Preparation of Multilayers Containing Conjugated Thiophene-Based Polyelectrolytes. Layer-by-Layer Assembly and Viscoelastic Properties

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We study the layer-by-layer assembly and properties of polyelectrolyte multilayers containing anionic and cationic poly(alkoxythiophene) derivatives, poly(3-(3′-thienyloxy)propanesulfonate) (P3TOPS) and poly-(3-(3′-thienyloxy)propyltriethylammonium) (P3TOPA), together with poly(diallyldimethylammonium chloride) (PDADMA) or poly(styrenesulfonate) (PSS). These polythiophenes are rigid-rod-type polyelectrolytes, which tend to aggregate in aqueous medium. Three types of multilayers have been prepared: (P3TOPS/P3TOPA)$_n$ (all-thiophene films), (P3TOPS/PDADMA)$_n$, and (PSS/P3TOPA)$_n$. The layer-by-layer adsorption of polythiophenes was followed by UV−vis spectroscopy and surface plasmon resonance (SPR). Adsorption of P3TOPS and P3TOPA took place within 10 min from dilute aqueous solution (1 mM with respect to monomers). The adsorption of a new polyion layer on top of polythiophene was always accompanied by a partial loss of the polythiophene layer. As the result, the amount of polythiophene in the film oscillated as a function of the number of layers. This behavior was attributed to the adsorption and partial desorption of aggregated polythiophene, supported by atomic force microscope (AFM) images of dry films. Per bilayer, the amount of polythiophene remaining in the film increased linearly and corresponded approximately to the formation of a thiophene monolayer. The viscoelastic properties of the films also exhibited a marked terminal layer effect in cases, where the length and hydrophobicity of the polyions were different. This effect was studied with (PSS/PDADMA) multilayers and was attributed to the formation of loops and tails. All multilayers studied appeared very soft, comparable to protein layers. This softness was attributed mainly to the film/solution interface with a hydrogel-like outer part of the films (zone III).

Introduction

The sequential layer-by-layer adsorption of polycations and polyanions has been shown to be an extremely versatile and facile technique for the preparation of thin organic films, polyelectrolyte multilayers (PEMs), on a variety of substrates.[1−3] PEMs are usually prepared by alternate adsorption from dilute solutions of oppositely charged polyions, but multilayers can also be formed by spin-casting or spraying.[4,5]

The multilayer assembly process itself is not completely understood yet. The adsorption of a polyelectrolyte on a charged surface leads to surface charge reversal, and the multilayer assembly, which is practically irreversible, is influenced by kinetic and thermodynamic constraints.[2,6−8] In general, the increase of the ionic strength of the deposition solution leads to a monotonic increase in the layer thickness.[7,9] Oppositely charged polyions intrinsi-

cally compensate each other in as-made water-rinsed multilayers, but exposure to electrolyte solutions leads to partial extrinsic compensation and incorporation of small ions.[7,10] The multilayers of flexible polyelectrolytes are strongly interpenetrated and do not exhibit distinct stratification.[1,8] The interpenetration of a layer depends critically on the ionic strength used in that particular adsorption step.[11] In addition, the charge density of polyelectrolytes has been shown to affect the layer-by-layer assembly, and with weak polyelectrolytes, this can produce interesting variations in the film structure.[12] On the other hand, with strong polyelectrolytes a critical linear charge density has been observed in several cases.[13−15] In addition, nonelectrostatic interactions may contribute significantly to the assembly process.[16] Other studies suggest that, instead of the charge density, the mismatch between the distances of the fixed charges in a pair of oppositely charged polyelectrolytes is decisive for a regular film growth.[2,17] In the layer-by-layer assembly of medium-charged polyelectrolytes, a partial removal of the previous

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(1) Decher, G. *Science* **1997**, *277*, 1232−1237.
(2) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319−348.
(3) Hammond, P. T. *Curr. Opin. Colloid Interface Sci.* **2000**, *4*, 430−442.
(4) (a) Cho, J.; Char, K.; Hong, J.-D.; Lee, K.-B. *Adv. Mater.* **2001**, *13*, 1076−1078. (b) Chiarelli, P. A.; Johal, M. S.; Holmes, D. J.; Casson, J. L.; Robinson, J. M.; Wang, H.-L. *Langmuir* **2002**, *18*, 168−173.
(5) Schlenoff, J. B.; Dubas, S. T.; Farhat, T. *Langmuir* **2000**, *16*, 9968−9969.
(6) Lowack, K.; Helm, C. A. *Macromolecules* **1998**, *31*, 823−833.
(7) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153−8160.
(8) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* **2001**, *34*, 592−598.

(9) Lösche, M.; Schmitt, J.; Decher, G.; Bouwman, W. G.; Kjaer, K. *Macromolecules* **1998**, *31*, 8893−8906.
(10) Schlenoff, J. B.; Ly, H.; Li, M. *J. Am. Chem. Soc.* **1998**, *120*, 7626−7634.
(11) Lukkari, J.; Salomäki, M.; Viinikanoja, A.; Ääritalo, T.; Paukkunen, J.; Kocharova, N.; Kankare, J. *J. Am. Chem. Soc.* **2001**, *123*, 6083−6091.
(12) (a) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309−4318. (b) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213−4219. (c) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017−5023.
(13) Fleer, G.; Hoogeveen, N. G.; Cohen Stuart, M. A.; Böhmer, M. R. *Langmuir* **1996**, *12*, 3675−3681.
(14) Steitz, R.; Jaeger, W.; v. Klitzing, R. *Langmuir* **2001**, *17*, 4471−4474.
(15) Schoeler, B.; Kumaraswamy, G.; Caruso, F. *Macromolecules* **2002**, *35*, 889−897.

layer upon adsorption of the next layer has been observed in several cases, and a recent work by Caruso et al. suggests that the existence of the critical charge density may be the result of the removal of the loosely bound film material in the form of a soluble polyelectrolyte–polyelectrolyte complex.[11,13,15,18]

