Polarity of Layer-by-Layer Deposited Polyelectrolyte Films As Determined by Pyrene Fluorescence

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Abstract: The polarity of polyelectrolyte (PE) multilayer films is investigated with pyrene as a polarity-sensitive probe. Multilayer films of poly(styrene sulfonate) (PSS) and various polycations were prepared by the layer-by-layer self-assembly technique. Pyrene (PY) molecules were inserted into the films by exposing the multilayers to pyrene solutions. By this method a homogeneous distribution of pyrene molecules at low concentration within the film was obtained. The ratio of the fluorescence intensities of the first (I) to the third (III) vibronic band (Py-value) of the pyrene emission spectrum is employed here to determine the polarity of the PE films. PSS and poly(allylamine hydrochloride) (PAH) multilayer films yielded a pyrene value close to the solvent polarity of acetone, while multilayers of PSS and poly(diallyldimethylammonium chloride) (PDADMAC) displayed a value higher than the one corresponding to water. The pyrene values of the polyelectrolyte films were independent from the solvent employed for probe dissolving. Although no direct relationship between solvent polarity and dielectric constant (ϵ) is available, an estimate of the static dielectric constant of the films can be provided by comparing the Py-values of the films with those of various solvents. Changes in the humidity conditions of the film environment in a closed cell did not affect the film polarity. However, a drastic and irreversible reduction of polarity could be induced by actively drying the samples by a nitrogen flow.

Introduction

The layer-by-layer (L-by-L) self-assembly technique[1] has been widely used to build up multilayer films on a nanometer length scale. The technique, originally developed for the sequential adsorption of oppositely charged polyelectrolytes (PEs) on planar substrates, has been successively adapted to prepare films containing various other macromolecular species. By using electrostatic attraction between alternately deposited charged species, inorganic nanoparticles,[2−4] biological macromolecules,[5−7] and several polyelectrolytes and dyes[8,9] have been deposited. Because of the possibility of building up vertically structured multilayer films on almost arbitrary substrates, the L-by-L technique provides a useful synthetic path for fabricating interesting functional supramolecular systems.[10] For example, the assembly of electroluminescence[11−13] and photovoltaic[14,15] devices has been achieved. The electronic properties of such devices are strongly related to intermolecular charge-transfer processes between a donor and an acceptor molecule. The rate and hence efficiency of an electron-transfer process is known to depend on the polarity of the surrounding medium.[16,17] It is a common difficulty to define quantitatively the polarity of the environment closely surrounding a molecule. In a macroscopic view a medium is considered as a homogeneous continuum and it is essentially described by physical constants such as the static dielectric constant (ϵ_r), for example. On a molecular length scale the bulk characteristics of solutions and of more highly organized systems are not easy to describe. Intermolecular interactions determine the properties of the chemical system and factors such as molecular structure and conformation, electrostatic, dipolar, and multipolar interactions, as well as short-range dispersive forces have to be taken into account. For solvents, the term *solvent polarity* has been introduced to describe all these interactions and it defines the overall solvation capability of solvents.[18,19]

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Although various electronic and optical properties of several poleyelectrolyte multilayer systems have been investigated, less attention has been paid until now to their dielectric properties. Only recently have a few investigations of the dielectric constant[20] or refractive index[21] of polyaion/polycation multilayers been reported.

In this work we investigate the micropolarity of multilayer films by using the fluorescence emission of pyrene molecules. Pyrene (PY) is one of the most commonly used polarity-sensitive probes. The $\pi^* \to \pi$ emission spectrum of monomer pyrene exhibits five well-resolved major vibronic bands between 370 and 400 nm, generally labeled I, II, III, ..., V, in progressive order. Due to coupling of the electronic and vibronic states,[22−24] the first vibronic band (0−0 transition, labeled as I) undergoes significant intensity enhancement with increasing solvent polarity compared to the third band (0−2 transition, labeled as III).[25,26] By the ratio of emission intensities of the vibronic bands I and III (indicated as I/III) measured in different solvents, the so-called Py-scale of solvent polarity has been established and the values I/III are generally referred as Py-values.[27] The Py-scale has been widely used to characterize the polarity of structured or anisotropic media like micelles, biological membranes, or polymer blends.[28,29]

In this work pyrene molecules are inserted into preformed polyelectrolyte multilayer films prepared by the layer-by-layer self-assembly technique. Although the probe molecules in the polymer matrices may be distributed on different sites having a distinct type of polarity, the measured spectra represent an average of the emission characteristic of the environment sensed by individual probe molecules. Thus, the polyelectrolyte multilayers are here considered as homogeneous media and their polarity is macroscopically estimated by using the Py-scale of the solvent polarity.

