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Effect of thickness, chemical nature of dopants and an alkyl substituent on absorption bands of polyaniline

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Abstract The effect of thickness, an alkyl substituent in the *ortho* position and the chemical nature of the counterion on the absorption spectra of polyaniline films was studied. Previous work performed using the electrochemical quartz crystal microbalance technique (EQCM) has shown a greater participation of anions in the ionic exchange process when the thickness of the film is increased. This fact was attributed to morphological changes leading to different densities of the polymer film, which was demonstrated by SEM experiments. Changes in absorption spectra provoked by conformational changes due to the presence of a substituent and the effect of the chemical nature of the anions are analyzed for Cl^- , ClO_4^- and *p*-toluene sulfonate (PTS^-).

Introduction

In the last decades, intrinsically conductive polymers have been widely studied because of their electronic and electrochromic properties. Electrochromism is the phenomenon produced by the change in the optical properties of a material caused by a passage of electric current. This phenomenon takes place in some transition metal oxides and some organic materials, making their potential utilization as non-emissive optical modulators [1] possible.

Among conductive polymers, polyaniline (PANI) would appear to be specially attractive because of its application possibilities: ionic exchange [2], corrosion protection [3], semiconductor devices [4], batteries [5], electrochromic devices [6–8] and microelectronics [9]. These applications are possible because PANI has many advantages such as ease of preparation from aqueous solutions and the stability of its conductive form [10]. However, this material presents the complication of having two oxidized forms, with the possibility of passing from one form to the other by different redox reactions and/or protonation of the different species [11].

Polymeric films present many complicated mechanical aspects due to electronic transfer through the film, especially to sites which are remote from the polymer/substrate interface. The movement of polymeric chains, allowing the accommodation of different species such as ions and solvent molecules inside the film, is very important. Consequently, the form of the voltammograms depends on all these factors, and thus a wide variety of E/j profiles have been found [12].

Kaufman et al. [13] have proposed a model for charge transportation through polymeric films in which the propagation of charge takes place by auto-exchange electronic reactions between oxidized and reduced species positioned at neighboring sites in the film. This model has been also suggested for PANI films.

Ionic exchange processes during the oxidation of PANI have been studied by the quartz crystal microbalance (EQCM) technique. It was shown that thickness is a very important parameter in this ionic process because the amount of ions and solvent molecules exchanged in the process of electro-neutralization of electric charges depends on the thickness of the polymeric film [14–17]. On the other hand, SEM micrographs have shown important changes in the morphology of the films, depending on their thickness, leading to different chain-packing patterns [17]. The presence of an alkyl substituent in the *ortho* position will affect the torsion angle (dihedral angle) between adjacent rings of the polymer backbone, modifying the electronic properties.

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The aim of this paper is to study the effect of thickness on absorption spectra of polyaniline films and to compare changes produced in absorption spectra of polyaniline and 2-ethylpolyaniline films in different electrolytic media. The chemical nature of different dopants is also an important parameter, because this will also modify the polymer structure, depending on the charge/size relationship.

Experimental

Polyaniline (PANI) films of different thicknesses were grown onto transparent glass/SnO₂ conducting substrates (resistivity 16 Ω/□), from a 1 M HCl + 0.5 M aniline solution by applying triangular potential sweeps (0.05 V s⁻¹) over the potential range -0.2 to 0.7 V (SCE). Poly-*o*-ethylaniline (2-ethyl PANI) films were prepared on the same substrates from a 1 M HCl + 0.5 M 2-ethylaniline solution by applying triangular potential sweeps (0.05 V s⁻¹) over the potential range -0.2 to 0.85 V. After deposition, films were rinsed with distilled water and placed in a one-compartment cell with two optical windows. The working electrolytes were 1 M free monomer HCl, HClO₄ or *p*-toluenesulfonic acid (PTSA) solutions. A platinum wire was used as counter electrode, and all potentials are referred to the saturated calomel electrode (SCE).

Spectroelectrochemical experiments were performed under potentiodynamic and potentiostatic conditions with an EG & G PAR Model 362 potentiostat/galvanostat by placing the electrochemical cell in the optical pathway of a HP 8452 diode array spectrophotometer. Thicknesses of PANI films were determined by interferometry. Working temperature during electrochemical experiments was 25 °C, and all solutions were prepared from analytical grade chemicals and triply distilled water. Aniline and 2-ethylaniline were distilled under reduced pressure in order to ensure that only the monomeric form was present, and all other chemicals were used as received.

