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Low-Defect Neutral, Cationic, and Anionic Conducting Polymers from Electrochemical Polymerization of *N*-Substituted Bipyrroles. Synthesis, Characterization, and EQCM Analysis

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Various 2,2′-bipyrroles *N*-substituted with alkyl, alkylsulfonate, or alkylammonium moieties have been anodically coupled to polymers. The polymers were characterized by cyclic voltammetry, UV−vis and FTIR spectroscopies, EQCM, and in situ conductivity. Coupling of dipyrroles instead of pyrroles minimizes the introduction of overoxidative defects into the polymer chain (from FTIR spectroscopy). The polymer of *N*-alkylammonium-*N*-hexyldipyrrole is soluble in acetonitrile. EQCM analysis of the oxidative doping process of the polymers in acetonitrile has shown that the alkyl- and alkylammonium-substituted polymers increase their mass with doping, whereas the mass decreases in the case of alkylsulfonate-substituted polymers provided with tetralkylammonium counterions. Electrochemical muscles built from the most representative polymers show marked deflections that follow the EQCM mass/charge changes.

Introduction

Conducting polymers undergo volumetric changes that can be exploited to perform work.[1,2] Polymer expansion is generally the result of ionic and molecular ingress that occurs as the oxidation state is changed either chemically or electrochemically.[3−7] Electrochemical experiments show that the related strain is proportional to the amount of charge transferred. This was particularly evidenced in conducting polymer bilayers in which the relative expansion or contraction of the conducting polymer layer with respect to the other nonelectroactive layer leads to a bending of the structure, with small material strains being amplified to create large deflections. Recently, Baughman[1] reviewed the use of conducting polymers as artificial muscles and described potential applications in areas including robotics and prosthetics, microvalves, and anti-vibration systems. Many other workers have demonstrated simple actuator devices using conducting polymers.[8−13]

Polyanionic and polycationic polyconjugated polymers, which might be particularly interesting for the construction of artificial muscles because of their ability to modulate the direction and amount of the volume change, have been frequently investigated in the past.[14−25] They are often called self-doped polyconjugated polymers because the potentially doping counter-

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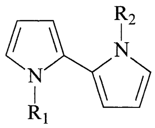
Chart 1



$R_1 = R_2 = CH_3$ (**1**)
$R_1 = R_2 = C_6H_{13}$ (**2**)
$R_1 = R_2 = C_6H_{12}N^+(CH_3)_3$ (**3**)
$R_1 = C_6H_{12}N^+(CH_3)_3$; $R_2 = C_6H_{13}$ (**4**)
$R_1 = C_3H_6N^+(CH_3)_3$; $R_2 = CH_3$ (**5**)
$R_1 = C_6H_{12}N^+(CH_3)_3$; $R_2 = H$ (**6**)
$R_1 = R_2 = C_4H_8SO_3^-$ (**7**)
$R_1 = C_4H_8SO_3^-$; $R_2 = C_6H_{13}$ (**8**)
$R_1 = C_3H_6SO_3^-$; $R_2 = CH_3$ (**9**)
$R_1 = C_6H_{12}SO_3^-$; $R_2 = H$ (**10**)

ion is covalently bound to the polyconjugated backbone.

In addition to their ability to act as artificial muscles, there are two more features the make these materials attractive. The synthesis of polyconjugated polyionic polymers has the main purpose of producing electroactive and/or conducting polymers soluble in water or other polar solvents. Soluble polyanionic and polycationic polymers are, in fact, commonly used in multilayer deposition from solution.[26−28] The second interesting aspect is their use in the construction of VOC (volatile organic compound) sensors taking advantage of the modulation of their selectivity with ionic character.

An easy way of producing such polymers is the anodic coupling of pyrrole monomers functionalized with the appropriate ionic substituent. The disadvantage is that *N*-substitution of pyrrole leads to poorly conducting materials (10^{-3} S cm^{-1} or less),[29,30] which can be attributed to the high torsional angle between adjacent pyrrole rings. In fact, the polymers were found to be particularly defective because of the presence of carbonyl groups,[30] which could be the main cause of their poor conduction.

Overoxidation defects are introduced into the polymer structure by the high voltage required for oxidative polymerization of pyrroles. Much less defective materials can be obtained from oligomers that are oxidized at less positive potentials, as found, for example, for polyfuran from terfuran.[31] Accordingly *N*,*N*′-dimethyl-2,2′-bipyrrole produces a low-defect polymer with a conductivity (0.3 S cm^{-1}) 30-fold higher than that for the polymer of *N*-methylpyrrole.[32]

Following this indication, we investigated the polymerization of *N*-substituted 2,2′-bipyrroles (Chart 1). These monomers were selected to provide neutral alkyl-substituted polymers as typical nonionic polymers, whereas alkylsulfonate- and alkylammonium-substituted polymers were chosen as typical examples of strong polyanionic and polycationic polymers. Also, variations of the substitution pattern, such as monosubstitution and disubstitution and the use of different alkyl chain lengths, were considered. We have characterized the polymers extensively by cyclic voltammetry, UV−vis and FTIR spectroscopies, and in situ conductivity. Moreover, focusing in this report on the ability of these materials to act as electrochemical muscles, we have provided a detailed EQCM analysis of their doping−dedoping processes and realized with them some all-plastic bilayer muscles.

Experimental Section

Chemicals and Reagents. All melting points are uncorrected. All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions were dried by conventional methods and freshly distilled under nitrogen. Acetonitrile was reagent-grade (Uvasol, Merck) with a water content of <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. All other chemicals were reagent-grade and used as received.

