J. Am. Chem. Soc. **2000,** *122,* 5841−5848

Adsorption and Desorption Behavior of an Anionic Pyrene Chromophore in Sequentially Deposited Polyelectrolyte-Dye Thin Films

Concetta Tedeschi, Frank Caruso,*,[†] Helmuth Möhwald, and Stefan Kirstein*,[‡]

Contribution from the Max-Planck-Institute of Colloids and Interfaces, D-14424 Potsdam, Germany

Received November 15, 1999

Abstract: Alternating thin films of the anionic dye pyrenetetrasulfonic acid (4-PSA) and poly(allylamine hydrochloride) (PAH) were formed by the squential deposition of 4-PSA and PAH from aqueous solution onto solid substrates. Film growth was followed by absorption spectroscopy, and the resulting polyelectrolyte-dye multilayer assemblies were characterized by using fluorescence spectroscopy, X-ray reflectivity, and atomic force microscopy (AFM) measurements. 4-PSA was successfully deposited in alternation with PAH when the ionic strength of the PAH solution was greater than 0.1 M. At each PAH adsorption step a given amount of previously adsorbed 4-PSA was extracted. The amount of dye released depended on the film thickness and the salt concentration in the PAH solution from which PAH was subsequently adsorbed. However, the total amount of dye remaining in the film after PAH deposition was essentially independent of the salt content in the PAH solution. Both X-ray reflectivity and AFM measurements revealed a high roughness of the 4-PSA/PAH multilayer films (ca. 20 Å). To gain a better understanding of the parameters that control dye adsorption and extraction, dye adsorption was also investigated by immersion of preformed PAH and poly(styrene sulfonate) (PSS) multilayer films of various thickness into 4-PSA solutions. The amount of 4-PSA absorbed by the films increased with film thickness, and saturated at a thickness above about 20 nm. For these films, subsequent adsorption of a PAH layer extracted most of the dye, except for a small amount approximately equal to that present in one 4-PSA/PAH bilayer prepared by the alternate adsorption process. These observations indicate that the dye molecules are adsorbed to a finite depth of about 20 nm, and after deposition of the oppositely charged PAH, a small amount that is independent of film thickness remains. The presence of this remaining 4-PSA is necessary to complex and bind the next PAH layer, hence allowing continued multilayer film growth. It was also found that the 4-PSA adsorption/desorption process depended on the drying process that was employed during the formation of the PSS/PAH multilayer films. The amount of dye as well as the penetration depth was reduced when the film was dried between deposition of each layer, and minor changes in the film structure were observed by X-ray reflectivity measurements.

Introduction

One promising method to fabricate structured organic thin films on solid substrates is the layer-by-layer self-assembly technique.[1] This process is based on the sequential adsorption of polycations and polyanions from dilute aqueous solution onto a solid support, utilizing the electrostatic interaction and complex formation between the oppositely charged polyelectrolytes for film build-up. The electrostatic nature of the interaction allows a variety of polyelectrolytes (PE) to be deposited, thereby forming pure polyelectrolyte multilayer films. This approach has been extended to various other materials, including inorganic nanoparticles,[2−4] dyes,[5,6] and biological macromolecules such as DNA[7,8] and proteins.[9,10] An attractive feature of the technique is that it allows the organization of different macromolecular species on a nanometer length scale. This enables the arrangement of "reactants" (e.g., optically active molecules or chemically active functional groups) at a molecular level, to produce cooperative electronic and optical properties including electroluminescence,[11−13] second-harmonic generation,[14] and photoinduced electron transfer.[15] Experimental studies on pure PE

---

* To whom correspondence should be addressed.

[†] FAX: +49-331-567-9202. E-mail: frank.caruso@mpikg-golm-mpg.de.

[‡] Present address: Humboldt University of Berlin, Institute of Physics, Invalidenstrasse 110, 10115 Berlin. FAX: +49-30-2093-7632. E-mail: kirstein@physik.hu-berlin.de.

(1) Decher, G. *Science* **1997**, *277*, 1232.

(2) Schmitt, J.; Decher, G.; Dressik, W. J.; Brandow, S. L.; Geer, R. E.; Shashidbar, R.; Calvert, J. M. *Adv. Mater.* **1997**, *9*, 61.

(3) Gao, M. Y.; Richter, B.; Kirstein, S.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102* (21), 4096.

(4) Kaschak, D. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118* (17), 4222.

(5) Ariga, K.; Lvov, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1997**, *119*, 2224.

(6) Yoo, D.; Lee., J.; Rubner, M. *Mater. Res. Symp. Proc.* **1996**, *413*, 395.

(7) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6117.

(8) Lvov, Y.; Haas, H.; Decher, G.; Möhwald, H.; Michailov, A.; Mtchedlishvily, B.; Margunova, B.; Vainshtain, B. *Langmuir* **1994**, *10*, 4232.

(9) Caruso, F.; Möhwald, H. *J. Am. Chem. Soc.* **1999**, *121*, 6039.

(10) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. *Langmuir* **1997**, *13*, 3427.

(11) Gao, M. Y.; Richter, B.; Kirstein, S.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102*, 4096.

(12) Ferreira, M.; Cheung, J. H.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 806.

(13) Cheung, J. H.; Fou, A. F.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 985.

(14) Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, *254*, 1485.

(15) Keller, S. W.; Johnson, S. A.; Yonemoto, E. H.; Brigham, E. S.; Mallouk, T. E. *J. Am. Chem. Soc.* **1995**, *117*, 12879.

10.1021/ja994029i CCC: $19.00

multilayer films have provided information on film thickness, surface roughness, adsorbed amount of polyelectrolyte, and internal film structure.[1,16−20] More recently, a number of investigations have been performed to gain a better understanding of the factors that govern the multilayer build-up process. The binding of dye molecules to preformed layers provides information on the extent of electrostatic association between oppositely charged polyelectrolytes in the multilayer films.[21,22] The layer-by-layer build-up of such films has also been closely examined with respect to the preparative conditions (e.g., drying, intermediate washing).[23] Incorporating dyes into the films enables one to use them as a probe to obtain detailed information about local features such as polarity or molecular mobility.

