



Iodine vapour doped polyaniline

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ABSTRACT

The physical characteristics of the polyconjugated polymer polyaniline in its emeraldine base form (EB-PANI) doped with iodine vapour have been investigated. Iodine doping occurs by the oxidation of the benzenoid diamine units of the polymer, rather than of the quinoid diimine units. The formation of triiodide anion (I_3^-) was confirmed by the appearance of a peak at 133 cm^{-1} in far-IR spectrum. The degree of doping of the polymer by I_3^- was determined as 8.2% by gravimetric analysis. The intensity of the electron paramagnetic resonance (EPR) signal in EB-PANI increased after doping with iodine vapour, similarly to the behaviour upon acid doping and in contrast to the behaviour upon exposure of the polymer to oxygen or 1-diphenyl-2-picrylhydrazyl (DPPH) radicals. This is attributed to differences in the acidity of the species that result from reduction of the oxidizing species involved in these reactions, resulting in subsequent acid doping of the polymer in the case of oxidation by iodine. This also results in a five orders of magnitude increase in the conductivity of the polymer upon doping with iodine.

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1. Introduction

The polyconjugated polymer polyaniline (PANI) has attracted considerable attention over the last three decades due to its straightforward polymerization, chemical and environmental stability and high electrical conductivity. Interest in polyaniline was generated after the fundamental discovery in 1977 that iodine-doped polyacetylene [1] has a metallic conductivity, which triggered research interest in other polyconjugated polymers in the hope that these would provide new and/or improved electrical, magnetic, optical material or devices.

Ammonium persulphate, potassium ferricyanide, potassium iodate and hydrogen peroxide have been employed as oxidants for the polymerization of aniline in acidic media. The most suitable of these are ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and potassium iodate (KIO_3). Ammonium persulphate is the most extensively used oxidant and the yield, elemental composition, conductivity and degree of oxidation of the resulting polymer are essentially independent of the value of the initial aniline/persulphate mole ratio r for $r \leq 1.15$ [2]. In a study of aniline polymerisation using a number of different oxidizing agents, it was claimed that potassium iodate is the most convenient, since it gives good quality samples for a wide range of synthesis parameters [3]. Armes and Aldissi carried out a detailed study of the potassium iodate oxidation route to polyaniline [4], and used this method for the preparation of colloidal polyaniline [5]. Based on Armes' ammonium persulfate

procedure for the synthesis of PANI, Cataldo and Maltese introduced a further step involving purification by treatment with acetone to eliminate undesired and potentially carcinogenic by-products [6]. The acetone extract consists of a mixture of impurities, which are low molecular weight oligomers of aniline such as *N*-phenyl-*p*-phenylene-diamine and other by-products such as hydrazobenzene, benzidine, *p*-aminophenol, quinone diimine and *p*-benzoquinone. The purification of EB-PANI is very important for its use in biomedical applications [7].

There have been only a few reports on the reaction of PANI with iodine, and there is a considerable variation in the experimental results and their interpretation. The result of treatment of PANI in its emeraldine base (EB-PANI) and leucoemeraldine base (LEB-PANI) forms with I_2 in *n*-heptane solution showed that both involved oxidation of benzene diamine units into quinone diimine units, resulting in more highly oxidized forms of the polymer [8]. Surprisingly, it was claimed that the product of this reaction in the case of EB-PANI is not a conductor, despite the fact that the proposed reaction mechanism involves protonation of the polymer by hydriodic acid, HI, formed as a result of the oxidation process, and resulting in the presence of iodide, I^- , as the anionic dopant [8]. In contrast to this, Zeng and Ko [9] found that reaction of EB-PANI with I_2 in ethanol solution resulted in an eight orders of magnitude increase in conductivity. These authors proposed a reaction mechanism involving oxidative attack of iodine on the nitrogen atoms of the quinone diimine units, rather than the benzene diamine units, and the formation of I_3^- and I_5^- anions, which were identified by an XPS study. An early study of the oxidative polymerization of aniline with KIO_3 claimed that this resulted in a product that contained no iodine [3]. However, a subsequent study carried out under very

