Synthesis and Characterization of Polyaniline Derivatives: Poly(2-alkoxyanilines) and Poly(2,5-dialkoxyanilines)

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A series of 2-alkoxyanilines and 2,5-dialkoxyanilines with alkyl chains containing $n = 1$, 2, 4, and 6 carbon atoms have been electropolymerized in acidic conditions and characterized by several techniques. The corresponding neutral polymers were found to be soluble in chloroform and tetrahydrofuran. On the other hand, chronoamperometry experiments have shown that the presence of long alkoxy groups ($n = 4$ and 6) decreases the rate of polymerization, giving materials with a lower degree of polymerization. Electrochemical and spectroscopic measurements have demonstrated that the electron-donating effects of the side chains are more significant for 2,5-dialkoxyanilines and for the corresponding polymers. Moreover, the presence of electron-donating substituents has allowed a better characterization of the charge carriers in fully oxidized polyanilines. Indeed, in agreement with electrochemical results, in situ ESR experiments displayed two signals with similar g values, related to the presence of radical cations formed during the leucoemeraldine–emeraldine transition and the emeraldine–pernigraniline transition. However, these radical cations were found to be more localized, with respect to polyaniline. Fully oxidized poly-(2,5-dialkoxyanilines) were found to be partially protonated at pH between −0.5 and 3, by electrochemical quartz crystal microbalance (EQCM) analysis. On the other hand, in situ conductivity measurements suggested that protonated imines do not act as efficient charge carriers. Finally, conductivity of 0.1 S/cm were found for disubstituted materials with short alkoxy groups ($n = 1$ and 2), whereas a decrease of 3−5 orders of magnitude were observed for materials bearing longer alkoxy groups ($n = 4$ and 6).

Introduction

Although studies devoted to polyaniline (PANI) date from the beginning of this century,[1] it is only since Diaz et al.[2] have reported its electrochemical synthesis as a thin film, that this electronically conducting polymer has attracted considerable interest. Many publications revealed that this material exhibits an increase of its electrical conductivity by 10 orders of magnitude, either by a simple protonation, which has been called protonic acid doping,[3] or by oxidative chemical[4] or electrochemical[5] doping. Furthermore, it was also found that PANI exhibits electrochromic effects, from pale yellow to green to blue-violet.[2,3,6] The reversibility of these unusual

electrical and optical properties, combined with its good environmental stability and its low cost of fabrication, make this polymer very attractive for the development of many technological devices, such as biosensors,[7] light-emitting diodes,[8] molecular devices,[9] conducting photoresists,[10] optical switches,[11] smart windows,[12] and transistors.[5b,13]

To be used in such applications, materials must be soluble or melt-processable. Like many other aromatic

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polyconjugated materials, PANI is insoluble in common organic solvents, although it has been found to be partly soluble in *N*-methylpyrrolidinone.[14] Recently, it has been reported that the use of dodecylbenzenesulfonic acid or camphorsulfonic acid improves the solubility of the conducting form of PANI.[15] However, some applications still require the use of common organic solvents, such as chloroform and tetrahydrofuran. Therefore, many studies have been devoted to the synthesis of soluble polyaniline derivatives. These studies have shown that 2-substituted polyanilines, with alkyl[16] or alkoxy[17] substituents, are more soluble than unsubstituted PANI. On the other hand, these polymers exhibit a lower electrical conductivity, with repect to PANI. However, as recently reported[18,19] double-substitution using alkoxy substituents at the 2- and 5-positions gives more regular materials with reduced side couplings and, mainly, a good conductivity of 10^{-1} S/cm. Moreover, earlier studies on poly(2-decyloxyaniline) and poly(2-octadecyloxyaniline)[20] have shown that the presence of the alkoxy group allow the formation of monolayers, at the air—water interface, and to an enhancement of the stability of the Langmuir—Blodgett films, with respect to poly(2-alkylanilines).[21] Hence, the design of new poly(2,5-dialkoxyanilines) bearing long lateral chains becomes particularly interesting.

Therefore, electrochemical polymerization of a series of 2-alkoxyanilines and 2,5-dialkoxyanilines, with a different number of carbon atoms in the side chains (n = 1, 2, 4, 6, Scheme 1), have been carried out. The effect of the double substitution on the formation of electroactive polymers, as well as the effect of the side-chain length on the physical properties were investigated by electrochemical, spectroscopic, electron spin resonance, microgravimetry, conductivity, and steric exclusion

Scheme 1
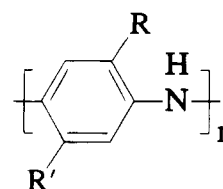
R = OCH$_3$; R' = H (PMOA)
R = OC$_2$H$_5$; R' = H (PEOA)
R = OC$_4$H$_9$; R' = H (PBOA)
R = OC$_6$H$_{13}$; R' = H (PHOA)

R = R' = OCH$_3$ (PDMOA)
R = R' = OC$_2$H$_5$ (PDEOA)
R = R' = OC$_4$H$_9$ (PDBOA)
R = R' = OC$_6$H$_{13}$ (PDHOA)

Table 1. Summary of the Electrochemical and Optical Data of the Aniline Derivatives

monomers	E_p (V vs SCE)	λ_{max} (nm)
ANI	1.03	254
MOA	0.75	270
DMOA	0.67	290
EOA	0.75	270
DEOA	0.65	292
BOA	0.81	270
DBOA	0.68	293
HOA	0.80	270
DHOA	0.68	293

chromatography measurements. These results should lead to a better knowledge of the structure—property relationships in polyanilines. Finally, the syntheses of poly(2,5-diethoxyaniline), poly(2-butoxyaniline), poly-(2,5-dibutoxyaniline), poly(2-hexyloxyaniline), and poly-(2,5-dihexyloxyaniline) are reported for the first time.

Results and Discussion

Cyclic Voltammetry of the Monomers. The cyclic voltammogram of the different monomers display an irreversible oxidation peak in acidic conditions. From results shown in Table 1, it can be observed that the incorporation of an alkoxy group, at the 2-position, decreases the oxidation potential, E_p, of the aniline. This decrease is related to the strong electron-donating properties of the alkoxy groups. The electronic effect of these groups can also be seen in the position of the maximum of absorption of the monomers, in acidic conditions (Table 1). The addition of a second alkoxy group, at the 5-position, reduces further the oxidation potential of the monomer, with respect to 2-alkoxyanilines and aniline (Table 1). This is in agreement with the strong red shift of the maximum of absorption of 2,5-dialkoxyanilines: ca. 25 nm with respect to 2-alkoxyanilines and almost 40 nm with respect to aniline. It can also be observed that there is no significant effect of the length of the pendant group on the oxidation potentials and on the electronic spectrum (Table 1) on both mono- and disubstituted anilines.

