

# Potential-Driven Conductivity of Polypyrroles, Poly-*N*-Alkylpyrroles, and Polythiophenes: Role of the Pyrrole NH Moiety in the Doping-Charge Dependence of Conductivity

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The in situ conductivity vs p-doping charge of low-defect polypyrroles, *N*-substituted polypyrroles, and polythiophenes has been investigated in acetonitrile in the presence of the weakly coordinating perchlorate ion as supporting electrolyte. In-situ ESR and EQCM measurements have given supporting information on polymer structure and conduction carriers. The structures of the polymers cover a wide range of conjugative, geometrical, and solvation conditions, but the conductive pattern follows simply the polymer ring type (pyrrole, *N*-substituted pyrrole, or thiophene). In polythiophenes an initial region of low conductivity, due to strongly spin-dimerized polarons, is followed by an increase of conduction to a plateau of high conductivity. *N*-substituted polypyrroles display a linear increase of conductivity with charge followed by a plateau of conductivity. Polypyrroles without *N*-substitution show an increase of conductivity to a maximum followed by a symmetrical decrease to zero at a charge corresponding to one bipolaron per tetrapyrrole unit. A redox-type bipolaron model of conduction, based on stabilization of the bipolaron positive charge by H-bonding with the counteranion, is suggested. The parent polypyrrole shows the uncomplicated conductivity pattern (increase of conductivity to a plateau) due to a uniquely strong stabilization of the  $\pi$ -stacked polymer chains.

## 1. Introduction

The doping-charge dependence of conductivity in conjugated polymers has received scarce attention since it was shown that in polypyrrole (as the perchlorate<sup>1</sup> or tetrafluoroborate<sup>2</sup> salt) the conductivity increases linearly with charge and then attains a plateau. On the other hand the conductivity in polyacetylene also, after a slight increase at the early levels of doping (ca 1%), increases almost linearly with doping and then saturates at a level of ca. 10% doping.<sup>3</sup> The independence of

conductivity from charge at the higher levels of doping was predicted for free charges hopping within a narrow potential range with constant density of states.<sup>4</sup>

This simple picture has proven to be oversimplified. In fact, conjugated polymers are quite different from typical inorganic semiconductors. The organic molecules which constitute these materials are oxidized to radical cations or dications and the former may interact magnetically to form dimers; moreover, anions are incorporated and interact with various strength with the positive charges of the polymer chain; and, finally, solvent molecules may be involved. All these factors seriously affect the conductive properties. Thus, it was no surprise that later investigations<sup>5,6</sup> have shown that

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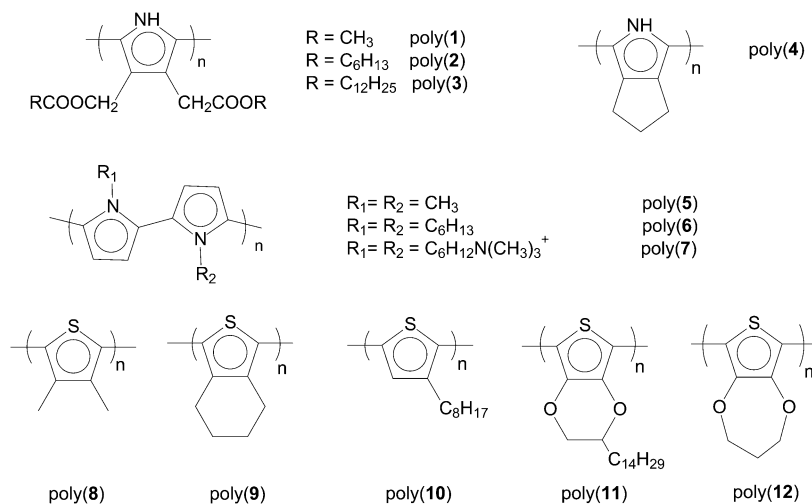
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Chart 1



polythiophenes, at least those investigated, are scarcely conducting at the first stages of doping and that in some instances polypyrrole displays a decrease in conductivity with charge after attaining a maximum.

We intend to make a more extended and possibly general survey covering different electronic (conjugative), geometric (steric), and solvation situations of these polymers. Of most importance in these studies is the use of polymers with a reasonable level of regularity (low defect content). In electrochemical samples, which are extremely practical for this kind of investigation as they are directly produced on the electrode for conductivity measurements, defects are generated during polymerization. These arise from the occurrence of undesired  $\alpha,\beta$  and  $\beta,\beta$  couplings<sup>7</sup> and from the overoxidative introduction (at the  $\beta$  positions) of carbonyl and hydroxyl moieties in the polymer chain,<sup>8–11</sup> with dramatic changes of the conductive properties of the polymer.

To prevent this problem 3,4-disubstituted polypyrroles<sup>7,12–19</sup> and polythiophenes<sup>20–22</sup> have been prepared

over the past years. These polymers also allow the investigation of conductivity with a more positive potential limit. We previously reported on poly(3,4-dialkoxythiophene)s and poly(3,4-dialkoxythiophene)s<sup>6</sup> in which the electron-rich substituent does not cause twisting along the polyconjugated chain. Here we extend the investigation to include the cases in which twisting of the polypyrrole chain is forced by alkyl moieties and/or the electron density is decreased. To this end we selected some poly(3,4-bis(alkoxycarbonylalkyl)pyrrole)s, poly(cyclopenta[c]pyrrole), poly(3,4-dimethylthiophene), and poly(cyclohexa[c]thiophene) (see Chart 1). Moreover, to confirm the previous observations made in poly(3,4-dialkoxythiophene)s<sup>6</sup> we considered also a more extended selection of polythiophenes of that type, including poly(tetradecyl-3,4-ethylenedioxythiophene) and poly(3,4-propylenedioxythiophene). Finally, regio-regular head-to-tail coupled poly(3-octylthiophene), in which absence of defects is guaranteed by the synthetic procedure, has been included as a good example of 3-substituted polythiophene with high conjugation (see Chart 1).