Additionally, the polarity of the polymer films has been studied with respect to different conditions of the humidity of the air and the drying process used for film preparation. Previous studies on pure polyelectrolyte multilayer films by neutron reflectivity measurements have demonstrated that a significant amount of water is retained in the films.[30,31] This amount was dependent on the drying process employed for film preparation.[31] However, to date there have been no investigations on the influence that the water content within the PE films could have on their polarity.

Experimental Section

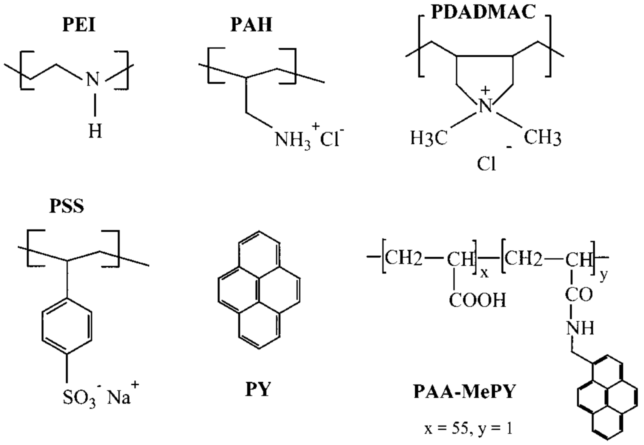

Figure 1. Chemical structures of the monomer units of poly(ethylenimine) (PEI), poly(allylamine hydrochloride) (PAH), poly(styrenesulfonic acid) (PSS), and poly(diallyldimethylammonium chloride) (PDADMAC). The fluorescent dye molecules were unsubstituted pyrene (PY) and poly(acrylic acid) (PAA) labeled with 1-pyrenylmethylamine (MePY).

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(diallyldimethylammonium chloride) (PDADMAC), M_w 200000−350000, as polycations, and poly(styrenesulfonic acid) (PSS), M_w 70000, as polyanion. All were purchased from Aldrich Chemical Co. and were used as received, except for PSS, which was dialyzed (Millipore GmbH, France, Filter type PBGC 07610, molar weight exclusion 10000 g/mol) against Milli-Q water and freeze-dried. No additional buffers were added to the polyelectrolyte solutions to adjust the pH value. The pH was in the range of 5.7 for PSS and PAH and 9 for PEI. For all samples PEI was used as the first layer of the film forming process to positively charge the substrates. Pyrene (PY), M_w 202.26, (purity > 99%), was obtained from Aldrich Chemical Co. and used without further purification. The pyrene-labeled copolymer poly(acrylic acid) (PAA), M_w 150000, labeled with 1-pyrenylmethylamine (MePY), was prepared by amidation of a commercial PAA sample[32] and obtained as a donation of D. F. Anghel. The chemical structures of the polymer monomer units and the 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. All organic solvents were of UV spectroscopic grade and were used without further purification. To vary the relative humidity (RH) of the atmosphere saturated aqueous salt solutions of sodium hydroxide (NaOH, 6% RH at 20 °C)[33] and sodium hydrogen phosphate (Na_2HPO_4, 95% RH at 20 °C)[33] in contact with excess salt were employed. The purity of all salts was higher than 99% (Fluka). Slides (1.25 × 12 × 46 mm or 1.2 × 9 × 35 mm for humidity measurements) and cuvettes (45 × 12.5 × 12.5 mm, five windows, light path 10 × 10 mm) were made of quartz suprasil and purchased from Hellma Optik (Jena, Germany).

Substrate Cleaning and Preconditioning. Quartz (Qz) substrates were cleaned by using the RCA protocol,[34] which means immersion 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 polyanions and polycations. All polyelectrolyte solutions were prepared at a

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concentration of 10^{-3} M (monomer) and contained 1 M salt (NaCl). The samples were manually dipped into the polyelectrolyte solutions for 20 min each. Immediately after rinsing with water, each layer was dried by an argon stream. Each prepared film, after the PEI-coated substrate, consisted of *n* assembled polyanion/polycation *bilayers*. The term *bilayer* is here used without reference to the internal structure of the PE films.

Dye insertion into the films was performed by using either unsubstituted pyrene (PY) molecules or the pyrene-labeled copolymer (PAA-MePY). For unsubstituted pyrene, preformed *PSS/polycation* multilayer films were prepared (as previously described) and pyrene was adsorbed onto the films by simply exposing the multilayers to a solution containing the dye. After being rinsed with water, the samples were dried by an argon stream. Due to the rinsing with water approximately 30% of the dye molecules was removed from a film of four bilayers, as examined by absorption spectroscopy. Additionally, remaining impurities of the solvents were washed aout. The concentration of the dye solutions was of the order of 10^{-6} M, otherwise stated. Employing the pyrene-labeled copolymer sequential adsorption of PAA-MePY and PAH was performed by the layer-by-layer technique. The aqueous solution of the pyrene-labeled copolymer was 10^{-3} M (with respect to the COOH groups), so that the pyrene concentration was 1.7×10^{-5} M. The measured pH value of the aqueous solution (ca. 4.5) was adjusted to 7 by adding NaOH to fully dissociate the carboxylic groups.

