Conductive and Magnetic Properties of 3,4-Dimethoxy- and 3,4-Ethylenedioxy-Capped Polypyrrole and Polythiophene

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Electrochemically prepared poly(3,4-dimethoxypyrrole), poly(3,4-dimethoxythiophene), poly(3,4-ethylenedioxypyrrole), and poly(3,4-ethylenedioxythiophene) have been characterized by cyclic voltammetry (CV) and ultraviolet−visible (UV−vis) and Fourier transform infrared (FTIR) spectroscopy and were subsequently investigated by in situ conductivity, in situ electron spin resonance spectroscopy (ESR), and electrochemical quartz crystal microbalance (EQCM) analysis. Blocking the 3 and 4 positions of the heteroaromatic ring allows the display of a complete potential window of conductivity for the polypyrroles during the oxidative doping process, whereas a potential window of conductivity wider than usual, but still open, is displayed for the polythiophenes. The combination of redox-type conduction and solvation in poly(3,4-dimethoxypyrrole) gives this material unusual solvatoconductive properties.

Introduction

Over the past two decades the field of π-conjugated polymers has attracted the attention of many scientists due to the interesting electrical and optical properties of these compounds.[1] Two types of polymers that have been studied extensively are polypyrrole (PPy) and polythiophene (PTh). PPy displays a good conductivity in combination with high stability in its oxidized form but suffers from the occurrence of undesired $\alpha-\beta$ and $\beta-\beta$ couplings during polymerization, which deteriorate its properties.[2] To prevent this problem, several 3,4-disubstituted pyrroles have been prepared over the past years.[3−10] One of these compounds, 3,4-dimethoxypyrrole (DMP), synthesized and studied by Merz and co-workers,[3−5] gives free-standing films with a conductivity of 200 S cm^{-1} after electrochemical polymerization. The latter is higher than that of PPy itself (100 S cm^{-1}), a difference that was attributed to the lack of the above-mentioned undesired β-couplings. Very recently, Reynolds and co-workers[10] reported on the electrochemical polymerization of 3,4-ethylenedioxypyrrole (EDP), which showed unique electrochromic properties.

The thiophene family also contains several 3,4-disubstituted derivatives. The most famous one is 3,4-ethylenedioxythiophene (EDT), being the monomer for the well-known and industrially produced conducting polymer poly(3,4-ethylenedioxythiophene).[11] This polymer, often abbreviated as PEDT (or PEDOT), was initially developed to give a soluble conducting polymer that lacked β-couplings within the polymer backbone. Prepared by standard oxidative chemical or electrochemical polymerization methods, PEDT was found to be an insoluble polymer yet exhibited some very interesting properties. In addition to a high conductivity (ca. 500 S cm^{-1}), PEDT was found to be almost transparent in thin, oxidized films and showed a very high stability in the oxidized state.[12] Due to these excellent properties, PEDT is nowadays applied as an antistatic coating in photographic films from AGFA, as an electrode material

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(1) For an overview on conducting polymers, see the following: (a) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998. (b) *Handbook of Organic Conductive Molecules and Polymers*; (Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, England **1997**; Vol. 1−4. (c) Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017. (d) Stenger-Smith, J. D. *Prog. Polym. Sci.* **1998**, *23*, 57. (e) *Polymeric and Organic Electronic Materials and Applications* Epstein, A. J., Yang, Y., Guest Eds.; in *MRS Bull.* **1997**, *22* (6), 13−62.

(2) (a) Street, G. B.; Clarke, T. C.; Kroumbi, M. T.; Kanazawa, K. K.; Lee, V. Y.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253. (b) Clarke, T. C.; Scott, J. C.; Street, G. B.; *IBM J. Res. Dev.* **1983**, *27*, 313.

(3) Merz, A.; Schwarz, R.; Schropp, R. *Adv. Mater.* **1992**, *4*, 409.

(4) Merz, A.; Graf, S. *J. Electroanal. Chem.* **1996**, *412*, 11.

(5) Gassner, F.; Graf, S.; Merz, A. *Synth. Met.* **1997**, *87*, 75.

(6) Goedel, W. A.; Holz, G.; Wegner, G.; Rosenmund, J.; Zotti, G. *Polymer* **1993**, *34*, 4341.

(7) Street, G. B.; Clarke, T. C.; Geiss, R. H.; Lee, V. Y.; Nazzal, N.; Pfluger, P.; Scott, J. C. *J. Phys. Colloq. C3* **1983**, *44*, 599.

(8) Ruhe, J.; Krohnke, C.; Ezquerra, T.; Kremer, F.; Wegner, G. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 885.

(9) Ruhe, J.; Ezquerra, T.; Mohammadi, M.; Enkelmann, V.; Kremer, F.; Wegner, G. *Synth. Met.* **1989**, *28*, C217.

(10) Gaupp, C. L.; Zong, K.; Schottland, P.; Thompson, B. C.; Thomas, C. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 1132.

(11) For a review on (P)EDT and derivatives, see Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

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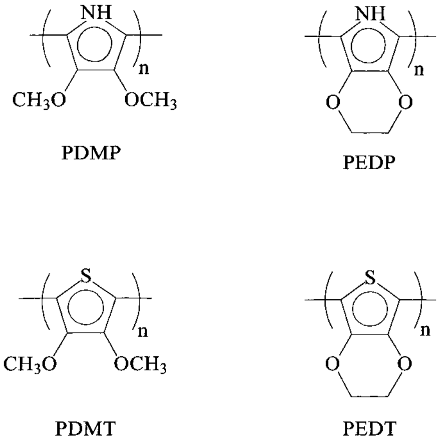
Chart 1



for solid electrolyte capacitors, and in several other applications.[11,13] Besides PEDT, several other 3,4-disubstituted thiophene derivatives were synthesized and electrochemically polymerized, one being 3,4-dimethoxythiophene (DMT)[14] (see Chart 1 for polymer structures).

The above-mentioned polymers allow the investigation of conductivity in a wide potential range extended both into the cathodic limit, due to the electron donor properties of the alkoxy moieties as well as for the fact that their presence does not cause twisting along the chain,[15] and into the anodic limit, due to protection against overoxidation along the 3 and 4 positions.

In this paper we report the electrochemical polymerization of 3,4-dimethoxypyrrole (DMP), 3,4-dimethoxythiophene (DMT), 3,4-ethylenedioxypyrrole (EDP), and 3,4-ethylenedioxythiophene (EDT) in acetonitrile, the characterization of the resulting polymer films with several techniques [cyclic voltammetry and UV−vis and Fourier transform infrared (FTIR) spectroscopy] and their analysis by in situ techniques such as potential-modulated conductivity, electron spin resonance (ESR) spectroscopy, and electrochemical quartz crystal microbalance (EQCM) analysis. The results will give more insight into the structure−property relationship of 3,4-disubstituted polythiophenes and polypyrroles as well as into the mechanism of conduction within these species.

Experimental Section

Chemicals and Reagents. 3,4-Dimethoxypyrrole (DMP),[3] 3,4-ethylenedioxypyrrole (EDP),[10,16] and 3,4-dimethoxythiophene (DMT)[17] were synthesized according to the literature. 3,4-Ethylenedioxythiophene (EDT) was purchased from Bayer (commercial name Baytron M).[11−13]

The supporting electrolytes tetrabutylammonium perchlorate (Bu_4NClO_4) and tosylate (Bu_4NTos) were previously dried under vacuum at 70 °C. All other chemicals were reagent-grade and were used as received.

