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The reaction of polyaniline with iodine

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Abstract

Polyaniline (PANI) (emeraldine) base has been exposed to iodine in an ethanol–water suspension. The conductivity of PANI increased from 10^{-9} S cm^{-1} to 10^{-4} S cm^{-1} already at the molar ratio $[I_2]/[\text{PANI}] = 1$, and a higher content of iodine had only a marginal effect. This is the result of the protonation of PANI base with hydriodic acid, which is a by-product of the oxidation of the emeraldine form of PANI to pernigraniline constitutional units. The reaction is discussed on the basis of FTIR spectra. An alternative reaction, a ring-iodination of PANI, is marginal. Only one iodine atom substitutes a hydrogen atom in about 12 aniline units, even at high iodine concentration, $[I_2]/[\text{PANI}] = 8$. The film of polyaniline base can be used in sensing iodine; after exposure to the iodine vapor, the conductivity of the polyaniline film increased.

Keywords: Conducting polymer; Polyaniline; Iodine

1. Introduction

Conducting polymers represent a class of materials with "intelligent" properties, the "intelligence" being defined as the ability of conducting polymers to respond to various external stimuli by changes in electrical, optical, chemical and/or mechanical properties. Polyaniline (PANI) is a typical representative of conducting polymers. The present study reports the reaction of PANI (emeraldine) base with iodine, and the consequent changes in the conductivity of this polymer.

The reactions of conducting polymers with iodine have historical importance. The reaction of polyacetylene with iodine has led to a marked increase in the conductivity, and laid the basis for the Nobel Prize awarded in 2000 for the discovery and development of conducting polymers [1,2]. The present study illustrates the chemistry of a conducting polymer, PANI, which could be exploited in the design of sensors or other analytical tools. So far, a few papers have reported on this topic. PANI base exposed to iodine increased its conductivity, which was explained by the charge-transfer complexes between iodine and imine nitrogens in PANI [3] or by the non-protonic doping [4]. The oxidation of aniline with potassium iodate has led to PANI and iodine [5]. The interaction of PANI with iodine was discussed but no concrete conclusion was offered, although covalent bonding was considered to be unlikely. Iodine has otherwise been introduced into PANI by copolymerization of aniline with 2-iodoaniline [6,7], or by the oxidation of 2-iodoaniline [7–10]. The textbooks of organic chemistry teach that the halogenations of aniline proceeds easily [11] and that a completely iodinated aniline can be obtained. It is not known whether similar ring-substitution of hydrogen atoms with iodine could take place with PANI, and what effect on the molecular structure and conductivity of this conducting polymer it might have.

Moreover, the anti-microbial activity of PANI has been reported only recently [12] and cannot be considered as being proved. Yet, the combination of PANI with iodine and the potential synergetic effect of both components justify the present introductory study.

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2. Experimental

2.1. Preparation of PANI and its reaction with iodine

Polyaniline was prepared by the oxidation of 0.2 M aniline hydrochloride (purum p.a., Fluka, Switzerland) with 0.25 M ammonium peroxydisulfate (APS; p.a., Lachner, Czech Republic) in aqueous solution [13]. The polymer precipitate was separated on a filter, and dried at room temperature; its conductivity was 4.4 S cm^{-1}. After immersion in excess of 1 M ammonium hydroxide for 2 days, the resulting PANI base was isolated by filtration followed by drying. The conductivity of the PANI base was 1.0×10^{-9} S cm^{-1}.

Portions of PANI base (2.5 mmol, 905 mg) were placed in flasks together with the iodine (puriss, Fluka, Switzerland) in various molar proportions (1 mmol of PANI base was taken to be 362.44 mg, *i.e.* based on the constitutional unit composed of four aniline molecules, 1 mmol of iodine, I_2, 254 mg). Water (50 mL) was added, followed by 20 mL of ethanol to increase the solubility of iodine. The contents were shaken from time to time, and left to react for one week. The solids were collected on a sintered-glass filter, and rinsed with copious portions of ethanol until unreacted iodine was removed and the filtrates were colorless. The samples then were dried at room temperature in a desiccator over silica gel.

Part of a sample on a sintered-glass filter was immersed in excess 1 M hydriodic acid for two days, then removed, rinsed with ethanol, and dried. The mass change was recorded. Another part of the PANI samples was similarly converted to the PANI bases by immersion in 1 M ammonium hydroxide, and handled as above.

