

Spectroscopic Investigation of Iron Salts Doped Polyaniline

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ABSTRACT: Iron salts have been doped into emeraldine base (EB) successfully using a chemical route. Both FeCl_3 and FeSO_4 were doped separately into EB in acetonitrile with metal ion and tetramer in the ratio of 4 : 1. The doped samples were characterized by UV-vis absorption, Mössbauer and fourier transform infrared (FTIR) spectroscopy. UV-vis spectra showed a suppression of the characteristic band of EB at 660 nm with an extended absorption towards the infrared regions for both the doped samples. FeSO_4 showed electronic absorption behavior similar to the features of acid doped EB. Mössbauer spectroscopy confirmed the presence of single oxidation and high spin

states of Fe(III) and Fe(II) in the respective doped polymers. No signature of Fe^{2+} was observed in the Fe^{3+} doped EB from the Mössbauer spectrum. FTIR spectroscopy showed a shift towards the lower wave number for the iron salts doped EB as compared to the pristine polymer. An increase in the intensity of the band at 1140 cm^{-1} is observed, which corresponds to the electronic like absorption confirming the doping of EB. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2792–2797, 2009

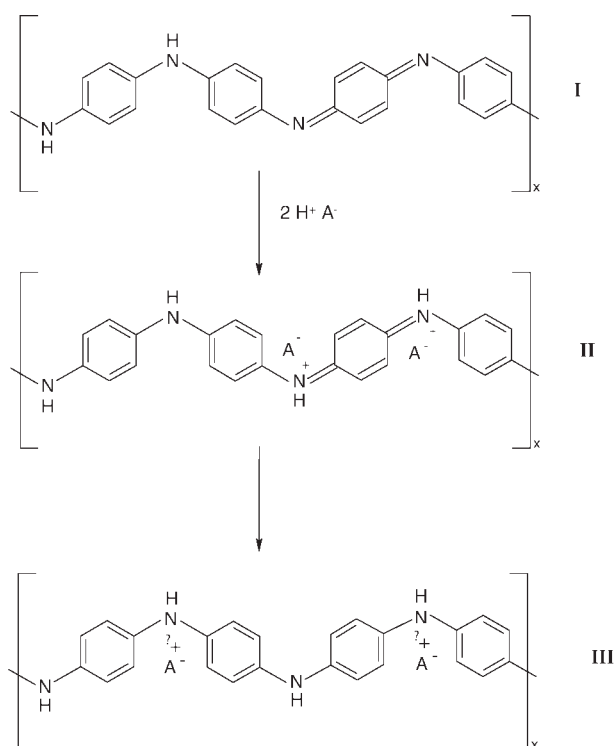
Key words: Polyaniline; iron salts; emeraldine base; Mössbauer spectroscopy; transition metal doping; polaron

INTRODUCTION

Polyaniline (PANI) is unique among the family of conjugated polymers since its doping level can be readily controlled through an acid doping/base dedoping process.¹ Potential applications of PANI include organic lightweight batteries, microelectronics, electrochromic displays, electromagnetic shielding and sensors.² Depending upon the oxidation state and potential level, PANI is either totally insulating or exhibits high conductivity. The fully reduced leucoemeraldine (LB) and the fully oxidized pernigraniline are insulating materials. Doping of PANI has, until now, relied strongly upon the protonic acid doping and its transformation to the electrically conducting form emeraldine salt (ES). Protonation is the simplest way to get the highly conductive ES but the polymer obtained is insoluble in the conventional organic solvents. There are few methods, which are used to overcome the insoluble nature. The first approach is to modify the backbone by the use of substituted aniline monomer in the synthesis^{3–5} which gives rise to soluble polymers. But, the drawback of this method is a decrease in the conductivity. The second approach is the counter ion-induced processability: by using an organic acid instead of inorganic salt and thus the polymer obtained becomes soluble in common solvents such as DMF or

DMSO. The acid commonly used is camphor sulphonic acid^{6,7} or dimethylsulphonic acid.^{8–10}

The protonation in PANI base is accompanied by a charge redistribution (internal redox reduction), which leads to the formation of a polysemiquinone radical type (III), called polaron lattice. The transformation of II in to III renders all rings equivalent and strongly favors charge delocalization.



