

Electrochemical Synthesis, Characterization and Application of poly (4-vinyl pyridine-co-aniline)

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Abstract A novel copolymer, poly (4-vinyl pyridine-co-aniline) [poly (4VP-co-Ani)] has been synthesised. Formation of copolymer was simple and readily achieved at room temperature. Poly (4VP-co-Ani) was synthesized electrochemically using a conventional three-electrode system. Redox processes were studied with cyclic voltammetry (CV). Effect of pH on the electro copolymerization process was also investigated. Acidic medium was favoured for efficient polymerization. Result of electrochemical and spectroscopic analyses were discussed at length. FT-IR spectroscopy has indicated that traits from both 4-vinyl pyridine and aniline were coherently present in the copolymer structure. Since both Ani and 4VP have been known for their abilities to incorporate metal ions in their homopolymeric chains, the poly (4VP-co-Ani) has been utilised as a membrane for cadmium ion selective electrodes (ISE).

Keywords: Aniline; Copolymer; Electro copolymerization; 4-vinyl pyridine

1 INTRODUCTION

SINCE the early 1980s, elaborate researches have been carried out to study the characteristics of the PANI both in its doped and undoped forms [1]. PANI is known for its brittleness, low mechanical stability and poor processability among others. Therefore, researchers have utilized different methods of PANI synthesis ranging from composites to copolymers to overcome these limitations [2-4].

PANI may exist in three oxidation states: leucoemeraldine state (white or colourless), emeraldine state (green or blue) and also pernigraniline state (blue or violet). Among all three, emeraldine state is regarded as the most practical form of PANI as it has high stability and also is electrically conducting upon doping with acid. Treatment of the conducting emeraldine in any acid medium can visibly alter the degree of conductivity.

Copolymer, composites and blends of PANI improve the versatility of PANI as an advanced material. Its properties such as simplicity of synthesis, low cost, good environmental stability and also high conductivity make it more desirable for usages in various applications. PANI may also incorporate functional groups into its main chain, possesses distinct redox properties and with the ability to exist in different oxidation states.

PANI has been used for light-emitting diodes (LEDs) [5], rechargeable batteries [6] and sensors [7,8]. Previously, poly (4-vinyl pyridine) (P4VP) was used as a cadmium sensor [9].

In this work, electrochemical copolymerization of PANI with poly (4-vinyl pyridine) (P4VP) was carried out. Synthesis and characterization of the copolymer were extensively studied with SEM and FTIR. The e.m.f. response of cadmium salts on the copolymer was also investigated.

2 EXPERIMENTAL

2.1 Reagent and apparatus

Aniline (Aldrich, USA) was purified by double distillation under nitrogen atmosphere. The 4VP (Fluka Chemicals, Switzerland), tetraethyl ammonium tetrafluoroborate (Et_4NBF_4) and acetonitrile (MeCN) (Merck, Germany), were used as received. All solutions were prepared using ultrapure water from Milli-Q plus (Millipore, USA).

All electrochemical measurements were carried out using a Potentiostat/Galvanostat Model 273A c/w related softwares and frequency response analyser FRD100 (Princeton Applied Research, USA). A three-electrode cell comprising working electrode, a 2B pencil graphite lead (Steadtler, Nuremberg, Germany), platinum wire (99.99%) (Advent, UK) as the counter electrode and Ag/AgCl (3M KCl) reference electrode were employed throughout the studies. FTIR spectra were recorded by spectrophotometer model 2000 (Perkin Elmer, USA). Morphological studies were carried out with scanning electron microscope (SEM) Jeol JSM 6300.

