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Stabilization and Characterization of Pernigraniline Salt: The "Acid-Doped" Form of Fully Oxidized Polyanilines

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ABSTRACT: The electrochemical polymerization of ring-substituted anilines (e.g., 2-methylaniline and 2-ethylaniline) gave uniform electroactive polymer films which were analyzed by cyclic voltammetry and in-situ spectroelectrochemistry in different acidic conditions. It has been found that the fully oxidized polymers undergo an acid–base transition at pH ~0 which leads to the formation of a protonated (bipolaronic) form. This electronic structure is characterized by an absorption band at 630 and 680 nm for poly(2-methylaniline) and poly(2-ethylaniline), respectively. A similar structure has also been obtained in the fully oxidized poly(*N*-methylaniline), and this bipolaronic form exhibits a maximum of absorption at 770 nm, whatever the pH of the electrolyte. However, in-situ conductivity measurements have revealed an insulating behavior for this charged and fully oxidized form, whereas the partially oxidized (polaronic) structure is conducting. These results are explained by a strong localization of the charge carriers in the fully charged polymers.

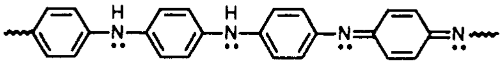
Introduction

Since the discovery that polyacetylene can be doped by oxidizing and reducing agents to metallic regimes,[1] many works have been devoted to the electrical properties of conjugated polymers.[2-5] Polyaniline (PANI) is certainly one of the most studied conjugated polymers[6] and was first reported in 1862 by Letheby.[7] In 1910, PANI was described as an octamer existing in four different oxidation states.[8] This material was analyzed later by de Surville et al.,[9] but it is only recently that PANI has attracted considerable interest because of its stability in the presence of oxygen and water and its unusual electrical and optical properties.[5,10-12] Indeed, upon chemical and electrochemical doping, PANI shows reversible insulator-to-metal transitions and electrochromic effects (pale yellow–green–blue–violet) which can be useful for the development of light-weight batteries,[13-15] electrochromic display devices,[16,17] sensors,[18-20] diodes, and transistors.[11,21,22]

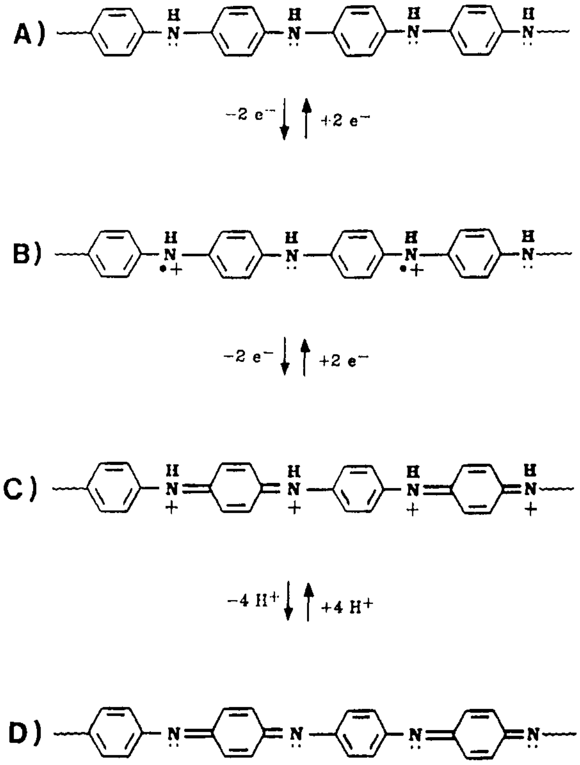
However, the main disadvantages of this polymer are its insolubility in common organic solvents and its infusibility. It has been found that ring-substituted (alkyl and alkoxy)[23-28] and *N*-alkyl-substituted polyanilines[29a-33] are more soluble than unsubstituted PANI, but, on the other hand, they exhibit lower molar masses and lower electrical conductivities.