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter-electrode was platinum; reference electrode was silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The working electrode for cyclic voltammetry was a platinum microdisk electrode (0.003 cm^2). For electronic spectroscopy, 0.8 × 2.5 cm indium−tin oxide (ITO) sheets (ca. 20 ohm/square resistance, from Balzers, Liechtenstein) were used. A platinum sheet (15 cm^2) was used in reflection−absorption FTIR spectroscopy. The voltammetric apparatus (Amel, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

ESR spectra were taken on a Bruker ER 100D following the procedure previously described.[18] Absolute spin calibration was performed with $VOSO_4{\cdot}5H_2O$ crystals; g-value calibration was performed with thin films of DPPH ($g = 2.0036$[19]).

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; IR spectra in reflection−absorption were taken with a Perkin-Elmer System 2000 FTIR spectrometer.

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.[20] The relevant working electrode 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} [21]) was used as conductivity standard.

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 model 5316B. Data were collected by a microcomputer with homemade analyzing software by which frequency changes were monitored as mass changes m.

EQCM measurements of the mass of the polymer films were performed outside the depositing solution. The reactivity toward air of the neutral polymers imposed the condition of measuring the mass in the oxidized state and, as a consequence, to taking into account the oxidation level of the polymer. The procedure was therefore that of depositing the polymer potentiostatically, extracting, washing with acetonitrile, and drying in a nitrogen stream to constant mass m. Subsequently the film was placed in monomer-free solution and its charge content Q_r was measured by reduction to the neutral state.

Simple correlation of mass m and charge Q_r stored in the as-deposited polymer, through

$$(Q_r)/F = m_X/W_X \tag{1}$$

$$m = m_0 + m_X \tag{2}$$

(where m_0 and m_X are the masses of the neutral polymer and of the dopant anion and W_m and W_X are the molar masses of the monomer and of the anion), allowed the determination of the mass of the neutral polymer m_0. The mass of polymer films in the solvated state was obtained by the frequency decrease in the solvent compensated for the frequency shift of the bare electrode.

Results and Discussion

Electrodeposition of the Polymers. As previously reported, the anodic coupling of 2,2′-bipyrrole in aceto-

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[12] (a) Bayer AG. EP 339 340, 1988. (b) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41−43*, 831. (c) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116. (d) Winter, I.; Reece, C.; Hormes, J.; Heywang, G.; Jonas, F. *Chem. Phys.* **1995**, *194*, 207. (e) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87. (f) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347.

[13] (a) Bayer AG. EP 553 671, 1993, (b) Bayer AG. EP 686 662, 1995, (c) Bayer AG. US 5 792 558, 1996. (d) Jonas, F.; Heywang, G. *Electrochim. Acta* **1994**, *39*, 1345. (e) Hupe, J.; Wolf, G. D.; Jonas, F. *Galvanotechnik* **1995**, *86*, 3404. (f) Jonas, F.; Morrison, J. T. *Synth. Met.* **1997**, *85*, 1397. (g) Lerch, K.; Jonas, F.; Linke, M. *J. Chim. Phys.* **1997**, *95*, 1506. (h) Jonas, F.; Lerch, K. *Kunststoffe* **1997**, *87*, 1401.

[14] *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999.

[15] Leclerc, M.; Daoust, G. *Synth. Met.* **1991**, *41−43*, 529.

[16] Merz, A.; Schropp, R.; Dotterl, E. *Synthesis* **1995**, 795.

[17] Leclerc, M.; Daoust, G. *Chem. Commun.* **1990**, 273.

[18] Zotti, G.; Schiavon, G. *Synth. Met.* **1989**, *31*, 347.

[19] Inzelt, G.; Day, R. W.; Kinstle, J. F.; Chambers, J. Q. *J. Phys. Chem.* **1983**, *87*, 4592.

[20] Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209.

[21] Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1983**, *87*, 2289.

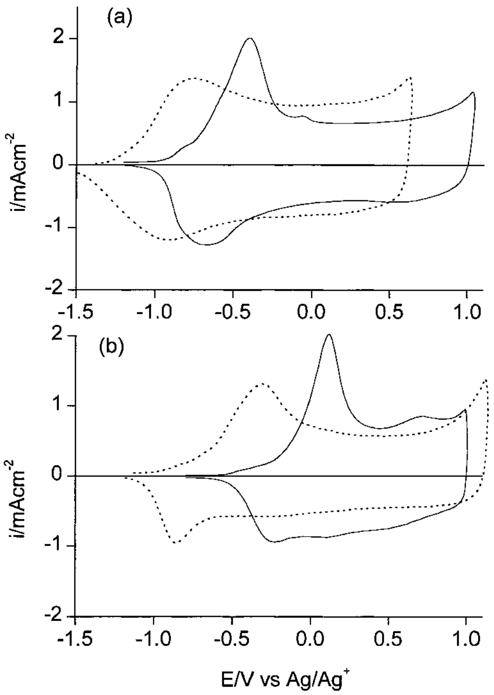

Figure 1. CV for (a) (—) PDMP and (- - -) PEDP and (b) (—) PDMT and (- - -) PEDT in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate 0.1 V s^{-1}.

Table 1. Redox Potential $E°$, Solvation[a] in the Neutral (S_n) and Oxidized (S_{ox}) State, Maximum Absorption λ (as Neutral), and Maximum in Situ Conductivity σ (as Oxidized) for Polymers in Acetonitrile + 0.1 M Bu_4NClO_4

polymer	$E°$/V	λ^b/nm	σ/S cm^{-1}	S_n	S_{ox}
PEDP	−0.9	505 (222)	15	1	0
PDMP	−0.6	460 (222)	15	2	2
PEDT	−0.6	610 (257)	600	1	0.4
PDMT	−0.1	552 (253)	90	3	3

[a] As acetonitrile molecules per repeat unit; polymers neutral or oxidized at 1 V. [b] Monomer maximum absorption in acetonitrile is given in parentheses.

nitrile is strongly dependent on the type of anion, with a particular difference between perchlorate and tosylate and on the water content.[22] This was also found to hold for DMP and EDP. The monomers were oxidized in acetonitrile + 0.1 M Bu_4NClO_4 in a one-electron irreversible peak at 0.6 and 0.5 V, respectively. Potentiostatic cycling in the same solution, however, did not produce polymer on the electrode. This drawback, which was previously explained by protonation of the formed oligomers,[22] is usually overcome by the use of water as a proton scavenger, but in this case addition of 1% water did not have any effect. We subsequently tried the polymerization in 0.1 M Bu_4NTos in acetonitrile. In this case, the polymer deposited nicely. After this result, which is attributed to an increased polymerization rate through ion pairing of the radical cations with the tosylate anion,[22] PDMP and PEDP films were produced potentiostatically at 0.2−0.3 V by use of 0.1 M monomer and 0.1 M Bu_4NTos in acetonitrile.

DMT and EDT display oxidation peaks at 1.06 and 1.04 V, respectively, in acetonitrile + 0.1 M Bu_4NClO_4 with buildup of the corresponding polymer. Both PDMT and PEDT were best potentiostatically deposited at 1.0 and 1.1 V, respectively, from 0.1 M monomer in acetonitrile.