2.2. Characterization

Infrared spectra in the range of 400–4000 cm^{-1} were recorded at 64 scans per spectrum at 2 cm^{-1} resolution using a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. The spectra were corrected for the presence of moisture and carbon dioxide in the optical path. Conductivity was measured with a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. For less conducting samples, a two-point method using a Keithley 6517 electrometer was applied. Before the latter measurements, circular gold electrodes were deposited on both sides of the pellets. The density was determined by the Archimedes method with a Sartorius R160P balance by weighing the pellets both in air and immersed in decane.

2.3. Iodine sensing test

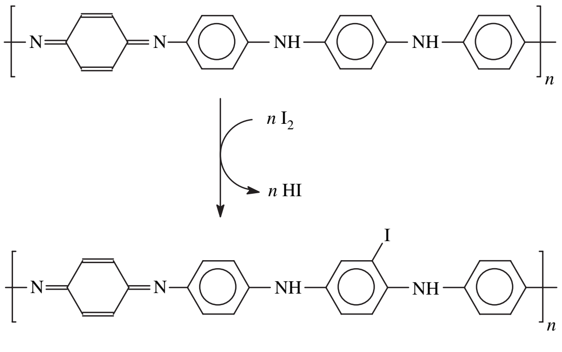
Two gold electrodes were sputtered on a ceramic support. PANI film was deposited *in situ* over the electrodes during the “standard” polymerization [14], *i.e.* by oxidizing 0.2 M aniline hydrochloride with 0.25 M APS, and converted to the PANI base by immersion in 1 M ammonium hydroxide. The area of the PANI film between the gold electrodes was 1×1 cm^2, and the film thickness was ∼100 nm [14]. Thus the constructed element was placed in the measuring unit located in a metallic box screening electromagnetic interference, and the resistance was recorded as a function of time. A grain of iodine, *ca.* 1 mm^3, was later laid next to the PANI film, the box was closed, and the resistance measurement continued. After some time, the iodine was removed. This procedure was repeated several times.

3. Results and discussion

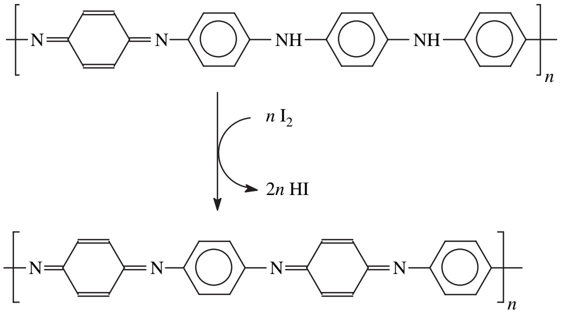
3.1. Reaction of PANI with iodine

The suspensions of PANI base was exposed to various proportions of iodine in ethanol–water mixtures, the presence of ethanol increases the solubility of iodine. The reaction between PANI base and iodine takes place; when PANI base is added to solid iodine, the brown iodine vapor immediately disappears. After addition of ethanol–water mixture, the brown color of the iodine disappeared only at the lowest iodine concentration.

If the reaction of PANI with iodine took place similarly like with bromine [15], the iodination of benzene rings might be anticipated (Scheme 1). During such a reaction, the iodine replaces the hydrogen atoms in the benzene rings. Hydrogen atoms recombine with iodine and produce hydriodic acid. The oxidation of PANI has also to be considered as an alternative pathway [4]. Polyaniline, in its emeraldine form, can be oxidized to the pernigraniline form, and iodine was reduced to hydriodic acid (Scheme 2). In both cases, hydriodic acid is a by-product, which protonates the emeraldine base (Scheme 3). This is easily proved: the conductivity of PANI base increases from 1.0×10^{-9} S cm^{-1} to 0.40 S cm^{-1} after immersion in an excess of 1 M HI. A similar protonation of the pernigraniline form has also been proposed [4]. In aqueous media, however, this reaction takes place only at high acidity [16,17], pH < 2. Such protonation is thus unlikely in the present case, when the reaction with iodine takes place in water



Scheme 1. Iodine replaces a hydrogen atom in polyaniline (emeraldine) base. Hydriodic acid is a by-product.