The following compounds were prepared according to literature procedures: 4,5-dihydro-3*H*,1′*H*-[2,2′]bipyrrole (**11**),[33] 1*H*,1′*H*-[2,2′]bipyrrole (**12**),[33] and 1,1′-dimethyl-1*H*,1′*H*-[2,2′]-bipyrrole (**1**).[32] The synthetic procedures used for the other bipyrroles, i.e., 1,1′-dihexyl-1*H*,1′*H*-[2,2′]bipyrrole (**2**), {6-[1′-(6-trimethylammonium-hexyl)-1′*H*-[2,2′]bipyrrol-1-yl]hexyl}-trimethylammonium ditetrafluroborate (**3**), [6-(1′-hexyl-1′*H*-[2,2′]bipyrrol-1-yl)hexyl]trimethylammonium tetrafluroborate (**4**), [3-(1′-methyl-1′*H*-[2,2′]bipyrrol-1-yl)-propyl]trimethylammonium tetrafluroborate (**5**), [6-(1′*H*-[2,2′]bipyrrol-1-yl)hexyl]-trimethylammonium tetrafluroborate (**6**), 4-[1′-(4-sulfobutyl)-1′*H*-[2,2′]bipyrrol-1-yl]butanesulfonic acid disodium salt (**7**), 4-(1′-hexyl-1′*H*-[2,2′]bipyrrol-1-yl)butanesulfonic acid sodium salt (**8**), 3-(1′-methyl-1′*H*-[2,2′]bipyrrol-1-yl)propanesulfonic acid sodium salt (**9**), and 6-(1′*H*-[2,2′]bipyrrol-1-yl)hexanesulfonic acid sodium salt (**10**), and their precursors are provided in the Supporting Information.

The sodium salts of the sulfonate monomers are so sparingly soluble in acetonitrile that polymerization is difficult or even prevented. For this reason, their tetrabutylammonium salts were also prepared. These salts were obtained from aqueous solutions of the sodium salts by ion exchange with H^+-exchange resin (Dowex HCR-W2 by Sigma) followed by neutralization with tetrabutylammonium hydroxide and evaporation to dryness.

Polypyrrole films were prepared as the perchlorate salt as reported in the literature.[34]

^1H NMR spectra were recorded on a Bruker FT 300 spectrometer (300 MHz for ^1H), whereas ^{13}C, JMOD, HMQC, HMBC, $^1H-^1H$ COSY, and $^1H-^1H$ COSY long-range NMR spectra were recorded on a Bruker FT 500 spectrometer (500 MHz for ^1H) and are referred to tetramethylsilane.

Electrosynthesis of Soluble Poly(4). A solution of **4** (44 mg, 0.1 mmol) in acetonitrile (25 mL) + 0.1 M $NaClO_4$ was fully electrolyzed at 0.5 V with the passage of 3 F mol^{-1}. The electrode became covered with ca. 3 mg of insoluble polymer. The dark electrolyte solution was then fully reduced at −1 V with the passage of the same amount of charge. After treatment with a few drops of ammonia (to complete the reduction, which makes the solution light olive green), the solvent was

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evaporated to dryness. The resultant green solid was washed with water and finally dried under vacuum to give 35 mg of product (77% yield). Anal. Calcd. for $C_{23}H_{38}ClO_4N_3$: C, 60.62; H, 8.34; N, 9.22. Found: C, 60.36; H, 8.52; N, 9.07.

Electrochemical Apparatus and Procedure. 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, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and was coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm^2). For electronic spectroscopy, 0.8 × 2.5 cm gold-coated silica plates were used. Electrochemical muscles were produced on one-side-conducting all-plastic foils (ORGACON from Bayer, 300 Ω sq^{-1}).

FTIR spectra of the polymer films were recorded in reflection−absorption mode on a Perkin-Elmer 2000 FTIR spectrometer; electronic spectra were obtained with a Perkin-Elmer Lambda 15 spectrometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were taken on a Reflex TOF spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as the matrix.

ESR spectra were recorded on a Bruker ER 100D X-band spectrometer. Absolute spin calibration was performed with $VOSO_4 \cdot 5H_2O$ crystals, g-value calibration with thin films of DPPH ($g = 2.0037$).

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited. Absolute polymer mass measurements were performed outside the depositing solution to measure the mass of polymer films in the dry state as well as to avoid errors due to polymer roughness. The oscillator circuit was homemade, and the frequency counter was Hewlett-Packard model 53131A.

The apparatus and procedures used for the in situ conductivity experiments were previously described in detail.[35] The electrode for conductivity measurements was a microband array platinum electrode (5-μm bandwidth, 100-nm thickness) with an interband spacing of 5 μm. The deposit was thick enough to ensure minimum resistance, under which conditions the conductivity σ is given by $\sigma = k/(R - R_0)$, where R is the measured resistance, R_0 is the lead resistance (100 Ω) and k is the cell constant (0.2 cm^{-1}).

Results and Discussion

Synthesis of the Monomers. Monomer **1** has already been reported in the literature,[32] whereas monomers **2**−**10** were prepared for the first time in the context of this work. Their synthetic access is depicted in Schemes 1 and 2 of the Supporting Information. The dihexyl derivative **2** was prepared from 1*H*,1′*H*-[2,2′]-bipyrrole **12** by reaction with bromohexane in the presence of KOH. The ammonium-funtionalized monomers **3**−**6** were prepared through nucleophilic substitution with trimethylamine of the bromo derivatives **13**, **16**, **19**, and **20**. The butylsulfonate-functionalized monomers **7** and **8** were obtained from **12** and **15**, respectively, through reaction with BuLi and then with 1,4-butanesultone. Finally, monomers **9** and **10** were prepared from the bromo derivatives **19** and **20**, respectively, by reaction with Na_2SO_4.

