



Synthesis and Characterization of Poly(aniline-co-sulfamethazine)

KEYWORDS

Sulfamethazine, oxidative polymerization, electrochemical method, Glassy carbon electrode, SEM

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ABSTRACT Poly(aniline-co-sulfamethazine) was prepared by electrochemical and chemical oxidative polymerization. The copolymer thin film of aniline with sulfamethazine on glassy carbon electrode was synthesized by using cyclic voltammetry in aqueous sulfuric acid medium. The formation of copolymer, the electrochemical behavior and the structure were studied. The analogous copolymer was prepared via a chemical oxidative polymerization in 1M HCl in the presence of potassium persulphate as an oxidant. The characterization of the copolymer by IR, ¹H NMR, XRD and SEM studies reveal the formation of aniline-co-sulfamethazine in amorphous nature.

1. Introduction

Polyaniline (PANI) has been in the forefront of commercially available conducting polymers because of its unique proton dopability, low cost, ease of synthesis, excellent redox recyclability, variable electrical conductivity, thermal and chemical stability. PANI can be used as an electrode material in the fabrication of secondary batteries in microelectronics and in electrochromic display material[1-4]. PANI has a rigid and planar backbone providing good conductivity but the same feature makes it insoluble in common organic solvents and incompatible with common polymers. This necessitates modification of the PANI structure to achieve better processability.

Considerable progress has been made in the modification of the PANI chain leading to better processibility by the post treatment of parent PANI base, the synthesis of polymer blends and composites, soluble substituted anilines and copolymers of aniline with substituted anilines. Among these methods copolymerization is considered to be an important method to improve the properties of homopolymers.

Sulfamethazine (SMZ, Fig-1) is 4-amino-N-(4,6-dimethyl-2-pyrimidine) benzenesulfonamide is a commonly used sulfonamide in veterinary medicine as an antibacterial compound to treat livestock diseases such as gastrointestinal and respiratory tract infections. Its uses include the treatment of chronic and acute bacterial infections in food-producing animals. SMZ depresses dihydrofolic acid synthesis[5-8]. This action is effective against a range of Gram-positive and Gram-negative organisms (Richards, Taylor & Zhu, 1996).

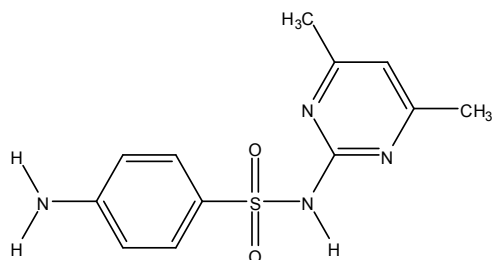


Fig-1 structure of sulfamethazine

Copolymerization is a simple way of preparation of new polymers, and it greatly increases the scope of tailor-making materials with specifically desired properties[9]. The copo-

lymerization 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[10]. Changing the monomer concentration ratio[11] 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[12].

In the present investigation, the cyclic voltammetry method was used for the electrochemical copolymerization of aniline and sulfamethazine 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.

2. Experimental

2.1 Materials

Chemicals used for this synthesis were of analytical grade purchased from Sigma-Aldrich. 5mM sulfamethazine stock solution was prepared in 1:1 aqueous ethanol. Aniline was distilled under reduced pressure. Potassium persulfate, sulfuric acid and methanol were used as received. All solutions were prepared by using bidistilled water.

2.2 Synthesis of polymerization of aniline and sulfamethazine

2.2.1 Electrochemical polymerization

Electrochemical polymerization of aniline and sulfamethazine was carried out using a software controlled Electrochemical analyzer Model CHI 620D provided with a three electrode single compartment cell assembly. A Glassy carbon with the surface area of 0.0314cm², a platinum wire and Ag/AgCl were used as working, counter and reference electrodes, respectively. The polymerization was carried out in an aqueous medium of 1M H₂SO₄ with aniline and sulfamethazine using cyclic voltmetric technique. The polymerization in all supporting electrolytes and their voltammograms were recorded on PC. Purified Nitrogen gas was purged in the solution to maintain oxygen free condition in all the experiments.

2.2.2 Chemical Copolymerization

Copolymer of poly(aniline-co-SMZ) was chemically synthesized using potassium persulphate as initiator in an aqueous acidic medium at 0-4^oC in a similar manner to that previously described[13-15]. A typical procedure for preparation of the

copolymer is as follows.

