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Electrochemical and XPS Studies toward the Role of Monomeric and Polymeric Sulfonate Counterions in the Synthesis, Composition, and Properties of Poly(3,4-ethylenedioxythiophene)

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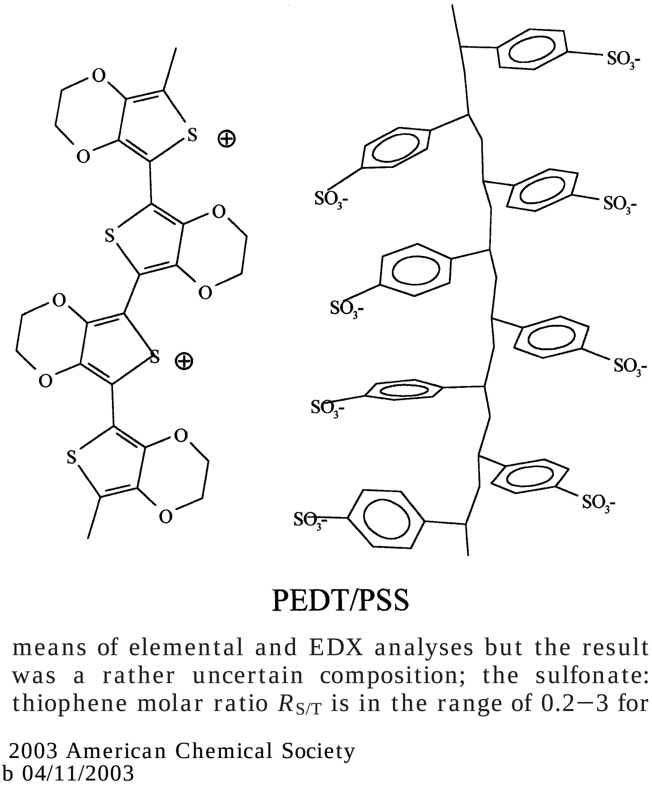
ABSTRACT: Electrochemically prepared poly(3,4-ethylenedioxythiophene) (PEDT) poly(styrenesulfonate) (PSS), produced from acidic (PSSH) and basic (PSSNa) PSS, was characterized by cyclic voltammetry CV, UV−vis spectroscopy, in situ conductivity, and XPS spectroscopy and was compared with electrochemically prepared PEDT/tosylate and chemically prepared PEDT/PSS. CV analysis shows that the polymer synthesis is strongly affected by the nucleophilic character of the counteranion. Although CV and UV−vis spectroscopy show that the structure and degree of polymerization (oligomeric, ca. 10 EDT units) of the PEDT backbone is the same for all polymers, XPS is able to explain the different conductivity values for these materials (ranging from 1 S cm^{-1} for PEDT/PSSNa to 400−450 S cm^{-1} for PEDT/tosylate) based on doping level and composition. In particular, critical results are observed to be the ratios between sulfonate and thiophene units in the polymers: the higher the PEDT concentration, the higher the conductivity. XPS also explains by solvent-induced nanometer-scale segregation between PEDT/PSS and excess PSS particles the often reported conductivity enhancement of chemically prepared PEDT/PSS upon treatment with polar solvents.

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDT) is one of the best known π-conjugated polymers that, due to its excellent conducting and electrooptical properties, has found its way into the market for several applications (e.g., electrode material for solid electrolyte capacitors, antistatic coating in photographic films, etc.).[1] Prepared via standard oxidative chemical or electrochemical polymerization methods, PEDT is an insoluble polymer with some very interesting properties. In addition to a very high conductivity (ca. 550 S cm^{-1}), PEDT is highly transparent in thin, oxidized films and is extremely stable in its oxidized state. Its solubility problem can be circumvented by using a water-dispersible polyelectrolyte, poly(styrenesulfonic acid) (PSSH), as the charge-balancing dopant during polymerization, yielding PEDT/PSS (Chart 1).[2,3] This material displays good film-forming properties, high conductivity (ca. 10 S cm^{-1}), high visible light transmissivity, and excellent stability.[1]

Chart 1



A first, still unclear point concerning this material is its composition. The polymer obtained from poly(sodium-*p*-styrenesulfonate) (PSSNa), chemically via Fe(III) salts[2] or electrochemically,[3] was investigated by means of elemental and EDX analyses but the result was a rather uncertain composition; the sulfonate:thiophene molar ratio $R_{S/T}$ is in the range of 0.2−3 for

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chemical samples[2] and is ca. 0.2 for electrochemical ones.[3] Conductivity appears to increase with a decrease of $R_{S/T}$ with typical values around 1 and 10 S cm^{-1} for $R_{S/T}$ = 2.5 and 0.25, respectively.[2] Within this general picture, an important yet still unclear point is the role of the sulfonate anion in the polymerization process.

In this paper, we describe detailed cyclic voltammetry, UV−vis and XPS spectroscopic, and in situ conductivity measurements performed on PEDT/PSS prepared by electrochemical polymerization in acetonitrile/water applying poly(styrenesulfonic acid) (PSSH) or its sodium salt (PSSNa). The results are compared with those obtained from chemically prepared PEDT/PSS and electrochemically prepared PEDT/perchlorate. The peculiar role of the sulfonate anion has also been considered investigating the EDT polymerization using *p*-toluenesulfonate (tosylate) as counterion; the latter may be considered as the monomeric homologue of PSS.