General Electrochemical Deposition and Characterization of the Polymers. The electrochemical investigation of all dipyrroles was performed in a 10^{-2} M solution of the compounds in acetonitrile + 0.1 M Bu_4NClO_4 with added 1% H_2O, which favors the electrodeposition of polypyrroles.[36,37] CV cycling was performed at a scan rate of 0.1 V s^{-1}. The obtained electrochemical parameters (oxidation peak potentials E_p) are summarized in Table 1.

Table 1. Oxidation Peak Potential E_p for Monomers, Redox Potential $E°$, and Conductivity σ for Polymers

monomer	E_p (V)	$E°$ (V)	σ (S cm^{-1})
1[32]	0.30	0.00	0.3
2	0.35	0.25	0.02
3	0.42	0.13	0.005
4	0.39	0.15	0.007
5	0.39	0.15	0.03
6	0.19	−0.15	0.2
7	0.40	0.15	0.001
8	0.40	0.15	0.005
9	0.40	0.15	−[a]
10	0.10	−0.39	0.05

[a] Not measurable.

With continuous cycling of the potential beyond (or potentiostatic oxidation at) the peak potential, the polymer deposited on the electrode. Subsequently, the polymer film was examined by CV in blank solution (solvent plus electrolyte), where it shows its reversible oxidation redox cycle. The relevant redox potentials $E°$, measured as the average of forward and backward peak potentials, are also summarized in Table 1.

The effectiveness of the deposition was evaluated from the charge yield (ratio between the reversible charge, measured between −0.2 and 0.5 V, and the deposition charge). This parameter was ca. 20% with only a few specified exceptions.

Electrochemical Deposition and Characterization of Poly(*N*,*N*′-dihexyldipyrrole). The cyclic voltammogram of *N*,*N*′-dihexyldipyrrole **2** displays a single oxidation peak at $E_p = 0.35$ V. This dipyrrole is oxidized at a higher potential than the dimethyl analogue **1** (E_p = 0.30 V[32]) because of its more bulky substituents, which induce a higher torsion of the rings along the chain.

The polymer shows its reversible oxidation redox cycle in blank solution at $E° = 0.25$ V (Figure 1a). For comparison, the CV of poly(**1**) exhibits the process at $E° = 0.0$ V,[32] i.e., once more at a lower potential. The polymer is remarkably stable toward overoxidation because its CV can be brought to a switching potential of 1.0 V without oxidative degradation.

The reversible charge, measured at 0.8 V and related to the EQCM mass, corresponds to ca. 0.5 electrons per pyrrole ring.

Electrochemical Deposition and Characterization of Poly(alkylammonium dipyrrole)s. The dialkylammonium-substituted monomer **3** displays its oxidation peak at $E_p = 0.42$ V, whereas the mixed alkyl−alkylammoniun monomers **4** and **5** are oxidized at $E_p = 0.39$ V, i.e., a potential just slightly less positive.

The CV of the deposits is shown to be a redox process at $E° = 0.13-0.15$ V (Figure 1b). It should be remarked that, for poly(**3**), poly(**4**), and poly(**5**), the CV can be brought to a switching potential of 1.0 V without

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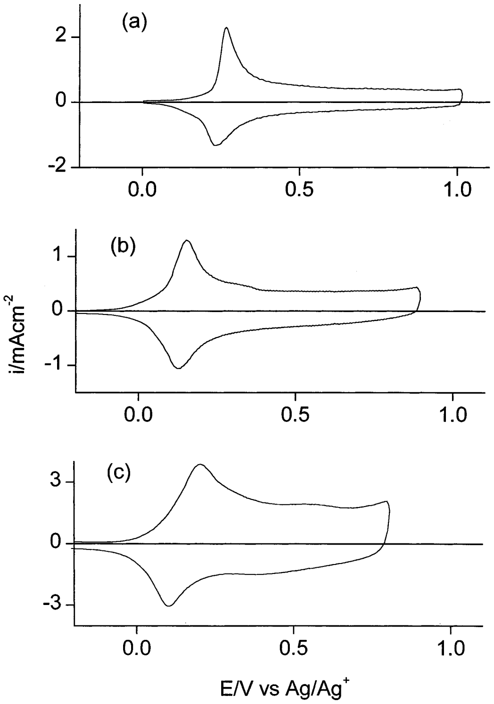

Figure 1. CV of (a) poly(**2**), (b) poly(**3**) and (c) poly(**7**) films in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Redox charge: (a) 4; (b) 5; (c) 16 mC cm^{-2}.

oxidative degradation, as for poly(*N*,*N*′-dihexyldipyrrole) (see before).

The EQCM results allow us to state that the reversible charge, measured at 0.8 V and related to the mass, again corresponds case to ca. 1 electron per monomeric unit (0.5 electrons per pyrrole ring). It is therefore suggested that poly(*N*-substituted pyrrole)s in general are dopable to this level.

The monosubstituted alkylammonium monomer **6** displays its oxidation at $E_p = 0.19$ V, i.e., much less positive than for **3**−**5** because of the unsubstituted pyrrole ring, which does not cause twisting along the pyrrole Cα−Cα bond. For the same reason, the CV of the deposits is characterized by a redox process at $E° = -0.15$ V, i.e., with a strong negative shift (ca 0.3 V) compared to the others.

Electrosynthesis and Characterization of Soluble Poly(4). Unlike the other materials, the solid polymer of **4** was produced potentiostatically with a low charge yield (less than 1%). After this result, which was addressed by extensive dissolution of the produced polymer, poly(**4**) could be prepared via acetonitrile solution in the undoped form as detailed in Experimental Section.

