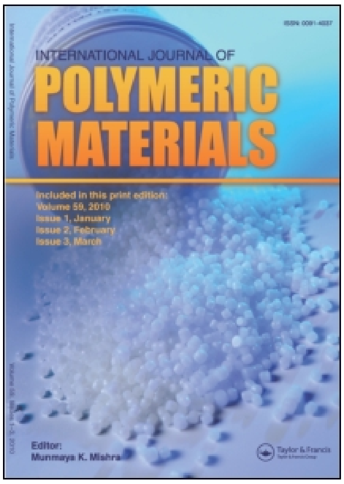

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IN-SITU SPECTROELECTROCHEMICAL INVESTIGATION OF INDOLE POLYMERIZATION

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Electrochemical polymerization of indole (In) was studied on Pt and Pd electrode by in-situ spectroelectrochemical method in acetonitrile (ACN) and in the mixture of ACN and water. Pd electrode seems to work better than Pt for the electropolymerization of In. The formation of oligomers could be followed by spectroscopic means during the electrochemical polymerization of In. One to one correlation between current (I) and obsorbance (A) values for oligomeric species were found. The electrochemical behavior of film formation of Indole was studied by cyclic voltammetry under various conditions. Polyindole film was soluble in ACN to certain extent, which allowed spectroscopic investigation of polyindole formation through the oligomeric stages in solution.

Keywords: electropolymerization, indole, polyindole, spectroelectrochemical polymerization, in-situ spectroelectrochemisty

INTRODUCTION

The electroactive properties of heterocyclic conducting polymers containing nitrogen atoms like polypyrrole, polycarbazole, and its substituted derivates [1–3] have been known for many years. The first stage of electropolymerization involves the oxidation of monomer to the cation radical. Then, depending on the electrochemical conditions several pathways of polymerization are possible and, in consequence, the obtained films reveal different structures and properties [4].

Electrochemical polymerization of indole, can occur after anodic oxidation of In in electrolytic solutions of salts such as $NaClO_4$ or $LiClO_4$ dissolved in ACN [5–8].

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The deposition of the polymer at the surface of a metallic anode (platinum, gold, nickel,) leads to a film-like conducting material, which is green in color in the oxidized state [9].

Recently, Talbi et al. [10] studied the polymerization of indole. An analysis of IR spectra of doped and dedoped polyindole suggested that the polymer structure contains 2,3 couplings. In that study the appearance of N–H bond at 1540 cm^{-1} in the dedoped polymer confirms the presence of the N–H bond and therefore supports the fact that the nitrogen atom is not a polymerization *site*. Quantum mechanical calculations indicated that the C_2 atom was the most positive in the radical-cation from of indole. In neutral indole the C_2 atom bonded to hydrogen is the most negatively charged. The preferential linkage sites C_2 and C_3 lead to a regular 2,3 structure of the polymer [11].

In this work, the authors report in-situ spectroelectrochemical study of the oxidation of indole in the mixture of acetonitrile and water. A three electrode cell system has been adopted for obtaining conducting polymers in an electrooxidation system. It is well known that the physical properties of polymers prepared in the three-electrode system are better than those of polymers obtained in the two-cell system. Oligomer formation of In can be followed by electrochemical and spectroscopic measurements by means of in-situ spectroelectrochemical technique. One to one correlation was expected for some species determined by CV and absorbance measurements of species formed during the electrochemical polymerization. This *technique* will help to understand more about the mechanism of the electropolymerization that may give information for the mass production of conductive polymer instead of thin films mostly obtained on the electrode surface. The polymerization reactions of film were performed under different experimental conditions.

EXPERIMENTAL

Materials

Indole (In), Acetonitrile (ACN), and Sodium Perchlorate were all Merck reagent chemicals of the highest purity and were used without further purification.

Polymerization Procedure

The polyindole formation on Pt electrodes and as a result of this polyindole electrodes were prepared by cyclic voltammetry technique, in a standard three-electrode cell using a platinum and a palladium working electrode, a platinum counter electrode, and a Ag/AgCl electrode as the reference. A Wenking POS 73 Model Scanning Potentiostat was employed for the electrolysis and cyclovoltammetric measurements: (I) constant potential electrolysis, (II) cyclic voltammetry (CV) of film growth, and (III) formation of oligomeric species.