Previous studies that have applied the alternate assembly process to small charged organic molecules, including dyes,[5,24,25] have shown that due to the high water solubility of ionic dyes,[5] regular multilayer film formation depends critically on several factors: for example, polymer concentration[5] and ionic strength of the employed polymer solutions.[26] A common difficulty in the preparation of dye/multilayer films is the extraction of the preadsorbed dye that occurs with subsequent polyelectrolyte deposition. Studies on the influence of salt concentration on this process indicated that under conditions of high polymer concentration, dye incorporation into a polyelectrolyte matrix depends significantly on the ionic strength of the polymer solutions.[26] However, to date there have been no systematic investigations on the influence of multilayer film thickness on the dye extraction process during the alternate assembly process.

In this work, we investigate the incorporation of a charged dye molecule into the polyelectrolyte films using a model dye that exhibits four negative charges and a chromophore moiety that is sensitive to the local environment, namely, pyrenetetrasulfonic acid (4-PSA). It was further shown[27] that 4-PSA complexes the cationic polyelectrolyte chains in solution with a very high binding constant. Therefore, this dye was considered as most promising for the alternate adsorption with plyelectrolytes. In particular, we have studied the following: (1) the stepwise adsorption and desorption of 4-PSA during its alternate deposition with poly(allylamine hydrochloride) (PAH) on planar surfaces (this is expected to yield a defined position of the dye within the film; additionally, it is an interesting question, if the electrostatic dye/polymer bond will be released during the film forming process, since the dye is a building block that can diffuse through the film; this could be of importance for applications of controlled release) and (2) the extent of dye adsorption to preformed PAH/poly(styrene sulfonate) (PSS) multilayer films of various thickness (this may become the most simple technique to incorporate dyes in films).

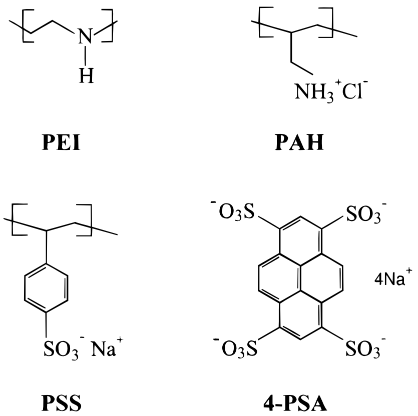

Figure 1. Chemical structures of the monomer units of poly(ethylenimine) (PEI), poly(allylamine hydrochloride) (PAH), poly(styrenesulfonic acid) (PSS), and the anionic fluorescent probe 1,3,6,8,-pyrenetetrasulfonic acid, tetrasodium salt (4-PSA).

In previous work,[22] we showed that the amount of dye adsorbed and extracted from PSS/PAH multilayer films assembled on polystyrene latex spheres depends on the film thickness (up to approximately 15 nm). Construction of the films on planar surfaces, however, allows examination of the multilayer build-up process by using absorption and fluorescence spectroscopy, while a detailed structural analysis of the film can be obtained by X-ray reflectivity and atomic force microscopy (AFM). Combining the data obtained from the various methods leads to a model describing dye penetration and binding, and dye removal from within polyelectrolyte films.

Experimental Section

Materials. The polyelectrolytes used for the preparation of the self-assembled films were poly(ethylenimine) (PEI), M_w 55000, poly(allylamine hydrochloride) (PAH), M_w 50000−65000, and poly(styrenesulfonic acid) (PSS), M_w 70000. All were obtained from Aldrich Chemical Co. and used as received, except for PSS, which was dialyzed against Milli-Q water and freeze-dried. PEI was used as the first layer of the film forming process to positively charge the substrates. The anionic fluorescent dye, 1,3,6,8,-pyrenetetrasulfonic acid, tetrasodium salt (4-PSA), M_w 610.42, was obtained from Molecular Probes (Oregon, USA). The chemical structures of the polymer monomer units and the anionic dye are shown in Figure 1. NaCl was from Merck (purity $>$99%). The ultrapure water used in all experiments was obtained by reversed osmosis followed by ion-exchange and filtration (Milli-Q purification system, Millipore, France) with a specific resistance better than 18 MΩ cm. Quartz slides ($1.25 \times 12 \times 46$ mm) were purchased from Hellma Optik (Jena, Germany).

Substrate Cleaning and Preconditioning. Quartz (Qz) substrates were cleaned using the RCA protocol:[28] that is, by immersing them in 5:1:1 (vol %) $H_2O/H_2O_2/NH_3$ at 80 °C for ca. 15 min, followed by extensive rinsing with Milli-Q water. After this cleaning procedure, the slides were completely hydrophilic. For all experiments, a prelayer of PEI was adsorbed on the Qz substrate by immersion (30 min) into a 10^{-3} M (monomer) aqueous solution of PEI. After adsorption, the films were rinsed by consecutively dipping them three times for 1 min in Millipore water and then dried with a gentle stream of argon.

Preparation of Multilayer Films. Multilayer films were formed on the PEI-coated Qz substrates by sequential deposition of PAH and 4-PSA or PAH and PSS. The concentration of the aqueous dye solution was 10^{-4} M, while that of the polyelectrolytes was 10^{-3} M (monomer). Solutions were with or without additional salt (NaCl). The samples were manually prepared by immersion in the polyelectrolyte and dye

---

[16] Decher, G. In *Comprehensive Supramolecular Chemistry*; Sauvage, J. P., Hosseini, M. W., Eds; Pergamon Press: Oxford, 1996; Vol. 9, pp 507−528.

[17] Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, *277*, 1225.

[18] Lowack, K.; Helm, C. A. *Macromolecules* **1998**, *31*, 823.

[19] Schmitt, J.; Grünewald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Lösche, M. *Macromolecules* **1993**, *26*, 7058.

[20] Hong, H.; Steitz, R.; Kirstein, S.; Davidov, D. *Adv. Mater.* **1998**, *10*, 1104.

[21] Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309.

[22] Caruso, F.; Lichtenfeld, H.; Donath, E.; Möhwald, H. *Macromolecules* **1999**, *32*, 2317.

[23] Lvov, Y.; Ariga, K.; Onda, M.; Ichinose, I.; Kunitake, T. *Colloids Surf.* A **1999**, *146*, 337.

[24] Araki, K.; Wegner, M. J.; Wrighton, M. S. *Langmuir* **1996**, *12*, 5393.

