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Synthesis and Characterization of Poly (Pyrrole-co-Flutamide)

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Abstract: Poly (Pyrrole-co-flutamide) was prepared by electrochemical and chemical oxidative polymerization. Using the electrochemical method, homo and copolymer thin films of pyrrole and flutamide were synthesized under cyclic voltammetric conditions in acetonitrile on the surface of the working Glassy carbon electrode. The copolymer formation, their electrochemical behavior 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, NMR and X-ray powder diffraction (XRD), and the surface morphology was studied using SEM analysis.

Keywords: copolymerization, Flu amide, pyrrole, Cyclic voltammetry and, Glassy carbon electrode

Introduction

The studies aiming to develop conducting polymer films for various applications (electrochromic devices¹, photoelectrochemical devices², rechargeable batteries and corrosion protection) frequently involve structural modification of the polymer backbone to enhance the properties, eg. Incorporation of various functional groups changes conductivity and porosity. Polyaniline, polypyrrole and their derivatives have been regarded as the most important conducting polymers. Owing to their stability and synthesis advantages. The electro polymerization of aniline and its derivatives brings about some difficulties like slow nucleation and film growth, but its high stability and interesting electrochemical properties have attracted much attention. On the other hand, polypyrrole films generally exhibit better conductivity and are more easily synthesized by electropolymerization, when compared to polyaniline. There are some reports concerning the copolymerization of pyrrole with aniline and thiophene derivatives, but no report on the chemically oxidative copolymerization of pyrrole with flutamide is found hitherto.

Flutamide 4-nitro-3-trifluoromethyl-isobutylanilide (Fig-I), is a synthetic antiandrogenic agent devoid of hormonal agonist activity. It seems to have antiandrogenic specificity only in genitalia organs androgen-

dependent, and its therapeutic use in prostatic cancer^{3,4}. Flutamide is an unusual example of an antiandrogenic drug lacking a steroidal structure.

After human oral administration Flutamide is quickly metabolised, producing about 10 metabolites, mainly 2-hydroxyflutamide and 3-trifluoro methyl- 4-nitroaniline.

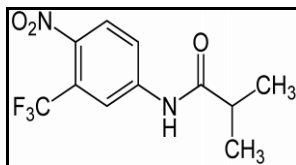


Fig-1. Chemical structure of Flutamide

Copolymerization is a simple way of preparation of new polymers, and it greatly increases the scope of tailor-making materials with specifically desired properties⁵. 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 alloy⁶. Changing the monomer concentration ratio⁷ 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 films⁸.

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

Experimental

Materials

Chemicals for the polymer syntheses were pyrrole and flutamide were of analytical grade purchased from Sigma-Aldrich. 0.1M Flutamide 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.

Synthesis of Copolymer of pyrrole and flutamide

Electrochemical polymerization

Electrochemical polymerization of pyrrole and flutamide 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 flutamide films were deposited with 20 cycles for the polymerization in all supporting electrolytes and their voltammograms were recorded on PC. Throughout the studies, anaerobic conditions were maintained with nitrogen gas atmosphere.

Chemical Copolymerization

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

Monomers, pyrrole (0.5M) and flutamide (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 0-4⁰C. 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 violet mixed 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 60°C for 4 hours.

Result and Discussion

Copolymerization of pyrrole and flutamide

The cyclic voltammogram of 0.001M flutamide 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 the reduced

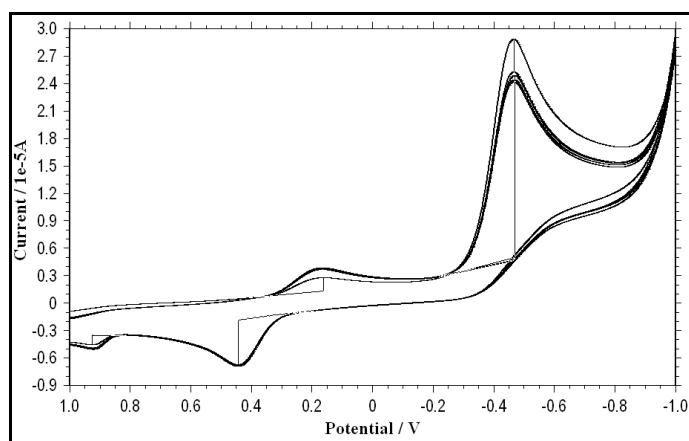


Fig-2. Cyclic voltammetric behavior of 0.001 M flutamide on GCE in 0.1 M H₂SO₄ at scan rate 100 mV/s.

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.

The cyclic voltammogram of 0.01 M pyrrole in acetonitrile was shown in Fig.3. The electro-oxidation and reduction was on a stationary glassy carbon electrode, the potential ranging from 0.6 to -1.0V at a scan rate of 100 mV/sec.