PANI and its ring-substituted derivatives are represented by the general following formula: $-[(\mathrm{B{-}NH{-}B{-}NH})_y(\mathrm{B{-}N{=}Q{=}N})_{1-y}]_n-$ where B denotes a benzenoid reduced unit and Q a quinoid oxidized unit. These polymers may exist in various oxidation states characterized by the ratio of amine to imine nitrogen atoms.[34-36]

When $y = 1$, the polymer is fully reduced (structure A, Scheme I) and is found to be insulating and yellow. It is called leucoemeraldine base. The half-oxidized polymer ($y = 0.5$) is called emeraldine base and has the following structure:



Scheme I



Upon protonic acid doping, this insulating violet polymer undergoes an internal redox reaction, the number of π electrons in the chains remaining constant, which gives a green conducting polymer,[37] named emeraldine salt (structure B, Scheme I). This structure can also be obtained by the oxidation of the leucoemeraldine in acidic conditions. Emeraldine salt may be viewed as a polaron lattice model[35,38] which confers metallic properties to the polymer. Finally, pernigraniline base (structure D, Scheme I) is the fully oxidized PANI form ($y = 0$) and is insulating and violet. It is obtained from the oxidation and the deprotonation of the polaronic lattice. It is important to note that these processes could involve the formation of an intermediate state (which is characterized by bipolarons;

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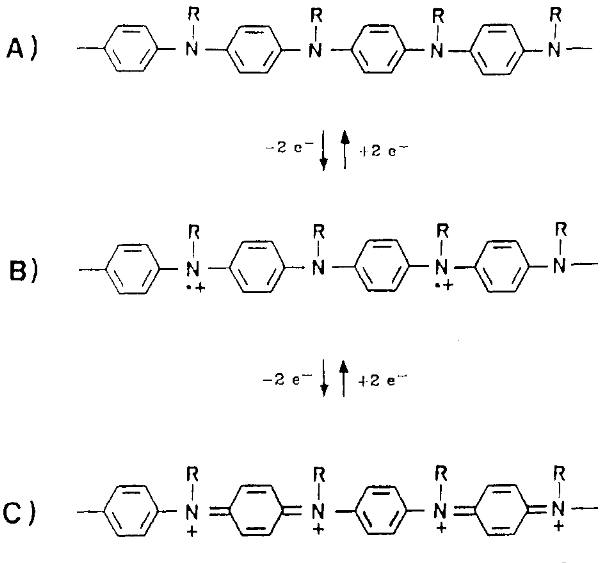
Scheme II



structure C, Scheme I) which represents the fully oxidized PANI in an acidic form.

The purpose of this work is the stabilization and the characterization of this charged fully oxidized lattice by two different approaches: (i) from the preparation of poly(alkylanilines) (e.g., poly(2-methylaniline) (P2MA) and poly(2-ethylaniline) (P2EA)) since the electron-donating effect of these substituents increases the basicity of the imine units[27] and, therefore, should stabilize the bipolaronic form at reasonable pH[39] and (ii) from the preparation of *N*-alkyl-substituted polyaniline derivatives (e.g., poly(*N*-methylaniline) (PNMA)) since, as previously shown,[29] the chemical particular structure of these polymers involves necessarily the formation of a charged fully oxidized form (structure C, Scheme II).

The characterization of the different electronic structures of these polymers as a function of the electrochemical potential and pH will also be part of the present work as well as the study analysis of the structure-property relationships occurring in these materials.

Experimental Section

Materials. Aniline derivatives: 2-methylaniline (2MA), 2-ethylaniline (2EA), and *N*-methylaniline (NMA) were obtained from Aldrich Chemical Co. and used without further purification. Hydrochloric acid, perchloric acid, sulfuric acid, and commercial buffer solutions (Fisher Scientific Co.) were used as received.

Electrochemical Synthesis. Electrochemical polymerizations were performed in a one-compartment cell equipped with 1-cm^2 platinum foils as working and auxiliary electrodes and a saturated calomel electrode (SCE) as the reference electrode; the given potentials are referred to SCE. The electrolyte was an aqueous solution of (a) a 0.5 M monomer in 3 M H_2SO_4 for 2MA and 2EA and (b) a 0.1 M monomer in 1 M $HClO_4$ for NMA. Oxidative electrodeposition of the polymer films was carried out by cycling the electrochemical potentials between 0.00 and 0.85 V vs SCE at a scan rate of 100 mV/s. The polymerizations were done at room temperature and under stirring. At the end of the polymerization, the potential was stopped at 0.3 V (emeraldine form) and the thin films were then carefully washed with the electrolyte solution without monomer.