The UV−vis spectrum of poly(**4**) in acetonitrile solution exhibits a maximum absorption at 285 nm (with a shoulder at 380 nm) with the same intensity as that of the monomer. These features are typical of poly(*N*-alkylpyrrole)s.[38]

MALDI analysis reveals a single peak at 2633 *m*/*z*, corresponding to the hexamer (12 pyrrole rings) less one perchlorate anion.

The FTIR spectrum displays, in addition to the bands of the monomer, a new band at 770 cm^{-1} (due to the inner pyrrole rings) ca. 4 times higher than that at 720 cm^{-1} (terminal rings), thus indicating an average chain length of ca. 10 pyrrole rings, in fairly good agreement with the length measured by MALDI.

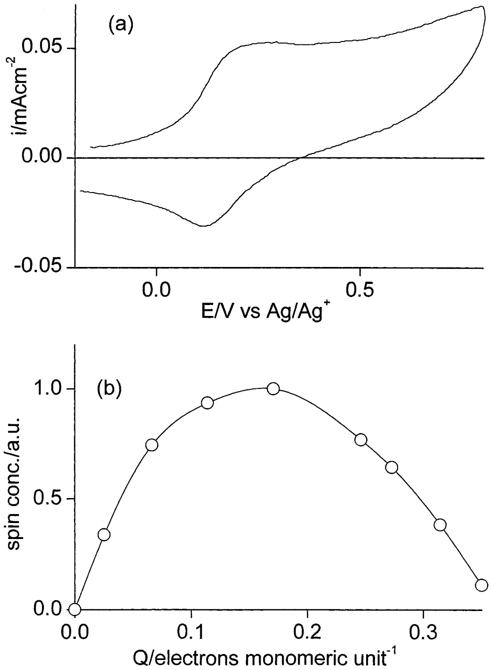

Figure 2. (a) CV at 0.1 V s^{-1} and (b) ESR intensity vs oxidation charge of poly(**4**) (9×10^{-4} M) in acetonitrile + 0.1 M Bu_4NClO_4.

A solution of undoped poly(**4**) in acetonitrile + 0.1 M Bu_4NClO_4 exhibits reversible oxidative CV at $E° = 0.2$ V (Figure 2a). The solution was electrochemically oxidized by charge steps. The ESR spectrum of the oxidized solution shows a featureless signal ca. 2 G wide at $g = 2.0029$. Its maximum intensity occurs at 0.15−0.20 electrons per repeat unit or 1 electron per 10−15 pyrrole rings (Figure 2b). This result, which might correspond to the one-electron oxidation of a dodecapyrrole, agrees with the results of the FTIR and MALDI analyses.

Because of its solubility in acetonitrile, poly(**4**) could be characterized by NMR spectroscopy. The full ^1H NMR spectrum is reported in the Supporting Information. In the aliphatic region, the spectrum strictly resembles that of the corresponding monomer. In the polymer spectrum, the signals are obviously broader and less resolved. In the aromatic region, only one broad signal, assigned to protons H-3, H-3′, m H-4, and H-4′, is present in the polymer spectrum. In contrast, in the monomer spectrum three multiplets at 6.04 (H-3, H-3′), 6.12 (H-4, H-4′), and 6.80 ppm (H-5, H-5′) are present.

The full ^{13}C JMOD (CH_3 and CH in the negative part, CH_2 and quaternary carbons in the positive part) spectra of the monomer and the corresponding polymer are reported in the Supporting Information. A careful analysis of the JMOD, HMQC, HMBC, and $^1H-^1H$ COSY spectra led to the assignment of almost all of the carbons present in the monomer, which gave the values reported in the Experimental Section. Also in the case of ^{13}C, the spectrum of the polymer resembles that of the monomer in the aliphatic region, with broader and less resolved signals. In the aromatic region, the polymer spectrum shows one broad CH signal at 112.25

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ppm, assigned to carbons C-3, C-3′, C-4, and C-4′, and one quaternary-carbon signal at 127.06 ppm, assigned to carbons C-2, C-2′, C-5, and C-5′. In contrast, in the aromatic region, the monomer spectrum shows six CH signals and two quaternary carbons. All of these data led us to assign a regioregular strucure to poly(**4**), in which the monomeric units are linked to each other through the α-pyrrole positions.

Electrochemical Deposition and Characterization of Poly(alkylsulfonate dipyrrole)s. The cyclic voltammetry of **7**−**9** as tetrabutylammonium salts in acetonitrile + 0.1 M Bu_4NClO_4 displays the oxidation peak of the monomer at 0.40 V. The best polymer deposits were obtained potentiostatically at 0.5 V.

FTIR analysis (see below) has evidenced that, in the case of the monosulfonate monomers **8** and **9**, the polymers are produced in the fully protonated form (i.e., with $-SO_3H$ moieties) because of the excess protons released during coupling (2 protons per sulfonate moiety). In this form, the polymer does not exchange the protons easily with Bu_4N^+ in acetonitrile + 0.1 M Bu_4NClO_4. In any case, the protons are easily replaced by Bu_4N^+ cations via treatment of the polymer films with Bu_4NOH in acetonitrile or with reduction at −2 V in acetonitrile + 0.1 M Bu_4NClO_4.

The CV of the pristine (acidic) deposits from **8** and **9** is shown to be a redox process at $E° = 0.25$ V. After deprotonation, the single process is negatively shifted to $E° = 0.15$ V, which can be explained by stabilization of the sulfonate anion with the positive charge on the polypyrrole chain.

The polymer produced from **7** contains both anionic $-SO_3^-$ and acidic $-SO_3H$ functions because of the lower amount of protons (relative to sulfonate moieties) released during coupling. This fact was demonstrated by FTIR bands of both functions (see below). The CV of the deprotonated deposits is shown as a redox process at $E° = 0.15$ V (Figure 1c). It is noteworthy that for the deprotonated polymers, CV beyond 0.8 V causes overoxidation, which can be attributed to the nucleophilic character of the sulfonate moiety in the aprotic medium.