Polymer Synthesis. Polymers were electrodeposited by potentiostatic oxidation or potential cycling over the monomer oxidation potential in acidic solutions. Owing to the hydrophobicity nature of butoxy and hexyloxy groups, 2,5-dibutoxyaniline and 2,5-dihexyloxyaniline were found to be insoluble in aqueous acid

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solution. As reported for other aniline derivatives,[22] a mixture of an aqueous acid (70%) and an organic solvent (acetonitrile) (30%) was necessary to solubilize these monomers and, hence, for the electrosynthesis of the corresponding polymers and subsequent electrochemical characterization. In the case of 2-butoxyaniline and 2-hexyloxyaniline, both monomers were found to be soluble in perchloric acid and electroactive polymers were obtained in such a media. However, we have noticed that only nonelectroactive reddish materials were obtained when hydrochloric acid or sulfuric acid were used.

In all cases, bulk materials were attained from bulk electrolysis as a dark-green powder. A large amount of soluble reddish side products were found only in the case of poly(2-alkoxyanilines). After deprotonation in 10% NH_4OH (emeraldine-base state), these derivatives were found to be completely soluble in chloroform and tetrahydrofuran.

Unlike doubly alkylated derivatives, double substitution of the aniline ring with alkoxy groups of different length allow the synthesis of electroactive polymers. In fact, only the presence of two methyl groups allow the formation of a polymer,[23] whereas dimers are mainly formed with longer alkyl groups, such as propyl group and butyl group.[23,24]

Mechanism of Polymer Electrodeposition. The mechanism of polymer deposition was investigated by chronoamperometry (CA) in a mixture of 1.0 M $HClO_4$ (70%) and acetonitrile (30%). Poly(2,5-dialkoxyanilines) ($n = 1, 2, 4, 6$) were selected in order to investigate the effect of the length of the pendant group. The chronoamperometric response for a diffusion-controlled process can be described by the Cottrell equation:

$$i = nFACD^{1/2}\pi^{-1/2}t^{-1/2} \qquad (1)$$

where i is the current, F the Faraday constant, A the area of the working electrode, C the concentration of the monomer, D the diffusion constant, and t the time. In these cases, the transient current decreases initially as expected from eq 1 and then reaches a plateau (Figure 1). The limiting current is related sigmoidally to the potential with $E_{1/2}$ corresponding to the second redox potential of the polymer $E^{\circ\prime}_2$ (viz. the emeraldine–pernigraniline transition), according to the following equation:

$$i = i_L[1 + \exp(nF/RT)(E_{1/2} - E)]^{-1} \qquad (2)$$

These results mean that there is a nucleation and growth of a conducting phase on the electrode surface as also indicated by the nucleation loop observed in the cyclic voltammogram.[25-27] In other words, there is a polymer deposit onto which the monomer is oxidized.

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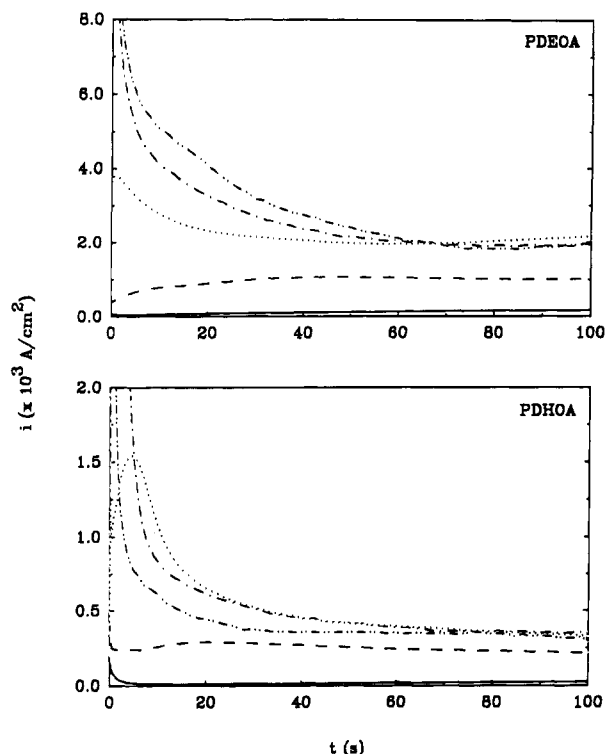

Figure 1. Current–time transients for the polymerization of 2,5-diethoxyaniline (DEOA) and 2,5-dihexyloxyaniline (DHOA). The solution was 0.05 M of monomers in 1 M $HClO_4$ (70%) and CH_3CN (30%). At $t = 0$ the potential was stepped from 0.45 (—), 0.50 (— — —), 0.55 (···), 0.60 (— · —), 0.65 V (— ··).

Indeed, it has been reported[27,28] that aniline oxidation is catalyzed by the fully oxidized polymer (pernigraniline). The initial decay of the current is due to the diffusion-controlled oxidation of the aniline to form the polymer, onto which aniline is oxidized catalytically. In agreement with this suggestion, and as reported for other polyconjugated materials,[25,26] the limiting current was found to increase as the monomer concentration increased (from 0.01 to 0.2 M) and as the potential of deposition is made more anodic (viz. until E_p). Moreover, the process is essentially controlled by the catalytic rate constant, since it has been found that there is no significant diffusion control of this process. Therefore, the limiting current is a measure of the catalytic activity of the polyaniline for monomer oxidation.

The CA sigmoidal transient was not observed when the monomer concentration was below 0.05 M. In this case, the current follows the $i = f(t^{-1/2})$ decay for a diffusion-controlled process and the current measured, at a given time increase with the applied potential showing a sigmoidal relationship with half-wave potential $E_{1/2}$ corresponding to the monomer oxidation potential. This result indicates that under this condition, no polymer deposit is formed (no nucleation loop was observed in the cyclic voltammograms). The sigmoidal transient was instead obtained when the monomer concentration was higher.

For poly(2,5-dimethoxyaniline) (PDMOA) a stable current is obtained when the applied potential is higher than 0.45 V and has a value of ca. 1.8 mA/cm², for a concentration of DMOA equal to 0.05 M. In the case of

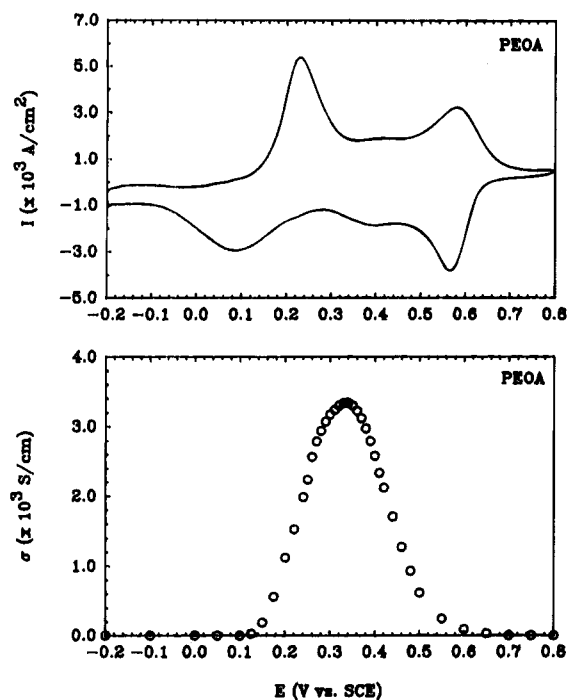(28) Manohar, S. R.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1991**, *41–43*, 711.