Absorption and Fluorescence Measurements. UV/vis spectra were recorded with a Varian Cary-5 UV/vis spectrophotometer. Steady-state fluorescence spectra were recorded using a Spex Fluorolog-2 (model FL-2T2) spectrofluorometer (ISA, Olching, Germany) at room temperature. Emission spectra of PY in the PE multilayer films were measured in a front face arrangement. The excitation wavelength used throughout the experiments was 340 nm and the excitation and emission slit widths were both adjusted to a resolution of 0.8 nm. It was verified by measuring the emission spectrum of pyrene in pure solvents that with this settings the Py-values can be measured with an accuracy of 3%. Except for *PAA-MePY/PAH* multilayer films, the emission spectra of undoped PE multilayers films were subtracted from the measured PY spectra. To study the influence of humidity on the polarity of PE multilayer films the samples were fixed on a Teflon holder and enclosed into a quartz cuvette in which the humidity was controlled by using saturated acqueous salt solutions.

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). The experimental data were fitted by a least-squares algorithm to a model by using the Fresnel equations and the Parratt formalism[35,36] as described in a previous work.[9,30]

Results

Polarity Determination. To examine the polarity of self-assembled polyelectrolyte films, six samples of the type PEI/[PSS/PAH]$_4$ were prepared on quartz substrates. Each film was exposed to a pyrene solution and each solution was prepared with a different solvent. *n*-Hexane and water were chosen as the two representative solvents for the most aprotic apolar and protic polar, respectively. After the samples were rinsed with water and dried with an argon stream, fluorescence measurements were performed. When the fluorescence of Py molecules is detected in different solvents as shown in Figure 2a (here the spectra are normalized at the first band I), the intensity of the third band (III) decreases with increasing solvent polarity. In Figure 2b the emission spectra of pyrene-doped samples, normalized to peak I, do not reveal any change in the intensities of peak III. The films, although dipped in pyrene solutions of different polarity, always yield a Py-value of 1.72 ± 0.03. In Table 1 the Py-values determined for PSS/PAH multilayer films and different pyrene solutions are listed together with values available from the literature.

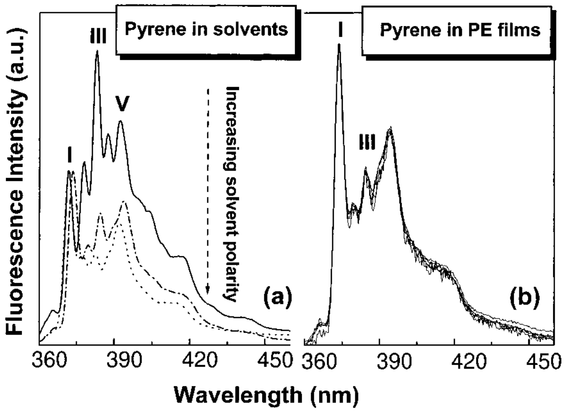

Figure 2. Fluorescence spectra of (a) pyrene dissolved in solvents characterized by different polarities [(−) *n*-hexane, (− • −) chloroform, and (···) water] and (b) pyrene adsorbed in polyelectrolyte multilayer films. The spectra normalized at the first band I are for six samples of the type Qz/PEI/[PSS/PAH]$_4$ exposed to six pyrene solutions prepared with n-hexan, *n*-butanol, cloroform, methanol, acetonitrile, and water, respectively.

The pyrene distribution normal to the film plane has been examined measuring the amount of dye absorbed by multilayer films of various thickness. Preformed [PSS/PAH] multilayers with a different number of bilayers ($n = 3, 6, 9, 12$) were prepared and exposed to a methanol solution containing pyrene in a concentration of ca. 10^{-4} M. Pure water was used to rinse the samples to remove excess pyrene from the surface. Figure 3 shows the pyrene absorbance at 338 nm and the fluorescence intensity of the dye versus the number of PSS/PAH bilayers. On the upper *x*-axis the film thickness, as determined by X-ray reflectivity measurements, is reported. The pyrene absorbance increases with bilayer number reaching saturation at a thickness above about 30 nm. In the range of small thicknesses (i.e., for samples between 3 and 9 bilayers), the absorbance per bilayer is of the order of 1.5×10^{-3}, which corresponds to a dye density of 1 molecule per 7000 Å^3. The intensity of pyrene emission also increases with increasing film thickness. Moreover, the fluorescence spectra of all multilayer films did not show any emission due to excimer formation (broad band centered at ca. 480 nm) and no changes in the shape of the spectra were observed. This indicates a low fraction of pyrene clusters.