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similar conditions produced material with a substantial iodine content, and Raman studies indicated that this was mainly due to the presence of triiodide, I_3^- [4,10]. Very recently Stejskal et al. have reported the results of a study of the reaction of EB-PANI with iodine in an ethanol–water suspension. They observed a five orders of magnitude increase in conductivity upon treatment with iodine, and attributed this to the protonation of EB-PANI with HI that is produced in the oxidation of the emeraldine base to the pernigraniline form [11]. The dopant anion was assumed to be I^- , although no evidence was presented to exclude the other previously proposed possibilities, I_3^- and I_5^- [4,9]. These authors also showed that the reaction of EB-PANI with I_2 vapour results in an increase in conductivity, and suggested that this might form the basis of an iodine sensor [11]. However, no characterisation of the material produced by the reaction with I_2 vapour was reported.

From the above, it is clear that several aspects concerning the reaction of PANI with iodine remain unclear, especially the nature and the extent of oxidation of the resulting oxidized polymer, and the nature of the dopant anion in the product. In the present paper we report a quantitative study of the reaction of EB-PANI with I_2 vapour, and the characterisation of the product by mid- and far-IR spectroscopy, CP MAS NMR spectroscopy, and EPR spectroscopy. These experiments were carried out in order to resolve the ambiguities and contradictions in the previously published studies, and to provide data for the product resulting from reaction with I_2 vapour, where potential complications from the presence of solvent and the perturbing effects of washing procedures are absent. The results provide a contrast with those for reaction of EB-PANI with other oxidizing agents, and this is attributed to differences in the acidity of the species that result from reduction of the oxidizing species involved in these reactions.

2. Experimental

2.1. Synthesis of EB-PANI and its reaction with iodine

The emeraldine base form of polyaniline (EB-PANI) was chemically synthesised by the method of Cataldo and Maltese [6]. Reaction of EB-PANI with iodine vapour was carried out by placing EB-PANI powder (0.0395 g) in an open glass tube suspended over solid iodine (4.73 g) in the bottom of an enclosed container. The container was evacuated to 10^{-3} Torr using a rotary vacuum pump and then closed by means of a vacuum tap. The reaction was allowed to proceed in the closed container over a period of 2 days at a temperature of 20 °C.

2.2. Characterisation

2.2.1. Gel permeation chromatography (GPC)

Molecular weight determinations were made using a gel permeation chromatography (GPC) system consisting of an HPLC pump (Waters 2690) with two columns in series (Waters HR 4E and Waters HR 5E). Both a PDA (photo diode analysis) detector and an RI (refractive index) detector were used. Polystyrene standards, with 10 different molecular weights were used to calibrate the column.

The sample was prepared to 0.02 wt% in *N*-methyl-2-pyrrolidone (NMP) solvent.

2.2.2. FT-IR spectroscopy

Mid-Infrared spectra were recorded on KBr discs in a dry nitrogen atmosphere at 8 cm^{-1} resolution using a Bio-RAD FTS-60 FTIR spectrometer. Far-infrared spectra were recorded on polyethylene discs under vacuum at 2 cm^{-1} resolution using a Bio-Rad FTS-40 V spectrometer.

2.2.3. Electron paramagnetic resonance (EPR) spectroscopy

EPR spectra were measured at 9.5 GHz using a Varian E-4 spectrometer with an E-231 multipurpose cavity. Fixed amounts of sample powders ($m_0 = 0.0085\text{ g}$) in a conventional quartz EPR tube were used for recording the spectra. EPR measurements were carried out under an N_2 atmosphere in order to avoid any possibility of re-oxidation. The EPR spectra were recorded with a modulation amplitude of 0.5 G and a scan time of 4 min for each sample.