2.2 Electrochemical polymerization

Both monomer solutions (Ani and 4VP) were first purged with oxygen-free-nitrogen (OFN) for 15 minutes. Polymerization of 0.05M of 4VP in MeCN was carried out in 0.1M Et_4NBF_4 by sweeping the potential between -0.4V to +0.6V with 50 mVs^{-1} scan rate. The polymer film modified

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electrode (PME) was washed with de-ionized water and was left to cure overnight. Next, electrochemical polymerization of 0.15M aniline in H_2SO_4 was carried out with PME as the working electrode. Scanning potential range of -0.3V to +0.8V and scan rate 100 mVs^{-1} was employed. The electropolymerized copolymer was taken out and washed with a mixture of water and MeCN in order to remove unreacted monomers.

2.3 Characterization

FT-IR spectroscopy system was used to study the membrane structure. Solid membrane samples are milled with potassium bromide (KBr) to form fine powder. The powder is then compressed into a pellet to be analyzed. FT-IR spectrums were recorded in the wavelength range of 400 to 4000 cm^{-1} at room temperature. Polymer film coated onto the graphite pencil was also analyzed by scanning electron microscopy (SEM) to compare morphology and porosity. The analytical conditions were at accelerating voltage 20 kV , beam current $2 \times 10^{-9} \text{ A}$, and working distance 15 mm .

3 RESULTS AND DISCUSSION

3.1 Electrochemical polymerization

Figure 1 shows progressive cyclic voltammogram (CV) of the electropolymerization of poly (4VP-co-Ani). At steady state (10^{th} cycle) and scan rate of 100 mVs^{-1} , the observed onset oxidation potential, E_{pa} is 1.00V and a cathodic peak potential, E_{pc} , of 3.55V . E_{pc} of 4VP obtained is at 2.25V and Ani at 2.85V and 5.50V . Both E_{pc} obtained from the respective homopolymers are different from the E_{pc} obtained from the polymerization of the copolymer. Thus, this signifies polymeric interaction has occurred between the individual monomers.

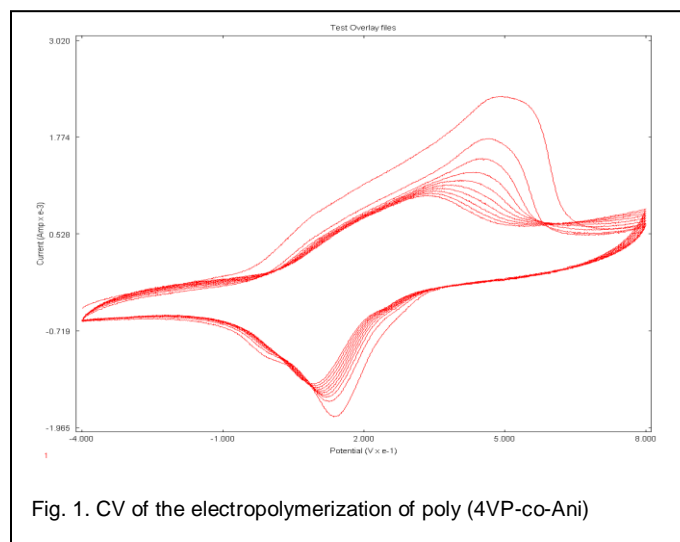


Fig. 1. CV of the electropolymerization of poly (4VP-co-Ani)

Figure 2 shows the CV obtained in a solution of 0.015M potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$) in 0.1 M KNO_3 solution of (a) copolymer modified (PME) and (b) bare pencil graphite lead (GPL). As can be seen, the PME has exhibited a relatively much faster kinetic of electron transfer as compared to the bare GPL electrode [10].