To investigate the influence of the molecular structure of polyelectrolytes on the film polarity, multilayers prepared with different polycations were doped with pyrene molecules. As in the case of PSS/PAH multilayers, four bilayers of PSS/PEI and PSS/PDADMAC were prepared and subsequently dipped into a methanol−pyrene solution. The fluorescence spectra of each type of multilayer film are shown in Figure 4 and the correspondent pyrene values, as estimated by the intensity ratio I/III, are listed in Table 2. The spectra in Figure 4 are normalized to the third band for a better vision. The emission spectrum obtained from a pyrene-doped sample of the type PEI/[PSS/PAH]$_4$ is added for comparison. The intensity peaks at around 373 nm correspondent to peak I, clearly change for each spectrum indicating that the film polarity is different for different kinds of multilayers. PSS/PEI and PSS/PDADMAC multilayer films were also exposed to pyrene solutions prepared with solvents of different polarities. As it was the case for the samples of the type PEI/[PSS/PAH]$_4$ shown in Figure 2b, the intensity ratios I/III did not change according to the type of solvent used

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Table 1. Py-Values of PSS/PAH Polyelectrolyte Multilayers and of Different Pyrene Solutions[a]

		I/III (literature values)				**I/III** present investigation[b]
solvents	ϵ	Kalyanas[d]	Karpovich[e]	Stahlberg[d]	Dong[f]	⟨I/III⟩ ± Sd
n-hexanol	1.89	0.61	0.56	0.61	0.58	0.60 ± 0.01
n-butanol	17.5	1.02		1.09	1.06	1.13 ± 0.03
chloroform	4.80	1.28			1.25	1.36 ± 0.03
methanol	32.7	1.33	1.30	1.45	1.35	1.37 ± 0.09
FILM[c]						**1.72 ± 0.03**
acetonitrile	37.50	1.75	1.70	1.92	1.79	1.87 ± 0.06
water	78.54	1.59		1.96	1.89	1.96 ± 0.03

[a] For solvents, the dependence of vibronic band intensities of pyrene monomer fluorescence is evident. [b] All the spectra were solvent blank corrected and were verified by repetitive measurements (eight repetitions, four being on the same sample). For film values, four repetitions on each sample were performed. [c] Film type: PEI/[PSS/PAH]$_4$/PY. [d] Reference 26. [e] Reference 22. [f] Reference 27.

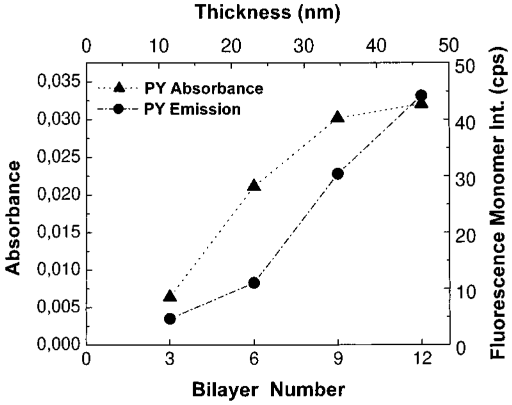

Figure 3. Absorbance at 338 nm and fluorescence monomer intensity (band at 373 nm) for samples of the type Qz/PEI/[PSS/PAH]$_n$/PY where $n = 3, 6, 9, 12$. The thickness of the films, as obtained by fitting of X-ray reflectivity data, is indicated on the top axis.

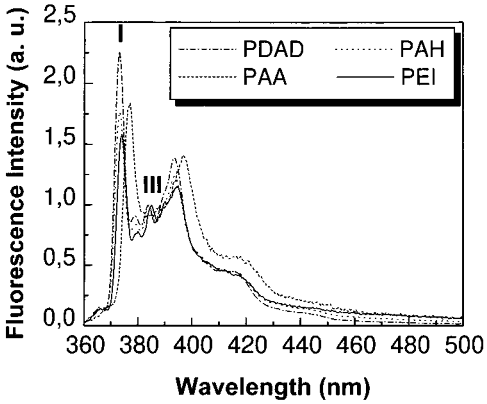

Figure 4. Fluorescence spectra of pyrene adsorbed in preformed polyelectrolyte multilayers of the type PEI/[PSS/PDADMAC]$_4$ (PDAD), PEI/[PSS/PEI]$_4$ (PEI), and PEI/[PSS/PAH]$_4$ (PAH). Spectrum PAA refers to a film of the type PEI/[PSS/PAH]$_2$/[PAA-MePY/PAH].

for probe dissolving, indicating that the organic solvents do not remain within the films.