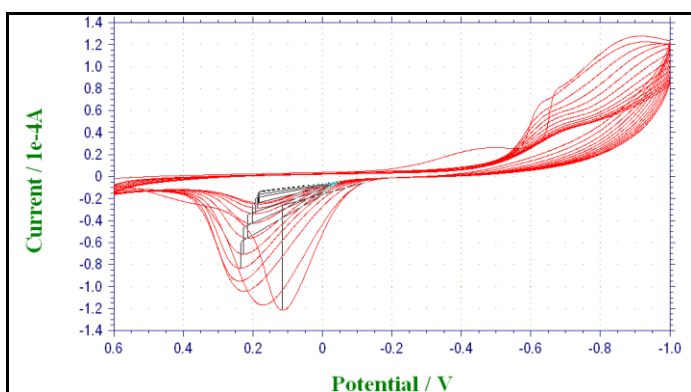


Fig-3. Cyclic voltammetric behavior of 0.01M pyrrole on GCE in acetonitrile at scan rate 100 mV/s.

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 flutamide 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.

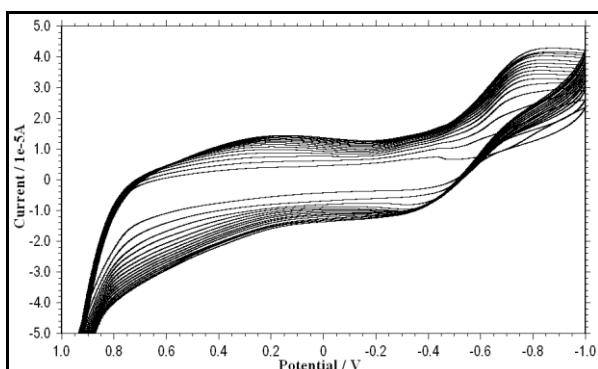


Fig-4. Cyclic voltammetric behavior of 0.01M pyrrole and 0.005M flutamide on GCE in acetonitrile at scan rate 100 mV

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 Ppzaformation was disappeared in the copolymerization of pyrrole and flutamide (pyrrole-co-flutamide) Such different and newer type of behavior suggests the copolymerization of both pyrrole and flutamide (pyrrole-co-FLA). The bluish-green-color film seen on the working electrode indicates the difference in the color of the polymer formed.

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

The IR spectral analysis of poly(pyrrole-co-FLA) is shown in Fig-9

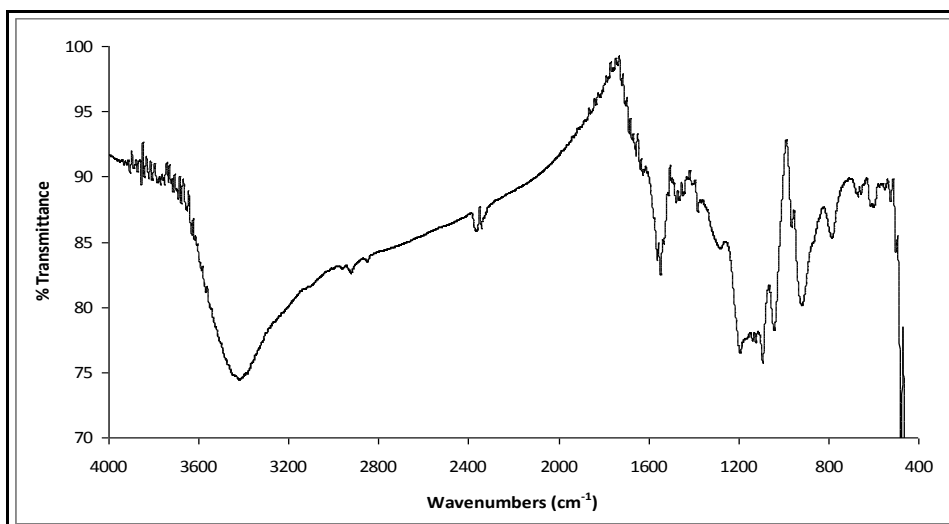


Fig-5 FT-IR spectra of Poly(pyrrole-co-flutamide)

The band observed at 3422cm^{-1} is attributed to the N-H stretching, since both monomer units contain -NH_2 and N-H groups. The bands observed around $2930, 2849\text{ cm}^{-1}$ is attributed to the C-H stretching and anti-symmetric stretching aromatic.

A prominent band at 1548cm^{-1} is attributed to aromatic pyridyl $\text{C}=\text{N}$ stretching. The band observed at 1198cm^{-1} is assigned as the C-N stretching of aromatic secondary amine. The occurrence of band at 1043 cm^{-1} assigned as carbon ring in cyclic, the band at 477 cm^{-1} assigned as C-N-C bending. The broad band around 3422 cm^{-1} is due to the involvement of -NH_2 group in one of the monomer in intermolecular electrostatic binding.

The band at 1180 cm^{-1} assigned as the $-\text{C}-\text{N}-$ in aromatic ring. The band observed at 1382 cm^{-1} assigned as $-\text{CF}_3$ in aromatic and as well as NO_2 substitution in aromatic ring.