Treatment of the Bu_4N^+ polymers with 0.1 M $HClO_4$ in acetonitrile, followed by washing with acetonitrile, causes the complete protonation of the sulfonate groups, as evidenced by the EQCM mass decrease and by the FTIR spectrum in which the Bu_4N^+ bands are lost and a single sulfonate ($-SO_3H$) absorption is shown.

The behavior of the alkylsulfonate dipyrrole **10** as a tetrabutylammonium salt is singular. The cyclic voltammetry of the monomer displays its oxidation peak at 0.10 V, i.e., at a very low voltage, because of the specific interaction of the positively charged pyrrole unit in the produced radical cation with the sulfonate moiety.[39]

Potentiostatic oxidation of **10** at 0.1 V results in progressive deposition of the polymer, whereas CV deposition proceeds with a low yield. The polymer was therefore produced potentiostatically, and in this way, it was found to be in an electrolyte-free form as for the tosylate salt of polypyrrole.[34] Preliminary reduction at −2 V is required for developing its CV properties: only after this step does the CV display a regular voltammogram at $E° = -0.39$ V. Such a strongly negative redox potential is once again due to the above-mentioned interaction of the pyrrole ring with the sulfonate anion as in polypyrrole ($E° = -0.65$ V fo tosylate vs −0.30 V for perchlorate[40]).

Electrochemical Deposition of Poly(alkylsulfonate dipyrrole)s in Water. Given their solubility in water, the sodium salts of the sulfonate-substituted monomers can be oxidatively polymerized from water. To this end, we have selected **7** and **10** as typical cases.

7 has an oxidation peak at 0.54 V vs SCE in 0.1 M HCl. The strongly acidic conditions are required by the relatively high oxidation potential. The oxidation of **10** occurs in 0.1 M NaCl at 0.35 V vs SCE, i.e., at a much lower potential, which allows its polymerization at a neutral pH. Extensive electrolysis at 0.6 V for **7** and at 0.4 V for **10** requires 2.4 F mol^{-1} with production of insoluble polymer on the electrode and a colorless solution.

FTIR Spectroscopy. FTIR reflection−adsorption spectroscopy was applied to polymers of **2**, **3**, **7**, and **8** as the most representative examples of the substitution pattern.

The spectrum of an undoped poly(**2**) film (see the Supporting Information) exhibits the bands present in the monomer (essentially the strong bands of the methylene groups at 2950, 2860, and 1490 cm^{-1}) and a single strong band in the CH deformation region at 770 cm^{-1} due to the out-of-plane deformation of the pyrrole β-hydrogen atoms in an α-coupled polymer. The corresponding CH stretching band at 3100 cm^{-1} is also displayed. The absence of other CH deformation bands (such as the terminal-ring band at 715 cm^{-1}) rules out a short length of the polymer chain. Moreover, overoxidation bands in the 1600−1750 cm^{-1} region are completely absent. These characteristics indicate the production of a low-defect polymer.

Similarly, the FTIR spectrum of the undoped poly(**3**) film, which is dominated by the strong bands of the perchlorate anion at 1110 and 620 cm^{-1} and of the methylene groups, shows the strong CH deformation band at 780 cm^{-1} of the regularly α-coupled polymer and no sign of overoxidation bands.

The FTIR spectrum of the undoped proton-free polymer of **8** is dominated by the strong bands of the sulfonate $-SO_3^-$ moiety at 1200 and 1040 cm^{-1}, whereas the as-prepared polymer shows only one strong band at 1140 cm^{-1} due to the $-SO_3H$ moiety. The as-prepared polymer of **7** shows both the $-SO_3^-$ and the $-SO_3H$ bands indicating that the sulfonate group is only partially protonated.

Both undoped polymers show the CH deformation band at 790 cm^{-1} of the regularly α-coupled polymer. From the appreciable intensity of the terminal-ring band at 720 cm^{-1} related to the intensity of the band at 790 cm^{-1}, we assign poly(**8**) a degree of polymerization of ca. 20 pyrrole rings.

UV−Vis Spectroscopy. The maximum absorption of the *N*,*N*′-disubstituted dipyrrole polymers occurs at 280−300 nm, which corresponds to the value extrapolated from oligomers for the infinite polymer.[38] In the case of monosubstituted dipyrroles, the maximum absorption of the relevant polymers is red-shifted to 360

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[39] Zotti, G.; Schiavon, G.; Zecchin, S.; Sannicolo', F.; Brenna, E. *Chem. Mater.* **1995**, *7*, 1464.

[40] Zotti, G.; Schiavon, G.; Comisso, N. *Synth. Met.* **1991**, *40*, 309.

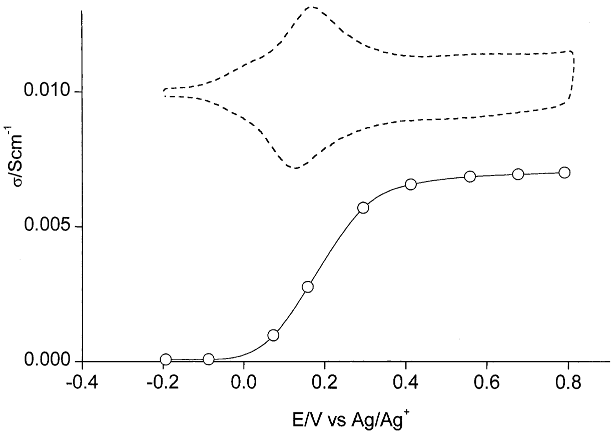

Figure 3. In situ conductivity vs potential of poly(**4**) in acetonitrile + 0.1 M Bu_4NClO_4.

nm, paralleling the shift for the monomers from 253 nm of disubstituted to 266 nm for monosubstituted dipyrroles.

