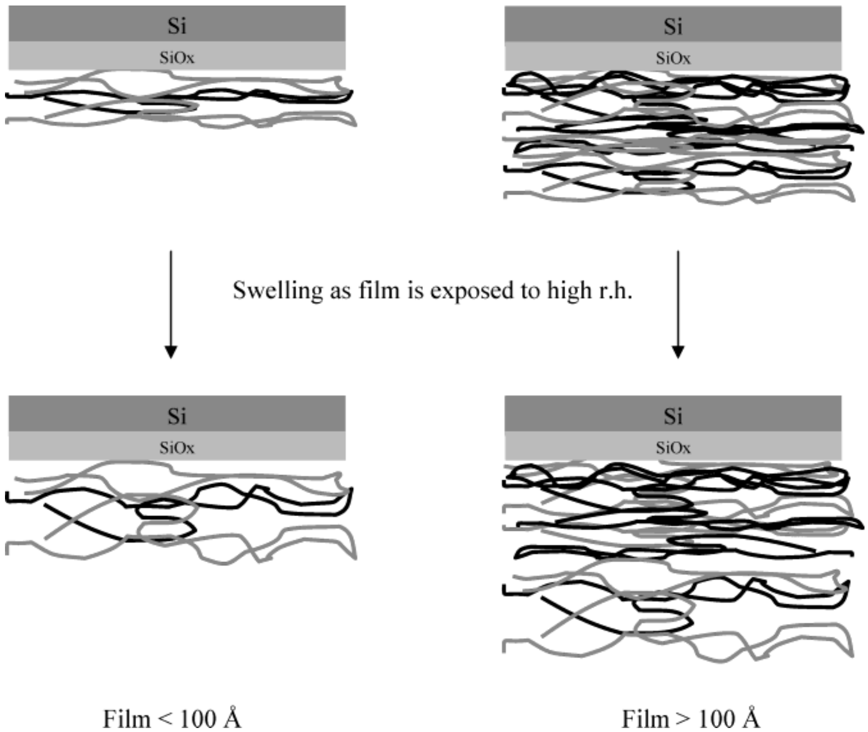


**Figure 5.** Proposed model for the structure of dry and swollen PAH/PSS multilayers for different number of adsorbed layers.

creases with increasing number of layers. The data indicate a smearing out of the "odd−even effect" with increasing number of deposited layers. This suggests that the loosely packed "outer layers" close to the multilayer/air interface contain more water and react in a more pronounced way to the environmental humidity.

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