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Synthesis and Characterization of Poly (Pyrrole-Co-Pyrazinamide)

KEYWORDS: Copolymerization, Pyrazinamide, Pyrrole, Cyclic Voltammetry, Glassy carbon electrode

D.Lakshmanan
Department of Chemistry, Dhanalakshmi College of Engineering, Manimangalam, Tambaram, Chennai-601301

G. Selvanathan
Department of Chemistry, AVC College (Autonomous), Mannampandal, Mayiladuthurai, Nagapattinam district, TamilNadu

ABSTRACT *Poly(Pyrrole-co-pyrazinamide) was prepared by electrochemical and chemical oxidative polymerization. Using the electrochemical method, homo and copolymer thin films of pyrrole and pyrazinamide were synthesized under cyclic voltammetric conditions in acetonitrile on the surface of the working Glassy carbon electrode. The copolymer formation, their electrochemical behaviour and the structure were examined. The analogous copolymers were prepared via a chemical oxidative polymerization in 1M HCl in the presence of potassium persulfate as an oxidant. The structure of the copolymer was systematically studied by IR, and X-ray powder diffraction (XRD) and the surface morphology was studied using SEM analysis.*

1. Introduction

Electrically conducting polymers are the subject of continuous research and development of potential applications in optical and electronic devices, electromagnetic shielding, energy storage systems, corrosion protection, sensors and microelectronic devices[1]. Polypyrrole of aromatic nitrogenous polymers is the most attractive one because of its higher oxygen/nitrogen separation factor up to 8[2]. However, the polypyrrole membrane used here is usually prepared by electropolymerization or interphase oxidative polymerization, where the membrane area is dependent on the size of the electrode and interphase. Polypyrrole could not be prepared by an easy solvent cast technique because polypyrrole is an insoluble material like most of other conductive polymers. Attempts have been made to solubilize pyrrole polymer by copolymerizing with other monomers. There are some reports concerning the copolymerization of pyrrole with aniline and thiophene derivatives[4-7], but no report on the chemically oxidative copolymerization of pyrrole with Pyrazinamide is found hitherto.

Pyrazinamide, (PZA, Fig-1) pyrazine-2-carboxamide is an antimicrobial agent that is most commonly used for treatment of active tuberculosis (TB) during the initial phase of therapy (generally the first two months of treatment), in combination with other agents. The spectrum of PZA is relatively narrow; it demonstrates clinically significant antibacterial activity only against Mycobacterium tuberculosis and M. africanum [8]. The parent compound is metabolized via pyrazinamidase (PZase) to pyrazinoic acid. pyrazinoic acid is the active form of the drug [9]. The mechanism of action for PZA is unknown. PZA and its analog, 5-chloro-PZA, may inhibit the fatty acid synthetase I (FASI) enzyme of M. tuberculosis [10,11]. PZA is generally considered to be a bacteriostatic agent.

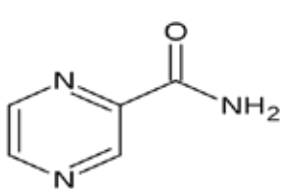

Fig-1. Chemical structure of pyrazinamide

Copolymerization is a simple way of preparation of new polymers, and it greatly increases the scope of tailor-making materials with specifically desired properties [12]. The copolymerization potential of two different monomers plays an important role in the properties of a copolymer as well as the deposition potential of two different kinds of metallic ion for the electrochemical preparation of a metallic alloy [13]. Changing the monomer concentration ratio [14] can readily control the copolymerization potential of two monomers. Among the various techniques available for the electrochemical synthesis of conducting polymers, the cyclic voltammetry (CV) has been used for the fast production of the good quality polymer films [15].

In the present investigation, the voltammetry (CV) method was used for the electrochemical copolymerization of pyrrole and pyrazinamide aiming at correlating the growth behaviour of copolymer film deposition with experimental conditions. For comparison the copolymers were synthesized by chemical oxidative polymerization and characterized.

2. Experimental

2.1 Materials

Chemicals for the polymer syntheses were pyrrole and pyrazinamide were of analytical grade purchased from Sigma-Aldrich. 0.1M pyrazinamide stock solution was prepared in 1:1 ethanol:water. Pyrrole was distilled under reduced pressure. Potassium persulfate (Merck), sulfuric acid and methanol (Merck) were used as received. All solutions were prepared using bidistilled water.