Characterization of the Polymers. Figure 1 and Table 1 summarize the cyclovoltammetric characteristics of the above-mentioned polymers. The CVs of the deposited PDMP and PEDP in acetonitrile + 0.1 M Bu_4NClO_4 show neat processes (Figure 1a) quite similar to that of PPy. The redox potentials $E°$ are −0.6 and −0.9 V, respectively. PDMT in acetonitrile + 0.1 M Bu_4NClO_4 shows a CV process with a single oxidation peak and two reduction peaks (Figure 1b) similar to that of poly(3-methylthiophene).[23] The redox potential $E°$ is ca −0.1 V. The CV of the deposited PEDT (Figure 1b) shows a process quite similar to that of PDMP. The redox potential $E°$, ca. −0.6 V, however, is much lower than for PDMT.

The CVs are stable up to 1 V, beyond which oxidation of the electrolytic medium (for the polypyrroles) becomes important or overoxidation at the sulfur atom (for the polythiophenes) takes place. For comparison, under the same conditions PPy cannot stand voltages higher than 0.5 V, whereas PTh starts undergoing overoxidation at voltages higher than 0.7 V. These observations are generally explained by the absence of substituents capping the β positions.

Spectroelectrochemical data on the neutral polymers are shown in Figure 2 and Table 1. Neutral PDMP displays multiple absorption peaks with the main maximum at 460 nm and two smaller absorption peaks at 433 and 500 nm. This vibronic fine splitting is due to high regularity along the polymer backbone[24] and in particular the vibronic progression of 0.2 eV, corresponding to a C=C Raman vibration frequency, indicates that the conjugated backbone adopts a rigid planar structure. Similar features have been observed in other polyconjugated systems, including poly(3,4-propylenedioxythiophene).[25] In contrast, neutral PEDP displays its maximum at 505 nm with no vibronic fine splitting.

Neutral PDMT displays multiple absorption peaks with a maximum at 552 nm and shoulders at 507 and 595 nm, which appear as the vibronic structure mentioned above. Neutral PEDT displays a broad absorption with a maximum at 610 nm [25] and a shoulder at 680 nm.

The lower E_g and the more negative $E°$ values for the ethylenedioxy polymers compared with the dimethoxy polymers cannot be due to electronic effects of the substituents or different dihedral angles between the planes of adjacent aromatic units, since no significant bathochromic shift can be observed in the spectra of the monomers (see Table 1), nor does significant ring decoplanarization exist.[26] It is therefore suggested that a higher degree of polymerization is responsible for this phenomenon.

Considering the optical properties of these polymers in their oxidized state, it is clearly shown that the

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(22) Zotti, G.; Schiavon, G.; Zecchin, S.; Brenna, E.; Sannicoló, F. *Chem. Mater.* **1995**, *7*, 1464.

(23) Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804.

(24) Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *J. Polym. Sci.* **1987**, *25*, 1071.

(25) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87.

(26) Meille, S. V.; Farina, A.; Bezziccheri, F.; Gallazzi, M. C. *Adv. Mater.* **1994**, *6*, 848.

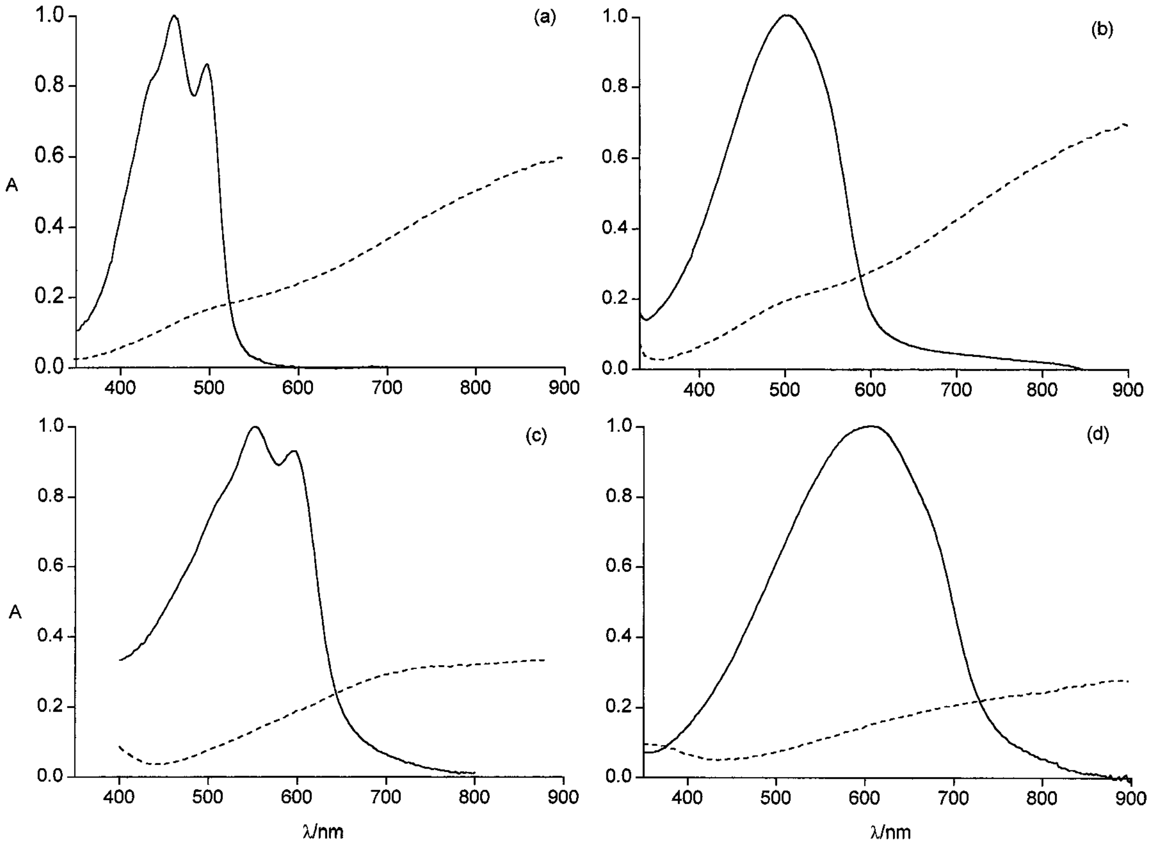

Figure 2. UV−vis spectra of (a) PDMP, (b) PEDP, (c) PDMT, and (d) PEDT in the (—) neutral and (- - -) oxidized states.

polythiophenes are more transparent in their conducting form than the polypyrroles (Figure 2). This feature is of importance for possible applications where color and especially transmittance are important (e.g., electrochromic windows); PEDT and PDMT display a nice sky-blue and transparent appearance, whereas their corresponding polypyrroles give an undesirable blue-gray and less transparent coating.

High-Potential Degradation of the Polymers. Though β-capped, the investigated polymers are subject to degradation upon high-potential polarization. We will consider this feature for PDMP and PEDT taken as typical examples.

