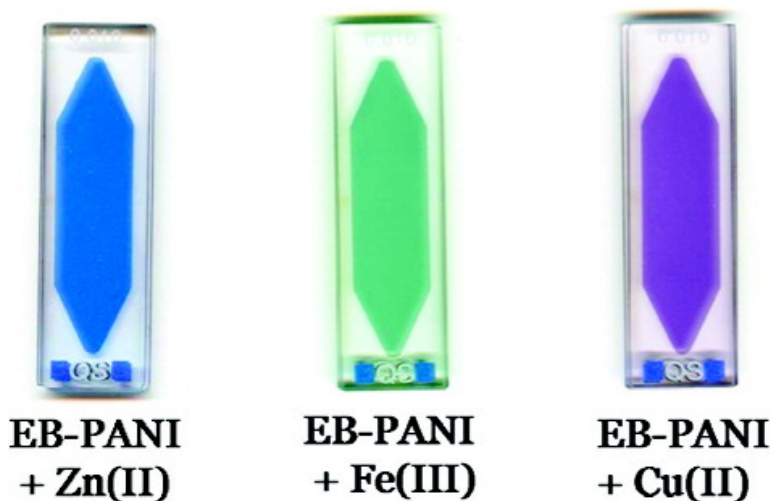


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Studies on the Interaction of Emeraldine Base Polyaniline with Cu(II), Fe(III), and Zn(II) Ions in Solutions and Films

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ABSTRACT: The interaction of emeraldine base polyaniline (EB) with Cu(II), Fe(III), and Zn(II) in 1-methyl-2-pyrrolidinone (NMP) solution was monitored using electronic UV–vis–NIR, resonance Raman, and electron paramagnetic resonance (EPR) spectroscopies. The films prepared from these solutions were also spectroscopically characterized. It was demonstrated that the nature of the products (semiquinone and quinone segments) formed from the interaction of EB and metal ions is strongly dependent on the nature of the cation, the metal/EB molar ratio, and the concentration of the components. The presence of semiquinone segments (radical cation) in EB solutions with Cu(II) and Fe(III) was undoubtedly confirmed by the observation of an electronic absorption band at ca. 900 nm, a characteristic Raman band at ca. 1330 cm^{-1} ($\nu_{\text{C-N}^{\cdot+}}$), and also an EPR signal at $g = 2.006$. The influences of metal/EB molar ratio and metal ion concentration on the formed species were investigated in Cu(II) and Fe(III) solutions, and it was verified that diluted solutions favor the formation of oxidized segments (pernigraniline) instead of doped ones (emeraldine salt). No matter the nature of metal ion solutions, all the polymeric films show a spectroscopic behavior of ES (doped polymer) according to electronic and Raman spectroscopic data.

Introduction

Polyaniline (PANI) electrical properties are reversibly controlled through redox or protonation reactions.^{1,2} The oxidation state of PANI can vary from the fully reduced (leucoemeraldine base, LB) to half oxidized (emeraldine base, EB) and then to the fully oxidized form (pernigraniline base, PB). The conducting form of PANI, emeraldine salt (ES), can be obtained by protonation of emeraldine base (EB).³ This protonation reaction causes an increase in PANI electrical conductivity of ca. 10 orders of magnitude.³ The protonation occurs preferentially at imine nitrogen atoms and is followed by an internal redox reaction that results in the formation of semiquinone segments (radical cation).^{2,4} The interconversion process of different forms of PANI and their structures are shown in Scheme 1.

Another way to increase the PANI conductivity is through complexation reaction of EB with alkali metal salts,^{5–8} Lewis acids,^{9–13} and transition metal salts.^{14–21} Doping process with alkali metal salts proceeds through coordination to the lone pair on imine nitrogen atoms in the chain backbone of EB; this process is called pseudo-protonation.⁸ Lewis acids doping consists in the treatment of EB with Lewis acids such as FeCl_3 , AlCl_3 , SnCl_4 , and GaCl_3 in strictly anhydrous conditions. It was shown that this type of doping occurs on both amine and imine nitrogen atoms.¹⁰ Transition metal salts are also employed for polyaniline doping, and the mechanism depends on the nature of the metal ions.^{16,19} In the case of Zn(II), which does not have an oxidizing character, the radical cation segments formation was assigned to the pseudo-protonation at imine nitrogen atoms without redox reaction between the metal ion and EB.⁸ On the other hand, the obtained products from the interaction of Eu(III) and EB were doped ES and Eu(II) ions.¹⁸ Dimitriev¹⁹ proposed the following steps in the doping mechanism for metal salts which could act as oxidizing agents: the metal ions oxidize

the amine nitrogen atoms giving imine nitrogen of EB and the reduced form of metal cations; after this, the reduced metal ions coordinate to the lone pair on imine nitrogen in the chain backbone; then, reduced cations are oxidized by the imine groups, resulting in radical cation segments and the oxidized cations.

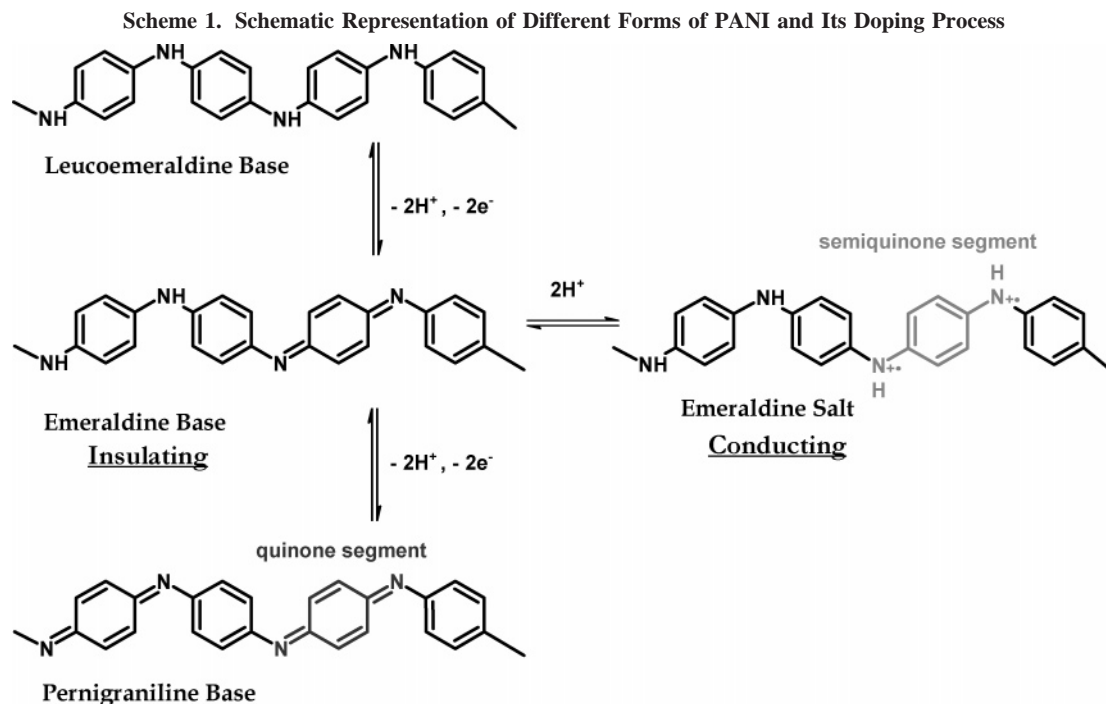
The EB–transition metal cationic complexes can be prepared both in suspension and in solution media. In the suspension route, an EB suspension (e.g., in nitromethane) is treated with a solution of a transition metal salt in the same solvent.^{14,17,21} In the solution route, EB dissolved in 1-methyl-2-pyrrolidinone (NMP) is mixed with transition metal salts dissolved in the same solvent.²² The resulting solution is used to prepare films by drop-casting.^{5,7,16}

The interest in the study of conducting polymer–transition metal salts complexes is related not only to the doping process but also to their applications in corrosion control,^{23–25} catalysis,^{22,26} and sensors.²⁷

Our group has been using resonance Raman spectroscopy for the characterization of conducting polymers. This technique allows selecting each chromophoric segment present in the polymeric chain by changing the exciting radiation.²⁸ In a previous work using this approach,²¹ we demonstrated the formation of semiquinone segments (radical cation) upon coordination of Cu(II), Fe(III), and Zn(II) ions to EB prepared by suspension route. It was also observed the formation of oxidized segments (pernigraniline-like) in the early stages of the doping reaction with Cu(II) and Fe(III). These metal ions were focused because Fe(III) and Cu(II) are usually employed as oxidizing agents in PANI synthesis;^{1,2} on the other hand, Zn(II) was chosen because it is a nonactive redox ion.