2.2.4. NMR spectroscopy

Solid-state ^{13}C cross-polarisation magic angle spinning (CP MAS) NMR spectra were recorded on dry powder samples using a Bruker AVA 300 spectrometer operating at 300.13 MHz proton frequency. Experiments were carried out with 4800 scans at ambient temperature using freshly prepared samples enclosed in a 7 mm zirconia rotor. The ^{13}C chemical shift scale is referenced to TMS. Samples were rotated at $5000 \pm 1\text{ Hz}$. The magic angle was adjusted by maximizing the sidebands of KBr.

2.2.5. Conductivity measurements

The electrical conductivity (σ) of the samples was measured by compressing the powder samples into pellets and using the standard four-probe method (Eq. (1)) [12] to minimize the effect of large surface resistance on the sample disks.

$$\sigma = \frac{l}{V} \frac{I}{dw} \quad (1)$$

where l is the probe spacing (pin distance), d is sample thickness and w is sample width.

The average thickness of the disk samples was 0.4 mm. Fresh samples were used for conductivity measurement to reduce any aging effects. The experiments were carried out using a DC current source at room temperature under ambient conditions.

3. Results and discussion

3.1. GPC

The GPC results for EB-PANI are given in Table 1 and Fig. 1. The weight average molar mass is $M_w = (61,000 \pm 1000)\text{ g mol}^{-1}$ and the polydispersity (PDI) = 5.4, which is in agreement with previously obtained results in literature [13–15] for EB-PANI synthesised at 7 °C.

3.2. UV-vis spectroscopy

The two characteristic peaks [16–18] in the UV-vis spectrum of EB-PANI/NMP solutions were observed: (a) the peak at $\sim 330\text{ nm}$ (called the B peak) corresponds to a $\pi \rightarrow \pi^*$ transition in the benzenoid ring [19] and (b) the second peak at $\sim 630\text{ nm}$ (called the Q peak) which is assigned to the transition of an electron from the highest occupied molecular orbital (HOMO, π_B) of the benzenoid part of EB-PANI to the lowest unoccupied molecular orbital (LUMO, π_Q) of the quinoid ring [17,20,21]. The intensity ratio of the peak at 630 nm to the peak at 330 nm which is proportional to the ratio of the quinoid units to benzenoid units along the EB-PANI backbone

Table 1
GPC results for EB-PANI sample

Sample	Method	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI	Comments/cutoff (min)
EB-PANI	PDA	60,600	11,100	5.4	Slight high molecular mass shoulder/19.0
EB-PANI	RI	61,800	11,500	5.4	Slight high molecular mass shoulder/19.0

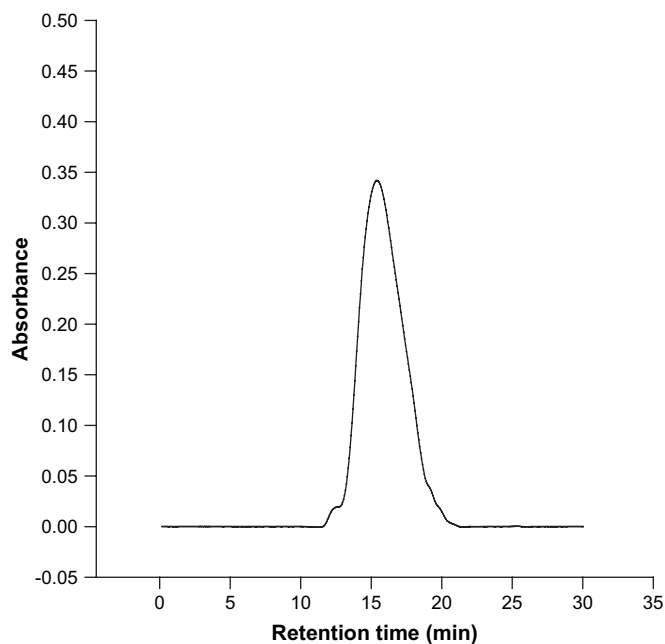


Fig. 1. Gel permeation chromatogram for EB-PANI sample.

(quinoid/benzenoid; Q/B) ratio was calculated. From the UV-vis spectrum (Fig. 2) of EB-PANI sample, 0.02 wt% in an NMP solvent, the Q/B ratio = 0.81 was calculated, which is in the range 0.8–0.9 that is characteristic for EB-PANI [22–26].