Reasonably defect-free materials may also be obtained from oligomers, which are oxidized at less positive potentials than the corresponding monomers. In fact, variously *N*-substituted 2,2'-bipyrroles have recently been coupled anodically to low-defect polymers.<sup>23</sup> We included some of these polymers (see Chart 1) in the present investigation to assess the role of *N*-substitution in the conductivity of polypyrroles.

This paper reports the synthesis and characterization (when not previously published) of these polymers, their electrochemical quartz crystal microbalance analysis (to establish the electron stoichiometry of the doping process and the relevant solvation changes), and in-situ ESR spectroscopy (to identify spin-bearing and spinless possible conductivity carriers). A detailed in-situ conductivity investigation of these polymers as a function of the doping charge constitutes the main part of the work. The investigations were performed in acetonitrile using a nonnucleophilic ("innocent") anion (perchlorate) to minimize anion effects on the conductivity. Finally,

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**Table 1. Monomer Oxidation Peak Potentials ( $E_p^m$ ); Polymer Oxidative Redox Potentials ( $E_p^o$ ), Half-Height CV Width ( $W$ ), Maximum Spin Concentration ( $s$ ), Maximum Doping Level at 0.8 V (dl), Maximum Conductivity ( $\sigma$ ), and Maximum UV-Vis Absorption Wavelength ( $\lambda_{\max}$ )**

| monomer     | $E_p^m/V$ | $E_p^o/V^a$ | $W/mV$ | $s/\text{spins ring}^{-1}$ | $dl/e \text{ ring}^{-1}$ | $\sigma/S \text{ cm}^{-1}$ | $\lambda_{\max}/nm$ |
|-------------|-----------|-------------|--------|----------------------------|--------------------------|----------------------------|---------------------|
| NH-pyrroles |           |             |        |                            |                          |                            |                     |
| <b>1</b>    | 0.88      | 0.16        | 160    | 0.12                       | 0.5                      | 0.002                      | 355                 |
| <b>2</b>    | 0.85      | 0.12        | 120    | 0.06                       | 0.5                      | 0.0003                     | 355                 |
| <b>3</b>    | 0.80      | 0.21        | 90     | 0.03                       | 0.5                      | 0.001                      | 355                 |
| <b>4</b>    | 0.66      | -0.60       |        | 0.01                       | 0.5                      | 3                          | 415                 |
| NR-pyrroles |           |             |        |                            |                          |                            |                     |
| <b>5</b>    | 0.30      | 0.00        | 280    | 0.10                       | 0.5                      | 0.3                        | 310                 |
| <b>6</b>    | 0.35      | 0.25        | 100    | 0.02                       | 0.5                      | 0.02                       | 310                 |
| <b>7</b>    | 0.42      | 0.13        | 100    | 0.02                       | 0.5                      | 0.005                      | 310                 |
| Thiophenes  |           |             |        |                            |                          |                            |                     |
| <b>8</b>    | 1.40      | 0.70        |        | 0.015                      | 0.3                      | 1                          | 330                 |
| <b>9</b>    | 1.30      | 0.35        |        | 0.008                      | 0.4                      | 90                         | 400                 |
| <b>10</b>   |           | 0.18; 0.52  |        | 0.004                      | 0.26                     | 80                         | 555                 |
| <b>11</b>   | 0.97      | -0.35       |        | 0.020                      | 0.6                      | 800                        | 650                 |
| <b>12</b>   | 1.09      | -0.3        |        | 0.020                      | 0.6                      | 300                        | 565                 |

the results are compared with previously published data and discussed.

## 2. Experimental Section

**2.1. Chemicals and Reagents.** Acetonitrile was reagent grade (Uvasol, Merck) with a water content of <0.01%. The supporting electrolyte tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) was previously dried under vacuum at 70 °C.

The monomers 3,4-bis[(methoxycarbonyl)methyl]pyrrole (**1**), 3,4-bis[(hexyloxycarbonyl)methyl]pyrrole (**2**) and 3,4-bis[(dodecyloxycarbonyl)methyl]pyrrole (**3**) were prepared according to the literature.<sup>24</sup> Preparation methods of the monomers cyclopenta[c]pyrrole (**4**),<sup>17</sup> 1,1'-dimethyl-1*H*,1'*H*-[2,2']bipyrrole (**5**),<sup>25</sup> 1,1'-dihexyl-1*H*,1'*H*-[2,2']bipyrrole (**6**),<sup>25</sup> {6-[1'-(6-trimethylammonium-hexyl)-1'*H*-[2,2']bipyrrol-1-yl]-hexyl}-trimethylammonium ditetrafluoroborate (**7**),<sup>23</sup> 3,4-dimethylthiophene (**8**),<sup>21</sup> cyclohexa[c]thiophene (**9**),<sup>20</sup> 2-tetradecyl-2,3-dihydro-thieno[3,4-*b*][1,4]dioxine (tetradecyl-3,4-ethylenedioxythiophene, **11**),<sup>26</sup> and 3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (3,4-propylene-dioxythiophene, **12**)<sup>26</sup> were also as previously reported.

Regioregular head-to-tail coupled poly(3-octylthiophene) (poly(**10**)) has been produced chemically according to McCullough.<sup>27</sup>

**2.2. Deposition of the Polymer Films.** With the exception of poly(**10**) films, which were cast from 1%  $\text{CHCl}_3$  solution, the polymer films were electrodeposited by potentiostatic oxidation of the relevant monomers in acetonitrile with 0.1 M  $\text{Bu}_4\text{NClO}_4$ . The cyclic voltammogram CV of the monomers shows the oxidation process at peak potentials given in Table 1. Electrodeposition was performed by potentiostatic oxidation at the foot of the oxidation process in concentrated solutions (typically  $10^{-1}$  M) for **4**, **8**, and **9**, but even from relatively diluted solutions ( $10^{-2}$  M) for **1**–**3**, **5**–**7**, **11**, and **12**. Water (1%) favors deposition for pyrroles **1**, **4**–**6**, and **7**, whereas its presence is adverse in the case of **2** and **3**. Table 1 reports the redox potentials of the polymers as average of the CV forward and backward peak potentials.