In the present work, reactions between EB solution in NMP and metal salts of Fe(III), Cu(II), and Zn(II) were monitored through electronic UV–vis–NIR, resonance Raman, and EPR (electron paramagnetic resonance) techniques for the first time. These spectroscopic techniques permitted to identify the species

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formed in NMP solution containing EB and Cu(II), Fe(III), or Zn(II) ions. The influence of PANI and metal ion concentrations in NMP and also of their molar ratio on the formed species was investigated. Further, the polymeric films obtained from these solutions were spectroscopically characterized.

Experimental Section

Synthesis of PANI Forms. Aniline (Merck) was distilled under reduced pressure prior to use. The polymerization was done in aqueous HCl solution (1 mol L⁻¹) using (NH₄)₂S₂O₈ (Merck) as oxidant, following the procedure already described in the literature.²⁹ PANI was obtained in the emeraldine salt form, ES. The emeraldine base form (EB) was obtained by treating ES with aqueous solution of NH₄OH (0.1 mol L⁻¹), as described previously.²⁹

Preparation of NMP Solutions. 0.5 g of EB was slowly added to 100 mL of NMP (Merck), and the mixture was stirred for 24 h at room temperature. Undissolved polymer particles were removed by filtering the mixture through a 0.7 μm Millipore membrane. The concentration of EB solution in NMP was spectrophotometrically determined by measuring the excitonic absorption band centered at 630 nm. The molar absorption of 5500 mol⁻¹ L cm⁻¹ determined by Yamamoto et al.³⁰ was used, in which the molarity was calculated on the basis of monomeric units. The molecular weight of one monomeric unit was calculated considering that the EB repetitive unit is (-NH-C₆H₄-NH-C₆H₄-N=C₆H₄=N-C₆H₄-); i.e., it contains four units derived from aniline. Thus, the monomeric unit weight was considered 90.6 g mol⁻¹.

The stock solutions of metal ions in NMP at concentration of 2 × 10⁻¹ mol L⁻¹ were prepared from analytical grade metal ion salts, CuCl₂·2H₂O, FeCl₃·6H₂O, and ZnCl₂ (Merck). PANI/transition metal solutions were prepared by mixing adequate EB and salt solutions to obtain the desired concentration.

Films were prepared using these solutions by drop-casting onto glass slides at about 60 °C.

Instrumentation. Raman spectra at 632.8 nm exciting wavelength (He-Ne laser, Spectra Physics model 127) were recorded in a Renishaw Raman imaging microscope (system 3000) containing an Olympus metallurgical microscope and a CCD detector at 4 cm⁻¹ resolution. The laser beam was focused on the sample in a ca. 1 μm spot by a 50× lens. Laser power has always been kept below 0.7 mW at the sample in order to avoid sample degradation. The FT-Raman spectra were recorded in a FT-Raman Bruker FRS-100/S spectrometer, using 1064 nm exciting radiation (Nd:YAG laser

Coherent Compass 1064-500N) and a Ge detector. Also, laser power has always been kept below 20 mW to avoid sample degradation.

The electronic UV-vis-NIR spectra were recorded on a Shimadzu UV3101PC UV-vis-NIR scanning spectrophotometer. The UV-vis-NIR spectra of the solutions were measured using quartz cell (0.1 mm thickness).

EPR spectra of powdered samples were recorded in a Bruker EMX instrument, operating at X-band frequency, at 77 K, using DPPH (α,α'-diphenyl-β-picrylhydrazyl) as frequency calibrant (*g* = 2.0036).

Results and Discussion

The electronic UV-vis-NIR spectra of EB solution in NMP (10.3 mmol L⁻¹) and solutions of EB with Fe(III), Cu(II), and Zn(II) (10.3 mmol L⁻¹ of EB and 11.1 mmol L⁻¹ of transition metal salts) are shown in Figure 1. The UV-vis-NIR spectrum of EB in NMP presents the bands at 325 and 630 nm; the former band is assigned to the π-π* transition while the last is due to the charge transfer from the benzenoid to quinoid rings.³¹ It was reported in the literature that upon protonic acid doping

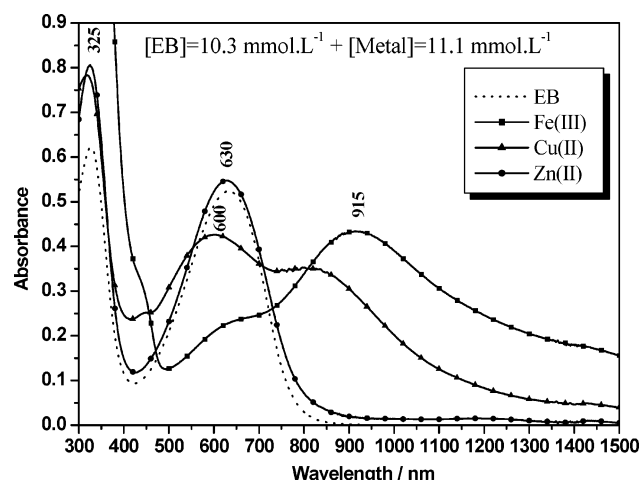


Figure 1. Electronic UV-vis-NIR spectra of EB and metal ion solutions in NMP. [EB] = 10.3 mmol L⁻¹ and [Mⁿ⁺] = 11.1 mmol L⁻¹.

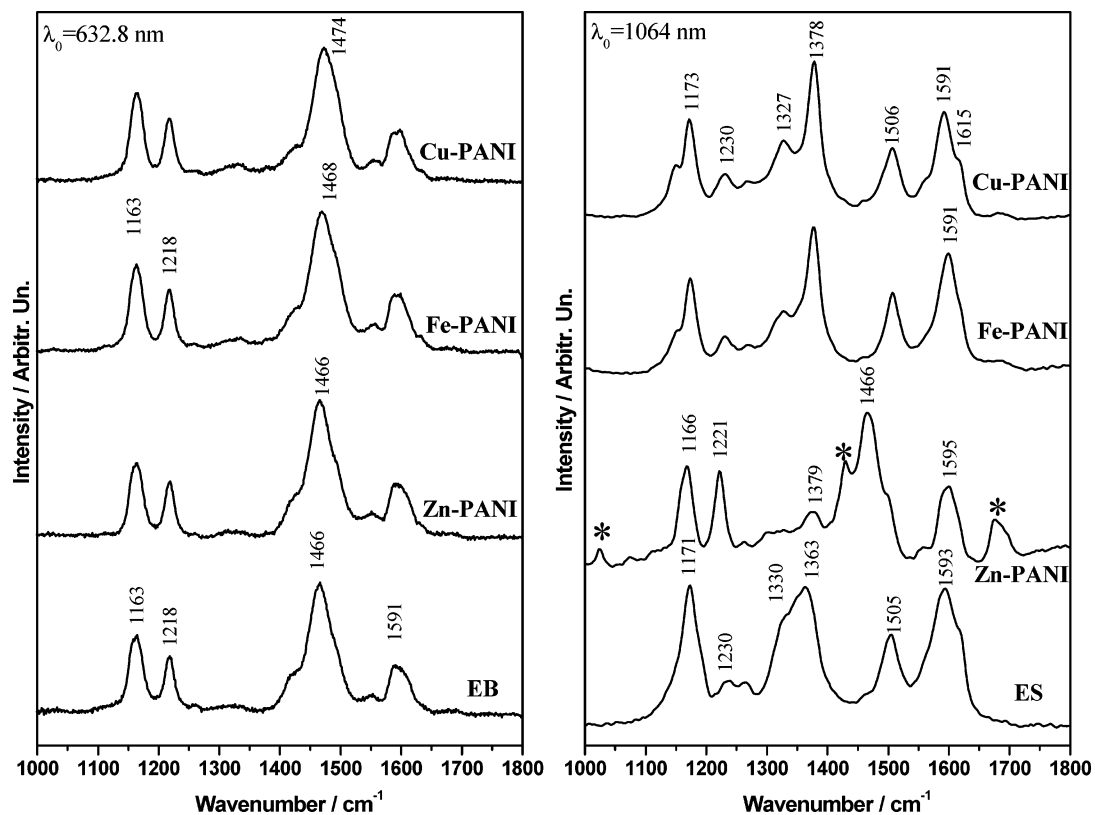


Figure 2. Resonance Raman spectra of EB solutions in NMP. [EB] = 10.3 mmol L⁻¹ and [metal cation] = 11.1 mmol L⁻¹. * indicates NMP bands.

