



Electrochemical synthesis and characterization of co-polymers of aniline and pyrrole

A M Pharhad Hussain* and A Kumar

Department of Physics Tezpur University Napaam Assam 784 928 India

E mail abu@tezu.ernet.in

Abstract Conducting polymer (CP) films of polyaniline (PAni) polypyrrole (Ppy) and copolymers of aniline and pyrrole are synthesized electrochemically in sulfuric acid (H_2SO_4) aqueous electrolyte on indium doped tin oxide (ITO) coated glass substrate Cyclic voltammetry (CV) studies are carried out for electrochemical characterization and the polymer films showed high electroactivity in acidic media X-ray diffraction study revealed polyaniline as completely amorphous and polypyrrole and co-polymer as polycrystalline Electrical (dc) conductivity of the co-polymer films was measured by four probe method and found to lie between those of polyaniline and polypyrrole UV-VIS spectra of the co-polymer show a peak at 370 nm which is in between the characteristic $\pi - \pi^*$ transition peak of polyaniline polypyrrole suggesting formation of copolymer FTIR spectra also suggest formation of copolymer poly (aniline-co-pyrrole)

Keywords Electrochemistry, co-polymer cyclic voltammetry UV-Vis, FTIR

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1. Introduction

Conducting polymers (CPs) have drawn much attention in the past decade since polyacetylene was first prepared [1] with a high conductivity [2] of about 10^3 S/cm They are promising materials for supercapacitor, batteries, sensors, electronic displays, smart windows, actuators, drug delivery *etc* because of their processability, low cost, high specific charge capacity, cycle life and redox property [3,4,9-12] CPs like polyaniline, polypyrrole, polythiophene *etc.* are ideal electrode materials [13] for energy storage and conversion systems which satisfy the requirements of high specific power and energy like all polymer redox supercapacitors [14] and all polymer rechargeable batteries [15] Most applications of the conjugated polymers are based on their electrochemical and optical properties, both the properties are closely related to the electrochemical reactions of the polymers [6]. Polyaniline is unique because it has a conductivity that can be reversibly controlled

both by charge transfer reaction with the conjugated backbone and by protonation of the nitrogen [3]. Polypyrrole has higher electrical conductivity, relatively better environmental stability and is polycrystalline [16-18]. However it is infusible and decomposes before melting [17].

Electrochemical studies on conducting polymers mainly include analysis of growth mechanism, doping/dedoping process and charge transfer characteristics. Major problems in most conducting polymers are their processability and environmental stability. They are insoluble or very poorly soluble in common organic solvents. Sulphonated polyaniline with SO_3 groups attached with the benzene ring is soluble but the conductivity is reduced [19]. Copolymers of conducting polymers are expected to show good conductivity as well as mechanical stability from two components at the cost of some of their properties such as electrical conductivity [20]. Copolymers of pyrrole and N-methyl pyrrole [21], pyrrole and phenol [22], pyrrole and terthienyl [23], pyrrole and tetra alkyl ammonium pyrrole [24], pyrrole and acrylamide [25] have been prepared by electrolytic oxidation of the mixture of monomers. Electro-co-polymerization of aniline and pyrrole have some advantage as both the monomers were added to the electrolyte and the oxidative polymerization takes place simultaneously. In this study an attempt has been made to synthesize copolymer films of aniline and pyrrole in aqueous medium with protonic acid H_2SO_4 as the supporting electrolyte. The CV of the polymer films has been carried at different scan rates to investigate the redox response. UV-VIS and FTIR spectra of the polymer films have been taken for understanding the optical and chemical nature of the polymers. Conductivity measurements of the films are carried out with four probe technique. X-ray diffractogram has been carried out to study the degree of crystallinity of the polymer films.