The conducting PIn was formed as a green film on the Pt electrode surface in an ACN solution containing 0.1 M $NaClO_4$ as a supporting electrolyte 0.01 M Indole with an electrolysis potential (+1.2 V).

Measurements

FT-IR analysis for the PIn was performed (Mattson 1000 FT-IR). The measurements were carried out by the KBr pellet method. The sample pellet was pressed in a vacuum to protect from the air-mixing phenomenon. UV-visible measurements were performed using a Shimadzu 160A Recording spectrophotometer. In-situ and ex-situ spectroelectrochemical measurements were made in a UV cell having working electrode (WE:Pt), counter electrode (CE:Pt), reference electrode (RE:Ag) without interfering the UV-vis. light passage through the solution where oligomeric species formed.

RESULTS AND DISCUSSION

Acetonitrile (ACN) Medium

A typical voltammogram of indole with platinum electrode is shown in Figure 1a and b. A single peak (Figure 1a) is observed in the first positive scan up to switching potential of +1.15 V due to the oxidation of indole. When the current in the first scan is reversed there is no complementary peak, but on subsequent reverse scans an electrochemical follow-up reaction produces the products detected as II and III (at +0.30 and 0.60 V) (Figure 1b). Similar results were obtained in the literature [12]. By continuous cycling it is observed that the peak (II) increases, beside showing the characteristic behavior of a deposited electroactive substance. Biindoles were perpared and examined in ACN by CV and mass spectrometric measurements were performed in literature previously [13]. 3,3′-biindole showed two one-electron steps at 0.28 and 0.62 V. These peaks, corresponding to tetrameric and hexameric species, were obtained ($m/e = 462$ and 690) in the mass spectrum. In this study, the authors also found development of two peaks (at about 0.3 and 0.6 V) (Figure 1b) during the electrolysis. These peaks can be assigned to electrogrowth of film of the oligomeric species.

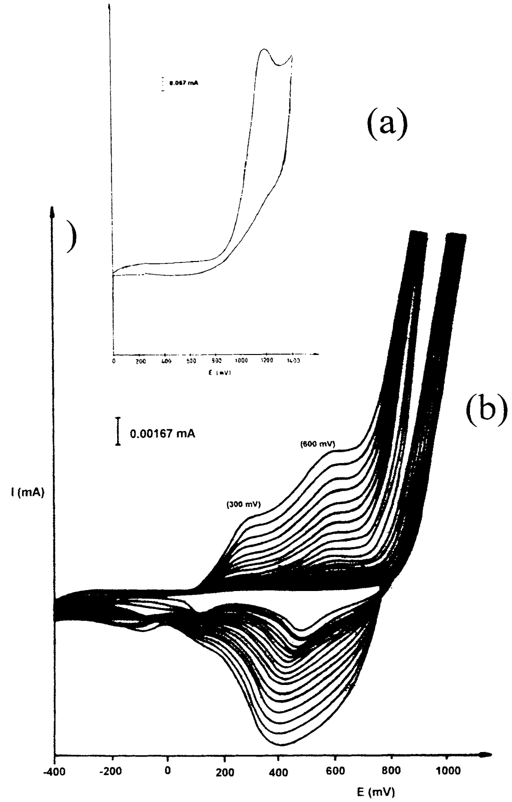


FIGURE 1 Cyclic voltammogram of In in ACN. (a) Oxidation of monomer, (b) during the polymer growth (reference electrode: Ag/AgCl; working electrode: Pt; counter electrode: Pt; scan rate: 100 mV/s; supporting electroylte: 0.1 M $NaClO_4$).

At Pd electrode, which is used as a working electrode, the rate of deposition of indole is higher than Pt electrode, probably because of the higher hydrogen absorption on Pd electrode (Figure 2).

UV-visible absorption measurements of In was performed during the electrochemical polymerization of In in ACN and the mixture of ACN and water. The absorption spectrum of In gives two peaks at different wavelengths, i.e. 220 nm and 268 nm. The peak at 220 nm belongs to π-π^* of benzene ring, whereas the peak at 268 nm belongs to π-π^* of pyrrole ring. The absorbance measurements during the electrochemical polymerization of In is given in Figure 3, where two peaks were observed at two different wavelengths, that is, 347 nm (I), 390 nm (II). These peaks may correspond to oligomer formation of In.