[25] Cooper, T.; Campbell, A.; Crane, R. *Langmuir* **1995**, *11*, 2713.

[26] Linford, M. R.; Auch, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, *120*, 178.

[27] Caruso, F.; Donath, E.; Möhwald, H.; Georgieva, R. *Macromolecules* **1998**, *31*, 7365.

[28] Kern, W. *Semicond. Int.* **1984**, 94.

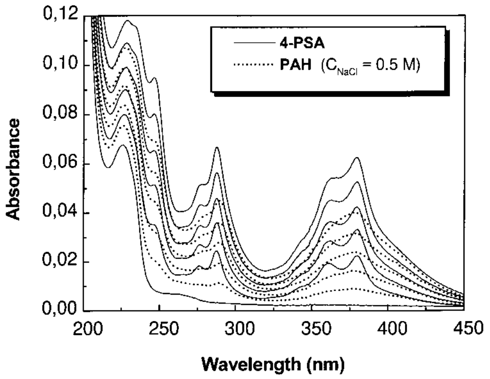

Figure 2. Absorption spectra of five 4-PSA/PAH bilayers, measured after each deposition cycle. The solid spectra are recorded after 4-PSA adsorption, and the dotted spectra after PAH deposition.

solutions for 20 min each. Immediately after rinsing with water, each layer was dried by an argon stream (unless otherwise stated).

All investigations on 4-PSA/PAH multilayer films were performed on films with the structure Qz/PEI/[PSS/PAH]$_2$/[4-PSA/PAH]$_n$. Here and throughout the text, each film, after the PEI-coated substrate, consists of n assembled *bilayers*. We note that the term *bilayer* does not imply a given structural property of the films.

Dye penetration was studied on preformed multilayer films with the structure Qz/PEI/[PSS/PAH]$_n$ with $n = 3$, 6, 9, or 12. The concentration of the polyelectrolyte solutions used to form these films was 10^{-3} M (monomer), while the salt concentration was adjusted to 1 M (NaCl). Some of these samples were prepared using an automated device (Riegler und Kirstein GmbH, Berlin).

Absorption and Fluorescence Measurements. UV/vis spectra were recorded with a Varian Cary-5 UV/vis spectrophotometer. Steady-state fluorescence measurements were performed with a Spex Fluorolog-2 (model FL-2T2) spectrofluorometer at room temperature. Emission spectra of 4-PSA in the PE multilayer films were measured in the front face arrangement using a solid sample holder. The excitation wavelength used throughout the experiments was 380 nm. The excitation and emission bandwidths were both 0.8 nm. Emission spectra for PE multilayer films were subtracted from the measured 4-PSA spectra.

Small-Angle X-ray Scattering (SAXS) Measurements and Data Analysis. X-ray reflectivity measurements were performed with a commercial $\theta/2\theta$ instrument (STOE and CIE GmbH Darmstadt, Germany, $U = 40$ kV, $I = 50$ mA, $\lambda = 1.54$ Å (Cu Kα)). The divergence of the incoming beam was 0.1°, and the 2θ resolution was 0.05°. The experimental data were fitted by a least-squares algorithm to a model using the Fresnel equations and the Parratt formalism.[29,30] The electron density of the film and the substrate perpendicular to the substrate plane was modeled assuming a constant density whereas the steps are smeared out by a Gaussian error function[31] to take into account the roughness at the interface ("one-box model").

Atomic Force Microscopy (AFM) Measurements. For the AFM measurements a commercial microscope (D-3000, Digital Instruments, Santa Barbara, CA) was used. Imaging was performed in tapping mode (TM) in air employing commercially available cantilevers (Nanosensors, Wetzlar, Germany) with a nominal tip radius of less than 10 nm. Tapping amplitude and especially the damping factor were carefully chosen to allow imaging of the polyelectrolyte surface structure without inducing alterations by the imaging process.

Results

Sequential Adsorption of 4-PSA and PAH. The growth of 4-PSA/PAH multilayer films formed by the sequential adsorption of 4-PSA and PAH was examined by using UV/vis absorption spectroscopy. A typical series of absorption spectra for the formation of 4-PSA/PAH films is shown in Figure 2. These spectra show the pyrene absorption after 4-PSA (solid spectra) and PAH (dotted spectra) deposition, respectively. The pyrene absorption is clearly identified by the characteristic peaks between 250 and 400 nm. The lowest solid line corresponds to the quartz substrate covered by PEI/[PSS/PAH]$_2$, which was used as a precursor film for all 4-PSA/PAH multilayer assemblies. The presence of salt in the PAH solution was necessary for 4-PSA/PAH multilayer formation. The spectra of Figure 2 are for 4-PSA/PAH multilayer films assembled using a PAH solution containing 0.5 M NaCl. The absorbance of the 4-PSA/PAH films is larger when 4-PSA was deposited as the last layer (i.e., 4-PSA as the outermost layer). More than 65% of the 4-PSA absorbance at 380 nm is lost when PAH is adsorbed after one layer of 4-PSA, indicating that 4-PSA has been extracted from the film. The removal of dye is accompanied by a broadening of the pyrene absorption spectra.

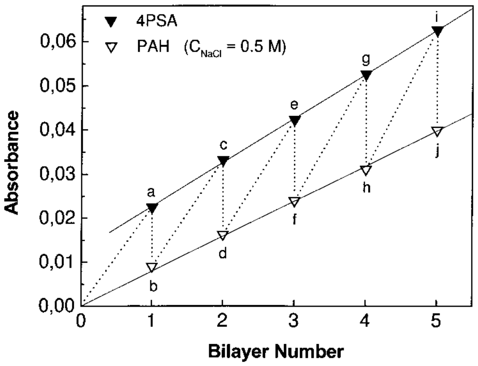

Figure 3. Absorbance at 380 nm versus the number n of 4-PSA/PAH bilayers, extracted from the data set shown in Figure 2. The initially adsorbed film of [PSS/PAH]$_2$ assembled on PEI-coated quartz substrate corresponds to zero absorbance. The dotted line is a guide to the eye to outline the stepwise dye adsorption/extraction process.