3.3. FT-IR spectroscopy

The mid-FT-IR spectra of EB-PANI and iodine-doped PANI (I-PANI) are shown in Fig. 3. After EB-PANI was doped with iodine vapour, the absorption peaks of the quinoid units shifted from 1586 cm^{-1} and 1162 cm^{-1} to 1582 cm^{-1} and 1158 cm^{-1} , respectively. A new peak at 133 cm^{-1} appeared in the far-IR spectrum, which is assigned to the ν_3 mode of I_3^- [27] (Fig. 4).

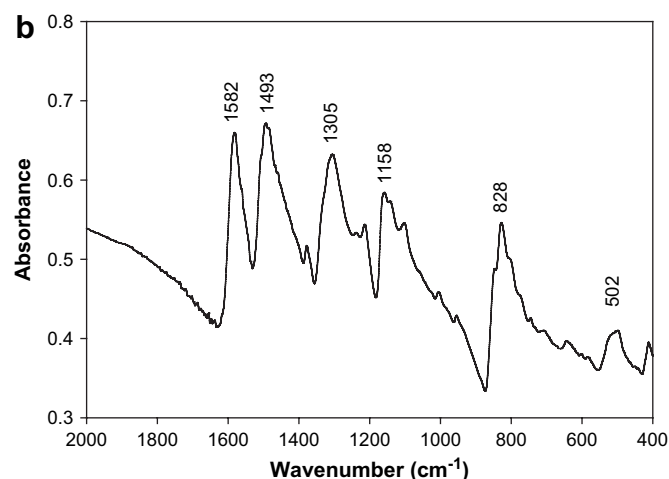
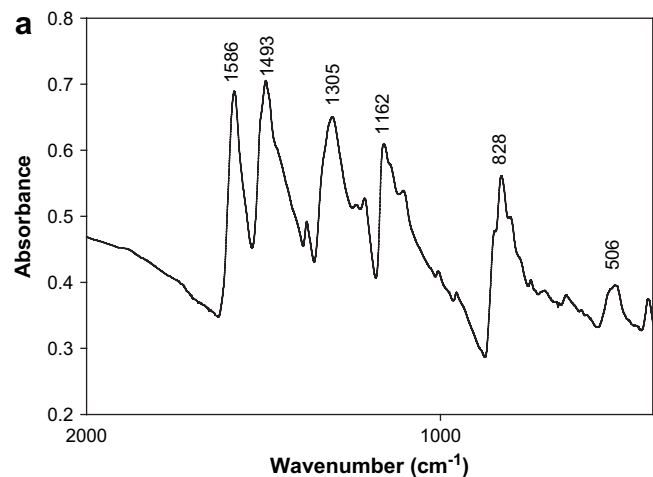


Fig. 3. Mid-FT-IR spectra of (a) EB-PANI and (b) I-PANI.

In a previous XPS study, iodine in the iodine-doped polyaniline, prepared by iodine doping of EB-PANI in ethanol solutions, was reported to exist in the form of I_3^- and I_5^- anions [9]. From the deconvolution of the $I_{3d(5/2)}$ XPS spectra of iodine-doped EB-PANI, the ratio I_3^-/I_5^- of the percentage of total area peaks was found to be 2:1. A doping level of 25–30% of iodine was calculated; so approximately one quarter of iodine was found to be present as I_5^- anion. Even after repeating the experiment and measuring the