2.2 Synthesis of Copolymer of pyrrole and pyrazinamide

2.2.1 Electrochemical polymerization

Electrochemical polymerization of pyrrole and pyrazinamide was carried out using HCH Electrochemical analyser Model 620D equipment provided with a three electrode cell assembly. A Glassy carbon (GC) microelectrode with the surface area of 0.0314 cm2, a platinum rode and Ag/AgCl were used as working, counter and reference electrodes, respectively. The homo and copolymerization was carried out in acetonitrile medium. The homo and copolymers of pyrrole and pyrazinamide films were deposited with 20 cycles for the polymerization in all supporting elec-

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trolytes and their voltammograms were recorded on PC. Throughout the studies, anaerobic conditions were maintained with nitrogen gas atmosphere.

2.2.2 Chemical Copolymerization

Copolymer of poly(pyrrole-co-PZA) was chemically synthesized using potassium persulphate as initiator in an aqueous acidic medium at 0-40C in a similar manner to that previously described[16-18]. A typical procedure for preparation of the copolymer is as follows.

Monomers, pyrrole (0.5M) and pyrazinamide (0.1M) were dissolved in 50 ml of 1 M HCl aqueous solution and cooled to 0-40C. The oxidant potassium persulphate (0.05M) was dissolved separately in 50 ml of 1 M HCl and cooled to 0-4OC. Then the oxidant solution was added drop wise to the monomer solution for 1 hour with constant stirring in the nitrogen atmosphere at 0-40C. After complete addition of the oxidant stirring was continued for another 7 hours to ensure the completion of the reaction. The bluish black precipitate was obtained and the reaction mixture was kept overnight in the refrigerator. Then the copolymer precipitate was filtered, washed with distilled water until the filtrate became colorless and finally with methanol and dried in an air oven at 600C for 4 hours.

3. Result and Discussion

3.1 Copolymerization of pyrrole and pyrazinamide

The cyclic voltammogram of 0.001M pyrazinamide in 0.1 M H2SO4 was shown in Fig-2. The electro-oxidation was on a stationary glassy carbon electrode, the potential ranging from 1.0 to -1.0V at a scan rate of 100mV/sec. The voltammogram exhibited one well defined cathodic at 0.5476V and anodic peak at 0.5242V potential in first cycle. As the cycling process continued, the peak current increased in two successive cycles and then reduced.

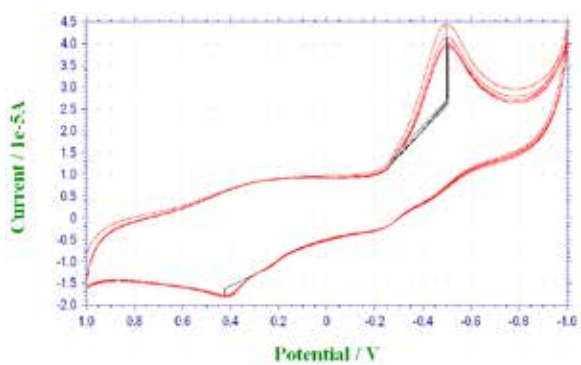

Fig-2. Cyclic voltammetric behaviour of 0.001 M pyrazinamide on GCE in 0.1 M H2SO4 at scan rate 100 mV/s.

The Fig-2 shows that the current decreases with increases in the number of scanning cycles. After the completion of 20 cycles, the working electrode was washed with ultra pure water, and then a violet coloured film was seen on the surface of the working electrode. This film was thin, and the film growth was inhibited further because of lesser conductivity.

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The cyclic voltammogram of 0.01 M pyrrole in acetonitrile was shown in Fig.3. The electrooxidation and reduction was on a stationary glassy carbon electrode, the potential ranging from 0.6 to -1.0V at a scan rate of100 mV/sec.