The predominant band for Carbonyl ($\text{C}=\text{O}$) which is present in the monomer at 1710 cm^{-1} is vanished in the copolymer. This clearly shows that these copolymers are Linked in the Carbonyl ($\text{C}=\text{O}$) unit. This is the strong evidence for the presence of flutamide unit in the copolymer. The band observed at 489 cm^{-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 flutamide took place most probably at the given conditions. The IR spectrum of the copolymer indicates that there are the $-\text{NH}_2$ group, $-\text{NH}$ group, NO_2 group, $-\text{CF}_3$ group and C-N-C in the copolymer film. Thus, the pyrrole and flutamide units are contained in the copolymer.

^1H NMR spectral analysis of poly(pyrrole-co-flutamide)

The signals around 7 and 7.2 -7.4 ppm are attributed due to respective aromatic protons. The signal at 3.55 ppm can be attributed to the N-H protons and secondary amine. The signals at the region 2.5 - 3.5 pm can be again attributed to the aromatic substituted NH and NH_2 protons. Based on the IR and ^1H NMR spectra, it is concluded that the greenish black polymer deposited on the working electrode is a copolymer.

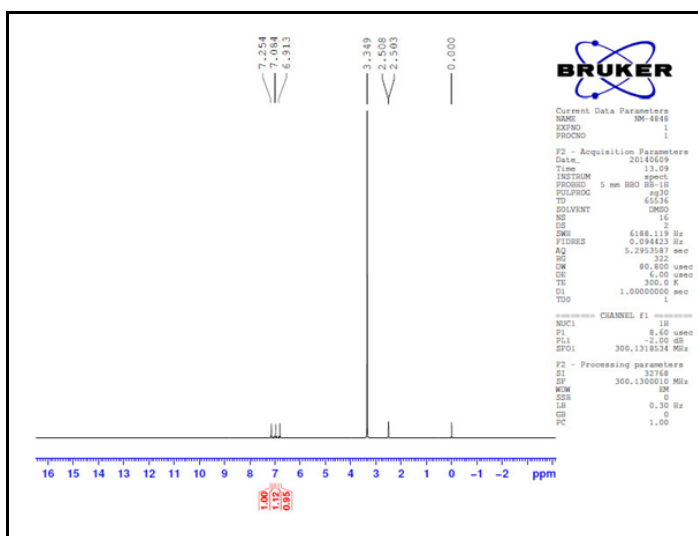


Fig- 6 NMR spectra of Poly(pyrrole-co- flutamide)

Morphology of Poly(pyrrole-co-flutamide)

Scanning electron micrographs (SEM) of the copolymer provide a clear morphology of the copolymer. The SEM images of the Poly(pyrrole-co-flutamide) is shown in Fig-11

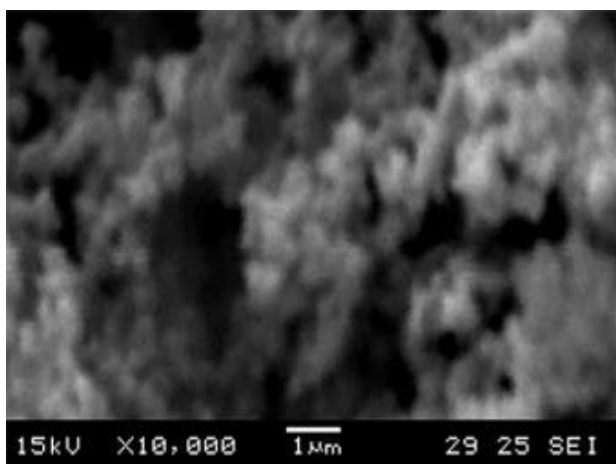


Fig-7 SEM images of the Poly(pyrrole-co- flutamide)

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.

XRD of Poly(pyrrole-co- flutamide)

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.

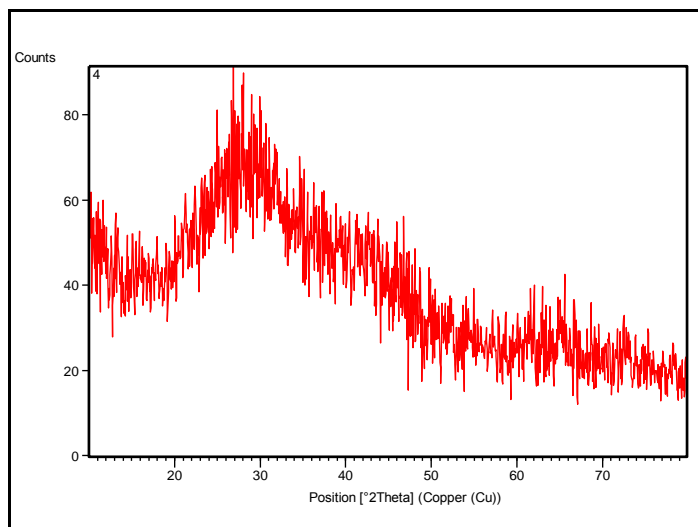


Fig-8 shows X-ray diffraction pattern of Poly(pyrrole-co- flutamide)

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

Conclusion

The Poly (pyrrole-co- flutamide) 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 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 (polymerization) new Poly(pyrrole-co- flutamide) has been proved by IR results. The X-ray diffraction of Poly(pyrrole-co- flutamide) suggests, it has amorphous nature. The SEM studies show the presence of nano particles.

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