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This fact severely impedes its large-scale technological applications. To overcome these difficulties, in past few years research effort has been directed toward the improvement of solution and processability of PANI. Lewis acid doping is one of the methods, which allow converting the emeraldine base (EB) form of PANI to its conductive form and the Lewis acid doping renders PANI soluble in different types of solvents, which is not possible in the case of Bronsted acid doping. The other way to achieve highly conductive PANI films is to employ the alkali-metal salts as dopants.¹¹ Light metal ions, such as Li^+ or Na^+ , are able to coordinate to imine nitrogen atoms of the polymer backbone, thus playing the role of protons and leading to a pseudo-protonation of the polymer. However, because of the mass difference of the metal ion and the proton, the highly symmetrical structure of the polymer backbone is not possible upon the doping with alkali metal ions. As a result, the conductivity of PANI films doped by alkali metal salts is lower by orders of magnitude as compared with those of protonic acid doped films.¹²

From the literature available for PANI doped with Lewis acid^{13–15} and transition metal salts,^{11,12,16} it can be learnt that the conductivity of PANI films doped with EuCl_3 [Ref. 13] approaches that of the hydrochloric acid doped films, and this phenomenon was explained via successive oxidation, pseudo-protonation, and protonation of the polymer backbone during doping. In addition to the above salts, which serve as dopants, there are salts of other metals that have electrode potentials intermediate between that of alkali metal ions and that of oxidative metal ions. It appears that such ions cannot directly oxidize the polymer chains or function as protons. There are several articles reporting the effect of doping EB by various transition metal salts,^{12–19} where the mechanism of doping by these salts was assigned to either pseudo-protonation or Lewis acid doping of the polymer. The mixed valent iron oxalate doping of EB was carried out and studied by Mathur et al.²⁰ The recent study detailed the molecular interaction between functional group in polydiphenylamine, *N*-aryl substituted aniline and ferric ions (Fe^{3+}) for the possible use in sensor applications.²¹ The problem of interaction of PANI and metal atoms or metal cations is of great importance due to the growing use of this polymer in organic electronics,²² electroluminescent devices,^{23,24} as protective coating against corrosion of metal surfaces.²⁵

The main purpose of this research was to prepare FeCl_3 and FeSO_4 doped EB and to study the interactions of the same metal cation with EB using complementary spectroscopic techniques such as Mössbauer, UV-visible and FTIR spectroscopy. We have selected these dopants because of the two different charges of the same metal cation.

EXPERIMENTAL

In a “standard” procedure, aniline hydrochloride was oxidized with ammonium peroxy disulphate in aqueous medium at ambient temperature. PANI was synthesized according to Stejkal et al.²⁶ Aniline hydrochloride (2.59 g, 20 mmol) and ammonium peroxydisulfate (5.71 g, 25 mmol) were dissolved separately in 50 mL of distilled water. Both solutions were kept for 1 h at room temperature, then mixed in a beaker, briefly stirred, and left at rest overnight to polymerize. PANI precipitate thus obtained was collected on a filter, washed with three 100-mL portions of 0.2 M HCl, and similarly with acetone. PANI (emeraldine) hydrochloride powder was dried in air and then in vacuum at 60°C. Additional polymerizations were carried out in an ice bath at 0–2 °C. The freshly prepared ES was dedoped using 0.2 M aqueous ammonia solution by stirring for 6 h, at pH 9. Then EB was doped with the iron salts, FeCl_3 or FeSO_4 , by calculating the metal ion-EB (tetramer) stoichiometric ratio, which was fixed at 4 : 1. The tetramer of EB has two imine and two amine nitrogen atoms, which can be possible sites for metal ion complexation. In a typical procedure of doping of EB with FeCl_3 , 1.076 g of anhydrous FeCl_3 was dissolved in 80 mL of acetonitrile and mixed with 0.60 g vacuum dried EB. The doping process was carried out for 18 h. Lewis acid-base complexation rendered PANI soluble in acetonitrile. FeSO_4 doping was also carried out following the same procedure taking 278 mg of FeSO_4 and 45 mg of EB.