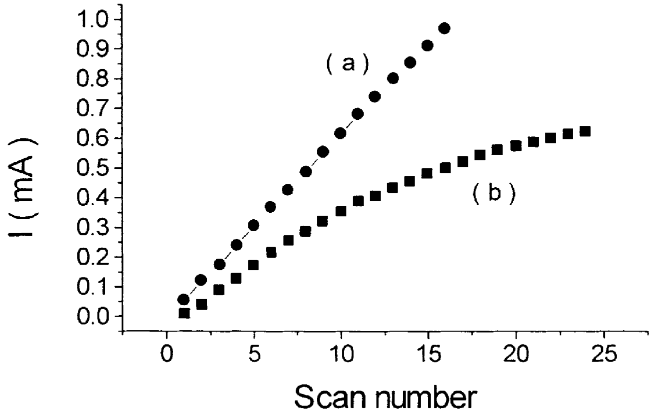


FIGURE 2 The effect of scan number on the current during the electrochemical polymerization of In. Reference electrode: Ag/AgCl; counter electrode: Pt; scan rate: 100 mV/s; [In] = 0,01 M, supporting electrolyte: 0.1 M $NaClO_4$ working electrode: (a) Pd; (b) Pt electrode.

Two peaks at 375 and 425 nm were also obtained from the final solution [14]. Mackintosh et al. have found evidence for the formation of a trimer in addition to the polymer during the electropolymerization of indole-5-carboxylic acid in ACN [15].

The in-situ spectroelectrochemical measurement is an effective way to follow the current and absorbance values of oligomeric species

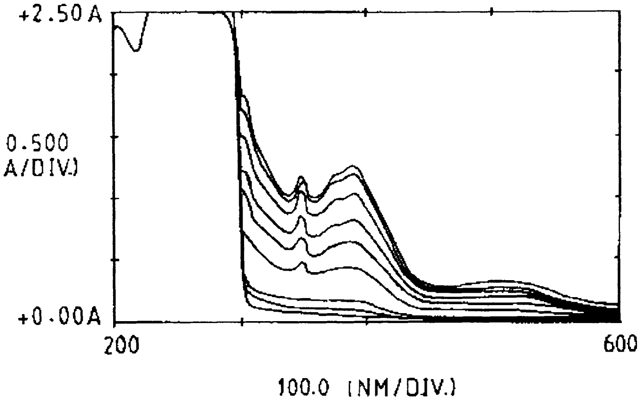


FIGURE 3 UV spectra of In during the electrochemical polymerization in ACN. Reference electrode: Ag/AgCl; working electrode: Pt; counter electrode: Pt; V: 1.1 volt; supporting electroylte: 0.1 M $NaClO_4$).

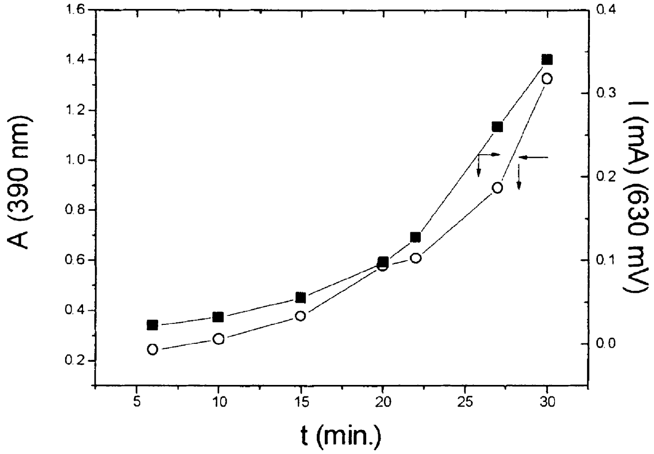


FIGURE 4 The results of the absorbance (at 390 nm) and the current value (at 630 mV) during in-situ spectroelectrochemical polymerization of indole in ACN.

at the same time. The results of changes of absorbance (at 390 nm) and current values (at 630 mV) with time during the insitu polymerization measurements of indole in ACN are given in Figure 4, which shows one to one correlation between changes in absorbance and current. This peak may correspond to formation of indole oligomers during electrolysis.