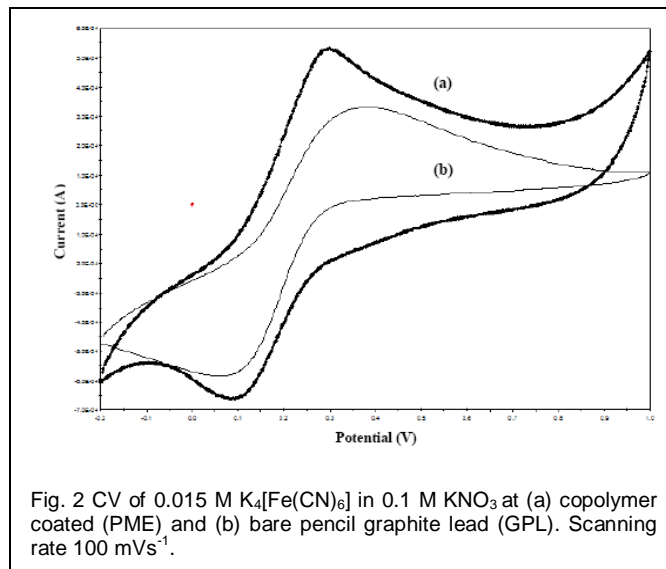


Fig. 2 CV of $0.015 \text{ M K}_4[\text{Fe}(\text{CN})_6]$ in 0.1 M KNO_3 at (a) copolymer coated (PME) and (b) bare pencil graphite lead (GPL). Scanning rate 100 mVs^{-1} .

3.2 Effect of pH on electrocopolymerization

Figure 3 shows the effects of different pH on the electrocopolymerization of poly(4VP-co-Ani). This study showed that the redox peak potentials were dependent on pH. The polymerization seems to favour low pH values, especially at pH 3.9 probably proton initiate radical formation in the monomers before polymerization takes place. The results were consistent with the fact that the pK_a value for pyridine groups of P4VP is 3.3. Thus the pyridine group actually deprotonates at this particular pH. Thus, pH 3.9 was chosen as the optimum pH for electrocopolymerization.

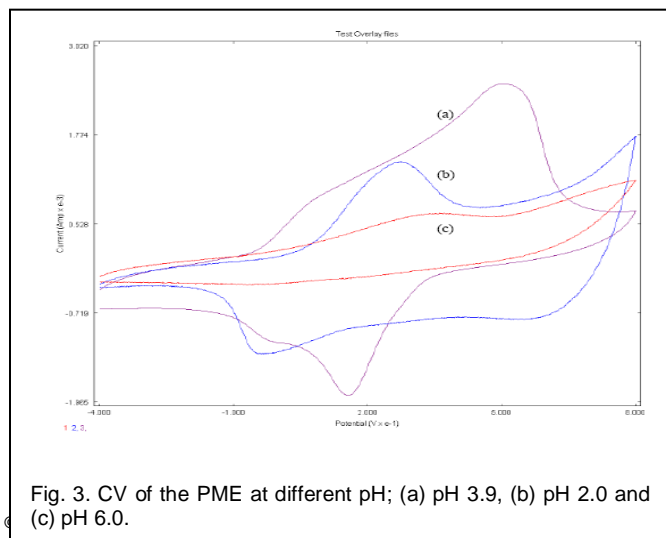


Fig. 3. CV of the PME at different pH; (a) pH 3.9, (b) pH 2.0 and (c) pH 6.0.

3.3 Stability test

To evaluate the electrochemical stability of the copolymer film, continuous sweeping at potential -0.2V to 1.0V at a scan rate of 100mVs⁻¹ was carried out (Figure 4) in a monomer free solution. After 400 cycles, the anodic and cathodic peak current dropped to around 9.54 % and 8.90 % respectively. The small percentage drop reveals a high environmental and redox stability of the copolymer film [11].