The oxidized film shows a broad absorption giving the polymer the blue color typical of oxidized polypyrrole.

In situ Conductivity. As for the generality of polypyrroles, oxidation of the polymers makes them conductive. Their in situ conductivity vs potential relationship is sigmoidal (Figure 3). The plateau value of poly(**2**) is relatively high (2×10^{-2} S cm^{-1}). It is considerably higher than that reported in the literature for other *N*-alkyl-substituted polypyrroles (10^{-3}–10^{-5} S cm^{-1})[29] because of the better quality of the material.

The oxidized polymers are generally conducting in the range 10^{-2}–10^{-3} S cm^{-1} (see Table 1). The exceptions are poly(**6**) and poly(**10**), which are more conductive with maximum conductivities of 0.2 and 0.05 S cm^{-1}, respectively. This difference is attributed to the fact that these polymers are *N*-alkylpyrrole/pyrrole copolymers, so their conduction takes advantage of the increased conjugation given by the increased coplanarity of the pyrrole rings.

Solubility. With the only exception of poly(**4**), the polymers are insoluble in the common solvents both in the undoped and in the oxidized forms and, for the sulfonate-substituted polymers, both in the deprotonated and in the protonated state.

We have investigated whether chloride rather than perchlorate would make ammonium-substituted polymers other than poly(**4**) soluble. Yet neither the use of the chloride salt of **6** as a monomer nor the treatment of poly(**3**) with concentrated HCl gave soluble polymers.

The generally encountered insolubility is particularly surprising because the literature reports that copolymers of pyrrole and *N*-alkylsulfonate pyrrole are water-soluble.[16] The reason for the insolubility of our polymers is possibly accounted for by the high degree of polymerization, i.e., the relatively long polymer chains. Cross-linking, which is generally an efficient process of insolubilization, is not particularly favored because FTIR analyses have shown the good efficiency of anodic coupling of the reported dipyrroles. Moreover, it is noticeable that poly(**4**) is highly soluble. Nonetheless, low amounts of cross-links are often sufficient to depress strongly the solubility so that their presence and action cannot be ruled out completely.

Ion Exchange during Doping. *Poly(N,N′-dihexyldipyrrole).* During the oxidative process, poly(**2**) is

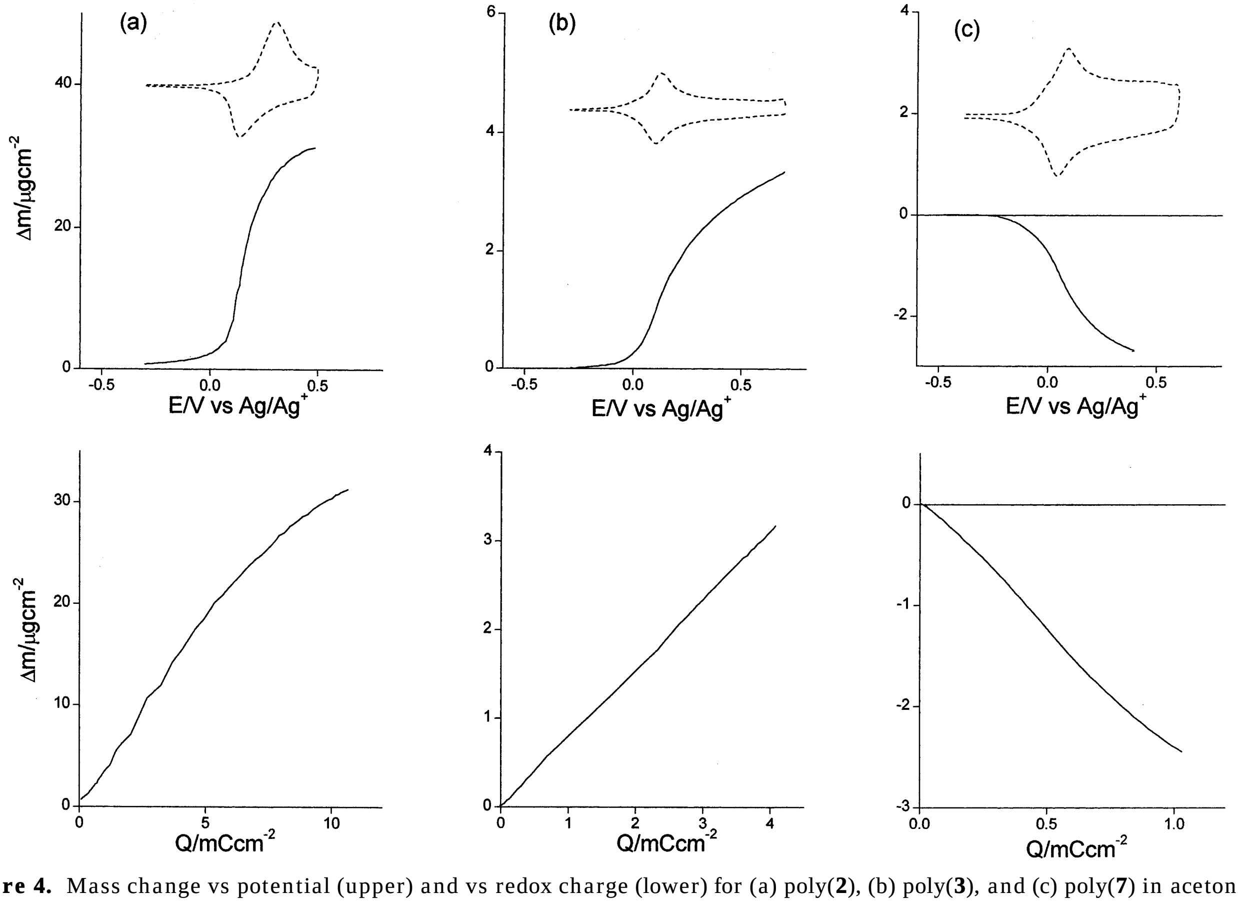

Figure 4. Mass change vs potential (upper) and vs redox charge (lower) for (a) poly(**2**), (b) poly(**3**), and (c) poly(**7**) in acetonitrile + 0.1 M Bu_4NClO_4. Backward scan only for clarity. Upper: CV for comparison.