Free standing films were prepared from the iron salts doped EB solutions on quartz substrates by dip-coating method. These films were used for the UV-visible spectrometry. UV-visible spectra of these films were carried out using a Shimadzu (UV-1601 PC) in a single scan at a scanning speed of 120 nm/min with a resolution of 2 nm. The films were dried in vacuum. The iron salts doped PANI powder was obtained by evaporation of the solvent in vacuum over a period of one week. Mössbauer spectra of EB doped with iron salts were measured in room temperature in a standard PC based spectrometer working in the constant acceleration mode. ^{57}Co in Rh matrix was used as source. The as-seen spectrum was deconvoluted using a least squares fitting program. FTIR spectral measurement of FeCl_3 and FeSO_4 doped EB samples were done using KBr pellets of the respective samples using Perkin-Elmer FTIR system (Spectrum GX) having a resolution of 2 cm^{-1} .

RESULTS AND DISCUSSION

UV-vis spectroscopy

The UV-vis Spectra of the EB thin film, FeCl_3 and FeSO_4 doped EB doped are shown in [Fig. 1(a–d)].

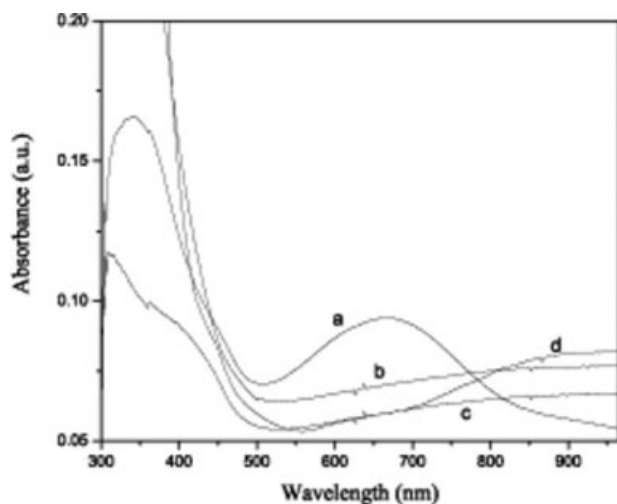


Figure 1 UV-vis spectra of (a) emeraldine base, (b) Fe (II) doped in 4 : 1 ratio, (c) Fe (II) doped in 8 : 1 ratio, and (d) Fe (III) doped emeraldine base.

The spectrum of EB show strong absorption peak around ~ 660 nm, which is attributed to the exciton like transition from the benzenoid rings to the quinoid rings²⁷ [Fig. 1(a)]. EB doped (in two different tetramer-Fe ratio of 4 : 1 [Fig. 2(b)] by FeSO_4 showed electronic absorption similar to the features of acid doped emeraldine films i.e. the strong absorption corresponding to polarons at ~ 440 nm and extending absorption tail towards the IR region, with suppression of the benzenoid to quinoid exciton like transition at ~ 660 nm. In Figure 2(c) typically illustrates that higher Fe-tetramer ratio (8 : 1) had also similar effect with more pronounced suppression at 660 nm band. On the contrary, EB doped with FeCl_3 showed only an extending of absorption tail with increase from visible to IR region with complete suppression of the benzenoid to quinoid exciton like transition at ~ 660 nm.

