Mono- and Multilayers of Oligoethylene Oxide-Modified Poly(3,4-ethylenedioxythiophene) on ITO and Glass Surfaces

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Dichloromethane-soluble poly(3,4-ethylenedioxythiophene)s modified with oligoethylene oxide chains of different lengths (PEDT−EO and PEDT−PEO) were produced by anodic coupling. PEDT−EO solutions were used to produce mono- and multilayer films on ITO−glass electrodes and float glass sheets. Layer-by-layer alternation of doped PEDT−EO with poly(*p*-styrene sulfonate) (PSS) or doped poly(3,4-ethylenedioxythiophene) sulfonate produced electroactive and robust multilayered surfaces with low surface resistivity (5×10^5 Ω/□ for a PEDT−EO/PSS 10-bilayer). Analogous multilayers could be built from doped PEDT−EO and polyammonium polycations. Doped PEDT−EO forms with PSS the first reported electrostatically bound polyionic multilayers in which the positive charge is delocalized over a polythiophene backbone.

1. Introduction

Since the discovery that π-conjugated polymers can be electrically conductive,[1] this part of polymer chemistry has grown enormously.[2] This has resulted in the fact that the Nobel Prize for Chemistry in 2000 was awarded to its pioneers[3] as well as the fact that several applications based on conductive polymers have been commercialized. One of the main (volume-wise) applications nowadays is the use of the conductive polymer poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDT/PSS) as an antistatic material (antistatic means that the surface resistivity is in the range of 10^6−10^9 Ω/□).[4] Examples of antistatic PEDT/PSS-based layers can be found in photographic film from AGFA (on PET) and in modern TV screens (on glass). Because of the large areas, antistatic materials are one of the main applications for conductive polymers. Thus, quite a lot of research and development is being performed on this topic in academia and industry.

One of the concepts that has been studied frequently over the past years concerns the self-assembly of polyconjugated polymers as multilayers on surfaces.[5−15] Multilayer films have been prepared through a film deposition technique that utilizes the electrostatic attraction of oppositely charged polyelectrolytes to create thin films with a layer-by-layer (LBL) technique. The electrostatic multilayer adsorption of positive and negative polyelectrolytes has been widely exploited as an alternative method to the Langmuir−Blodgett technique. This method provides a simple means of deposit-

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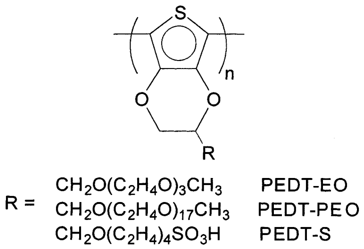
Chart 1



ing robust polymer films in a controlled and defined manner.

The literature reports on poly(3-carboxymethylthiophene) in alternation with polycationic polyammonium layers,[5,6] polyaniline sulfonate (PANI$-$SO$_3$) and polyallylamine (PAH),[7] PANI$-$SO$_3$ or PPV polymer bilayers,[8] water-soluble poly(*p*-phenylene)s with sulfonate and quaternary ammonium functionalizations,[9] polypyrrole,[10,11] and polyaniline.[12] All-polythiophene multilayer films with poly(cyclopentadithienyl-alkyl sulfonate) as the polyanion and poly(cyclopentadithienyl-alkylammonium) as the polycation have been produced;[13] similarly, poly-3-(3′-thienyloxy)propane sulfonate/poly-3-(3′-thienyloxy)propyltriethylammonium[14] and poly(3-octanic acid)thiophene/poly(3-hexylammonium thiophene)[15] have been assembled in multilayers.

The multilayered polymers reported above are all in the undoped state. Multilayers based on polyconjugated polymers in the conducting state have been recently prepared from water-soluble PEDT$-$S (Chart 1) in alternation with PAH.[16] The polyanionic character of the PEDT polymer requires polycationic polymers. In fact, a polythiophene in the doped state is by itself a polycation so that a soluble polymer of this type may in principle act as a polycation in the LBL production of multilayers. This requires that the polymer is stable in the doped state, which suggests that 3-alkoxy-substituted polymers are good candidates. Plain PEDT is stable but insoluble in the doped state. The literature reports on polythiophenes bearing an oligoethylene oxide chain at the 3-position;[17−19] these are soluble in certain organic solvents. Moreover, a recent paper reports on an EDT-based polymer with a 5-unit oligoethylene oxide chain.[20] These oligoethylene oxide-modified polythiophenes could thus be a good choice for our purposes.