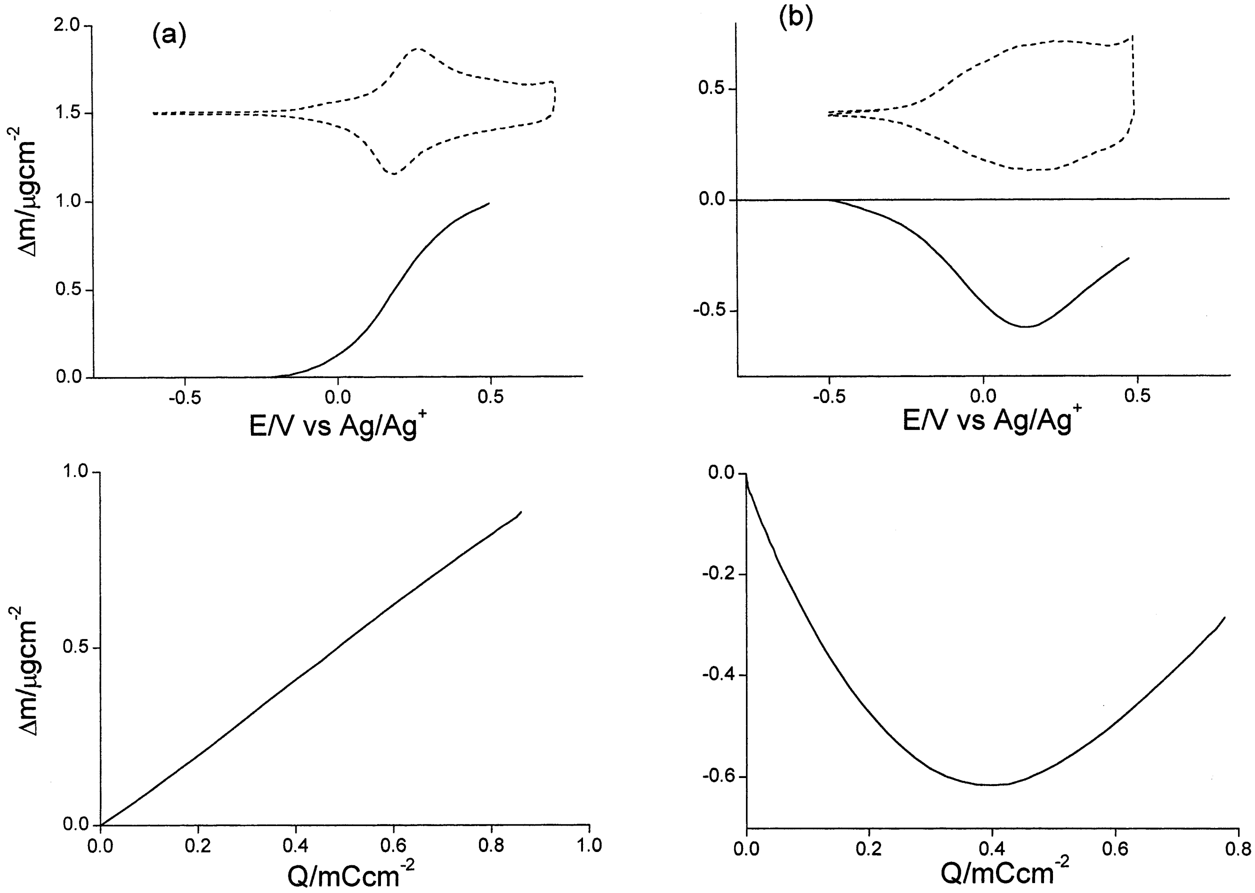

Figure 5. Mass change vs potential (upper) and vs redox charge (lower) for (a) as-grown and (b) Bu_4NOH-treated poly(**8**) in acetonitrile + 0.1 M Bu_4NClO_4. Backward scan only for clarity. Upper: CV for comparison.

expected to take in anions. We have checked the EQCM response of the polymer films upon CV in acetonitrile + 0.1 M Bu_4NClO_4. The mass change during CV (Figure 4a) shows clearly that anions are taken in during positive doping. The relationship of the mass change Δm to the charge Q is almost linear (Figure 4a), and the slope corresponds to $F\Delta m/Q = 300$ g mol^{-1}, i.e., that expected from the perchlorate anion mass plus extra (ca. 5) acetonitrile molecules. The very high value of the mass/charge ratio favors the use of this material in electrochemical muscles.

Poly(alkylammonium dipyrrole)s. Poly(**3**) incorporates anions with oxidation (Figure 4b). The relationship of mass change Δm and charge Q (Figure 4b) has a slope $F\Delta m/Q = 75$ g mol^{-1}, i.e., essentially that expected for the perchlorate anion mass less some solvent. Similar behavior is shown by poly(**4**), with a slope of the mass/charge relationship corresponding to $F\Delta m/Q = 65$ g mol^{-1}.