Two different types of spectral changes have been observed in FeCl_3 doped and FeSO_4 doped emeraldine base samples. It may be noted that the binding affinity of the different metal cations with the PANI chain, particularly with the two basic groups in the benzenoid and quinoid rings can vary, Transition metal ions with low electrode potential, such as Zn^{2+} , has the ability to coordinate to the nitrogen atoms of the quinoid rings, whereas transition metal

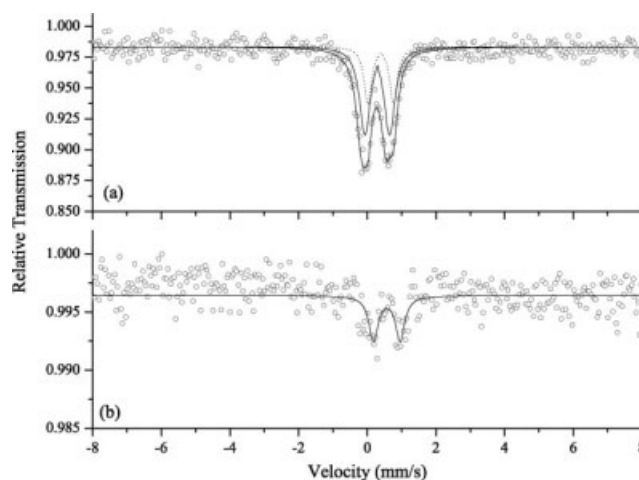
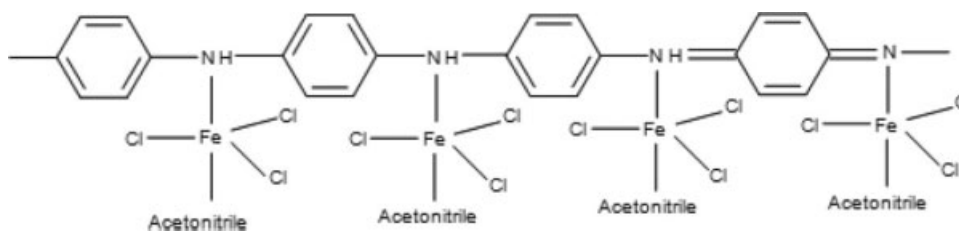


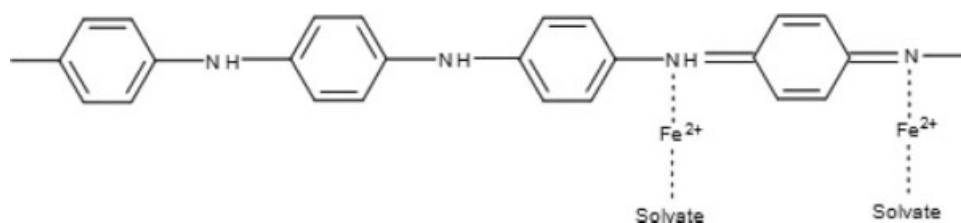
Figure 2 Mössbauer spectra of (a) Fe (III) and (b) Fe (II) doped emeraldine base.

ions with intermediate electrode potential have the ability to coordinate to the nitrogen atoms of both benzenoid and quinoid rings of the polymer matrix.^{12,28,29} From the reduction potential table, it is known that Fe^{2+} has lower reduction potential than Fe^{3+} ($V_{\text{red}}, \text{Fe}^{2+} = -0.409$ V, $V_{\text{red}}, \text{Fe}^{3+} = 0.771$ V). Therefore, it is quite difficult for Fe^{2+} to oxidize the electron rich benzenoid ring. So, in this case partial oxidation of polymer occurs, and the doping must proceed via pseudo-protonation of the polymer.^{28,29} The UV-vis spectra of FeSO_4 doped EB show the features similar to the protonated emeraldine base. So, its clear that Fe^{2+} which has low electrode potential is able to coordinate only with the imine nitrogen atoms of the polymer backbone, thus playing the role of protons and leading to the pseudo-protonation of the polymer.^{28,29} The formation of semiquinone segments that coordinate with the high spin Fe (III) ions was observed by electron paramagnetic resonance spectroscopy.^{30,31}

The tetramer of EB has two imine and two amine nitrogen atoms, which can be possible sites for metal ion complexation. Scheme 1 shows the possibility of complexation in the case of FeCl_3 doped EB through all four sites (two imine and two amine nitrogen atoms). Scheme 2 shows the possibility of complexation occurs in the case of FeSO_4 doped EB in two imine sites only.