This paper reports on the production of organosoluble conducting PEDTs bearing a short (PEDT$-$EO) or long (PEDT$-$PEO) oligoethylene oxide chain (Chart 1). These polymers were prepared by anodic coupling in acetonitrile and characterized by several techniques. Subsequently, we studied the adsorption of PEDT$-$EO as conducting (antistatic) and fast electroactive mono- and multilayer films on ITO and float glass surfaces and characterized the layers by cyclic voltammetry (CV), UV$-$vis spectroscopy, and surface conductivity.

2. Experimental Section

Chemicals and Reagents. Acetonitrile was reagent grade (Uvasol, Merck) with a water content $<0.01\%$. The supporting electrolyte, tetrabutylammonium perchlorate (Bu$_4$NClO$_4$), was previously dried under vacuum at 70 °C. 3-Aminopropyltrimethoxysilane (ATS) was purchased from Fluka. The polycations poly(allylamine hydrochloride) (PAH) ($M_w = 15000$) and poly(diallydimethylammonium chloride) (PDDA) ($M_w = 250000-400000$), the polyanion poly(sodium-*p*-styrene sulfonate) (PSS) ($M_w = 100000$), and all other chemicals were reagent grade and used as received.

2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxymethyl}-2,3-dihydrothieno-[3,4-b][1,4]dioxine (EDT$-$EO) and poly(ethylene oxide)-modified (2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methanol (EDT$-$PEO) ($M_w =$ ca. 930) were prepared as reported in the literature.[20] Poly(3,4-ethylenedioxythiophene) sulfonate (PEDT$-$S) was produced electrochemically as previously reported.[21]

ITO/glass electrodes were 1×4 cm^2 indium tin oxide one-side coated float-glass sheets (20 Ω/□, Merck-Balzers). Float glass sheets (1×4 cm) were previously etched with concentrated HCl, washed, and dried at 120 °C for 12 h.

The ITO/glass electrodes and the float glass sheets were cleaned with acetone and dried prior to use.

Apparatus and Procedures. Experiments were performed at 25 °C under nitrogen (unless otherwise stated), in three electrode cells, in acetonitrile, and in the presence of 0.1 M Bu$_4$NClO$_4$. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and was coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm^2).

UV$-$vis spectra were obtained with a Perkin-Elmer Lambda 15 spectrometer. GPC measurements were performed with a Waters 2690 instrument. SIMS analysis of the ITO/glass electrodes was performed with a custom-built instrument.[22]

Conductivity. The apparatus and procedures used for the in situ conductivity experiments were previously described in detail.[23] The electrode for conductivity measurements was a two-band platinum electrode (0.3×0.01 cm for each band) with interband spacing of 20 μm, typically polymer-coated with the passage of 20 mC, which assured the attainment of limiting resistance conditions. Poly(3-methylthiophene) (60 S cm^{-1}) was used as a conductivity standard.

Measurements of the sheet resistance of the multilayers were performed on the glass side of the substrate with the four-probe technique using a Kuliche-Soffa head (UK) with a Keithley 220 programmable current source and a Keithley 195A digital multimeter.

EQCM. Electrochemical quartz crystal microbalance (EQCM) analyses were performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade and the frequency counter was Hewlett-Packard mod.5316B. Data were collected by a microcomputer with homemade analyzing software by which frequency changes were monitored as mass changes m.

Method for Layering. Layering was performed on both the ITO and the glass surfaces of the ITO/glass electrodes as such. In some instances surface silanization with ATS was previously performed according to the literature.[24] In the latter case the clean ITO/glass substrate was immersed for 1 h in 5% ATS solution in nitrogen-degassed dry toluene and then washed with dry toluene and dried. Ammonium conversion of

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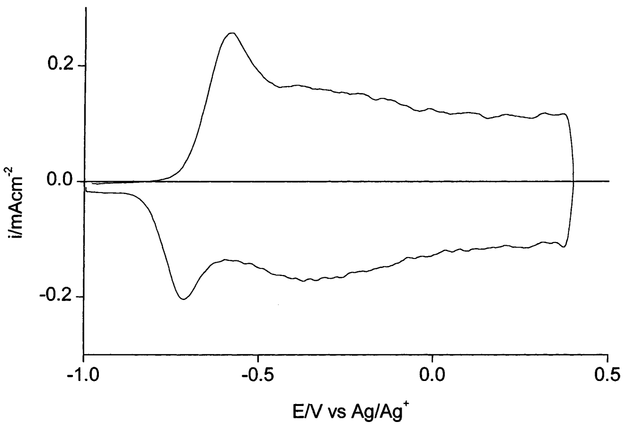

Figure 1. Cyclic voltammograms for PEDT−EO film in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V/s.

the primer layer (from ATS to ATS−H) was performed by dipping for 5 min in 10^{-2} M $HClO_4$ in acetonitrile followed by washing with acetonitrile and drying.