Acetonitrile-Water (ACN–H_2O) Medium

The spectroelectrochemical polymerization of indole was also investigated in a mixture of ACN and water. In the ACN and water solutions (%20 H_2O – %80 ACN %30 H_2O – %70 ACN) there is no deposition of In on the electrode; only oligomers were obtained in solution (Figures 5–6). From Figure 7a, b, and c, respectively it is obvious that there is more deposition of indole on the electrode in ACN rather than in the mixture of ACN and water. Water and acetonitrile interact, forming hydrogen bonds and giving an inter-component complex. These interactions affect the organic polymerization process in two ways. The coupling of the water molecules to an organic molecule such as acetonitrile enhances the proximity of water to the organic (polymeric) electrode. On the other hand, the water discharge is helped by formation of these hydrogen bonds with acetonitrile, due to the increment in nucleophilic character of the

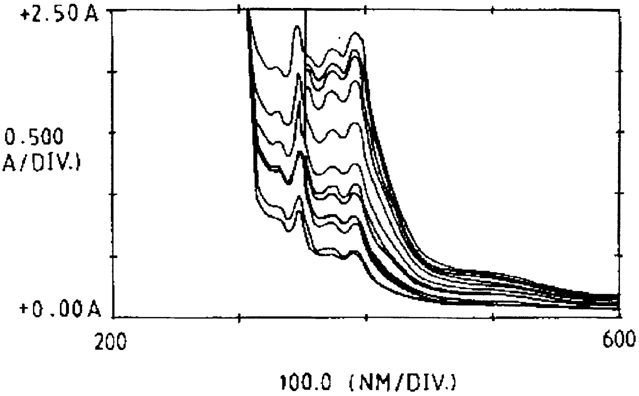


FIGURE 5 UV spectra of In during the electrochemical polymerization in %20 H_2O – %80 ACN (reference electrode: Ag/AgCl; working electrode: Pt; counter electrode: Pt; V: 1.1 volt; supporting electrolyte: 0.1 M $NaClO_4$).

hydroxylic oxygen [16–17]. Their oxidation and rection with the growing radical cations could be responsible for the observed electrode passivation (Scheme 1).

It was reported in Ref. [13] that with water the neutral radical is formed to a limited extent, compared with the absence of water (Scheme 2, III).

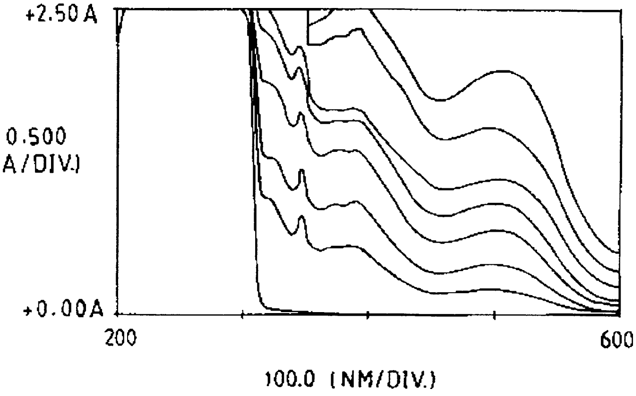


FIGURE 6 UV spectra of In during the electrochemical polymerization in %30 H_2O – %70 ACN (reference electrode: Ag/AgCl; working electrode: Pt, counter electrode: Pt; V: 1.1 volt; supporting electrolyte: 0.1 M $NaClO_4$).

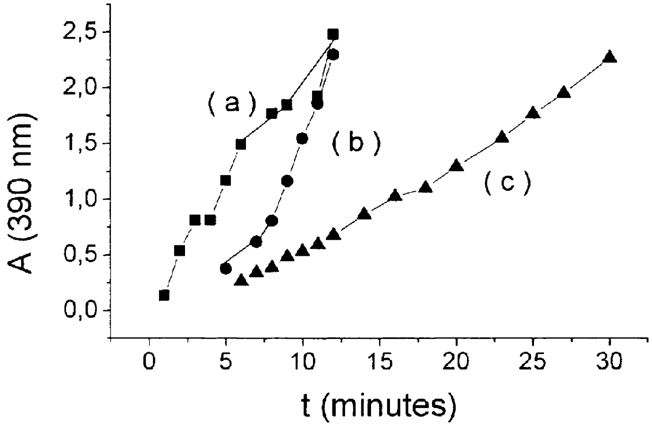
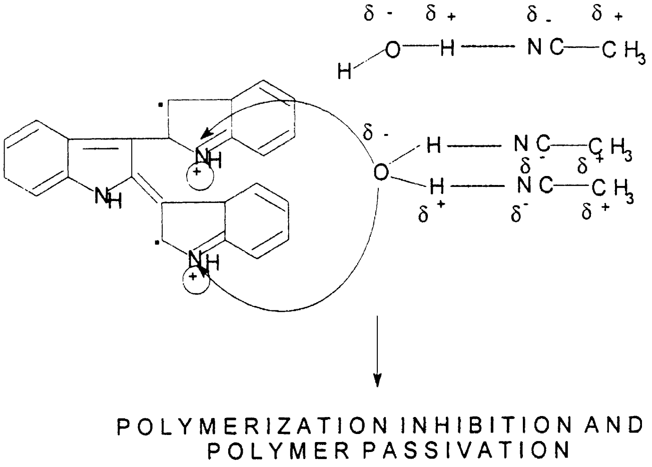