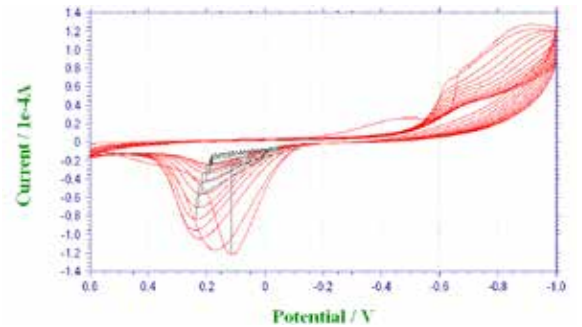

Fig-3. Cyclic voltammetric behaviour of 0.01M pyrrole on GCE in acetonitrile, scan rate 100 mV/s.

The voltammogram shows an anodic peak at 0.1177V in the first cycle. The peak current increased very quickly with increase in the number of cycles and the peak potential was shifted anodically. This is probably due to autocatalytic polymerization, which causes quick polypyrrole (Ppy) film growths as the electrolysis proceeds. After completion of the 30th cycle, a dark blue color polymer film on the working electrode was observed.

The monomers of 0.01 M pyrrole and 0.005 M pyrazinamide were electrolyzed on GCE in acetonitrile by repeated cycling between 0.6 and -1.0 V. The cyclic voltammogram (Fig-4) shows a well defined anodic peak entered at a potential of 0.0195V in the first cycle and the peak potential shifted anodically.

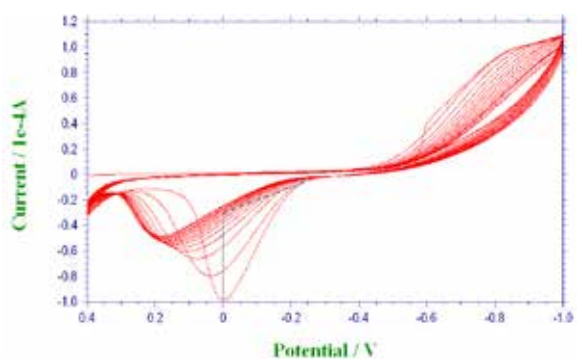

Fig-4. Cyclic voltammetric behaviour of 0.01M pyrrole and 0.005M pyrazinamide on GCE in acetonitrile, scan rate 100 mV

As the scanning cycle increased anodic and peak was observed. When the cycling process continued, there was a gradual shifting in the anodic potential anodically in each cycle. Though the oxidation peak pattern is somewhat similar to that of pure Ppy, there was significant difference in the peak potential. The cathodic peak which observed in the polypyrrole formation was disappeared in the copolymerization of pyrrole and Pyrazinamide (pyrrole-co-PZA) Such different and newer type of behaviour suggests the copolymerization of both pyrrole and pyrazinamide (pyrrole-co-PZA). The bluish-green-color film seen on the working electrode indicates the difference in the color of the

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polymer formed.

3.2 FT-IR spectral analysis of poly(pyrrole-co-pyrazinamide)

The IR spectral analysis of poly(pyrrole-co-PZA) is shown in Fig-5

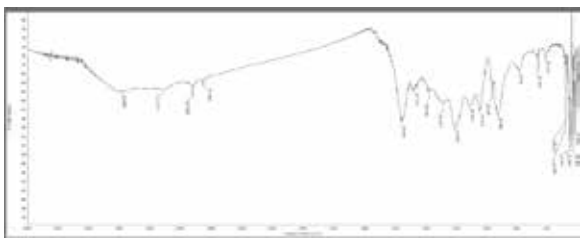

Fig-5 FT-IR spectra of Poly(pyrrole-co-pyrazinamide)

The band observed at 3366cm−1 is attributed to the N-H stretching, since both monomer units contain –NH2 and N-H groups. The bands observed around2651, 2922 cm−1 is attributed to the C-H stretching and anti-symmetric stretching aromatic.

A prominent band at 1559cm-1 is attributed to aromatic pyridyl C=N stretching. The band observed at 1209cm−1 is assigned as the C-N stretching of aromatic secondary amine. The occurrence of band at 1047 cm−1 assigned as carbon ring in cyclic, the band at 865 cm−1 assigned as C-N-C stretching. The broad band around 3116 cm−1 is due to the involvement of -NH2 group in one of the monomer in intermolecular electrostatic binding.

The predominant band for Carbonyl (C=O) which is present in the monomer at 1720 cm−1 is vanished in the copolymer. This clearly shows that these copolymers are Linked in the Carbonyl (C=O) unit. This is the strong evidence for the presence of pyrazinamide unit in the copolymer. The band observed at 489cm−1 is attributed to the C-N-C bend stretching in aromatic amine.