Scheme 1 Possible structure of FeCl_3 doped EB.



Scheme 2 Possible structure of FeSO_4 doped EB.

The UV-vis spectra of FeCl_3 doped EB show features different from the FeSO_4 doped one. In this case, FeCl_3 is a Lewis acid having high electrode potential compared to Fe^{2+} and thus the doping occurs via oxidative process. An extended absorption tail with increase from Vis to NIR region can be attributed to the delocalization of charge carriers (polarons).³²

Mössbauer spectroscopy

Mössbauer spectroscopy was performed to ascertain the oxidation states of iron after doping and to establish the doping mechanism of both Fe^{3+} and Fe^{2+} to the polymer backbone. Mössbauer spectra of both Fe^{3+} and Fe^{2+} doped EB are shown in [Fig. 2 (a,b)] respectively. In the case of EB doped with Fe^{3+} , the as-seen doublet is deconvoluted into two doublets signifying the presence of two inequivalent sites that Fe^{3+} can be complexed to, in the polymer backbone. These two sites are the amine and imine sites of the EB. The obvious difference in the isomer shift (IS) of the two sites signifies the difference in the electron densities around the iron nucleus complexed to these two sites (Table I). The doublet with lower IS is attributed to the amine sites.¹⁵ From the relative intensities of the doublets it is clear that the affinity of Fe^{3+} is much greater for amine sites than for imine sites. The hyperfine parameters obtained for both the deconvoluted doublets are characteristic of high spin Fe^{3+} oxidation state. It is worth mentioning here that Genoud et al.¹⁵ carried out the doping of EB with Fe^{3+} but could not avoid the reduction of ca. 8% of FeCl_3 to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as was evident from their Mössbauer spectra. In our case, however, there is no signature of Fe^{2+} in the Mössbauer spectrum of Fe^{3+} doped EB. The absence of reduction of Fe^{3+} in the present study may be due to the use of acetonitrile as a solvent in place of hygroscopic nitromethane used earlier in the doping process. However, impurities of Fe^{2+} in Fe(III) doped PANI prepared in nitromethane can be removed by using hexafluoroacetylacetone.³³

The Mössbauer spectrum of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ doped EB clearly shows a doublet with a large value of quadrupole splitting and a high value of IS, which

are characteristic of Fe^{2+} oxidation states. Presence of only one doublet further confirms that Fe^{2+} complex with only one site and that is the imine site. This confirms that the doping mechanism of Fe^{2+} is similar to pseudoprotonation. This is due to the fact that the metal cation (Fe^{2+}) having low electrode potential has the ability to coordinate to the imine nitrogen atoms only.

Fourier transform infrared (FTIR) spectroscopy

The infrared spectroscopy can be conveniently used to study the interconversions of PANI structure. In the spectrum of EB, the characteristic vibrational modes are observed at 1587 cm^{-1} and 1498 cm^{-1} which corresponds to the $\text{N}=\text{Q}=\text{N}$ and $\text{N}-\text{B}-\text{N}$ respectively (Q- quinoid unit and B- benzenoid unit) [Fig. 3(a)]. The mode at 1380 cm^{-1} is assigned to C-N stretching frequencies in QB_tQ . Another mode