Physical Measurements. Cyclic voltammograms were recorded at a scan rate of 100 mV/s and performed with a potentiostat/galvanostat EG&G PAR Model 273 in different acidic media. Commercial buffer solutions were used for pH $\geq$ 1.0, while for more acidic solutions, they were prepared from aqueous HCl solutions of different concentrations. The pH values given for these solutions are taken from Hammett acidity functions which reflect more accurately the proton-donating ability of highly acidic solutions.[40] The Coulombic yields are expressed as the ratio of reversibly exchanged charge Q_r to net irreversible charge Q_i, at the end of each cycle. The $E_{1/2}$ values were calculated as the average of anodic and cathodic peak potentials.

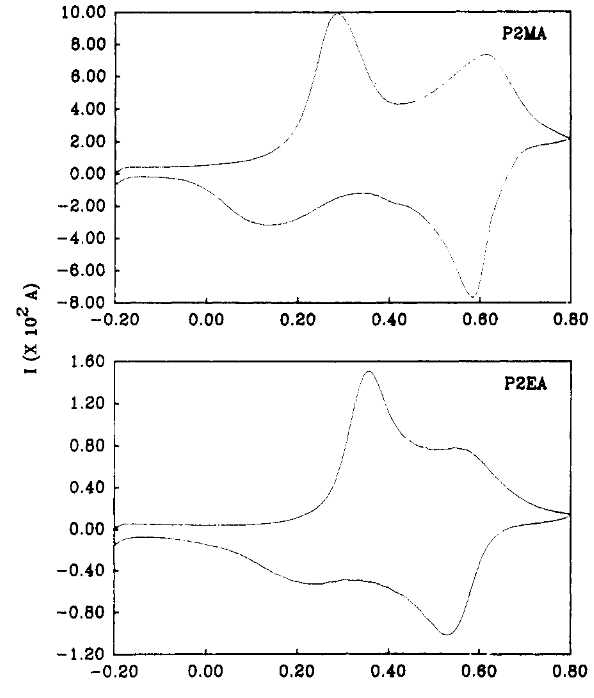


Figure 1. Cyclic voltammogram of poly(2-methylaniline) (P2MA) and poly(2-ethylaniline) (P2EA) in 2 M HCl (pH −0.7).

Electronic absorption spectra were taken using a HP 8452A diode array or a Varian DMS 100 spectrophotometer. For the in-situ spectroelectrochemical measurements, an indium-tin oxide (ITO) coated glass electrode (Applied Films 20-50 Ω/sq) and a platinum wire were used as the anode and cathode, respectively. All measurements were started at −0.20 V, and before recording each absorption spectrum, the potential was kept at the desired value for 2 min. A new polymer sample was synthesized for each cyclic voltammetry or spectroelectrochemistry measurement to prevent any degradation of the polymer sample.

The apparatus and procedures used in the in-situ conductivity experiments were previously described.[41] The working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with an interband spacing of 6 μm, typically polymer coated until the attainment of limiting resistance conditions. Whenever semiinfinite conditions could not be achieved, data were extrapolated using the calibration curves relevant to PANI.[41] The deposit was cycled at a low scan rate (typically 10 mV/s) between the neutral and the oxidized state, by sweeping the potential from 0.0 to 0.7 V (to prevent any degradation of the polymer) with the three-electrode potentiostat, while a small-amplitude (typically 10 mV) dc voltage was applied between the bands with an additional potentiostat in the two-electrode configuration and the relevant current was recorded.

Results and Discussion

Poly(2-alkylanilines). Thin P2MA and P2EA films were easily prepared electrochemically in acidic media with a Coulombic yield of 30%. As shown in Figure 1, these polymers exhibit two well-defined quasi-reversible redox processes in acidic conditions. The use of the Nernst equation[12] can give useful information concerning the mechanisms involved in these two electrochemical processes, since a plot of $E_{1/2}$ vs pH will give a straight line of slope −59 (m/n) mV per pH unit where m is the number of protons and n the number of electrons involved in the electrochemical reaction. The slope allows then the de-