The adsorption/desorption process of 4-PSA is illustrated in more detail in Figure 3, where the absorption maximum of 4-PSA at 380 nm is plotted against the number of 4-PSA/PAH bilayers. It is seen that the extent of dye extraction increases with increasing number of bilayers (i.e. film thickness) while the increment of absorbance measured after adsorption of PAH is constant; i.e., the lines connecting the data points measured before and after PAH adsorption diverge with increasing bilayer number. This strongly suggests that the extraction process involves not only dye molecules adsorbed at the surface but also those that are more deeply incorporated within the polymer matrix. The absorbance measured after PAH deposition varies linearly with bilayer number, indicating that the amount of dye remaining in the film is linearly dependent on the film thickness.

The amount of dye bound to the film structure per 4-PSA/PAH bilayer can be estimated from the slope of the line in Figure 3 for data measured after PAH adsorption (b, d, f, h, j). Taking into account that the measured absorbance corresponds to film on both sides of the quartz substrate, an average absorbance of 0.004 per bilayer at 380 nm is obtained. Assuming a two-dimensional distribution of 4-PSA and using a molar extinction coefficient of 2.06×10^4 cm^{-1} M^{-1} for 4-PSA in solution at 380 nm, a mean area density of ca. 1.5 dye molecules per nm^2 is calculated from the Beer–Lambert law.

To understand the role played by salt in the formation of [4-PSA/PAH]$_n$ multilayer films, samples were prepared using PAH solutions with different NaCl concentrations. Figure 4 summarizes the multilayer growth of the films, as followed by UV/vis spectroscopy. The ionic strength in the polymer solution clearly influences the amount of dye that is adsorbed and

---

(29) Parratt, L. G. *Phys. Rev.* **1954,** *95*, 359.
(30) Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171.
(31) Névot, L.; Croce, P. *Rev. Phys. Appl.* **1980**, *15*, 761.

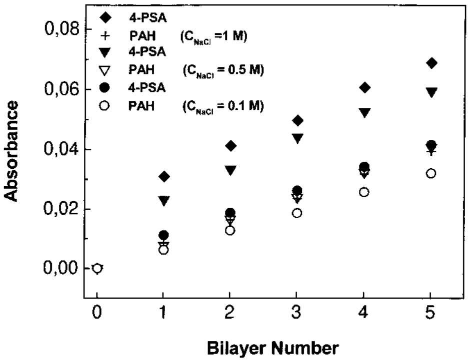

Figure 4. Absorbance at 380 nm versus bilayer number for multilayer films of the type PEI/[PSS/PAH]$_2$/[4-PSA/PAH]$_5$ prepared with different concentrations of NaCl in the PAH solutions. Closed symbol data points correspond to 4-PSA adsorption and open data points to PAH adsorption.

Table 1. List of Parameters To Describe the X-ray Reflectivity Data of the Sample of the Type PEI/[PSS/PAH]$_2$/[4-PSA/PAH]$_5$[a]

	samples	d/Å	$10^5\rho_{\mathrm{Film}}$/Å^{-2}	$\sigma_{\mathrm{film/air}}$/Å
a	0.1 M NaCl	70	1.27	19
b	0.5 M NaCl	86	1.57	22
c	1 M NaCl	96.5	1.67	21
d	PSS/PAH only	92	1.46	16

[a] The last line corresponds to a sample of type PEI/[PSS/PAH]$_3$. For all data the same parameters were used to describe the quartz substrate: $\rho_{\mathrm{quartz}} = 2.14 \times 10^{-5}$, μ_{quartz}=1.5×10^{-6}, $\sigma_{\mathrm{quartz/film}} = 6.5 \pm 0.5$.

Table 2. List of Relevant Parameters To Describe the X-ray Reflectivity Data of 12 DL of PSS/PAH after Different Drying Procedures[a]

samples	drying process	d/Å	$\sigma_{\mathrm{film/air}}$/Å
a	Ar-flow, every step	481 ± 1	10 ± 2
b	air, every step	510 ± 1	12 ± 2
c	Ar-flow, at end	510 ± 1	14 ± 2
d	air, at end	496 ± 1	12 ± 2

[a] For all data the same parameters were used to describe the quartz substrate and the scattering density of the film: $\rho_{\mathrm{quartz}} = 2.14 \times 10^{-5}$, $\mu_{\mathrm{quartz}} = 1.5 \times 10^{-6}$, $\sigma_{\mathrm{quartz/film}} = 5$, $\rho_{\mathrm{film}} = 1.43 \times 10^{-5}$. The electron densities were held at the same value in the fits of all the samples.

extracted from the film. The largest amount is observed for salt concentrations of 1 M, whereas the lowest amount of dye is extracted at NaCl concentrations of 0.1 M. However, the resulting amount of dye in the film after adsorption of PAH is only slightly different for the various salt concentrations.

The quality of the 4-PSA/PAH multilayer films was examined by X-ray reflectivity. The data could be described by a simple one-box model, assuming a constant electron density across the film. The parameters obtained from a best fit of the model to the experimental data are listed in Table 1. The roughness of the air/film interface for the 4-PSA/PAH films is more than 20 Å, whereas typical roughness values for PSS/PAH multilayer structures are in the range 10−16 Å (see Tables 1 and 2). The total thickness of the 4-PSA/PAH sample increases with the salt concentation of the polyelectrolyte solution from 70 Å for 0.1 M NaCl to 97 Å for 1 M NaCl. For comparison, the data of a film of three double layers of PSS/PAH are also given in Table 1.

The surface roughness of the 4-PSA/PAH samples and a three double layer sample of PSS/PAH was additionally examined by atomic force microscopy. In Figure 5 two images are presented which were recorded in tapping mode. Both samples were prepared with a salt concentration of 1 M NaCl. The root-mean-square value of the surface roughness, as extracted from the commercial software, was 1.1 and 3.3 nm for the PSS/PAH (a) and 4-PSA/PAH (b) multilayer films, respectively. These data are consistent with the trend seen in the X-ray reflectivity data.