Relatively little is known about the correlation between the structure of the adsorbing polyelectrolytes and the multilayer assembly process. Reducing the stiffness of the flexible chains by increasing the ionic strength leads to the formation of thicker layers above the critical polyelectrolyte charge density.[15] However, most of the studies of PEM formation have dealt with flexible polyelectrolytes. Conjugated aromatic polyelectrolytes are examples of rigid-rod polymers typically possessing a strongly hydrophobic backbone with pendant ionic groups, which renders them very liable to aggregation.[19] Ionically substituted polythiophenes are electronically conducting polyelectrolytes, which can be used for the preparation of conducting multilayers.[11,20] Conducting polymers have unique electrical, optical, and luminescence properties, and multilayers prepared from these materials are interesting for both basic science and applications in the field of sensors, electrooptics, and light-emitting diodes.[20c,21,22] Poly- and oligothiophenes, in particular, have a strong tendency to aggregate in poor solvents, and this should affect the layer-by-layer assembly process in water, a very poor solvent for the aromatic backbone.[23] We have previously observed a clear effect of the oxidation state of polythiophene (i.e., its charge density) on the multilayer formation.[11,20e]

To understand the factors influencing the multilayer buildup, it is important to study the process in situ during the adsorption of polyelectrolyte and to characterize the film after each adsorption step. In this work, we describe the layer-by-layer assembly process of conjugated rigid-rod polyelectrolytes based on polythiophenes as a function of film composition, hydration state, and ionic strength using UV–vis spectroscopy, surface plasmon resonance (SPR), quartz crystal impedance, and atomic force microscopy (AFM) using materials shown in Scheme 1. There are very few papers on the assembly process with conjugated polyelectrolytes and, especially, those dealing with the quartz crystal impedance characterization of the PEMs.[24–26] This technique can give invaluable information about the properties and formation of multilayers in situ, which is difficult to obtain by other existing techniques. While quartz crystal microbalance has been extensively

Scheme 1. Structures and Abbreviations of the Polyelectrolytes Used in This Work
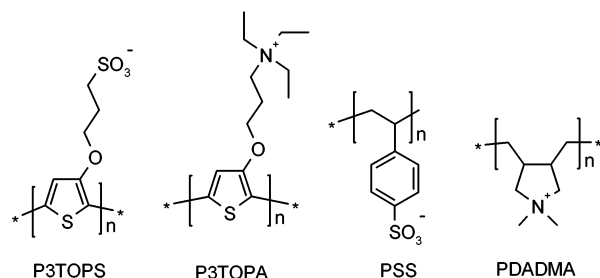
used for the characterization of PEMs, the question about the validity of the famous Sauerbrey equation,[27] i.e., the possible viscoelasticity of the film, always remains suspicious, especially with wet films. In this work we also discuss the viscoelastic behavior of our polyelectrolyte multilayers in water, in light of the recently presented quartz crystal impedance theory, and present a qualitative picture of the layer-by-layer assembly of conjugated polythiophene-based polyelectrolytes.[28]

Experimental Section

Materials. Synthesis, polymerization, and polymer characterization of thiophene derivatives sodium 3-(3′-thienyloxy)-propanesulfonate (3TOPS) and 3-(3′-thienyloxy)propylammonium bromide (3TOPA) (Scheme 1) have been described earlier.[11] 2-Aminoethanethiol hydrochloride (MEA, from Aldrich), *N*-(trimethoxysilylpropyl)-*N,N,N*-triethylammonium chloride (TMSPA, from ABCR), poly(diallyldimethylammonium chloride) (PDADMA, M_w = 400–500 kDa, from Aldrich), and poly(sodium-4-styrenesulfonate) (PSS, M_w = 70 kDa from Aldrich and 263 kDa from Polysciences, Germany) were used as received. Low-molecular-weight PDADMA (Aldrich; M_w very low but unknown) was dialyzed using a membrane with a nominal M_w cutoff of 3500 in order remove extremely short oligomers (ca. half of the original material was lost in this process). All aqueous solutions were prepared in Millipore water (18 MΩ/cm).

Preparation of Polyelectrolyte Multilayers. The gold-plated quartz crystals (10 MHz, International Crystal Manufacturer, Oklaholma) were cleaned in hot piranha solution (concentrated H_2SO_4:30% H_2O_2 3:1—*warning*! piranha solution is very corrosive and must be treated with extreme caution; it reacts violently with organic material and must not be stored in tightly closed vessels), rinsed with water, and dried. The crystals were cleaned in oxygen and hydrogen plasma immediately before use.[29] The surface of the gold-plated crystals was primed with a self-assembled monolayer of MEA (1 mM aqueous MEA solution for 1 h, which results in a positive surface charge) and placed in a flow through cell. The adsorption of polyelectrolytes was carried out using 10 mM solutions (with respect to monomer) of PSS and PDADMA (in 0.1 M $NaNO_3$ solution) for 15 min and 1 mM solutions of P3TOPS and P3TOPA (in 0.1 M $NaNO_3$ solution) for 30 min. After each step the cell was rinsed with water and soaked three times for 1 min in pure water. These multilayers (so-called wet films) were not exposed to a drying step during the assembly. For the measurements of dry films the adsorption was carried out with a droplet of polyelectrolyte solution on the gold surface. The surface was then rinsed thoroughly with running water and after that soaked three times for 1 min with water and dried. Multilayers on evaporated gold (SPR) and quartz (UV–vis) were prepared similarly as described for the wet films above. The

(16) (a) Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. *Langmuir* **1997**, *13*, 1385–1387. (b) Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717–2725.

(17) Fischer, P.; Laschewsky, A.; Wischerhoff, E.; Arys, X.; Jonas, A.; Legras, R. *Macromol. Symp.* **1999**, *137*, 1–24.

(18) Lvov, Y.; Ariga, K.; Onda, M.; Ichinose, I.; Kunitake, T. *Colloids Surf. A: Physicochem. Eng. Asp.* **1999**, *146*, 337–346.

(19) Bockstaller, M.; Köhler, W.; Wegner, G.; Vlassopoulos, D.; Fytas, G. *Macromolecules* **2000**, *33*, 3951–3953.