Results and discussion

UV/Vis spectra: general features

Spectroelectrochemical studies were carried out by obtaining absorption spectra of PANI and 2-ethyl PANI films *in situ* for different oxidation potentials. All data obtained in this paper are in agreement with previous results presented by other authors [10, 18–20]. Stiwell and Park [10] have shown four different optical species depending on the applied potential: a “leuco” form absorbing at ca. 3.9 eV, the radical cation presenting an absorption band at ca. 2.8 eV, the quinoid form absorbing at 1.9 eV, and, finally, delocalized free electrons absorbing at ca. 1.55 eV. Even though in this work absorption spectra were taken for the entire potential range where the transition from leucoemeraldine to pernigraniline occurs, the analysis is only done for the first transition: leucoemeraldine-emeraldine. The effect of the degree of doping is clearly revealed by shifting of the band corresponding to the formation of the radical cation. The first redox process in the polymeric chains involves the insertion/deinsertion of electrons and, consequently, the formation of positive charges in the

polymer, which is compensated by the incorporation/expulsion of ions. The insertion of counter ions into the polymeric matrix strongly perturbs the polymer geometry, not only by its size but also by the formation of an ionic complex. In the case of polyaniline, the charge compensation is achieved by the participation of protons and anions ejected/incorporated from the electrolyte.

In Fig. 1, absorption spectra obtained for 89-nm thick PANI film in HCl electrolytic solution are shown. The observed absorption bands can be explained using the electronic transitions diagram proposed by MacDiarmid and Huang (Fig. 7 in [21]) and based on theoretical calculations. In the potential range between -0.25 and 0 V, the polymer is completely reduced in the form of leucoemeraldine. In this case, an increase in the absorption from ca. 3.5 eV that leads to an absorption band centered at 3.9 eV is observed. This band corresponds to the π - π^* electronic transition that takes place from the highest occupied band to the lowest unoccupied band. When the polymer begins to be oxidized (0.1 to 0.3 V) to form emeraldine, half of the electrons of the occupied band are removed. In this way, the band is destabilized and is moved slightly to form the polaron band lying in the intergap space. Now, two absorption bands appear, at ca. 1.5 and ca. 3.0 eV, corresponding to the electronic transitions from the underlying bands to the polaronic band. The intensity of the absorption band centered at ca. 3.0 eV is a maximum at 0.25 V, this potential being approximately equal to that of the first peak in the voltammetry when the number of radical cations is at its maximum. On the other hand, when the potential is increased from 0.30 to 0.55 V, there is a shift of the polaronic band to higher energy values together with an increase in intensity of the band centered at 1.5 eV. These phenomena occur because the polaronic band always becomes more destabilized on moving to higher energy values. When the polymer is completely oxidized (0.75 V), it can be seen that the spectrum is completely changed: the bands at 1.5 V and 3.0 eV are no longer observed and the spectrum shows only one

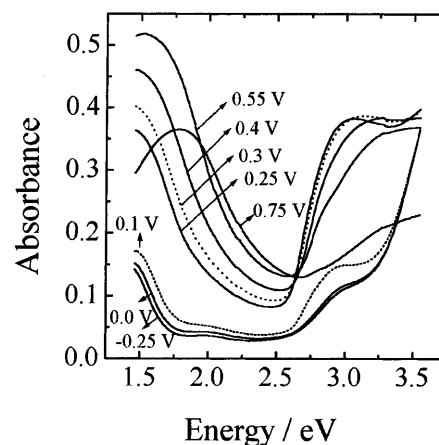


Fig. 1 Absorption spectra obtained at different polarization potentials for an 89-nm thick PANI film in 1 M HCl electrolytic solution

band centered at ca. 2.2 eV, corresponding to the $\pi-\pi^*$ electronic transition in the pernigraniline form.

Effect of thickness

As mentioned above, all the analysis in the present paper is performed for the first oxidation process and the modifications in the position of the polaronic band (ca. 3.0 eV). In Fig. 2, the spectra for three different film thicknesses, recorded at 0.10 V in the region of the polaronic band, are shown as an example. The band centered at ca. 2.8 eV and a rise corresponding to the "leuco" form can be seen in the figure. All the forward analysis is carried out by determining the maximum of the polaronic band for each spectrum by a deconvolution method by multiple gaussian functions. Both experimental (points) and fitted curves (full lines) are shown in the figure, and the deconvoluted curves (dotted lines) for one spectrum are also depicted. This procedure was carried out for each spectrum in order to establish the maximum energy of the polaronic band.