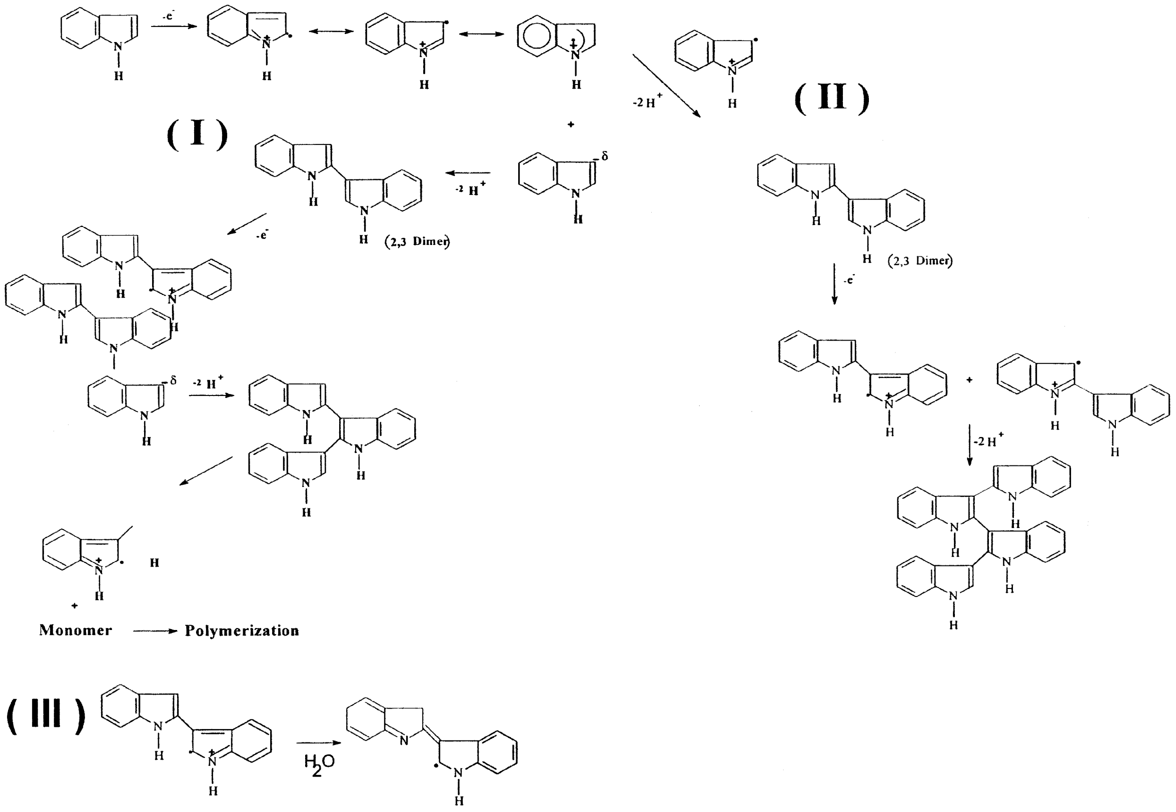
FIGURE 7 UV-Vis. Results of indole during in-situ spectroelectrochemical polymerization of indole in %30 H_2O – %70 ACN (a), %20 H_2O – %80 ACN (b), ACN (C) (at 390 nm, 1.0 V, reference electrode: Ag/AgCl; working electrode: Pt; counter electrode: Pt).