PEDT−EO, PEDT−S, and PEDT−PEO (prepared in the doped state, see also Results) were used as 0.1 wt % solutions in CH_2Cl_2, water, and acetonitrile, respectively. PAH, PDDA, and PSS were used as 10^{-2} M water solutions.

The buildup of the multilayers was performed according to the methodology introduced by Decher and co-workers,[24,25] that is, by dipping the ITO/glass electrodes alternatively into the solutions of the two polymers. Immersion times were 5 min. After each immersion step the substrate was carefully washed with the relevant solvent for 1 min and dried in air.

The layer buildup was monitored by CV and UV−vis spectroscopy. For the latter the absorbance data are given as measured, that is, for the sum of the ITO and glass sides.

Film thicknesses were measured with a KLA-Tencor P10 profilometer.

3. Results and Discussion

3.1. Polymer Synthesis and Characterization.

Electrochemical Polymerization of EDT−EO. The cyclic voltammogram of EDT−EO in acetonitrile + 0.1 M Bu_4NClO_4 displays an oxidative process at a peak potential $E_p = 1.06$ V as for the parent EDT.[26] Oxidation at this potential leads to the growth of polymer film on the electrode.

Bulk polymer was routinely prepared from a stirred 10^{-2} M solution of the monomer in acetonitrile + 0.1 M Bu_4NClO_4 or $NaClO_4$ by applying a potential of 1 V. Polymerization was continued to completeness with the passage of ca. 2.4 e monomer^{-1}. In the former case (0.1 M Bu_4NClO_4) the polymer was produced as a deposit which was washed with acetonitrile and dried (yield 1.3 mg C^{-1}). Only a fraction (depending on the electrolytic batch) of this polymer is soluble in CH_2Cl_2. In the latter case (0.1 M $NaClO_4$) the product is completely dissolved in the electrolyte batch and is separated from the electrolyte by CH_2Cl_2 extraction from water.

Characterization of PEDT−EO Film. (1) CV and UV−Vis Spectroelectrochemistry. The CV of PEDT−EO film in acetonitrile + 0.1 M Bu_4NClO_4 is shown in Figure 1. The redox potential $E°$, taken as the average of forward and backward peak potentials, is −0.60 V as for PEDT.[26] The undoped polymer film displays in the UV−vis spectrum (Figure 2a) the vibronic fine-splitting usually found when regularity (order) along a rigid polymer backbone is present.[27] The absorption maxima occur at 625 and 675 nm, the latter corresponding to the low-energy shoulder in the known EDT polymers. At the same time the films show a strong color contrast between the undoped and the doped state (Figure 2a).

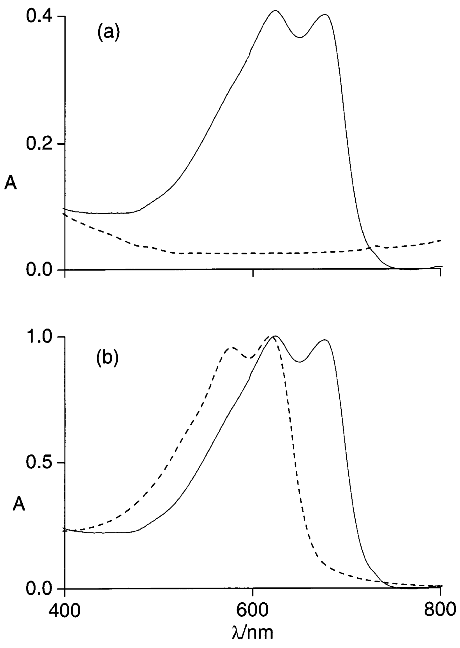

Figure 2. (a) Spectroelectrochemistry for PEDT−EO films in acetonitrile + 0.1 M Bu_4NClO_4, (—) undoped and (- - -) doped; (b) UV−vis spectra of undoped PEDT−EO (—) film on an ITO electrode and (- - - -) in chloroform solution.

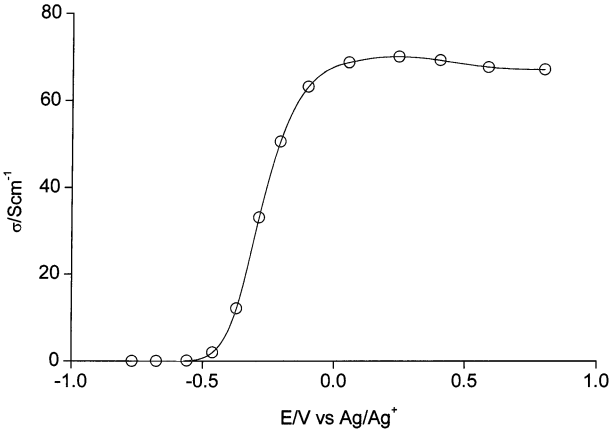

Figure 3. In situ conductivity vs potential for PEDT−EO films in acetonitrile + 0.1 M Bu_4NClO_4.