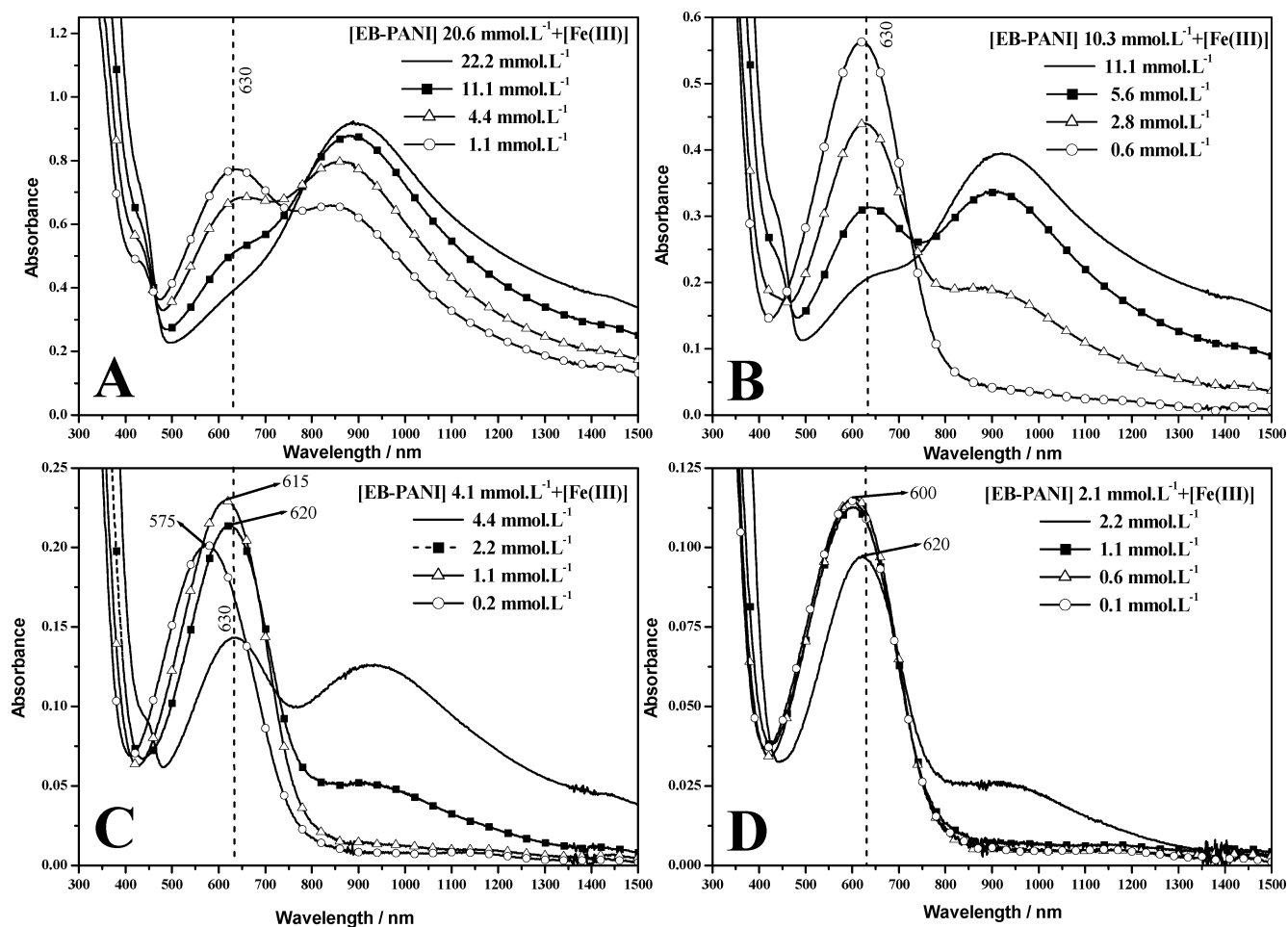


Figure 3. Electronic UV-vis-NIR spectra of Fe-PANI solutions in NMP with different Fe/EB molar ratios.

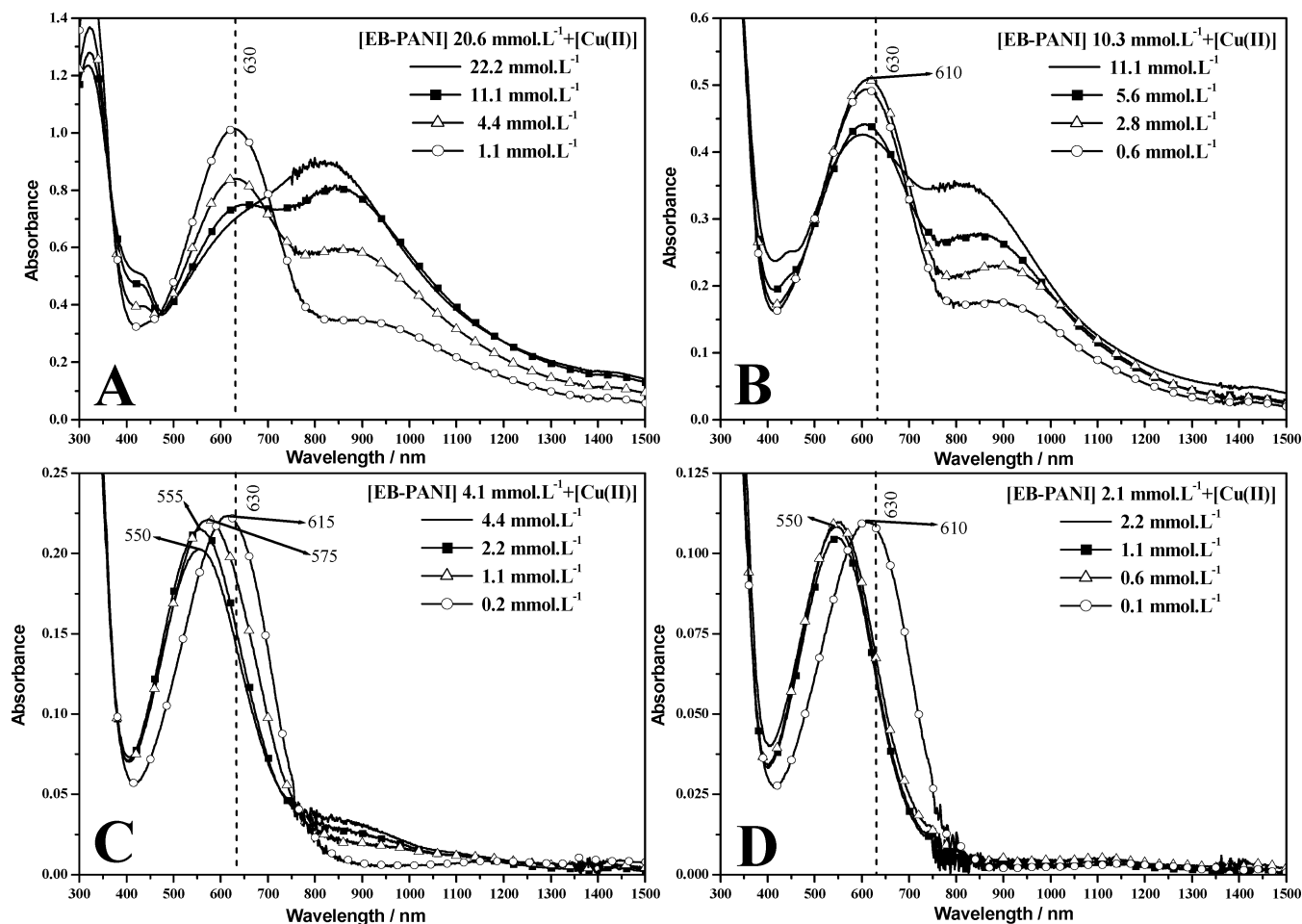


Figure 4. UV-vis-NIR spectra of Cu-PANI solutions in NMP with different Cu/PANI molar ratios.