(20) (a) Ferreira, M.; Cheung, J. H.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 806–809. (b) Ferreira, M.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7107–7114. (c) Faïd, K.; Leclerc, M. *J. Am. Chem. Soc.* **1998**, *120*, 5274–5278. (d) Kim, J.; Wang, H.-C.; Kumar, J.; Tripathy, S. K.; Chittibabu, K. G.; Cazeca, M. J.; Kim, W. *Chem. Mater.* **1999**, *11*, 2250–2256. (e) Lukkari, J.; Viinikanoja, A.; Paukkunen, J.; Salomäki, M.; Janhonen, M.; Ääritalo, T.; Kankare, J. *J. Chem. Soc., Chem. Commun.* **2000**, 571–572. (f) Zotti, G.; Zecchin, S.; Berlin, A.; Schiavon, G.; Giro, G. *Chem. Mater.* **2001**, *13*, 43–52.

(21) Kumpumbu-Kalemba, L.; Leclerc, M. *J. Chem. Soc, Chem. Commun.* **2000**, 1847–1848.

(22) (a) Ho, P. K. H.; Granström, M.; Friend, R. H.; Greenham, N. C. *Adv. Mater.* **1998**, *10*, 769–774. (b) Ho, P. K. H.; Kim, J.-S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. *Nature (London)* **2000**, *404*, 481–484.

(23) Xia, C.; Locklin, J.; Youk, J. H.; Fulghum, T.; Advincula, R. C. *Langmuir* **2002**, *18*, 955–957.

(24) Calvo, E. J.; Etchenique, R.; Bartlett, P. N.; Singhal, K.; Santamaria, C. *Faraday Discuss.* **1997**, *107*, 141–157.

(25) Picart, C.; Lavalle, Ph.; Hubert, P.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J.-C. *Langmuir* **2001**, *17*, 7414–7424.

(26) Plunkett, M. A.; Claesson, P. M.; Rutland, M. W. *Langmuir* **2002**, *18*, 1274–1280.

(27) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206–222.

(28) Kankare, J. *Langmuir*, in press (ASAP article, DOI: la025911w).

(29) Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir* **1992**, *8*, 357–359.
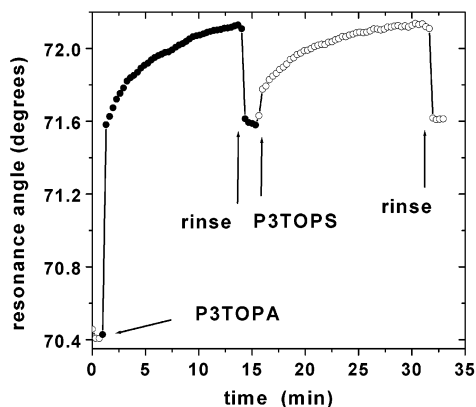
Figure 1. Change of the surface plasmon resonance angle during the adsorption of (i) P3TOPA on Au/MEA/P3TOPS/P3TOPA/P3TOPS (solid symbols) and (ii) followed by the adsorption of P3TOPS (open symbols). The aqueous polyelectrolyte solutions were 1 mM and contained 0.1 M $NaNO_3$. Times of rinsing are indicated in the figure.

quartz cuvette was cleaned inside with piranha solution, rinsed with water, and dried. Then it was silanized with TMSPA in oxygen and water free atmosphere in order to obtain a positively charged surface.[30]

Multilayer Characterization. The crystal parameters were measured at 25 °C using a prototype quartz crystal (QC) analyzer with impedance detection.[31] In the measurements involving dry films the multilayer was equilibrated over a saturated aqueous LiBr solution (relative humidity 6% at 25 °C).[32] Before the multilayer assembly, the parameters of an unloaded resonator were determined for each crystal attached to the crystal holder under appropriate conditions (in water or air). The UV–vis spectra during the multilayer assembly were recorded with a HP-8453 spectrophotometer using a quartz flow-trough cuvette. The deposition of polyelectrolyte multilayers was carried out in the cuvette. Surface plasmon resonance (SPR) curves were measured with a SPREETA surface plasmon resonance liquid sensing system (Texas Instruments). For the contact mode atomic force microscopy studies in air (AFM, AutoProbe CP from TM microscopes) the multilayers were prepared on TMSPA silanized glass in a class 100 clean room.

Results and Discussion

Kinetics of Adsorption. The surface plasmon resonance (SPR) spectroscopy is a good technique for following the kinetics of polyelectrolyte adsorption, but it is less ideal for following the multilayer assembly step-by-step with the highly colored polythiophenes. In this case, the high optical thickness of the multilayers causes saturation in the SPR signal after a few layers. The resonance angle of incidence, at which the reflectance minimum is observed, depends on changes in the optical thickness at the interface between the metal electrode and solution. To the first approximation, the thickness of the adsorbed layer is proportional to the change in the angle corresponding to the minimum.[33] Figure 1 shows an example of the change in the surface plasmon resonance angle during the adsorption of P3TOPA and P3TOPS. The change in the resonance angle levels off in both cases within ca. 10 min. The adsorption of P3TOPA causes a large change in the resonance angle with a rapid initial increase while the changes are smaller upon adsorption of P3TOPS. Rinsing with water after P3TOPS resulted in a very small net change in the apparent thickness. However, P3TOPS
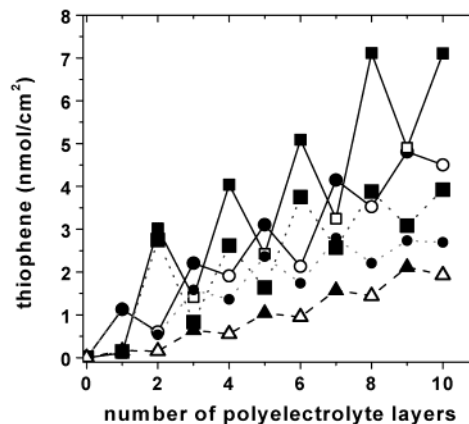
(30) Szentirmay, M.; Campbell, L.; Martin, C. *Anal. Chem.* **1986**, *58*, 661–662.

(31) Kankare, J.; Loikas, K., patent pending.

(32) Lide, D. R., Ed.; *Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL, 1996–1997; p **15**-25.

(33) Garland, P. B. *Q. Rev. Biophys.* **1996**, *29*, 91–117.