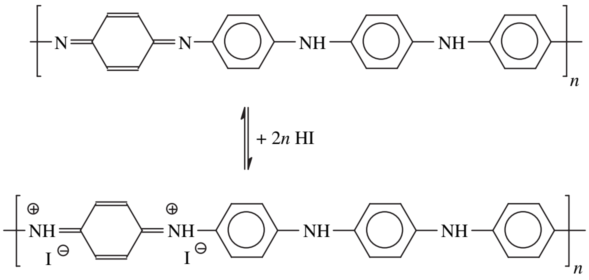


Scheme 2. Polyaniline (emeraldine) base is oxidized with iodine to pernigraniline base. Hydriodic acid is a by-product.

and only 0.072 M HI would be produced under such concentration conditions according to Scheme 2.

The fact that the PANI base becomes protonated after reaction with iodine manifests itself by an increase in the conductivity from 10^{-9} S cm^{-1} to 10^{-4} S cm^{-1} (Table 1), the maximum conductivity, 6.9×10^{-4} S cm^{-1}, being reached at the ratio $[I_2]/[PANI] \approx 3$. The molar concentration of PANI is expressed as the concentration of the constitutional units composed of four aniline molecules (Schemes 1–3). The increase, however, is much smaller than with PANI base reprotonated with 1 M HI, when the conductivity reached 0.40 S cm^{-1}. This is explained by the partial conversion of the emeraldine form of PANI to pernigraniline as discussed below.

The incorporation of iodine into PANI is also reflected by the increasing density (Table 1). Here, however, the saturation limit was reached only after $[I_2]/[PANI] \approx 4$. Such a result could be interpreted by assuming that, at low iodine concentration, the protonation with hydriodic acid is the reaction controlling the conductivity while, at high iodine concentration, the conductivity decreases due to the modification of PANI chains, either by oxidation or ring-substitution, or both. An increase in the conductivity has also been reported by other authors with the saturation limit at $[I_2]/[PANI] = 0.25–0.5$ and was explained by the charge-transfer reaction between iodine and quinonediimine nitrogens [3] or by non-protonic doping by these nitrogens [4]. A similar increase in the conductivity after "doping" with iodine has also been mentioned by Chaudhari and Kelkar [18], without specific reference to its mechanism. The nature of the reaction between PANI and iodine, producing hydriodic acid – a ring-substitution (Scheme 1) or oxidation (Scheme 2) – is thus not obvious.



Scheme 3. Polyaniline (emeraldine) base reacts with hydriodic acid to form the corresponding salt, polyaniline hydriodate. The product can be deprotonated with ammonium hydroxide back to the polyaniline base.

Table 1
The density and conductivity of PANI base, after exposure to various proportions of iodine

$[I_2]/[PANI]$[a]	Density (g cm^{-3})	Conductivity (S cm^{-1})
0	1.233	1.0×10^{-9}
1	1.638	2.2×10^{-4}
2	1.752	6.2×10^{-4}
3	1.789	6.9×10^{-4}
4	1.832	5.0×10^{-4}
5	1.836	2.4×10^{-4}
6	1.834	2.2×10^{-4}
7	1.836	1.7×10^{-4}
8	1.837	1.7×10^{-4}

[a] The ratio of the molar concentration of iodine to the molar concentration of PANI (1 mol of PANI base is taken as 362.44 g, a constitutional unit being represented by four aniline units linked at their *para*-positions).

3.2. Reprotonation and deprotonation

The fact that PANI exposed to iodine is protonated with hydriodic acid can be proved in two ways. When immersed in 1 M HI, there is virtually no increase in density, mass, or conductivity for samples prepared at $[I_2]/[PANI] > 1$ (Table 2). This means that all the imine nitrogens in PANI have already been associated with hydriodic acid, and the reaction shown in Scheme 3 does not take place.

This is further supported by the deprotonation of the products with ammonium hydroxide, in which the hydriodic acid associated with PANI is abstracted, producing ammonium iodide (Scheme 3). Deprotonation according to Scheme 3 would result in a mass loss of 41.4 wt.%. A value close to this is indeed found in the experiments with the samples prepared at $[I_2]/[PANI] > 1$ (Table 3). This amount corresponds to about one molecule of hydriodic acid per two aniline constitutional units, and again confirms that fact that the hydriodic acid was produced, and that reaction between PANI and iodine took place. The observation that, in thermogravimetric analysis, the iodine is removed from PANI at relatively low temperature [19] is also in accordance with these results. The complete removal of an acid is also demonstrated by the

Table 2
The reprotonation of PANI base, after exposure to iodine, with 1 M hydriodic acid

