ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

Electrocatalysis at copolymer of 3- Methylthiophene and 3- Hexylthiophene modified electrodes

By Beniam Tadesse

Advisor Dr. Teketel Yohannes

A Project Submitted To The School Of Graduate Studies In Partial Fulfillment Of The Requirements For The Degree Of Master Of Science In Chemistry

March, 2007

ACKNOWLEDGEMENT

I would like to express my gratitude to my advisor Dr. Teketel Yohannes for his valuable advise, helpful discussions, devoted support and guidance.

I would also acknowledge and express my thanks to Ato Assefa Sergawi, a PhD candidate, for sharing his expertise and helpful discussions.

I would like to express my thanks also to Dr.Shimelis Admassie, Dr. Yonas Chebude, and Dr. Wondimagen Mamo for their technical assistance and cooperation and to all my instructors at the department of chemistry.

My heartfelt appreciation and honor goes to my late father Ato Tadesse Abdissa and my mother W/r Shewaye Asfaw for the material assistance, moral support and everything.

Finally, I would like to express my thanks to Hormat Engineering Factory and The General Manager, Col. Asfawessen Tegene, for moral support and sponsoring my education.

CONTENTS

LIST OF FIGURES

Figure **Page**

ABSTRACT

The electrochemical polymerizations and characterization studies were made for the monomers 3-hexylthiophene (3HT) and 3-methylthiophene (3MT) with respect to Pt, GC and Au electrodes. The electrochemical properties of the corresponding polymers poly(3-hexylthiophene) (P3HT) , poly(3-methylthiophene) (P3MT) were also studied in a monomer free $LiClO_4$ - acetonitrile solutions. Copolymers were shown to be electrochemically synthesized from the monomers 3HT and 3MT and showed intermediate electrochemical properties between their corresponding homopolymers. The optimum copolymer ratio, polymerization potential and deposition time that are required to obtain the best electrocatalytic effect was also demonstrated using various redox species. The electrocatalytic effect of this copolymer was studied on selected inorganic and organic samples. It was found that poly(3HT-co-3MT) modified platinum electrode is highly selective and sensitive towards these redox species. The detection limits for poly(3HT-co-3MT) modified Pt electrode were also shown for these redox species.

Key words; *poly(3-hexylthiophene), poly(3-methylthiophene), poly(3HT-co-3MT), Electrochemical Polymerization, Electrocatalysis.*

1. INTRODUCTION

Polymers are large molecules or macromolecules produced by the union of many (10^2 -10^6) small repeating units called monomers. Many polymers are strong, elastic, plastic, tough, friction - resistant, and insulating [1].

Starting in 1970s new materials having high electrical conductivity became available. In 1974, the first polymer capable of conducting electricity, polyacetylene, was prepared by accident in Shirakawa group [2]. The subsequent discovery by Heeger and MacDiarmid [2] increased the conductivity to 12 orders of magnitude. An intensive search for other conducting polymers soon followed. The target was (and continues to be) a material, which could combine the processibility and environmental stability of a fully organic polymer with the useful electrical properties of a metal.

Copper has a conductivity of about $5x10^5$ S/cm and polystyrene has a value of $10x10^{-18}$ S/cm. Typically undoped conducting polymers have values comparable to those of other insulating polymers (10^{-12} S/cm), which on doping are increased to 10^{2} S/cm [3].

The main focus of the early research activity on conducting polymers was on their electrical conductivity. Neutral conjugated polymers are insulators or semiconductors. To make these polymers electrically conducting, one should introduce species, which are electron accepting (oxidizing agents) or electron donating (reducing agents). The oxidation and reduction reactions, which induce high conductivity, are termed, using the language of semiconductor physics, p-doping and n-doping, respectively. However, the process of doping in conducting polymers is different from that of semiconductors. In semiconductors doping involves replacing some of the atoms with atoms that have either more or less electrons while in conducting polymers the dopant molecules never replace any of the atoms of the polymer, rather they simply act as associates that accept or donate electrons. The doping process of conducting polymers can be represented by the following general scheme:

For an oxidation process

$$\text{Polymer} + \text{X} \rightleftharpoons \text{Polymer}^{n+} + \text{X}^{n-}$$

And for a reduction process

$$\text{Polymer} + \text{M} \rightleftharpoons \text{Polymer}^{n-} + \text{M}^{n+}$$

Where X is the oxidizing agent and M is the reducing agent. X^{n-} and M^{n+} are the dopant counter anion and cation, respectively. By appropriately adjusting the doping level, conductivity anywhere between that of the undoped (inslulating or semiconducting) and that of the fully doped (metallic) forms of the conjugated polymer may be obtained. The doping process may be achieved either electrochemically *via* application of a potential or chemically by using an oxidizing or a reducing agent. Oxidizing agents such as I_2, Br_2, Cl_2, AsF_5, $FeCl_3$ and $NOPF_6$, and reducing agents like Li, Na, and K have been used. p -type doping is more common and gives higher conductivity and a better stability. Polymer synthesis could be carried through chemical and electrochemical routes.

Electrochemical polymerization of conducting polymers is generally carried by (1) constant current (galvanostatic) (2) constant potential (potentiostatic) and (3) potential scanning (potentiodynamic). Standard electrochemical technique, use a three electrode electrochemical cell containing a working electrode, a counter electrode and a reference electrode. The commonly used working electrodes are gold, platinum, silver, glassy carbon and indium-tin oxide coated glass plates. Electrochemical synthesis can be used to prepare free standing homogeneous and self doped films [4].

Modification of the form, structure and property of a conducting polymer is mandatory to meet the specific requirements for different technological applications. The selection of the proper method of modification depends on both the desired property and the level at which the modification will occur.

Copolymerization is one of the methods of modification and result in copolymers with properties intermediate between the individual polymers. Many types of copolymers have been prepared by chemical or electrochemical polymerization from mixtures of different monomers [5]. The properties of the copolymers are determined by the structure ratio and sequence of the repeating units of the monomers in the copolymer. The various copolymers differ by mode of polymerization (chemical or electrochemical) by the structure of the obtained copolymer (random or block), and also by the conservation or not of a fully π conjugated system in the copolymer backbone. As to modification of electrodes, there are different approaches.

Although different approaches for electrode modification, including adsorption, covalent attachment, and coating the surface with thin polymeric films have been developed, improving, and developing of new approaches still remains an important research topic. Among the wide range of electrode modifiers, conducting polymer films such as polythiophene and polypyrrole, have acquired a wide popularity, since they are easy to generate at the electrode surface compared with other common chemical immobilization technique [6-7].

One of the most interesting properties of conducting polymers is their ability to catalyze some electrode reactions. A thin layer of a conducting polymer, deposited onto the surface of substrate electrode, is able to enhance the kinetics of electrode processes of some solution species. These electrocatalytic processes, proceeding at conducting polymer electrodes, present a fast growing area of investigation, which may yield many unexpected application in various fields of applied electrochemistry.

For electroanalytical purposes, electrocatalysis at chemically or electrochemically modified electrode are used to amplify the detection signal. It accelerates the heterogeneous electron transfer of the target analyte, which is slow at the same potential at a bare electrode, induced by an immobilized charge mediator i.e., catalyst. Slow electrode reactions of many important analytes require a potential greatly exceeding their formal redox potentials in order for the reactions to proceed at desirably high rates. The acceleration of such kinetically hindered electrode reactions by electrode - confined charge mediator permits the quantification of these analytes at less extreme potentials, because catalyzed electrode reactions usually occur near the formal potential of the mediator. By applying less extreme potentials, both detectability and selectivity can be improved significantly as compared with those obtained at non-modified electrodes.

In the present study, a stable film of poly(3- methylthiophene-co-3-hexylthiophene) was coated on platinum and/or glassy carbon electrodes by an electropolymerization of a mixture of 3-methylthiophene and 3-hexylthiophene. The stability of the copolymer film was explored and compared to similar system. Characterization of the synthesized film was done using various electroanalytical techniques. The new electrode modification gave better electrochemical performance for various redox systems.

2. LITRERATURE REVIEW

2.1 Conjugated polymers

Conjugated polymers having semiconductor and conductor properties become the most promising materials to be used in electrochromic devices [8], as catalysts [9], as sensors [10], as electrochemomechanical devices [11], as electrode modifiers [12], as photovoltic devices [13], and a corrosion protection [14], etc. Most of the known conducting polymers today were first synthesized chemically as insulating powder or film. The interest in organic conducting polymer increased when one was able to synthesize a polymer in its conductive state (doped form) using electrochemical technique. Furthermore, the possibility of modifying the polymers through side chains and copolymerization has opened up new options for use as active components in photoelectrochemical [15-17] and electrochemical devices [18-21].

Electronic Conduction in conjugated polymers takes place by the facile migration of electrons through the molecular and solid – state structure. This process occurs because large molecules that have a delocalized unsaturated, electronic structure (many double or triple bonds in communication with each other) generate properties that are not found in simple molecules. The electrical properties are different because the electronic structures are different.

Consider a simple diatomic molecule derived from two identical atoms that have only one electron available for bonding. The energy levels of these two electrons before and after the formation of the bond are shown in Fig.1. Bond formation involves the generation of two new energy levels- the bonding level, occupied by the two electrons and unoccupied anti- bonding level. This higher level can be populated temporarily if bonding- level electrons acquire sufficient energy from heat or light to make the transition.