**2.3. Apparatus and Procedure.** Experiments were performed at room temperature under nitrogen in three electrode cells. 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 coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry was a platinum minidisc electrode ( $0.003 \text{ cm}^2$ ). For electronic spectroscopy, a  $0.8 \times 2.5 \text{ cm}$  indium–tin-oxide (ITO) sheet (ca 20 ohm/square resistance, from Balzers, Liechtenstein) was used.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer.

Electrochemical quartz crystal microbalance (EQCM) analyses were performed with a platinum-coated AT-cut quartz electrode ( $0.2 \text{ cm}^2$ ), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade and the frequency counter was Agilent model 53131A. Data were collected by a microcomputer with homemade analyzing software. The dry mass and charge measurements were performed according to the procedure previously published.<sup>6</sup>

ESR spectra were taken on a Bruker ER 100D following the procedure previously described.<sup>28</sup> Absolute spin calibration was performed with  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  crystals, and  $g$ -value calibration was done with thin films of DPPH ( $g = 2.0036$ ).<sup>29</sup>

The apparatus and procedures used for the in-situ conductivity experiments were previously described in detail.<sup>30,31</sup> The electrode for conductivity measurements was typically a two-band platinum electrode ( $0.3 \text{ cm} \times 0.01 \text{ cm}$  for each band) with interband spacing of 20  $\mu\text{m}$ . In case of conductivities lower than  $10^{-2} \text{ S cm}^{-1}$ , the electrode was a microband array platinum electrode (5  $\mu\text{m}$  bandwidth, 100 nm thick) with interband spacing of 5  $\mu\text{m}$ . The deposit was thick enough to ensure minimum resistance, under which condition the conductivity  $\sigma$  is given by  $\sigma = k/(R - R_0)$ , where  $R$  is the measured resistance,  $R_0$  is the lead resistance, and  $k$  is the cell constant. Though the conductivity device is a 2-probe one, contact effects are minor as proven by the identical results obtained with a more complex 4-probe device.

## 3. Results and Discussion

**3.1. Characterization of Polymers.** Although the synthesis of polymers prepared from 3,4-bis[(alkyloxy-carbonyl)methyl]pyrrole)s poly(**1**) – poly(**3**) was previously reported,<sup>32</sup> their characterization will be reported here below for the first time.

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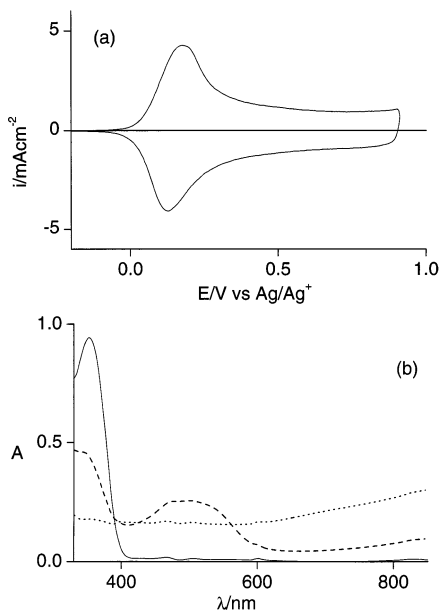
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**Figure 1.** (a) Cyclic voltammogram of poly(1) in acetonitrile with 0.1 M  $\text{Bu}_4\text{NClO}_4$ ; scan rate,  $0.1 \text{ V s}^{-1}$ ; reversible oxidation charge,  $14 \text{ mC cm}^{-2}$ . (b) Spectroelectrochemistry of poly(3) in acetonitrile with 0.1 M  $\text{Bu}_4\text{NClO}_4$ : (—)  $-0.2$ , (---)  $0.2$ , and (···)  $0.8 \text{ V}$ .

The characteristics of the other polypyrroles and polythiophenes produced for this investigation were in agreement with those previously reported. Particular comments are deserved to poly(4) and poly(10).

The poly(4) films are reversibly oxidized at  $E^\circ = -0.60 \text{ V}$ , i.e., at a potential much lower than that reported in the literature ( $-0.12 \text{ V}$ ).<sup>17</sup> The UV-vis spectrum of the undoped polymer shows a maximum at  $415 \text{ nm}$ , i.e., at a lower energy than previously reported ( $390 \text{ nm}$ ).<sup>18</sup> Both these results indicate the production of polymer films with enhanced conjugation.

The CV of poly(10) films in acetonitrile with  $0.1 \text{ M Bu}_4\text{NClO}_4$  shows a twin reversible oxidation process at  $E^\circ = 0.18$  and  $0.52 \text{ V}$ , compatible with that reported in the literature.<sup>33</sup> CV responses of this type, but at higher potentials (ca.  $0.6 \text{ V}$ ) and unresolved, were previously reported for electrochemically prepared samples<sup>34</sup> for which it is easy to argue a defective texture.

**3.1.1 Poly(3,4-bis[(alkyloxycarbonyl)methyl]pyrrole)s.** The polymer films show a clean reversible oxidation process (Figure 1a) at  $E^\circ = \text{ca. } 0.15 \text{ V}$  which is positive enough to make their undoped form stable in the air. The redox potential  $E^\circ$  shifts positively from **2** to **3**, as expected for an increase of the size and as previously observed for a series of alkyl substituted polythiophenes.<sup>35</sup> In contrast,  $E^\circ$  shifts negatively from **1** to **2**, which is accounted for by the change of the polymer chain from a naked to an alkyl-coated polyester rod. As it will be shown later the former is strongly solvated and loses solvent upon oxidation, whereas the latter increases its solvation when oxidized. These contrasting solvent

effects are reflected in the different redox potentials of the polymers.