$[I_2]/[PANI]$[a]	Density (g cm^{-3})	Conductivity (S cm^{-1})	Mass change (wt.%)
0	2.056	0.40	+54.0
1	1.857	3.3×10^{-3}	+19.8
2	1.864	1.9×10^{-3}	+4.6
3	1.851	1.0×10^{-3}	+5.1
4	1.884	7.4×10^{-4}	+5.2
5	1.856	4.2×10^{-4}	+2.4
6	1.830	1.9×10^{-4}	−0.7
7	1.845	1.8×10^{-4}	+0.6
8	1.851	1.1×10^{-4}	−0.6

[a] *Cf.* Table 1.

Table 3
The deprotonation of PANI base exposed to iodine with 1 M ammonium hydroxide

$[I_2]/[PANI]$	Density ($g\ cm^{-3}$)	Conductivity ($S\ cm^{-1}$)	Mass change[a] (wt.%)	Iodine content[b] (wt.%)
1	1.235	8.7×10^{-13}	−36.7	3.2
2	1.256	1.5×10^{-13}	−41.3	4.7
3	1.244	5.6×10^{-13}	−43.2	5.9
4	1.253	4.7×10^{-13}	−44.9	7.1
5	1.283	5.6×10^{-13}	−43.1	8.3
6	1.322	5.7×10^{-13}	−45.0	8.7
7	1.308	4.9×10^{-13}	−44.1	8.6
8	1.345	4.9×10^{-13}	−43.4	8.7

[a] Deprotonation according to Scheme 3 would result in a mass loss of −41.4 wt.%.

[b] If one hydrogen atom per four aniline constitutional units were substituted by iodine (Scheme 2), the iodine content would be 26.0 wt.%.

reduction of conductivity from 10^{-4} S cm^{-1} to 10^{-13} S cm^{-1} (Table 3).

3.3. Ring-substitution

If the PANI were ring-substituted with iodine then, after deprotonation, the iodine content would be reduced only marginally, while after the deprotonation of non-substituted PANI, no iodine would be left in the product. The dramatic decrease in the density after deprotonation (Table 3) provides strong evidence for the latter situation.

The residual content of iodine, found by elemental analysis in deprotonated samples, is indeed low, with a maximum at 8–9 wt.% when $[I_2]/[PANI] > 4$. If each aniline constitutional unit were substituted by a single iodine atom (Scheme 1), the content of iodine would be 26.0 wt.%. This means that the actual degree of substitution is much lower. This conclusion is also confirmed by the measurement of density, which is relatively low and close to that of the PANI base, 1.24 g cm^{-3}. Yet a small but steady increase in the density with increasing amount of iodine in the reaction, and thus increasing ring-iodination, can be discerned (Table 3).

The oxidation of emeraldine constitutional units to pernigraniline ones is thus the main reaction which takes place (Scheme 2). Depending on the iodine concentration, the conversion of emeraldine to pernigraniline need not be complete and PANI chains can attain various intermediate degrees of oxidation. The reaction of the PANI base with iodine, leading to an increase in conductivity, can be probably extended to other halogens. It could be used in the detection of halogens or for their removal from various media.

3.4. FTIR spectroscopy

The course of the reaction between the PANI base and iodine is also supported by the changes observed in the FTIR spectra. The infrared spectrum of the original PANI base (Fig. 1, spectrum a) is compared with that of the product of the reaction (spectrum b). A broad absorption band at wave numbers higher than 2000 cm^{-1} (only the beginning of this band is shown in Fig. 1) is typical of the conducting form of PANI [20,21]. It is believed to indicate an increase in the polymer conductivity. The red shift of the main vibration bands at 1592 cm^{-1} and 1497 cm^{-1} in the spectrum of the PANI base, corresponding to quinone and benzene ring-stretching deformations, respectively, observed after reaction with iodine, confirms the protonation of the PANI base. The next band characteristic of the conducting protonated form is observed at 1240 cm$^{-1,}$ and is interpreted as a C–N$^{+\bullet}$ stretching vibration in the polaron structure [22]. The prominent 1139 cm^{-1} band is assigned to a vibration mode of the $-NH^{+\bullet}=$ structure, which is formed during protonation [23]. Partial conversion of the emeraldine form of PANI to pernigraniline is strongly supported by the presence of the peak at about 1378 cm^{-1}, attributed to C–N stretching in the neighborhood of a quinonoid ring, which is typical for the PANI base but it is still present in the spectrum of the protonated product of the reaction. This peak is found in the oxidized pernigraniline form of PANI [24,25].