2. Experimental Section

2.1. Chemicals and Reagents. Acetonitrile was reagent grade (Uvasol, Merck) with a water content < 0.01%. The polyanions poly(sodium-*p*-styrenesulfonate) (PSSNa) (M_w = 100 000, Aldrich) and poly(*p*-styrenesulfonic acid) (PSSH) (M_w = 70 000, Polysciences) were used as received. Tetrabutylammonium perchlorate (Bu_4NClO_4) and tosylate (Bu_4NTos) were previously dried under vacuum at 70 °C. 3,4-Ethylenedioxythiophene (EDT) and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDT/PSS) are commercial products from Aldrich. 2,2′-Bis-EDT was prepared as reported previously.[4] *p*-Toluenesulfonic acid (TosH), sodium *p*-toluenesulfonate (TosNa), *N*-methylpyrrolidinone (NMP), and all other chemicals were reagent grade and were used as received. Poly(3,4-ethylenedioxythiophene) perchlorate (PEDT/ClO_4) films were prepared as previously reported.[5]

2.2. Apparatus and Procedure. Electrochemistry and UV−Vis Spectroscopy. Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter electrode was platinum; unless otherwise stated the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a glassy carbon minidisk electrode (0.06 cm^2).

For UV−vis spectroscopy a 0.8 × 2.5 cm indium−tin−oxide (ITO) sheet (ca. 80% transmittance, ca. 20 Ω sq^{-1} resistance, from Balzers) was used. Spectra were obtained with a Perkin-Elmer Lambda 15 spectrometer.

2.3. Electrical Conductivity. The apparatus and procedures used for the in situ conductivity experiments were previously described in detail. The electrode for conductivity measurements was a two-band platinum electrode (0.3 cm × 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 the conductivity standard.

2.4. 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 a Hewlett-Packard model 5316B.

EQCM measurements of the mass of the polymer films were performed outside the depositing solution. The reactivity toward air of the undoped polymers imposed the condition of measuring the mass in the oxidized state and, as a consequence, to take into account the oxidation level of the polymer. The procedure was therefore that of depositing the polymer potentiostatically, then leaving the polymer at open circuit until attainment of equilibrium (steady o.c. potential), extracting, washing with acetonitrile, and drying in a nitrogen stream to constant mass. Subsequently the film was placed in monomer-free solution, its potential checked (it was reproducibly unchanged from the previous equilibrium value), and its charge content measured by reduction to the undoped state.

2.5. XPS. X-ray photoelectron spectroscopy (XPS) of polymer films deposited on platinum sheets was done using a Scienta ESCA200 spectrometer with a base pressure of 2 × 10^{-10} mbar (UHV) and monochromatized Al(K_α) radiation ($h\nu$ = 1486 eV). The binding energy of the gold Au($4f_{7/2}$) line was calibrated to 83.9 eV. The experimental conditions are such that the full width at half-maximum (fwhm) of the gold Au($4f_{7/2}$) line is 0.65 eV.

The S(2p) signal of PEDT/PSS and derivatives is analyzed and deconvoluted in components described by an envelope of Gaussian−Lorentzian sum function with an asymmetry tail.[6,7] Note that the natural S(2p) line is a doublet S($p_{1/2,3/2}$), due to the spin−orbit coupling. The doublet splitting and relative intensities are taken as input in the curve-fitting scheme of the XPS spectra. During the fitting procedure, the parameters of the peaks, defining shapes and positions, are not allowed to go outside physically reasonable limits, as described elsewhere.[8] To compare the binding energies of the core levels from the measurements performed on the conductive (PEDT/PSS) and insulating (PSSH and PSSNa) samples, the hydrocarbon C(1s) line is used as common reference. For the conductive samples PEDT/PSS, PEDT/Tos, and PEDT/ClO_4, the Fermi level is the reference level.

3. Results and Discussion

3.1. Electrochemical Polymerization. PEDT/Tos was conveniently deposited from 0.1 M EDT in acetonitrile + 0.1 M Bu_4NTos by potentiostatic oxidation at 0.8 V. Comparable products were prepared from 0.1 M EDT in 1:1 vv acetonitrile/water + 0.1 M TosH or TosNa, and these samples will be hereafter named PEDT/Tos(H) and PEDT/Tos(Na), respectively.

As previously reported[2] 0.1 M EDT in 1:1 vv acetonitrile/water + 0.1 M PSSNa are good conditions for electropolymerization. Potentiostatic oxidation at 0.6 V lead to the growth of PEDT/PSS(Na) films on the anode.

The polymer was conveniently prepared also from 0.1 M EDT in 1:1 vv acetonitrile/water + 0.1 M PSSH and will be hereafter named PEDT/PSS(H).

A sample, named PEDT/PSS(H)$_w$, was prepared from a 0.05 M EDT dispersion in 0.1 M PSSH potentiostatically grown at 0.8 V (vs SCE). The resulting deposits are very smooth and transparent and are, in this respect, the best in the series herein reported.

3.2. Tosylate Effect upon Polymerization. Since tosylate may be considered as the monomeric homologue of poly(styrenesulfonate), we have considered this monomeric anion to investigate the role of arylsulfonates in EDT polymerization.

The tosylate anion is known to promote the electropolymerization of pyrrole to a polypyrrole with greatly improved conductivity and mechanical properties;[9] the latter was attributed to ion pairing with the electrogenerated radical cation of the monomer.[10] We have checked whether the same mechanism is valid for EDT. Therefore, we used the EDT dimer (2,2′-bis-EDT) due to its lower oxidation potential and thus absence of undesired water-involving reactions.

2,2′-Bis-EDT is oxidized in acetonitrile in the presence of 0.1 M Bu_4NClO_4 at an irreversible peak (E_p = 0.51 V at 0.1 V s^{-1} in 10^{-3} M solution).[4] The shape of the CV peak ($E_p - E_{p/2}$ = 48 mV) is typical for an EC (electrochemical plus a follow-up chemical reaction) scheme.[11] The number of exchanged electrons apparent from the peak current (n_{app}) is ca. 1.6 electron per molecule.

Polymer is produced upon potential cycling, which accounts for the n_{app} value being higher than 1. In any case the n_{app} value expected for an infinitely long polymer is 3, since two electrons are required for coupling and ca. one electron for doping, the latter given by the doping level at the deposition potential (see Figure 4 after section 3.5). Therefore, the polymer should in fact be a short oligomer. This is what usually occurs when dimers (or oligomers) are used as starting monomers, as observed for e.g.polythiophene deposition from thiophene oligomers (DP = 10−35 thiophene rings from thiophene,[12] ca. 12 from bithiophene[13] and 6 from terthiophene[14]).