The CV response is stable up to ca.  $0.9 \text{ V}$ . The voltammogram is  $x$ -axis symmetrical (at  $0.1 \text{ V s}^{-1}$ ) for thin films (reversible charge  $Q_r = 3\text{--}10 \text{ mC cm}^{-2}$ ) of poly(1) and poly(2). Thinner films ( $Q_r \leq 1 \text{ mC cm}^{-2}$ ) are required for poly(3) in which the longer alkyl chain introduces into the CV some hysteresis for higher thicknesses. The CV width at half-height  $W$ , measured at the reduction side of the potential scale as  $2(E_p - E_{p/2})$ , decreases progressively from poly(1) to poly(3) (see Table 1). Also poly(dipyrrole)s poly(5)–poly(7) display a CV response  $x$ -axis symmetrical with  $W$  higher for poly(5) than for poly(6) and poly(7) (see Table 1).

The UV-vis spectrum of the undoped polymers (Figure 1b) shows a maximum at  $355 \text{ nm}$ , i.e., intermediate between that of polypyrrole ( $420 \text{ nm}$ )<sup>36</sup> and poly *N*-methylpyrrole ( $310 \text{ nm}$ ),<sup>37</sup> which reflects the partial decoplanarization of the pyrrole rings operated by the methylene substitution of the  $\beta$ -positions. Oxidation gives a blue-green color to the film. Spectroelectrochemistry shows an intermediate band at  $500 \text{ nm}$  which attains its maximum absorption at 50% oxidation (Figure 1b). This band has been assigned to polarons (radical cations).<sup>38</sup>

Poly(1) and poly(2) are insoluble in the common solvents whereas poly(3) is soluble in chloroform.

**3.2. EQCM Analysis.** **3.2.1. In-situ Mass and Charge.** During the oxidative cycle the mass of the polymers increases reversibly. For poly(4), poly(5), poly(8), poly(9), poly(11), and poly(12) the increase is linear with charge with a slope  $F\Delta m/Q = \text{ca. } 100 \text{ g mol}^{-1}$ , corresponding to the simple uptake of the perchlorate anion. A lower value ( $65 \text{ g mol}^{-1}$ ) was found previously for poly(7) which indicates a decrease of solvation of approximately one solvent molecule.<sup>23</sup> The mass of poly(10) also increases linearly with charge but the slope ( $F\Delta m/Q = \text{ca. } 200 \text{ g mol}^{-1}$ ) corresponds to the uptake of the perchlorate anion plus 2–3 extra solvent molecules. It appears that the alkyl chain favors solvation of the oxidized polymer. Poly(6) with its hexyl chains displays an even higher slope ( $300 \text{ g mol}^{-1}$ ) corresponding to the uptake of 5 extra solvent molecules.<sup>23</sup>

A complex behavior is displayed by the poly(3,4-bis[(alkyloxycarbonyl)methyl]pyrrole)s. Quite different mass changes upon oxidation (at  $0.8 \text{ V}$ ) are observed depending on the substitution pattern. The mass decreases heavily (by ca. 60%) for poly(1) and increases similarly (by ca. 70%) for poly(2) whereas it increases only moderately (by ca. 15%) for poly(3). Taking into account the reversible uptake of one perchlorate anion per two pyrrole rings (see below), the mass changes during oxidation correspond to acetonitrile loss for poly(1) and acquisition for poly(2) of ca. 4–5 molecules per pyrrole ring, whereas less than one molecule is lost by poly(3). The undoped polymers are in fact differently swollen by the solvent as shown by EQCM in the dry state and in acetonitrile. Whereas undoped poly(2) and poly(3) are in practice not solvated, poly(1) is heavily swollen by

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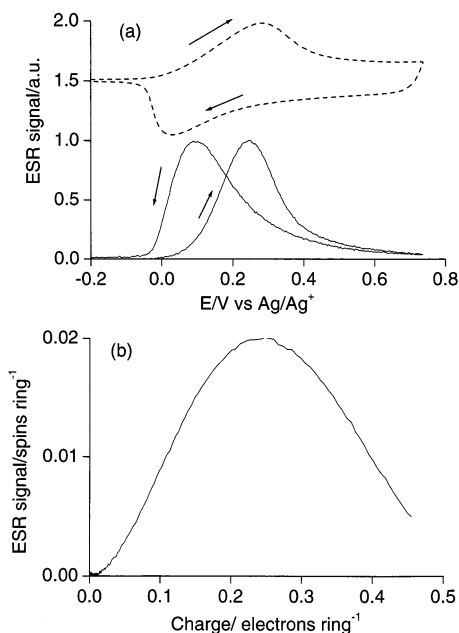
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**Figure 2.** In situ ESR vs (a) potential and (b) charge of poly(2) in acetonitrile with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.

acetonitrile due to the polar characteristics of the substituents, attaining a degree of solvation of 6–8 acetonitrile molecules per pyrrole ring.

**3.2.2. Dry Mass and Charge.** Through correlation between the EQCM mass of the undoped polymer and the total reversible charge involved in the redox process, the stoichiometry of the oxidation could be provided for all the investigated polymers.

For all the polypyrroles it was found that 0.5 electrons per ring are exchanged at 0.8 V.

In polythiophenes the values are different depending on the substituent. Thus 0.3 and 0.4 electrons per ring are exchanged at 0.8 V by poly(8) and poly(9), respectively. For poly(10) the doping level is somewhat lower (0.26 electrons per ring).