UV Results of PIn in Acetonitrile (ACN) Medium

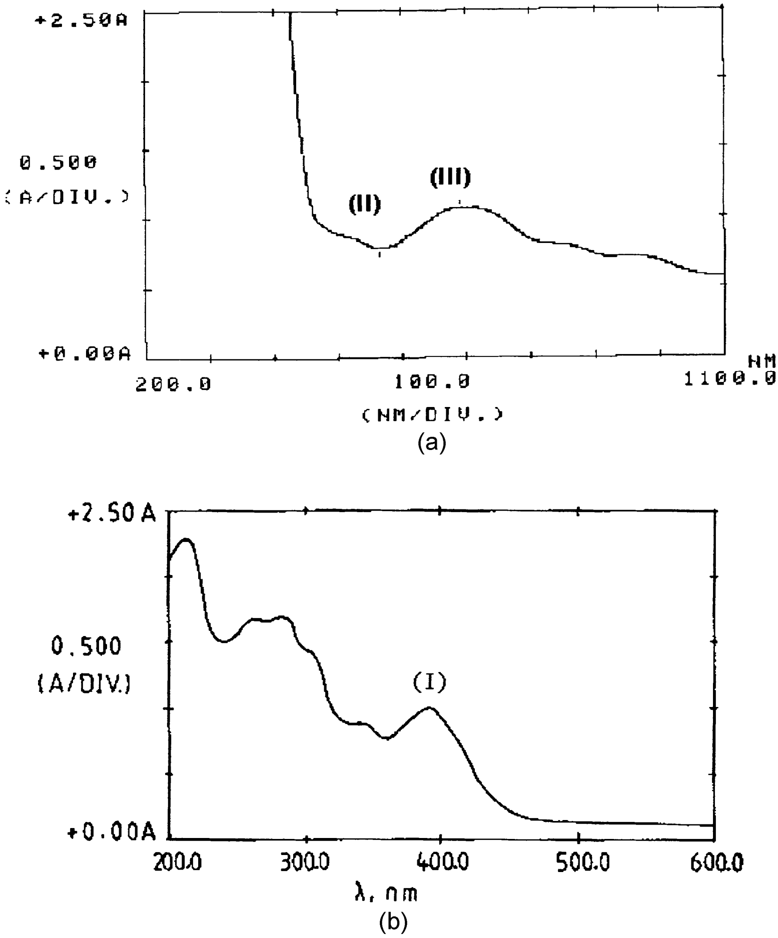
One of the problems in that conducting polymers are difficult to dissolve in any solvent because of their delocalized π-electronic structures, which are the very same molecular characteristics that give rise to properties necessary for practical application [18]. Poly-



SCHEME 1


-e⁻
-2 H⁺
(I)
(II)
(III)
(2,3 Dimer)
(2,3 Dimer)
-e⁻
-2 H⁺
-e⁻
-2 H⁺
-δ
Monomer ⟶ Polymerization
H₂O

SCHEME 2



(a)

(b)

FIGURE 8 UV Spectrum of PIn (a), in dilute condition (b) in ACN.

indole was investigated with an aim of obtaining soluble products in ACN. Absorbance measurements are given in Figure 8a and b. Peaks were observed at 390, 500, and 680 nm (I, II, and III), which correspond to the soluble oligomeric species in as yet undefined order.

FT-IR Results

A strong and narrow peak at 3412 cm^{-1} is observed in the spectrum of indole. The same peak was observed in the spectrum of polyindole (Figure 9a). The appearance of this bond at 3412 cm^{-1} in the polymer