Oxidation of 2,2′-bis-EDT produces a polymer film which shows a reversible oxidation process at $E° = -0.45$ V and a maximum absorption at 575 nm in the UV−vis spectrum (in the undoped state). The redox potential is more positive than that of PEDT, and the absorption maximum is at somewhat higher energy; both results thus confirm the expected low degree of polymerization.

The tosylate anion changes both the number of exchanged electrons and the peak potential of the electrochemical oxidation of 2,2′-bis-EDT. Upon addition of Bu_4NTos, the n_{app} of the oxidation peak height increases up to 2.5 electron mol^{-1} at 1:1 molar ratio (or higher), and E_p shifts to a less positive potential (by ca. 25 mV). These data indicate that tosylate speeds up the polymerization process. The difference with the behavior of 2,2′-dipyrrole[10] is that the potential shift is much lower (25 instead of 100 mV). The potential shift allows one to determine[11] that the coupling rate is less than 10 times higher in tosylate than in perchlorate.

The results may be accounted for as follows. The radical cation forms an ion pair with the tosylate anion; the resulting ion pair may dimerize at a faster rate than the free radical cation due to the shielding of the positive charge and the consequent elimination of Coulomb repulsion. The observation that tosylate is better able to promote the coupling reaction than perchlorate is attributed to the disability of the latter to form ion pairs,[15] a consequence of its poor electron-donating property. The scarce effect compared with that on polypyrrole is accounted for by the absence of the strong ion pairing given by the pyrrole H-bonding moiety.

This difference between the tosylate and the perchlorate counteranion is not observed in the final product as shown by EQCM analysis. Polymer films were produced from 10^{-3} M 2,2′-bis-EDT solution in the presence of 0.1 M perchlorate and 2×10^{-3} M tosylate salt. The deposit was formed with the ratio of mass increase over polymerization charge expected for the intervention of perchlorate anion solely. This result, which is the opposite of that obtained with 2,2′-dipyrrole where tosylate was the only anion present in the polymer,[10] indicates that the (weak) kinetic dominance of tosylate in the coupling step is not operating thermodynamically.

A negative property of tosylate is that of preventing anodic coupling under certain circumstances. The deposition of PEDT/Tos occurs regularly in acetonitrile + 0.1 M Bu_4NTos only if the monomer concentration is 0.1 M or higher. No polymer is electrodeposited in 10^{-2} M EDT concentration or less. In contrast, EDT polymerization in acetonitrile + 0.1 M Bu_4NClO_4 occurs regularly even at 10^{-3} M EDT concentration. This result is accounted for by the basic properties of tosylate anion. Aryl- and alkylsulfonic acids are strong in water but weak in aprotic solvents like acetonitrile so that in this medium the sulfonate anion acts as a proton scavenger. For this reason in the course of thiophene oxidation the initially formed radical cation of thiophene is deprotonated by tosylate and the produced neutral radical undergoes further oxidation to an inert overoxidized species, with the result that no polymerization occurs. In the case of pyrrole, polymerization is not hindered by tosylate since pyrrole is much more electron rich than thiophene and consequently its radical cation is less acidic. EDT is also more electron rich than thiophene, but tosylate does not allow its polymerization unless the monomer concentration is so high that protons released during coupling are sufficiently concentrated to block tosylate through its neutralization.

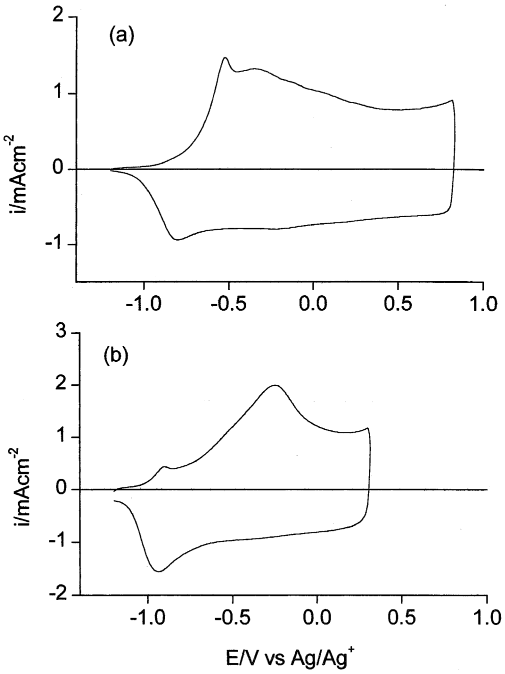

Figure 1. Cyclic voltammograms of (a) PEDT/Tos in acetonitrile + 0.1 M Bu_4Tos and (b) PEDT/PSS(Na) in acetonitrile/water + 0.1 M PSSNa. Scan rate: 0.1 V/s. Reversible charge (at 0.8 V): 13 mC cm^{-2}.

3.3. Electrochemical and UV−Vis Spectroscopic Analysis of the Electrochemically Prepared Polymers. Electrochemistry of PEDT/Tos, PEDT/Tos(H), PEDT/Tos(Na), PEDT/PSS(Na), and PEDT/PSS(H) films was performed in the monomer-free solution used for polymerization. The CVs (see, e.g., Figure 1) show a process similar to that of $PEDT/ClO_4$. The redox potentials $E°$, taken as the average of forward and backward peak potentials, are in all cases at ca −0.55 V, which indicates that the electroactive part of the polymer, i.e., the polythiophene backbone, is identical for the monomeric and the polymeric anions. The real difference between the polymers is the separation between forward (oxidation) and backward (reduction) peak potentials which at the same polymer thickness is higher for the PSS-based polymers than for the monomeric (Tos or ClO_4) anion-based polymers. Typically for films storing reversible charges of ca. 10 mC cm^{-2} and at a scan rate of 0.1 V s^{-1} the peak separation increases from 0.45 V (PEDT/Tos) to 0.7 V (PEDT/PSS) (Figure 1). This result may be attributed to a slowing down of the electrolyte motion in the polyanion polymer during charging−discharging.