Poly(alkylsulfonate dipyrrole)s. The Bu_4N^+ salt of poly(**7**) is expected to eject cations during the oxidative process, thus exhibiting its ability as a self-dopable polymer. The mass change during CV in acetonitrile + 0.1 M Bu_4NClO_4 (Figure 4c) shows clearly that cations are ejected during positive doping. The linear mass/charge relationship (Figure 4c) gives $F\Delta m/Q = -240$ g mol^{-1}, i.e., that expected for the Bu_4N^+ cation mass. The data indicate that cation ejection is the only process of ion exchange during doping.

For the purpose of the electrochemical muscles described below, it is important to report the response of as-prepared (partially protonated) poly(**7**). In this case, the slope of the mass/charge relationship is still negative ($F\Delta m/Q = -120$ g mol^{-1}) although ca. 50% lower than that of the Bu_4N^+ salt of the polymer.

FTIR analysis of poly(**7**) films before and after being dipped in acetonitrile + 0.1 M $LiClO_4$ indicates the substitution of the Bu_4N^+ bands by those of lithium-coordinated water. The substitution with Li^+ causes a shift of $E°$ to 0.25 V, similar to that of the protonated polymer. This indicates that the coordination of $-SO_3^-$ with Li^+ is similarly strong. After exchange, the linear EQCM mass/charge relationship has a positive slope ($F\Delta m/Q = 70$ g mol^{-1}) close to that expected for the insertion of the perchlorate anion. Thus, it appears that the lithium cation [as well as the proton; see below for poly(**8**)] is more strongly bound to the sulfonate group than the tetralkylammonium cation.

During oxidation, the as-prepared (SO_3H-containing) poly(**8**) does not eject cations but takes in anions (Figure 5a). The EQCM slope (Figure 5a) corresponds to $F\Delta m/Q = 100$ g mol^{-1}, i.e., that expected for the perchlorate anion mass. It appears that the protonated polymer behaves as a totally alkyl-substituted polymer, i.e., protonation of the $-SO_3^-$ moiety shields its negative charge completely.

If the protons of as-prepared poly(**8**) are replaced by Bu_4N^+ cations with Bu_4NOH treatment, the mass decreases initially during doping and then increases (Figure 5b). Thus, Bu_4N^+ is ejected first, but subsequently the low amount of negative charge in the polymer favors anion entry.

Electrochemical Muscles. To exploit the ability of the investigated polymers as electrochemical muscles, evidenced by the EQCM measurements, we selected the polymers with the highest mass/charge ratio, both positive such as poly(**2**) and negative such as poly(**7**). Poly(**1**) and polypyrrole were selected as reference polymers. All polymers were investigated as-prepared.

ORGACON strips 15 mm long and 5 mm wide, with a mechanical interruption of the conductive layer along a line 7 mm from the bottom, were immersed by 12 mm in the monomer solution and polymer-coated with a deposition charge of 0.4 C. They were subsequently washed and immersed to the same level in a monomer-free solution for the doping−dedoping tests. The forced localization of the polymer in the upper end of the immersed strip (5 × 5 mm^2) confines the bending action there. The expected result is a rigid deflection of the foil at the deposited zone during the doping−dedoping processes.

Switching the potential from the oxidized (0.5 V) to the undoped (−0.1 V) state, which requires ca. 70 mC of reversible charge, makes the foil deflect. The process, which requires 5−10 min for full deflection, is completely reversible for several cycles. Moreover, the deflection is proportional to the redox charge.

In the case of poly(**2**), the deflection of the 12-mm bilayer electrode occurs in the direction of the deposit because of the shrinking of the material and is particularly high (5 mm at the tip), in agreement with the EQCM slope. For comparison, poly(**1**) and polypyrrole deflect in the same direction by ca. 1 mm only.

As predicted, the response of the poly(**7**) deposit occurs in the opposite direction. Following the EQCM slope, its full deflection at the tip is ca. 2 mm.

Conclusions

A series of nine previously unreported 2,2′-bipyrroles *N*-substituted with alkyl, alkylsulfonate, or alkylammonium moieties have been synthesized and coupled to polymers. FTIR analysis of the polymers has confirmed the expectation that using dipyrroles instead of pyrroles minimizes the introduction of overoxidative defects into the polymer chain.

In contrast with the materials studied in previous reports, the *N*-alkylsulfonate-substituted polymers are not soluble. Solubility in acetonitrile is shown by the polymer of *N*-alkylammonium-*N*-hexyldipyrrole, which has been fully characterized in this medium.

From an EQCM analysis of the oxidative doping process in acetonitrile, it has been shown that the alkyl- and the alkylammonium-substituted polymers increase their mass with doping (counteranion and solvent ingress). The alkylsulfonate-substituted polymers bearing tetralkylammonium as the counterion undergo a mass decrease (counterion elimination), whereas they increase in mass (counteranion and solvent ingress) with strongly bound hydrogen and lithium cations.

Electrochemical muscles in the form of plastic bilayers have been built from these polymers. The observed deflections followed the EQCM mass/charge changes so that a large choice of responses, different in direction and amplitude, were obtained. This makes these polymers good candidates for the production of electrochemical actuators.

The produced polymers also provide a noticeable substitution pattern that can produce various specific conductivity changes to organic vapors (VOCs). The ability of these polymers to act as VOC sensor materials will be reported in a forthcoming paper.

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Supporting Information Available: Synthetic procedures and relevant schemes for bipyrroles and their precursors; FTIR spectrum of poly(1,1′-dihexyl-1*H*,1′*H*-[2,2′]bipyrrole); NMR spectra of poly[6-(1′-hexyl-1′*H*-[2,2′]bipyrrol-1-yl)hexyl]-trimethylammonium tetrafluroborate. This material is available free of charge via the Internet at http://pubs.acs.org.

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