Figure 2. Cyclic voltammogram and in situ conductivity measurements (during the oxidation process) of poly(2-ethoxyaniline) (PEOA) in 1 M HCl.

Table 2. Summary of Some Physical Properties of the Polyaniline Derivatives

polymers	$\lambda_{max}{}^a$ (nm)	$E°'_1$ (V vs SCE)	$E°'_2$ (V vs SCE)	σ (S/cm)	DP
PANI	315	0.12	0.70	5	80[b]
PMOA	325	0.08	0.62	0.1	80[b]
PDMOA	350	0.03	0.44	0.3	50[b]
PEOA	320	0.12	0.59	3×10^{-3}	35
PDEOA	355	0.07	0.50	0.1	20
PBOA	340	0.09	0.58	2×10^{-3}	25
PDBOA	370	0.09	0.46	7×10^{-4}	15
PHOA	340	0.09	0.56	1×10^{-5}	15
PDHOA	375	0.09	0.53	1×10^{-6}	10

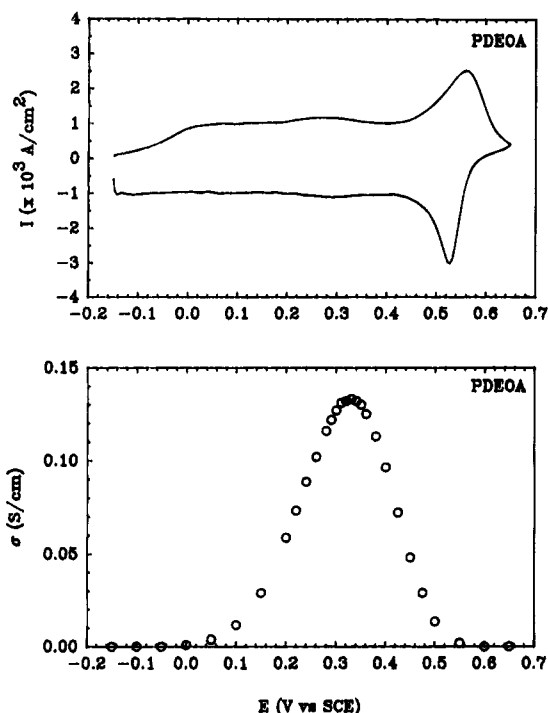*[a]* Of the leucoemeraldine form. *[b]* Data from ref 19.

Figure 3. Cyclic voltammogram and in situ conductivity measurements (during the oxidation process) of poly(2,5-diethoxyaniline) (PDEOA) in 1 M HCl.

poly(2,5-diethoxyaniline) (PDEOA), the nucleation was observed when the applied potential was higher than 0.5 V, showing a saturated current value of 1.7 mA/cm^2 for $C = 0.05$ M, which is comparable to the value found for PDMOA. As shown in Figure 1, when $E = 0.5$ V, the current is about the half of the transient, because only ca. 50% of pernigraniline is formed.

For poly(2,5-dibutoxyaniline) (PDBOA), the increase of the lateral chain length has a more dramatic effect. Indeed, the plateau occurs at a value of 0.4 mA/cm^2 for a 0.05 M concentration of the monomer, viz., the catalytic action is 4 times lower with respect to PDMOA and PDEOA. For poly(2,5-dihexyloxyaniline) (PDHOA) the increase of the side-chain length does not seem to alter the rate of polymerization with respect to PDBOA. Indeed, a saturated current of 0.3 mA/cm^2 was observed (Figure 2), which is comparable to the value found for PDBOA.

These chronoamperometric results suggest that an increase in the length of the alkoxy side groups decreases the rate of polymerization. Two factors may explain these results: first, the steric hindrance of both butoxy or hexyloxy groups may limit the couplings; second, the hydrophobicity of the polymer, which is higher compared to that of PDMOA and PDEOA, may favor the precipitation of oligomers. This account for the low degree of polymerization (DP) values observed for these materials (Table 2).

Cyclic Voltammetry and UV−Visible Spectroscopy of the Polymers. As shown in Figures 2−5, in acidic conditions poly(2-alkoxyanilines) and poly(2,5-dialkoxyanilines) exhibit a electrochemical behavior similar to that of polyaniline, ca. two quasi-reversible redox processes with a third redox couple between these processes. This third peak was related to irregular couplings,[29] degradation,[30] dimers, and oligomers.[31] As stated in a recent study,[19] the third redox couple seen in monosubstituted polyanilines may be related to

structural defects (irregular couplings), whereas in disubstituted polyanilines, it may be related to the presence of dimers and oligomers trapped in the polymer matrix.

The incorporation of electron-donating groups on the ring, which decreases the oxidation potential of the monomers, acts in the same direction for the redox potential $E°$ of the corresponding polymers (Table 2). The first redox process of poly(2-alkoxyanilines) occurs around 0.1 V. These fully reduced polymers (viz. the *leucoemeraldine* form) display also an absorption maximum at longer wavelengths, compared to the unsubstituted polyaniline: from 315 nm for PANI, to 325 nm for PMOA and PEOA, to 340 nm for PBOA and PHOA. Once again, this behavior can be related to the electron-donating effects of the alkoxy groups, which go in the

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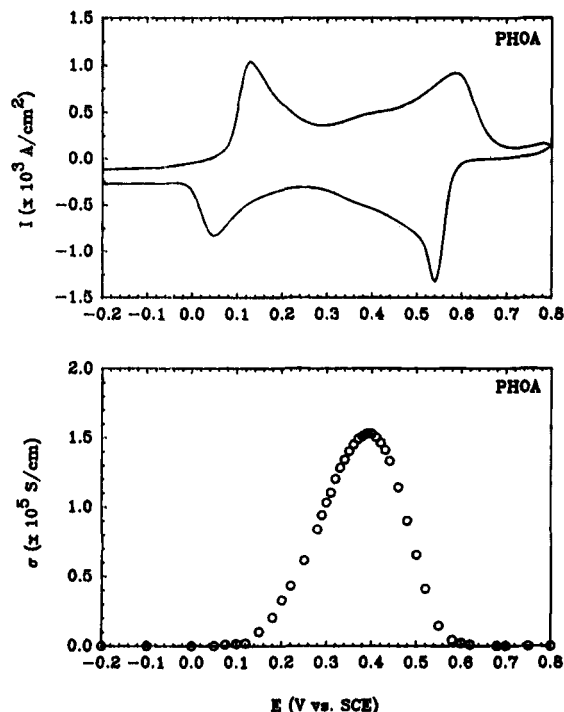(31) Hand, R. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 850.