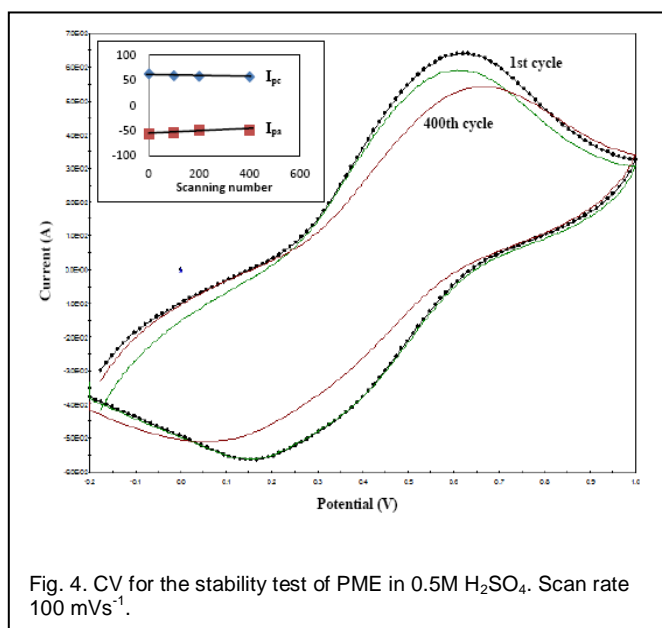


Fig. 4. CV for the stability test of PME in 0.5M H₂SO₄. Scan rate 100 mVs⁻¹.

3.4 FT-IR analysis

The FT-IR spectra of poly (4VP-co-Ani), P4VP and PANi are recorded in the range 400 - 4000 cm⁻¹ (Figure 5). The pyridine stretching seen at 1616 cm⁻¹ is the trait of 4VP. The absorption peak at 3409 cm⁻¹ is attributed to the N-H stretching vibrations from both 4VP and Ani. Vibrational band at 2915 cm⁻¹ is due to -CH₂ stretching while peak found at 1499 cm⁻¹ can be attributed to benzenoid C=C stretching vibration. Peaks observed from 1000 cm⁻¹ - 1350 cm⁻¹ correspond to in-plane bending mode of aromatic C-H bonds [12]. Peaks below 1000 cm⁻¹ are due to out of plane bending mode of C-H bonds. After immersion in 0.01 M Cd²⁺ the N-H stretching bands of the co-polymer at 3409 cm⁻¹ disappears while the intensity of the bands at 1499 cm⁻¹ become sharper.

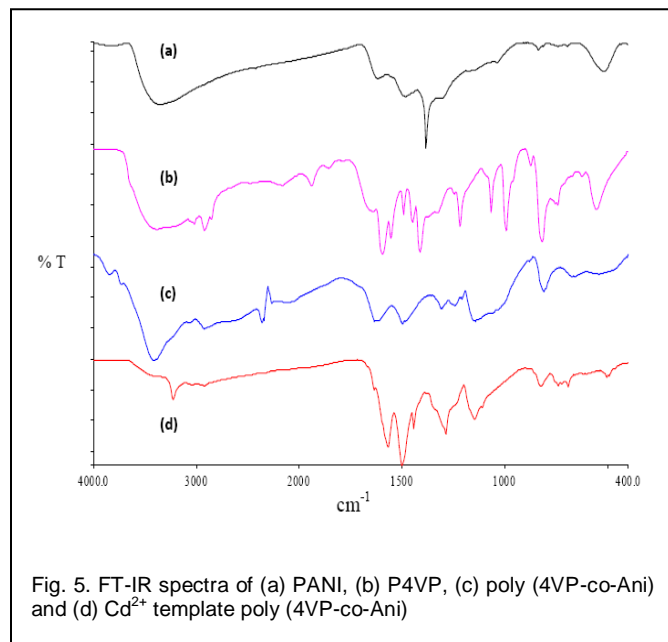


Fig. 5. FT-IR spectra of (a) PANI, (b) P4VP, (c) poly (4VP-co-Ani) and (d) Cd²⁺ template poly (4VP-co-Ani)

An expected schematic representation of poly (4VP-co-Ani) is shown in Figure 6.