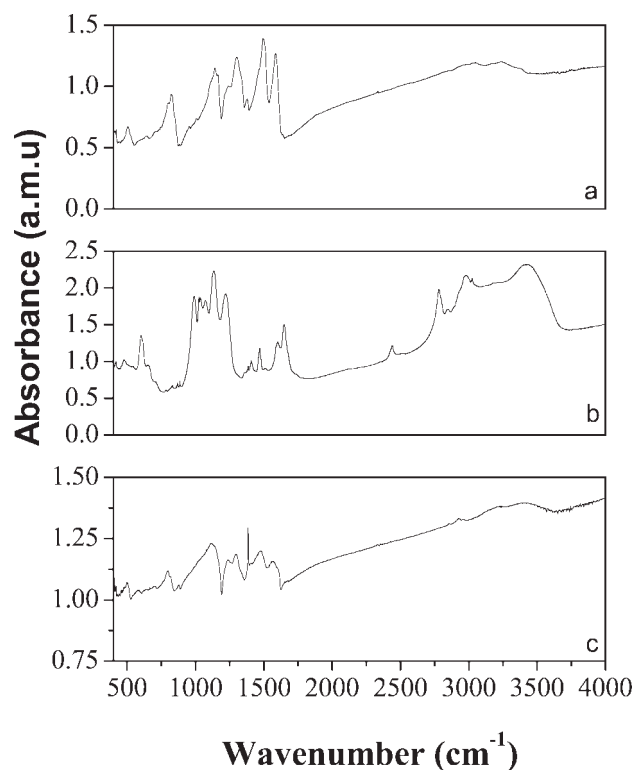


Figure 3 FTIR spectra of (a) emeraldine base, (b) Fe(II) doped emeraldine base, and (c) Fe(III) doped emeraldine base.

TABLE I
Mössbauer Parameters of Iron Doped PANI

Sample	IS (mm/s)	Quadrupole splitting (mm/s)	F.W.H.M (mm/s)	% Intensity
FeCl ₃ doped EB	0.20	0.70	0.38	68.6
	0.39	0.74	0.27	31.4
FeSO ₄ doped EB	0.60	0.80	0.37	100

at 1315 cm⁻¹ is attributed to QBQ, QBB, and BBQ. C—N stretching frequency in BBB was noted at 1240 cm⁻¹ (B_t- *trans* benzoid unit, B_c- *cis* benzoid unit). The mode of N = Q = N was found at 1160 cm⁻¹.⁺ The band observed at 832 cm⁻¹ corresponds to an aromatic C—H out-of-plane bending.³⁴

After doping FeSO₄, the vibrational bands observed for EB i.e. 1587, 1380, 1315, 1240, 1160, and 832 cm⁻¹ shift to 1559, 1373, 1302, 1235, 1142, and 800 cm⁻¹ respectively [Fig. 2(b)]. The shifting frequency indicates longer effective conjugation length of the polymer. In addition to shifting of the observed frequencies, the peaks observed in the case of FeSO₄ doped EB were remarkably intense. This effect is due to an enhancement of the oscillator strength of backbone related vibrations due to vibronic coupling with the π -electron charge oscillation along the chain.³⁵ The vibration mode at 1498 cm⁻¹ corresponds to stretching of N—B—N remain unchanged in the spectrum, which indicates that the doping by the FeSO₄ mainly affects only the electronic structure of the quinoid units and have no significant effects on the benzenoid units. From the above observation we may conclude that the doping of FeSO₄ is not an oxidative process but occurs via pseudo-protonation. And one more notable change in the doped one is that there is a drastic increase in the intensity of the band at 1140 cm⁻¹. The intensity of this peak may be considered as a measure of the degree of doping of the polymer backbone.³⁶

In the case of FeCl₃ doped EB there is shift in vibration mode at 1498 cm⁻¹ (stretching mode of N—B—N) but no change is observed in the stretching band of quinoid indicating an occurrence of oxidative doping at amine nitrogens¹¹ [Fig. 3(c)].

CONCLUSIONS

In this work we have shown that the plausible mechanism for doping of Fe(III) salts in EB proceeds via Lewis acid-base complexation whereas doping of Fe(II) is similar to pseudo-protonation. It is also demonstrated that Fe(III) gets attached to both the amine and the imine nitrogens whereas Fe(II) gets attached to only the imine nitrogens. This is clear from the Mössbauer spectra of the doped polymers. Also no signature of Fe²⁺ was seen for the Fe³⁺

doped EB from the Mössbauer spectrum. UV-vis and Fourier transform infrared (FTIR) spectroscopy further corroborates the attachment of the iron atoms to the nitrogen sites with characteristic change in their spectra obtained.

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