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Figure 4. Cyclic voltammogram and in situ conductivity measurements (during the oxidation process) of poly(2-hexyloxyaniline) (PHOA) in 1 M HCl (70%) and CH_3CN (30%).
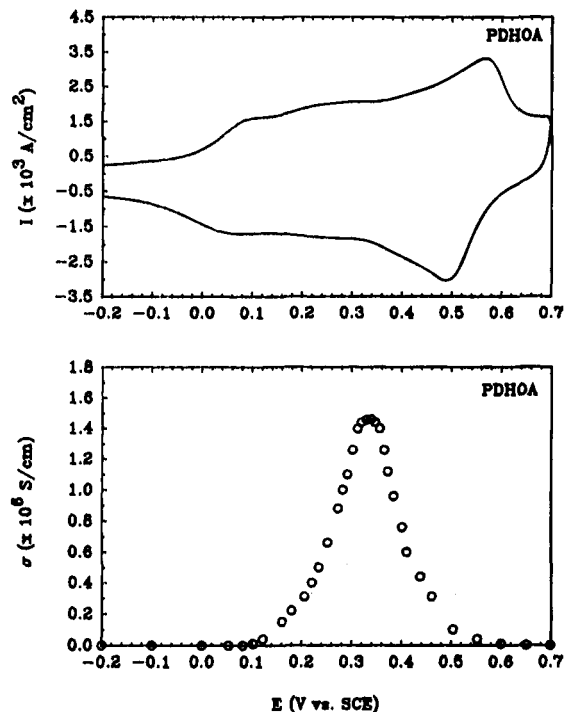

Figure 5. Cyclic voltammogram and in situ conductivity measurements (during the oxidation process) of poly(2,5-dihexyloxyaniline) (PDHOA) in 1 M HCl (70%) and CH_3CN (30%).

same sense that the potential of the first redox process. It is important to underline that for longer substituents ($n = 4$ and 6, Scheme 1), the absorption maximum is characterized by a broad band. A similar red-shift is also found in fully reduced poly(2,5-dialkoxyanilines): from ca. 350 nm for PDMOA and PDEOA to ca. 370 nm for PDBOA and PDHOA. The red shift may be attributed to an increase of the electronic effects with the length of the alkoxy groups, which seems to saturate

when $n \geq 4$. As regard the polyanilines bearing butoxy or hexyloxy groups, the red shift is found to be more pronounced. This may be explained by the interdigitation of these longer side chains, which stabilizes a slightly more planar conformation of the backbone.

It is important to point out that such a red-shift is also observed for the neutral half-oxidized polymers (viz. the *emeraldine-base* form). However, only the absorption maxima of the fully reduced polymers are reported in Table 2, since these values may be directly related to the potential of the first redox transition ($E^{o'}_1$). In addition, the steric effects of the side chains which affect the electrical conductivity of the charged half-oxidized polymer (viz. the *emeraldine-salt* form), may be correlated to the λ_{max} of the fully reduced form, since the leucoemeraldine form shows a molecular structure which is close to the emeraldine-salt form. Indeed, each structures have benzenoid rings, whereas quinoid rings are present in the emeraldine-base structure.

A weak dependence of the length of the lateral chain has been observed for disubstituted polyanilines. Indeed, the first redox process occurs at a very low potential for PDMOA, whereas an increase has been observed with the increase of the lateral chain length: namely, from 0.03 to 0.09 V (Table 2), indicating a minor modification of the backbone conformation. In all cases, these values still remain lower than those found in PANI. The electron-donating effects of the alkoxy groups should decrease the redox potential, which is actually observed for the first members of the series. However, there is a progressive increase of the potential with the length of the substituents, which seems to saturate with longer side-chains ($n = 4$ and 6, Scheme 1), namely, at 0.09 V vs SCE (Table 2). This might be related either to an increase of the torsional angle between the monomeric units in the polymer backbone or to a decrease of the degree of polymerization. For the first point, it has been reported that the presence of substituents can induce nonplanar conformation that increases the redox potential and the bandgap values.[32] However, it has been reported that the steric hindrance of alkoxy groups was not important in polythiophenes.[33] This increase of the redox potential may be better explained by a decreased Coulombic interaction between the polycationic chain and the anion as the alkoxy group becomes larger, as recently found for poly(dialkylcyclopentadithiophenes).[34] On the other hand, this increase of the value, as well as its stabilization may also be related to the lower molar masses in disubstituted polyanilines. This is further confirmed by chronoamperometric and steric exclusion chromatography experiments (Table 2).

The optical properties of the electrochemically prepared polyaniline films on an ITO electrode were studied by in situ spectroelectrochemistry in 1 M HCl (for $n = 1$ and 2, Scheme 1) or in a mixture of 1 M HCl (70%) and CH_3CN (30%) (for $n = 4$ and 6, Scheme 1). Figure 6 show the absorption spectra of PDHOA, at different electrochemical potentials. As reported for PANI[2,3,6] and other disubstituted polyanilines,[18] PDHOA exhibits multiple reversible color changes from yellow-orange to

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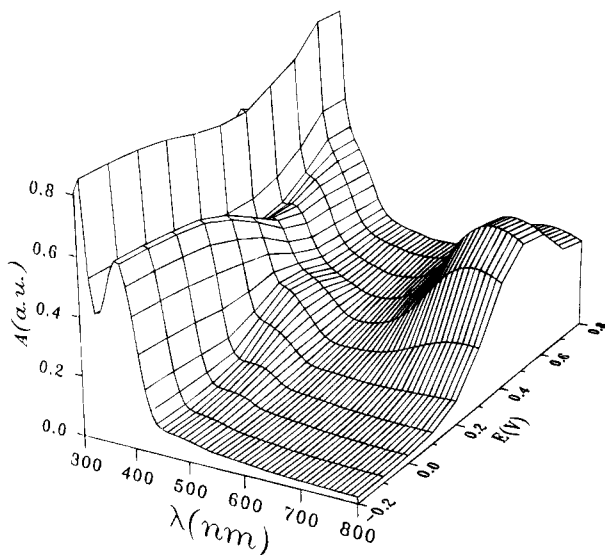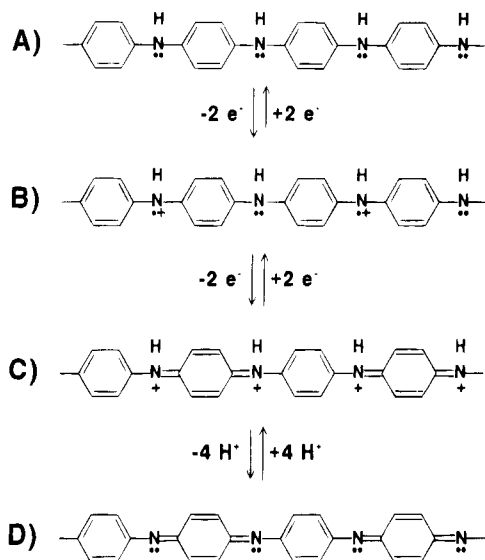
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Figure 6. Spectroelectrochemistry of PDHOA in 1 M HCl (70%) and CH₃CN (30%).