2. Experimental

Monomers aniline (Aldrich) and pyrrole (SRL-India) are distilled under reduced pressure and stored in darkness prior to use in inert condition. H_2SO_4 (Qualigen) is used as received and double distilled deionized water is used in all experimental purpose. CP films of polyaniline, polypyrrole and their copolymer were deposited on ITO (BHEL, India) coated glass substrates using stainless steel counter electrode and SCE reference electrode in a three electrode electrochemical cell using a potentiostat/galvanostat (AEW2, Sycopel Scientific Ltd. UK). Five polymer films are synthesized, two of them are of pure polymer films of 0.1M pyrrole and 0.01M aniline monomer and other two films with 0.1M aniline and 0.01M and 0.02M pyrrole monomer. The polymerizations are carried out potentiostatically at 1000 mV in an aqueous solution containing the monomers and sulfuric acid as the supporting electrolyte for polymerization. The cyclic voltammograms of the polymer films have been recorded using the same potentiostat/galvanostat. The dc conductivity measurements of the polymer films are carried out by four probe technique using a standard four probe setup. The x-ray diffractogram [Philips X-pert pro] of the polymer films are recorded. UV-VIS spectra of the polymers are recorded by using a double beam UV-VIS spectrometer (Shimadzu) taking ITO coated glass in the reference

beam line. The FTIR spectra of the polyaniline samples have been taken by using Nicolet Impact 410 FTIR spectrophotometer.

3. Results and discussion

3.1 Electrical conductivity :

The conductivity of the polymer films is measured by four probe method using a standard four probe set up at room temperature. The dc conductivity for the polyaniline films was found to be 35 S/cm and that for polypyrrole is about 100 S/cm. The conductivity of the co-polymers films were found to be in the range of 50-70 S/cm. Conductivity of the co-polymer films lies between the conductivity of polypyrrole and polyaniline, which could be explained in terms of decreased crystallinity of the copolymer. To co-polymer films with lower concentrations of pyrrole (0.01 and 0.02M) and higher concentration of aniline monomer (0.1M) exhibited lower conductivity, around 50-55 S/cm and the co-polymer films with higher concentration of pyrrole monomer (0.1M) and lower concentration of aniline (0.01M) showed higher conductivity on the order of 70 S/cm. This behaviour is attributed to the fact that polypyrrole films are more conducting as compared to polyaniline.

3.2 Cyclic Voltammetry

The cyclic voltammetry of the polymer films is carried out at different scan rates of 10, 20, 40 and 50 mV/s in a three electrode electrochemical cell, potentials are applied against saturated calomel electrode (SCE) and are shown in Figure 1(a-e). Every CP shows an electrochemical window within which the doping/dedoping (redox) process is largely reproducible, beyond which oxidative or reductive decomposition of the CP occurs. The CV is observed to be related with the electrochromism of the CP, i.e. the redox peaks observed in the CV usually coincide with the CP's colour changes. Polyaniline films change colour from dark green to bottle green with increase in potential in the forward sweep and again back to dark green in the reverse sweep. The co-polymer films in the forward sweep change colour from blackish green to dark brown and in the reverse sweep it becomes again blackish green. The results are consistent with the results reported in the literature [26-31]. The CV of CP depends on several parameters like substrate, electrolyte concentration, p^H of the electrolyte etc. The cathodic and anodic currents increase with increase in scan rates in all CV. The CV of pure polyaniline (Figure 1a) shows distinct oxidation-reduction peaks at 1.5 V and 0.6 V respectively which also depicts a slight increase in oxidation potential at higher scan rate. The peak current in forward scan in case of pure polypyrrole (Figure 1b) was obtained at 1.8 V and the peak in the reverse sweep was obtained at 0.2 V. In this polymer film a slight shift of the peak towards higher and lower potential, in forward and reverse sweep respectively, was also observed with increase in scan rate. In the CV of copolymer with 0.1 M aniline and 0.01 M pyrrole, interestingly two peaks are observed in the forward sweep (Figure 1c). The first peak at 1.55 V which coincides with the peak position of pure polyaniline, may be due to the oxidation of aniline part of the co-polymer chain and the second one at 1.8 V which coincides with the peak position of polypyrrole, may be attributed to oxidation of the pyrrole part of

the copolymer chain. In Figure 1d, the CV of the copolymer with 0.1M aniline and 0.02M pyrrole, at lower scan rate again two oxidation peaks with small potential position difference was observed but at higher scan rate instead of two peaks one broad peak was obtained. This is may be due to overlap of the two independent oxidation peaks of pyrrole and