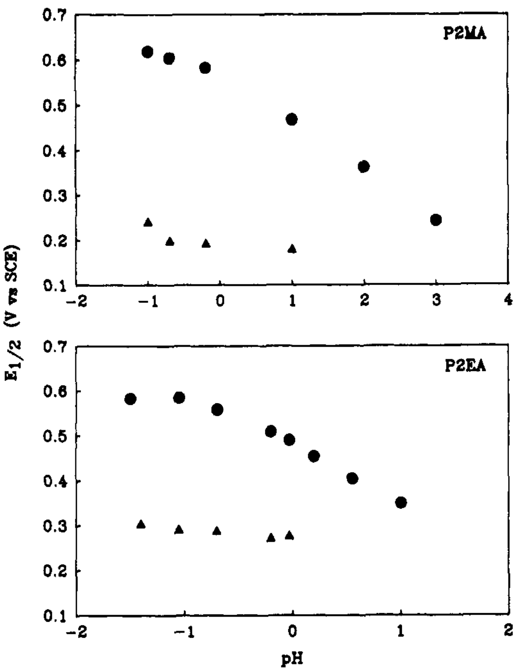


Figure 2. Oxidation potential ($E_{1/2}$) of the first (▲) and the second (●) redox processes of P2MA and P2EA at different pH.

termination of the proton/electron ratio exchanged during a redox process.

It has been found that the first redox process (Figure 2) is almost independent upon pH between pH –0.7 and 1.0 for P2MA and between pH –0.7 and 0.0 for P2EA (at higher pH values, the first peak could not be resolved), indicating that no proton participates in this electrochemical reaction. According to the electrochemical reactions reported for PANI,[34-36] the first redox process might be related to the oxidation of the amine nitrogen atoms (Scheme I, structure A) to radical cations (structure B). This reaction does not involve protonation or deprotonation in agreement with the independence of this process upon pH. However, it must be noted that, at pH <–0.7 (2 M HCl), $E_{1/2}$ moves to higher potentials, which can be related to a partial protonation of the amine nitrogen atoms in highly acidic conditions.

For the second redox process (Figure 2), two different behaviors were found. In the first part, a linear relationship was observed between $E_{1/2}$ and pH of the electrolyte with a slope of about –120 mV/pH unit, indicating that two protons with each electron are exchanged during this redox reaction. This linear relation holds between pH 0.5 (0.5 M HCl) and 3 for P2MA and between pH 0 (0.75 M HCl) and 1 for P2EA. As shown in Scheme I, the second redox process involves the oxidation of the radical cations (structure B) to give the fully oxidized form (structure D) with a ratio of 2 protons for each electron released. On the other hand, at more acidic pH (pH ~ 0 for P2MA and pH ~ –0.5 for P2EA), the second redox process becomes almost independent upon the pH of the electrolyte (Figure 2), which means that deprotonation of the intermediate form (structure C) does not occur. The same behavior was observed by Wei et al.[27] for P2MA.

From these results, it therefore seems that the fully oxidized polyanilines can exist in two different forms depending on the pH of the solution: a protonated form (structure C) or a deprotonated one (structure D). In order to better characterize these chemical structures, in-situ spectroelectrochemical measurements have been performed. Figure 3 shows the absorption spectrum of P2EA recorded in 0.75 M HCl (pH 0) and 1 M HCl (pH –0.2) at various electrochemical potentials. This polymer exhibits multiple reversible color changes from pale yellow to green to blue–violet as the potential is swept from –0.2 to 0.8 V. In both cases, when the polymer is fully reduced (E_{ox} = –0.2 V), an absorption peak is observed at 310 nm related to the π–π^* transition, while the half-oxidized (E_{ox} = 0.35 V) P2EA exhibits two absorption bands near 420 and 800 nm. These two absorption bands are characteristic of the presence of polarons (structure B).[34-36] Moreover, the similar UV–visible absorption spectra for P2EA between –0.20 and 0.35 V in different acidic conditions are consistent with the independence of the first redox potential upon the pH of the electrolyte. In contrast, the fully oxidized P2EA displays a different absorption spectrum depending on the pH of the solution. As shown in Figure 3, at pH 0, the completely oxidized form exhibits a maximum of absorption near 590 nm which can be related to the formation of a deprotonated quinoid form (structure D).[42] On the other hand, at pH –0.2, the fully oxidized polymer shows a maximum of absorption at 680 nm. This band could correspond to a protonated form (structure C). A similar behavior was also found for P2MA[39] and the unsubstituted PANI.[43,44] For example, an absorption band at 590 nm was observed for the fully oxidized PANI in strongly acidic media whereas the completely oxidized deprotonated PANI (pernigraniline base) exhibits an absorption peak near 520 nm. Some authors have related the presence of the 590-nm absorption band to the formation of a bipolaronic lattice (structure C),[43] but this absorption band can also be viewed as a transition from the valence (HOMO) band to the conduction (LUMO) band.[45]