Scheme 2

green to blue-violet, as the potential is swept from −0.2 to 0.7 V. For the fully reduced polymer (Scheme 2, structure A), an absorption peak is observed near 375 nm, which is related to the π−π* (HOMO to LUMO) transition. Upon oxidation, new peaks appear at ca. 450 and ca. 820 nm, at half-oxidation (emeraldine state), both being related to the presence of radical cations in the polymer backbone (Scheme 2, structure B).[35] Further oxidation to the pernigraniline form causes a disappearance of the 450 nm band and a shift of the 820 nm band to a shorter wavelengths (ca. 745 nm). The latter band seems to be related to the fully charged oxidized polymer (Scheme 2, structure C).[36] Similar results were also observed with PDBOA and poly(2-alkoxyanilines).

Conductivity of the Polymers. The results of conductivity measurements are listed in Table 2. The

electrochemically synthesized poly(alkoxyanilines) and poly(dialkoxyanilines) showed conductivities ranging from 10⁻¹ to 10⁻⁶ S/cm, depending upon the substitution pattern. To measure clearly the maximum conductivity of these polymers, in situ conductivity measurements were also performed. As previously reported for polyaniline and its derivatives,[19,36,37] these new polyaniline derivatives display a finite window of conductivity (Figures 2−5), with a maximum close to values obtained using the four-probe technique (ex situ). As expected, the materials are insulating in the fully reduced form (leucoemeraldine state), reach a conductivity maximum at a potential intermediate between the two redox processes (emeraldine state), and become insulating again in the fully oxidized form (pernigraniline state).

In all cases, the conductivity (of the emeraldine state) is lower than that of PANI and decreases as the length of the lateral chain increases. We must state that the trend is not perfectly clear; in any case, the longer the chain of the lateral group, the lower the conductivity, with some exceptions (see below).

It is well-known that interchain hopping is the dominant transport in these materials.[38a] In agreement with this transport mechanism, the conductivity values were found to be independent upon the average molecular weight.[38b] Hence, the presence of long substituents increases the interchain distance, which reduces the transport of the charge carriers between the polymer chains (hopping) and gives thus lower electrical conductivity values. It is noteworthy that the ring-twisting might also explained the lower conductivity, of the ring-substituted derivatives.[32] However, as stated above the steric effect of alkoxy substituents is not so significant,[19,33] which is further confirmed by the red-shift of the absorption maximum (Table 2).

For short substituents, such as methoxy and ethoxy groups, the presence of a second alkoxy group at the 5-position gives materials with improved conductivities: e.g., PDMOA (σ ~ 0.4 S/cm) vs PMOA (σ ~ 0.1 S/cm) and PDEOA (σ ~ 10⁻¹ S/cm) vs PEOA (σ ~ 10⁻³ S/cm). These results may be explained by a more regular structure in disubstituted polyanilines, as proposed in a previous study.[19] Materials with longer substituents do not display any improvement of the conductivity: e.g., PDBOA (σ ~ 10⁻⁴ S/cm) vs PBOA (σ ~ 10⁻³ S/cm) and PDHOA (σ ~ 10⁻⁶ S/cm) vs PHOA (σ ~ 10⁻⁵ S/cm). Once again, these results can be related to an increase of the interchain distance. Obviously, the interchain distance is more important with the presence of a second long substituent, and this should explain why PDHOA is less conducting than PHOA. Moreover, as reported for polythiophene derivatives,[39] the diluting effects of the charge carriers caused by the presence of insulating alkoxy groups in the polymer chain should also be considered.

These results, together with those reported previously on methyl- and methoxy-substituted polyanilines,[19] have demonstrated that whatever the number and the length

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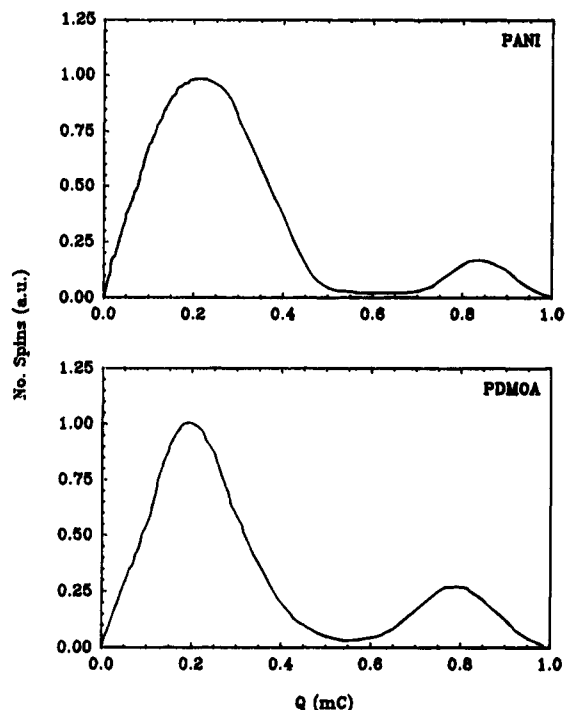
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Figure 7. Spin concentration vs oxidation charge for PANI and PDMOA in CH_3CN + 0.1 M TEAP.

of the side chains, the use of alkoxy groups gives materials with an electrical conductivity higher than that found with poly(alkylanilines): poly(2,5-dimethoxyaniline) (10^{-1} S/cm) vs poly(2,5-dimethylaniline) (10^{-6} S/cm)[19,23] and poly(2-hexyloxyaniline) (10^{-5} S/cm) vs poly(2-hexylaniline) (10^{-7} S/cm).[16g]

In Situ ESR of the Polymers. To investigate the effect of the substitution on the paramagnetic behavior of the polymers, in situ ESR measurements were carried out on PMOA and PDMOA, and compared to those obtained with PANI.

Figure 7 shows the ESR signal as a function of the reversible charge for PANI and PDMOA. As one can see, the disubstituted polymer displays a behavior similar to that of the unsubstituted polyaniline.[40-42] Upon oxidation, paramagnetic species are produced with two maximum spin concentrations in correspondence with the two oxidation processes. From the relationship between the ESR signal intensity and the redox charge, the first signal appears at around one-quarter of the oxidation charge and the second signal appears at around three-quarters of the oxidation charge, whereas spin activity drops to lower values when conductivity reaches its maximum value (at one-half of the oxidation charge, viz. emeraldine state).

The first oxidation step yields radical cations,[35] although the in situ ESR signal shows an increase followed by a decrease. The ESR signal decrease during the oxidation of conducting polymers (e.g., polythiophene and polypyrrole) is generally interpreted as a polaron–

bipolaron recombination,[43,44] but this is quite different in the case of PANI: this decrease results from spin–spin interactions between radical cations.[41] However, this cannot be viewed as a π-dimerization, which by definition is an interchain process. Indeed, it has been found that the π-dimerization process does not occur during the oxidation of oligoanilines: the position of the absorption bands of radical cations in phenyl-protected oligomer did not vary with the concentration.[45] Moreover, a linear relationship was observed between the concentration of the oxidized oligoanilines and ESR measurements.[45] Consequently, the pairing can be described as an intrachain phenomenon.