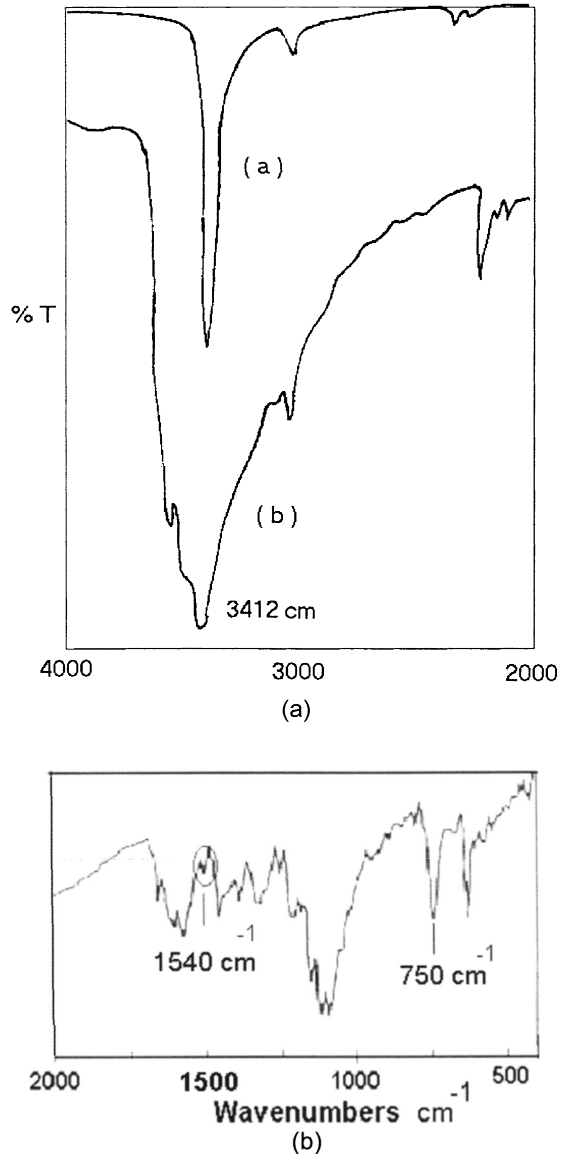


FIGURE 9 FT-IR spectra of In (a), PIn (b).

indicates the presence of an N–H bond and therefore supports the fact that the nitrogen atom is not a polymerization site. Similar results were obtained in the literature [10,19]. In Figure 9b the bands at 1475 and 1600 cm^{-1} are induced by aromatic alkene, the absorption peak at

1320 cm^{-1} induced by (C—N) amine, and the single peak peak at 750 cm^{-1} is induced by the bending mode of aromatic alkene. Those band indicate that coupling does not involve the benzene ring, in agreement with previous suggestions [6,13]. In this figure, a band at 1540 cm^{-1}, induced by the bending mode of N—H bond, was observed. As a result, the polymerization mechanism of indole was suggested to be by the 2,3 polymerization mechanism shown in Scheme 2.

CONCLUSION

Electrochemical polymerization of In is thought to be initiate by the formation of unstable In radical cations at the vicinity of anode and anode surface depending on the substituent of In, where the presence of steric effect transfers the reaction to the solution. Oxidation of In can probably proceed to form radical cations that can first form oligomers (see Figure 3,390 and 500 nm) and then continue to grow as long as indole is available. One to one correlation between Absorbance (at 390 nm) and current values (at about 600 mV) was observed for oligomeric species that are formed during in-situ spectroelectrochemical measurements (see Figure 4). FTIR results indicate that benzene ring does not participate in the coupling reaction. N-position of indole is not involved in the coupling because N—H band appears in FTIR scans.

The different coupling reactions that involve the 2,3 dimers and monomers in their neutral or radical cation forms lead preferentially to trimers and tetramers (case of dimer-dimer coupling) in which the monomeric units are linked together by C_2-C_3 bonds reported in the literature [20]. The electrochemical polymerization of N-methyl indole and 2-methyl indole were also studied by the author's group which found that although oligomer formation of N-methyl indole was obtained by in-situ UV measurements (at 390 nm), there was no detectable oligomeric species during the electrochemical polymerization of 2-methyl indole. C_2 atoms of the radical cation monomers are the most positively charged and C_3 atoms of neutral forms are the most negatively charged, as previously indicated [19]. It can be concluded that the electrochemical polymerization takes place via the 2 and 3 position of indole ring, as this position is shown to be the most reactive [10,11,20].

The authors' results, suggest a tentative mechanism (Scheme 2, I and/or II). Polymerization growth may continue by radical cation-monomer and/or radical cation-radical cation coupling. In the presence of water, it was noted that an increase in the amount of water decreases the deposition of indole on the electrode. In the presence of water, neutral radical can form from radical cation due to nucleophilic attack of OH^- on the cationic site therefore the yield decreases (Scheme 2, III). Further investigation is necessary for clarifiying the mechanism, by the use of other substituted indoles.

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