The above results in the IR spectral data's of copolymer demonstrate that an electrochemical copolymerization of pyrrole and pyrazinamide took place most probably at the given conditions. The IR spectrum of the copolymer indicates that there are the –NH2 group, –NH group and C-N-C in the copolymer film. Thus, the pyrrole and pyrazinamide units are contained in the copolymer.

3.3 Morphology of Poly(pyrrole-co-pyrazinamide)

Scanning electron micrographs (SEM) of the copolymer provide a clear morphology of the copolymer. The SEM images of the poly(pyrrole-co-PZA) is shown in Fig-6

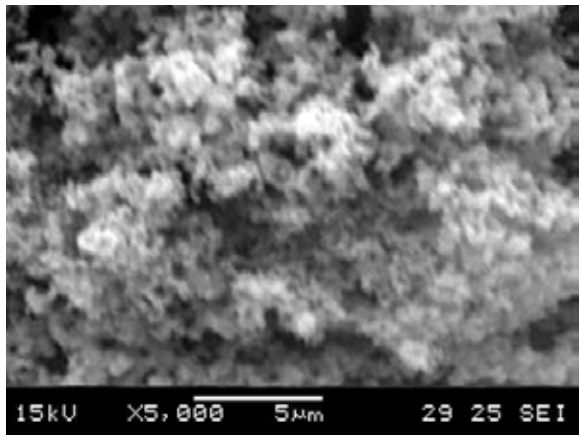

Fig-6 SEM images of the poly(pyrrole-co-PZA)

The SEM images show a microstructure with homogeneous spongy and fibrous structure with uniformity in the surface. The SEM morphology obtained indicates the presence of polymer overgrowth leading to agglomeration.

3.4 XRD of poly(pyrrole-co-pyrazinamide)

The X-ray diffraction analysis is also a powerful tool to determine the structure and crystallization of polymer matrices. The phase in which the polymer chains are parallel and ordered in close packed array is the crystallites region, whilst the phase where the chains are not ordered and do not have parallel alignment is the amorphous region. This ordered arrangement of polymer chains in the crystalline phase may be of different types depending on the nature of the polymer and can be detected from X-ray diffraction. Fig-7 shows X-ray diffraction pattern of poly(pyrrole-co-PZA) .

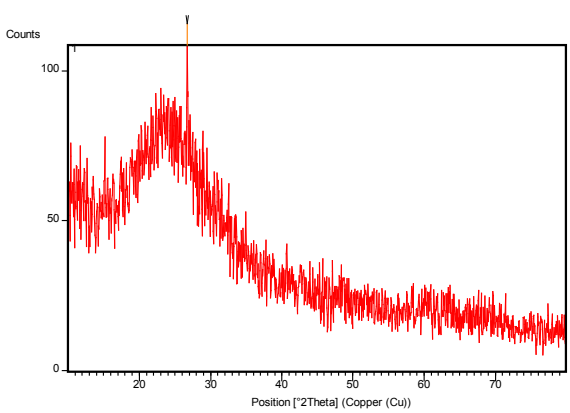

Fig-7 X-ray diffraction pattern of poly(pyrrole-co-PZA)

The XRD patterns of the poly (pyrrole-co-PZA) seems to be comprised with one broad peak situated at approximately 11.3689o and do not show sharp peaks characteristic of crystalline materials. Careful analysis of X-ray diffraction of poly(pyrrole-co-PZA) suggests that it has amorphous nature.

4. Conclusion:

The poly(pyrrole-co-PZA) was synthesized under cyclic voltammetric conditions in acetonitrile medium on the surface of the working Glassy carbon electrode. The analogous copolymers were prepared via a chemical oxidative polymerization in 1M HCl in the presence of Potassium persulfate as an oxidant. The structure of the copolymer was

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systematically studied by IR, and X-ray powder diffraction (XRD) and the surface morphology was studied using SEM analysis. The participation of -C=O group in the chemical synthesis of new poly(pyrrole-co-PZA) has been proved by IR results. The X-ray diffraction of poly(pyrrole-co-PZA) suggests, it has amorphous nature. The SEM studies show the presence of nano particles.

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