Figure 2. Spectrophotometric determination of the thiophene-based polyelectrolytes in multilayers: solid symbols, polythiophene on top; open symbols, PDADMA or PSS on top. Assembly in water: ■, □ (solid line): PSS/P3TOPA; ●, ○ (solid line): P3TOPS/PDADMA; ● (dotted line) and ■ (dotted line): P3TOPS and P3TOPA, respectively, in P3TOPS/P3TOPA. Assembly in DMSO–H_2O (80/20 v/v): ▲, △ (dashed line): P3TOPS/PDADMA. Even layers correspond to polycation on top.

evidently adsorbs on P3TOPA because all-thiophene multilayers can be formed, and the mechanism of polythiophene adsorption cannot be reached on the basis of SPR data alone. On the other hand, the results show that the layer formation with these conjugated rigid rod polyelectrolytes follows the general path commonly observed with flexible polyelectrolytes, in which a fast initial step is followed by a slower process in a time scale of minutes.[2]

Characterization of the Assembly Process by UV–vis Spectroscopy and AFM. Both polythiophenes, P3TOPS and P3TOPA, are highly colored (λ_{max} 620 and 580 nm, respectively), which makes possible to follow the buildup of multilayers spectrally. The variation of the amount of polythiophenes, calculated as moles of the monomer repeat units, is shown in Figure 2 for (P3TOPS/PDADMA)$_n$ and (PSS/P3TOPA)$_n$ multilayers. In both cases the surface coverage of thiophene oscillates regularly, and a large portion of polythiophene left on the surface after the standard washing procedure is removed upon addition of the next layer of PDADMA or PSS. While the average addition of polythiophene per layer is ca. 1.0 nmol/cm² for P3TOPS and 2.8 nmol/cm² for P3TOPA, the average amount of thiophene remaining on the surface per bilayer is only ca. 0.5 and 1.2 nmol/cm², respectively. This suggests that part of the previously adsorbed polythiophene forms a soluble complex with the added polyelectrolyte. While low charge density generally prevents multilayer formation and high charge density leads to stable films, partial desorption of the polyelectrolyte multilayer upon the adsorption step has been observed with polyelectrolytes having medium charge density.[13,15] However, the charge density of P3TOPS and P3TOPA is high, and because of the flexibility of the side chains and inert polyelectrolytes, the charge separations should not pose constraints for multilayer formation. The amount of polythiophene remaining in the multilayer increases linearly with the number of bilayers in both cases, in accordance with previous reports.[11,20e] In all-thiophene multilayers (P3TOPS/P3TOPA)$_n$ the spectral data can yield separately the surface coverage of both polythiophenes because P3TOPS is in the oxidized form and absorbs also at wavelengths above 700 nm (Figure 2).[11] The average additions of P3TOPS and P3TOPA are ca. 0.95 and 1.7

nmol/cm² per layer, respectively, but the next poly-thiophene adsorption step always removes part of the previous layer. However, the amount of each component remaining in the film increases linearly (ca. 0.54 and 0.74 nmol/cm² of P3TOPS and P3TOPA per bilayer, respectively).

Standard washing procedures similar to ours have been widely used between the adsorption of oppositely charged polyelectrolyte layers and are considered sufficient for the reproducible preparation of PEMs, removing the loosely bound material from the surface.[6,9,12a,13,15] We have also studied the effect of extended washing period for the multilayer formation. If the (P3TOPS/PDADMA) film is left soaking in water for 15 min after the standard washing procedure, part of the outermost P3TOPS layer is removed. In this case, the amount of polythiophene does not decrease during the adsorption of the next PDADMA layer. Similarly, soaking in water (15 min after the standard washing) after the adsorption of the PDADMA layer does not lead to additional desorption of P3TOPS. Therefore, adsorption of the next polyelectrolyte layer and extended washing with water are alternative procedures leading to similar film growth.

The surface coverage of polythiophene per polyelectrolyte bilayer is quite low, in the range 0.5−1.2 nmol/cm². Standard molecular models yield theoretical monolayer coverage estimates of ca. 0.75 or 1.3 nmol/cm² for oxygen-substituted thiophene rings oriented parallel or perpendicular to the surface, respectively. This implies that the thiophene coverage per bilayer is close to or below a monomolecular film. Similar surface coverage has been reported for other thiophene-based polyelectrolytes.[20f,21] A low increase of surface coverage per layer is usually observed with flexible polyelectrolytes with no added electrolytes, but it increases significantly with the ionic strength (here the increase of the ionic strength to 0.5 M had only a negligible effect, vide infra).[7] It should be pointed out, however, that the absolute surface coverages are only semiquantitative because they are based on molar absorptivities measured in solution. In addition, scattering of light due to noncolored polyions results in a small bias for the absorbance readings, which is difficult to take quantitatively into account. In any case, the surface coverage is low, and it results from the partial desorption of the uppermost layer, which has been observed previously in some cases involving a small number of ionic groups in the polymer.[13,15] Although the charge density of P3TOPS is reduced due to oxidation, we have shown that the multilayer growth proceeds regularly irrespective of the oxidation state of the polythiophene electrolyte.[11,20e] The desorption caused by oppositely charged polyelectrolyte or extensive rinsing implies, therefore, that aggregation of the polythiophene chains may be responsible for this behavior. In aggregates the chains are held together by weak hydrophobic and stacking interactions, and only those chains electrostatically bound to the oppositely charged polyelectrolyte on the surface are likely to survive the rinsing or the tendency to form soluble complexes in the next assembly step (Figure 3). In addition, the rather low molecular weight of our thiophene-based polyelectrolytes also favors the formation of soluble polyelectrolyte complexes.[34] Residual aggregates in the film (and the inaccuracies in the spectral quantification) may also explain the apparent inequality of the positive and negative components in the all-thiophene films.
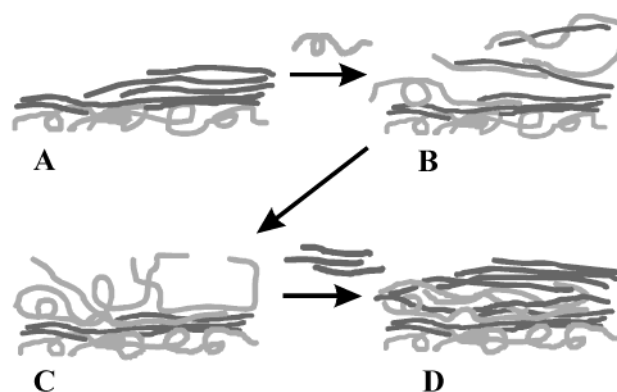

Figure 3. Schematic representation (only the topmost layers) of a multilayer formation with a flexible (e.g., PDADMA, gray lines) and polythiophene-based polyelectrolyte (black lines). (A) Electrostatically bound and aggregated polythiophene on the surface of a multilayer. (B) The next polyelectrolyte solubilizes part of the aggregated polythiophene as a polyelectrolyte−polyelectrolyte complex. (C) The flexible polyelectrolyte form a layer with loops and tails. (D) The addition of poly-thiophene-based polyelectrolyte (aggregated in aqueous solution) leads again to a situation similar to that in (A).