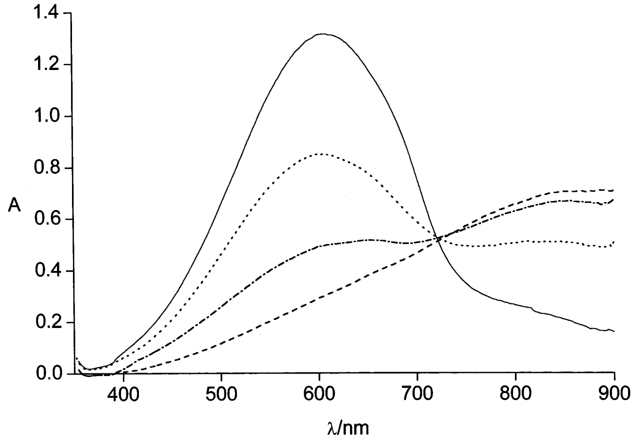

Figure 2. UV−vis spectroelectrochemistry of PEDT/PSS(Na) in acetonitrile/water + 0.1 M PSSNa from the undoped (—) to the fully doped (---) state.

Table 1. Electrical Conductivities of p-Doped Polymers[a]

polymer	σ/S cm^{-1}
PEDT/PSS(Na)	1
PEDT/PSS(H)	80
PEDT/PSS(H)$_w$	50
PEDT/Tos(Na)	400
PEDT/Tos(H)	450
PEDT/PSS[b]	0.03
PEDT/PSS[c]	30
PEDT/Tos[d]	125
PEDT/ClO$_4$[d]	650

[a] Taken ex situ on the pristine material; [b] Chemically prepared, pristine; [c] Chemically prepared, treated with NMP; [d] From acetonitrile.

The UV−vis spectra of undoped PEDT/Tos, PEDT/Tos(H), PEDT/Tos(Na), PEDT/PSS(Na), and PEDT/PSS(H) display a single featureless band around 610−620 nm (see, e.g., Figure 2), identical to PEDT/ClO$_4$. This indicates the same conjugation length and thus the same degree of polymerization. Extrapolation of the maximum absorption λ_{max} of the EDT dimer and trimer,[1] according to the linear relationship between energy gap and the inverse number of monomeric units,[16] suggests that the degree of polymerization is low (around 10). It should be remembered that the PSS chains are formed by a much higher number of repeat units (400−500).

Electrochemical and UV−vis spectroscopic analyses, both on films and in bulk material, did not show any significant difference between the polymers. Since in any case the electrochemical and spectroscopic properties, i.e., the electronic characteristics, are related to the polyconjugated polythiophene backbone of the polymers, differences may be expected to be present in the outer nonelectroactive anionic component of the polymers. This aspect of the polymer structure, namely the anion composition, is expected to bear consequences on the conductivity as reported in the following sections.

3.4. Conductivity of Electrochemically Prepared Polymers. The conductivity values obtained for the as-prepared polymers are summarized in Table 1. In situ conductivity measurements (Figure 3) show that oxidation causes the insulating-to-conducting transition generally found in polyconjugated polymers. This effect is fully reversible. The maximum in situ conductivity (e.g., 40 S cm^{-1} for PEDT/Tos) is generally somewhat lower than the ex situ conductivity of the pristine material (125 S cm^{-1} for the same polymer); the latter is attributable to electrolyte insertion in the matrix. The relationship between in situ conductivity and doping charge evidences an initial region of low conductivity, followed by an approximately linear increase of conduction with charge after which the conductivity attains a very extended plateau. The whole plot is the same previously reported for PEDT/ClO$_4$.[5]

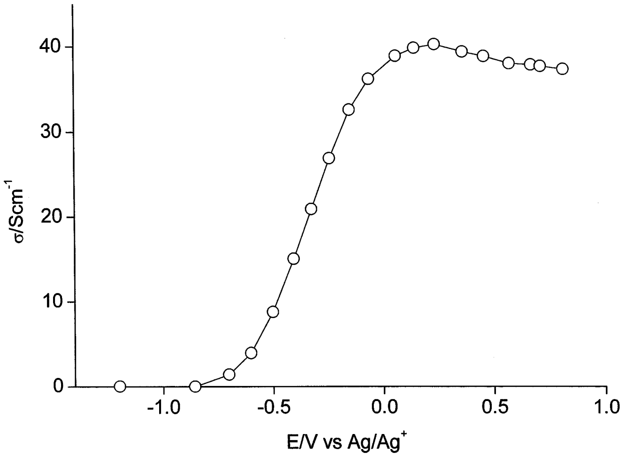

Figure 3. In situ conductivity vs potential for PEDT/Tos films in acetonitrile + 0.1 M Bu$_4$NClO$_4$.

As-prepared PEDT/Tos(H) and PEDT/Tos(Na) are the most conductive (450 and 400 S cm^{-1} respectively). In contrast the polyanion-based materials give lower conductivities; PEDT/PSS(H) displays a conductivity of 80 S cm^{-1} and PEDT/PSS(Na) is even less conductive (1 S cm^{-1}).