PDMP undergoes degradation if anions just a little more nucleophilic than perchlorate, such as tosylate, are used. The CV of the deposited PDMP film in acetonitrile + 0.1 M Bu_4NTos displays a potential $E^\circ = -0.47$ V (Figure 3). At higher potentials one can also observe a second oxidation process at $E^\circ =$ ca. 0.4 V; the latter marks the closure of a potential window of conductivity[27] as discussed in a further section. The tosylate polymer is unstable at potential values higher than 0.6 V. As a result the repetitive CV displays distortion and conductivity decreases progressively. This result may be due to nucleophilic attack of the tosylate anion to the oxidized polymer with deprotonation of the NH moiety made acidic by the high oxidative charge. This suggestion was confirmed by FTIR analysis of polymer films after oxidation at 1.2 V and backward reduction at −1.2 V (Figure 4b). The comparison with the monomer (Figure 4a) shows, in addition to the disappearance of the aromatic CH stretching mode at 3005 cm^{-1} and out-of-plane bending mode at 742 cm^{-1}, the complete disappearance of the NH stretching band at 3400 cm^{-1}, whereas a strong band at 1600 cm^{-1} is observed. This band may be assigned to a vibrational contribution from quinoidal C=N and C=C modes.[28] This result shows that degradation of the oxidized polymer is in fact

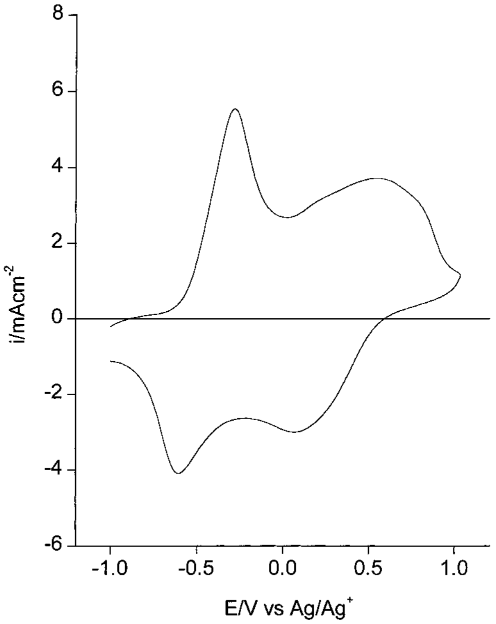

Figure 3. CV for PDMP in acetonitrile + 0.1 M Bu_4NTos. Scan rate 0.1 V s^{-1}; reversible charge 13 mC cm^{-2}.

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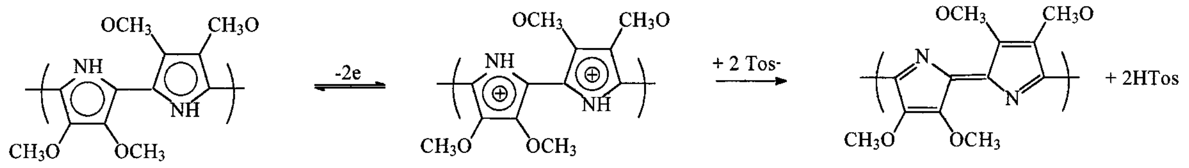
[27] Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Borgonovo, M.; Lazzaroni, R. *Chem. Mater.* **1997**, *9*, 2876.

[28] Shacklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1986**, *88*, 3955.

Scheme 1



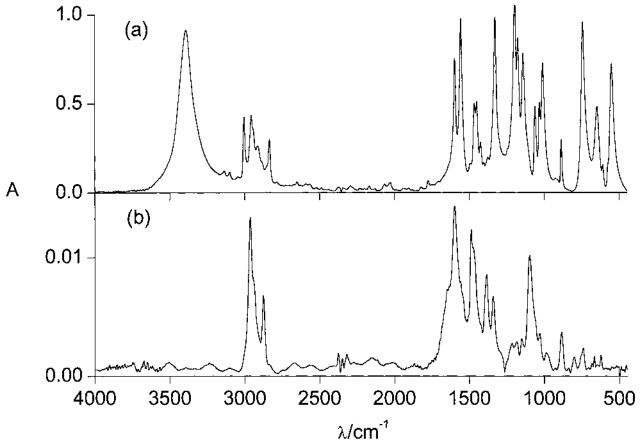


Figure 4. FTIR spectra of (a) DMP (KBr pellet) and (b) overoxidized PDMP (reflection−absorption).

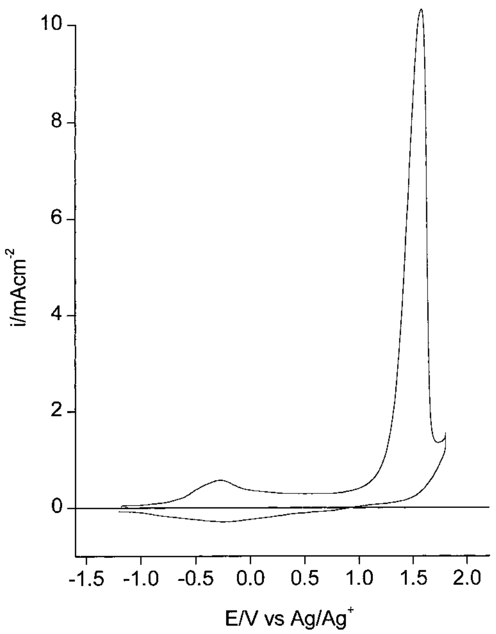


Figure 5. CV for PEDT in acetonitrile + 0.1 M Bu_4NClO_4 beyond the overoxidation peak. Scan rate 0.1 V s^{-1}; deposition charge (neutral state) 20 mC cm^{-2}.

Scheme 2

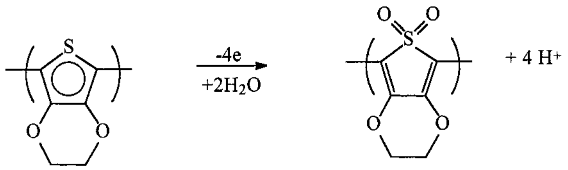


Table 2. Some Typical EQCM Analysis Values for Polymer Films[a]

Q_d/mC	m/μg	Q_r/mC	m_0/μg	Q_{rmax}/mC	electrons mol^{-1}
		PNMP-Tos			
8.0	4.35	1.05	2.55	2.05	1.05
16.0	9.95	2.15	6.30	4.30	0.95
		PEDT-ClO_4			
15.0	8.50	1.50	7.00	2.80	0.58
16.0	8.95	1.75	7.20	3.10	0.63
23.5	14.5	2.60	12.0	4.75	0.58

[a] Q_d = deposition charge; Q_r = reversible charge of the as-prepared tosylate polymer; Q_{rmax} = maximum reversible charge; m = measured mass; m_0 = mass of neutral polymer.

deprotonation to an imine polymer (Scheme 1). The role of proton scavenger, which in this case has been played by the tosylate anion, does not pertain to perchlorate, which appears to act as a truly non nucleophilic anion.