Essentially, within the experimental errors, the addition of one or two methoxy substituents did not modify the ratio of the maximum number of spins n_s to the total injected electrons n_e (n_s/n_e 0.09, i.e., ca. 1 spin/12 monomeric units[46]) of the first oxidation process. The main difference appears in the relative intensity of the two maximum spin concentrations. For the unsubstituted PANI, the intensity of the first signal is 6:1 with the second signal, whereas it decreases to ca. 3:1 in PMOA and PDMOA, which indicates an absolute increase of the maximum spin concentration at the second oxidation process. The nature of the second paramagnetic state of PANI was not clear because of the instability of fully oxidized PANI.[30,40b,42] This is not the case for these new materials, since the presence of electron-donating groups gives more stable polymers, by lowering the redox potentials. As mentioned above, the paramagnetic species responsible for the first ESR maximum can be attributed to radical cations (polarons) formed in the leucoemeraldine–emeraldine transition.[35] We may infer that the second paramagnetic species is related to similar polarons produced at the emeraldine–pernigraniline transition. This suggestion is supported by the observation that the g values for the two species are the same (2.0027). It is then proposed that these radicals are related to a depairing process during the emeraldine–pernigraniline transition.

Moreover, the ESR signal line width can bring also valuable information. The line width of both signals increases with the number of the substituents in the ring, from 1.5 (PANI) to 1.8 (PMOA) to 2.4 G (PDMOA). According to previous studies,[40,47,48] a larger ESR line width is associated with low mobility (localization) of the spin. In other words, this indicates that the radical cations are more localized as the number of substituents on the aniline ring increases. Similar results were recently reported for poly(2-methylaniline), where the localization effect was related to an increase separation between neighboring chains.[48] Furthermore, the in-

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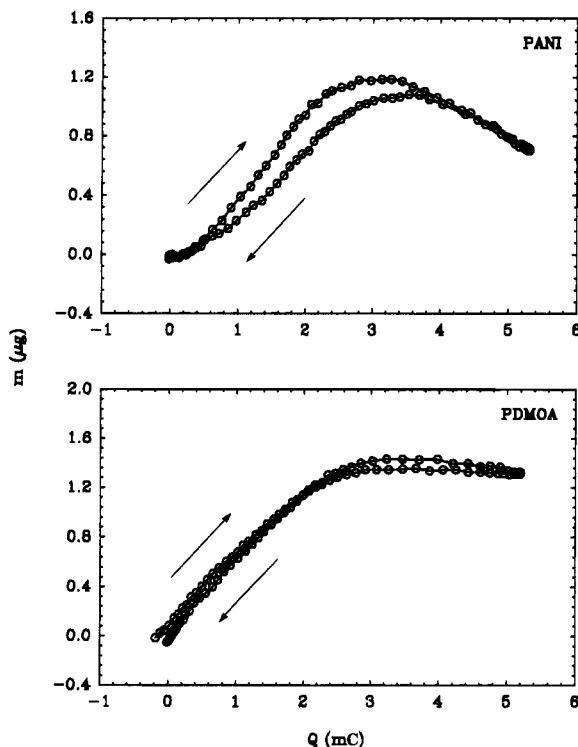
Figure 8. Mass change during the oxidation and reduction processes of PANI and PDMOA in 0.1 M HClO₄.

creased localization is reflected in a much smaller conductivity value for substituted polyanilines (see above).

Ion Exchange in the Electrochemical Doping of the Polymers. The ion exchange during the oxidation of the polyanilines was measured with the electrochemical quartz crystal microbalance (EQCM). Similar investigations were previously reported for PANI in nonaqueous solvents and in aqueous acid.[49-51] We have tested the behavior of the first members of the series, namely, PMOA and PDMOA, and compared the results with those obtained on PANI.

In acetonitrile (+0.1 M TEAP), PANI, PMOA, and PDMOA exhibit the same behavior: there is a linear increase of the mass with the charge during both oxidation processes, with a slope of ca. 100 g/mol of electrons. If it is assumed that no solvent transport occurs during both oxidation processes,[50,51] this mass increase is simply related to insertion of perchlorate counterions ($M_W = 99.5$ g/mol). Moreover, this is a proof that, in organic conditions, the pernigraniline form of these polyanilines is protonated (stucture C, Scheme 2).[49]

As reported in the literature,[50,51] the $m = f(Q)$ plots for PANI in acidic solutions show an increase of the mass with the oxidation charge during the first oxidation process and a decrease of the mass during the second oxidation process. We have found that for pH ≤ 1, the slopes are ca. 50 and ca. −30 g/mol, respectively (Figure 8). Assuming, once again, that no solvent transport occurs during both oxidation processes,[50,51] the mass increase of 50 g/mol is related to insertion of one

perchlorate anion per two released electrons, indicating that, since the emeraldine form contains one perchlorate anion per two monomeric units, the leucoemeraldine form is partially (50%) protonated, in agreement with the results reported by Buttry et al.[50] The mass decrease of 30 g/mol is related to the expulsion of both protons and anions; since this value is much lower than 100, we can assume that the pernigraniline form is still protonated (one-third of the monomeric units). At higher pH (2–3), the slope found are ca. 100 and −50 g/mol of electrons. These values indicate that at higher pHs, the leucoemeraldine is unprotonated, but the pernigraniline form remains partially protonated (one-quarter of the monomeric units).

The addition of an electron-donating group at the 2-position (PMOA) influences the ion exchange during the electrochemical doping. Indeed, an increase of the mass is observed during the first oxidation process with a slope of ca. 50 g/mol of electrons at pH ≤ 1 and ca. 100 g/mol of electrons at higher pH values. On the other hand, the mass does not change during the second oxidation process (zero slope). This means that all perchlorate ions inserted during the leucoemeraldine–emeraldine transition remain in the polymer matrix during the emeraldine–pernigraniline transition. Unlike PANI, the pernigraniline form of PMOA is protonated one unity over two.

PDMOA behaves similarly to PMOA for the second oxidation process, viz. no change in the mass is detected: one monomeric unity over two is protonated in the pernigraniline form (Figure 8). Unlike PMOA, where the leucoemeraldine form is protonated only at pH ≤ 1, fully reduced PDMOA is found to be partially protonated at pH ranging between −0.5 and 3. In all cases, the slope for the first oxidation process is 50 g/mol (Figure 8).

The EQCM differences of the poly(alkoxyanilines) with PANI, namely, the reduced mass increase during the first oxidation step and the absence of mass changes during the second, are explained by a progressive increase of the polymer basicity, both in the leuco and in the pernigraniline forms, related to the presence of electron-donating alkoxy groups. These results are in good agreement with the electronic spectra of these polymers.