3.5. Conductivity of Chemical PEDT/PSS. It is known that PEDT/PSS as commercially obtained, attains its best conductivity after treatment with NMP; the latter increases the conductivity by a factor of ca. 10^3.[17] Thus, films were cast from the commercial solution as such or with 20 wt % NMP added. We indeed observed (see Table 1) that the conductivity increases 1000 times (from 0.03 to 30 S cm^{-1}) upon using NMP. Since the open-circuit potential of both pristine and NMP-treated polymer films, measured in aerated acetonitrile + 0.1 M Bu$_4$NClO$_4$, is 0.0 ± 0.1 V vs Ag/Ag$^+$, the doping level is 0.30−0.35 (see Figure 4 after section 3.5). From the relationship between conductivity and potential given in Figure 3 it appears that the conductivity change within this range of doping is negligible. Moreover the UV−vis spectra of both films are identical, both in the undoped and in the oxidized state, which clearly rules out that the increase of conductivity may be due to secondary doping as found for polyaniline.[18,19] The dramatic conductivity change might be instead explained by the assumption that the organic solvent NMP induces segregation between PEDT/PSS and the excess free PSS on a nanometer scale, thus allowing better pathways for conduction.

3.6. EQCM Analysis of the Electrochemically Prepared Polymers. EQCM was applied to evaluate the dopant and nondopant components of the investigated polymers. EQCM analysis was first performed on the tosylate-based polymer PEDT/Tos since in this case all sulfonate moieties are dopant anions. Thus, the dry mass only consists of polythiophene and tosylate dopant and the content of the latter is determined by the doping charge. The relationship between mass and charge stored in the polymer at different potentials has allowed to draw the curve in Figure 4, from which the polymer

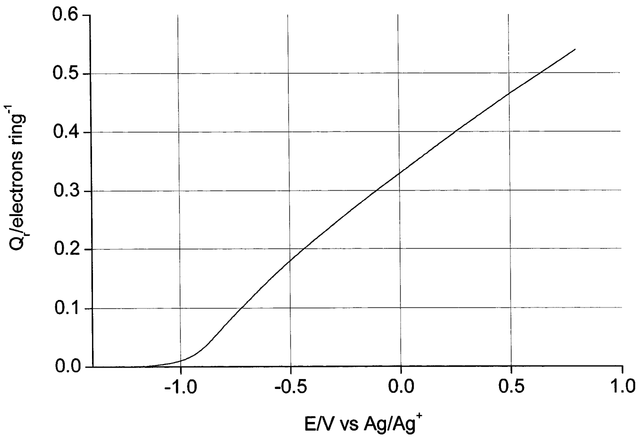

Figure 4. Reversible charge (as electron ring^{-1}) vs potential for PEDT/Tos in acetonitrile + 0.1 M Bu_4NTos.

at the equilibrium potential (0.0 V) results to store a reversible charge of 0.33 electron per thiophene ring. The result is the same obtained for the perchlorate polymer.[5]

The EQCM analysis was then performed on PEDT/PSS(H) deposits produced from solutions containing 0.1 M concentration of both EDT and PSSH. In this case, the mass contains extra nondopant sulfonate moieties. Measurements were also performed on samples produced at solutions with a 10-fold higher PSS/EDT molar ratio, giving similar results. It thus appears that the polymer composition is in practice not dependent on the anion concentration. For a better determination of the sulfonate composition in these polymer films, we applied XPS as reported below.

4. XPS Analysis of the Polymers

4.1. Link between the $R_{S/T}$ Ratio and Conductivity. Both PEDT and PSSH contain one sulfur atom per repeat unit. The sulfur atom in PEDT is within the thiophene ring whereas in PSS it is included in the sulfonate moiety. Because of those different chemical environments, the S(2p) electrons of PEDT and PSSH have different binding energies so that the composition of PEDT/PSS(H) as well as PEDT/Tos(H) polymer mixtures can be analyzed by XPS.[20,21] This is illustrated in Figure 5a. The sulfur signal for pure PSSH appears at higher binding energy (167.8 eV) due to the three electronegative oxygen atoms withdrawing the electron density of the sulfur atom. The S(2p) doublet at 163.3 eV comes form PEDT/ClO_4^-. The asymmetric tail on the higher binding energy side of this component is due to the positive charge stored along the doped PEDT chain and partially localized on the sulfur atoms.

The intensity ratio between the signal from PSS and PEDT gives directly the $R_{S/T}$ ratio. Figure 5b shows the S(2p) spectrum of the chemically polymerized PEDT/PSS dispersion (s = 0.03 S cm^{-1}). For this polymer mixture, a higher $R_{S/T}$ ratio has been observed at the surface,[21] attributed to an excess of PSSH undergoing phase segregation. This has also been observed with XPS. Indeed, it is possible to be more surface sensitive by tilting the sample (takeoff-angle TOA = 80°) during the XPS measurements since then only the photoelectrons coming from a depth of about 20 Å in the organic film are collected, while for TOA = 0° (bulk mode) XPS probes down to a 100 Å depth. The analysis at glazing angle reveals an enhancement of the PSSH component but, even with the bulk mode of XPS, the $R_{S/T}$ ratio is high (3.8). This suggests that the concentration of the excess insulating polymer PSSH in the film is important.