Sexithiophene bolaform amphiphiles have recently been shown to adsorb in an aggregated state from water.[35]

The AFM data of dry films with 10 polyelectrolyte layers (for the AFM images please see Supporting Information) also support aggregation. The (P3TOPS/PDADMA)₅ and (P3TOPS/P3TOPA)₅ multilayers appeared smooth but were decorated with larger features having width in the range of 200−300 nm and height of ca. 10−30 or 100−200 nm (former or latter film, respectively). These features are most probably polyelectrolyte aggregates on the surface. However, significantly larger features (width up to 1 μm and height ca. 50−70 nm) were observed in a (PSS/P3TOPA)₅ film, and the largest corrugations on the surface could be seen in the (PSS/PDADMA)₅ multilayer, in which they covered almost half of the surface. Therefore, not only polythiophenes but also other polyelectrolytes, PSS in particular, appear to form aggregated structures. In fact, several polyelectrolytes form metastable clusters consisting of likely charged polyions in solution.[36] Poly-(styrenesulfonate) has been shown to form large aggregates in solution, similar in size with the features observed in the PSS-containing multilayers (the features are probably compressed due to drying).[37] The rms roughness (corresponding to an area of 7 × 7 μm²) of the dry multilayers studied increased in the order P3TOPS/PDADMA (1.6 nm) < P3TOPS/P3TOPA (5.7 nm) ≈ PSS/P3TOPA (5.8 nm) ≪ PSS/PDADMA (18.2 nm). However, between the large aggregates the surface roughness is ca. 1−2 nm with all multilayers.

The role of aggregates in the layer-by-layer adsorption of polythiophenes finds further support from the measurements carried out in DMSO−water mixtures (Figure 2). In this medium the UV−vis spectrum of P3TOPS indicates deaggregation.[11] The surface concentration of thiophene increases linearly, but the average increase is only ca. 0.45 nmol/cm² per bilayer. Addition of PDADMA leads to a small decrease in the amount of P3TOPS, but the desorption of polythiophene is less pronounced than

(34) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **2001**, *34*, 3736−3740.

(35) Locklin, J.; Youk, J. H.; Xia, C.; Park, M.-K.; Fan, X.; Advincula, R. C. *Langmuir* **2002**, *18*, 877−883.

(36) Sedlák, M. In *Physical Chemistry of Polyelectrolytes*; Radeva, T., Ed.; Marcel Dekker: New York, 2001.

(37) (a) Tanahatoe, J. T.; Kuil, M. E. *J. Phys. Chem. B* **1997**, *101*, 5905−5908. (b) *J. Phys. Chem. B* **1997**, *101*, 9233−9239. (c) *J. Phys. Chem. B* **1997**, *101*, 10839−10844.

in water. This implies that in DMSO–water the adsorption of polythiophene takes place mainly by strong attachment of individual polymer chains instead of large aggregates.

Quartz Crystal Impedance Characterization of the Multilayers. The quartz crystal microbalance (QCM) technique has been extensively used for the characterization of polyelectrolyte multilayer assembly. The results have generally been interpreted by the classical Sauerbrey equation, which linearly relates the frequency decrease to the mass increase.[27] This equation has been derived for completely rigid films in a vacuum, and its application to real films composed of soft materials must always be done with caution. This is especially true when measurements are carried out under liquid. The viscoelastic properties of polyelectrolyte multilayers are generally not known. Caruso et al. have argued using indirect evidence that dry multilayers behave as rigid films, and consequently, measurements on these films can be interpreted in a gravimetric manner.[38] On the other hand, a recent paper revealed the viscoelastic behavior of poly(L-lysine)/hyaluronic acid multilayers immersed in water.[25] In situ studies of poly(allylamine)/glucose oxidase multilayers showed that the film viscoelastic properties were modified upon addition of the enzyme component.[24] Studies of polyelectrolyte adsorption using QCM with the energy dissipation technique suggest that while the first polyelectrolyte chains in the forming layer adopt a flat conformation the last chains adsorb with loops and tails protruding into the solution.[26] We have previously studied the same systems as in this work and found a nonmonotonic behavior under liquid.[11,20e]

The transmission line and Butterworth–van Dyke (BVD) models are in general use to describe the behavior of a loaded quartz crystal resonator.[39] These models describe the mechanical properties by electrical equivalents, and they have the advantage of giving a relatively simple picture of the properties of the loaded resonator. However, the precise physical interpretation of the elements and parameters involved is questionable.[28,39b] In this work we discuss the properties of a loaded resonator in terms of the complex local acoustic impedance $\zeta_0 = \zeta' + j\zeta''$ ($j = \sqrt{-1}$).[28] The viscoelastic properties of a material can be described by its complex shear modulus G with its real (G', storage modulus) and imaginary (G'', loss modulus) components (eq 1).[40]

$$G = G' + jG'' \tag{1}$$

The treatment of a resonator covered with a film and immersed in a Newtonian liquid medium (complex shear moduli G_f and G_l for the film material and liquid, respectively) leads to the following first-order approximations for the changes of the real and imaginary parts of the local acoustic impedance due to the film:[28]

$$\Delta\zeta' = \mathrm{Re}(\zeta_0 - Z_l) \approx \omega m_f \frac{\rho_l}{\rho_f} \mathrm{Im}\!\left(\frac{G_l}{G_f}\right) \tag{2}$$

$$\Delta\zeta'' = \mathrm{Im}(\zeta_0 - Z_l) \approx \omega m_f \left[1 - \frac{\rho_l}{\rho_f} \mathrm{Re}\!\left(\frac{G_l}{G_f}\right)\right] \tag{3}$$