On the other hand, the use of the quartz crystal microbalance has demonstrated that alkoxy groups allow one to obtain a protonated pernigraniline form. It is well-known that the fully reduced (structure A, Scheme 2) and deprotonated oxidized (structure D, Scheme 2) forms are insulating, whereas the half-oxidized from (structure B, Scheme 2), which is charged, is conducting.[3-5] By analogy, a fully charged oxidized polyaniline (structure C, Scheme 2) was expected to be conducting. As shown in Figures 2–5, charged oxidized polyanilines are found to be insulating. These results are in good agreement with those reported previously on poly(alkylanilines).[36] It was believed that this insulating behavior was related to a strong localization of the charge carriers.[36] However, it was not clear whether protonated imines in structure C might act as charge carriers, even in a partially protonated polyaniline.[36] The EQCM experiments have shown that fully oxidized poly(alkoxyanilines) may be partially protonated. These results combined to in situ conduc-

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tivity measurements indicate clearly that protonated imines do not act as efficient charge carriers. Thus, an insulating or conducting behavior is also related to the nature of the charge carriers.

Conclusion

Novel alkoxy derivatives of polyanilines have been prepared electrochemically, namely, poly(2,5-diethoxy-aniline) (PDEOA), poly(2-butoxyaniline) (PBOA), poly-(2,5-dibutoxyaniline) (PDBOA), poly(2-hexyloxyaniline) (PHOA) and poly(2,5-dihexyloxyaniline) (PDHOA), with electrical conductivity values ranging from 10^{-1} to 10^{-6} S/cm.

This study has shown that double-substitution, at the 2- and 5-positions, displays some advantages, in terms of regularity, electrical conductivity and basicity. Indeed, with short alkoxy groups, materials with an improved conductivity by 2 orders of magnitude were obtained: e.g., PDEOA vs PEOA. However, longer alkoxy groups, such as butoxy and hexyloxy, increase the distance between the polymer chains, thus giving a lower conductivity. Moreover, the increase of the hydrophobicity of the monomers yields low molecular weight polymers. Double substitution with alkoxy substituents increases the stability of the fully oxidized form, by lowering the redox potential. This made then possible the investigation of the charge carriers in the pernigraniline form. In fact, the second ESR signal is not related to degradation, but rather to a depairing process during the formation of the quinonediimine structure. EQCM data revealed a progressive increase of the polymer basicity (from PDMOA to PMOA to PANI), giving partially protonated structures, both in the leucoemeraldine and in the pernigraniline forms. We have shown, by in situ conductivity measurements, that these structures are insulating and consequently the conducting behavior is also related to the nature of the charge carriers.

Finally, all these novel polyanilines derivatives were found to be soluble in chloroform and in tetrahydrofuran. This property will be exploited by processing these new materials, using the Langmuir–Blodgett technique, to make negative photoresists for microlithography applications. Moreover, these materials might be excellent candidates for the fabrication of light-emitting diodes. All these properties are currently under investigation.

Experimental Section

Chemicals and Reagents. Aniline (ANI), 2-methoxyaniline (MOA), 2-ethoxyaniline (EOA), 2,5-dimethoxyaniline (DMOA), 2,5-diethoxynitrobenzene, 1-iodobutane, 1-iodohexane, 2-nitrophenol, and palladium on activated carbon were obtained from Aldrich Co. All other chemicals were reagent grade and used as received.

Synthesis of the Monomers. 2,5-Disubstituted anilines were prepared in three steps: first, the oxidation of 2-nitrophenol by ammonium persulfate, in alkaline solution, yielded 2-nitro-1,4-hydroquinone;[52] second, double alkylation of this compound with the desired iodoalkane[53] yielded 2,5-disubstituted nitrobenzenes; finally, the hydrogenation of the nitro compounds, with 10% Pd on charcoal in ethanol,[54] gives the

desired aniline. The latter procedure is illustrated for the preparation of 2,5-dihexyloxyaniline (DHOA), since to our knowledge it is reported for the first time: A mixture of de 2,5-dihexyloxynitrobenzene (2.883 g, 8.9 mmol) and 10% of Pd/C (0.960 g) in absolute ethanol (10 mL) was saturated with hydrogen for 30 min and then stirred under a static pressure for 30 h; 2.291 g (yield 88%) of 2,5-dihexyloxyaniline was obtained:

^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.74 (1H, d, J = 8.93 Hz), 6.69 (1H, dd, J = 8.79 and 2.89 Hz), 6.44 (1H, d, J = 2.89 Hz), 6.18 (2H, s), 3.94 (2H, t, J = 6.68 Hz), 3.87 (2H, t, J = 6.50 Hz), 1.87–1.64 (4H, m), 1.54–1.21 (12H, m), 0.99–0.78 (6H, m). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 153.38, 142.79, 130.89, 112.76, 107.32, 105.61, 69.17, 68.34, 31.47, 31.42, 29.18, 25.59, 25.56, 22.46, 13.90. IR (KBr, cm^{-1}) 3475, 3370. MS (EI/HR) 293.2354 (δ = 2.6 ppm).

We present below the spectral characteristics of the other disubstituted anilines synthezised:

2,5-Dibutoxyaniline (DBOA):[55] ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.68 (1H, d, J = 8.79 Hz), 6.34 (1H, d, J = 2.81 Hz), 6.23 (1H, dd, J = 8.68 and 2.90 Hz), 3.94 (2H, t, J = 6.29 Hz), 3.88 (2H, t, J = 6.50 Hz), 1.95–1.62 (4H, m), 1.59–1.36 (4H, m), 1.04–0.89 (6H, m). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 153.57, 140.74, 137.20, 112.31, 102.50, 102.26, 68.42, 67.61, 31.29, 31.19, 19.05, 18.98, 13.57. IR (neat, cm^{-1}) 3480, 3370. MS (EI/HR) 237.1729 (δ = 3.2 ppm).

2,5-Diethoxyaniline (DEOA):[56] Mp 82–83 °C (lit.[56a] mp 84 °C and lit.[56b] mp 81–82 °C). ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.69 (1H, d, J = 8.75 Hz), 6.36 (1H, d, J = 2.91 Hz), 6.24 (1H, dd, J = 8.75 and 2.94 Hz), 4.00 (2H, q, J = 6.97 Hz), 3.95 (2H, q, J = 6.97 Hz), 3.80 (2H, s), 1.40 (3H, t, J = 7.01 Hz), 1.37 (3H, t, 7.00 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 153.53, 141.00, 136.84, 112.67, 103.17, 102.76, 64.48, 63.59, 14.98, 14.84. IR (KBr, cm^{-1}) 3470, 3370. MS (EI/HR) 181.1103 (δ = 0 ppm).

2-Substituted anilines were obtained by alkylation of 2-nitrophenol,[53] followed by the reduction of the resulting 2-alkoxynitrobenzene.[54] The spectral data of these monosubstituted anilines are also reported below:

2-Hexyloxyaniline (HOA):[55] ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.86–6.72 (5H, m), 4.03 (2H, t, J = 6.57 Hz), 1.87 (2H, m), 1.57–1.39 (6H, m), 0.99 (3H, t, J = 6.96 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 146.50, 135.94, 120.62, 118.17, 114.80, 111.16, 67.92, 31.35, 29.09, 25.55, 22.35, 13.77. IR (neat, cm^{-1}) 3485, 3390. MS (EI/HR) 193.1467 (δ = 0.2 ppm).