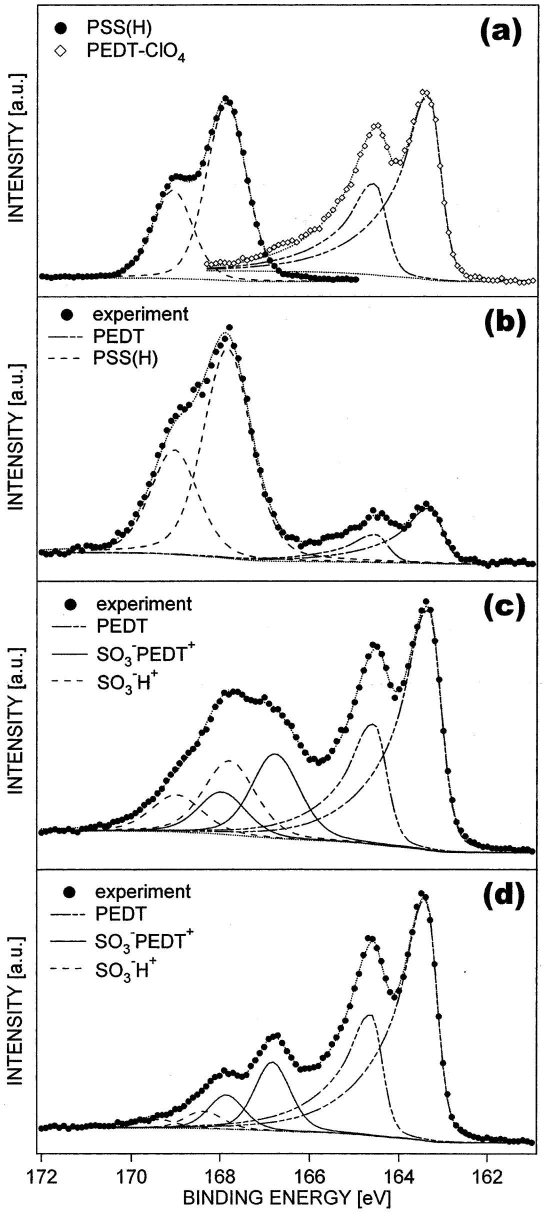

Figure 5. S(2p) signals from (a) PSSH and PEDT/ClO_4, (b) chemically prepared PEDT/PSS, (c) electropolymerized PEDT/PSS(H), and (d) electropolymerized PEDT/Tos.

Graph c displays the S(2p) signal from the electrochemically prepared PEDT/PSS(H) for which a much lower $R_{S/T}$ ratio (0.68) is found. In this case the spectrum is similar for TOA = 80° and TOA = 0°, which indicates that the layer is homogeneous. Hence, the electrochemical PEDT/PSS(H) sample contains more PEDT than PSS. As a result, we deduce that (i) a single PSS chain interacts electrostatically over its length with many shorter PEDT chains and (ii) the distance between adjacent PEDT chains is small, which favors hopping of charge between PEDT chains. Hence the electropolymerized PEDT/PSS(H) can be seen as an organic salt, very compact and conductive. This explains the higher conductivity found for the electrochemical PEDT/PSS(H) (80 S cm^{-1}) compared with the chemically prepared PEDT/PSS (0.03 S cm^{-1}). An even higher conductivity (450 S cm^{-1}) is found when PSS is replaced by Tos. Once

Table 2. Values of Binding Energy (in eV) of Various Components of the S(2p) Signal in Polymers (Shifts from the PEDT Peak in Parentheses)

polymer	PEDT	$SO_3^-PEDT^+$	$SO_3^-Na^+$	$SO_3^-H^+$
PEDT/PSS(H)	163.3	166.8 (3.5)		167.8 (4.5)
PEDT/PSS(Na)	163.4	166.8 (3.4)	167.1 (3.7)	167.8 (4.4)
PEDT/Tos(H)	163.4	166.8 (3.4)		168.3 (4.9)
PEDT/Tos(Na)	163.3	166.7 (3.4)		168.1 (4.8)

Table 3. Amount (Molar Fraction) of the Three Different Sulfonate Groups and of Their Sum ($R_{S/T}$) Relative to the EDT Content in Polymers[a]

polymer	$SO_3^-PEDT^+$	$SO_3^-Na^+$	$SO_3^-H^+$	$R_{S/T}$	σ/S cm^{-1}
PEDT/PSS(H)	0.35		0.33	0.68	80
PEDT/PSS(Na)	0.25	0.19	0.52	0.96	1
PEDT/Tos(H)	0.22		0.06	0.28	450
PEDT/Tos(Na)	0.19		0.09	0.28	400
PEDT/PSS[b]	0.30−0.35		3.5	3.8	0.03

[a] Comparison is made with conductivity (σ). [b] Chemically prepared, pristine.

more this increase of conductivity is related to the $R_{S/T}$ ratio, since the PEDT/Tos has a ratio of 0.28. In this case, the organic layer is mainly composed of PEDT and the tosylate groups in the film are uniquely involved in the charge neutralization of the doping positive charge carried by PEDT. This is in agreement with the study by K. E. Aasmundtveit et al.[22] who demonstrated that PEDT/Tos is an organic crystal composed of one tosylate anion every four EDT units in the unit cell. The hopping distance between two chains that are π-stacked is 3.4 Å which leads to a significant increase of hopping rate between PEDT chains.[23] Hence, the transport of charge is expected to be efficient along the conjugated PEDT chains and between π-stacked PEDT chains.

4.2. XPS Estimate of Doping Level. The S(2p) spectrum of the electropolymerized PEDT/PSS(H) film is shown in graph c of Figure 5. The intensity at higher binding energy (168 eV) arises from the presence of PSS in the film. Surprisingly, the response is composed of two types of sulfur atoms, since only one S(2p) doublet with a 2:1 ratio cannot fit this spectrum. The doublet residing at 167.8 eV originates from the sulfonic acid group $SO_3^-H^+$. The additional doublet, with S(2p) line appearing at 166.8 eV comes from the sulfonate group, $SO_3^-PEDT^+$, neutralizing the positive charge in the PEDT chains. The S(2p) signal of $SO_3^-PEDT^+$ appears at a lower binding energy than $SO_3^-H^+$ because of the different chemical environments.[24] In practice, there is an equal amount of $SO_3^-PEDT^+$ and $SO_3^-H^+$ moieties. The ratio between the $SO_3^-PEDT^+$ and the PEDT signals (0.35) therefore gives a direct estimation of the doping level.

Graph d in Figure 5 displays the S(2p) spectrum of the electropolymerized PEDT/Tos(H). The results of the curve fitting procedure are summarized in Tables 2 and 3. The S(2p) signal from the high binding energy side comes from the tosylate, very similar to the signal generated by the sulfonic group in PSSH. Beside the impressive PEDT concentration in the film, a noticeable feature is that the main contribution from tosylate (S(2p) = 166.8 eV) appears at a binding energy similar to that for the $SO_3^-PEDT^+$ component observed in the electropolymerized PEDT/PSS(H). Thus, for PEDT/Tos(H), the tosylate contribution arises essentially from tosylate anions $SO_3^-PEDT^+$ involved in the doping process. The doping level of PEDT/Tos(H) is estimated to be 0.22, equivalent to one charge for 4−5 EDT monomeric units.