the band at 630 nm disappears, whereas new bands at 440 and 850 nm, characteristic of polaronic segments, are observed.^{31,32} Albuquerque et al.³³ reported that an addition of oxidizing agent (persulfate) to an EB solution causes a gradual shift of the band at 630 nm to lower wavenumbers that depends on the oxidation level of PANI. This band is observed at 530 nm in the PB spectrum. The UV-vis-NIR spectrum of EB solution with Zn(II) (Zn-PANI) presents only the characteristic bands of EB, at 325 and 630 nm, suggesting that interaction of this metal cation and EB is not occurring. On the contrary, for Fe-PANI solution new absorption bands at 440 and 915 nm are observed. These bands are characteristic of polaronic segments, indicating that doped polymer are formed upon interaction of EB and Fe(III) in NMP. The spectrum of Cu-PANI solution shows bands at 600 and 820 nm. The presence of the band at 820 nm could be explained by the presence of doped polymer while the band at 600 nm could be attributed to the formation of oxidized polymer (pernigraniline, see Scheme 1). These results show that the products formed from the interaction of EB and transition metal cations in NMP solution are strongly dependent on the nature of the metal ion.

Figure 2 shows the resonance Raman spectra of the same solutions presented in Figure 1 for two exciting radiations. The resonance Raman spectrum of EB in NMP solution at 632.8 nm shows the characteristic bands of quinone segments at 1163 (β_{C-H}), 1218 (ν_{C-N}), 1466 ($\nu_{C=N}$), and 1591 cm^{-1} ($\nu_{C=C}$).^{34,35} The spectrum of Zn-PANI at 632.8 nm shows the same bands observed in EB spectrum and also a very weak and broad band at 1379 cm^{-1} observed in the ES spectrum, assigned to ν_{C-N^+} of radical cation segments. These segments can be easily

detected using the 1064 nm exciting radiation (Figure 2) since doped segments are in resonance in this condition, showing that a small amount of doped segments are formed in EB solution with Zn(II). For Fe-PANI and Cu-PANI, the resonance Raman spectra at 1064 nm present bands at 1173, 1230, 1327, 1378, 1506, 1591, and 1615 cm^{-1} (Figure 2). These bands are characteristic of radical cations,^{36,37} showing the formation of semiquinone segments upon Cu(II) and Fe(III) complexation. For 632.8 nm exciting radiation (Figure 2), the EB band at 1466 cm^{-1} assigned to $\nu_{C=N}$ is shifted to higher wavenumber in Cu-PANI spectrum when compared with the other metal-PANI spectra. In the PB spectrum this band occurs at 1485 cm^{-1} (spectrum not shown); so, the shift could indicate a partial oxidation of EB to PB by the Cu(II) ions. This hypothesis is confirmed by the electronic band at 600 nm in the Cu-PANI UV-vis-NIR spectrum (Figure 1).

The UV-vis-NIR spectra of EB and Fe(III) solutions with different EB/metal molar ratio are shown in Figure 3. As can be seen from Figure 3A, as the Fe(III) concentration is gradually increased, there is a decrease of the band at 630 nm together with an increase of the band at ca. 900 nm. This is an evidence that semiquinone segments are formed as the Fe(III)/EB molar ratio is increased. The same behavior is observed for a set of spectra (Figure 3B) of other solutions with different concentrations but with the same variation in the metal/polymer ratio. On the other hand, in Figure 3C, for the same metal/polymer ratio but with much more diluted solution, as Fe(III) concentrations is decreased, there is a shift of the band at 630 to 575 nm, and the relative intensity of the band at 900 nm does not overcome the intensity of other bands. This spectral behavior

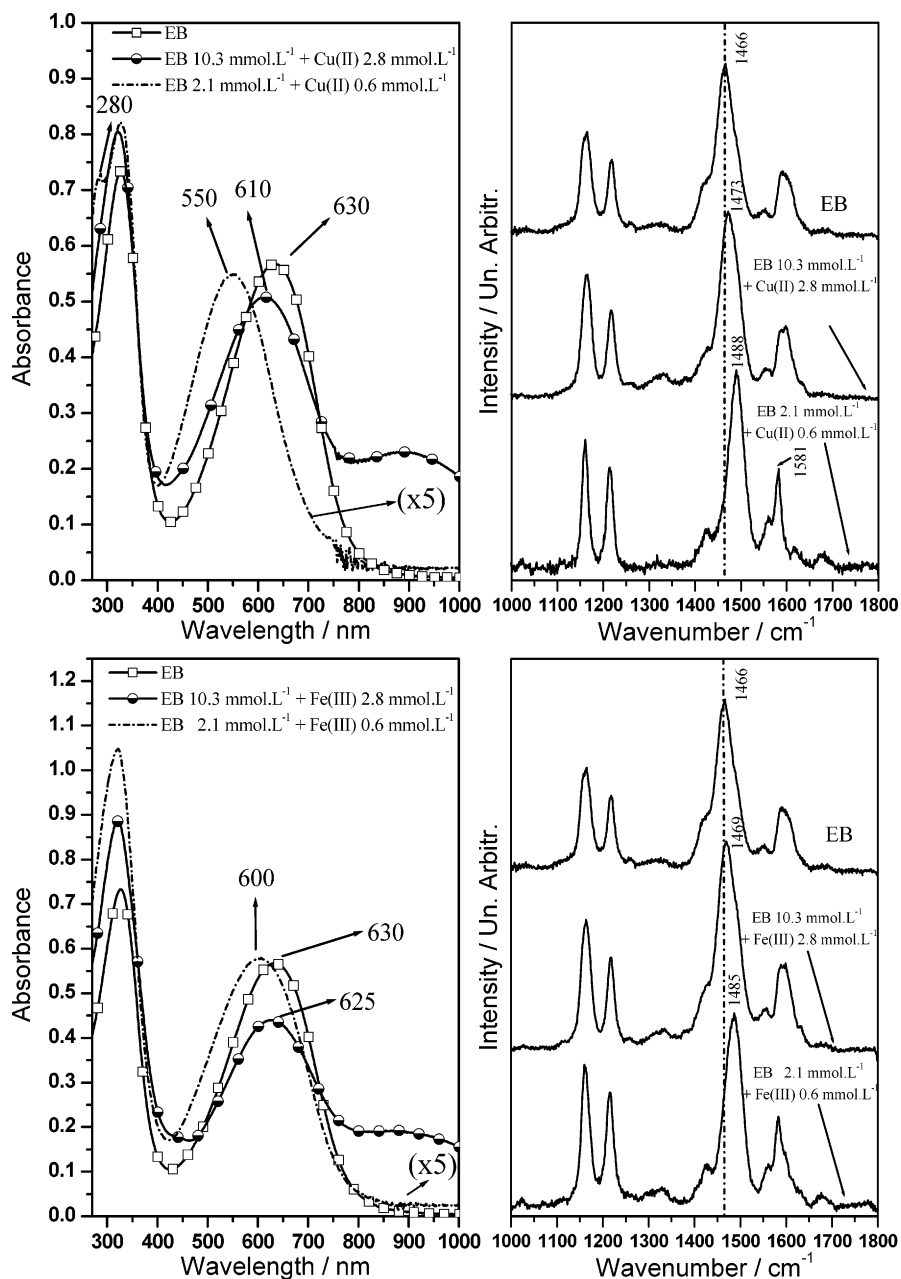


Figure 5. UV-vis-NIR and resonance Raman spectra ($\lambda_0 = 632.8$ nm) of Fe-PANI and Cu-PANI solutions in NMP. Concentrations are indicated in the figure.

is indicative that not only semiquinone segments are formed but also an oxidation of polymer is occurring, as indicated by the band at 575 nm. Figure 3D presents the spectra of lowest concentrations employed, but with the same metal/polymer ratio. Again, the relative intensity of the band at 900 nm is very low, and there is only a continuous shift of the band at 630 to 600 nm that can be assigned to the presence of pernigraniline-like segments. So, it can be observed that the UV-vis-NIR spectra of Fe-PANI solutions are dependent on the polymer/metal ratio and also on the concentration used.