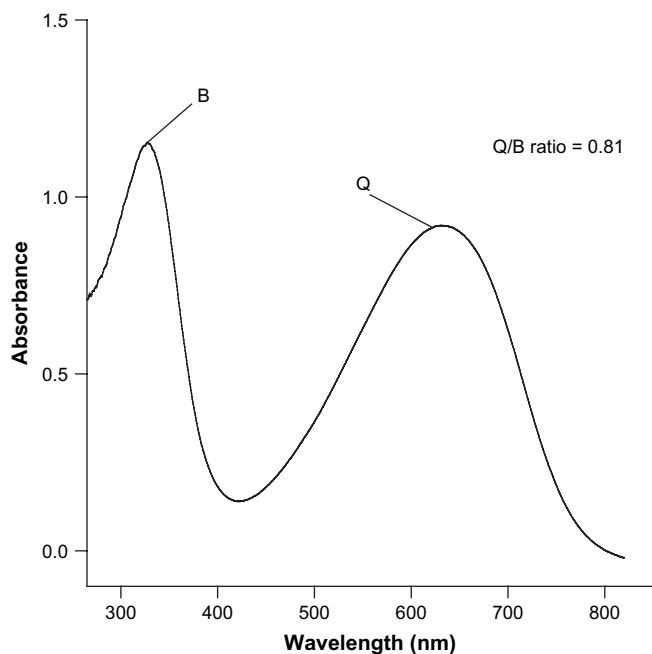


Fig. 2. UV spectrum of 0.02 wt% EB-PANI sample in NMP.

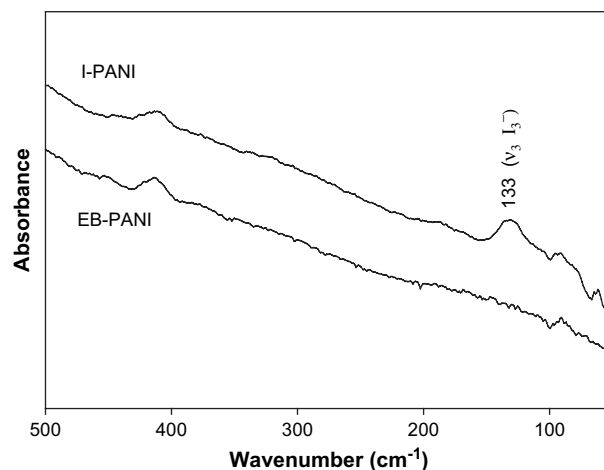


Fig. 4. Far-FT-IR spectra of EB-PANI and I-PANI.

sample immediately after doping with iodine, we found no evidence of the presence of I_5^- anion, which is known to show an IR band at 165 cm^{-1} [27]. This result is consistent with the result obtained by Chen et al. [27] in the iodine-doped poly-(isothianaphene) by iodine vapour where the absence of an I_5^- band in the far-IR spectrum was also confirmed. The discrepancy between the XPS and far-IR results might be due to an incorrect assignment of the XPS peaks. It seems more likely that the two sets of $I_{3d(5/2)}$ peaks that were reported in the previous study [9] are due to the two chemically distinct iodine sites in the I_3^- ion, rather than to the presence of I_3^- and I_5^- ; peaks at the same position and in the same 2:1 intensity ratio have been reported in the $I_{3d(5/2)}$ XPS spectrum of I_3^- in CsI_3 , and were assigned to the two terminal and one central iodine atoms in the linear triiodide ion [28]. This interpretation agrees with a previously reported Raman study of EB-PANI prepared by oxidative polymerization with KIO_3 , which showed a Raman peak at 107 cm^{-1} , assigned to the ν_1 mode of I_3^- [4,10]. Therefore, the XPS, far-IR and Raman results are consistent and indicate that I_3^- is the dominant form of iodine present in the product of reaction of EB-PANI with iodine. This contrasts with the recent results of Stejskal et al., who assumed that the product contains only iodide anions [11].

3.4. Gravimetric measurements

The doping level of the I-PANI sample is calculated (Table 2) by measuring the mass of the EB-PANI sample before ($m_0 = 0.0395\text{ g}$) and after doping with iodine vapour (m_i). In accordance with the discussion above, it was assumed that the dopant is present only as I_3^- anions in the sample. The amount of I_3^- (n_i) present in the sample after doping the polymer with iodine vapour is calculated as follows:

$$n_i = \frac{(m_i - m_0)}{M_r(I_3^-)} \quad (2)$$

where $M_r(I_3^-) = 380.71\text{ g mol}^{-1}$ is the molar mass of I_3^- .