The fundamental difference between a polymeric (PSS) counteranion and a small (Tos) counteranion lies in the presence in the former case of sulfonate groups that are not involved in the doping process. Their amount is very high which is due to the density of sulfonate groups in PSSH being higher than the density of positively doping charge carried by PEDT. Therefore, while half of the sulfonate groups are used to neutralize the doping charge, the other half cannot be excluded from the film since they are attached to the PSS chain. This is in contrast with the case of small anions like tosylate for which only the amount necessary to neutralize the doping charge in PEDT is taken in the film during the electropolymerization. Another difference between the monomeric and the polymeric counterions is the obtained doping level, namely 0.35 for PEDT/PSS(H) and 0.22 for PEDT/Tos(H). Although the doping level is higher for PEDT/PSS(H), this polymer is much less conductive than PEDT/Tos(H). In fact, from Figures 3 and 4, the increase of conductivity for an increase of doping level from 0.22 to 0.35 is observed to be 2-fold at most. Thus, the reduced conductivity of PEDT/PSS(H) is largely explained by the higher average hopping distance which appears to rule the magnitude of the electrical conductivity, since it overwhelms the doping level effect.

4.3. Acidic vs Basic PEDT/PSS and PEDT/Tos. To shine light on the conductivity difference observed between PEDT/PSS(H) (80 S cm^{-1}) and PEDT/PSS(Na) (1 S cm^{-1}), both electrochemically prepared, XPS was applied to analyze the composition of these films. For the sake of comparison, similar XPS investigations were performed on PEDT/Tos(H) and PEDT/Tos(Na) that have similarly high conductivities (400−450 S cm^{-1}).

Graph b in Figure 6 presents the deconvoluted S(2p) spectrum of PEDT/PSS(Na) while graph a presents the references recorded for electropolymerized PEDT/ClO_4 and pure PSS in basic and acidic form. The amount of sodium in the film, measured via the integrated intensity of the Na(1s) photoelectric line, is much lower than expected. Indeed, the pure PSSNa has a 1/1 Na/S ratio, while the Na/S ratio in PEDT/PSS(Na) is 0.19. Moreover, the comparison with the reference spectra of PSSNa does not explain the high binding energy side of the S(2p) contribution in PEDT/PSS(Na). In other words, the S(2p) peak cannot be deconvoluted with only contributions from $SO_3^-Na^+$ and $SO_3^-PEDT^+$ moieties. The additional high binding energy contribution corresponds to the sulfur in the sulfonic acid group $SO_3^-H^+$ (167.8 eV) already observed for PEDT/PSS(H) (see Figure 6c). The low sodium content of the PEDT/PSS(Na) film is due to the replacement of sodium ions by protons from the depositing solution. This is easily understood since on one hand the sulfonate anion has a basic character and on the other the electropolymerization of EDT releases two protons per polymerized monomer.

Although there is no well-defined fine structure present in S(2p) peak of PEDT/PSS(Na), we can propose a physically reasonable curve fitting scheme. The intensity of introduced S(2p) line from $SO_3^-Na^+$ groups (dotted line) is imposed to follow the amount of sodium present in the samples, while the peaks' shape and position were allowed to adjust within reasonable limits. The sensitivity factors for Na(1s) and S(2p) lines were carefully calibrated using PSSNa powder as a reference sample, to achieve exact concentration. The position of

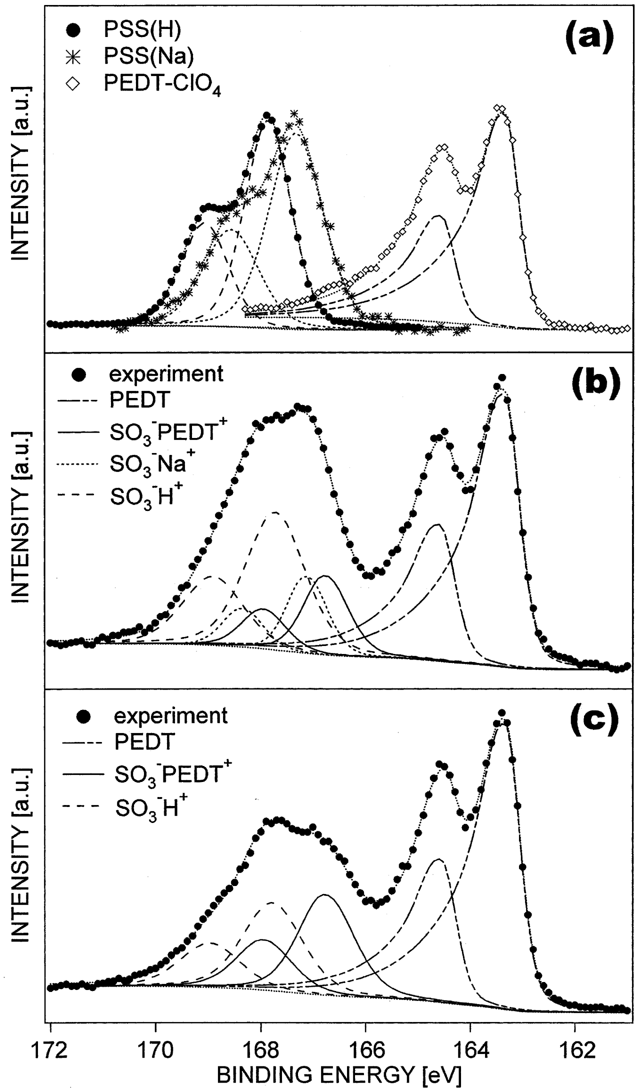

Figure 6. Comparison between the S(2p) signals from (b) PEDT/PSS(Na) and (c) PEDT/PSS(H). The reference spectra are presented in graph a: pure PSSH, pure PSSNa, and PEDT/ClO$_4$.

the S(2p) doublet of $SO_3^-Na^+$ corresponds to that found in pure PSSNa. The two other S(2p) doublets to fit the PSS part of the spectrum are due to $SO_3^-H^+$ (dashed line) and $SO_3^-PEDT^+$ (full line) groups. The positions of $SO_3^-PEDT^+$ line is fixed and equal to the values obtained for PEDT/PSS(H) blend (see Figure 6c).