Both poly(11) and poly(12) exchange 0.6 electrons per thiophene unit at 1.0 V. This value, which corresponds to that previously obtained for poly(3,4-ethylenedioxythiophene) PEDT,<sup>6</sup> is much higher than that shown by the other polythiophenes (0.3–0.4 electrons per ring) because of the electron donor properties of the alkoxy-substituents.

The maximum doping charges are summarized in Table 1.

**3.3. In situ ESR.** Oxidation of the polymer films produces an ESR signal, which after an initial increase with charge attains a maximum at the oxidation peak potential and then decreases to zero with further oxidation (see, e.g., Figure 2). The process is fully reversible.

The *g* value of the signal is 2.0029 for polypyrroles (as for polypyrrole<sup>39</sup>), 2.0025 for poly(10) (as for polythiophene<sup>40</sup>), and 2.0035 for poly(11) and poly(12) (as for PEDT<sup>6</sup>). For poly(8) and poly(9) the *g* value is 2.0029. The signal width is  $(1-2) \times 10^{-4}$  T, with the exception of poly(8) and poly(9) for which it is ca.  $7 \times 10^{-4}$  T.

**3.3.1. Poly(pyrrole)s.** For polypyrroles poly(1)–poly(7) except poly(4) the plot of ESR signal vs doping charge (as electrons per pyrrole ring, Figure 2) shows that spins attain the maximum concentration at a doping charge of 0.25 electrons ring<sup>-1</sup> (1 electron per 4 pyrrole rings) and tend to disappear at 0.5 electrons ring<sup>-1</sup>.

The maximum spin concentration (see Table 1) decreases progressively from poly(1) to poly(3) and from poly(5) to poly(6). The value for poly(1) is comparable with that measured for polypyrrole (1 unpaired electron per 10 pyrrole rings<sup>41</sup>) and indicates a relatively high concentration of free polarons. The maximum spin concentration is in principle controlled by either spin pairing in  $\pi$ -dimers or destabilization of the polaron vs the neutral-bipolaron state. The former is commonly known in oligothiophenes<sup>42</sup> and has recently also been found for some oligopyrroles<sup>43</sup> but is hindered by steric factors<sup>44</sup> and therefore appears to be ruled out in our case by the scarce allowed overlapping of the twisted and substituent-shielded polypyrrole chains. In contrast, the observed decrease of spin concentration as the alkyl chain length is increased suggests a progressive destabilization of the polaron state favoring the neutral-bipolaron state. This indication is confirmed by the trend of the CV width values *W* given in Table 1. *W* is in fact the potential separation between the two subsequent one-electron steps producing the polaron and the bipolaron states and measures the stability of the polaron state. The correspondence of *W* with the spin concentration gives strong support to the proposed hypothesis.

In poly(4) the maximum spin concentration is the lowest and is recorded at a minimum value of charge (ca 0.07 electrons ring<sup>-1</sup>), which appears to indicate a minimum stability of the polaron form in this polymer.

**3.3.2. Poly(thiophenes).** The maximum spin concentration, reported in Table 1, is 0.004–0.02 unpaired electrons per thiophene ring (one electron per 50–250 rings) and indicates a concentration of free polarons significantly lower than that for polypyrroles. The maximum spin concentration is in practice controlled by the spin pairing in  $\pi$ -dimers commonly known in oligothiophenes.<sup>42</sup>

Plotting the ESR signal intensity vs doping charge shows that the maximum spin concentration occurs at a low value of charge. In the PEDT-type polymers poly(11) and poly(12) the charge of maximum spin concentration is 0.06 electrons ring<sup>-1</sup>. For the alkyl substituted polythiophenes the maximum is attained at doping charges increasing from 0.04 for poly(10), to 0.10 for poly(9), and 0.15 electrons ring<sup>-1</sup> for poly(8). This trend follows the optical and electrochemical trend of conjugation degree ( $\lambda_{\max}$  and *E*<sup>o</sup> values in Table 1) which decreases in the same order. The reported progressive

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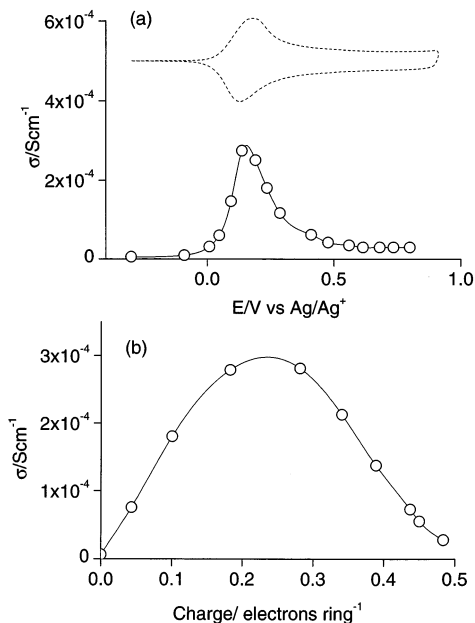
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**Figure 3.** In situ conductivity vs (a) potential and (b) charge of poly(2) in acetonitrile with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.

increase of  $\pi$ -dimerization with the oligothiophene chain length<sup>45</sup> appears to be accounted for by a favorable effect of the degree of conjugation on such  $\pi$ -interaction.

**3.4. In situ Conductivity.** As will soon appear, the conductive behavior of the polymers with the applied charge depends essentially on the type of aromatic ring. The maximum conductivities are given in Table 1.

**3.4.1. Poly(1)–Poly(4).** In situ conductivity measurements of these polypyrroles show that oxidation causes the progressive transition from a low-conductivity to a conductive state. Then the polymer passes to a second low-conductivity state (fully oxidized) via a maximum located at the redox potential (Figure 3a).