As previously observed[25] the CV of PEDT displays a strong oxidation peak at ca. 1.5 V, i.e., far beyond the reversible oxidation process, in which the polymer loses its conductive properties (Figure 5). The charge involved in this process (Q_{ox}) is ca. 7 times the reversible charge Q_r measured at 1 V. It must be remarked that this occurs with thin films (deposition charge $Q_d < 5$ mC cm^{-2}); with increasing thickness, this process becomes more difficult. Since Q_r corresponds to 0.6 electron $ring^{-1}$ (see below), Q_{ox} corresponds to ca. 4 electrons $ring^{-1}$. The latter agrees with overoxidation of the sulfur atom to a sulfone (Scheme 2). Unfortunately this could not be confirmed by FTIR analysis of polymer films after overoxidation at 1.5 V since the products dissolved into solution and their amount was too small to be collected. The suggested degradation is in any case in agreement with the results of PTh overoxidation as reported by Barsch and Beck.[29]

EQCM Analysis of the Polymers. EQCM analyses show that PDMP and PEDP (as tosylate salts) are deposited with a 30% deposition yield, PDMT with a 23% yield, and PEDT with the highest (65%) deposition yield.

The EQCM technique also shows that in perchlorate solution both polypyrroles totally exchange tosylate within some minutes even in the oxidized form. This fact, which is in contradiction with that found for PPy,[30] may be accounted for by easy polymer solvation.

The correlation between the mass of the neutral polymer m_0 and the total reversible charge Q_r involved in the redox process (at 1 V) allowed us to state that 1 electron is exchanged per pyrrole unit and 0.6 electron per thiophene unit. This holds for all the investigated polymers. Typical determinations are reported in Table 2.

The mass vs potential or charge relationships are reversible (Figure 6). In the case of the ethylenedioxy polymers PEDP and PEDT, the mass vs charge relationships show a linear regime with a $F\Delta m/Q_r$ value of 60 g mol^{-1}, indicating the acquisition of one perchlorate anion and the loss of one acetonitrile molecule per

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(29) Barsch, U.; Beck, F. *Electrochim. Acta* **1996**, *41*, 1761.

(30) Schiavon, G.; Zotti, G.; Comisso, N.; Berlin, A.; Pagani, G. *J. Phys. Chem.* **1994**, *98*, 4861.

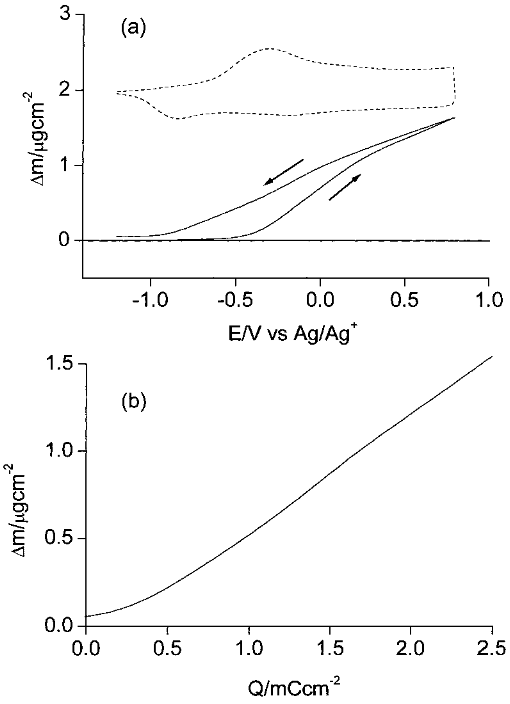

Figure 6. In situ EQCM vs (a) potential and (b) charge for PEDT in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

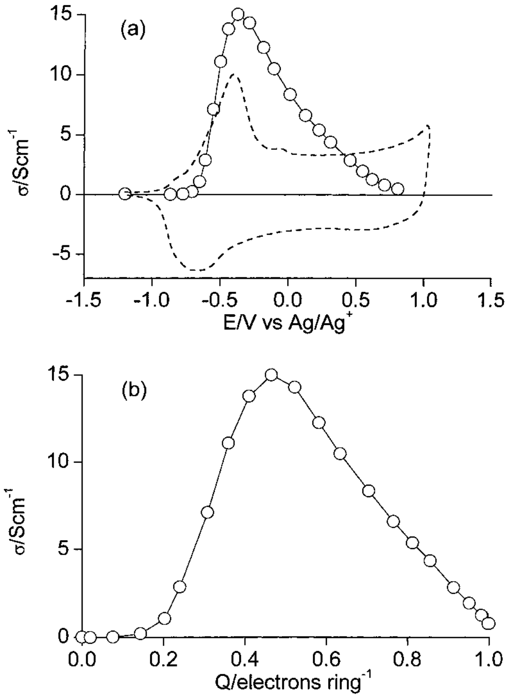

Figure 7. In situ conductivity vs (a) potential and (b) charge for PDMP in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

oxidizing electron. In the case of the dimethoxy polymers PDMP and PDMT the mass vs charge relationship gives a $F\Delta m/Q_r$ value of 100 g mol^{-1}, indicating the exchange of one perchlorate anion per electron (no solvent change).

All four polymers are to a various degree swollen by acetonitrile (Table 1). Neutral dimethoxy polymers PDMP and PDMT contain 2 and 3 acetonitrile molecules per repeat unit, respectively, whereas the neutral ethylenedioxy polymers PEDP and PEDT are less swollen (one acetonitrile molecules per repeat unit). From the above-reported relationships of mass and charge, PDMP and PDMT hold the solvent in the oxidized state whereas PEDP and PEDT lose it upon oxidation. In their fully oxidized (at 1 V) state the ethylenedioxy polymers are practically not swollen, whereas a high solvation is observed for the dimethoxy polymers.

In Situ Conductivity of the Polymers: PDMP and PEDP. In situ conductivity measurements of all four polymers in acetonitrile + 0.1 M Bu_4NClO_4 show that oxidation causes the transition from a low-conductivity to a conductive state as generally found in polyconjugated polymers. PDMP passes to a second low-conductivity state (fully oxidized) via a maximum (15 S cm^{-1}) located at ca. −0.4 V (Figure 7a). A complete valence band depletion of PDMP at the anodic limit of 1 V is ruled out by the presence at this potential of a high CV capacitive current, but a sub-band is in fact depleted by the one-electron oxidation process. This conductive behavior is completely different from that of PPy perchlorate, which is conducting through an extended potential plateau.[31]

The relationship between conductivity and reversible charge (the latter given as electrons per pyrrole ring) for PDMP is shown in Figure 7b. It can be observed that the conductivity maximum occurs at 50% of the total charge (0.5 electron per pyrrole unit), which is reminiscent of the maximum conductivity of a half-oxidized redox state.[32] In any case a significant asymmetry of the curve is apparent. This result may be accounted for by the dominance of mixed-valence conduction between polaron and bipolaron (rather than neutral and polaron) forms in the 25−50% range of charge. The occurrence of spin pairing in the first oxidation stage (up to 25% of doping charge) is suggested and confirmed by ESR measurements (see below).

The in situ conductivity of PEDP as the perchlorate salt both vs potential and vs charge shows a picture similar with that of PDMP, also with a maximum conductivity of 15 S cm^{-1}.

A particular comment is deserved for the ex situ conductivity of PDMP films. When they are produced at low current densities (0.5−1 mA cm^{-2}), high conductivities (100−200 S cm^{-1}) are displayed.[4] In our case (current density around 10 mA cm^{-2}) we found similar values (ca 80 S cm^{-1}). It should be observed that the maximum in situ conductivity (15 S cm^{-1}) is much lower than that of the ex situ material. This unusual result, which is due to solvation effects, will be considered in detail in the last section.