In Fig. 3, the maxima of the polaronic absorption bands as a function of film thickness for five potential values are plotted for both HCl and HClO₄ electrolytes. The potentials of 0.10, 0.20, 0.25, 0.30 and 0.40 V were chosen because they are positioned around the first voltammetric peak corresponding to the formation of the radical cation. It can be seen from the plots that the thicker the polymer film, the lower is the electronic transition energy. On the other hand, in all cases, the energy of the band increases with the potential according to the scheme reported by MacDiarmid and Huang [21]: on increasing the degree of doping the polaronic band is more destabilized, so that the electronic transition is observed at higher energies. In a previous paper [17], SEM micrographs of different thickness PANI films were analyzed. It was shown that thicker films present a

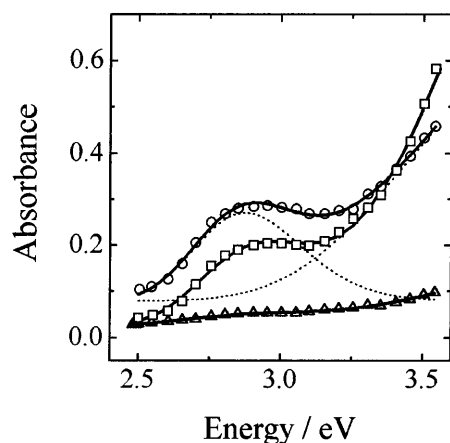


Fig. 2 Absorption spectra obtained at 0.1 V in 1 M HClO₄ electrolytic solution for three different thick PANI films: 40 nm (Δ), 89 nm (\square) and 214 nm (\circ). Fitted curves (—) and deconvoluted curves (.....) using the multiple gaussian method

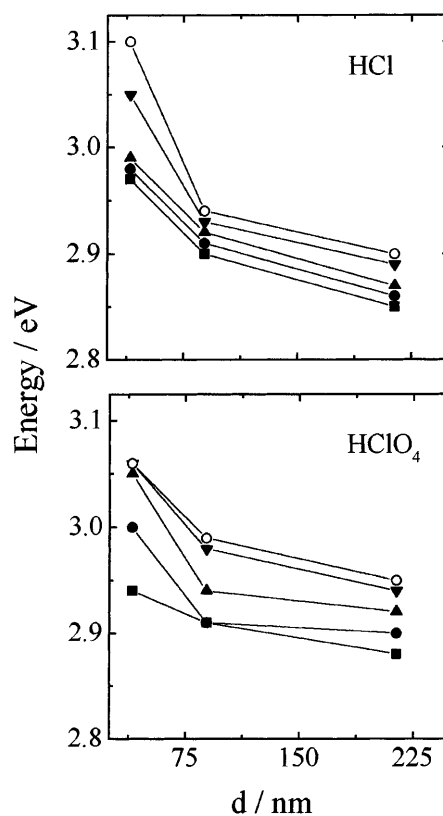


Fig. 3 Maxima of the polaronic absorption band as a function of film thickness for different potentials in HCl and HClO₄ electrolytes: 0.1 V (\blacksquare), 0.2 V (\bullet), 0.25 V (\blacktriangle), 0.3 V (\blacktriangledown), 0.4 V (\circ)

spongy globular structure which leads to a higher surface/volume ratio. It has already been pointed out [22–24] by means of optical and ellipsometric observations that film density changes from a more compact structure near the electrode surface to a less dense structure at an increasing distance from the metal substrate. This density variation is also predicted by the theory of de Gennes [25], and it leads to a diminution of the chain packing factor, modifying the volume fraction of the conducting species in the percolation limit. This produces an increase in conductivity [26], and it is an explanation for the shift of the polaronic band to lower energies when the film thickness is increased.