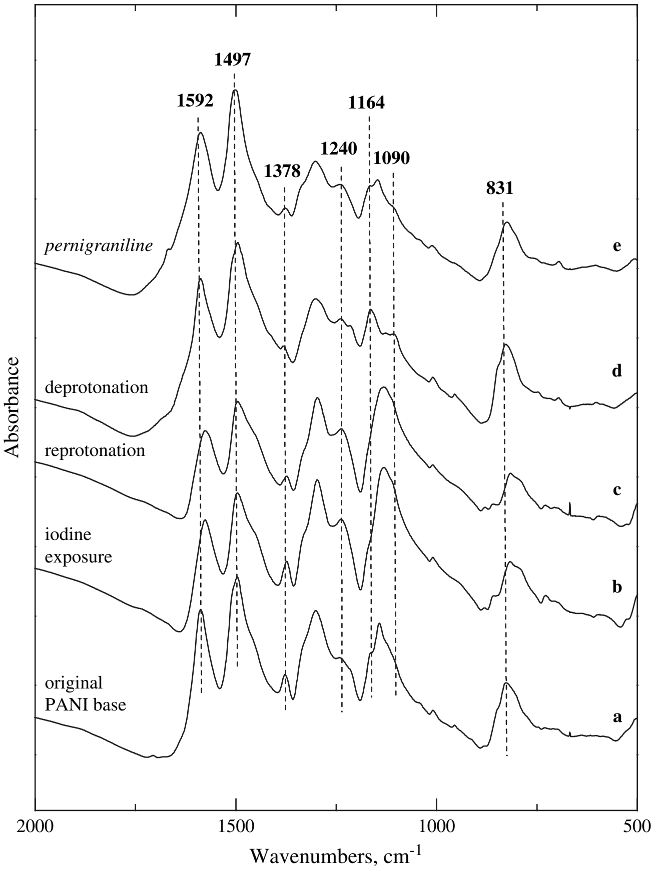


Fig. 1. FTIR spectra of (a) the original PANI base; (b) PANI base exposed to iodine, $[I_2]/[PANI] = 5$; (c) PANI base exposed to iodine and then protonated with 1 M hydriodic acid; (d) PANI base exposed to iodine, and then deprotonated with 1 M ammonium hydroxide; and (e) the spectrum of PANI prepared with an excess of APS oxidant, *i.e.* rich in pernigraniline constitutional units, and deprotonated, is shown for comparison.

Finally, we have proved that PANI exposed to iodine is protonated with hydriodic acid by observing that no change occurs in the spectra after the reprotonation of the reaction product by this acid (Fig. 1, spectrum c).

The different structures of the reaction product in the base form (Fig. 1, spectrum d) are well documented by comparison with the spectrum of the initial PANI base (spectrum a). The baseline above 2000 cm^{-1} decreased after reaction with iodine, and the band close to 1140 cm^{-1} decreased, too. The spectrum of deprotonated PANI differs from the spectrum of the original PANI base by the shape of bands at about 1240 cm^{-1}, the presence of the band at 1164 cm^{-1} interpreted as a mode of N=Q=N vibration [26], and of the peak at 1090 cm^{-1}, assigned to C−H in-plane bending of the ring observed in the pernigraniline form of PANI [27].

In order to support the observation that a partial conversion of the emeraldine constitutional units to the pernigraniline ones occurs after exposure to iodine, we have prepared PANI by using higher oxidant-to-monomer molar ratio [APS]/[aniline] = 2, instead of common [14] [APS]/[aniline] = 1.25, to obtain PANI rich in pernigraniline units. The similarity between the spectra of the PANI after reaction with iodine (Fig. 1, spectrum d) and the spectrum of deprotonated pernigraniline prepared with excess APS (Fig. 1, spectrum e) is well documented. Especially the presence of the peaks at 1164 and 1090 cm^{-1} is recognized in the last spectrum. The different shapes of the spectrum of the deprotonated sample observed at about 1100 cm^{-1} may be connected with the presence of X-sensitive modes of C−H in-plane bending vibrations corresponding to ring-iodination of PANI [28].