Here $Z_l = (\rho_l G_l)^{1/2}$ is the bulk acoustic impedance of liquid, ω is the angular frequency, m_f is the film areal mass, and ρ_f and ρ_l are the density of the film and liquid, respectively. The effect of the complex shear modulus of the liquid medium and the film material on the crystal resonance frequency f_s is accounted for in the medium-corrected Sauerbrey equation (4) (d_q is the thickness of the quartz
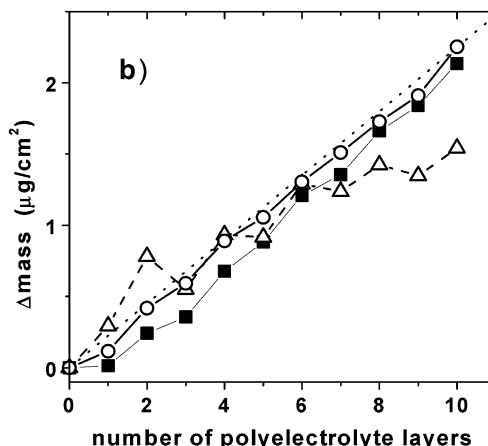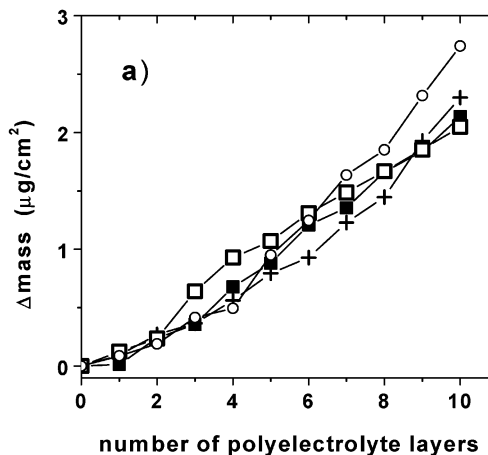

Figure 4. Mass calculated from the Sauerbrey equation during the assembly of dry (6% relative humidity) polyelectrolyte multilayers. Even layers correspond to polycation on top (substrate Au/MEA). (a) (■) P3TOPS/P3TOPA; (○) P3TOPS/PDADMA; (□) PSS/P3TOPA; (+), PSS/PDADMA. (b) The assembly of P3TOPS/P3TOPA from (■) 0.1 M, (○) 0.5 M NaNO₃, and (△) calculated from spectroscopic data (Figure 2). Dotted line is the calculated mass for a P3TOPS/P3TOPA multilayer with an addition of 1 nmol/cm² of thiophene per layer.

resonator). Here the correction term contains contributions from the medium density and viscosity (η_l) and the film properties in the form of the imaginary part of the film complex shear compliance J_f'' ($J = J' - jJ'' = G^{-1}$).

$$\frac{\Delta f_s}{f_s} = -\frac{m_f}{\rho_q d_q}\left[1 - \frac{\rho_l}{\rho_f}\mathrm{Re}\!\left(\frac{G_l}{G_f}\right)\right] = -\frac{m_f}{\rho_q d_q}\left(1 - \omega \rho_l \eta_l \frac{J_f''}{\rho_f}\right) \tag{4}$$

In a vacuum (and air) eq 4 reduces to the original Sauerbrey equation, and therefore, the data for the dry films can be analyzed gravimetrically irrespective of their thickness (if it is considerably below the penetration depth of the transverse acoustic vibrations). The mass increase calculated from the Sauerbrey equation for dry multilayers is presented in Figure 4, which also includes the mass calculated from spectroscopic data for comparison. The mass increase is approximately linear after 2–3 layers for all the films containing polythiophene (average mass increments ca. 0.72, 0.32, and 0.47 μg/cm^{-2} per bilayer for

(38) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. *Langmuir* **1997**, *13*, 3422–3426.

(39) (a) See, e.g., papers in: *Faraday Discuss.* **1997**, *107*. (b) Kanazawa, K. K. *Faraday Discuss.* **1997**, *107*, 77–90.

(40) Aklonis, J. J.; MacKnight, W. J. *Introduction to Polymer Viscoelasticity*, 2nd ed.; John Wiley & Sons: New York, 1983.

Table 1. Calculated "Softness Parameter" J_f'/ρ_f for Various Thin Films[a]

film type	J_f'/ρ_f ($m^3\ Pa^{-1}\ kg^{-1}$)
poly(*n*-butyl acrylate)[b]	2.85×10^{-11}
poly(3-methylthiophene)[c]	2.27×10^{-10}
mussel adhesive protein[d]	
before cross-linking	3.7×10^{-9}
after cross-linking	1.1×10^{-9}

[a] J_f' = real part of the complex shear compliance of the film material; ρ_f = film density. [b] Spin cast from toluene (ref 42). [c] Electropolymerized and reduced film in propylene carbonate (ref 43). [d] Reference 44.

(P3TOPS/PDADMA), (PSS/P3TOPA), and (P3TOPS/P3TOPA), respectively) whereas the curvature persists somewhat longer in the case of the (PSS/PDADMA) film. The surface loading per layer is close to the addition of 1 nmol/cm² of thiophene per layer, which corresponds roughly to a monomolecular coverage. (For the all-thiophene film the calculated mass increase using this value is shown as a dotted curve in Figure 4b.) The small difference in the film mass obtained from QCM and spectroscopic measurements can be attributed to the different substrates and the inaccuracies discussed above. The effect of ionic strength on the formation of conjugated polyelectrolyte multilayers is noteworthy (Figure 4b). The total mass and the mass increment per bilayer for (P3TOPS/P3TOPA)₅ multilayers prepared in 0.1 or 0.5 M NaNO₃ are practically identical (2.1 and 0.47 or 2.2 and 0.45 µg/cm⁻², respectively). This is in contrast with flexible polyelectrolytes, with which the layer thickness shows a nonlinear dependence on the ionic strength.[9,41]