When comparing the deconvolution scheme of PEDT/PSS(H) and PEDT/PSS(Na), the following conclusions can be drawn: (i) the amount of sulfonate in the PEDT/PSS(Na) film ($R_{S/T} = 0.96$) is higher than in PEDT/PSS(H) ($R_{S/T} = 0.68$), and the lower PEDT concentration in the film has a direct impact on the conductivity since larger distance for hopping are expected whith decrease of conductivity; (ii) the doping level decreases from 0.35 in PEDT/PSS(H) to 0.25 in PEDT/PSS(Na). The higher sulfonate content, the higher size of the sodium bearing sulfonate ends and, to a lesser extent, the lower doping level in PEDT/PSS(Na) are responsible for the 2 orders of magnitude conductivity drop of PEDT/PSS(Na) compared to PEDT/PSS(H).

To check the validity of this explanation, similar XPS analyses were performed on PEDT/Tos(H) and PEDT/Tos(Na). These materials have similar conductivity values. The comparison between PEDT/Tos(H) and PEDT/Tos(Na) in Figure 7 shows that both films have the same amount of tosylate ($R_{S/T} = 0.28$). Note that the possible presence of sodium is below the XPS detection limit in PEDT/Tos(Na). Hence the films formed in TosH or TosNa solutions in fact contain tosylate groups that neutralize the positive doping charges of PEDT. Moreover, the doping level is estimated to be 0.22 for PEDT/Tos(H) and 0.19 for PEDT/Tos(Na). The similarities in doping level and $R_{S/T}$ ratio are consistent with the equivalent conductivities of those films.

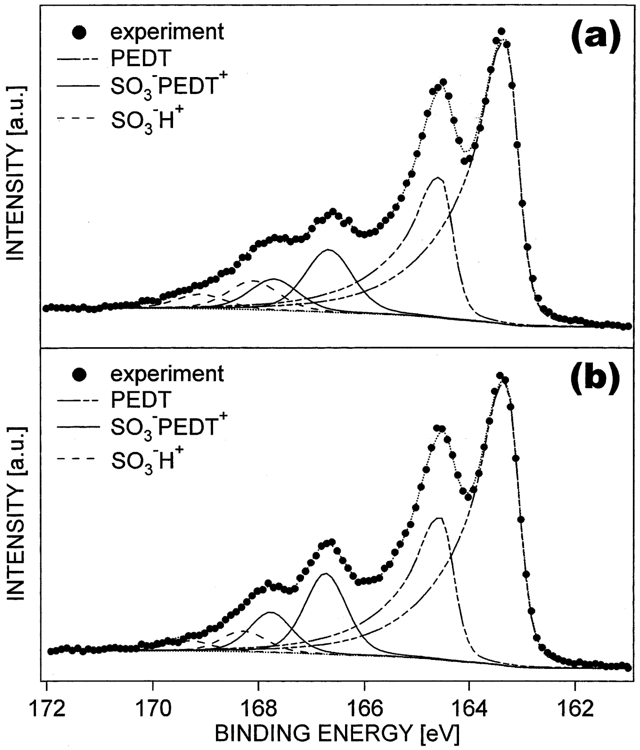

Figure 7. Comparison between the S(2p) signals from (a) PEDT/Tos(H) and (b) PEDT/Tos(Na).

5. Conclusions

Conducting polymers composed of poly(3,4-ethylenedioxythiophene) (PEDT) with a monomeric (tosylate) or polymeric (poly(styrenesulfonate), PSS) arylsulfonate counteranion cover a wide range of conductivity values (4 orders of magnitude) from 450 to 0.03 S cm^{-1}. Since their polyconjugated backbone is essentially the same (their optical and electrochemical properties are almost identical), the conductive behavior reflects the predominant role of the counterion.

When a monomeric anion (tosylate) is used, PEDT takes the minimum amount of anion to neutralize its doping charge and all tosylate molecules are involved in the doping process. The resulting polymeric material is simply made of PEDT chains and the conductivity is very high (400−450 S cm^{-1}; independent of the acidity of the counterion).

At the opposite side is the chemically prepared PEDT/PSS, which contains an excess of PSS likely due to the micellar nature of the emulsion. The resulting segregation gives the lowest conductivity to the material (0.03 S cm^{-1}). This conductivity value can however be upgraded (10^3 times) by adding NMP to the coating formulation. The latter might be explained by the assumption that the organic solvent induces segregation between PEDT/PSS and the excess free PSS on a nanometer scale, thus allowing better pathways for conduction.

The electropolymerized PEDT/PSS is homogeneous with a completely different composition. The oxidized PEDT chains formed at the electrode surface take just the minimum amount of PSS counterion to attain charge neutralization. However, since the density of the charge in PEDT is lower than the density of tosylate groups, some sulfonate groups are not involved in the doping process. Thus, the sulfonate anion is dopant and free acid in 1:1 ratio for PEDT/PSS produced from acid PSS and dopant, whereas it is as free acid and free sodium salt in PEDT/PSS produced from the sodium salt of PSS. The amount of sulfonate groups which are not involved in the doping process leads to an increased hopping distance for the charge carriers with the result of an intermediate range of conductivity (1−80 S cm^{-1}).

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