(2) Conductivity. In situ conductivity measurements, presented in Figure 3, show that oxidation causes the reversible transition from an insulating to a conductive state as for polyconjugated polymers in general. The relationship of conductivity vs potential is sigmoid with a plateau conductivity of 70 S cm^{-1}.

(3) EQCM of Polymer Films. Correlation between the EQCM mass of the undoped polymer m_0 and the total reversible charge Q_r involved in the redox process (at 1 V) shows that PEDT−EO exchanges 0.6 electrons per

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thiophene unit. This result corresponds to that previously obtained for PEDT.[28] The evaluation of reversible charge of the mono- and multilayers reported below was more conveniently made at 0.4 V (to avoid excess background currents) where the charge corresponds to 0.4 electrons per thiophene unit.

The mass vs potential (or charge) relationships are reversible and the latter shows a linear regime with a $F\Delta m/Q_r$ value of 100 g mol^{-1}, indicating the acquisition of one perchlorate anion per oxidizing electron.

EQCM analysis has been applied also to the study of lithium ion uptake. PEDT−EO films uptake Li^+ from acetonitrile solution according to Langmuir's law,

$$\Gamma/\Gamma_{max} = kC/(1 + kC)$$

with a limiting Li^+:(EDT−EO) mole fraction Γ_{max} of 0.6 and an adsorption constant $k = \approx 10$ M^{-1}. The uptake corresponds to an EO/Li ratio of ≈6, vs a value of ≈3 in polycrystalline PEO.[23] Despite the PEO nature of the polymer and its considerable alkali metal ion uptake, PEDT−EO films do not change their optical nor electrochemical response in the presence of 0.1 M $LiClO_4$, $NaClO_4$, or KPF_6 in acetonitrile. It appears that the long distance of the PEO segments from the polyconjugated backbone does not cause any significant twisting of the latter. The CV responses observed at difference in the homologous polymer bearing a 5-unit oligoethylene oxide chain[20] may be accounted for by different coordinative properties of the longer substituent chain.

Characterization of PEDT−EO Solution. (1) UV−Vis Spectroscopy. PEDT−EO/ClO_4 results in a blue material soluble in CH_2Cl_2 where it displays broad and weak adsorption due to the oxidized form of the polymer. Its spectrum in the same solvent after compensation with hydrazine is similar to that of the bulk polymer in the undoped state (fine structure included) but for a hypsochromic shift to 622 nm (Figure 2b). Since the spectrum of the multilayered (solid) material produced from the solution is identical to that of the bulk solid polymer (see below), the different spectrum of the solution is not attributable to a low-DP oligomeric fraction. The shift appears instead to be due to solvent-promoted twisting of the thiophene rings along the polyconjugated chain.

(2) Molecular Weight Determination. Neither MALDI-TOF nor electrospray ionization mass spectroscopy was able to provide M_w values for the polymer. The UV−vis characteristics of the polymer are identical to those of PEDT for which extrapolation of the maximum absorption λ_{max} of the EDT dimer and trimer,[29] according to the expected linear relationship between energy gap and the inverse number of monomeric units,[30] suggests that the degree of polymerization DP is low (around 10). GPC analysis of PEDT−EO in CH_2Cl_2/THF solution, applying THF as the eluent and with detection at 570 nm, results in $M_w = 1500$ g/mol. Given the uncertainty of both evaluations, a DP between 5 and 10 may be assigned to the polymer, in agreement with that recently found by MALDI-TOF MS in the case of PEDT−S.[21]

Electrochemical Synthesis and Characterization of PEDT−PEO. EDT−PEO is oxidized at $E_p = 1.15$ V in acetonitrile + 0.1 M Bu_4NClO_4. In this case however oxidation at the peak potential does not lead to the growth of polymer film on the anode since the formed oligomers are soluble.

Bulk polymer was produced by electrolysis in acetonitrile + 0.1 M $NaClO_4$. In this medium the monomer is oxidized at a more positive potential ($E_p = 1.25$ V). Typically, 100 mg in 25 mL of acetonitrile + 0.1 M $NaClO_4$ are fully electrolyzed at 1.3 V with the passage of 26 C (over 2 F mol^{-1}). The blue solution is evaporated, the solid washed with $CHCl_3$ (to extract nonreacted monomer and side products), and the blue polymer extracted with CH_2Cl_2 and dried (ca 115 mg). PEDT−PEO is soluble in water and polar organic solvents.