According to Figure 4, the spectral behavior of solutions containing EB and Cu(II) is dependent on the Cu(II)/EB ratio. In Figure 4A, as the concentration of Cu(II) is increased, there is a decrease of the band at 630 nm and an increase of the bands at 820 and 430 nm, indicating the formation of semiquinone segments upon interaction with Cu(II). From Figure 4B where the solutions are diluted keeping the same metal/polymer ratio, there is a decrease in the relative intensity of the band at 900 nm (due to semiquinone) and a shift of the band at 630 to 550

nm, indicating that oxidation of EB is occurring. The shift of the band at 630 nm to lower wavelengths is also observed in spectra of Figure 4C,D, and it is more pronounced as the concentration of solutions is decreased.

Comparing the UV-vis-NIR spectra from Figures 3A and 4A (the same concentration of EB and transition metal salts), it can be noticed that the ratio of the bands ~ 900 nm (doped)/630 nm (undoped) in Fe(III) spectra is greater than in Cu(II). This result suggests that doping process by Fe(III) is more effective than by Cu(II). On the other hand, the blue shift of the band at 630 nm, assigned to EB oxidation, is observed in Figure 4B (Cu-PANI) but is not observed in Figure 3B (Fe-PANI). Additionally, for diluted solutions (Figures 3D and 4D), the shift of the band at 630 nm is greater for solutions containing Cu(II) (550 nm) than for Fe(III) (600 nm). These results show that pernigraniline formation in Cu(II) solution is favored compared to Fe(III) solution.

From these results it can be seen that by changing the Fe(III) or Cu(II) concentration (Figures 3 and 4), there is not only

a change in the relative amount of the species (doped/undoped) but also oxidized polymer (PB) formation in diluted solutions. Aiming to confirm the role of metal cations and of EB concentrations on the nature of the species formed, the resonance Raman technique was also used (Figure 5). For both Cu-PANI and Fe-PANI solutions it, can be seen changes in the spectral profiles upon dilution. The UV-vis-NIR spectrum of the solution with EB 10.3 mmol L⁻¹ and Cu(II) 2.8 mmol L⁻¹ presents bands at 610 and 900 nm that can be attributed to partially oxidation and doping of EB, respectively (Figure 5). The presence of oxidized segments is also confirmed by the shift of the Raman band ($\nu_{C=N}$) from 1466 to 1488 cm⁻¹ (Figure 5). The band at 1488 cm⁻¹ ($\nu_{C=N}$) in the resonance Raman spectrum, the lack of the band at ca. 900 nm, and the shift of the absorption band at 630 to 550 nm in the UV-vis-NIR spectrum upon dilution suggest that oxidized polymer is the primary species present in the diluted solutions. For instance, the UV-vis-NIR spectrum of solution EB 2.1 mmol L⁻¹/Cu(II) 0.6 mmol L⁻¹ (Figure 5) presents the band at 280 nm and a shift of the band at 630 to 550 nm that are characteristic of PB formation.³³ In the same way, the resonance Raman spectrum presents a band centered at 1490 cm⁻¹ and a sharp band at 1581 cm⁻¹ that are characteristic of PB.^{21,35} On the basis of the results of both UV-vis-NIR and resonance Raman, we undoubtedly demonstrate that the blue shift of the band at 630 nm in EB solutions with Cu(II) or Fe(III) is due to the oxidation of EB. The absorption bands at 625 and 900 nm in the UV-vis-NIR spectrum of the solution containing EB 10.3 mmol L⁻¹ and Fe(III) 2.8 mmol L⁻¹ together with the Raman band ($\nu_{C=N}$) at 1469 cm⁻¹ indicate that this solution also presents doped and oxidized polymer. After dilution, the band at 900 nm is no more observed. Additionally, the absorption band related to quinone segments is shifted to 600 nm in the UV-vis-NIR spectrum, while the Raman band assigned to $\nu_{C=N}$ shifts to 1485 cm⁻¹, showing that Fe(III)/EB diluted solution also results in the oxidation of EB. Although EB oxidation is observed both in Cu(II) and Fe(III) solutions, the presence of Cu(II) ions results in a larger extent of oxidation than Fe(III). The correlation between the position of absorption band associated with the presence of quinoid segments (630 nm) and the Raman band of $\nu_{C=N}$ (1466 cm⁻¹) undoubtedly demonstrate that oxidized polymer (pernigraniline) is formed in EB solution with Cu(II) and Fe(III). Furthermore, it was observed that diluted solutions of EB with these ions in NMP favor the oxidation of EB instead of its doping. It is important to mention that no oxidation was observed for the PANI solutions containing the non-redox-active Zn(II) ion.

A blue shift of the EB absorption band at 630 nm was observed when PANI thin films are formed.^{38,39} This blue shift was assigned to conformational changes associated with ring torsion angle in the polymer backbone primarily due to polymer-substrate interaction rather than oxidation of polymer chain (PB formation). This assignment was done because IR spectra of PANI thin films did not show the characteristic PB spectral features. However, the blue shift observed in this study (Figures 3–5) could not be associated with conformational changes because resonance Raman spectra of EB/metal salts solutions present PB characteristic features.

Using the EPR technique, it is possible to monitor the semiquinone segments as well as the transition metal salts. The EPR spectra of Fe-PANI and Cu-PANI solutions are shown in Figure 6. The EPR spectra of CuCl₂·2H₂O and FeCl₃·6H₂O in NMP were also recorded for comparison purposes since Cu(II) and Fe(III) are paramagnetic ions. The EPR spectrum of

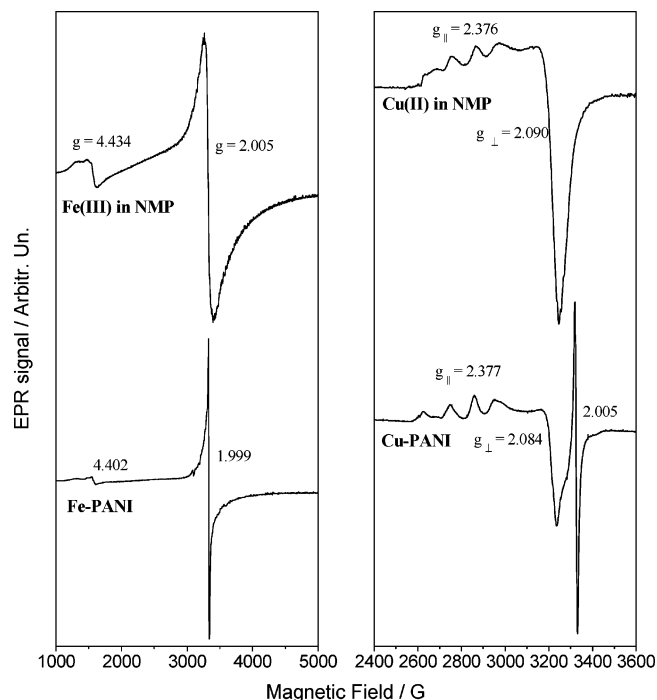


Figure 6. EPR spectra of Cu(II) and Fe(III) solutions in NMP ([metal] = 7.2 mmol L⁻¹) and metal/PANI solutions in NMP ([metal] = 22.2 mmol L⁻¹ and [EB] = 26.5 mmol L⁻¹).