2-Butoxyaniline (BOA):[57] ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.93–6.86 (5H, m), 4.07 (2H, t, J = 6.41 Hz), 1.91 (2H, m), 1.65 (2H, m), 1.12 (3H, t, J = 7.40 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 146.50, 135.03, 120.39, 118.36, 115.00, 110.95, 67.37, 30.95, 18.86, 13.40. IR (neat, cm^{-1}) 3480, 3380. MS (EI/HR) 165.1156 (δ = 1.7 ppm).

Characterization. NMR spectra were performed in deuterated chloroform or acetone on a 300 MHz Varian instrument. The infrared spectrum were run on a Perkin-Elmer 783 infrared spectrophotometer. The molecular mass of the synthesized amines was determined by mass spectrometry (MS) using a electronic impact high-resolution (EI/HR) Kratos MS-50 TCTA Manchester UK instrument.

Synthesis of the Polymers. Syntheses were performed with freshly prepared monomers. Electrodeposition of polymer films was carried out by cycling the electrochemical potentials at a scan rate of 100 mV/s, under stirring. Bulk polymers were produced by electrolysis at a constant potential. In all cases, the polymers were recovered at the emeraldine state to avoid any degradation of the polymers into quinones.[30] The polymers were washed with methanol and an aqueous acid solution to yield a dark green powder.

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The electrolyte solution used to obtain polyaniline (PANI), poly(2-methoxyaniline) (PMOA) and poly(2-ethoxyaniline) (PEOA) was an aqueous solution of 0.1 M of the monomer in 1.0 HCl, whereas it was an aqueous solution of 0.05 M of the monomer in 1.0 M HClO₄, for poly(2-butoxyaniline) (PBOA) and poly(2-hexyloxyaniline) (PHOA).

Poly(2,5-diethoxyaniline) (PDEOA) was elecropolymerized according to the procedure reported for poly(2,5-dimethoxy-aniline) (PDMOA).[18] Poly(2,5-dibutoxyaniline) (PDBOA) and poly(2,5-dihexyloxyaniline) (PDHOA) were obtained following the electrooxidation of a solution of 0.05 M of the monomer in a mixture of 1.0 M HClO₄ (70%) and CH₃CN (30%).

Apparatus and Physical Measurements. Electrochemical polymerizations were performed at 25 °C, under nitrogen, in a three-compartment cell. The working (anode) and auxiliary electrodes (cathode) were Pt foils. The reference electrode was a saturated calomel electrode (SCE). A platinum sheet (15 cm²) was used in preparative electrolysis.

Electrochemical measurements were carried out using a potentiostat/galvanostat EG & G PAR Model 273. At the beginning of each electrochemical study, films were washed with acetone to remove oligomers, after a base treatment. A treatment of the emeraldine-salt form with NH₄OH 10% (v/v)[58] (PANI, PMOA, PEOA, PDMOA, and PDEOA) or with a mixture of NH₄OH (50%) + CH₃CN (50%) (PBOA, PHOA, PDBOA, and PDHOA) gives rise to the emeraldine-base form.

Chronoamperometry measurements were performed with disubstituted polymers, in a mixture of 1 M HClO₄ (70%) + CH₃CN (30%); the working electrode was a Pt minidisc electrode (2.8 × 10⁻³ cm²).

Cyclic voltammograms were recorded at a scan rate of 100 mV/s in 1 M HCl for PANI, PMOA, PEOA, PDMOA, and PDEOA and in a mixture of 1 M HCl (70%) + CH₃CN (30%) for PBOA, PHOA, PDBOA, and PDHOA. Cyclic voltammograms of cast films are identical to those of electrochemically prepared films. Redox potential values (*E*°′) were calculated as the average of anodic and cathodic peak potentials.

For spectroelectrochemistry measurements, an indium–tin oxide (ITO)-coated glass electrode (Applied Films 20–50 Ω/□) and a Pt wire were used as the anode and the cathode, respectively. Electronic absorption spectra were taken using a UV–vis diode array spectrophotometer (HP 8452A). All measurements were started at the reduced (leucoemeraldine) state, ca. −0.2 V, and polymers were kept at the desired electrochemical potential for 2 min.

Protonic acid doping[3] was performed by treating pristine polymers with 1 M HCl (PANI, PMOA, PEOA, PDMOA, and PDEOA) or in 1 M HCl (70%) + CH₃CN (30%) (PBOA, PHOA, PDBOA, and PDHOA), leading the emeraldine-salt form. Conductivity measurements of pressed pellets (thickness 0.24–0.50 mm) of these acid-doped polymers were performed using the four-probe technique. In situ conductivity experiments were performed with a two-band microelectrode,[59] according to the procedure described elsewhere.[19] Plots of conductivity (σ) vs the oxidation potential (*E*) were calibrated using the conductivity value obtained from the four-probe technique, in

air (ca. 0.35 V/SCE).

Electrochemical quartz crystal microbalance (EQCM) were carried out with a gold-coated AT-cut quartz electrode (0.35 cm²), resonating at 6 MHz, onto which the polymers were deposited potentiodynamically, according to the procedure described elsewhere.[60] The oscillator was homemade, and the frequency counter was a Hewlett-Packard 5316B. Calibration of the quartz crystal microbalance was performed with silver deposition from a 10⁻² M solution of AgNO₃ in CH₃CN + 0.1 M tetraethylammonium perchlorate (TEAP). The voltammetric apparatus was coupled to a 731 digital integrator. Data were collected using a microcomputer with a homemade analyzing software, from which frequency changes Δν were monitored as mass changes Δm. EQCM experiments were performed in CH₃CN + 0.1 M TEAP and in HClO₄ at pH ranging from −0.5 to 3 (1.0, 0.1, 10⁻² M + 9 × 10⁻² M NaClO₄ and 10⁻³ M + 9.9 × 10⁻² M NaClO₄).[61]

In situ electron spin resonance (ESR) experiments were carried out in CH₃CN + 0.1 M TEAP as supporting electrolyte. The working electrode was a Pt wire (0.5 cm length, 0.05 cm² area) polymer-coated to a thickness of ca. 1 μm. The wire was inserted in an ESR quartz tube (2 mm diameter) bearing a Pt counter electrode at the bottom and a silver quasi-reference electrode at the top. Spectra were run on a Brucker Er 100D X-band spectrometer and simultaneous recording of the ESR signal and the current vs the applied voltage on a HP 7046A dual-trace recorder.[62] Absolute spin calibration was performed with VOSO₄·5H₂O crystals.

The degree of polymerization of the polymers was determined by steric exclusion chromatography (SEC), using solutions made with the emeraldine-base form (2.5 mg/mL) in tetrahydrofuran. SEC experiments were performed at 30 °C with a Waters apparatus using a series of three ultrastyragel columns with upper porosity limits of 10², 5 × 10², and 10³ Å. The calibration curve was obtained by running monodispersed polystyrene standards.

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