In Situ Conductivity of the Polymers: PDMT and PEDT. In situ conductivity measurements of PDMT as the perchlorate salt (Figure 8a) shows that oxidation causes the transition from a low-conductivity to a conducting state (fully oxidized) via a maximum located at ca. 0.2 V. The maximum conductivity is 90 S cm^{-1}, much lower than for PEDT (see below). Previously reported PDMT[33] showed even lower conductivities in the range 1.5−30 S cm^{-1}.

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(31) Feldman, B. J.; Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1985**, *107*, 872.

(32) Chidsey, C. E. D.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 1479.

(33) Yamamoto, T.; Kashiwazaki, A.; Kato, K. *Makromol. Chem.* **1989**, *190*, 1649.

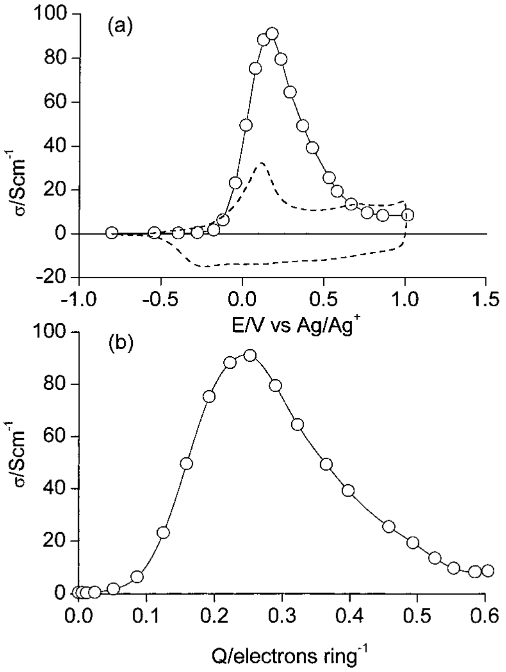

Figure 8. In situ conductivity vs (a) potential and (b) charge for PDMT in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

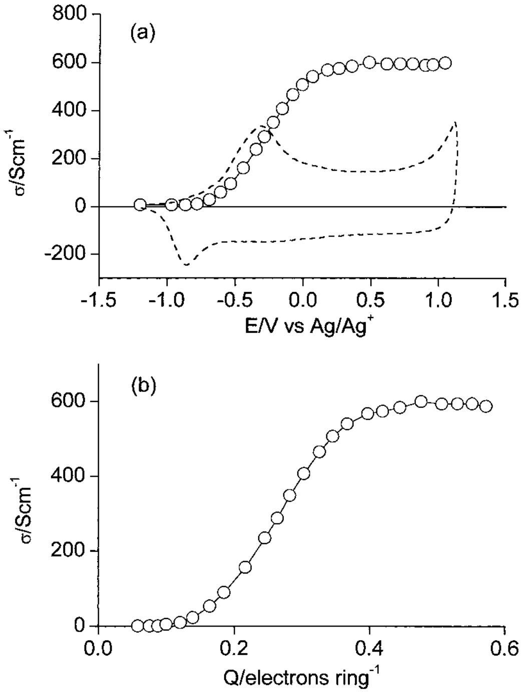

Figure 9. In situ conductivity vs (a) potential and (b) charge for PEDT in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

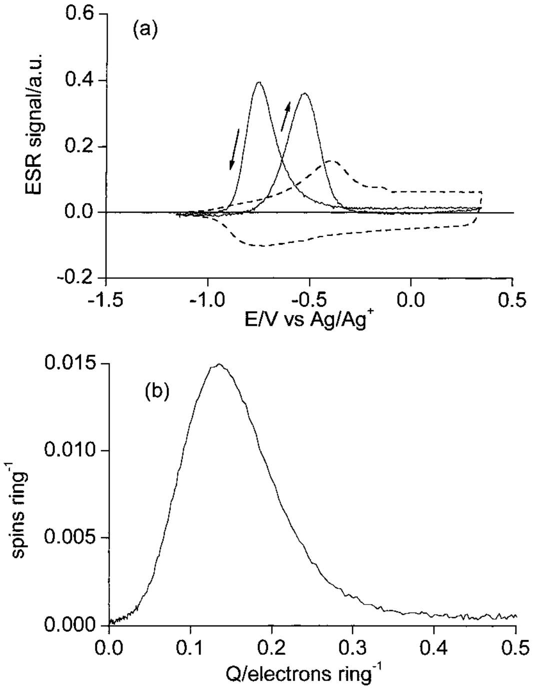

Figure 10. In situ ESR (a) potential and (b) charge for PDMP in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

The relationship between conductivity and reversible charge for PDMT (Figure 8b) apparently resembles that of PDMP. Before the conductivity starts rising, there is a wide charge range (from 0 to ca. 0.1 electron ring^{-1}) in which the material is scarcely conductive. The conductivity then attains a maximum at ca. 50% of the maximum charge (at a doping charge of 0.25 electron per thiophene unit), but in contrast with PDMP, the following decay of conductivity with charge does not proceed linearly yet the slope decreases until a low conductivity plateau is attained.

In situ conductivity measurements of PEDT, deposited as the perchlorate salt (Figure 9a), shows that oxidation of the polymer results in a conductivity that spans over a very extended plateau in the potential domain. The plateau conductivity is 600 S cm^{-1}, a very high value that is in good agreement with that reported in the literature (550 S cm^{-1}).[34] It is clearly evident that this potential dependence of conductivity is completely different from that of the investigated polypyrroles.

The relationship between conductivity and reversible charge (the latter given as electrons per thiophene ring) for PEDT is shown in Figure 9b. It can be observed that the conductivity plateau starts at ca. 0.4 electron ring^{-1} but also in this case there is a wide charge range (from 0 to ca. 0.15 electron ring^{-1}) in which the material is not conductive. The occurrence of spin pairing in this first oxidation stage is suggested and confirmed by ESR measurements (see below).

In Situ ESR of the Polymers. The next sections will consider this feature for PDMP and PEDT taken as typical examples; the responses of the others are substantially the same.

Oxidation of PDMP films produces an ESR signal, which after an initial increase with charge attains a maximum close to the oxidation peak potential and then decreases to zero (Figure 10a). The *g* value of the signal is 2.0032 and its width is 1.5 G. On the reverse scan the signal reappears with a peak in correspondence with the cyclic voltammetric backward peak.

The maximum spin concentration is 0.015 spin per pyrrole ring, considerably lower than that measured for PPy (1 unpaired electron per 10 pyrrole rings).[35] This result also appears from the plot of ESR signal vs charge (as electrons per pyrrole ring, Figure 10b), from which

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(34) Yamato, H.; Kai, K.; Ohwa, M.; Asakura, T.; Koshiba, T.; Wernet, W. *Synt. Met.* **1996**, *83*, 125.