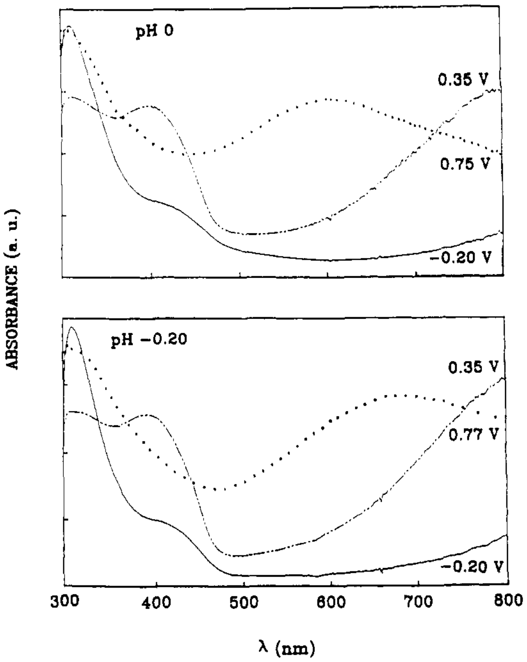


Figure 3. Optical absorption spectra of P2EA in 1 M HCl (pH –0.2) and 0.75 M HCl (pH 0.0) at various potentials vs SCE.

The optical absorption spectra of the fully oxidized P2MA and P2EA were also recorded in solutions of different pH, and these results are reported in Figure 4. In both cases, the presence of two different regimes clearly indicates that the fully oxidized poly(alkylanilines) undergo an acid–base transition from a deprotonated form (structure D) to a protonated one (structure C). At pH > 0.3, fully oxidized P2MA is characterized by a maximum of absorption at 570 nm, whereas at pH < 0.3, it exhibits

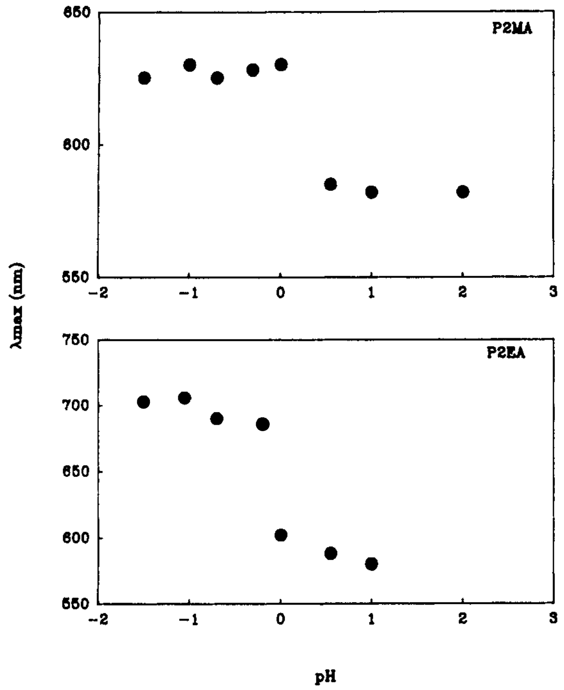


Figure 4. Maximum of absorption (λ_{max}) of the fully oxidized P2MA and P2EA in the UV-visible range at different pH.