The UV−vis spectrum of the dark blue solution in CH_2Cl_2 after hydrazine reduction shows the typical spectrum of undoped EDT polymers with a maximum at 623 nm (shoulder at 576 nm). The latter as a solid on ITO shows the maximum at 620 and a shoulder at 660 nm as for solid PEDT.[26] It is noticeable that in acetonitrile the spectrum resembles that in the solid state but with more pronounced peaks, which may be accounted for by a scarce solvation of the PEO side chains by acetonitrile. In acetonitrile the undoped polymer displays an extinction coefficient of 2×10^4 M^{-1} cm^{-1} (concentration M in repeat units) at the maximum (620 nm).

As-prepared bulk PEDT−PEO contains PEO-coordinated $NaClO_4$. EDX analysis, showing the sodium Na−K signal at 1.05 keV, the sulfur S−K signal of the thiophenes at 2.3 keV, and the chlorine Cl−K signal of perchlorate at 2.65 keV, has given an approximate composition of $(PEDT-PEO)_{2x}(NaClO_4)_3$. The sodium salt may be eliminated by ion exchange of the water solution on mixed cationic−anionic exchange resins. In fact, the polymer is converted by this procedure from the perchlorate to the hydroxide form, as confirmed by FTIR, showing the absence of perchlorate ion and the presence of the hydroxide ion. GPC analysis in water has given $M_w = 5040$ au (with detection at 600 nm) corresponding to a DP = ≈6.

3.2. Polymer Layering. *PEDT−EO Monolayers on ITO.* The CV of the ITO electrode after one dipping step (Figure 4a) shows a nice well-defined process with two redox signals at $E° = -0.6$ and 0.0 V, storing a reversible charge $Q_r = 30$ μC cm^{-2} (at 0.4 V). The CV is stable to repeated cycles. Adsorption from PEDT−EO solution occurs at the same level at the bare and at the ATS−H-primed ITO. This indicates that the interaction of the polymer with the surface is not necessarily via the ATS ammonium groups. For this reason only bare ITO was therefore used with PEDT−EO.

Differently from PEDT−EO, PEDT−PEO does not form monolayers on the ITO surface (either bare or ATS-primed), which is accounted for by its much higher solubility. Thus, a PEO side chain appears to be required for the adsorption but its length must be short.

The charge of the PEDT−EO layer is high since it compares with the value for the ideal close-packed ferrocene monolayer (45 μC cm^{-2}, i.e., 4.5×10^{-10} mol cm^{-2} [31]), though the charge stored per repeat unit is

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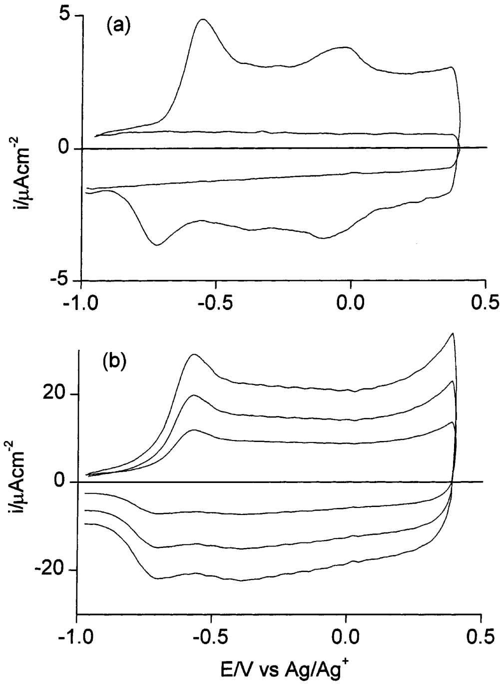
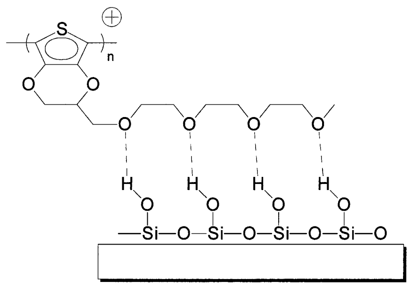


Figure 4. Cyclic voltammograms for (a) a PEDT−EO monolayer and (b) (PEDT−EO/PSS)$_n$ multilayers (n = 5, 10, 15) on ITO in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V/s.