Bond formation in more complex molecules follows the same principle. As each bond is formed an additional bonding and antibonding level is added to the over all electronic structure. Thus, the larger the number of atoms that are linked together in a molecule or ultrastructure, the greater will be the number of bonding and anti bonding orbitals. In a higher – polymer molecule, or a solid – state system, thousands or millions of atoms may be involved and the number of molecular orbitals becomes correspondingly large.

Beyond a certain size of "molecule" the bonding orbitals become crowded together on the energy scale to form a set of closely spaced energy levels. This set is known as a bonding band or, in physics or solid – state terminology, as the valence band, The term "band " is used because the energy levels are so closely spaced that for all practical purposes they form an energy continuum within which electrons can exchange places and are free to wander throughout the material. A similar crowding and band formation occurs with the anti bonding orbitals, which are described as the conduction band. The two bands are usually separated by an energy gap known as the band gap.

The height of the band gap and the degree to which the valence band is filled with electrons determine if the material is an insulator, a semiconductor, a metal, or a "semimetal." The possibilities are shown in Fig. 2

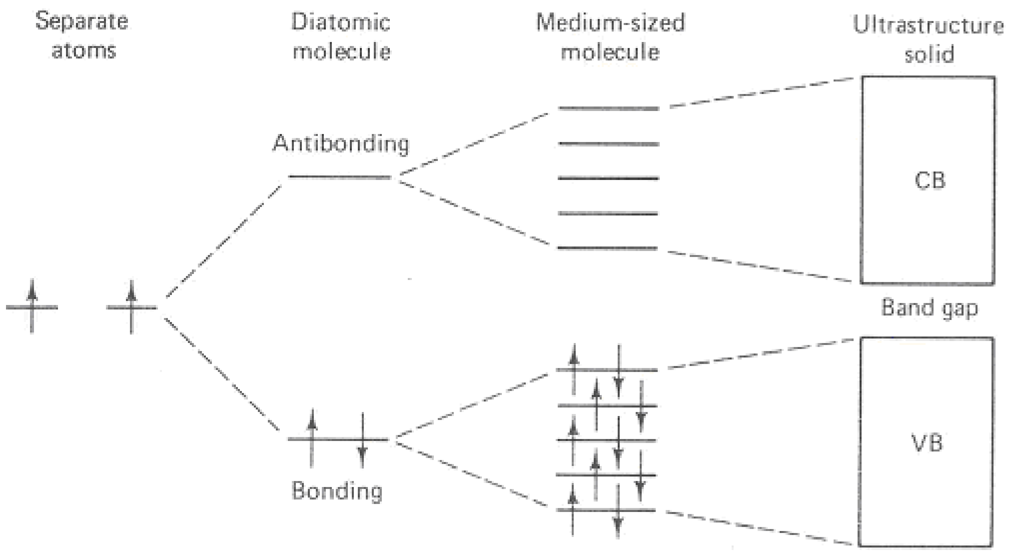


Figure 1. Progression from atomic orbitals in two isolated atoms, through the formation of a bonding orbital in a simple diatomic molecule, and the generation of several bonding orbitals in a medium-sized molecule, to a the coalescence orbital energy levels into bands.

It should be noted that although the electrons in a band are free to wander within the energy confines of the band, there would be no overall movement of electrons unless they have access to unoccupied energy levels and unless they can function as unpaired electrons or some derivative state.

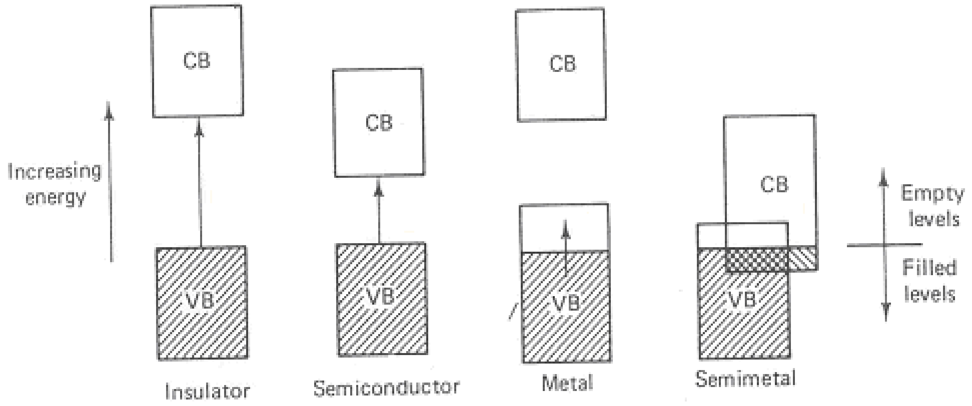
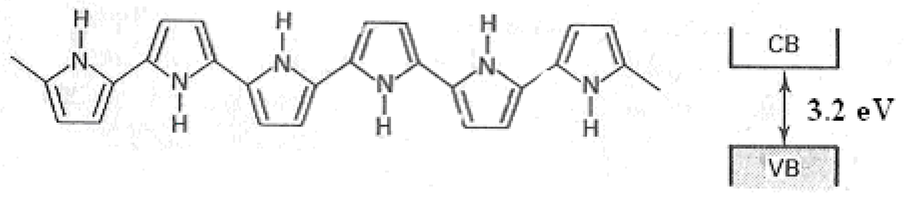


Figure 2. Simplified representation of the band structure found in an insulator, a semiconductor, a metal, and a semimetal. The shaded boxes indicate regions filled with electrons. Unshaded areas are regions that could accept electrons promoted from the filled levels.

2.2 Mechanism of the doping processes in conducting polymers.

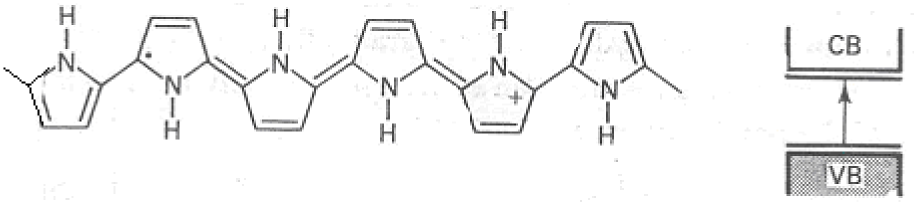
The doping process of conducting polymers is quite different from those of classic, inorganic semiconductors. The basic difference lies in the fact that while semiconductors have a rigid lattice and the evolution of their electronic structure upon doping is well described by band models, polymers consist of flexible chains which, in turn, favor localized chain deformations. Therefore, while in inorganic semiconductors the doping processes involve the introduction of impurities into the crystal lattice with the formation of intergap energy levels which are either close to the conduction band (for donor impurities) or to the valance band (for acceptor impurities), in the case of conducting polymers the processes are quite different. The impurities or doping agents do not become part of the structure but, rather, are inserted within the polymer chain and can be easily removed by applying an apposite electrical driving force. Consequently and most significantly the doping processes of conducting polymers are reversible and may be monitored by an external polarization, which may be promoted and controlled in suitable electrochemical cells.

In an attempt to illustrate in a simple way the general concept of the doping process in polymers, let us consider the p-doping (oxidation) process of polypyrrole. In the undoped state, polypyrrole is poor electronic conductor with an energy gap of 3.2 eV between the conduction band (CB) and the valance band (VB) (scheme (1)).



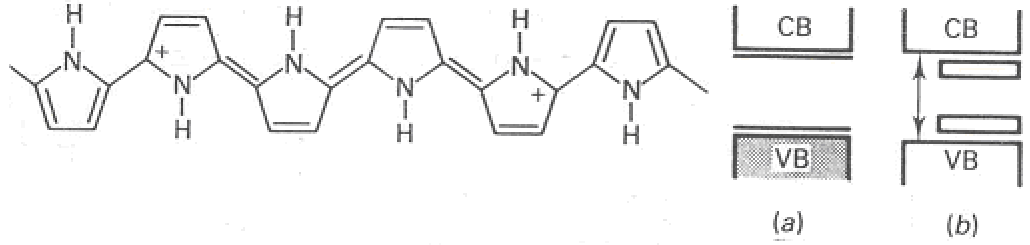
Scheme 1: Structure of polypyrrole in an undoped state.

The initial removal of electrons (following the oxidation, p-doping process) leads to the formation of a positive charge localized in the polymer chain (radical cation, accompanied by a lattice distortion which is associated with a relaxation of the aromatic structural geometry of the polymer chain towards a quinoid form. This form extends over four pyrrolic rings (scheme (2)).



Scheme 2: Formation of a polaron in polypyrrole upon doping.

This radical cation (which is partially delocalized over the polymer segment and is stabilized by polarizing the surrounding medium) is called a polaron. It is energetically described as a half-filled polaron level situated at approximately 0.5 eV from the band edges. When further electrons are removed from the chain, dications are formed, namely two positive charges localized in the same “defect site”. This defect has been referred as a bipolaron, defined as a pair of like charges associated with a strong localized lattice distortion, which again extends over four pyrrolic rings.