The pyrene-labeled copolymer was used to confine the pyrene probe within single polyelectrolyte bilayers. Films of the type Qz/PEI/[PSS/PAH]$_2$/[PAA-MePY/PAH] were prepared and a pyrene value of 1.89 ± 0.04 was measured. The sample emission spectrum is shown in Figure 4 and the Py-value is listed in Table 2.

Influence of Humidity on the Polarity of Polyelectrolyte Multilayers. The polarity of the polyelectrolyte multilayer films was additionally studied by pyrene fluorescence spectroscopy as a function of the humidity of the environment. Preformed PSS/PAH multilayer films of 15 bilayers doped with pyrene molecules were exposed to different conditions of relative humidity (RH) with use of over-saturated aqueous salt solutions. Fluorescence measurements were performed at two extreme conditions of relative humidity, i.e., 6 and 95%. The emission intensity ratio I/III did not change according to humidity variations: a Py-value of 1.68 ± 0.03 was determined in both environments as well as in the presence of silica gel, which was used to achieve the lowest possible value of relative humidity.

By collecting continuously fluorescence spectra, without any delay time between the acquisition of each of them, strong pyrene photobleaching was observed. Figure 5 shows a typical series of emission spectra together with their time trace (inset of Figure 5) for a sample stored, in this case, at 95% of constant RH. The total emission intensity decreases from the first recorded spectrum (upper in the series) until the last one, indicating photobleaching of the pyrene molecules. The strong decrease in the fluorescence intensity is a combination of a fast

Table 2. Py-Values of Different Polyelectrolyte Multilayer Films and Dielectric Constants Estimated from the Solvent Polarity Data Given in Figure 7

film type	Py-values[a]	ϵ
Qz/PEI/[PSS/PEI]$_4$	1.54 ± 0.05	30 ± 10
Qz/PEI/[PSS/PAH]$_4$	1.75 ± 0.06	50 ± 10
Qz/PEI/[PSS/PDADMAC]$_4$	2.22 ± 0.08	120?
Qz/PEI/[PSS/PAH]$_2$/[PAA-MePY/PAH]$_1$	1.89± 0.04	65 ± 10

[a] The estimated values are referred to four repetitive measurements performed on the same sample. For the first three type of samples the pyrene adsorption was performed by methanol–pyrene solutions.

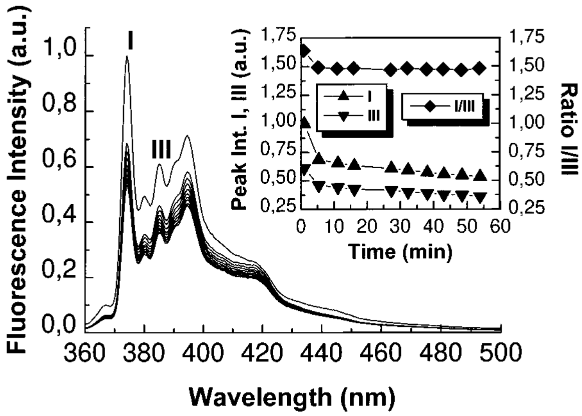

Figure 5. Series of 10 pyrene emission spectra in 15 [PSS/PAH] bilayers successively measured one after the other at 95% of constant RH. The first spectrum collected is normalized to peak I. The successive spectra are normalized to the peak intensity I of the first spectra to show pyrene photobleaching. The inset displays a plot of the peak intensity I and III (left ordinate axis) and of the emission intensities ratio I/III (right ordinate axis) versus acquisition time.