Scheme 1



lower (0.4 electrons) and the molecular size of the unit is higher (≈3 times from simple molecular modeling). This result is attributed to some aggregation of the oxidized polymer to form a more dense monolayer. In agreement with this suggestion CV cycling in CH_2Cl_2 + 0.1 M Bu_4NClO_4 shows a marked decrease (down to Q_r = 15 μC cm^{-2}) of the surface charge due to a 50% dissolution of the undoped polymer. Aggregation of ethyleneoxy-substituted thiophene polymers[19,20] or oligomers[32] is reported in the literature, though data refer to undoped samples. In our case an additional reason for aggregation could be that of formation of π-dimers or in any case of the occurrence of π-interactions among the oxidized polythiophene chains.

As further confirmation of the occurrence of aggregation, PEDT−EO solution in a $CHCl_3/CH_3CN$ 1:1 mixture produces on ITO a monolayer which shows a CV with a single well-defined process at $E°$ = −0.65 and a long flat plateau encompassing a charge Q_r = 15 μC cm^{-2}. This value is the same as that previously obtained on samples CV cycled in CH_2Cl_2, is reproducible, and fits monolayer coverage better.

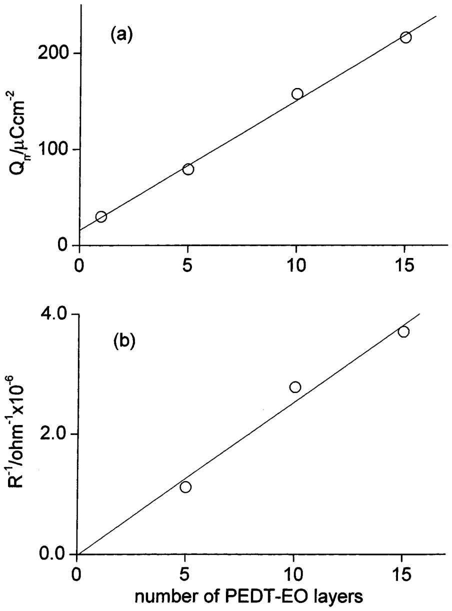


Figure 5. Charge (a) and surface conductance (b) vs number of PEDT−EO layers n in ITO/PEDT−EO/(PSS/PEDT−EO/)$_{(n-1)}$ multilayers. (a) Slope = 13 μC cm^{-2}; Q_0 = 30 μC cm^{-2}.

The interaction of PEDT−EO with the ITO/glass surface is suggested to occur via the oligoethylene oxide moieties (see Scheme 1). Adsorption of poly(ethylene oxide) on silica does in fact occur and it proceeds via coordination of the ether oxygen atoms to Bronsted acid (hydroxyl) sites of the surface.[33] In fact, polycationic (trimethylammonium-substituted) polymers are reported to adsorb on negatively charged sites (polysilicic acid chains) of glass[34] but this occurs in water. In the apolar solvent (CH_2Cl_2) used in this work no appreciable dissociation to produce such charged sites should occur so that the suggestion of H-bridges between the hydroxyl sites and the PEO segments is a more realistic one.

PEDT−EO/PSS Multilayers on ITO. Subsequent alternation of PEDT−EO (in CH_2Cl_2) with PSS (in water) increases the amount of adsorbed PEDT−EO (Figure 4b). The increase is linear up to at least 15 bilayers with a step increase of 13 μC per bilayer (Figure 5a). The step-by-step CV analysis of the multilayering process shows that at each PSS treatment the charge stored in the previous multilayer decreases so that the analysis shows an alternation of charge (Figure 6). This decrease, which does not occur in a PSS-free washing step, may be attributed to complexation and dissolution of PEDT−EO adsorbed excess with PSS. A zigzag behavior of this type in polyelectrolyte multilayering has been previously reported.[14]

From Figure 4b it is clear that the CV response is fast and complete up to at least 15 bilayers.

The four-probe conductivity of the multilayer PEDT−EO/PSS films has been measured. The surface resistance was obtained for the multilayers with more than

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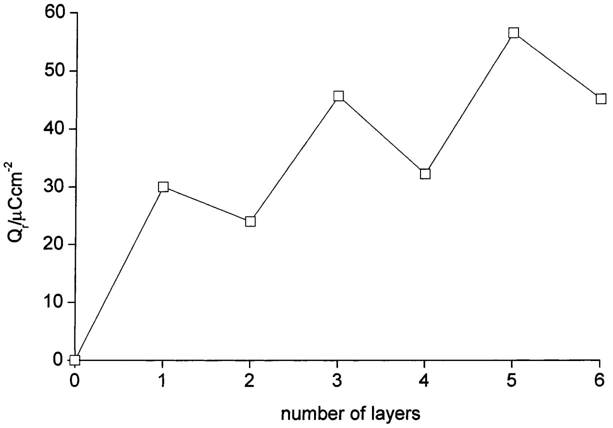

Figure 6. Charge vs number of layers in (PEDT−EO/PSS) multilayering.