Viscoelastic Properties of the Multilayers. For the multilayers under water (wet films, no added salt) the resonance frequency changes after each layer deposition and rinsing displayed similar zigzag behavior as reported previously.[11,20e] Qualitatively, this behavior can be partly explained by desorption of some material upon addition of a new layer. However, the medium-corrected Sauerbrey equation (eq 4) shows that for film-covered resonators immersed in a liquid medium the effects of the medium and film viscoelectric properties cannot be a priori neglected. On the other hand, elimination of the areal mass density of the film from eqs 2 and 3 yields eq 5, which contains only film parameters and experimentally measurable quantities:

$$\frac{\Delta\zeta''}{\Delta\zeta'} = \frac{1}{|Z_l|^2}\frac{\rho_f}{J_f'} - \tan\delta \qquad (5)$$

Assuming a value for the loss tangent ($\tan\delta = G_f''/G_f'$), the parameter J_f'/ρ_f can be determined. This parameter can be used as a measure of the "softness" of the thin film. The density of organic materials is usually close to 1000 kg m⁻³ and does not have much effect when considering films made of similar materials. On the other hand, the real part of the complex shear compliance scales with the inverse of the magnitude of the complex shear modulus ($J_f' = G_f'/|G_f|^2$). The larger the complex shear modulus, the stiffer the material and, therefore, the smaller the value of the parameter. This intuitive conclusion is supported by values of the parameter J_f'/ρ_f calculated on the basis of literature data (Table 1). For rubbery films above the glass transition temperature the value of J_f'/ρ_f is of the order of 10^{-11} m³ Pa⁻¹ kg⁻¹ and increases to ca. $(1-5) \times 10^{-9}$ m³ Pa⁻¹ kg⁻¹ for hydrogel-type layers. The
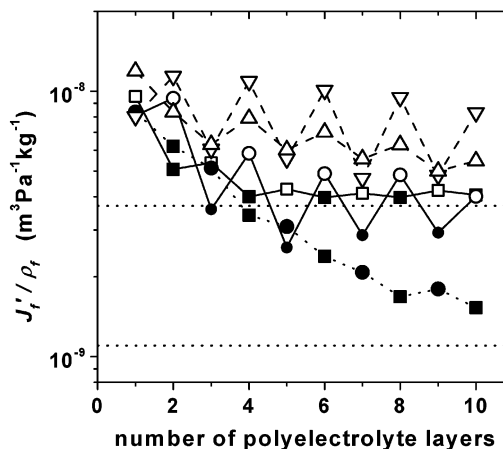

Figure 5. Film softness parameter J_f'/ρ_f (calculated from eq 5 using tan δ = 1) for the polyelectrolyte multilayers in pure water (no added salt) at different stages of the assembly. Filled symbols, polythiophene on top; open symbols, PSS or PDADMA on top (substrate Au/MEA). ■, □ (solid line): PSS/P3TOPA; ●, ○ (solid line): P3TOPS/PDADMA; ● and ■ (dotted line): P3TOPS and P3TOPA, respectively, in P3TOPS/P3TOPA; ▽ (dashed line) PSS(70 kDa)/PDADMA (400−500 kDa); △ (dashed line), PSS-(263 kDa)/PDADMA (low M_w). Even layers correspond to polycation on top. The J_f'/ρ_f values calculated for adsorbed mussel adhesive protein film (from ref 44) are shown by horizontal lines before and after cross-linking (Table 1). Stiffness increases downward in this figure.

data in Figure 5 have been calculated on the basis of eq 5 and assuming a loss angle of 45°. The results imply that the polyelectrolyte multilayers under water resemble very soft hydrogels. In addition, in the case of (P3TOPS/P3TOPA) and (PSS/P3TOPA) multilayers, J_f'/ρ_f shows a nearly monotonic decrease with the number of polyelectrolyte layers, but large oscillations can be seen with the (P3TOPS/PDADMA) film. To understand the origin of this behavior, (PSS/PDADMA) multilayers were studied, too. In both latter cases, the more hydrophobic or shorter the polyelectrolyte forming the outermost layer the smaller the value of J_f'/ρ_f. The measurements, in which the molecular weight of the long flexible polycation (PDADMA, with M_w = 400 kDa) was changed, give insight into this terminating layer behavior (Figure 5). For the (PSS/PDADMA) multilayers containing very short PDADMA the oscillations are markedly attenuated, but at the same time, the increase in the length of PSS from 70 to 263 kDa has only negligible influence on the apparent softness of the PSS terminated film. Surface force measurements have shown that loops and tails of flexible polyelectrolytes can extend far into the solution.[6,45] Under the ionic strength employed PSS and PDADMA are both close to the rod-to-coil collapse.[46] On the other hand, high molecular weight PDADMA is more hydrophilic and can form large loops and other protrusions on the film surface. (According to molecular models, the contour length of the 400 kDa PDADMA is in the range of 1 µm.) We, therefore, contribute the oscillations to a water-like diffuse gel formed on the surface of the multilayers with high molecular weight PDADMA as the top layer. Similar interpretation has been

(41) Ladam, G.; Schaad, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. *Langmuir* **2000**, *16*, 1249−1255.

(42) Lee, S.-W.; Hinsberg, W. D.; Kanazawa, K. K. *Anal. Chem.* **2002**, *74*, 125−131.

(43) Hillman, A. R.; Jackson, A.; Martin, S. J. *Anal. Chem.* **2001**, *73*, 540−549.

(44) Höök, F.; Kasemo, B.; Nylander, T.; Fant, C.; Sott, K.; Elwing, H. *Anal. Chem.* **2001**, *73*, 5796−5804.

(45) Ruths, M.; Sukhishvili, S. A.; Granick, S. *J. Phys. Chem. B* **2001**, *105*, 6202−6210.