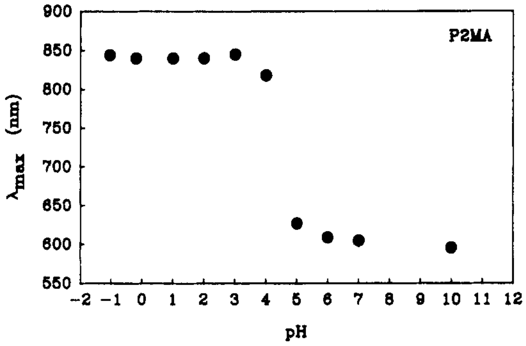


Figure 5. Maximum of absorption (λ_{max}) of the 50% oxidized P2MA in the UV-visible range at different pH.

a maximum of absorption at a different wavelength (630 nm). A similar transition can also be observed with the fully oxidized P2EA at pH ~ −0.1, the maximum of absorption shifting from 590 nm for the deprotonated form to a value of 680 nm for the protonated one. These results are in good agreement with those obtained by cyclic voltammetry with a transition occurring in the same pH ranges. Moreover, the fully oxidized polyaniline (pernigraniline) undergoes an acid–base transition which seems to be similar to that reported for the 50% oxidized form (emeraldine).[37] Indeed, as shown in Figures 4 and 5, similar optical transitions can be clearly observed for both acid–base transitions.

Poly(*N*-methylaniline). As a model compound, thin films of PNMA were also prepared by electropolymerization with a Coulombic yield of 14%. The voltammogram of this polymer (Figure 6) displays two well-defined quasi-reversible redox processes in strongly acidic conditions. As expected, the redox potentials did not show any dependence on the pH of the solutions, and that clearly indicates that no protonation or deprotonation reaction is involved in the two electrochemical processes (Scheme II). Since the nitrogen atoms do not bear any hydrogen atoms, it is obvious that the second redox process (Scheme II) cannot depend on pH. Therefore, the fully oxidized poly(*N*-alkylanilines) must be charged.

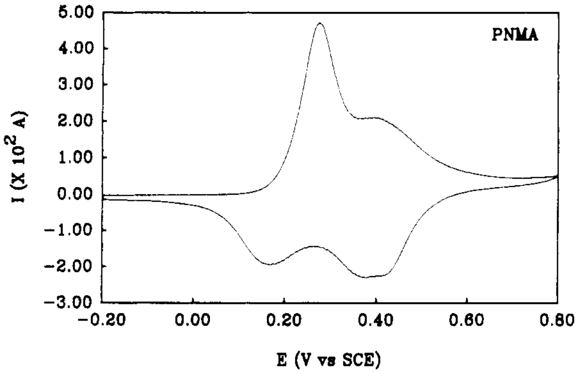


Figure 6. Cyclic voltammogram of poly(*N*-methylaniline) (PNMA) in 3 M $HClO_4$ (pH −2.0).

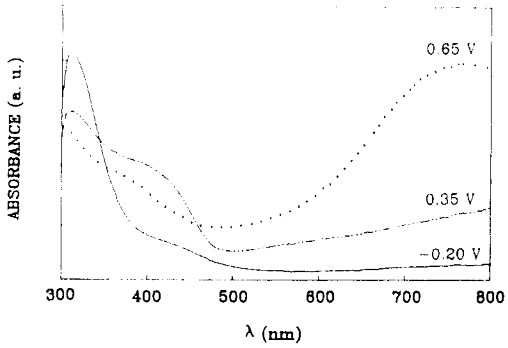


Figure 7. Optical absorption spectra of PNMA in 1 M $HClO_4$ (pH −0.7) at various potentials vs SCE.

As previously reported,[29a,33] PNMA exhibits multiple and reversible color changes from pale yellow to green to blue as the potential is swept from −0.20 to 0.65 V. The optical absorption spectra of the fully oxidized PNMA were also recorded in solutions of different pH, and these results are reported in Figure 7. A peak near 770 nm was observed for the completely oxidized PNMA in all aqueous solutions, and that confirms that the fully oxidized poly(*N*-alkylanilines) are always charged (Scheme II, structure C).

In-Situ Conductivity Measurements. It is well-known that the fully reduced (structure A) and deprotonated oxidized (structure D) forms are insulating, whereas the half oxidized form (structure B), which is charged, is conducting.[11,34] By analogy, structure C (Schemes I and II) could also be conducting. In order to study the influence of this electronic structure on the electrical conductivity of these materials, in-situ conductivity measurements were performed in 2 M HCl (pH −0.7) for the ring-substituted polymers and in 3 M $HClO_4$ (pH −2.0) for the *N*-alkyl-substituted polymer. On the basis of our previous optical and electrochemical measurements, these highly acidic media allow the formation of charged and fully oxidized polyanilines.