5 bilayers and its inverse was found to be proportional to the number of bilayers (Figure 5b).

The surface resistivity of 10-bilayer electrodes resulted in 0.35×10^6 Ω/□. The measured film thickness was 12 (±2) nm, in good agreement with that (10.5 nm) calculated on the basis of reversible charge (150 μC cm^{-2}), doping level (0.4 electrons per unit), M_w of the PEDT−EO unit (318 au) and PSS unit (183 au), ex situ doping level (0.33 electrons per unit[35]), and density (1.4 g cm^{-3}). From surface resistivity and thickness the conductivity of the material results in 2−3 S cm^{-1}. This value is lower than that of bulk PEDT−EO/ClO_4 (70 S cm^{-1}) due to the charge-separating action of the PSS counteranion polymer but remains still considerably high. This result can be compared with the analogous behavior of PEDT/ClO_4 and PEDT/PSS, in which the conductivity of 650 S cm^{-1} in PEDT/ClO_4 drops to 80 S cm^{-1} in PEDT/PSS.[35]

The PEDT−EO/PSS multilayer films, dedoped either electrochemically (in situ) or chemically (with hydrazine), show the same UV−vis spectrum of the analogously treated bulk PEDT−EO films. The absorbance of the hydrazine-dedoped multilayer electrodes, considered along with the reversible charge and the charge stoichiometry, corresponds to an extinction coefficient of 2×10^4 M^{-1}cm^{-1}, in perfect agreement with the value obtained by direct analysis of the polymer solution and with that measured for PEDT−PEO (see above).

PEDT−EO/PAH and PEDT−EO/PDDA Multilayers on ITO. Although both are polycationic polymers, also the alternation of PEDT−EO with PAH increases the amount of adsorbed PEDT−EO. After the first PEDT−EO layer is deposited, the increase of reversible charge is linear with the number of alternations (≈6 μC cm^{-2} per bilayer). Alternation with PDDA on the PEDT−EO monolayer increases similarly the amount of adsorbed PEDT−EO (≈8 μC cm^{-2} per bilayer).

The alternation of PEDT−EO and PAH (or PDDA) appears to be allowed by the interaction of the oligoethylene oxide moieties of PEDT−EO and the ammonium ends of PAH or PDDA, that is, by a nonelectrostatic coordination action. In this way a LBL alternation of polycationic polymers is feasible. It should be recalled that multilayers alternating neutral polymers may be regularly formed via nonelectrostatic (H-bonding) forces.[12b]

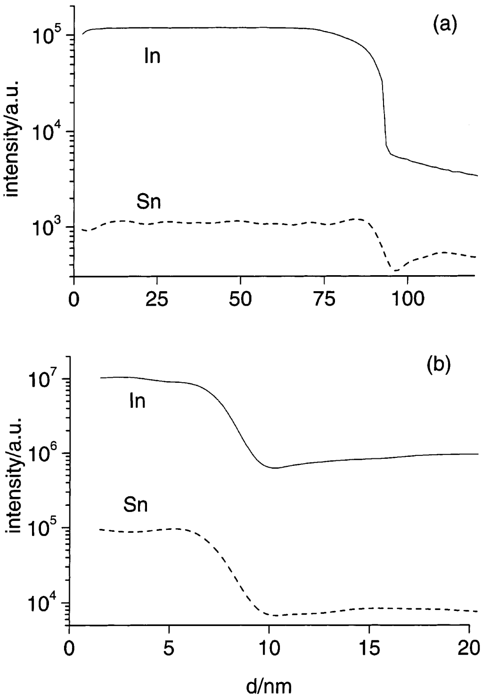

Figure 7. SIMS profile of (—) In and (- - -) Sn content of the ITO/glass electrode at the (a) ITO and (b) glass sides.

PEDT−EO/PSS Multilayers on Float Glass. After potentiostatic steps between 2 and −2 V, the PEDT−EO/PSS multilayer on the ITO side is removed. Subsequent chemical reduction with hydrazine evidences that 50% of the absorbance in the UV−vis spectrum has been lost. Thus, it is clearly shown that LBL proceeds at the same rate on both the ITO and the glass sides of the electrode. In fact, SIMS has shown that the glass side of the ITO/glass sheet is covered with a thin yet homogeneous ITO film (5 vs 100 nm of the ITO side, Figure 7) so that the layers are formed in any case on an ITO surface.