(46) McAloney, R. A.; Sinyor, M.; Dudnik, V.; Goh, M. C. *Langmuir* **2001**, *17*, 6655−6663.

given for the increase of the viscoelastic properties upon adsorption of a low charge density polycation on gold-plated quartz crystals.[26] The length of PSS has a much smaller effect, but the adsorption of a hydrophobic PSS or P3TOPS layer compresses the underlying PDADMA layer, resulting in lower J_f'/ρ_f value. Therefore, the results imply that the outermost layer is largely responsible for the layer-to-layer variation of the apparent viscoelastic properties during the growth of our films in cases where there is a large difference in the hydrophobicity or contour length of the polyions. It should be noted that in a very recent work the hydration of (PSS/PDADMA) multilayers was found to remain constant, which supports the interpretation of the oscillations as a pure terminating layer effect.[47]

As a whole, the polyelectrolyte multilayers appear surprisingly soft, the average J_f'/ρ_f value being comparable to that of adsorbed protein layers. This is especially astonishing for films containing hydrophobic rigid-rod polythiophenes. Electropolymerized polythiophene films exhibit J_f'/ρ_f values 1−2 orders of magnitude lower, a difference much too large to be explained by the inaccuracy in the value of the loss tangent.[43,48] Although the data in Figure 5 have been calculated by assuming a value of unity for the loss tangent ($\delta = 45°$), it should be pointed out that letting the loss angle vary between 10° (nearly totally elastic) and 80° (almost liquid) affects the J_f'/ρ_f value maximally by a factor of 2−3 (down and up, respectively). In general, several factors, including slip at the resonator−film interface, energy losses in the material, changes in the surface roughness, and water trapped inside the layers, can contribute to the observed viscoelastic behavior of the films.[49] Slippage at the surface is unlikely with polyelectrolyte multilayers, which are known to show good adherence to charged surfaces. On the other fact, polyelectrolyte multilayers are known to absorb large amounts of water.[9,50] In fact, the energy dissipation in protein layers has been attributed to water trapped within the film, in addition to losses due to the deformation of the proteins themselves.[49] A very rough estimation of water in a multilayer (actually, water mechanically coupled to the resonator) can be obtained by comparing the frequency changes observed for wet and dry multilayers. The mass of a dry multilayer is ca. 40% of the estimated wet mass for the (PSS/P3TOPA) and (PSS/PDADMA) films and ca. 20% for the (P3TOPS/PDADMA) and (P3TOPS/P3TOPA) films, which shows that considerable amount of water may be sensed by the resonator. However, the average stiffness of all multilayers studied initially increases with the number of polyelectrolyte layers, leveling off after ca. 4 layers with polythiophene-containing films. For thicker films, the average J_f'/ρ_f value seems to approach a "bulk" value of ca. $(2−6) \times 10^{−9}$ m³ Pa⁻¹ kg⁻¹. Our preliminary results indicate that an increase of the ionic strength in the bathing solution induces stiffening of all the films. At higher ionic strength the bulk of the film (zone II) should swell and incorporate more water whereas the outer zone III collapses.[41] This implies that the outer hydrated zone III has a large effect on the apparent softness of the polyelectrolyte multilayers studied. We are currently extending our measurements to the detailed effect of ionic strength and to films that are substantially thicker than the multilayers in the present

work, in which the outermost zone III makes a major contribution to the film.

At the moment we cannot decide the exact relative role of the zones II and III in the viscoelastic behavior. Water can be bound in the gel-like outer layer and trapped within the rough surface, but the whole film is hydrated and deformations within the material can also contribute to the softness. The AFM pictures show that the rms roughness values exhibit some correlation with the apparent softness of the wet films. However, the behavior of the (PSS/PDADMA) multilayer with large oscillations suggests that the formation of loops and tails on the surface exhibit a large effect, too. It is interesting to note that using the complex shear modulus data obtained at much lower frequency with the dynamic shear force technique for quaternized poly(4-vinylpyridine) layers yield the J_f'/ρ_f values close to those in Figure 5.[45] Although extrapolation into the megahertz frequencies cannot be done, the shear modulus data were explained by loops and tails of the polymer extending into the solution. In summary, the rough surface with trapped water and the gel-like outer surface of a thin film result in a water-like solvent−film interface, which gives the whole hydrated film an apparent hydrogel-like appearance, also in the case of multilayers prepared from rigid-rod polyelectrolytes.

Conclusions

Rigid polyelectrolytes based on anionic and cationic polythiophene derivatives P3TOPS and P3TOPA form multilayers with each other (all-thiophene films) and with flexible polyelectrolytes, such as PDADMA and PSS. During the aqueous assembly of multilayers containing polythiophenes the next layer, be it either PDADMA, PSS, or polythiophene, always partially removes the previous underlying polythiophene layer. The amount of polythiophene in the films, therefore, oscillates as the function of the number of the polyelectrolyte layers. The same partial desorption can be effected by extended rinsing with solvent. This effect is attributed to desorption of polythiophene from adsorbed aggregates, leaving only a nearly monomolecular layer of electrostatically bound polymer on the film surface.

Quartz crystal impedance data taken after each assembly and rinsing step revealed that all the polyelectrolyte multilayers studied appeared very soft. The films resemble hydrogels, and the average softness is comparable to that of adsorbed protein films. Multilayers containing rigid polythiophene derivatives appeared stiffer than (PSS/PDADMA) multilayers, but the difference was small and even the all-thiophene multilayer was significantly softer than electropolymerized poly(3-methylthiophene) films in organic solvents. A terminating layer effect was observed in all cases in which there was a clear difference in the contour length or hydrophobicity of the polyelectrolytes used. This effect of the outermost layer was attributed to the loops and tails of polymer extending deep into the solution. The diffuse film−solution interface probably dominates the viscoelastic behavior of these thin polyelectrolyte multilayers, but the relative effect of the film bulk and outer layers will be addressed in future work.

Supporting Information Available: AFM topography images of dry P3TOPS/P3TOPA, P3TOPS/PDADMA, PSS/P3TOPA, and PSS(70 kDa)/PDADMA(400−500 kDa) multilayers. This material is available free of charge via the Internet at http://pubs.acs.org.

(47) Schwarz, B.; Schönhoff, M. *Langmuir* **2002**, *18*, 2964−2966.
(48) Brown, M. J.; Hillman, A. R.; Martin, S. J.; Cernosek, R. W.; Bandey, H. L. *J. Mater. Chem.* **2000**, *10*, 115−126.
(49) Höök, F.; Rodahl, M.; Brzezinsky, P.; Kasemo, B. *Langmuir* **1998**, *14*, 729−734.
(50) Farhat, T.; Yassin, G.; Dubas, S. T.; Schlenoff, J. B. *Langmuir* **1999**, *15*, 6621−6623.