The doping level of the I-PANI sample is obtained by applying Eq. (3).

$$\text{Doping level (\%)} = \frac{n_i}{n_0} \times 100 \quad (3)$$

where $n_0 = 4.34 \times 10^{-4}\text{ mol}$ is the amount of the PANI repeat unit ($\text{C}_6\text{H}_5\text{N}$; $M_r = 91.11\text{ g mol}^{-1}$) in the sample. The I_3^- is formed from I_2 as a result of oxidation of the polymer and, Eq. (3) represents the incremental degree of oxidation, over and above the value 50% that corresponds to oxidation of LEB-PANI to EB-PANI.

The doping level of iodine in the I-PANI sample was thus found to be 8.2% (Table 2).

3.5. EPR spectroscopy

After doping the EB-PANI sample with iodine vapour the EPR signal increased in intensity (Fig. 5). From the second integral it was found that the polaron level had increased by a factor of 4.9 ($I_{\text{I-PANI}}/I_{\text{EB-PANI}} = 164/34 = 4.9$) following treatment with iodine vapour. This behaviour is similar to that observed upon doping EB-PANI with acids [29] and it is accounted for by the following reaction:

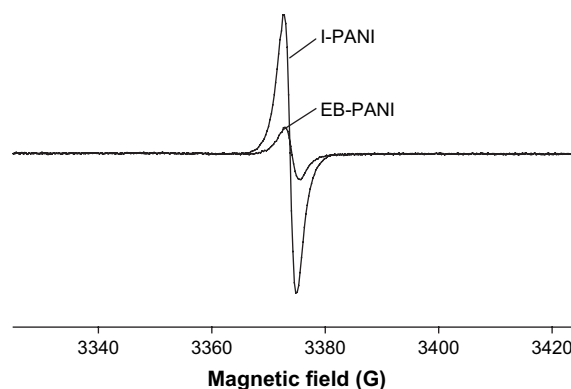
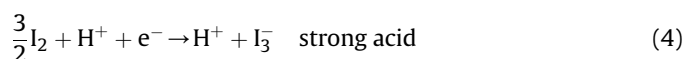
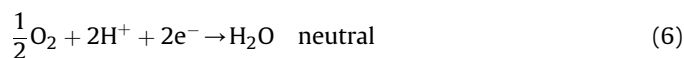


Fig. 5. EPR spectra of EB-PANI sample before and after doping with iodine (I-PANI).



This is in contrast to the case of interaction of EB-PANI with 1-diphenyl-2-picrylhydrazyl (DPPH) radicals [30] or with oxygen [29] where the concentration of polarons after doping decreases Eqs. (5) and (6).



The environment after doping also influences the EPR signal. If the environment is similar to that following addition of a strong acid, the concentration of polarons increases, while in the case of DPPH or oxygen as oxidant, due to formation of a neutral environment after doping, the EPR signal decreases. Thus, the effects of oxidizing agents on the EPR spectra of EB-PANI are complex, and depend strongly on the acidity of the species that result from reduction of the oxidizing species involved in these reactions.

3.6. CP MAS NMR spectroscopy

The EB-PANI sample showed six broad and well-defined resonances at 113.7 (shoulder), 123.7, 138.0, 141.4, 147.1 and 158.1 ppm (Fig. 6). The assignments of these peaks based on previous related work [31–35] are given in Table 3. The peak at 123.7 ppm is broad and consists of several resonances which indicate differences in the chemical environments of the protonated carbons C-2,3. The shoulder at 113.7 ppm is assigned to C-6. The peaks at 138.0 and 158.1 ppm originate from the protonated C-8 and the unprotonated C-7 carbons, respectively, in the quinoid part of the EB-PANI structure. The peaks at 141.7 and 147.1 ppm are associated with the C-4 and C-1 unprotonated carbons, respectively. In the I-PANI sample (Fig. 6) we observed a small increase in the intensity of the peak of the quinoid unit (8Q) at 138.0 ppm, which is consistent with the small increase in the degree of oxidation (8.2%) determined from the gravimetric measurements.