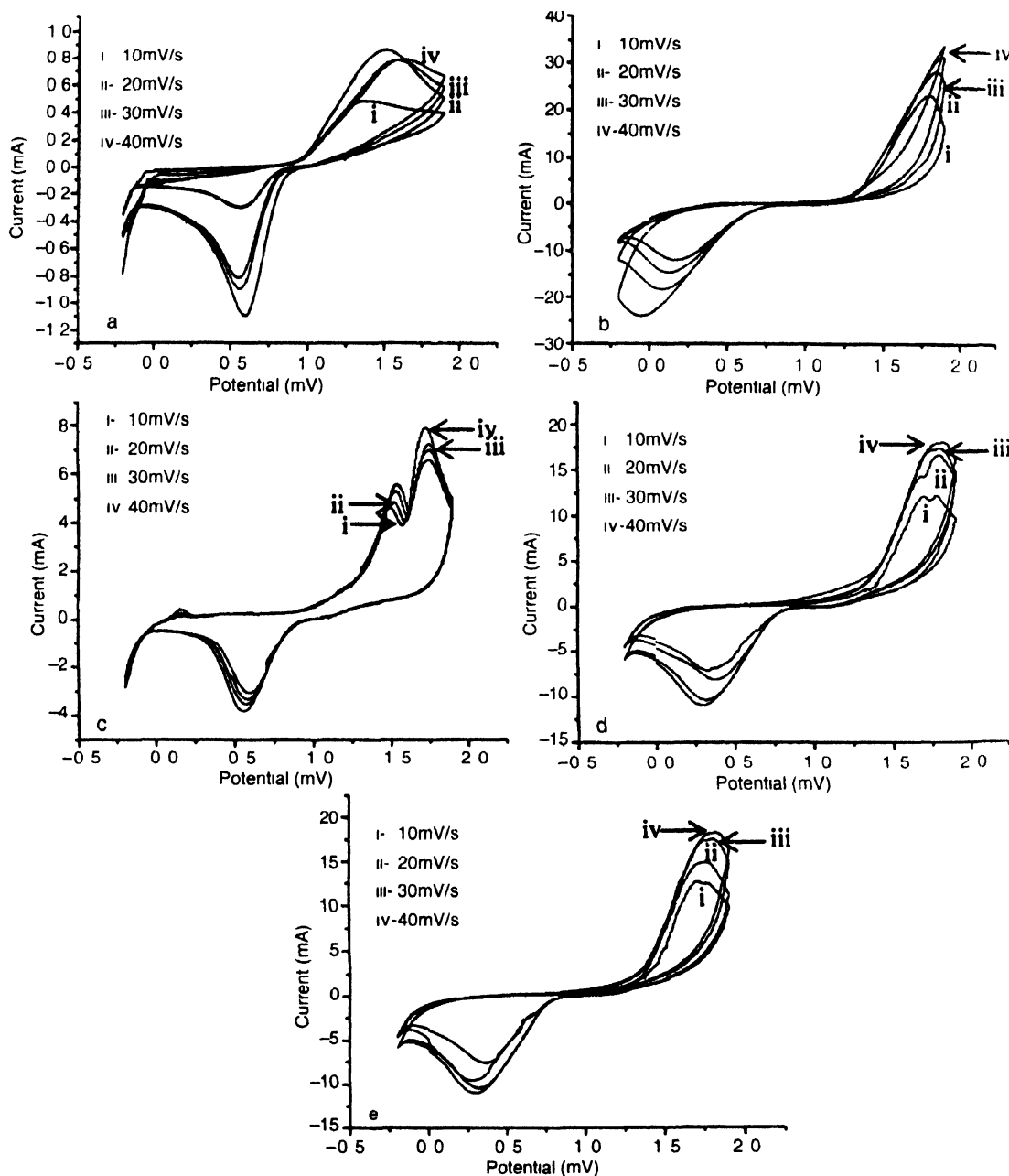


Figure 1. Cyclic Voltammograms of (a) polyaniline, (b) polypyrrole, (c) poly (aniline-co-pyrrole) [Aniline 0.1M + 0.01M Pyrrole], (d) poly (aniline-co-pyrrole) [Aniline 0.1M + 0.02M Pyrrole] and poly (pyrrole-co-aniline) [pyrrole 0.1M + aniline 0.01M] at different scan rates in aqueous H_2SO_4 with stainless steel counter and SCE as reference electrode.