Dye Adsorption to Preassembled PSS/PAH Multilayer Films. To examine the role of the film thickness on the 4-PSA adsorption process, preformed [PSS/PAH] multilayer films with a different number of bilayers (n = 3, 6, 9, 12) were prepared and exposed to a solution containing dye. Figure 6 shows the 4-PSA absorbance at 380 nm versus the number of PSS/PAH bilayers. The absorbance was measured after dipping the films into a 4-PSA solution for 20 min (closed symbols) and after additional dipping into a PAH solution containing 1 M NaCl (open symbols). The upper x-axis shows the mean film thickness obtained by X-ray reflectivity prior to the 4-PSA dipping. As in the case of the 4-PSA/PAH multilayers formed by the alternate assembly of 4-PSA and PAH, a significant amount of

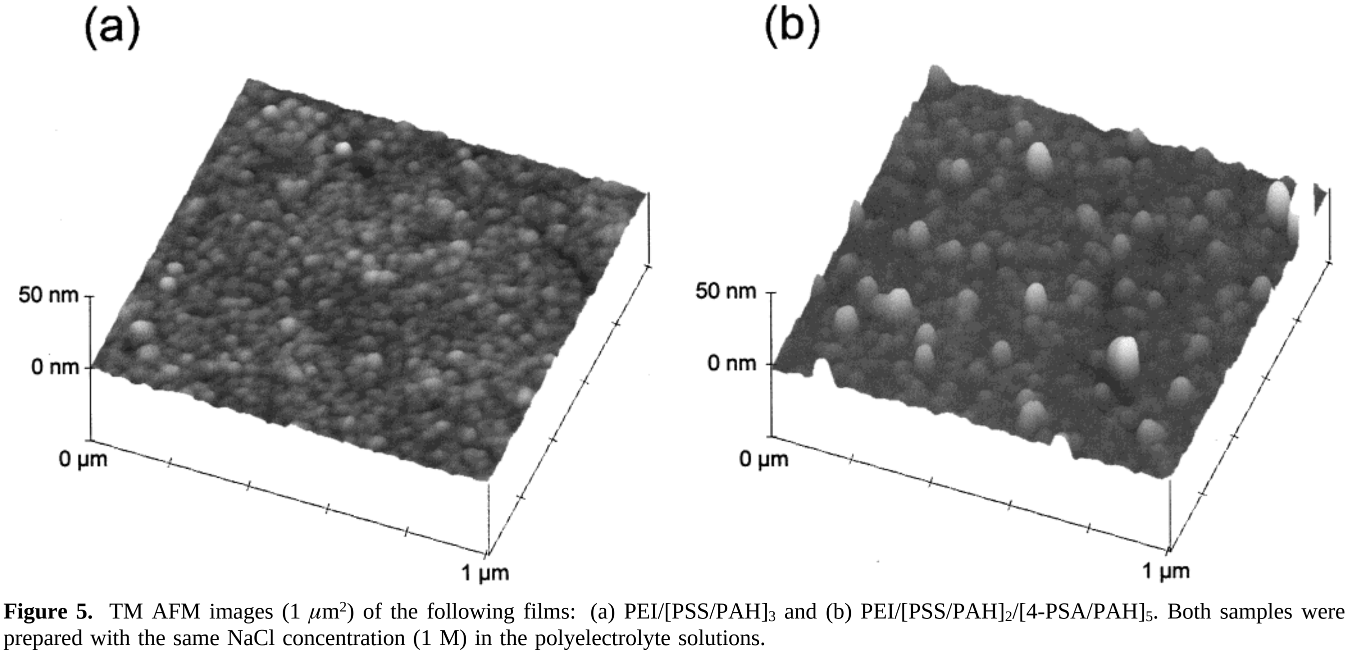

Figure 5. TM AFM images (1 μm^2) of the following films: (a) PEI/[PSS/PAH]$_3$ and (b) PEI/[PSS/PAH]$_2$/[4-PSA/PAH]$_5$. Both samples were prepared with the same NaCl concentration (1 M) in the polyelectrolyte solutions.

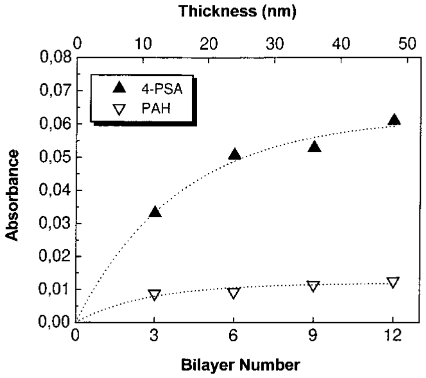

Figure 6. Absorbance at 380 nm for samples of the type PEI/[PSS/PAH]$_n$/4-PSA (solid symbols) and PEI/[PSS/PAH]$_n$/4-PSA/PAH (open symbols) where $n = 3, 6, 9$, and 12. The thickness of the films before adsorption of the 4-PSA/PAH layer is indicated on the top axis.

the adsorbed dye is extracted by exposure to a PAH solution. However, the amount of dye adsorbed does not increase linearly with film thickness but instead reaches saturation at a thickness above approximately 6 bilayers of PSS/PAH (i.e. film thickness of 20 nm). This finding is in agreement with our earlier work on 4-PSA binding to PAH/PSS multilayers assembled on polystyrene latex beads.[22] In that work saturation of 4-PSA binding was observed at about 11 PSS/PAH layers (or 5−6 PSS/PAH bilayers). After extraction of 4-PSA by PAH, the amount of dye remaining in the film is essentially constant at an absorbance of approximately 0.004 (the absorbance of the lower curve in Figure 6 divided by two). This value is surprisingly the same as that observed for each 4-PSA/PAH bilayer for films assembled by the sequential adsorption of 4-PSA and PAH.

Figure 7 displays the fluorescence spectra of 4-PSA adsorbed on [PSS/PAH]$_n$ multilayer films (a) before and (b) after the adsorption of an additional PAH layer. The peak at 404 nm is characteristic of the monomer emission of pyrene while the broad band centered around 500 nm is due to pyrene excimers. When 4-PSA forms the outermost layer, the spectra are dominated by excimer emission. After deposition of the outermost PAH layer, both the monomer and excimer emission intensities are dramatically reduced, reflecting extraction of 4-PSA from the film with PAH adsorption. This is in agreement with the absorbance data (see earlier). The high sensitivity of fluorescence spectroscopy allows detection of the remaining small amount of dye after subsequent deposition of a PSS layer onto PE multilayer films with preadsorbed 4-PSA. The measured spectrum after immersion of a 12 bilayer film into PSS solution is also shown in Figure 7. In this case, no excimer emission is visible, but a significant amount of monomer emission is observed.