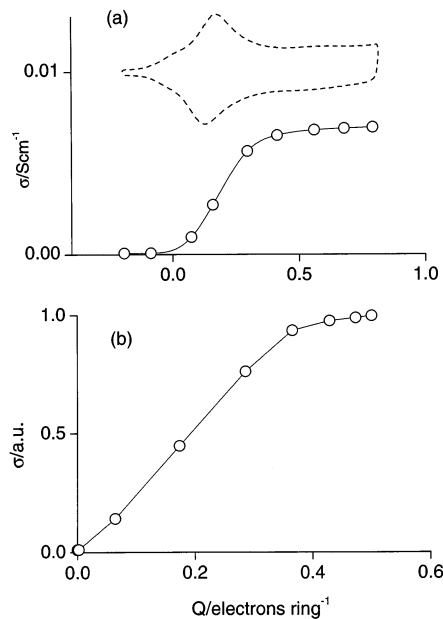
In poly(1)–poly(3) the maximum conductivity is low (ca  $10^{-3}$  S cm<sup>-1</sup>) which is attributable to decoplanarization of the pyrrole rings. In the case of poly(4) the maximum conductivity is 3 S cm<sup>-1</sup>, i.e., higher than that reported in the literature (0.1 S cm<sup>-1</sup><sup>17</sup>) though it must be recalled that the latter was measured ex situ.

The relationship between conductivity and reversible charge (the latter given as electrons per ring) is shown in Figure 3b. The parabolic shape is reminiscent of that of redox conductivity.<sup>46</sup> It can be observed that the conductivity maximum occurs at 0.25 electrons per pyrrole unit and approaches zero at 0.5 electrons per pyrrole unit.

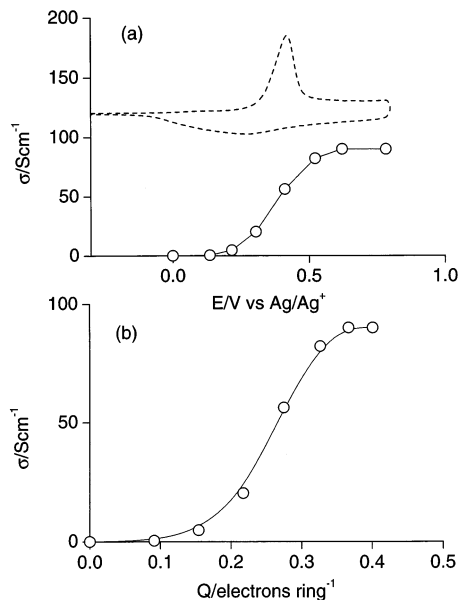
The conductive behavior of these polymers is different from that of poly(3,4-dialkoxypyrrole)s<sup>6</sup> in which a low-conductive initial range of oxidation charge is observed. Moreover, they are oxidized to bipolarons (dications) involving four pyrrole rings, i.e., the oxidation levels are half of those found in poly(3,4-dialkoxypyrrole)s.<sup>6</sup>

The conductive behavior of these polymers is also different from that of polypyrrole perchlorate which is conducting through an extended potential plateau.<sup>1</sup>

**3.4.2. Poly(5)–poly(7).** In situ conductivity in these *N*-substituted polypyrroles upon oxidation shows, after



**Figure 4.** In situ conductivity vs (a) potential and (b) charge of poly(7) in acetonitrile with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.



**Figure 5.** In situ conductivity vs (a) potential and (b) charge of poly(9) in acetonitrile plus 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.

the transition from a low-conductivity to a conductive state, a plateau of conductivity (Figure 4a). The relationship between conductivity and reversible charge shown in Figure 4b is simply linear at the initial stage, attaining the plateau at ca. 0.4 electrons per ring.

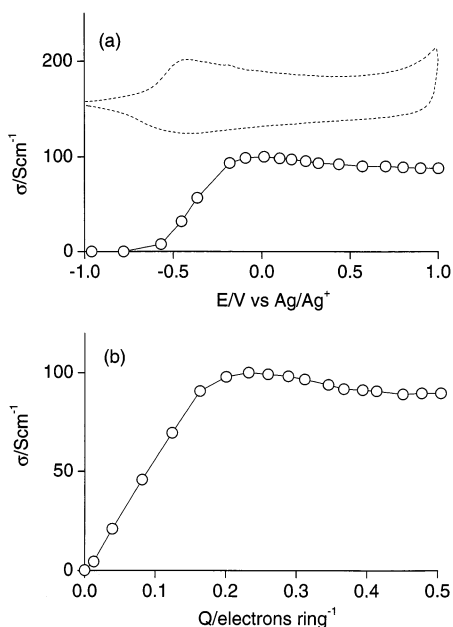
**3.4.3. Poly(8)–poly(12).** In relationship with the redox charge the in situ conductivity of these polythiophenes (and of the polythiophenes previously investigated<sup>5,6</sup>) show a three-segment plot, with an initial range (ca 20%) of charge in which the conductivity stays at low values and a final extended plateau of high conductivity.

Poly(9) (Figure 5) is nonconductive up to ca. 0.15 electrons ring<sup>-1</sup>. The maximum (plateau) conductivity is 90 S cm<sup>-1</sup>, which is particularly high compared with that ex situ for PF<sub>6</sub><sup>-</sup>-doped samples of the same polymer (8 S cm<sup>-1</sup><sup>20</sup>).

In poly(10) the nonconductive region extends up to ca. 0.1 electrons ring<sup>-1</sup>. The maximum conductivity is

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**Figure 6.** In situ conductivity vs (a) potential and (b) charge of polypyrrole in acetonitrile with 0.1 M  $\text{Bu}_4\text{NClO}_4$ .

$80 \text{ S cm}^{-1}$ , i.e., comparable with that reported in the literature for electrochemically doped samples.<sup>34</sup>

Poly(**8**) gives a maximum conductivity of  $1 \text{ S cm}^{-1}$ , in good agreement with the literature,<sup>21</sup> after a plateau of nonconductivity extending up to ca. 0.05 electrons per ring. The shape of the relationship with charge could not be measured beyond 0.8 V because of the start of oxidative degradation.