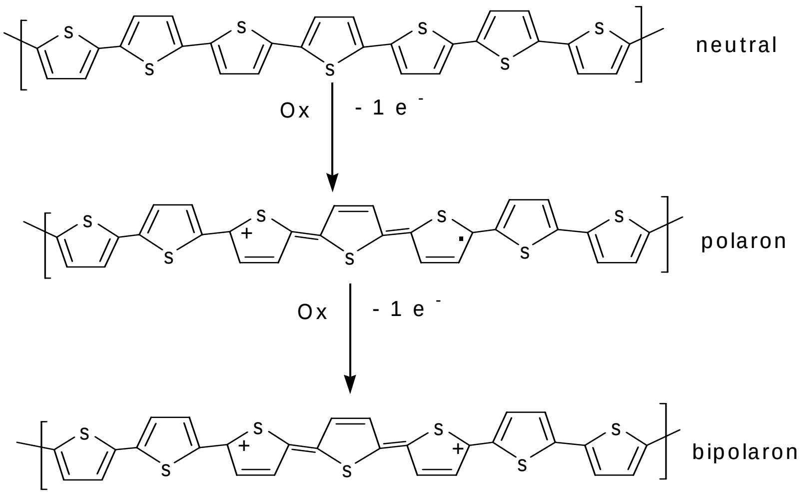
Scheme 3: Formation of a bipolaron in polpyrrole.

The bipolorans are energetically described as spinless bipolaron levels (scheme (3)) which are empty and which, at high doping levels, may overlap with the formation of bipolaronic bands (scheme 3b). Finally, for polymers with band gap, E_g values smaller than that of polypyrrole-such as polythiophene – the bipolaronic bands may also overlap with the valence and conduction bands, thus approaching the metallic regime.

In the doped state the conjugated polymers possess a very high electronic conductivity, up to 100 or even 1000 S/cm. The conventional theory attributes it to a high mobility of single charged polarons whose theoretical calculations of the electronic structure of the polymer lead to the conclusion that there is a gain in energy if two polarons form a bipolaron [22].

In the same way doping of poly(3-alkylthiophenes) (P3ATs) is achieved by either chemical oxidation with oxidants such as I_2 or $FeCl_3$, or by electrochemical oxidation of thin polymer films in the presence of an electrolyte such as tetraethylammonium tetrafluoroborate (TEATFB) or lithium perchlorate ($LiClO_4$). Apart from the drastic increase in electrical conductivity, other more important property changes have also been observed on doping. Doping greatly affects the flexibility of polymer chains. The barrier to rotation of the repeating units along the polythiophene chain has been found to increase by 10 to 100 times when doped. This results in an increase in stiffness, which renders the doped segments more planar and extended than the undoped portions. This can be translated into an increase in volume on doping. Based on this idea a class of conjugated materials prepared by cross-linking P3ATs or copolymers of P3ATs have been produced and investigated [23]. The structural changes that occur in conjugated polymer up on oxidation are illustrated in scheme (4) for polythiophene [24].

One of the major problems with conducting P3ATs is their thermal unstability that is closely related to the ease of undoping. At 100^0C, the conductivity of P3AT thin films is markedly decreased within minutes [25]. The rate of thermal undoping is controlled by the steric interaction between alkyl chains and dopants, which increases with enhanced movements of the side chains at high temperatures. One way to prepare materials, which are more thermally stable in terms of undoping, is to decrease the interaction between the side chains and dopants.



Scheme 4: Structural changes in polythiophene upon doping with a suitable oxidant.

2.3. Electrochemical Synthesis

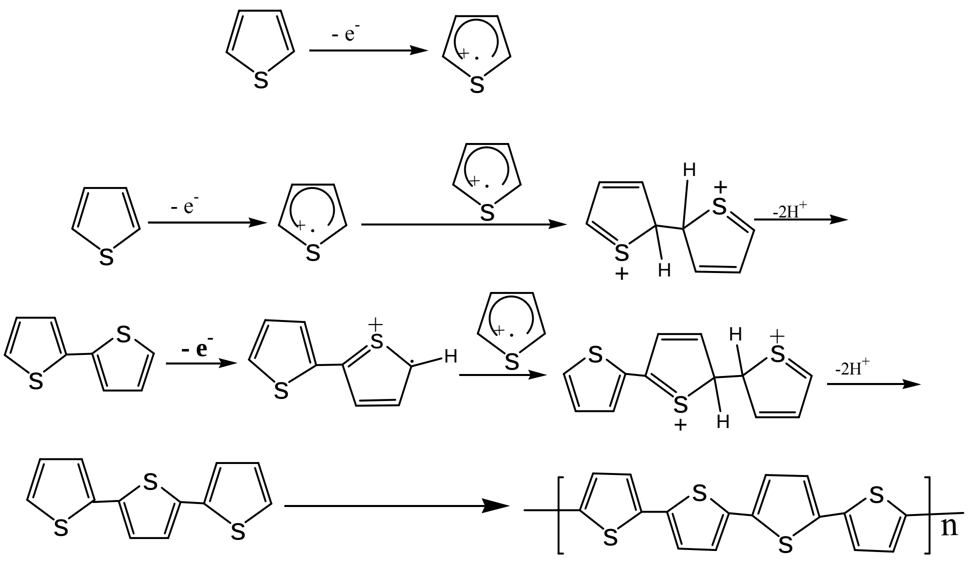
Electrochemical polymerization has been used to synthesise substituted polythiophenes from their monomers using both cathodic and anodic routes. The anodic route is the most convenient and widely used. The electrochemical polymerization may be carried out with a classical three-electrode electrochemical cell, consisting of a working electrode, a reference electrode, and a counter electrode, in a solution containing the monomer and a supporting electrolyte. The nature of the working electrode is critical for the preparation of these films and depends on the type of polymer to be synthesized and on the electrolytic medium. Since the films are produced by an oxidative or reductive process, it is important that the electrode does not oxidize or reduce concurrently with the monomer. Working electrodes such as gold, platinum, and transparent indium doped tin-oxide (ITO) coated glass can be used. The ITO-coated glass electrode is particularly suitable for spectroscopic studies.

For the synthesis, potentiostatic (fixed potential), galvanostatic (fixed current), or potentiodynamic (varying potential) methods can be used. A preliminary study is necessary in order to find a solvent in which the monomer is soluble and to determine the potential at which the polymerization may be performed. Very often, cyclic votammetry is a good tool to determine the best polymerization conditions. The polymerization potential should not be too low, since this causes the polymerization process to be very slow and to form soluble oligomers, nor too high in order to avoid a material having lower conductivity due to overoxidation. In general, the polymerization potential must be chosen not too far (±0.1 V) from the corresponding oxidation peak potential of the monomer. The electrodeposition potential is specific for any given electropolymerisation process. As potential needed for monomer oxidation is always higher than the charging of the existing polymer, both polymerization and doping processes may be driven by a single electrochemical operation which, starting from the monomer, first forms the polymeric chain and then induces its oxidation and deposition on the working electrode. The polymeric film coating the working electrode can be studied afterwards in a monomer free solution.

The general mechanism of the electrochemical polymerization reaction is as shown in scheme 5. The first step consists of the irreversible electrochemical oxidation of the neutral monomer to form delocalised radical cations. The radical cations are unstable and reactive. Since the electron transfer reaction is much faster than the diffusion of the monomer from the bulk solution, a high concentration of radicals is continuously maintained at the electrode/solution interface. The next step in the polymerization sequence involves the radical cation-radical cation coupling with dimer formation followed by a deprotonation and rearomatisation. As the dimer is more easily oxidized than the monomer, under the given experimental conditions it is immediately reoxidised to the cation. Chain growth proceeds between the radical cations of the monomer and those of the continuously forming oligomers. This in turn is followed by another proton elimination and oxidation of the propagated oligomeric unit to a cation. For the polymerization to continue, radical cations must be present in the vicinity of the working electrode and therefore, the electrode potential should be kept at the oxidation potential of the monomer. In the terminology of electrochemical reaction mechanisms, the electrochemical polymerization proceeds through successive electrochemical and chemical steps according to a general $E(CE)_n$ scheme, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface.

Once deposited as conductive films, the polymers can be repeatedly cycled from the undoped to the doped forms (and *vice versa*) in an electrochemical cell similar to that used for the electropolymerisation reactions in the absence of the monomer. The undoping-doping process involves transport of the counter ions from the electrolyte solution into the polymer matrix (between chains) during charging and out of the polymer matrix during discharging to neutralize the electronic charge on the polymer chain.

Although electrochemical synthesis gives rise to cross - linked, insoluble materials that are not dense or of high quality, it is widely used because of the following advantages over chemical synthesis. (a) The polymeric materials, directly grafted onto the electrode surface is produced in one step. (b) There is no need for a catalyst; therefore, the electrodeposited polymer is pure. (c) By controlling the amount of charge supplied, the thickness of the polymer film may be controlled from a few angstroms to many micrometers. (d) By changing the nature of the counter ions in solution, the electrical and physicochemical properties of the polymer may be changed for a particular purpose (e) There is the possibility of performing *in situ* characterization of the growth process or of the polymer by electrochemical and/or spectroscopic techniques.



Scheme5. Mechanism of electropolymerization of thiophene.