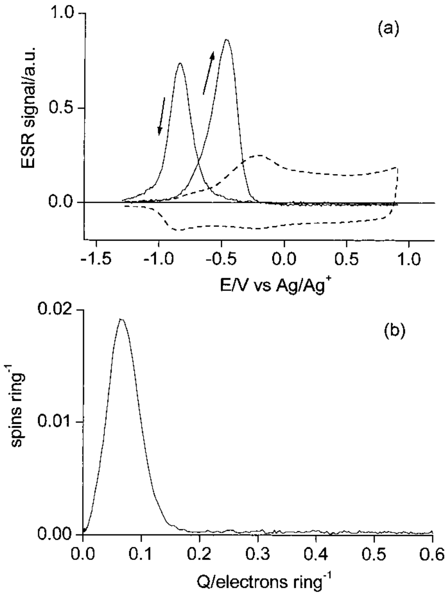

Figure 11. In situ ESR (a) potential and (b) charge for PEDT in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

it may be observed that spins disappear at 0.3 electron ring^{-1}. A low maximum spin concentration at low doping charge suggests the occurrence of spin pairing in π-dimers. The latter is commonly known in oligothiophenes[36] and has recently also been found for oligopyrroles.[37]

The overall picture for PEDT is similar to that for PDMP. Upon oxidation an ESR signal is generated, attains a maximum around the oxidation peak potential, and then decreases to zero (Figure 11a). The g value is 2.0035 and the width is 2.2 G. The maximum spin concentration is 0.02 spin per thiophene ring. In the ESR signal vs charge plot (Figure 11b), spins attain the maximum concentration at 0.06 electron per ring and disappear at 0.15 electron per ring.

A comparison of conductivity and spin concentration as a function of doping charge for all polymers shows once again, but more clearly than before, that free unpaired electrons and conductivity are noncorrelated.

A final consideration deals with the g values (2.0032 for PDMP and 2.0035 for PEDT), which are unusually high (PPy has been shown to display the signal at g = 2.0029[38] and PTh at g = 2.0025[39]). In fact the g values are related to the participation to the carbon, sulfur and oxygen atoms according to

$$\Delta g = g - g_e \propto \lambda / E_g$$

where g_e is the free-electron g-value (2.0023), λ is the spin–orbit coupling parameter (29 cm^{-1} for C_{2p}, 382 cm^{-1} for S_{3p}, 76 cm^{-1} for N_{2p}, 151 cm^{-1} for O_{2p}) and E_g is the band-gap of the polymer.[40] As a consequence the g values would always be higher than the free-electron value. The optical band-gap value of, e.g., PDMP (2.7 eV) is lower than that of PPy (2.85 eV),[41] but the calculation shows that this fact only minimally accounts for the higher measured g value of PDMP. It is therefore clear that spin delocalization at the oxygen atoms of the alkoxy β-substituents is particularly important.

Potential Windows of Conductivity. As for conducting materials in general, the conductivity of polyconjugated polymers is associated with the presence of partially filled bands so that conduction is limited in the potential range (for oxidation) by the depletion of the valence band. This was experimentally shown for many polymers including the main members polyaniline, polythiophene, and polypyrrole[42] and regular dipyrrole–arylene copolymers.[27]

In the case of polythiophenes the theory calculates a bandwidth of 2.6 eV for PTh.[43] Since the valence band of poly(4,4′-dimethoxydithiophene), which involves one electron per thiophene ring, displays a bandwidth of ca. 2.5 eV,[44] we may conclude that for such polymers there is a substantial agreement between theory and experiment.

Considering polypyrroles, the theoretical value of the bandwidth of PPy is 3.8 eV,[45] i.e., higher than that of PTh. In fact the bandwidth is lowered to 1.3 eV for poly(3,4-dimethylpyrrole)[42] and poly(3,4-cyclopentanepyrrole),[6] but responsible for this deviation is steric decoplanarization of the rings along the chain axis. The stored charge is in any case ca. 0.8 electron/pyrrole, i.e., close to the theoretically calculated value of 1.[6]

In the polymers investigated here, alkoxy substitution at the 3 and 4 positions, besides protecting the ring from undesired oxidation processes, allows coplanarization of the rings.[26] Therefore it is expected that the bandwidths are close to the calculated values. This may be true for PEDT but is definitely not the case for PDMP. Since 0.6 electron ring^{-1} is extracted from PEDT in the potential range in which 1 electron ring^{-1} is removed from PDMP, it is clear that the PDMP valence band is much narrower than that of PEDT, i.e., a situation opposite to that predicted.

The bandwidth of the polymers can be obtained from the potential range of the CV process $\Delta E°$ (= $E^0{}_2 - E^0{}_1$). In PDMP (tosylate response) it appears to be ca. 0.9 eV wide. This value confirms that the band of PDMP is narrower than its theoretical value and than that of polypyrroles with decoplanarized rings *without any*

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(35) Genoud, F.; Guglielmi, M.; Nechtschein, M. *Chem. Phys. Lett.* **1985**, *55*, 118.

(36) (a) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728. (b) Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113. (c) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106. (d) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620. (e) Bauerle, P.; Segelbacker, U.; Gaudl, K. U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76. (f) Hapiot, P.; Audebert, P.; Monnier, K.; Pernaut, J. M.; Garcia, P. *Chem. Mater.* **1994**, *6*, 1549. (g) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013.

(37) (a) VanHaare, J. A. E. H.; Groenendaal, L.; Gavinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *33*, 638; (b) VanHaare, J. A. E. H.; VanBoxtel, M.; Janssen, R. A. J. *Chem. Mater.* **1998**, *10*, 1166.

(38) Oudard, J. F.; Allendoerfer, R. D.; Osteryoung, R. A. *J. Electroanal. Chem.* **1988**, *241*, 231.

(39) Kaneto, K.; Hayashi, S.; Ura, S.; Yoshino, K. *J. Phys. Soc. Jpn.* **1985**, *54*, 1146.

(40) Tourillon, G.; Gourier, D.; Garnier, F.; Vivien, D. *J. Phys. Chem.* **1984**, *88*, 1049.

(41) Zotti, G.; Martina, S.; Wegner, G.; Schluter, A. D. *Adv. Mater.* **1992**, *4*, 798.

(42) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.

(43) Bredas, J. L.; Elsenbaumer, R. L.; Chance, R. R.; Silbey, R. *J. Chem. Phys.* **1983**, *78*, 5656.

(44) Dietrich, M.; Heinze, J. *Synth. Met.* **1991**, *41–43*, 503.

(45) Bredas, J. L.; Themans, B.; André, J. M. *J. Chem. Phys.* **1983**, *78*, 6137.

Table 3. PDMP Resistance Increase Δ*R* at Vapor Atmosphere of Different Solvents

solvent	$\Delta R/R_0$ (Tos)	$\Delta R/R_0$ (ClO_4)
H_2O	0	0
ethanol	2	0.6
acetone		0.8
acetonitrile	1.2	2.8
chloroform	13	3.6
toluene	0	0
hexane	0	0

[a] Data for polymer as perchlorate and tosylate. Deposition charge 50 mC; dry air resistance R_0 5 Ω.

twisting of the polymer chain. An alternative explanation must be found in the pyrrole nature of this polymer and more specifically in the presence of the NH function.

Comparison between conductivity and charge for all investigated polymers evidences an initial region of low conductivity, followed by an approximately linear increase of conduction, common to all polymers and due to magnetic interaction between polarons. Differentiation occurs at higher charges; PEDT then displays a substantial independence from charge, whereas PDMP shows a linear decrease with charge. The former behavior is expected for free charges hopping within a narrow potential range with constant density of states,[46] a condition we may call "metallic". The trend observed in PDMP may, on the contrary, be explained by a redox-type model of conduction based on bipolarons as carriers, which would account for the linear decrease of conductivity from 0.5 to 1 electron ring^{-1} doping charge.[32] A bipolaron conduction mechanism of this type, in fact, has been proposed for doped polyconjugated polymers.[47] In this case the bipolaron charge might be a dicationic dipyrrole unit (see Scheme 1) stabilized by the alkoxy substituents and pinned by NH interaction with the anion. Such an interaction, which in the case of the tosylate anion is so strong that deprotonation follows, is limited to the stabilization of the bipolaron in the case of the much less nucleophilic perchlorate anion.