For poly(**11**) and poly(**12**), like PEDT,<sup>6</sup> the initial noneffective charge corresponds to 0.15 electrons  $\text{ring}^{-1}$ . The plateau conductivities ( $300\text{--}800 \text{ S cm}^{-1}$ ) are the highest in the series as they are for PEDT-based polymers in general.<sup>47</sup>

**3.4.4. Polypyrrole.** The conductive behavior of polypyrrole as perchlorate salt has been reinvestigated to give a more clear picture of its behavior in the relationship of conductivity vs reversible charge. The in-situ conductivity, which could be measured up to 1.0 V, gives a linear increase up to ca. 40% of charge followed by an extended plateau of conductivity (Figure 6). Correlation of EQCM dry mass and reversible charge indicates that 0.5 electrons per pyrrole unit are exchanged at 1.0 V, which is the value common to all the polypyrroles here investigated.

### 3.5. Polymer Structure and Conduction Pattern.

The structures of the polymers studied here span a wide range of conjugative, geometrical, and solvation conditions.

We consider first the conjugative properties. In polythiophenes with good coplanarity of the rings such as cyclopenta[*c*]thiophene<sup>20</sup> and regioregular poly(3-alkylthiophene)s<sup>33,48</sup> the UV-vis absorption maximum occurs at 560 nm, which is in fair agreement with that (540 nm) extrapolated for ideal polythiophene.<sup>49</sup> In agreement with these data, an undoped regioregular poly-

(**10**) film on ITO shows a maximum at 555 nm, with additional shoulders at 525 and 610 nm<sup>33</sup> i.e., vibronic features characteristic for a regular backbone structure.<sup>48,50</sup> Undoped poly(**9**) shows a maximum at 400 nm,<sup>20</sup> a shorter wavelength which reflects the decoplanarization of the thiophene rings operated by the substitution at the  $\beta$ -positions. Finally in poly(3,4-dialkylthiophene)s such as poly(**8**), where a more severe twisting is operating, the maximum occurs at 330 nm.<sup>51</sup>

Similar considerations may be expressed for the conjugative variations in polypyrroles. The UV-vis spectrum of the undoped poly(**4**) shows a maximum at 415 nm which is in fact the same of polypyrrole (420 nm)<sup>36</sup> so that it indicates a good coplanarity of the pyrrole rings. At the opposite the *N*-substituted polypyrroles display their maximum at 310 nm,<sup>37</sup> due to the strong steric interaction of *N*-substituted pyrrole with its adjacent rings. Poly(**1**)–poly(**3**) show their maximum at 355 nm, i.e., intermediate between that of polypyrrole and of *N*-substituted polypyrroles, which reflects the intermediate degree of decoplanarization operated by the methylene substitution of the  $\beta$ -positions.

Also, the electron availabilities of the polymers span a wide range of values, as indicated by the redox values ranging from  $-0.35$  to  $0.7 \text{ V}$  for the polythiophenes and from  $-0.60$  to  $0.25 \text{ V}$  for the polypyrroles (Table 1).

Finally, the solvation properties are quite different such as, e.g., among poly(**1**)–poly(**3**), and doping may cause large differences in solvation, e.g., from null in poly(**5**) to a strong ingress of solvent in poly(**6**).

Despite these quite various and significant differences within the three polymer series (polythiophenes, *N*-substituted polypyrroles, and  $\beta$ -substituted polypyrroles), the conductivity behavior within a series is the same. Differences in conductive behavior are instead among the series, i.e., the pattern depends on whether the aromatic ring is a thiophene, a *N*-substituted pyrrole, or a  $\beta$ -substituted pyrrole. The difference in conductive behavior among representative members such as poly(**10**), poly(**7**), and poly(**3**) is nicely illustrated in Figure 7.

The conduction mechanisms which will be proposed are illustrated in Scheme 1, in which N, P, BP, and DP indicate neutral, polaron, bipolaron, and dimerized-polaron states, respectively, and the square frames evidence the conductivity carriers for each series.

The relationship between conductivity and charge for all polythiophenes evidences an initial region of low conductivity. Oxidation produces polarons which both on theoretical<sup>52,53</sup> and experimental grounds<sup>54,55</sup> are confined in a hexameric segment. They are strongly spin-dimerized and according to this sort of Peierls distortion the materials continues to be low-conducting.

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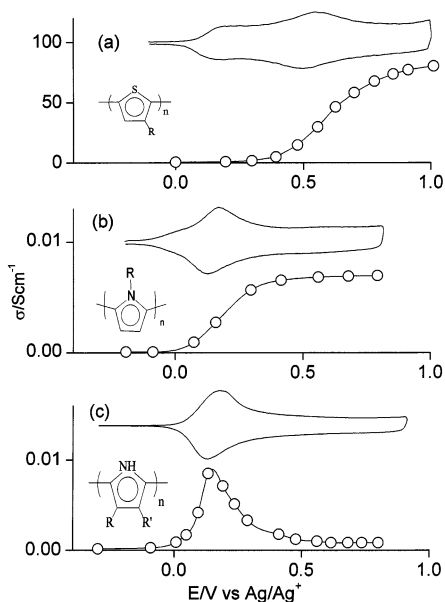
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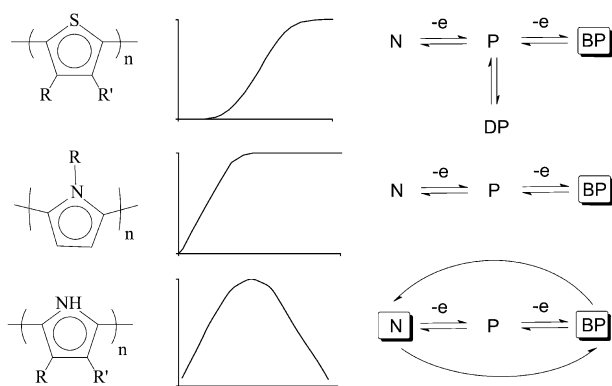
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**Figure 7.** In situ conductivity vs potential of (a) poly(**10**), (b) poly(**7**), and (c) poly(**3**) in acetonitrile with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.