As shown in Figure 8, the conductivity reaches a maximum (4 S/cm for P2MA, 0.2 S/cm for P2EA, and 0.02 S/cm for PNMA) at a potential intermediate between the two redox processes (emeraldine state), the materials being insulating in the fully reduced (leucoemeraldine) and charged oxidized (pernigraniline) forms. The asymmetry observed in the electrical response, in both intensities and potentials, during the redox cycles may be explained by the formation of a more homogeneous conducting phase after a first complete oxidation. In other words, the 50% oxidized polyanilines may have different morphologies depending on whether they are obtained from the reduction of the fully oxidized polymer or from the oxidation

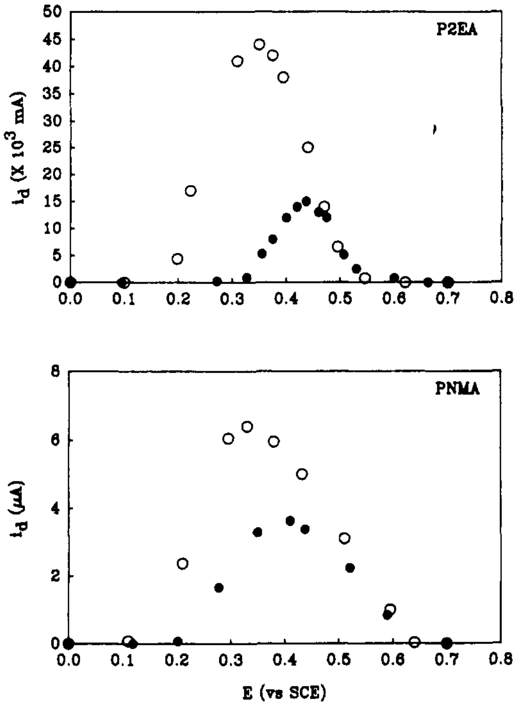


Figure 8. In-situ conductivity measurements of P2EA in 2 M HCl (pH -0.7) and PNMA in 3 M $HClO_4$ (pH -2.0) in the forward (●) and the backward (○) scans.

of the leucoemeraldine form. On the other hand, a decrease of the electrical conductivity was observed when the polymers were brought at too high potentials (e.g., 0.9 V vs SCE) or kept in a fully oxidized form for a too long period of time. This behavior can be explained by a partial degradation of the polymers.[46,47] Finally, the difference in the potential values for the conductivity maxima in the forward and backward scans is directly related to the asymmetry observed in the quasi-reversible redox processes (Figure 1).

On the other hand, it is important to note that, although they are charged, the fully oxidized polyanilines are insulating. A high electrical conductivity in conjugated polymers is related to a high mobility of the charge carriers along and between the polymer chains, and it seems that fully charged polymer chains do not allow an easy transport of the charge carriers. The strong Coulombic interactions between the bipolarons lead to a strong localization of the charge carriers. Similar arguments were developed for other types of conjugated polymers.[44,48,49] However, it must be pointed out that the effects of protonation on the electronic structure of the fully oxidized polyanilines are not completely understood,[43,45,50] and, therefore, it is still not clear if the protonated imines in structure C (Scheme I) can act as charge carriers, even in partially doped polyanilines. On the other hand, the electronic structure of fully oxidized poly(*N*-methylaniline) can be compared to those observed in polythiophenes and polypyrroles,[44,48] and since this fully oxidized structure is also insulating, it therefore seems that the high electrical conductivity in conjugated polymers is associated with mixed valence states of fractional charge per repeat unit.

Conclusion

This study has clearly shown that protonated fully oxidized poly(alkylanilines) can be stabilized in highly acidic conditions (pH ~ 0). This electronic structure (bipolaronic) has been characterized by electrochemical and in-situ optical measurements and has been found to be related to an acid-base transition similar to the one reported for the emeraldine form. By analogy with the nomenclature used previously for the unsubstituted polyaniline, this protonated form is called "pernigraniline salt". A similar charged and fully oxidized structure has also been obtained with poly(*N*-methylaniline). In this particular case, since no deprotonation reaction can occur, the polymer has to be charged in its fully oxidized form. In-situ conductivity measurements have revealed an insulating behavior for the pernigraniline salt form. These results can be explained by a strong localization of the charge carriers and, therefore, suggest that a high electrical conductivity in conjugated polymers can only be obtained with a partial doping of these materials.

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