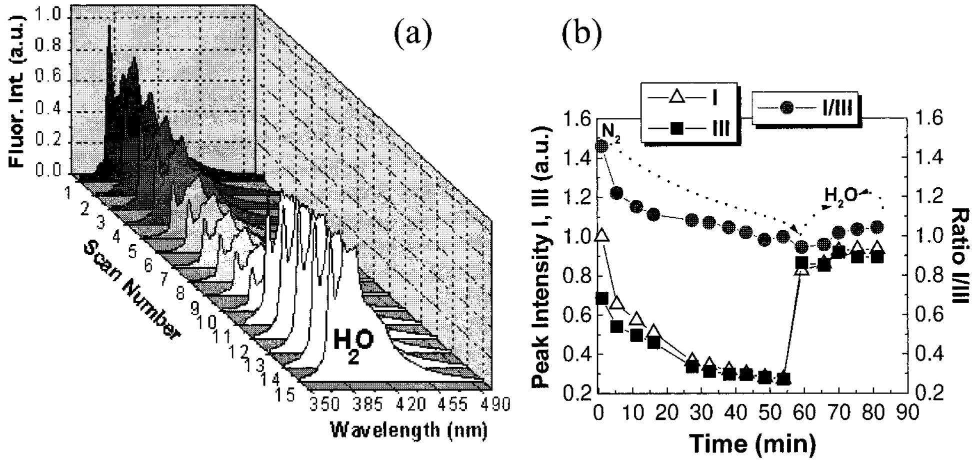

Figure 6. (a) Fluorescence spectra for a sample of the type PEI/[PSS/PAH]$_{15}$/PY. During the first 10 data collections the sample (enclosed in a Qz cuvette) was blown by nitrogen, while during the subsequent 5 spectra the sample was immersed into water. (b) Variation of the peak's intensity I and III and of their respective ratio I/III as a function of the spectra acquisition time.

component with decay time on the order of several minutes and a slow one, which has a decay time on the order of hours (see inset of Figure 5). After 1 h of irradiation the total fluorescence intensity is reduced by more than 50%. The ratio of the first to the third band decreased only within the fast decay time from 1.68 ± 0.01 to 1.48 ± 0.01 and remained constant afterward (inset of Figure 5). The same behavior was observed at 6% of relative humidity and for samples dried by silica gel. In all cases, the Py-values as well as the integrated intensity recovered to their initial values when keeping the samples in the dark for several hours.

Another parameter that was supposed to influence the polarity of the films was the drying procedure employed for film preparation. Thus, a sample of 15 [PSS/PAH] bilayers doped with pyrene molecules and kept at a relative humidity of 95% for 2 days was blown by a nitrogen flux and simultaneously fluorescence spectra were acquired. In Figure 6b the time traces of the peak intensities and the pyrene values are shown. The first 10 data points correspond to this drying procedure. Without interrupting the spectra collection, the cuvette containing the sample was filled with pure water and another five spectra were recorded, as demonstrated in Figure 6a. During the nitrogen exposure the total intensity decreases and recovers to the initial value when water is added. Moreover, also the intensity ratio I/III, i.e., the pyrene value, decreases during the drying process from an initial value of 1.46 to 0.99, and only slightly increases to 1.04 when the sample is immersed into water. By storing the sample in water for 1 h, no change in the intensity ratio I/III was detected.

Discussion

A homogeneous distribution of pyrene at low concentration in the polymer films should be achieved to ensure that the polarity sensed by the probe molecules is not influenced by contributions of dye molecules closely arranged in the vicinity of one another. The concentration and the vertical distribution of pyrene molecules within the film can be extracted from Figure 3. Here, the absorbance (which is a measure of the adsorbed amount of pyrene) clearly increases with increasing film thickness. By extrapolation of the data to zero thickness, no offset of the absorption is observed, proving that no excess of dye molecules at the film surface exists. The low solubility of unsubstituted pyrene in water (2−3 μM) enables one to remove the excess of dye molecules from the film surface by rinsing with water, avoiding simultaneously a complete probe desorption from the whole polymer matrix. At a film thickness above approximately 30 nm a saturation of the adsorbed amount of dye is observed. Such behavior, already reported in previous studies on charged dye molecules,[9,38] indicates a finite penetration depth of roughly 30 nm for the probe diffusion within the film. Thus, to avoid the saturation regime, which could have resulted in an inhomogeneous distribution of the dye within the film, preformed PE multilayers of only four bilayers were used to determine the film polarity by PY emission. The mean concentration of pyrene within the film has been estimated on the order of 1 molecule per 7000 Å^3 for a pyrene methanol solution at 335 nm. By exposing the multilayer films to pyrene solutions prepared with other solvents, such as water, the pyrene concentration within the film was even lower. No excimer emission could be detected in the pyrene emission spectra, which would indicate pyrene associations. In conclusion, there is significant experimental evidence that the pyrene molecules are homogeneously distributed at low concentration within the bulk of the polyelectrolyte films. On the other hand, under the assumption of a homogeneous distribution and a mean volume per molecule of 7000 Å, the distance between two molecules is on the order of 20 Å, which is small enough to ensure efficient energy transfer between molecules with a high oscillator strength.