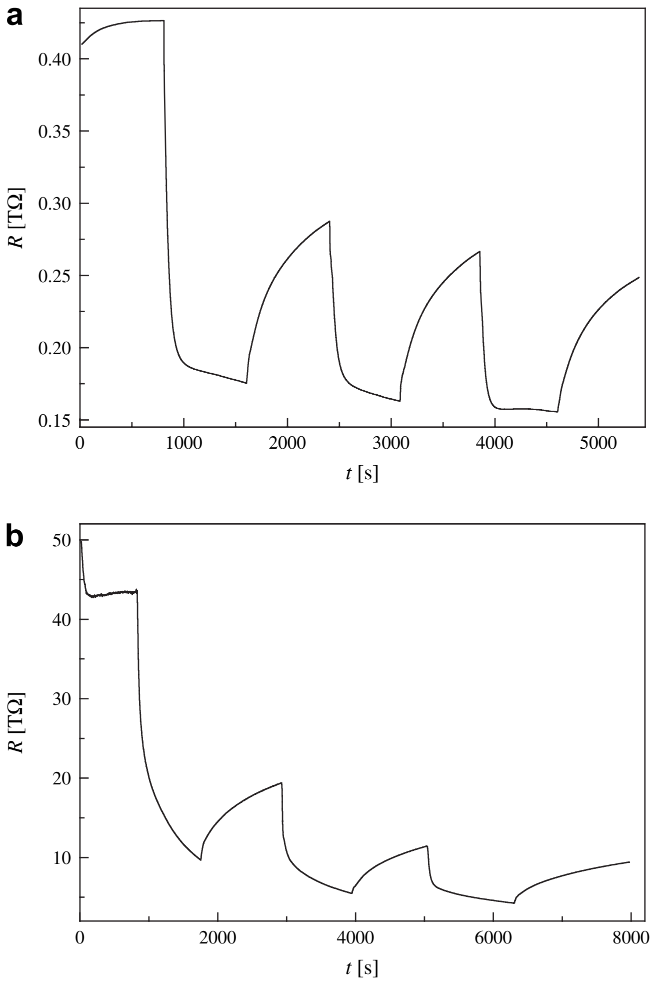


Fig. 2. (a) The resistance response of polyaniline base film deposited on a ceramic support to repeated exposures to iodine vapor and (b) the corresponding response of the ceramic support without a PANI film.

3.5. Polyaniline film as an iodine sensor

The fact that the conductivity of the PANI base increases after reaction with iodine can be used for the sensing of halogens in general and of iodine in particular. When a thin film of PANI base [14] deposited on a ceramic support is exposed to iodine vapor (a crystal of iodine was placed close to PANI film), the resistance decreases (Fig. 2a). The resistance partly recovers when the iodine is removed, and decreases again during repeated exposure. It should be noted that a qualitatively similar but much smaller response is obtained even without a PANI film (Fig. 2b), due to the adsorption of iodine on the ceramic support. The conductivity of iodine is 7.7×10^{-10} S cm^{-1}, which is low but not negligible in this type of experiment. Yet, the conductivity changes caused by iodine absorption on the support represent only a few percent of the corresponding change observed for PANI film. It is obvious that the processes of iodine interaction with PANI are partly reversible, based on adsorption and desorption of iodine, resulting in the chemical reaction of iodine with PANI. Yet, the response is slow and the response to iodine exposure decreases after each cycle. In general, the chemistry of the halogen interaction with PANI, although complex, could be used in the sensing of these elements, even though additional research would be needed to develop a sensor suitable for practical applications.

4. Conclusions

Polyaniline base reacts with iodine and its conductivity increases by five orders of magnitude to 10^{-4} S cm^{-1}. The increase in conductivity is due to the protonation of PANI with the hydriodic acid that is produced in the oxidation of the emeraldine base to the pernigraniline form. The results suggest that polyaniline structure could be approximated as a product of the coexistence of the emeraldine form protonated with hydriodic acid, and the non-protonated pernigraniline constitutional units. This reaction was nearly complete when $[I_2]/[PANI] = 1$. An alternative reaction, ring-iodination of PANI, is marginal, producing less than one iodine atom per 12 aniline units in the PANI chain, and it takes place at higher ratios $[I_2]/[PANI] = 1-4$. Further increase in the content of iodine up to $[I_2]/[PANI] = 8$ had no effect. The feasibility of making a sensor for iodine, based on the decrease of resistance after interaction of this halogen with a thin PANI film, has been demonstrated.

Acknowledgments

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