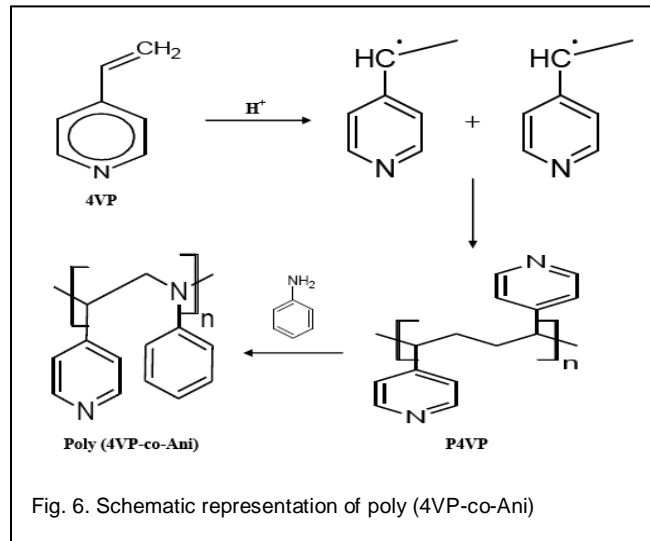


Fig. 6. Schematic representation of poly (4VP-co-Ani)

3.5 SEM morphological studies

Surface morphology of electropolymerized copolymer films was observed by SEM. Figure 7 shows the SEM images of the respective polymers. The differences observed between the homopolymer P4VP and PANi are obvious. However, the appearance of the copolymer tends to favour the morphology of PANi. Grain-like structures are observed on the copolymer surface before immersion while coral-like structures with small dendrites distributed

randomly throughout the copolymer are observed after immersion. Availability of mesoporous-like structure facilitates the formation of metal-copolymer complexes. This work has investigated on the possible fabrication of an ion selective electrode (ISE) making use of membrane prepared from such complexes, especially cadmium (Cd) complex. Also mesoporous structures normally characterise a good electrode as the electrode-solution interface is optimized [13]. The study of Cd-ISE is on-going and will be reported soon.

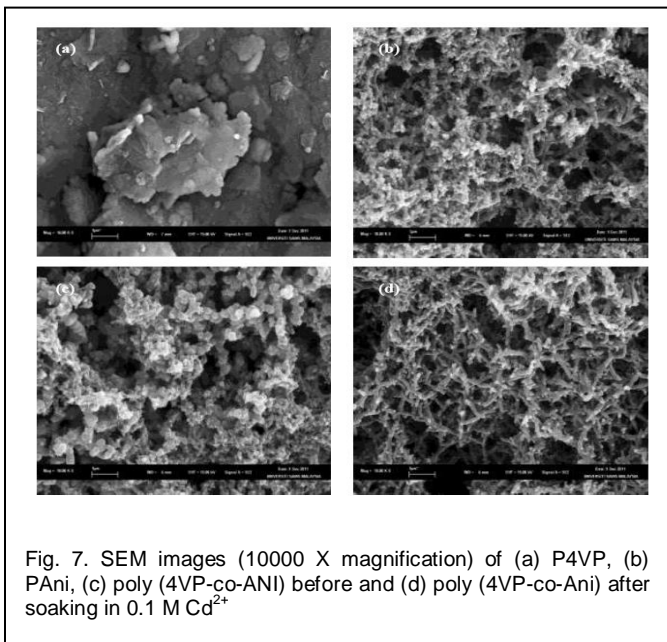


Fig. 7. SEM images (10000 X magnification) of (a) P4VP, (b) PANi, (c) poly (4VP-co-ANI) before and (d) poly (4VP-co-ANI) after soaking in 0.1 M Cd²⁺

4 CONCLUSION

Poly (4VP-co-Ani) was successfully deposited electrochemically onto a graphite lead electrode. The PME was proven to have high stability, good mesoporous structure and good electron transfer as compared to the GPL electrode. FT-IR analysis has also shown that the copolymer acquires the ability to incorporate cadmium ions in its polymeric chain. Thus, application of this copolymer in the field of sensor is promising.

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