The micropolarity sensed by the pyrene molecules in the self-assembled polyelectrolyte multilayer films is independent of the nature of the solvents used for dissolving probe. This is proved by the evaluated Py-values of the films which are constant when the dye adsorption is performed from dye solutions of different solvents (see Figure 2b and Table 1 for PSS/PAH multilayers). The film microenvironment was also found to be independent of the film thickness and the storage time of the samples (one year maximum in ambient conditions). The emission spectra shown in Figure 4, together with their intensity ratios I/III listed in Table 2, clearly show that the polarity of the PE multilayer films can be varied via the chemical structure of the polymers used for the multilayer build-up process. The variations in polarity can cover a broad range of Py-values measured for various solvents, like dioxane and water, for example. Multilayer films of PSS/PDADMAC display an anomalous Py-value (ca. 2.22) with respect to solvents. Within the Py-scale of solvent

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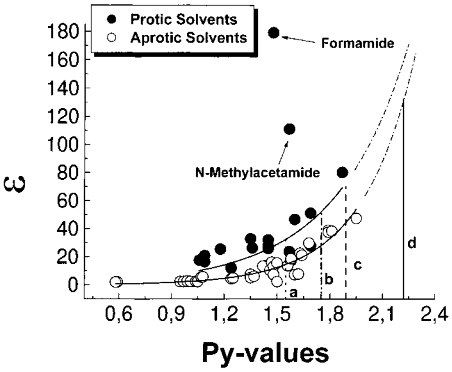

Figure 7. Static dielectric constant ϵ versus Py-values for homogeneous solvents. The protic and the aprotic solvents are marked. The exponential curves are least-squares fits to the data values and drawn as a guideline to the eyes. The pyrene values of the various polyelectrolyte films are indicated by the vertical lines (a = PSS/PEI, b = PSS/PAH, c = PAA-MePy/PAH, d = PSS/PDADMAC). The dielectric constant is estimated from the cross section of the vertical lines with the exponential fit curve of protic or aprotic solvents, respectively. For the case of PSS/PDADMAC extrapolations of the fit curves have been used.

polarity the highest reported Py-values are 1.87 and 1.95, which correspond to the values measured for the most polar solvents, i.e., water and dimethyl sulfoxide, respectively.[27] Nonetheless, the Py-value obtained for PSS/PDADMAC multilayers is not unreasonable since even higher values have been reported from Nakashima et al.[39] for block copolymer films.

However, caution has to be paid when comparing the Py-values of the PE films with those of solvents. The Py-scale is not sensitive to the protic or aprotic behavior of solvents, i.e., to their ability or inability, respectively, to act as hydrogen bond donors.[19] This becomes evident when a correlation is attempted against other solvent polarity scales, like Dimroth's $E_T(30)$-scale, or physical parameters, such as the dielectric constant, just as examples.[40,25] By plotting the static dielectric constant ϵ of various solvents against the corresponding Py-values (see Figure 7), an accumulation of data points along separated traces for protic and aprotic solvents can be observed as a trend. The ϵ values of protic solvents are generally higher compared to those of aprotic solvents. Since no significant functional relation has been found between ϵ and the Py-scale,[25] the literature data presented in Figure 7 have been arbitrarily fitted to an exponential curve, which should be considered as a guide for the eyes. From this graph a rough estimate of the dielectric constant of the polymer films can be derived by comparing the film Py-values with those of solvents. For doing this, a possible approach is to consider the chemical structure of the polyelectrolytes with respect to their proton-donating behavior. Due to the ability of primary and secondary amines, as well as that of carboxylic groups, to behave as hydrogen bond donors, the polyelectrolytes PEI, PAH, and PAA-MePy, which respectively contain these groups (see Figure 1), are expected to exhibit a protic-like behavior. On the contrary, PSS and PDADMAC can be better approximated to aprotic solvents because of the presence of sulfate groups and tertiary amines, respectively. However, these arguments become more difficult when considering the polyanions and polycations assembled into multilayer films. Within the polymer matrix a significant amount of water is retained,[30,31] suggesting a contribution to the film polarity. Nevertheless, since in this work no influence of the ambient humidity on the film polarity could be detected, the contribution of water molecules on the film polarity can be reasonably excluded. This finding leads to the conclusion that multilayers of PSS/PDADMAC exhibit an aprotic-like behavior, while films of PAA-MePy/PAH can be considered as protic materials. A protic behavior is assumed as well for PSS/PEI and PSS/PAH multilayers, because the hydrogen-donating groups of PEI and PAH are still present within the films when the polycations are assembled together with the PSS. Under these assumptions an estimate of the static dielectric constant for each type of polyelectrolyte multilayer film has been obtained from the values of the exponential fits of the protic and aprotic solvents corresponding to the Py-values of the films (see Figure 7). The values of the dielectric constants are listed in Table 2. The errors have been estimated by the variance of the solvent values with respect to the exponential curves. For PSS/PDADMAC multilayers it is nearly impossible to deduce a reliable value for ϵ, because as can be seen by Figure 7 no solvents are available as a reference, which exhibit so high polarity like the PSS/PDADMAC films. This explains the big error that is introduced in the evaluation of ϵ for these types of multilayers. However, these studies were not intended to measure the dielectric constant of the PE films, which obviously could be better determined by performing electric measurements. Here, we desired more to give information on the microenvironment of pure polyelectrolyte films, which could be additionally helpful in gaining a better understanding of factors that might be related to the polarity of the PE assemblies. Moreover, it is the local polarity that plays an important role in the control of photoinduced electron-transfer processes, the long-term aim of these studies.