Monomers, aniline (0.5M) and sulfamethazine (0.1M) were dissolved in 50 ml of 1M HCl aqueous solution and cooled to 0-4°C. The oxidant potassium persulphate (0.05M) was dissolved separately in 50 ml of 1M HCl and cooled to 0-4°C. Then the oxidant solution was added dropwise to the monomer solution for 1 hour with constant stirring in nitrogen atmosphere at 0-4°C. After complete addition of the oxidant stirring was continued for another 7 hours to ensure the completion of the reaction. A dark green precipitate was obtained and the reaction mixture was kept overnight. Then the copolymer precipitate was filtered, washed with distilled water until the filtrate became colourless and finally with methanol and dried in an air oven at 60°C for 8 hours.

3. Result and Discussion

3.1 Copolymerization of aniline and sulfamethazine

The cyclic voltammogram of 0.005M sulfamethazine in 0.1M H₂SO₄ was shown in Fig-2. The electro-oxidation was on a stationary glassy carbon electrode, the potential ranging from 1.2 to -1.2V at a scan rate of 100mV/sec. The voltammogram exhibited one broad anodic peak at 1.13V potential in first cycle. As the cycling process continued, the peak current reduced.

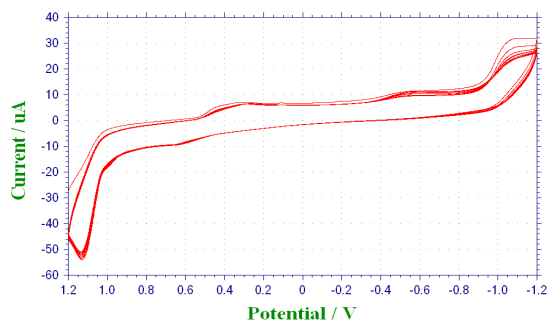


Fig-2. Cyclic voltammetric behavior of 0.005 M sulfamethazine on GCE in 0.1 M H₂SO₄ at scan rate 100 mV/s.

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

The cyclic voltammogram of 0.04 M aniline in 0.1 M H₂SO₄ on a stationary Glassy carbon electrode with a potential window from 1.2 to -1.0V at a scan rate 100mV/sec is given in Fig.3. The voltammogram shows an anodic peak at 0.32V and a cathodic peak at 0.39V in the first cycle. The peak current increased with the increase in number of cycles. After completion of the 30 cycles, a green-color polymer film was seen on the working electrode.

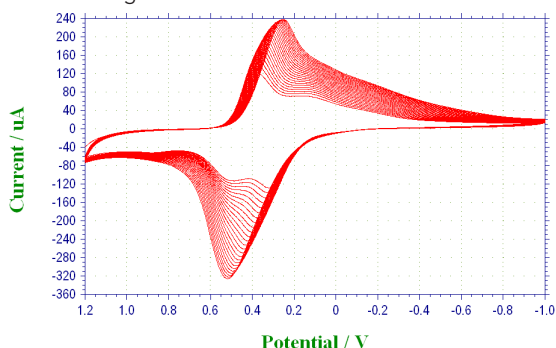


Fig-3. Cyclic voltammetric behavior of 0.04 M aniline on GCE in 0.1 M H₂SO₄, scan rate 100 mV/s.

The cyclic voltammogram was recorded for 0.01M aniline with 0.005M sulfamethazine on a GCE in 0.1 M H₂SO₄ medium with a potential range between 1.2 and -1.2V. The cyclic voltammogram (Fig-4) shows a broad cathodic wave entered at a potential of -1.0V in the first cycle

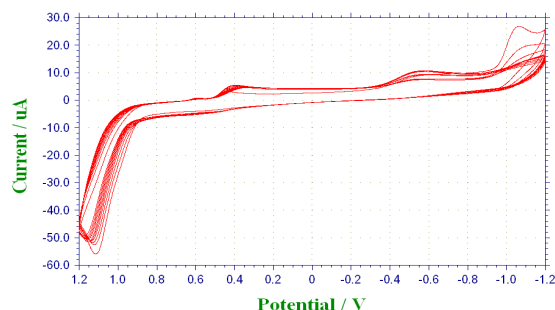


Fig-4. Cyclic voltammetric behavior of 0.01M aniline with 0.005M sulfamethazine on GCE in 0.1M H₂SO₄, scan rate 100 mV/s.