2.4 Copolymers

A copolymer is a polymer made from two or more different monomers. Many commercial synthetic polymers are copolymers. It should be noted that the sequence of monomer units along a copolymer chain can vary according to the method and mechanism of synthesis. Three different types of sequencing arrangments are commonly found.

2.4.1 Random copolymers:- In random copolymers no definite sequence of monomer units exists. A copolymer of monomers A and B might be depicted by the arrangement shown in scheme 6.

Scheme 6: - A - B - B - B - A - A - B - A - A - A - A - B - A - B - B - B -

2.4.2 Regular copolymers. As the name implies, regular copolymers contain a regular alternating sequence of two monomer units (scheme 7).

Scheme 7: - A - B - A - B - A - B - A - B –

Olefin polymerization that takes place through ionic- type mechanisms can yield copolymers of this type. Again, the properties of the copolymer usually differ markedly from those of the two related homopolymers.

2.4.3 Block copolymers:- Block copolymers contain a block of one monomer connected to a block of another, a illustrated in scheme 8.

Scheme 8: - A - A - A - A - A - A - A - A - A - B - B - B - B - B - B – B

Block copolymers are usually formed by ionic polymerization process unlike other copolymers they retain many of the physical characteristics of the two homopolymers.

2.5 Electrocatalysis at conducting polymer electrodes

At conducting polymer-modified electrodes, at least three processes should be considered, taking place during electrocatalytic conversion of solution species. One of them is a heterogeneous electron transfer between the electrode and a conducting polymer layer, and electron transfer within the polymer film. As usual, this process is accompanied by the movement of charge compensating anions and solvent molecules within the conducting polymer film, and possible conformational changes of polymer structure as well. The rate of this process is determined by many factors. Among these, electric conductivity of a polymer layer, electron self-exchange rate between the chains and/or clusters of polymer, and anion movement within polymer film seem to be of great importance. The second process is the diffusion of solution species to the reaction zone, where the electrocatalytic conversion occurs. As compared to simple electrode reactions, this process can be more complicated in cases where the electrocatalytic conversion occurs within the polymer film. Then, the diffusion of species within the film, as well as the possible electrostatic interaction of this species with the polymer film should be taken into account. Last, a chemical (heterogeneous) reaction taken place between solution species and conducting polymer. As a result of these complex processes, the kinetic behavior and voltammetric responses are difficult to interpret, and a great deal of attention has been paid to consider some simplified models.

From both theoretical and practical points of view, the question on the location of electro catalytic process seem to be of primary interest. If the charge transfer within the layer of conducting polymer proceeds much faster than the mass transfer of reacting species and their electrochemical conversion, the electrocatalytic process should proceed at the outer conducting polymer/solution interface. In an opposite case, if the mass transfer and electrochemical reaction proceed faster than the electron transfer in conducting polymer, an electrocatalytic process occurs at the inner substrate electrode/conducting polymer interface, assuming that the permeability of a porous conducting polymer layer is sufficiently high to penetrate the reacting species and solution ions. At last, if both the above processes occur at a comparable rate, the electrocatalytic process is located within the conducting polymer layer. The depth of the reaction zone within the conducting polymer layer will be determined in this case by the balance between charge and mass transfer, and the rate of electrocatalytic conversion as well. The problem on the location of electro catalytic process is often considered as the question on either metal-like (electrocatalysis at conducting polymer/solution interface), or semiconductor - like (electrocatalysis either within the polymer layer, or at inner substrate electrode/ conducting polymer interface) behavior, or in other words, on the chemical catalysis *versus* redox catalysis, respectively.

3. EXPERIMENTAL SECTION

3.1. Solution Preparation

0.1 M Lithium perchlorate ($LiClO_4$) in acetonitrile (Riedel-Dehaen) was used as a supporting electrolyte. 0.25 M of monomers 3-hexylthiophene (Aldrich), 3-methylthiophene (Aldrich) dissolved in 0.1 M $LiClO_4$ - acetonitrile solutions were used in the electrochemical polymerization. 1 M phosphoric acid (H_3PO_4) (Riedel-Dehaen) and 0.1M sodium hydroxide (NaOH) (BDH) were used for preparing the approprate pH of the phosphate buffer solutions (mixture of disodium orthophosphate

($Na_2HPO_4.12H_2O$) (BDH) and sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$) (BDH)), and 1M potassium nitrate (KNO_3) (BDH), were used as supporting electrolytes during the electrochemical characterization of the electrocatalytic effect of the polymers and copolymers formed on the working electrode. The analytes used in the aqueous system were potassium ferricyanide ($K_3Fe(CN)_6$) (BDH), catechol ($C_6H_4(OH)_2$) (Aldrich) and hydroquinone ($C_6H_4(OH)_2$) (May and Baker Ltd).

3.2. Preparation of electrodes

3.2.1. Reference Electrodes

The reference electrode used in organic solutions was quasi Ag/AgCl reference electrode. It was prepared by applying a potential of 4.60 V from a dc source between silver and a platinum wire immersed in a saturated potassium chloride solution. In aqueous solutions commercial standard Ag/AgCl reference electrode was used.

3.2.2. Counter Electrodes

Platinum foil in organic solutions and Pt wire in aqueous solutions were used as counter electrodes. These electrodes were cleaned using a blue flame from Bunsen burner.

3.2.3. Working Electrodes

Unmodified (bare electrodes) and modified platinum disc electrodes in the study of monomers and polymers in organic solutions were used. The unmodified electrodes were platinum disc (2 mm diameter), gold disc electrode (2 mm diameter), glassy carbon (GC) disc electrode (3 mm diameter), from CH Instruments were used. The working electrodes were polished with alumina powder to a mirror finish in every experiment.

The working electrodes in the electrocatalytic studies were bare platinum disc or platinum disc electrode modified with copolymers of 3-methylthiophene and 3-hexylthiophene and homopolymers poly(3-methylthiophene), and poly(3-hexylthiophene).

After electrochemical deposition of the polymer on the electrode surface it was removed from the monomer solution and rinsed with acetonitrile and deionized water successively. The electrode was then dipped in to 0.1 M aqueous phosphate buffer solution (pH = 0.5) for hydroquinone/catechol detection.

3.3 Experimental Setups and Procedure

All the electrochemical polymerization and electrochemical characterizations were carried in a three-electrode one-compartment electrochemical cell. An electrochemical analyzer (BAS CV-50W) was used to run all electrochemical experiments. The pH measurements were carried using pH/ION meter level 2. All potentials are reported *versus* Ag/AgCl reference electrode. Before each experiment was carried the solutions were purged with a stream of argon and blankated with argon throughout the experiment.

Before the electrochemical polymerizations and characterizations the appropriate working potential window was selected using the supporting electrolyte solution. Then the electrochemical behavior of the monomers, homopolymers and copolymers were studied. Finally the electrocatalytic behavior of the polymers and copolymers were studied on selected inorganic and organic analyates.

4. RESULTS AND DISCUSSION

4.1. Electrochemical Studies

The appropriate potential windows of the supporting electrolyte (0.1 M $LiClO_4$ - acetonitrile) solution were first determined before the electrochemical polymerization and characterization were carried out. It was found that there were no interfering electrochemical reactions with in the potential ranges where the monomers and polymers were electrochemically studied.

The electrochemical behavior of the monomers 3-hexylthiophene (3HT) and 3-methylthiophene (3MT) were examined using cyclic voltammetry within the potential window previously determined. The cyclic voltammograms for the two monomers at various electrodes are depicted in Fig. 3 and 4.

.

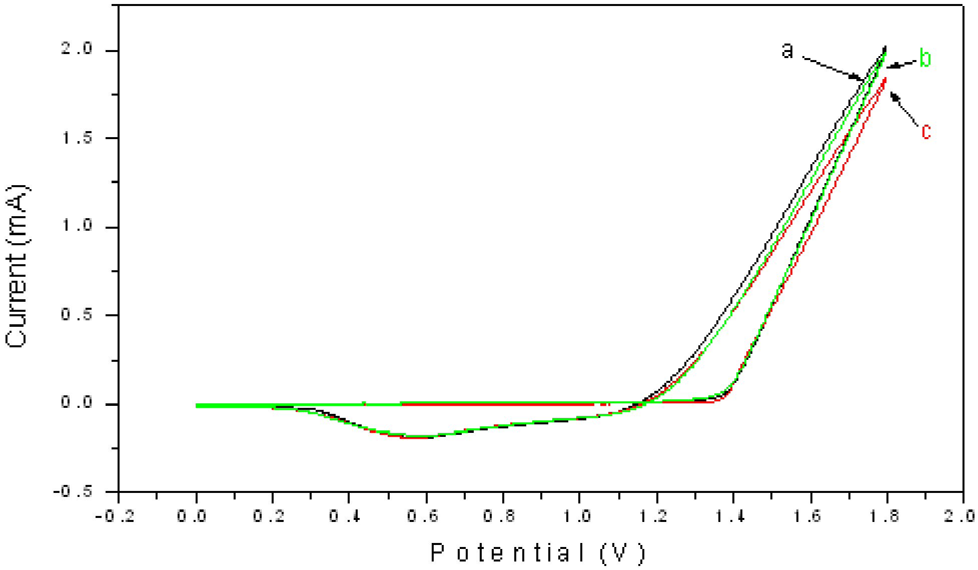


Figure 3. Cyclic voltammogram for the monomer 0.25 M 3HT in 0.1 M $LiClO_4$ - acetonitrile solution at a) Au b) GC c) Pt at a scan rate of 50mV/s

As can be seen from Fig 3. the first two segment for 3HT was run between the potential window of 0 V and 1.8 V using cyclic voltammetry at the three electrodes. The onset oxidation potential of 3HT is nearly the same for Pt, Au and glassy carbon electrodes. The different in the amount of current obtained is most probably attributed to the difference in polymer thickness at the respective electrodes.