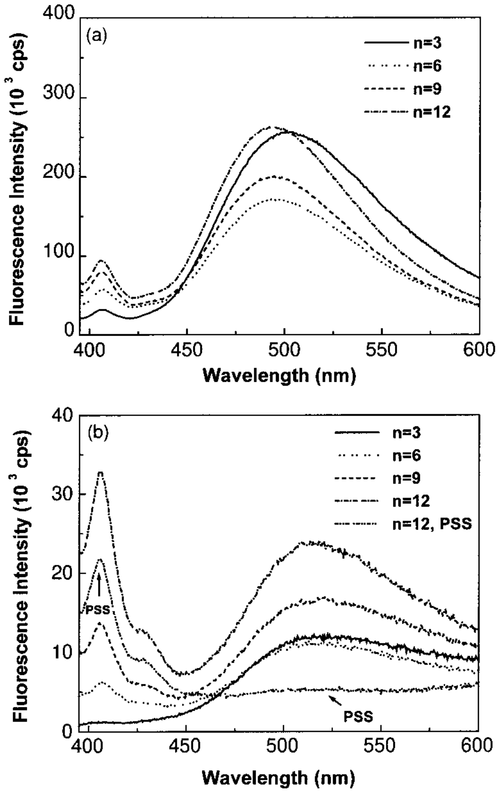

Figure 7. Fluorescence spectra of the same set of multilayer films specified in Figure 6. Spectra were measured after deposition of (a) 4-PSA and (b) 4-PSA and PAH. A spectrum is also shown after exposure of a PSS/PAH multilayer film with an outer 4-PSA layer to a solution of PSS. Note that the intensity scale differs by 1 order of magnitude between the spectra shown in panel a and those shown in panel b.

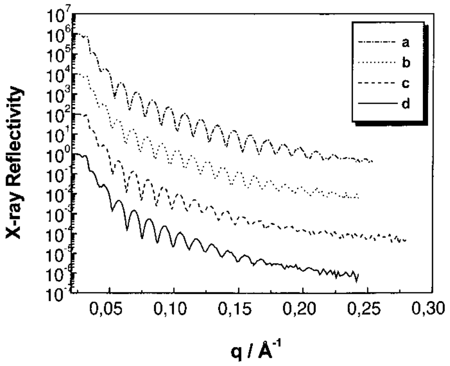

Figure 8. X-ray reflectivity spectra of four different multilayer films of the type PEI/[PSS/PAH]$_{12}$, prepared under different drying conditions: (a) drying after each layer deposition with a stream of argon; (b) drying by exposure to air after each layer; (c) drying after the assembly of 12 bilayers with a stream of argon; (d) as for c, but drying by exposure to air.

Influence of the Drying Procedure. The dye adsorption/desorption process was investigated by using films that were prepared under different conditions with respect to the drying process. Four different sets of samples were prepared, each consisting of films with 3, 6, 9, and 12 PSS/PAH bilayers. The different drying procedures were as follows: series a was dried by a stream of argon after each dipping process; series b by exposure to air for 7 min after each layer was deposited; and series c and d only at the end of the multilayer film formation by argon flow and air, respectively. X-ray reflectivity data of the 12 bilayer samples for all four sets are shown in Figure 8. The corresponding data extracted from the fits using a one-box-model are listed in Table 2. The structure of the films, as apparent from the X-ray reflectivity data, differs mainly in the film/air roughness, which is larger for samples c and d (drying at the end) compared to samples a and b (drying at every deposition step). The total film thickness also varies by ca. 5%, which is comparable to the variations in sample reproducibility.

The four differently prepared sets of PSS/PAH multilayers were subsequently exposed to 4-PSA solution for 20 min. The amount of dye adsorbed was measured by UV/vis absorption spectroscopy and the results are shown in Figure 9. Qualitatively, the same tendency of saturation is observed for all four films. However, a different saturation value is attained between the samples prepared by drying at each step (a and b) and those dried at the end of film assembly (c and d). The data can be

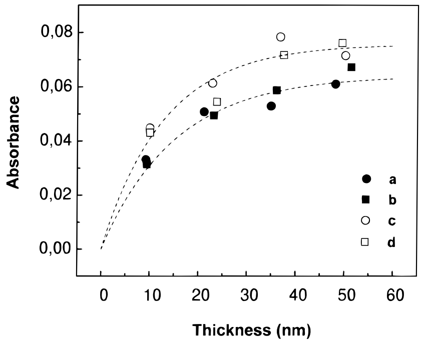

Figure 9. Absorbance of pyrene at 380 nm as a function of the thickness of the PSS/PAH multilayers, prepared under different drying conditions and after immersion into a solution of 4-PSA. The dotted lines are the best fits of an exponential curve $a = a_0[1 - \exp(-x/x_0)]$ to the averages of the values *a* and *b*, and *c* and *d*, respectively. The labels a, b, c, and d, refer to the same drying procedures as indicated in Figure 8. The parameters obtained from the best fits are $a_0 = 0.064$, $x_0 = 15.1$ nm and $a_0 = 0.076$, $x_0 = 12.8$ nm for the two sets a,b and c,d, respectively.

described by an exponential curve $a = a_0[1-\exp(-x/x_0)]$, as shown in Figure 9. The two dashed lines represent a best fit to the average values of the corresponding data sets. For the films a and b, the saturation value $a_0 = 0.064$, and for the films c and d, $a_0 = 0.076$.

Discussion

The experimental results can be explained within the framework of the proposed model illustrated schematically in Figure 10. The dipping of a preformed PSS/PAH multilayer film (Figure 10, step 1) into a solution of 4-PSA results in adsorption of the dye not only at the film surface but also into the polyelectrolyte film with a finite depth (Figure 10, step 2). This is concluded from the absorption measurements of preformed PSS/PAH multilayers exposed to a 4-PSA solution, which show a clear increase in the amount of 4-PSA adsorbed for thin films (less than 6 bilayers) followed by a saturation value reached above 10 bilayers. This behavior can be described by a smoothly decaying dye concentration with respect to the concentration at the film surface. The typical penetration depth as well as the depth profile in principle can be extracted from the data shown in Figure 6. Here, the absorbance (which is a measure of the total amount of dye within the film) versus film thickness is fitted by an exponentially increasing curve with a decay constant d_0 of 17 nm. This curve reflects the integral of the density profile and thus, within this model, the dye concentration decreases exponentially from the surface toward the interior of the film with a decay length, referred to as the *penetration depth*. This is of the order of 17 nm (Figure 10, step 2).