The fact that PDMT behavior is intermediate between that of PEDT and the polypyrroles may be explained as follows. After the nonconducting region of charge, a redox conduction operates at first as for the polypyrroles (at the lower charge of 0.5 electron ring^{-1}, the dication is located in four rings). After that the "metallic" conduction sets in at a lower value than for PEDT (the reason is possibly the increased interchain spacing introduced by the free dimethoxy substituents).

Finally, it is instructive to compare the relationships of conductivity and charge for the investigated polymers with those of other noncapped polypyrroles and polythiophenes previously investigated.[48] It then appears that the simple picture of a linear increase of conductivity with charge, followed by the plateau of conductivity originated by a constant density of carriers, has in fact only been observed in PPy with perchlorate or tetrafluoroborate as counteranions.[31,49] In the case of polythiophenes, polaron dimerization introduces a low-conductivity state at the early stages of charge. Similar effects are shown for polypyrroles with more nucleophilic counteranions. PEDT is therefore not an exception; it shows the initial region of low conductivity and at higher charge the plateau of conductivity of a true organic metal. In contrast, PDMP appears as a new entry in the family since it is the first polypyrrole (i) to show polaron dimerization, with the consequent 25% charge range of nonconduction and (ii) to exhibit a linear decrease of conductivity from the maximum at 50% charge to almost zero at 100% charge. This result is a completely new and unexpected relationship between conduction and doping charge.

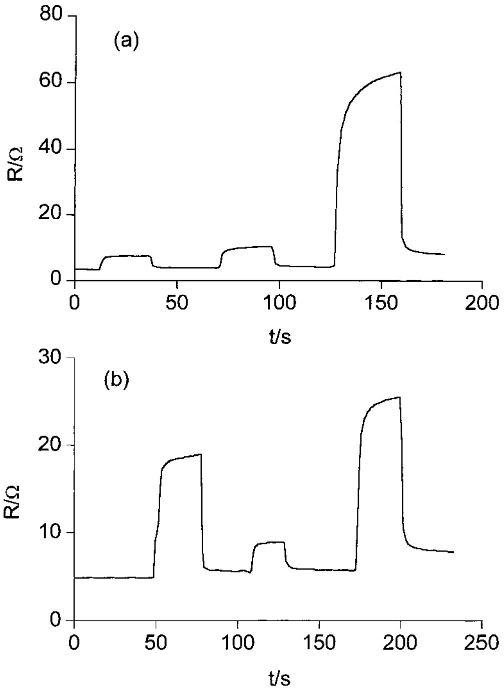

Figure 12. Resistance response of PDMP (a) tosylate and (b) perchlorate at (sequentially) acetonitrile-, ethanol-, and chloroform-saturated air.

PDMP as Vapor Sensor. The impressive reversible drop of conductivity observed for PDMP in acetonitrile was used for the construction of vapor-sensing devices. To this end we investigated the response of the polymer-coated conductivity device to vapors of different solvents ranging from water to hexane. Both the as-prepared tosylate and the ion-exchanged perchlorate polymers were tested. The changes of conductivity are given in Table 3 and illustrated in Figure 12. A typical time-resolved response is shown in Figure 13. The device has a time response of ca. 20−30 s.

It is observed that the highest increases in resistance are measured for acetonitrile and chloroform. In fact, these molecules solvate the polymer to the same level (2 molecules per pyrrole ring) as indicated by the EQCM changes. As a result the polymer chain separation is increased, and since the chloroform molecule is bigger, the charge hopping distance and consequently also the resistance increase. Polar solvents such as water and apolar solvents such as hexane or toluene, which do not swell the polymer, are not effective.

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(46) Focke, W. W.; Wnek, G. E. *J. Electroanal. Chem.* **1988**, *256*, 343.

(47) Chance, R. R.; Bredas, J. L.; Silbey, R. *Phys. Rev. B* **1984**, *29*, 4491.

(48) Zotti, G. *Synth. Met.* **1998**, *97/3*, 267.

(49) Waller, A. M.; Compton, R. G. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 977.

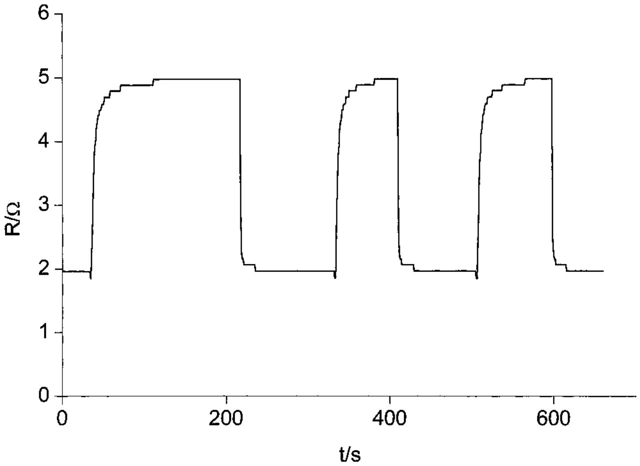

Figure 13. Resistance response of PDMP tosylate at acetonitrile-saturated air. Deposition charge 50 mC.

Analogous tests with the other polymers reported here did not show significant resistance changes in any of the solvents tested with PDMP.

Previous studies of this type have evidenced the (reversible) water[50] and (irreversible) alcohol[51] dependence of conductivity within PANI. In the latter cases the vapor causes an increase of conductivity of several orders of magnitude, which was attributed to solvent-induced solid-state ionic conductivity and structural ordering (crystallization) of the polymer, respectively. Recently a polypyrrole dodecyl sulfate conductivity sensor was reported, showing an increase of resistance of ca. 30% for methanol.[52]

Conclusions

The present in-situ conductivity vs doping charge studies on β-alkoxy-capped polythiophene and polypyrrole derivatives, coupled with in situ magnetic (ESR) and mass (EQCM) techniques, have allowed us to clarify roles and mechanisms of conduction within polyconjugated polymers. In particular, it was shown that dimerization of radical cations (polarons), which subtracts possible charge carriers, can also occur in polypyrroles and that in polypyrrole spinless carriers may be localized dications (bipolarons) operating according to a mixed-valence conduction mechanism. Different carriers (free polarons, dimerized polarons, free bipolarons, pinned bipolarons, and free electrons) and mechanisms (electron hopping or mixed-valence electron exchange) may be operating in the same polyconjugated polymer depending on the counteranion nucleophilicity and the substitution pattern.

The combination of redox-type conduction and solvation in poly(3,4-dimethoxypyrrole) gives this material unusual solvoconductive properties. The latter have been used to develop an organic solvent vapor sensor particularly responsive for chloroform and acetonitrile.

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(50) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 6627.

(51) Svetlicic, V.; Schmidt, A. J.; Miller, L. L. *Chem. Mater.* **1998**, *10*, 3305.

(52) Dobay, R.; Harsanyi, G.; Visy, C. *Electroanalysis* **1999**, *11*, 804.