aniline. The CV of the copolymer with 0.1M pyrrole and 0.01M aniline (Figure 1E) shows single broad peak in the forward sweep. As the aniline concentration is low, the dominant part is the pyrrole units in this case and hence oxidation of aniline peak is too weak and the oxidation of pyrrole unit dominates the current peak. The higher peak height *i.e.* peak current of pyrrole oxidation may be attributed to the higher conductivity of pyrrole in oxidized state

3.3 UV-VIS spectra :

The UV-VIS spectra of the polymer films of polyaniline, polypyrrole and the copolymer deposited on ITO coated glass are presented in Figure 2a-c. The absorption band at 310nm (Figure 2a) is associated with the $\pi - \pi^*$ transition of the benzenoid part in the polyaniline linear structure or simply the band gap of the polymer and the relatively broader band at 620 nm in the absorption spectra of pure polyaniline (Figure 2a) can be attributed to the intramolecular transition between benzenoid and quinoid ring in the polymer chain. Polyaniline is completely transparent in the 200-300 nm region. The UV-VIS spectra of pure polypyrrole (Figure 2b) shows absorption at 415nm which may be accounted for the $\pi - \pi^*$ electron transition or the characteristic transition of the polypyrrole. The theoretical study shows that the longer the absorption wavelength of the $\pi - \pi^*$ electron transition of the conjugated chain, the longer will be conjugation length of the chain [32]. UV-VIS spectrum of the co-polymer film shows the combined features of both polyaniline and polypyrrole (Figure 2c) one absorption peak is observed at 370nm which is in between the characteristic peaks of polyaniline and polypyrrole and may be the characteristic peak of the co-polymer. The second absorption band a broader one at 600nm may be due to the $\pi - \pi^*$ transition of the benzenoid and quinoid of the polyaniline part in the co-polymer chain.

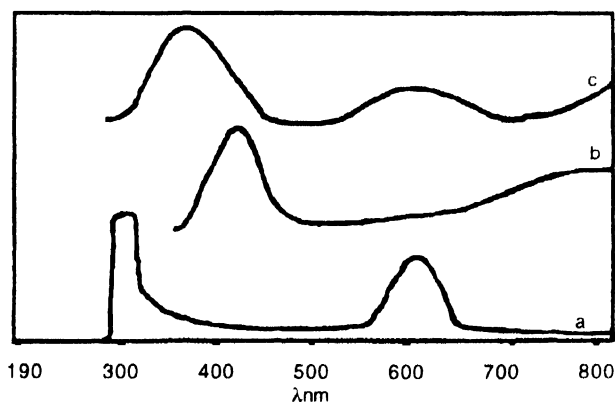


Figure 2. UV-VIS absorption spectra of (a) polyaniline (b) polypyrrole and (c) poly (aniline-co-pyrrole) with 0.1 M aniline and 0.1 M pyrrole

3.4 FTIR Spectra :

FTIR spectra of the polymer polyaniline, polypyrrole and the copolymer are presented in Figure 3a-c respectively. In Figure 3a peak at 3470 cm^{-1} is attributed to the N-H stretching

of the amine group of aniline [33]. The peak near 3000 cm^{-1} is due to the C–H stretching absorption. The peak at 1300 cm^{-1} is due to the C–N stretching of the polymer. The strongest band observed near 1100 cm^{-1} and the band at 1235 cm^{-1} are due to C–C stretching and C–C twisting, respectively [34]. The peak near 800 cm^{-1} is due to the N–H out-of-plane bending absorption. The peak due to N–H bending can be seen in the range of $1560\text{--}1640\text{ cm}^{-1}$. The stretching peak of N–H appears in the range of $3420\text{--}3450\text{ cm}^{-1}$. The C = C stretch absorption of aromatic compound (aniline) is obtained at 1477 cm^{-1} (Figure 3a) and the same C = C stretch absorption for hetero-aromatic compound (pyrrole) is obtained at 1527 cm^{-1} (Figure 3b). Both the characteristic C = C stretching absorption peaks for aromatic and hetero-aromatic compounds are present in the IR spectra of the co-polymer (Figure 3c) at around 1480 and 1525 cm^{-1} , and this may be the confirmation of formation of co-polymer chain in the electropolymerization.