**Scheme 1**



This region is then followed by a range of almost linear increase of conduction till, at higher charges, a substantial independence from further charge is shown. At this doping level a lattice of strongly  $\pi$ -interacting chains, providing electron-filled states able for conduction, is obtained. The observed conductive behavior is that expected for free charges hopping within a narrow potential range with constant density of states ("metallic" conduction).<sup>4</sup>

*N*-substituted polypyrroles (NR-polypyrroles) behave differently as the linear increase of conduction starts immediately, in agreement with the absence of  $\pi$ -dimerization in these materials. At higher charges a plateau-type of "metallic" conduction is shown like that in polythiophenes.

Polypyrroles without *N*-substitution (NH-polypyrroles) show at the beginning of charging a linear increase with charge like NR-polypyrroles do, but after attaining a maximum the conductivity decreases pointing to zero at 0.5 electrons per ring (one bipolaron per tetrapyrrole unit). This final part of the conductive pattern was previously observed only in poly(3,4-dialkoxypyrrole)s<sup>6</sup> with the bipolaron charge corresponding to a shorter (bipyrrole) subunit, as a consequence

of the much higher charge density on these polymers.

The role of the proton at the nitrogen atom appears therefore to be crucial for conduction. Its absence in NR-polypyrroles makes them similar to polythiophenes at high levels of doping charge (see Scheme 1).

**3.6. Role of the Pyrrole NH Moiety in the Conduction Mechanism.** First we must stress that the correspondence of unpaired electron density (Figure 2b) and conductivity (Figure 3b) in NH-polypyrroles does not mean that polarons are the carriers since their concentration is low and, more importantly, such correlation is clearly not present in NR-polypyrroles. Thus, bipolarons are the carriers also in this case.

3D-hopping of bipolaron charges within the polymer chain and between adjacent polymer chains has been described as a concerted transfer of the twin bipolaron charge to a bipolaron-free polymer segment.<sup>3</sup> In this model both bipolaron-carrying and bipolaron-free segments are required for conduction, and this therefore results in a parabolic relationship of conductivity vs doping charge. The behavior we observed in NH-polypyrroles fits this model. Thus, we may assume a redox-type<sup>46</sup> bipolaron model of conduction (see Scheme 1).

Such a model requires a reason for bipolaron stabilization. We believe that the bipolaron positive charge is stabilized by NH-interaction (H-bonding) with the counteranion which thus pins the charge. Such an interaction may be so strong that deprotonation follows even with weakly nucleophilic anions, as shown by FTIR for tosylate with poly(3,4-dialkoxypyrrole)s.<sup>6</sup> In polyanilines deprotonation of the fully oxidized form is even the general rule.<sup>56</sup> For the cases considered here this NH-interaction is limited to the stabilization of the bipolaron by the scarcely nucleophilic perchlorate anion, which therefore proves not to be so "innocent" as expected.

The conductivity of polyconjugated polymers is limited in the potential range (for oxidation) by the depletion of the valence band.<sup>57,58</sup> In polypyrrole the theoretical value of the bandwidth is high (3.8 eV<sup>59</sup>). In fact, it appears that the band is strongly reduced in NH-polypyrroles to less than 1 eV by this sort of charge pinning.<sup>6</sup>

The simple picture of a linear increase of conductivity with charge, followed by a plateau of conductivity has been observed in NH-polypyrroles in the case of the parent polypyrrole and with perchlorate or tetrafluoroborate as counteranions only.<sup>1,2</sup> We have here confirmed this result for a wide potential and charge range. The reason of this seemingly singular behavior may be traced to a high stabilization of the  $\pi$ -stacked polymer chains, due to the absence of substituents of any type, which contrasts the charge pinning action of the counteranions favoring the "metallic" state versus the bipolaron lattice.

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#### 4. Conclusions

A series of low-defect polypyrroles, *N*-substituted polypyrroles, and polythiophenes have been produced as films on electrodes to investigate the relationship between conductivity and p-doping charge (level). The study has been performed in situ in acetonitrile containing the weakly coordinating perchlorate ion to limit counteranion interactions. Polymer structures have been elucidated and conduction carriers were identified with ancillary techniques such as in situ ESR and EQCM. Although the structures of the polymers cover a wide range of conjugative and geometrical situations, and solvation changes within a polymer series or upon p-doping are often severe, the doping level dependence of conductivity depends on only the polymer ring type (pyrrole, *N*-substituted pyrrole, or thiophene). *N*-substituted polypyrroles are those which follow the expected and uncomplicated linear increase of conductivity with charge followed by a plateau of conductivity. A first complication appears in polythiophenes where the plateau of high conductivity is preceded by an initial region

of low conductivity, which may be attributed to strongly spin-dimerized polarons in a sort of Peierls-type insulating behavior. The most impressive deviation from expectations comes from polypyrroles without *N*-substitution in which the conductivity goes to a maximum and then symmetrically tends to zero at a doping charge corresponding to one bipolaron per tetrapyrrole unit. It is suggested that the bipolaron positive charge is pinned by H-bonding to the counteranion. Conduction then operates via bipolaron hopping between neutral and bipolaron segments in a redox-type bipolaron model of conduction. The parent polypyrrole singularly shows the uncomplicated conductivity pattern (increase of conductivity to a plateau) which may be due to a strong stabilization of the  $\pi$ -stacked polymer chains allowed by the absence of substituents.

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