Studies performed on polyelectrolyte films,[41] and similar systems such as monolayers of polyelectrolyte brushes,[42] showed significant film swelling upon exposure to humid air. This finding indicates that the relative amount of water in the films depends on the humidity. Here, experimental evidence has been obtained for an unchanged micropolarity of the films upon variation in the humidity conditions of the film environment. It seems that the water content in the polyelectrolyte films does not affect the microenvironment in the proximity of the pyrene molecules, or at least gives a constant contribution independently of the relative humidity of the air.

It has been further demonstrated that the film polarity dramatically changes by drying the films actively with a nitrogen stream (see Figure 6b). This finding seems to be contradictory with the previous result. However, by drying actively the PE films, changes in the internal film structure and total film thickness were observed in previous studies,[9,30] probably as a result of shear deformation. It was suggested that the drying procedure leads to a rearrangement of the polyelectrolytes, which in turn increases the number of ionic bonds between the polycations and polyanions. Thus, the observed changes in the film polarity upon the active drying process may be explained by this structural reorganization. Hong et al.[30] showed that the structural modification of the PE films by the drying procedure is irreversible. This finding is in agreement with our experiments which demonstrate irreversible changes in the film polarity, even by immersing the samples into water (see Figure 6 b).

The pyrene photobleaching observed in Figure 5 can be ascribed to the presence of oxygen, a well-known quencher of PY fluorescence.[43] It is interesting to note that the time decay

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of fluorescence under constant illumination can be described by two time constants (see inset of Figure 5) and that the pyrene value decreases during the fast bleaching process. This behavior is unexpected, since the I/III band intensity ratio usually is not sensitive to photobleaching in the presence of oxygen.[22] An explanation for this behavior could be given under the assumption of pyrene partitioning into two different environments within the film. One fraction of the dye molecules could be localized in sites characterized by a high polarity, which we assume to exhibit strong photobleaching, while the remaining molecules could be placed in a more apolar environment, showing only small photobleaching. Since the recorded fluorescence spectra (see Figure 5) represent an average of the emission of both fractions, at the acquisition of the first spectrum an average Py-value is observed (1.68 in our case). Simultaneously, the molecules localized in the polar environment are bleached and a consequent reduction of the recorded film Py-value results. However, at the present state of the studies this explanation can be rather speculative.

The recovery of photobleaching after storage in the dark may be explained by lateral diffusion of the pyrene molecules. The sample is illuminated only on a narrow stripe (1 mm) and the dyes are destroyed by photooxidation only within this zone. In the dark, undestroyed molecules will diffuse into the former illumination zone and thus fluorescence can be observed later on. This effect is well-known and has been used to measure the diffusion coefficient of dyes within polyelectrolyte multilayer films.[44]

Conclusions and Outlook

The work presented here is part of a program to prepare an ultrathin film with a polarity gradient along which a photoinduced electron-transfer process could be directed. To realize such a functional film, several tasks have to be achieved:

Functional molecules have to be incorporated into the film. Here, pyrene molecules were inserted in the films by exchange with an adjacent solvent. The pyrene concentration obtained by this method is sufficiently low to consider the dye molecules as isolated from each other, but high enough to enable energy transfer between them.

Dye molecules should be placed at a defined layer position within the film. This problem was solved by using a dye-labeled copolymer where the position of the probe molecules was controlled via the sequence of the adsorption process.

As a major task, control of the film polarity should be provided. Depending on the kind of polyelectrolyte employed for film formation, different polarities could be obtained, thus providing the opportunity to produce tailored systems for ET processes. One may criticize the conversion of the films Py-values into dielectric constants since the Py-scale is based on measurements with isotropic solvents of low molecular weight. However it should be kept in mind, with respect to the long-term goal of this work, that electron transfer (ET) processes are mainly influenced by the local polarity. It is a big advantage that pyrene as a dye probe for polarity investigations is also suitable for ET studies, due to its long lifetime of the excited state.

The polarity of the film structures should be inert against environmental conditions. It has been also shown that contact with different solvents or air of different humidity does not change the local polarity. However, actively rearranging the matrix via a nitrogen stream may reduce the water content in the film.

In conclusion, this work has established fundamental steps to prepare a film with a polarity gradient suitable for ET studies. Finally it should be stated that the employed method can be easily extended from planar films to colloidal templates, which exhibit higher specific surface area. This facilitates time-resolved optical spectroscopy as well as future applications in photoenergy conversion.

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