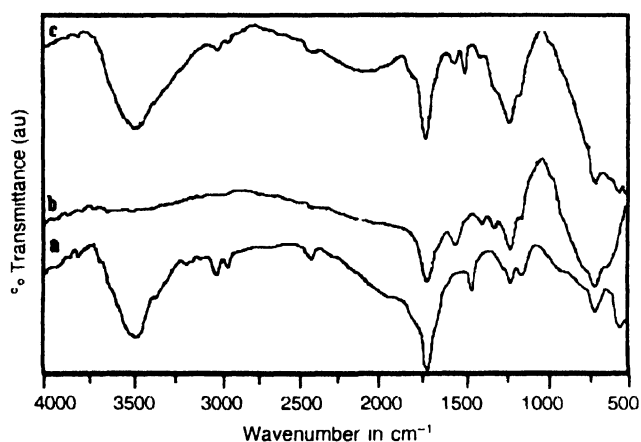


Figure 3. FTIR spectra of (a) polyaniline (b) polypyrrole and (c) poly (aniline-co-pyrrole)

3.5. X-ray diffractogram :

The XRD spectra of pure polyaniline film, pure polypyrrole and poly (aniline-co-pyrrole) are presented in Figures 4a, 4b and 4c respectively. Pure polyaniline deposited on ITO coated

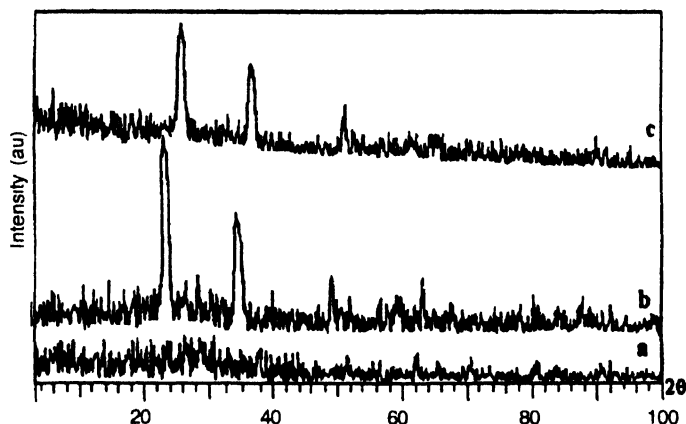


Figure 4. X-ray diffractogram of (a) polyaniline (b) polypyrrole and (c) poly(aniline-co-pyrrole).

glass is completely amorphous (Figure 4a), whereas polypyrrole (Figure 4b) on ITO coated glass is polycrystalline. The co-polymer poly (aniline-co-pyrrole) is also found to be polycrystalline but the degree of crystallinity is reduced (Figure 4c). The decrease in crystallinity in poly (aniline-co-pyrrole) may be attributed to the incorporation of aniline monomer in the co-polymer chain as polyaniline is completely amorphous.

4. Conclusion

From this study we have observed that free standing films of poly (aniline-copolyrrole), which can be removed from the substrate, can be synthesized by electro-copolymerization. XRD results show that polypyrrole is crystalline and polyaniline is amorphous. Though the degree of crystallinity of polypyrrole is more as compared to those of co-polymer films, the polypyrrole films are more adhesive to the ITO coated glass substrate and are not removable from the substrate. Conductivity of the co-polymer films lies between the conductivity of polypyrrole and polyaniline which could be explained in terms of decreased crystallinity of the copolymer. The absorption peak at 370 nm in the UV-VIS spectra of the copolymer may be attributed to the characteristic electronic transition absorption of poly (aniline-copolyrrole). Presence of aromatic and heteroaromatic characteristic C=C stretching peaks in the FTIR spectra of copolymer also suggest electro-copolymerization of poly (aniline-co-pyrrole).

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