It is interesting to ask if the dye concentration profile within the film is due to penetration kinetics or due to a variation of the structure along the film normal. In the first case, one could estimate the diffusion coefficient *D* from the measured width d_0 =17 nm of the distribution and the immersion time $t = 20$ min according to $D = d_0^2/2t = 10^{-15}$ cm^2/s. This value is not unreasonable with respect to recent experiments using similar dyes.[32] However, the values are known to vary by orders of magnitude for different dyes, and data for this specific system have not been measured. The second case is favored by the fact that diffusion coefficients have been shown to be strongly depth dependent,[32] suggesting a larger free volume near the surface that can be filled by the dye.

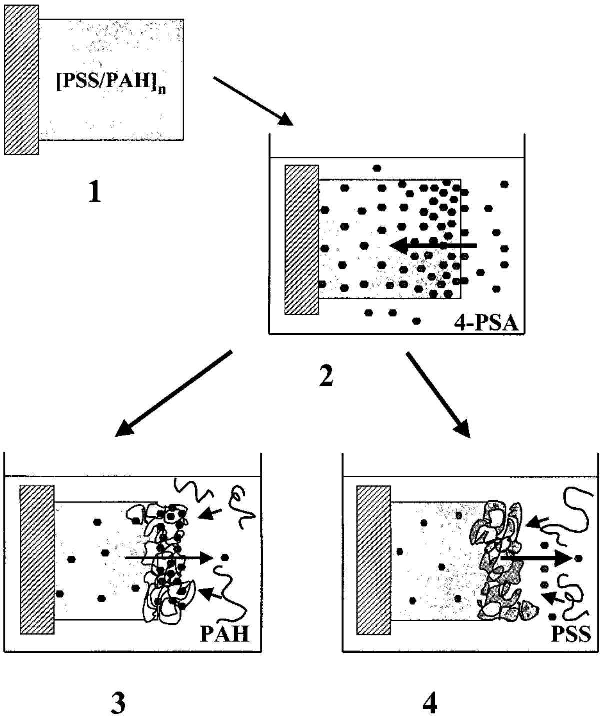

Figure 10. Schematic illustration of the adsorption and desorption process of 4-PSA molecules interacting with a PSS/PAH multilayer film: (1) Film of *n* PSS/PAH multilayers. (2) Film of *n* PSS/PAH multilayers after dipping into the dye solution, a high 4-PSA concentration is achieved within a certain depth from the top of the film, and dye molecules are distributed over the whole film with a lower concentration. (3) Film of *n* PSS/PAH multilayers after adsorption of an additional layer of PAH, most of the dye is released and the remaining molecules are concentrated in the vicinity of the surface. A small concentration remains equally distributed over the whole film. (4) Film of *n* PSS/PAH multilayers after deposition of a PSS layer instead of PAH, almost all dye molecules are extracted from the film. Only a very small concentration of distributed dye remains in the film.

When the film is immersed afterward into a solution of PAH, a large fraction of the dye is extracted and released into the polyelectrolyte solution (Figure 10, step 3). However, the amount of dye remaining is virtually independent of the thickness of the PSS/PAH multilayer (Figure 6, lower line); only a very slight increase in the amount of dye in the film with increasing film thickness is observed both in UV/vis and fluorescence spectroscopy. This rate of increase in absorbance with film thickness is found to be less than 3% of that found for the sequentially adsorbed 4-PSA/PAH films (Figure 3) and is attributed to a spurios amount of dye distributed throughout the whole film. However, the major amount of 4-PSA remaining is due to dye bound to the surface. This amount is identical with that which is found per bilayer in the sequentially assembled 4-PSA/PAH multilayer films after dipping them into a PAH solution (see Figure 4). This indicates that an amount of dye that enables the binding of a subsequent “layer” of PAH is retained. Therefore, most of the dye is localized in the vicinity of the surface, where it can interact with the incoming PAH for adsorption.

From the absorbance data, a mean surface coverage of one 4-PSA molecule per 0.7 nm^2 is calculated. This is less than that required for monolayer coverage of the surface. Taking into account that the dye should be distributed along the normal plane of the film over a range which corresponds to a typical thickness

---

[32] Klitzing, R. v.; Möhwald, H. *Macromolecules* **1996**, *29* (21), 6901–6906

of a single PAH layer, i.e., 2 to 3 nm, it is reasonable to assume that this amount of dye is not sufficient to bind large amounts of PAH to produce a complete and homogeneous new layer. Rather, a submonolayer will form. This is strongly supported by the X-ray reflectivity data of the stepwise adsorbed 4-PSA/PAH multilayer structures. The total thickness of a PEI/[PSS/PAH]$_2$/[4-PSA/PAH]$_5$ film is comparable to that for PEI/[PSS/PAH]$_3$. This means that the average thickness of five bilayers of 4-PSA/PAH is only of the order of a single bilayer of PSS/PAH, approximately 3 nm. Further, the surface roughness of the whole film, as deduced from fitting the X-ray reflectivity data, is comparable with the thickness of the dye/polycation film. Thus, although a linear growth of the absorbance in the 4-PSA/PAH films is observed (Figure 3), the formation of homogeneous and smooth 4-PSA/PAH films cannot be confirmed by the X-ray reflectivity data. Additionally, the AFM measurements reveal that the surface roughness of 4-PSA/PAH multilayers is a factor of 3 larger than that for PAH/PSS multilayer films (RMS of 3.3 and 1.1 nm, respectively) (Figure 5).

The adsorption of PSS instead of PAH (Figure 10, step 4) leads to almost total removal of the dye from the film. The small amount that is still detected by fluorescence spectroscopy is related to the fraction distributed homogeneously within the interior of the film; this amount is lower than that observed when PAH rather than PSS is adsorbed. Since the concentration of dye within the film is very low, no excimer emission is observed (Figure 7b).