The PEDT−EO attachment on bare glass has been checked with ITO-free float glass sheets. SA from PEDT−EO occurs on float glass similarly to the deposition on ITO/glass. This conclusion comes from the fact that subsequent alternation of PEDT−EO with PSS produces a multilayer as evidenced by UV−vis spectroscopy. Both the absorbance at 620 nm (for the undoped form) and the conductance (for the doped form) increase similarly at each deposition step. The increase is supralinear, which indicates a progressive increase of roughness.[36]

The surface resistivity resulted in 0.55×10^6 Ω/□ for the 10-bilayer, which is comparable with the value (0.35×10^6 Ω/□) for the same multilayer on an ITO-modified glass surface. Treatment with *N*-methylpyrrolidinone, which in the case of chemically prepared PEDT/PSS proved to be efficient in increasing the conductivity (by 3 orders of magnitude),[35] was not effective at all. This result is easily accounted for by the absence of extra

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PSSH, which is on the contrary heavily present in the chemically prepared PEDT/PSS.

PEDT−S/PAH and PEDT−S/PEDT−EO Multilayers. In this section we present a comparison of the here-described PEDT−EO with the reported PEDT−S multilayers.

PEDT−S solution in water does not produce a monolayer on bare ITO but it is reported to do so on the ATS-primed surface.[16] We previously reported that with this polymer the CV develops with difficulty due to slow ion permeation into the hydrophilic polymer[21] so that the addition of 1% water was required to promote the full display of the electrochemical response. The amount of PEDT−S adsorbed in the first layer stores a reversible charge $Q_r = 25\ \mu C\ cm^{-2}$, that is, comparable with the PEDT−EO monolayers described above. Subsequent alternation of PAH and PEDT−S following the prescription given in the literature[16] increases the amount of adsorbed PEDT−S, giving $Q_r = 550\ \mu C\ cm^{-2}$ for 10-bilayer electrodes. The layers are blue-gray with a flat absorption in the visible range, ≈0.25 absorbance for the 10-bilayer electrodes, in substantial agreement with the reported value.[16] The incomplete color (and doping) switching between the undoped and doped forms previously reported[16] has also been confirmed. The 10-bilayer electrode displays a surface resistivity of $1.0 \times 10^6\ \Omega/\square$.

LBL deposition using polycationic (0.33 positive charges per unit) PEDT−EO and polyanionic (0.66 negative charges per unit) PEDT−S has also been performed. The layers increase linearly by $\approx 17\ \mu C\ cm^{-2}$ per bilayer. The surface resistivity resulted in $1.8 \times 10^6\ \Omega/\square$ for the 10-bilayer electrode, that is, with a substantial 5-fold increase compared with that of the PEDT−EO/PSS multilayers. The replacement of the insulating PSS with the conducting PEDT−S polyanionic layer has given this unexpected result, for which structural differences (concerning, e.g., grain size and contact effects) may be responsible.

Conclusions

Soluble conducting poly(3,4-ethylenedioxythiophene)s (PEDTs) bearing oligoethylene oxide (EO) chains of different lengths were produced by anodic coupling. A PEDT−EO bearing a short oligoethylene oxide chain adsorbs as a stable, conducting, and electroactive monolayer on ITO and glass surfaces.

Layer-by-layer alternation of doped PEDT−EO with poly(sodium-*p*-styrene sulfonate) has given electroactive and robust multilayers with low surface resistivity (e.g., $5 \times 10^5\ \Omega/\square$ for a 10-bilayer) and fast switchability between the doped and the undoped forms. The first property may be useful for the production of high-quality antistatic layers on insulating surfaces such as glass or quartz. The second may be of interest for the production of efficient electrochromic devices and in contacting the ITO surface of organic LEDs and photodiodes.

Finally, two points deserve to be highlighted. The first concerns the fact that the polycationic component of common electrostatically bound multilayer films bear the positive charge localized at fixed, usually non-electroactive, sites. The doped PEDT−EO layers here reported are the first in which the whole positive charge is delocalized over a polythiophene backbone. Doped polyaniline[12a] and polypyrrole[10] layers previously used in multilayers delocalize the charge over a polyconjugated chain bearing NH handles absent in a polythiophene chain.

The second is that the common electrostatically bound multilayer films bear polycationic and polyanionic components. Due to specific oligoethylene oxide interactions, the polycationic PEDT−EO layers may be alternated with other polycationic layers. These results may be points of particular interest for the growing field of organized surfaces.

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