Effect of substituent and dopants

In Fig. 4, spectra obtained for a 2-ethyl PANI film (89-nm thick) in HCl at different oxidation potentials are shown. It can be seen that the set of spectra is quite similar to that corresponding to PANI film of the same thickness (Fig. 1), with differences related to the potential values in which intensities of the bands are at their maxima. While, for PANI films, the intensity of the polaronic band is a maximum at 0.25 V, in the case of 2-ethyl PANI this band is more intense at 0.4 V. This is in good agreement with electrochemical data shown in

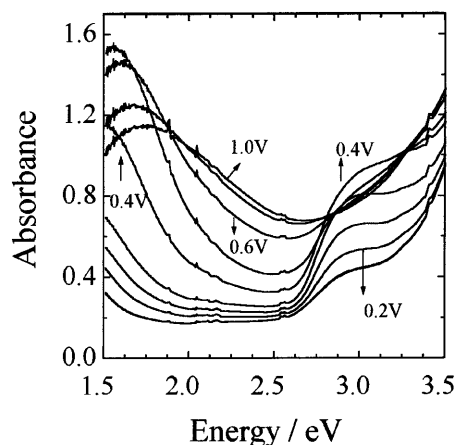


Fig. 4 Absorption spectra obtained at different polarization potentials for an 89-nm thick 2-ethyl PANI film in 1 M HCl electrolytic solution

Fig. 5, where the voltammograms of PANI and 2-ethyl PANI films are compared. It can be seen that the first oxidation process is polarized to more positive potentials for substituted PANI. It should be pointed out that, in 2-ethyl PANI, the second oxidation process is also shifted, but to less positive potentials, and spectra of the oxidized form present a band at lower energies (ca. 1.75 eV) than that of unsubstituted PANI. These shifts in alkyl-substituted polyanilines have been already reported [27] and can be rationalized by considering structure and conformational changes induced by the presence of the substituent. It is well known that electronic properties of aromatic polymeric systems will be affected by changes in the torsion angle (dihedral angle) between adjacent rings of the polymer chain. Introduction of a C_2H_5 -group on each phenyl ring will increase the torsion angle and, consequently, will decrease the degree of orbital overlapping between the π electrons of phenyl rings with the nitrogen lone pair (sp^3 hybridization). This diminishes the extent of conjugation and increases the energy of the first oxidation process, because

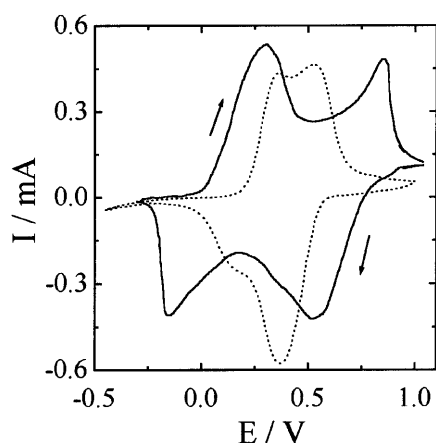


Fig. 5 Potentiodynamic I/E profiles of 40-nm thick PANI (—) and 2-ethyl PANI films (.....) in 1 M HCl solution. $v = 0.005 \text{ V s}^{-1}$

it is more difficult to oxidize the completely reduced form of polyaniline (amine form). At this point, it is important to direct the reader's attention to two effects that alkyl substituents produce on the polymer oxidation processes: electronic and steric effects. The electron-donating nature of the ethyl group (Hammett constant $\sigma_I = -0.05$ [28]) would indicate a shift of the first oxidation peak to less positive potentials than those observed in PANI. Experimental results (Fig. 5) show that steric effects due to the increase of the dihedral angle are stronger than electronic effects leading to the polarization of the first oxidation peak of the 2-ethyl polyaniline film. Results are consistent with conductivity measurements of PANI and alkyl-substituted polyanilines [27], where it was shown that conductivity diminishes in the sense of PANI, poly(*o*-toluidine) and poly(*o*-ethyl aniline). Electronic effects of the alkyl substituent are more important in the second redox process, because, once the radical cation is formed, its oxidation to the imide form must be facilitated by the presence of the sp^2 hybridized nitrogens that diminish the steric strain due to wide dihedral angles, leading to a lower oxidation potential for the emeraldine/permanganine couple. In some cases, when thicker films were prepared, these two processes appeared as a unique large voltammetric peak indicating that most amine units passed directly to imide units. Another striking feature that can be inferred by comparing Figs. 1 and 4 is the great difference of absorbance between PANI and 2-ethyl PANI films. Considering that both films have the same thickness, substituted polyaniline seems to be a better absorber than PANI, which makes it suitable for practical applications such as electrochromic devices [1].