Similarly in the case of 3MT (Fig. 4) no significant differences in oxidation onset potentials of the monomer were observed at the various electrodes. When the onset oxidation potentials of the two monomers are compared no significant difference was seen. This is clearly observed when using Pt electrode as shown in Fig. 5.

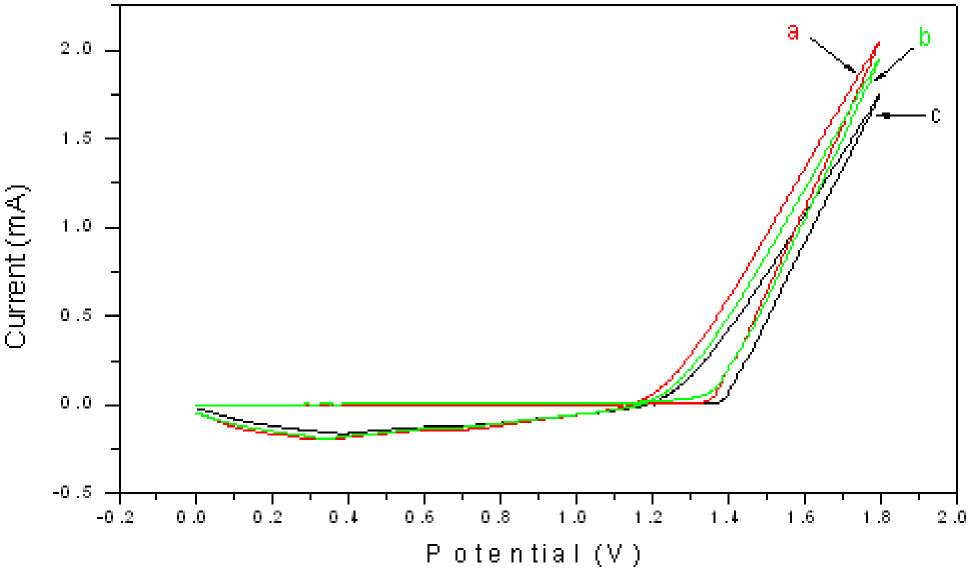


Figure 4. Cyclic voltammogram for the monomer 0.25 M 3MT in 0.1 M $LiClO_4$ - acetonitrile solution at a) Pt b) GC c) Au at a scan rate of 50 mV/s.

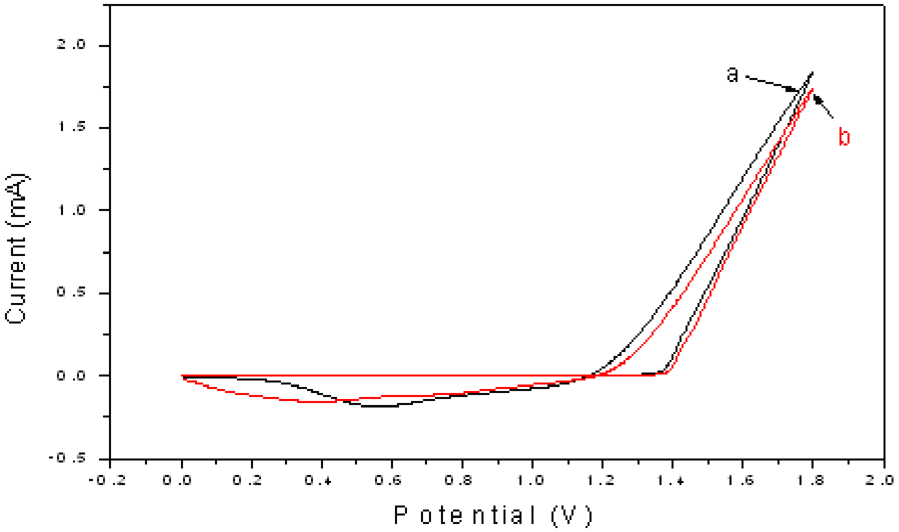
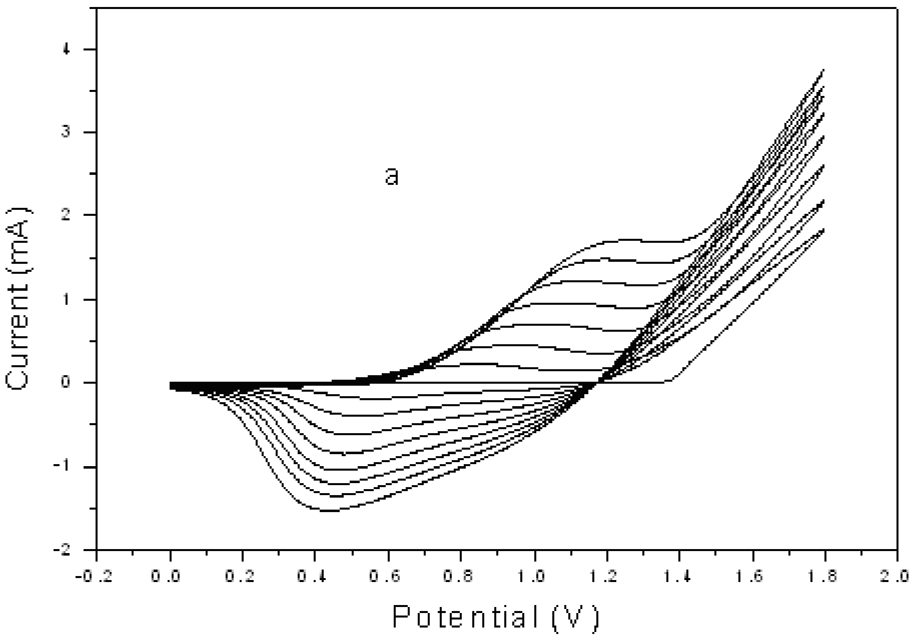
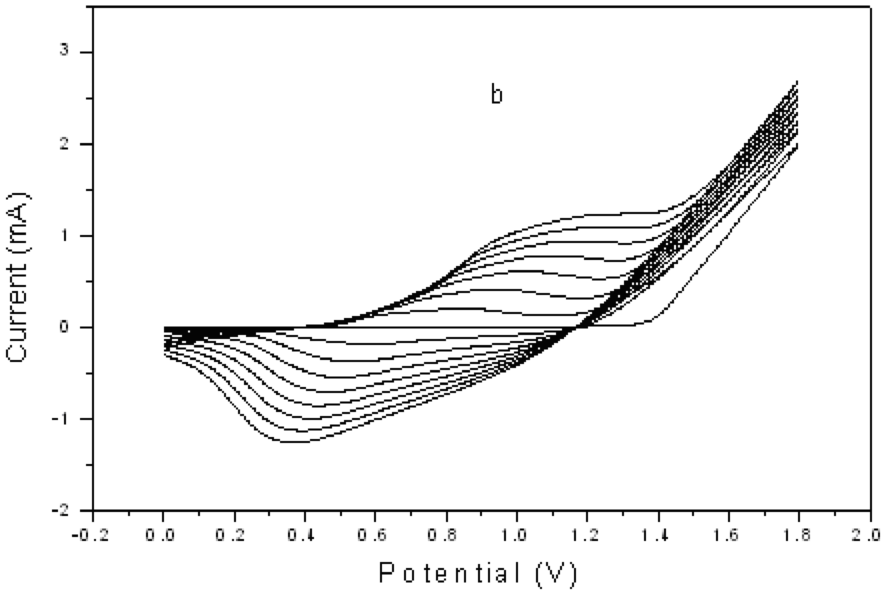


Figure 5. Cyclic voltammogram for the monomer 0.25 M 3MT and 3HT in 0.1 M $LiClO_4$ -acetonitrile solution (a) 3HT (b) 3MT at Pt electrode at a scan rate of 50 mV/s.