3.7. Mechanism for iodine doping of EB-PANI

In a previously proposed mechanism for iodine doping of EB-PANI by Zeng and Ko [9], it was proposed that the iodine-doping reaction takes place at the N-atoms of the quinoid diimine units, forming a charge-transfer complex, followed by further oxidation of the quinoid units, while the benzenoid units remain unaffected. According to the FT-IR, EPR and NMR results in the present study, this is very unlikely to occur. Also, it seems very unlikely that iodine would further oxidise the quinoid diimine part of the polymer

Table 2

Parameters for calculation of the doping level of iodine in I-PANI

Sample	m_i (g)	$(m_i - m_0)$ (g)	n_i ($\times 10^{-5}$, mol)	Doping level (%)
I-PANI	0.0530	0.0135	3.55	8.2

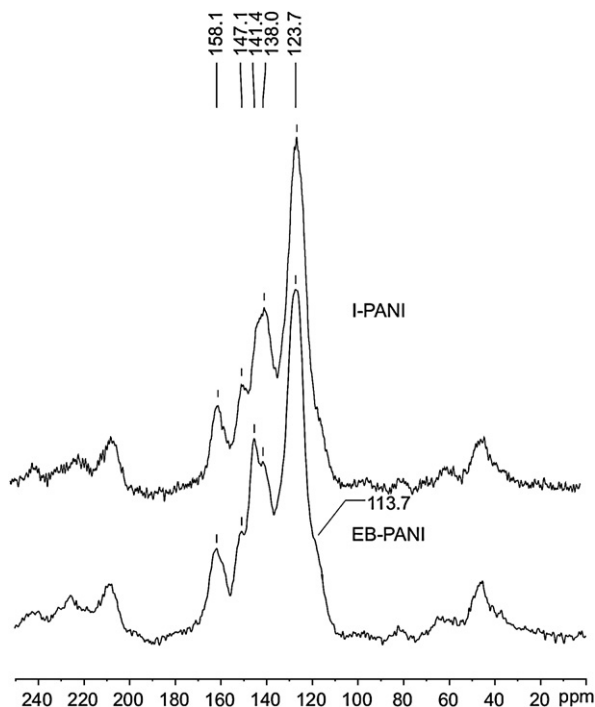
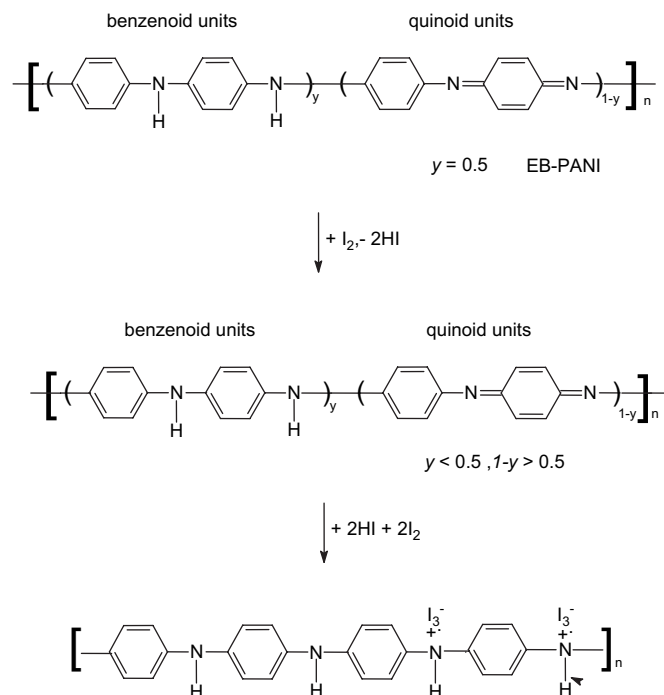


Fig. 6. ^{13}C CP MAS NMR spectra of EB-PANI and I-PANI.



Scheme 1. Mechanism for iodine doping of EB-PANI. The second step occurs for only a small proportion of the quinoid units, due to the limited amount of HI formed.

rather than oxidising the benzenoid diamine units. The mechanism proposed in the present study is shown in Scheme 1.