In Fig. 6, the energies of the maxima of the polaronic absorption bands, calculated by the same method as that shown in Fig. 2, for both PANI and 2-ethyl PANI films as a function of the potential, are plotted for HCl, $HClO_4$ and PTSA electrolytes. In all cases, the energy of the band increases with the potential according to the scheme proposed in [21]: increasing the degree of doping, causes the polaronic band to be more destabilized, so that the electronic transition is observed at higher energies. The effect of the substituent is also revealed on observing spectroscopic data. At all potentials, the band of substituted polyaniline shows a hypsochromic shift (towards higher energies) when compared with PANI films, indicating a decrease in the extent of conjugation due to the steric strain produced by the voluminous C_2H_5 -groups. Another possible explanation for this hypsochromic shift is the formation of a triplet state of the bipolaron, as demonstrated by theoretical calculations in which the Coulomb interaction between counterions is considered [29]. The effect of the substituent is more important when PTSA anions are used as dopants, the hypsochromic shift of the band of substituted PANI being much more pronounced for PTSA than for Cl^- or ClO_4^- ions. It should be pointed out that, for unsubstituted PANI films in the three different electrolytes, the smaller the charge/size ratio of the dopant the higher is

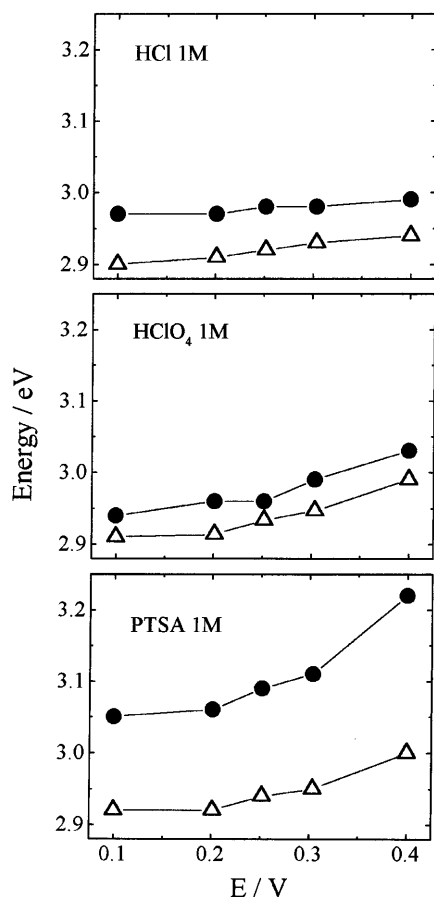


Fig. 6 Maxima of the polaronic absorption band in 1 M HCl, HClO₄ and PTSA electrolytes for same thickness PANI (Δ) and 2-ethyl (●) PANI films

the energy of the absorption band, but these differences are not very pronounced. When the three curves corresponding to poly(*o*-ethylaniline) are compared, there is not much difference between that for Cl⁻ and that for ClO₄⁻ ions; on the contrary, the curve obtained for PTSA is completely shifted to higher energies. This analysis demonstrates the important role played by the ethyl substituent, which produces high steric hindrance for doping with large PTSA ions. On the other hand, it is a general view that organic acids do affect the conductivity by altering the size of the crystalline fraction as well as the crystal phase. Moreover, PTSA is a planar molecule unlike Cl⁻/ClO₄⁻, and hence more anisotropy should be observed. Genies et al. [30] have reported results with substituted polyanilines with long alkyl chains such as C₆H₁₃⁻, and molecular modelling indicates that the alkyl substituent in the *ortho* position would lead to a less random conformation, with a tendency to form good linear chains. However, the low conductivity observed when compared with unsubstituted PANI is probably due to the screening effect of the alkyl group on the protonated nitrogen. Thus, this nitrogen is less accessible to the electrolyte, even more for a voluminous dopant such as PTSA, in good agreement with our spectroelectrochemical results.