After having the onset oxidation potentials of each monomer, the homopolymers of both 3HT and 3MT were produced by sweeping the potential from 0 V to 1.80 V. To see the effect of the electrodes on the oxidation potentials of the homopolymers the redox characteristics of the polymers were examined on Pt, Au, GC electrodes (Fig. 6 and 8) and in a monomer free electrolyte solution (Fig. 7 and 9)


a
Current (mA)
4
3
2
1
0
-1
-2
Potential (V)
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0


b
Current (mA)
3
2
1
0
-1
-2
Potential (V)
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

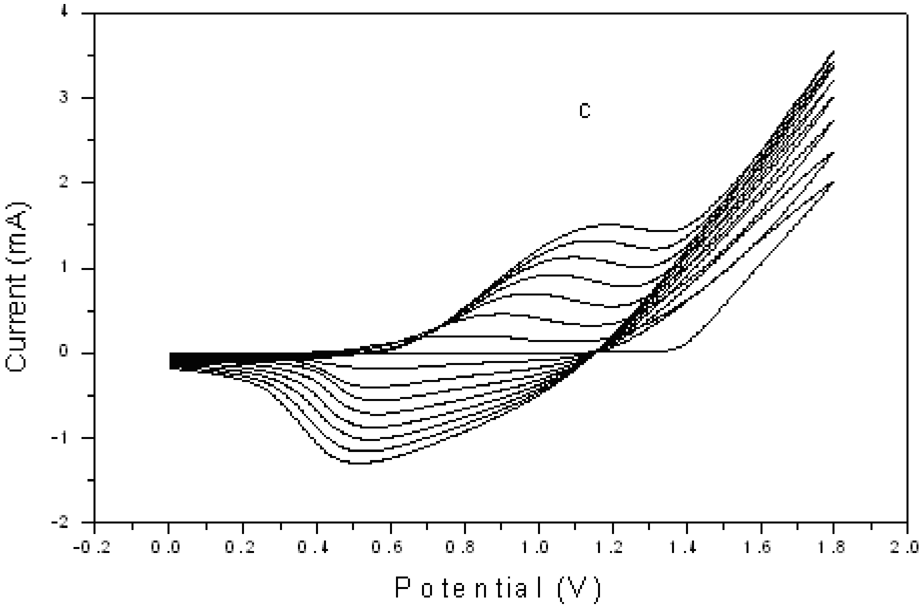


Figure 6. Cyclic voltammograms of polymerizations of 0.25 M 3HT in 0.1 M $LiClO_4$ - acetonitrile solution at a) Pt b) GC c) Au working electrodes at a scan rate of 50 mV/s.

As it can be seen from Fig. 6 and Fig. 8, an increase in oxidation peak current at the three electrode was seen for both monomers which is mainly because of a film growth after each cycle on each electrode. In addition, for all electrodes the oxidation onset potential for the first scan was higher than for the second and for higher scans. It is known that oligomers are oxidized at lower potentials than their corresponding monomers.

When the redox behavior of both P3HT and P3MT were examined in a monomer free solution (Fig. 7and 9) a slight difference in the oxidation peak potentials is observed. The difference in the oxidation peak current is mainly attributed to the difference in the amount of adsorption of P3HT and P3MT film on the electrode surfaces.

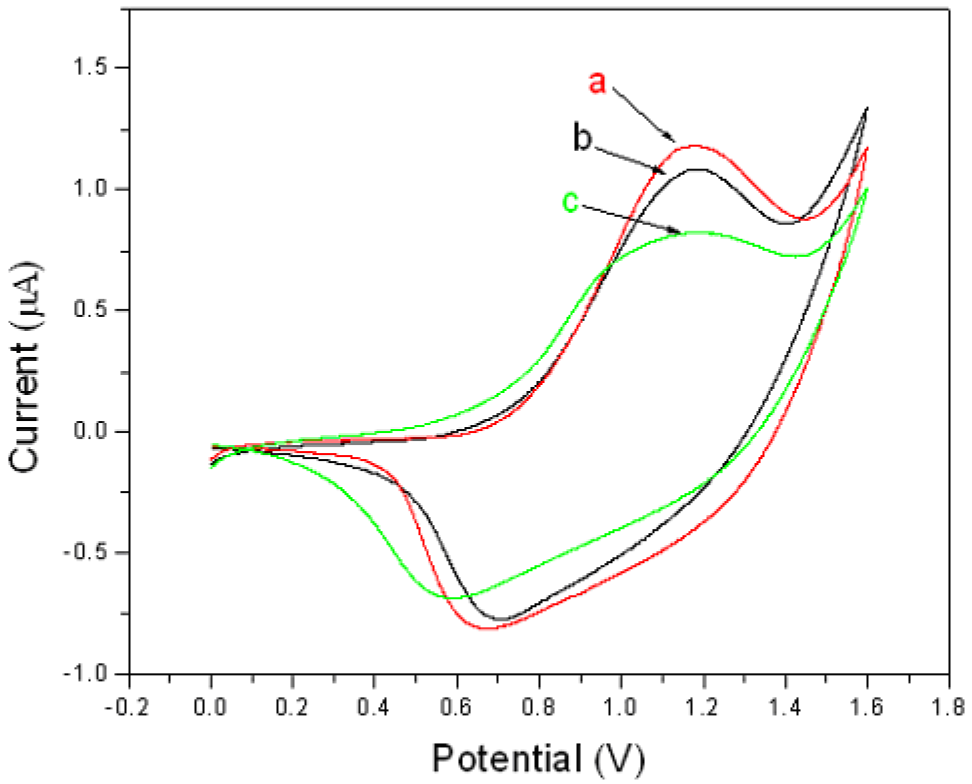
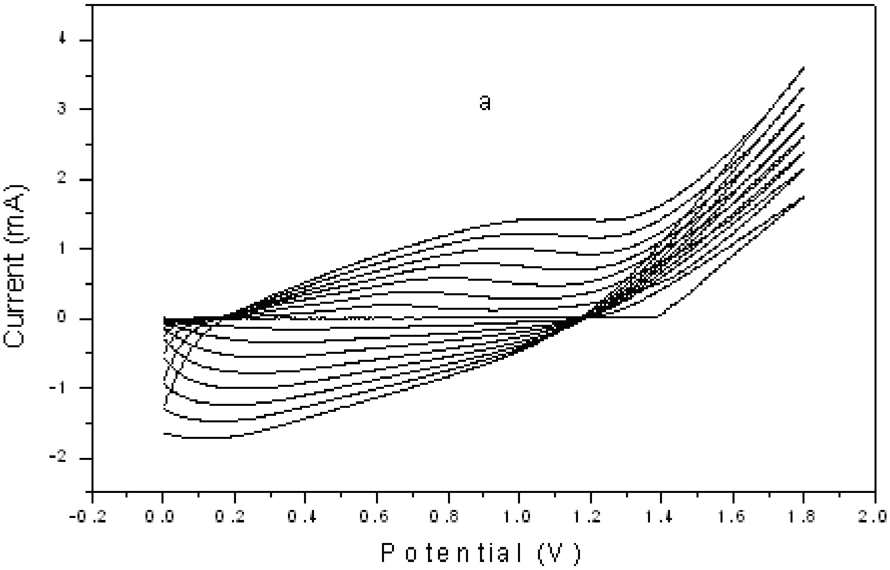
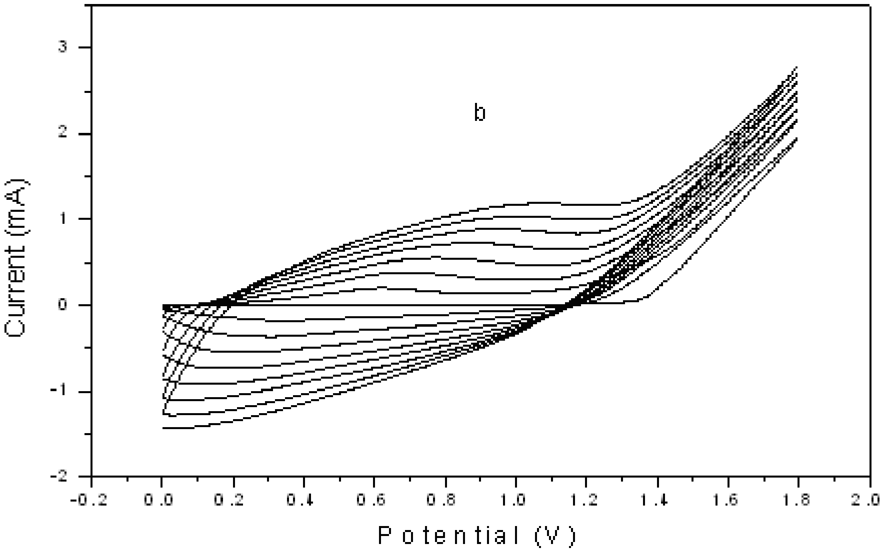


Figure 7. Cyclic voltammogram of P3HT in monomer free 0.1 M $LiClO_4$ - acetonitrile solution, polymerized by scanning 0.25 M 3HT at a) Pt b) Au c) GC working electrodes, at a scan rate of 25 mV/s.