As the scanning cycle increased both anodic and cathodic peaks were observed. The initial reduction peak disappeared and one reduction peaks at 0.4V and one oxidation peak at 1.1V appeared. When the cycling process continued, there was a gradual decrease in the reduction peak whereas anodic peak showed only small increase in the peak current. Though the reduction peak potentials at 0.4V is closer to that of pure PANI formation and one oxidation peak at 1.1V closer to the pure PSMZ formation, oxidation peak of pure PANI disappeared in the copolymer. A bluish-green-color film was seen on the working electrode. These indicate the copolymerization of aniline with sulfamethazine (aniline-co-SMZ).

The typical cyclic voltammogram of 0.01M aniline and 0.0025M sulfamethazine were recorded on GCE in 0.1M H₂SO₄ is given in Fig-5.

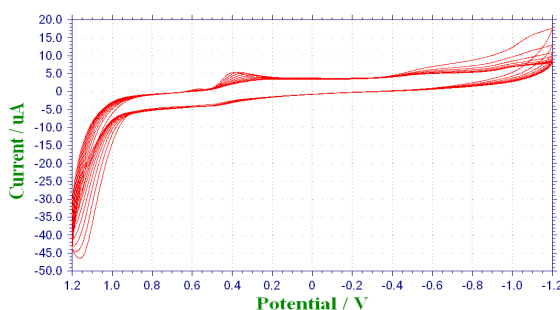


Fig-5 Cyclic voltammetric behavior of 0.01 M aniline and 0.0025M sulfamethazine on GCE in 0.1M H₂SO₄, scan rate 100 mV/s.

The cycling range and scan rate are same as previously. The voltammogram exhibited one cathodic peak at 0.39V and one anodic peak at 1.16V in first cycle. Here the voltammogram exhibited different behavior from PANI. The reduction peak potential at 0.389V is closer to that of pure PANI formation and oxidation peak of pure PANI disappeared in the copolymer. Similarly one oxidation peak at 1.16V closer to the pure PSMZ formation and this peak are disappeared in further cycles. When the cycling process continued, there was a gradual decrease in the reduction peak whereas anodic peak was disappeared. Such different type of behavior suggests the copolymerization of both aniline and sulfamethazine (aniline-co-SMZ). This type of incorporation of aniline monomer into sulfamethazine monomer leads to the formation of a random copolymer on the working electrode. The bluish-green-color film seen on the working electrode indicates the difference in the color of the polymer formed.

The cyclic voltammogram of 0.01M aniline and 0.001M sulfamethazine were electrolyzed on GCE in 0.1 M H_2SO_4 medium is presented in Fig-6.

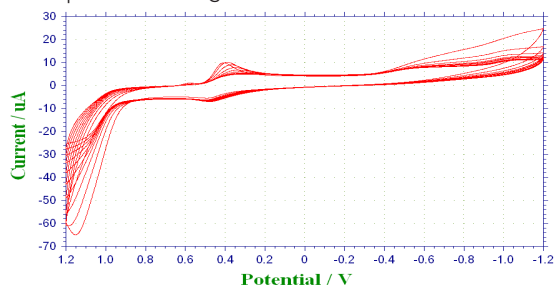


Fig-6 Cyclic voltammetric behavior of 0.01 M aniline and 0.001M sulfamethazine on GCE in 0.1M H_2SO_4 , scan rate 100 mV/s.

The cycling range and scan rate are same as previously. The voltammogram exhibited one cathodic peak at 0.409V and two anodic peaks at 0.492V and 1.15V in first cycle. Here also the voltammogram slightly exhibited different behavior from polyaniline. The redox peak potentials at 0.409V and 0.492V are closer to that of pure PANI formation. An oxidation peak at 1.15V closer to the pure PSMZ formation and this peak is disappeared in further cycles. When the cycling process continued, there was a gradual decrease in the redox peak potential whereas anodic peak was disappeared. These behaviors indicate the incorporation of more aniline units compared to the previous concentration studies. The green-color film seen on the working electrode indicates the difference in the color of the polymer formed.