This scheme simply involves the oxidation of some of the benzenoid diamine units of EB-PANI by iodine, resulting in a decrease in y from 0.5 in EB-PANI structure to a value $y = 0.42$, and a decrease in the ratio of the benzenoid to quinoid units in the EB-PANI structure. The number of quinoid diimine units increases, which is consistent with the increase in the quinoid peak upon doping in the ^{13}C NMR spectrum. In the final step, quinoid units are protonated, which results in an increase in the polaron concentration and a consequent increase in the intensity of the EPR signal as in the case of acid doping of EB-PANI and formation of the emeraldine salt of polyaniline (ES-PANI) form. Formation of I_3^- anions are confirmed by the appearance of the peak at 133 cm^{-1} in the far-IR spectrum.

The recent report by Stejskal et al. [11] described the chemical change occurring upon reaction of EB-PANI with iodine as a partial conversion of the emeraldine constitutional units ($y = 0.5$ in Scheme 1) to pernigraniline units ($y = 0$), but none of their reported measurements allowed the degree of conversion to be determined. The present study establishes that this is 0.082/0.5, i.e. about 16%, in the case of reaction with iodine vapour, so that the material is

Table 3
Assignment of the peaks in the CP MAS spectrum of EB-PANI

^{13}C chemical shift	Assignment (carbon number)
158.1	7 (Q)
147.1	1
141.4	4, 5
138.0	8 (Q)
123.7	2, 3
113.7	6

clearly much closer to the emeraldine base form than to the pernigraniline form.

The process in Scheme 1 has been divided into three steps to separate the oxidation and protonation processes, although these would most likely occur in concert in the actual reaction. The discussion of the ^{13}C CP MAS NMR spectrum above was given in terms of benzenoid and quinoid units, which applies to the deprotonated form of the polymer. To our knowledge, no ^{13}C assignments have been reported for the protonated form, but our results suggest that the chemical shifts do not change appreciably upon protonation, at least for the relatively small degree of incremental oxidation and protonation involved in the reaction with iodine.

3.8. Conductivity measurement

The conductivity of the EB-PANI was increased by five orders of magnitude through the iodine-doping process, attaining a value of $\sigma = 0.504\text{ S cm}^{-1}$. This is in a good correlation with the results obtained by Stejskal et al. [11] which showed that the conductivity of EB-PANI increased by five orders of magnitude. However, the increase of conductivity is much smaller than with EB-PANI base reprotonated with 1 M HI, when the conductivity reached 0.40 S cm^{-1} [8] which is similar to the result we obtained with iodine vapour doped EB-PANI.

4. Conclusion

The reaction of EB-PANI with iodine vapour was investigated. The presence of triiodide, I_3^- in the product was established by observation of its ν_3 vibrational mode as a band in the far-IR spectrum at 133 cm^{-1} . This is shown to be consistent with previously reported $\text{I}_{3d(5/2)}$ XPS and Raman spectroscopy results for closely related materials, which establishes that I_3^- is the predominant iodine-containing species present in such products. The incremental degree of oxidation and the doping level were determined to be 8.2% by gravimetric analysis. This result shows that, despite the oxidative nature of the reaction with iodine, the

resulting product is still much closer to the emeraldine base form than to the pernigraniline form. ^{13}C CP MAS NMR spectroscopy confirms that the electronic structure of the polymer is not greatly changed from that of EB-PANI, but a small increase in the amount of quinoid carbon atoms is consistent with the small incremental degree of oxidation determined from gravimetric analysis. The conductivity of the EB-PANI increases by five orders of magnitude as a result of protonation of the oxidized polymer by acid released in the oxidation process. This is accompanied by an increase in the polaron number by a factor of almost 5, as determined by EPR spectroscopy. This contrast with the results of studies of the reaction of EB-PANI with other oxidizing agents, and this is shown to be due to the fact that the nature and properties of the polymeric product depend strongly on the acidity of the species that result from reduction of the oxidizing species involved in these reactions.

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