Zn-PANI (not shown) does not present any signal, indicating that there are not paramagnetic species in this solution. It can be observed that the EPR spectrum of Fe(III) in NMP presents broad signals at $g = 4.434$ and 2.005 , characteristics of high-spin Fe(III). The Fe-PANI EPR spectrum presents signals of Fe(III) ions at $g = 4.402$ and ca. 2.0 superimposed to the organic radical signal at $g = 1.999$, which is broadened (width of 15 G) by the presence of metal ions. Therefore, these results indicate that semiquinone segments and high-spin Fe(III) ions are present in this sample. The EPR spectrum of Cu(II) in NMP shows a characteristic signal with hyperfine splitting and $g_{\perp} = 2.090$, $g_{\parallel} = 2.376$, and $A_{\parallel} = 118.2$ G. Similarly, the spectrum of Cu-PANI presents a broadened signal with line width of 10 G at $g = 2.005$, in addition to those of the metal ion. These features confirm the formation of radical cations upon interaction of EB with Cu(II). All these results are in agreement with those obtained using resonance Raman and electronic UV-vis-NIR spectroscopies.

Polymeric films were prepared from metal/EB solutions by drop-casting. The UV-vis-NIR spectra of the films and the metal/EB solutions used to prepare them are shown in Figure 7. For all samples, the UV-vis-NIR spectra of the films are different from the solutions. For Cu(II) the intensity ratio of 850/600 nm bands increases in the spectrum of the film. The solvent evaporation gives rise to semiquinone segments because after the solvent elimination more copper ions are available for coordination to the lone pair on nitrogen in the EB. Furthermore, for all the films the absorption at NIR is higher than in solution, suggesting that metal complexation is occurring for all cation samples. It is interesting to notice that even the film with Zn(II) shows absorption bands at 440 and 850 nm, which are characteristic features of doped polymer (ES). This result suggests that there is a competition between ion-solvent and ion-polymer interactions, and in the case of Zn(II), the coordination of the ion to the polymeric chains, resulting in doped polymer, is only reached through the solvent release.

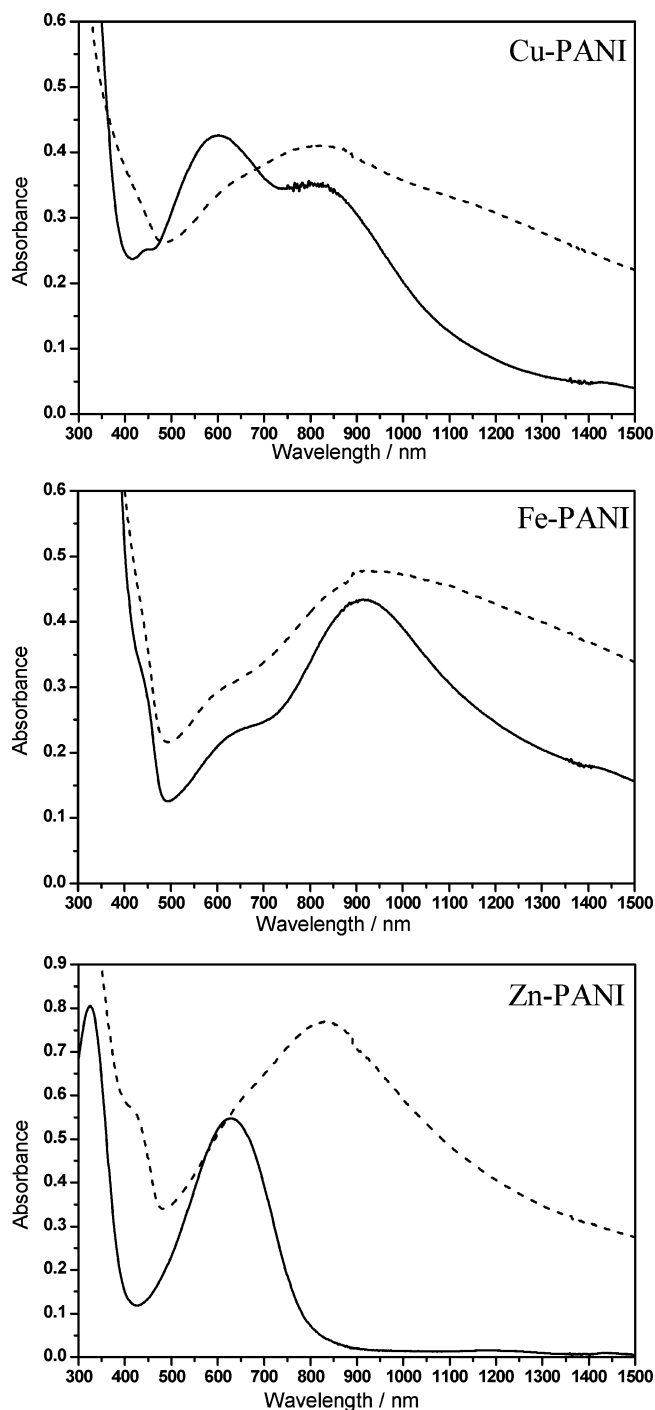


Figure 7. Electronic UV-vis-NIR spectra of Metal/PANI solutions (solid line) ($[\text{EB}] = 10.3 \text{ mmol L}^{-1}$ and $[\text{M}^{n+}] = 11.1 \text{ mmol L}^{-1}$) and films prepared from these solutions (dashed line).

The resonance Raman spectra of metal/EB films are shown in Figure 8. It can be observed drastic differences between the solutions resonance Raman spectra (Figure 2) and those of films (Figure 8), both excited at 632.8 nm. The main differences upon solvent evaporation are the decreasing of the bands at 1220 ($\nu_{\text{C-N}}$) and at 1466 cm^{-1} ($\nu_{\text{C=N}}$) assigned to quinone segments and the appearance of new bands, characteristic of semiquinone segments, at 1258 and 1330 cm^{-1} . Even in the film containing Zn(II), the semiquinone features were observed. This result points to the conversion of insulator EB to the conductive form of polyaniline (ES) upon film formation, corroborating the UV-vis-NIR spectroscopic results.

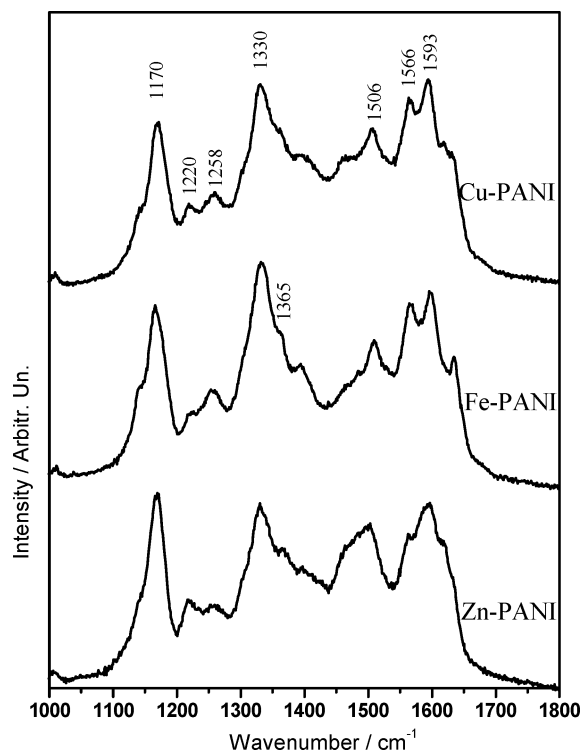


Figure 8. Resonance Raman spectra of metal/PANI films prepared from solutions of ($[\text{EB}] = 10.3 \text{ mmol L}^{-1}$ and $[\text{M}^{n+}] = 11.1 \text{ mmol L}^{-1}$), exciting radiation = 632.8 nm.