When the cyclic voltammogram of both P3HT and P3MT was examined during the polymer growth process, P3MT covers broader oxidation potential range, which is not the case for P3HT, where the corresponding voltammograms of the electrochemical polymerizations showed relatively sharper oxidation. This shows that P3MT is more conductive in wide range of potentials than P3HT in its oxidized form.


a
Current (mA)
4
3
2
1
0
-1
-2
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Potential (V)


b
Current (mA)
3
2
1
0
-1
-2
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Potential (V)

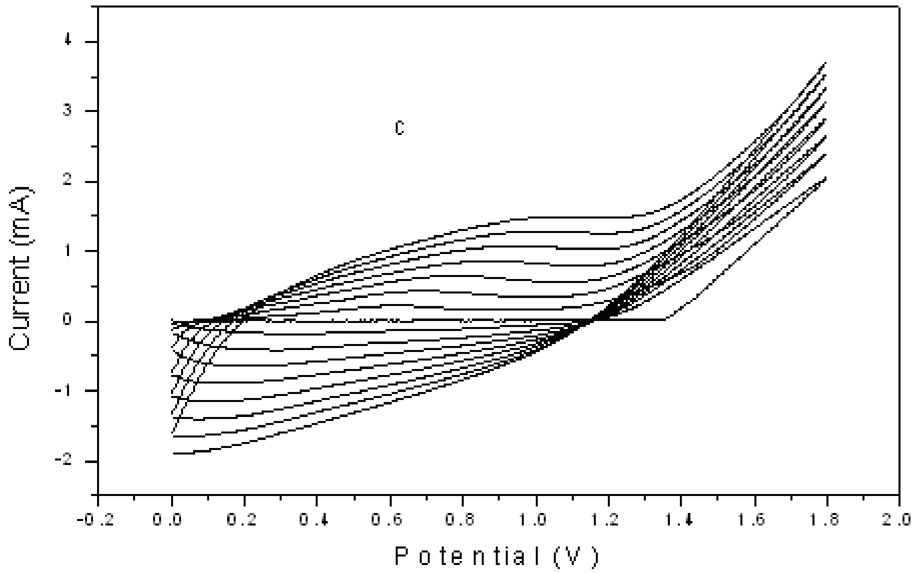


Figure 8. Cyclic voltammograms of the polymerizations of 0.25 M 3MT in 0.1 M $LiClO_4$ - acetonitrile solution at a) Pt b) GC c) Au working electrodes at a scan rate of 50 mV/s.

The redox behaviors of the two homopolymers were examined at a platinum electrode in Fig.10. As it can be seen the oxidation peak potential of P3MT is higher than that of P3HT.

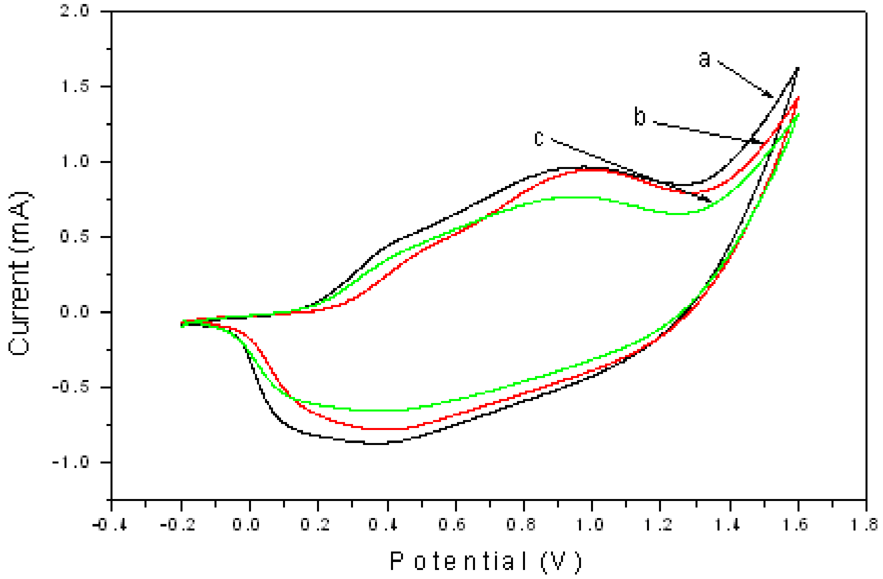


Figure 9. Cyclic voltammogram of P3MT in monomer free 0.1 M $LiClO_4$ - acetonitrile solution polymerized by scanning 0.25 M 3MT at a) Au b) Pt c) GC working electrodes, at a scan rate of 25 mV/s.

4.1.1 A Copolymer from 3-Hexylthiophene and 3-Methylthiophene

To determine whether a copolymer is formed from these two monomers, a 1:1 mixture of these two monomers were taken and electropolymerized at Pt-electrode. The characteristics of the polymer obtained as a result of mixing the two monomers was examined in monomer free solution (Fig. 10) in comparison to the two homopolymers.

As shown in Fig. 10, the oxidation peak potential of the polymer which is electropolymerized from the two monomer mixture, is at the intermediate position between the two hompolymers. This indicates that a new copolymer of 3HT and 3MT is formed.

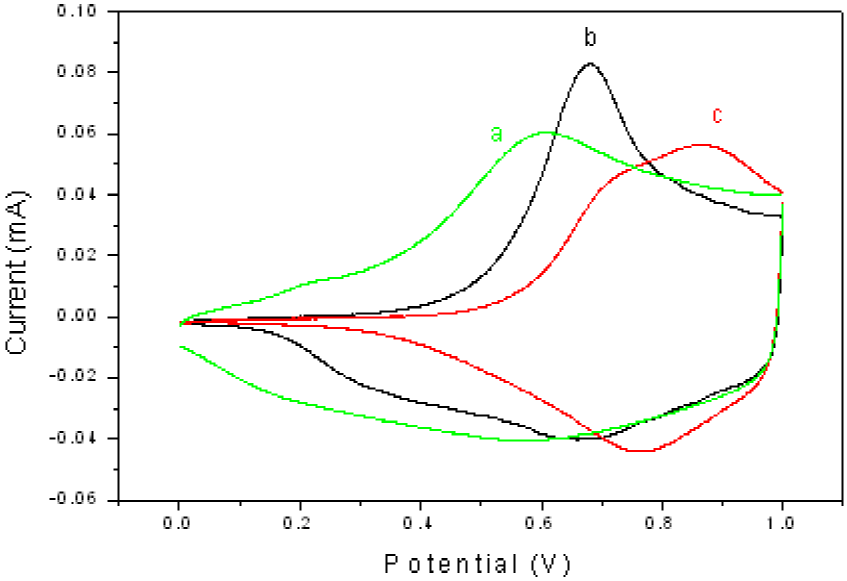


Figure.10 Cyclic voltammograms of (a) P3HT (b) poly(3HT-co-3MT) electropolymerized at 1.60 V from volume ratio of (1:1) 3HT to 3MT (c) P3MT electropolymerized at 1.60 V in a monomer free 0.1 M $LiClO_4$ -acetonitrile solution at a scan rate of 25 mV/s.

Once copolymer formation from the two monomer was determined, the behavior of the homopolymers (P3HT and P3MT) and the copolymer poly (3HT–co-3MT) (1:1) at various electropolymerization potential were studied (Fig. 11,12 and13).

As it can be seen from Figures.11, 12 and 13, there is no significant shift in oxidation peak potential as the electropolymerization potential changes for both the hompolymers and the copolymer. The relatively sharper peak characteristic of P3MT is more pronounced on the copolymer over the relatively broader peak characteristic of P3HT.

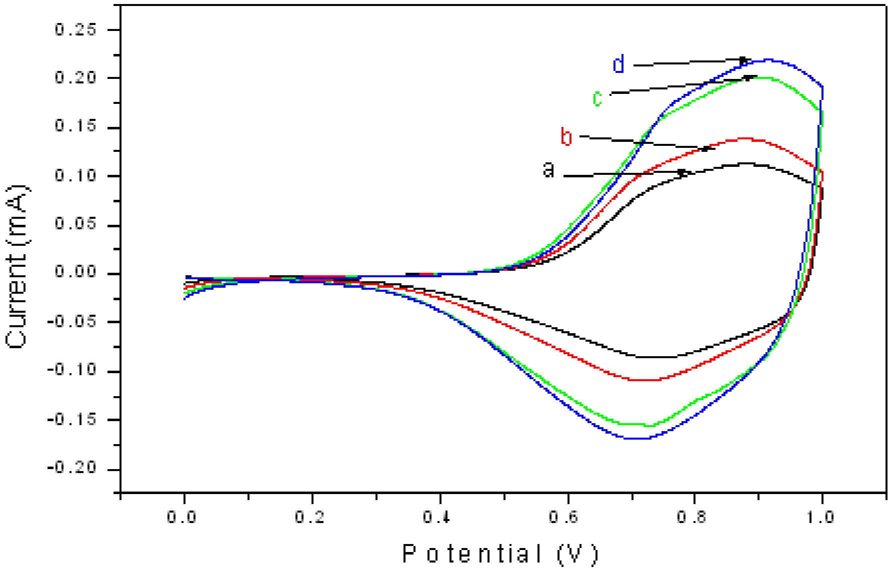


Figure 11. Cyclic voltammograms of P3HT electropolymerized at a) 1.60 V b)1.65 V c)1.7 V d)1.75 V in monomer free 0.1 M $LiClO_4$ acetonitrile solution at a scan rate of 50 mV/s.