The release of 4-PSA in the interior of the film (i.e. that which is not involved in binding of newly adsorbed PAH) is also confirmed by the shape of the absorption and fluorescence spectra (Figure 2). During the stepwise adsorption of 4-PSA and PAH, the absorption spectrum is not only reduced in intensity when PAH is adsorbed but it is also broadened. Since this is caused by inhomogeneous broadening, it is assumed that the dye used for PAH complexation experiences a broader range of environments than the dye simply diffusing into the film. Thus, the absorption spectra can be regarded as a superposition of a broad form, reflecting dyes bound to PAH at the surface region, and a sharp one, describing dyes within the film. Similarly, the excimer emission band of the fluorescence spectra shown in Figure 7b corresponds mainly to dyes bound in the surface region of the film.

Since the adsorption and desorption of dye mainly originates from the underlying layers of PSS/PAH and given that the coverage of the outermost 4-PSA/PAH layer cannot be considered as a complete monolayer, the following question remains: How can the dye adsorption and extraction during the 4-PSA/PAH "multilayer" formation (see Figures 2 and 3) be understood? Therefore, one has to remember that all of these samples were prepared on top of two precursor bilayers of PSS/PAH. Hence, the adsorption/desorption process observed in Figures 2 and 3 is simply due to "binding" and "extraction" of the dye to and from the PAH/PSS film. The absorbance values after the first immersion of the PEI/[PSS/PAH]$_2$ sample into the dye solution and after the adsorption of the next PAH layer (0.024 and 0.008) are in good agreement with those extracted from Figure 6 for two bilayers (0.027 and 0.008). Therefore, the release of dye is mainly from within the preformed PSS/PAH film.

The above finding is in qualitative and quantitative agreement with the earlier study on the binding and release of 4-PSA into PSS/PAH multilayer films assembled on colloids studied by using fluorescence spectroscopy.[22] In that work it was shown that the asdorption and release of 4-PSA depends on the thickness of the preformed PSS/PAH multilayers and a finite penetration depth of roughly 6 double layers was proposed.

It is still not completely understood why the dyes are removed from the bulk of the film when an additional layer of PAH is adsorbed. It is clear that this cannot be solely due to better solubility of the dyes within the aqueous polyelectrolyte solution, since the dyes are not removed by the intermediate washing process in water. In our previous work[22] it was suggested that the dye removal is due to a structural rearrengement of the film caused by long-range electrostatic interactions between the outermost layer and the charged groups within the film. However, an alternative explanation may be, since the films are porous enough to allow the dyes to penetrate and move freely within them,[32,33] that the concentation of dyes within the film is given by the surface potential created by the outermost layer. In the case of a positively charged layer (PAH), the negatively charged dyes are concentrated at the surface and either they are used for binding with the new PAH layer or they are more easily dissolved in the solution. If no PAH layer is adsorbed the dyes at the surface are forming a negative and hence repulsive potential for the dyes. Therefore, they are forced to penetrate more deeply into the film.

In any case, the amount of adsorbed dye material should depend on the internal structure of the film, i.e., the concentration of free sites for the dyes to go inside. A simple method that could affect the porosity of the films is the drying procedures employed during the film formation. The influence of drying on the structure of layer-by-layer deposited polyelectrolyte films has been studied previously by X-ray reflectivity measurements[33] and using a quartz crystal microbalance.[22] However, these studies present contradictory results. In the article of Hong et al.[20] it is shown that drying of the films after each layer deposition results in a smoother film/air interface and also thinner films. In contrast, Lvov et al.[23] demonstrate by means of electron microscopy that drying after each step results in thicker films and higher interface roughness. Here, no difference in film thickness for the different drying procedures could be observed and the differences in film/air roughnesses (see Table 2) are not significant.

It was argued in previous work[20] that drying affects the conformation and the mutual binding of the polyelectrolytes due to the removal of water. Here we have obtained direct evidence for a change of the internal structure of the polyelectrolyte films due to the drying process. In Figure 9, the two dotted lines representing an average adsorption of dye after different drying conditions of the PSS/PAH multilayer structure show a different saturation value, with a lower value when the film was dried after each layer. This indicates that films that are dried after each deposited layer absorb less dye. It was recently shown that the polyelectrolyte multilayers use only a fraction of their available charges for the mutual binding, while the other charges are compensated by small ions.[22] It was further demonstrated that an oppositely charged dye preferentially binds to charged groups that do not form ion-pairs. If less probe is absorbed by the film, fewer sites are present for the dye to bind to and/or some of these sites are not accessible. Since the dye only binds to polyelectrolyte charges that do not form ion-pairs, it is most probable that the drying process results in multilayer films which have fewer ion-pairs and/or reduced probe accessibility. The drying process alters mostly the conformation of the polymer backbone but does not influence the average density of the film.

---

(33) Caruso, F.; Donath E.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102* (11), 2011−2016.

This is in accordance with the results obtained from the X-ray reflectivity measurements.

Conclusions

The exposure of a polyelectrolyte multilayer film to a solution of a low molecular weight dye which is oppositely charged to the outermost polyelectrolyte layer results in adsorption of the dye at the film surface and within the film to a finite depth. The penetration depth is influenced by the method of preparation of the polyelectrolyte films, e.g., by drying. A large amount of dye adsorbed in the film is released upon dipping the dye saturated multilayer films into polyelectrolyte solution. A small amount of homogeneously distributed dye remains within the film when a polyelectrolyte of the same charge as the dye is adsorbed, whereas a polyelectrolyte of opposite sign uses preadsorbed dye molecules to form complexes, allowing multilayer growth.

The almost complete withdrawal of 4-PSA by a polyelectrolyte of the same charge is explained by an ion exchange process at the surface. The observed “multilayer” formation of 4-PSA/PAH does not reflect homogeneous layer by layer growth, but is due to the deposition of submonolayers of dye/polyelectrolyte material.

Acknowledgment. We thank Georg Papastavrou for performing the AFM measurements and Andrea Holzwarth for help with the X-ray measurements. F.C. acknowledges the Federal Ministry of Education, Science, Research and Technology (BMBF) for funding and C.T. the Max-Planck-Society for a research fellowship.

JA994029I