The EPR spectra of metals/EB films are shown in Figure 9. Zn-PANI film presents EPR spectrum with a narrow signal with $g = 2.003$ (line width of 11 G). This result indicates the presence of an organic radical due to doped polymer formation, confirming resonance Raman and UV-vis-NIR data. On the other hand, the Fe-PANI spectrum presents only a broad signal with $g = 2.044$ (line width of 494 G). The absence of a sharp signal indicative of an organic radical could be explained by the magnetic interaction between the metal spin and organic radical cations of the polymer. Similarly, Cu-PANI film shows the EPR spectrum with isotropic signal at $g = 2.152$ (line width of 225 G) with no hyperfine structure, indicating also a magnetic coupling of Cu(II) ions and organic radicals. Similar results have been described for PANI doped with Cu(II) and Fe(III) using the suspension synthetic route.²¹

This set of results shows that the species formed through the interaction of EB and transition metal cations are strongly dependent on the nature of the ion and on their concentration. For Cu(II) and Fe(III) in diluted solutions the oxidation of EB to PB was observed. The proposed mechanism involves the oxidation of amine groups by Fe(III) or Cu(II). The Cu(I) and Fe(II) ions formed could be reoxidized by action of O_2 , and subsequently, they could act as oxidizing agent again. For these ions in concentrated solution, doped polymer is formed (ES). The results with concentrated solutions are in agreement with those obtained using the suspension route.²¹ The doping process occurs both by pseudo-protonation and by a redox process. In the latter process, Cu(II) and Fe(III) ions could oxidize the amine segments resulting in pernigraniline moieties, Cu(I), and Fe(II) ions. After the oxidation of EB to PB, there is a second step where Cu(I) or Fe(II) ions interact with imine nitrogen atoms and reduce them, resulting in semiquinone segments and Cu(II) or Fe(III) ions. For all Zn(II) solutions no interaction with polymer was observed; semiquinone forma-

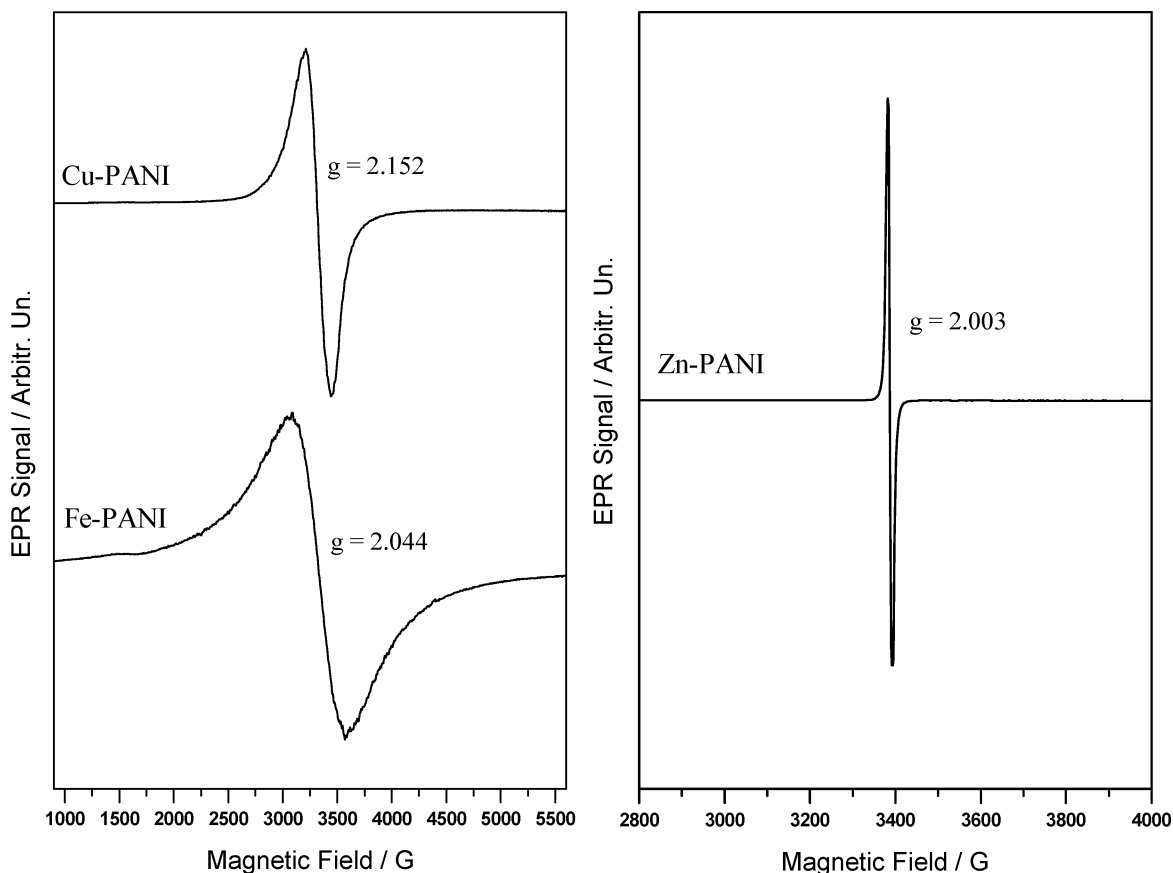


Figure 9. EPR spectra of metal/PANI films prepared from solutions of ([EB] = 10.3 mmol L⁻¹ and [Mⁿ⁺] = 11.1 mmol L⁻¹).

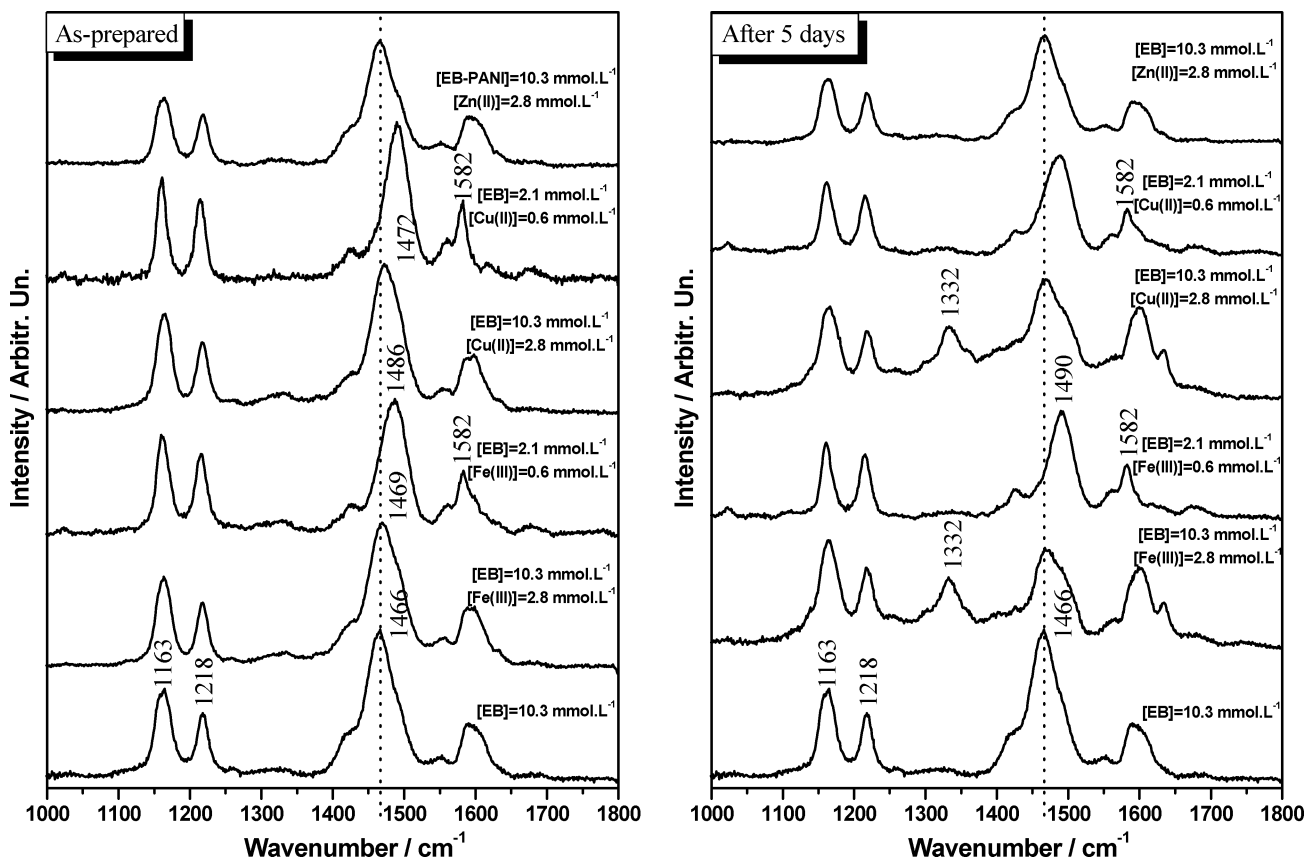


Figure 10. Resonance Raman spectra of metal/PANI solutions as-prepared and after 5 days; exciting radiation = 632.8 nm.

tion was only observed when films were prepared, i.e., when the solvent was eliminated.