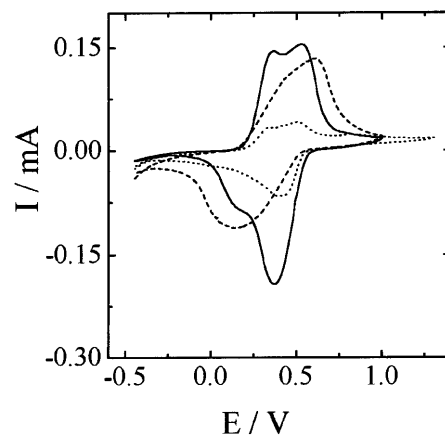


Fig. 7 *I/E* potentiodynamic profiles of 40-nm thick 2-ethyl PANI films in 1 M HCl (—), 1 M HClO₄ (---), and 1 M PTSA (.....). $\nu = 0.005 \text{ V s}^{-1}$

In Fig. 7, the voltammograms obtained with poly(*o*-ethylaniline) films of the same thickness in the three different electrolytes are shown. In all cases, the two redox processes can be observed, but it is clear that *i/E* profiles depend strongly on the nature of the anion of the electrolyte. The most striking feature is the diminution of current observed for PTSA electrolyte, this being ca. three times lower than that observed for Cl⁻ ions. This fact shows the difficulty for PTS⁻ ions to enter the polymeric matrix to neutralize positive charges. Differences among the three electrolytes are not so great when unsubstituted PANI films are analyzed (Fig. 8), in agreement with spectroscopic data. It can be observed that, even though the current in PTSA is lower than in HCl and HClO₄ solutions, differences of maxima of current peaks are not of the same order as in poly(*o*-ethylaniline). Attention must be paid to the fact that the second redox process of polyaniline is depolarized towards less positive potentials when the charge/mass ratio of the anion diminishes. EQCM experiments [17] have shown that this redox couple is accompanied by the

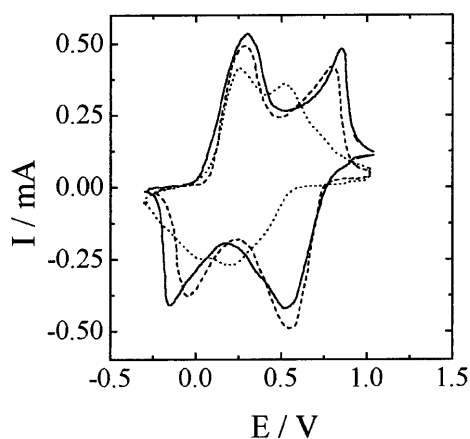


Fig. 8 *I/E* potentiodynamic profiles of 40-nm thick PANI films in 1 M HCl (—), 1 M HClO₄ (---), and 1 M PTSA (.....). $\nu = 0.005 \text{ V s}^{-1}$

ejection of anions from the polymeric matrix. Therefore, since chloride ions form very strong ionic pairs with the positively charged polymer chains, it is more difficult to remove than the voluminous PTS^- anion. This seems to be a possible explanation of potential shifts observed for the second redox process of PANI films as a function of the charge/mass ratio of the anion. The effect of anions on the electrochemical response of polyaniline has been reported in several papers [31, 32], especially regarding their influence on the polymerization process. It is well known that the structure of PANI films depends strongly on the counterion used in its formation, and obviously the electrochemical response of the films will change. In this case, both PANI and 2-ethyl PANI films were prepared in chloride media, controlling their thickness, and, after polymerization, they were cycled in different electrolytes. This procedure was adopted in order to be sure that in all cases the "depart material" was the same and to be able to perform a realistic comparative study of different dopants used. This is the reason why voltammetric results in PTSA solutions differ from literature data obtained with films formed in PTSA or DBSA solutions [32].

Raman resonance characterization of the redox behaviour of substituted PANI films is in progress with the purpose of obtaining more information about charged segments formed during the oxidation-reduction process in the different electrolytes.

Conclusions

In this paper, it has been shown that a large substituent such as ethyl and the chemical nature of the counterion are very important parameters, playing a very important role in determining the energy of the electronic bands of PANI films. The presence of the substituent significantly perturbs the geometry of the chains, leading to a hypsochromic shifting of the polaronic absorption band. It was shown that, depending on the size of the counterion, the presence of an alkyl group in the *ortho* position will influence the participation of this anion in the ionic exchange process by virtue of steric hindrance. The electron-donating effect of the ethyl substituent is completely negligible compared with the steric effect that produces an increase of the torsion angle between phenyl rings. The electronic effect will be important in the second oxidation processes, as is evidenced by the diminution of the redox potential of the emeraldine/ pernigraniline couple.

Morphological changes in the polymer film are also produced by difference in thickness. Thin films are compact, but their density diminishes on increasing the distance from the metallic electrode. This leads to changes in the packing factor of the chains, modifying the volume of the conducting units in the percolation

limit. This phenomenon is evidenced by the shift towards lower energies of the polaronic absorption band.

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