The typical cyclic voltammogram of 0.01M aniline and 0.01M sulfamethazine were electrolyzed on GCE in 0.1M H_2SO_4 , shown in Fig-7

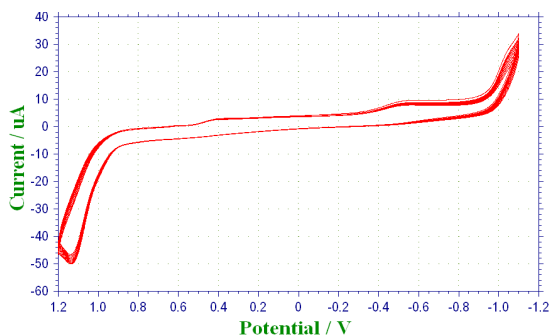


Fig-7 Cyclic voltammetric behavior of 0.01M aniline and 0.01M sulfamethazine on GCE in 0.1M H_2SO_4 , scan rate 100 mV/s.

The voltammogram exhibited only one anodic peak at 1.33V in first cycle. The anodic peak at 1.13V closer to the pure PSMZ formation, the peaks of PANI was disappeared. When the cycling process continued, there was a gradual increase in the anodic current. These behaviors indicate the incorporation of more sulfamethazine units compared to the previous concentration studies. The violet color film seen on the working electrode indicates the difference in the colour of the polymer formed.

The cyclic voltammetric studies suggest the incorporation of sulfamethazine in the copolymer formed and the copolymer is influenced by the concentration of sulfamethazine. The concentration of sulfamethazine monomer was plotted against the total charge for the formation of electro active oxidative conducting copolymer films shown in Fig-8. The

total charge decreases with an increase in sulfamethazine monomer concentration. There was a sudden decrease in the total charge from PANI formation when 0.001M sulfamethazine was employed. After this, increase in sulfamethazine concentration led to a slower decrease rate and at concentrations 0.0025 and 0.005M sulfamethazine only little change was observed in total charge. This indicates the incorporation of more and more sulfamethazine in the copolymer and decreases the electro active behaviour.

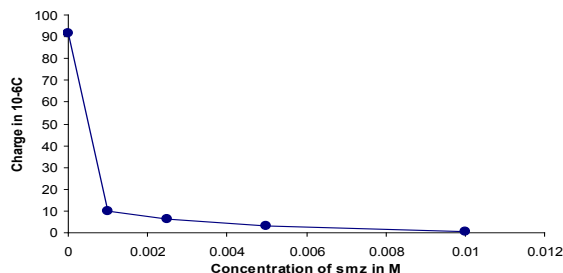


Fig-8 Plot of charge Vs Concentration of SMZ

3.2 FT-IR spectral analysis of poly(aniline-co-SMZ)

The IR band position of poly(aniline-co-SMZ) was prepared in a solution containing 0.01M aniline and 0.005M sulfamethazine is shown in Fig-9

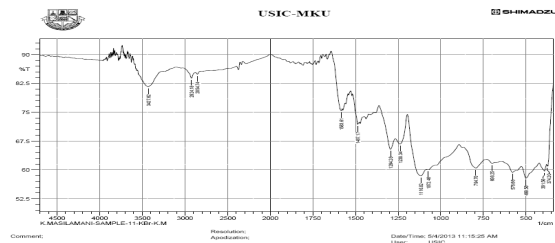


Fig-9 FT-IR spectra of Poly(aniline -co- sulfamethazine)

The band observed at $3427cm^{-1}$ is attributed to the N-H stretching, since both monomer units contain $-NH_2$ groups. The band observed at $2924cm^{-1}$ and $2854cm^{-1}$ is attributed to the C-H stretching and anti-symmetric stretching. A prominent band at $1583.61cm^{-1}$ is attributed to NH_2 deformation and a band at $1487cm^{-1}$ is attributed to N-H secondary amide deformation. The occurrence of this band clearly shows that these copolymers are composed of N-H units. A band at $1297cm^{-1}$ is attributed to the SO_2 in sulfones anti symmetric stretching, since sulfamethazine contain SO_2 group. This is strong evidence for the presence of sulfamethazine unit in the copolymer.

The copolymer shows that the band observed at $1238cm^{-1}$ is assigned as the C-N stretching of aromatic amine, for the C-N stretching in aromatic amines are in the range $1280-1180cm^{-1}$. The band at $1116cm^{-1}$ is attributed to the C=S stretching vibrations of the thiocarbonyl compound. A peak at $794cm^{-1}$ is attributed to the disubstituted amine or trisubstituted amine in benzene ring stretching. A band at $698cm^{-1}$ is attributed to the C-S stretching and a band at $578cm^{-1}$ is attributed to the SO_2 deformation. The band observed at $499cm^{-1}$ is attributed to the C-N-C bend stretching in amine.