Figure 10 shows the resonance Raman spectra ($\lambda_0 = 632.8$ nm) of EB solutions with Cu(II), Fe(III), and Zn(II) recently

prepared and after 5 days. The resonance Raman spectrum of Zn(II) solution recently prepared is similar to the spectrum of EB, and it remains the same after 5 days, indicating that interaction of Zn(II) and EB in these solutions is not occurring in this period of time. The solutions of EB with Cu(II) and Fe(III), $[EB] = 10.3 \text{ mmol L}^{-1}/[\text{metal}] = 2.8 \text{ mmol L}^{-1}$, present the band assigned to $\nu_{C=N}$ slightly shifted to higher wavenumbers (6 and 4 cm^{-1} for Cu(II) and Fe(III), respectively), indicating that oxidation of amine moieties is occurring. After 5 days, the band ascribed to $\nu_{C=N}$ assumes its original value, and a new band at 1332 cm^{-1} assigned to ν_{C-N^+} is observed. This result is consistent with the proposition that PB is converted to doped polymer in Cu(II) or Fe(III)/EB solutions as a function of time. On the other hand, it is not observed any signal of doped segments after 5 days in the resonance Raman spectra of diluted solutions of EB with Cu(II) and Fe(III), $[EB] = 2.1 \text{ mmol L}^{-1}/[\text{metal}] = 0.6 \text{ mmol L}^{-1}$. The observation of oxidized segments instead of doped segments in diluted solutions could be attributed to the very low concentration of metal cation, which is not sufficient to coordinate to the polymer, and so the doping process is not observed.

Conclusions

Resonance Raman, UV-vis-NIR, and EPR results obtained in this work showed that the products formed from the interaction of EB and transition metal cations are strongly dependent on the nature of the metal ion, their concentration, and the metal/polymer ratio. The formation of semiquinone and the oxidation of EB were undoubtedly demonstrated in the EB solutions with Cu(II) and Fe(III).

Furthermore, it was observed that the species present in NMP solutions depend not only on the metal/EB molar ratio but also on the concentration of each component. For Cu(II) and Fe(III), diluted solutions favor the formation of oxidized segments instead of doped ones.

Resonance Raman and UV-vis-NIR spectra of the films showed the spectral features of doped polymer (ES), indicating that for all these studied cations the solvent elimination leads to the formation of radical cations, even for Zn(II) solution in which no interaction of the metal cation and EB was observed. For solutions, there is a competition among the interactions ion-solvent, polymer-solvent, and ion-polymer; when the solvent is released, the ion can interact with the polymer and then doping it.

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References and Notes

- MacDiarmid, A. G.; Epstein, A. J. *J. Faraday Discuss. Chem. Soc.* **1989**, *88*, 317–332.
- Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139–182.
- Huang, W. S.; MacDiarmid, A. G.; Epstein, A. J. *Chem. Commun.* **1987**, *23*, 1784–1786.
- Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277–324.
- Sapirgin, A. V.; Breneman, K. R.; Lee, W. P.; Long, S. M.; Kohlman, R. S.; Epstein, A. J. *Synth. Met.* **1999**, *100*, 55–59.
- Giotto, M. V.; Bonagamba, T. J.; Panepucci, H.; Valenciano, G. R.; Mattoso, L. H. C. *Synth. Met.* **1999**, *101*, 756–757.
- Ryu, K. S.; Moon, B. W.; Joo, J.; Chang, S. H. *Polymer* **2001**, *42*, 9355–9360.
- Chen, S. A.; Lin, L. C. *Macromolecules* **1995**, *28*, 1239–1245.
- Genoud, F.; Kulszewicz-Bajer, I.; Dufour, B.; Rannou, P.; Pron, A. *Synth. Met.* **2001**, *110*, 415–416.
- Kulszewicz-Bajer, I.; Suwalski, J. *Synth. Met.* **2001**, *119*, 343–344.
- Bienkowski, K.; Kulszewicz-Bajer, I.; Genoud, F.; Oddou, J. L.; Pron, A. *Synth. Met.* **2003**, *135*, 159–160.
- Genoud, F.; Kulszewicz-Bajer, I.; Bedel, A.; Oddou, J. L.; Jeandey, C.; Pron, A. *Chem. Mater.* **2000**, *12*, 744–749.
- Kulszewicz-Bajer, I.; Pron, A.; Abramowicz, J.; Jeandey, C.; Oddou, J. L.; Sobczak, J. W. *Chem. Mater.* **1999**, *11*, 552–556.
- Hasik, M.; Drelinkiewicz, A.; Wenda, E. **2001**, *119*, 335–336.
- Neoh, K. G.; Young, T. T.; Looi, N. T.; Kang, E. T. *Chem. Mater.* **1997**, *9*, 2906–2912.
- Dimitriev, O. P. *Macromolecules* **2004**, *37*, 3388–3395.
- Anand, J.; Rao, P. S.; Palaniappan, S.; Sathyanarayana, D. N. *Synth. Met.* **1998**, *95*, 57–62.
- Dimitriev, O. P.; Kislyuk, V. V. *Synth. Met.* **2002**, *132*, 87–92.
- Dimitriev, O. P. *Polym. Bull. (Berlin)* **2003**, *50*, 83–90.
- Dimitriev, O. P.; Smertenko, P. S.; Stiller, B.; Brehmer, L. *Synth. Met.* **2005**, *149*, 187–192.
- Izumi, C. M. S.; Constantino, V. R. L.; Ferreira, A. M. C.; Temperini, M. L. A. *Synth. Met.* **2006**, *156*, 654–663.
- Higuchi, M.; Imoda, D.; Hirao, T. *Macromolecules* **1996**, *29*, 8277–8279.
- Fahlman, M.; Crispin, X.; Guan, H.; Li, S.; Smallfield, J. A. O.; Wei, Y.; Epstein, A. J. *Polym. Prepr.* **2000**, *41*, 1753.
- Epstein, A. J.; Smallfield, J. A. O.; Guan, H.; Fahlman, M. *Synth. Met.* **1999**, *102*, 1374–1376.
- Tallman, D. E.; Spinks, G.; Dominis, A.; Wallace, G. G. *J. Solid-State Electrochem.* **2002**, *6*, 73–84.
- Higuchi, M.; Ikeda, I.; Hirao, T. *J. Org. Chem.* **1997**, *62*, 1072–1078.
- Virji, S.; Fowler, J. D.; Baker, C. O.; Huang, J. X.; Kaner, R. B.; Weiller, B. H. *Small* **2005**, *1*, 624–627.
- Batchelder, D. N. In *Optical Techniques to Characterize Polymer Systems*; Brässlner, H., Ed.; Elsevier: Amsterdam, 1987; p 393.
- MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacér, L., Ed.; Riedel Publications: Dordrecht, 1987; p 105.
- Moon, D. K.; Ezuka, M.; Maruyama, T.; Osakada, K.; Yamamoto, T. *Macromolecules* **1993**, *26*, 364–369.
- Huang, W. S.; MacDiarmid, A. G. *Polymer* **1993**, *34*, 1833–1845.
- Lee, K.; Heeger, A. J.; Cao, Y. *Synth. Met.* **1995**, *72*, 25–34.
- de Albuquerque, J. E.; Mattoso, L. H. C.; de Faria, R. M.; Masters, J. G.; MacDiarmid, A. G. *Synth. Met.* **2004**, *146*, 1–10.
- Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. *Macromolecules* **1988**, *21*, 1297.
- Quillard, S.; Louarn, G.; Lefrant, S.; MacDiarmid, A. G. *Phys. Rev. B* **1994**, *50*, 12496–12508.
- Gruger, A.; Novak, A.; Regis, A.; Colomban, P. *J. Mol. Struct.* **1994**, *328*, 153–167.
- Quillard, S.; Berrada, K. D.; Louarn, G.; Lefrant, S.; Lapkowski, M.; Pron, A. *S. New J. Chem.* **1995**, *19*, 365–374.
- Dimitriev, O. P. *Synth. Met.* **2001**, *125*, 359–363.
- Dimitriev, O. P. *Synth. Met.* **2001**, *122*, 315–319.

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