The above results in the IR spectral data's of copolymer demonstrate that an electrochemical copolymerization of aniline and sulfamethazine took place most probably at the given conditions. The IR spectrum of the copolymer indicates that there are the $-NH_2$ group, $-NH$ group and SO_2 in the copolymer film. Thus, the aniline and sulfamethazine units are contained in the copolymer.

3.3 ¹H NMR spectral analysis of poly(aniline-co- SMZ)

The ¹H NMR spectra of Poly(aniline-co-SMZ) shown in Fig-10.

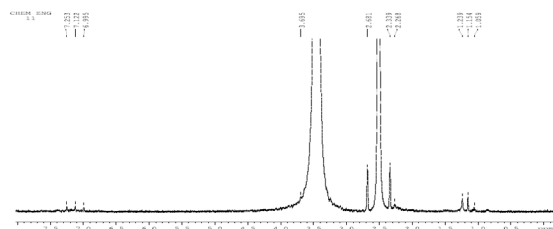


Fig-10 ¹H NMR spectra of poly(aniline -co- SMZ)

The main peaks are discussed here. The signals around 6.99, 7.12 -7.25ppm can be attributed due to aromatic protons respectively. The signal at 3.69ppm can be attributed to the N-H protons. The signals at the region 2.68ppm can be attributed to the aromatic substituted CH₃ protons. The signals at the regions 2.26-2.33ppm can be attributed to the NH₂ protons. Based on the IR and ¹H NMR spectra, we concluded that the green polymer deposited on the working electrode is a copolymer.

3.4 Morphology of poly(aniline-co- SMZ)

Scanning electron micrographs (SEM) of the copolymer provide a clear morphology of the copolymer. The SEM images of the poly(aniline-co-SMZ) was prepared in a solution containing aniline (0.5M) and SMZ (0.1M) is shown in Fig-11

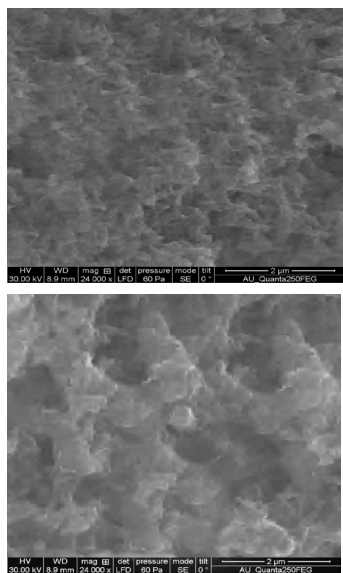


Fig-11 SEM images of the poly(aniline-co-SMZ)

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.

3.5 XRD of Poly(aniline-co-SMZ)

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, while 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-12 shows X-ray diffraction pattern of Poly(aniline-co-SMZ)

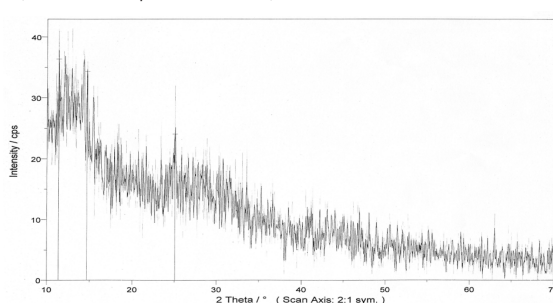


Fig-12 X-ray diffraction pattern of Poly(aniline-co- SMZ)

The XRD patterns of the poly(aniline-co-SMZ) 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(aniline-co-SMZ) suggests that it has amorphous nature.

4. Conclusion:

The poly(aniline-co-sulfamethazine) was synthesized by potential cycling in sulphuric acid medium (pH 1) 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, NMR and X-ray powder diffraction (XRD) and the surface morphology was studied using SEM analysis. The participation of NH group in the chemical synthesis of new poly(aniline-co-SMZ) has been confirmed by IR results. The X-ray diffraction of poly(aniline-co-SMZ) suggests the amorphous nature. The SEM studies show the nano structured copolymer.

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