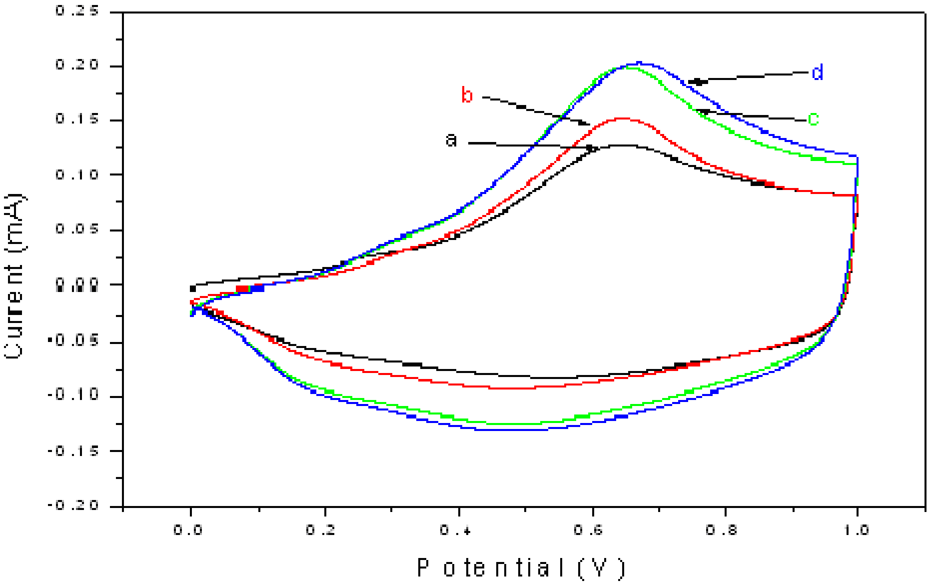


Figure 12. Cyclic voltammograms of P3MT electropolymerized at a) 1.60 V b) 1.65 V c) 1.7 V d) 1.75 V in monomer free 0.1 M $LiClO_4$ acetonitrile solution at a scan rate of 50 mV/s.

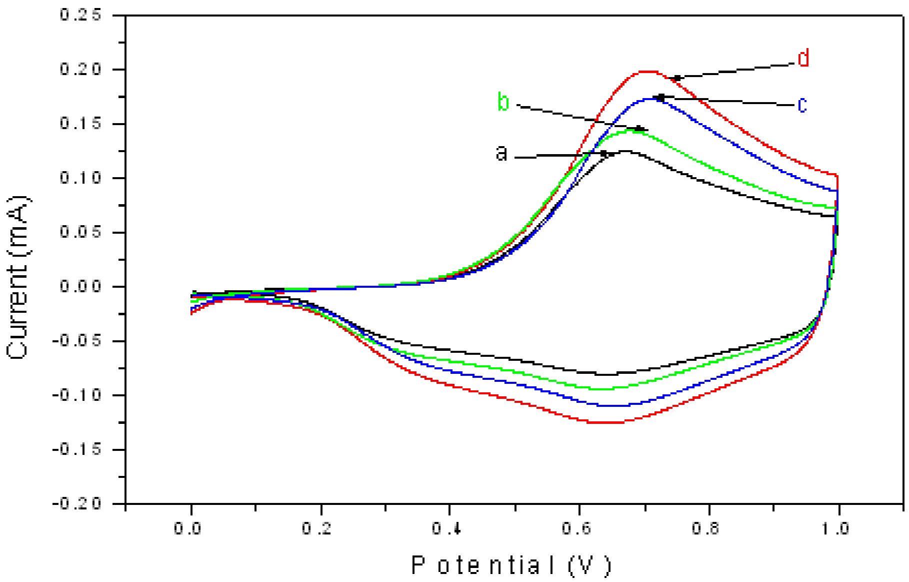


Figure 13. Cyclic voltammograms of poly (3HT-co-3MT) from volume ratio of 1:1 3HT to 3MT electropolymerized at a)1.60 V b)1.65 V c)1.7 V d)1.75 V in monomer free 0.1 M $LiClO_4$ - acetonitrile solution at a scan rate of 50 mV/s

Once the characteristics of both the homopolymers and the copolymer were studied at different electropolymerization potential, an intermediate electropolymerization potential of 1.7 V was chosen to study the effect of composition of the two monomers on the electrocatalytic activity of the redox system of 2 mM $K_3Fe(CN)_6$ in 1M KNO_3 solution. (Fig. 14).

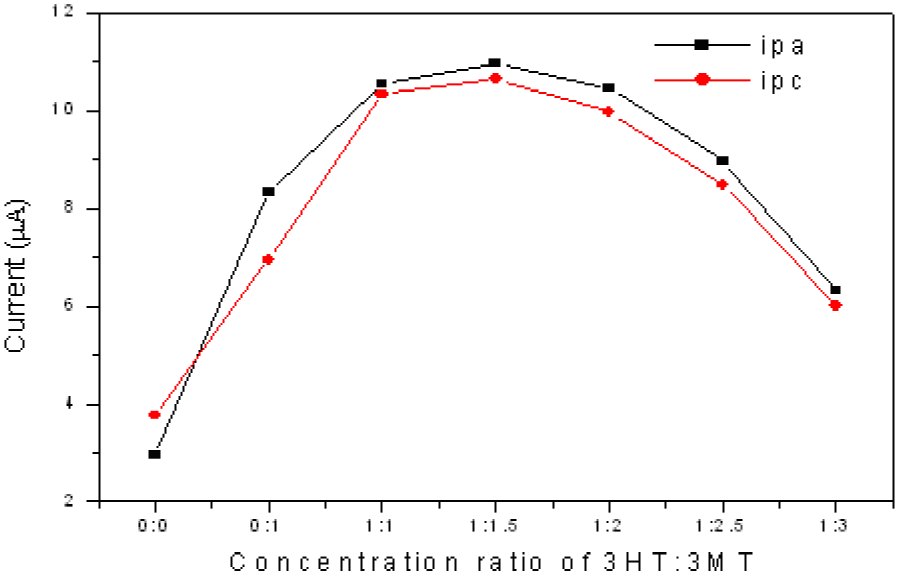


Figure 14. The effect of composition of poly(3HT-co-3MT) at a Pt electrode on the electrocatalytic activity of the redox system of 2 mM $K_3Fe(CN)_6$ in 1 M KNO_3 solution, at a polymerization potential of 1.7 V and a deposition time of 10s.

After the electrocatalytic effect of the copolymers electropolymerized from different composition of the monomers were examined, the optimum composition of the two monomers was found to be 1:1.5 since the relative current obtained for these composition is higher than the others (Fig.14).

Once the optimum ratio of the two monomers is determined, the effect of polymerization potential was examined on the behavior of the copolymer electro- polymerized from the monomer mixture of 3HT: 3MT (1:1.5) with respect to their electrocatalytic activity on the redox system of 2 mM $K_3Fe(CN)_6$ in 1 M KNO_3 solution (Fig. 15).

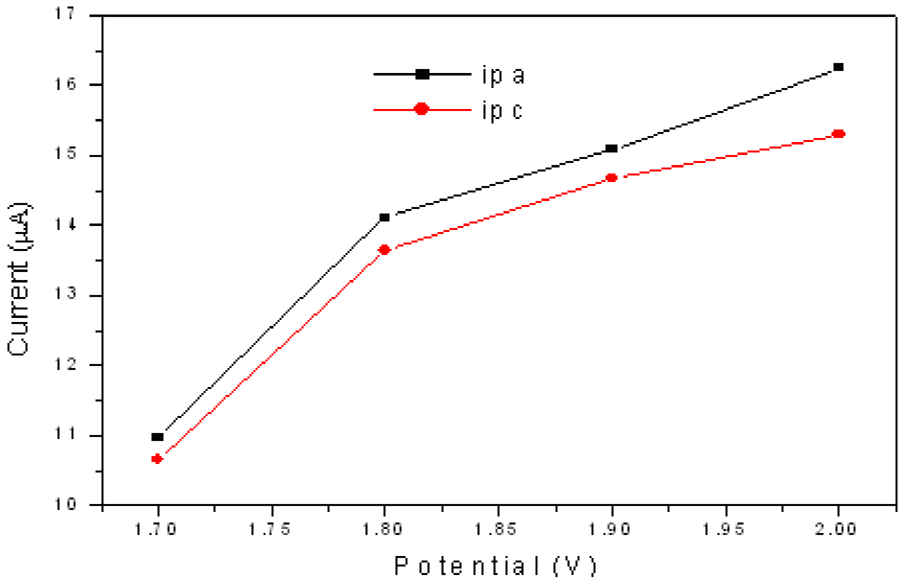


Figure 15. The effect of polymerization potential of poly(3HT-co-3MT)(1:1.5) at a Pt electrode on the electrocatalytic activity of the redox system of 2 mM $K_3Fe(CN)_6$ in 1 M KNO_3 solution.

As it can be seen from Fig. 15, the relative increase in the amount of current obtained as the electropolymerization potential changes from 1.7 V to 1.8 V is much higher than the relative increase in current as the electropolymerization potential is raised from 1.8 V to 2.0 V. Because of the decrease in relative increase in current, as the electro-polymerization potential is raised above 1.8 V, the optimum electropolymerization potential with a value 1.8 V was chosen.

After determining the optimum composition and electropolymerization potential, the effect of deposition time were also examined in Fig. 16. As it is shown from Fig. 16 the optimum deposition time was found to be at 15 sec.

Being able to produce the copolymer poly(3HT-co-3MT) (1:1.5) with electro polymerization potential of 1.8 V and with a deposition time of 15 sec, its applications in the electrocatalysis of organic analytes were studied and presented in the following section

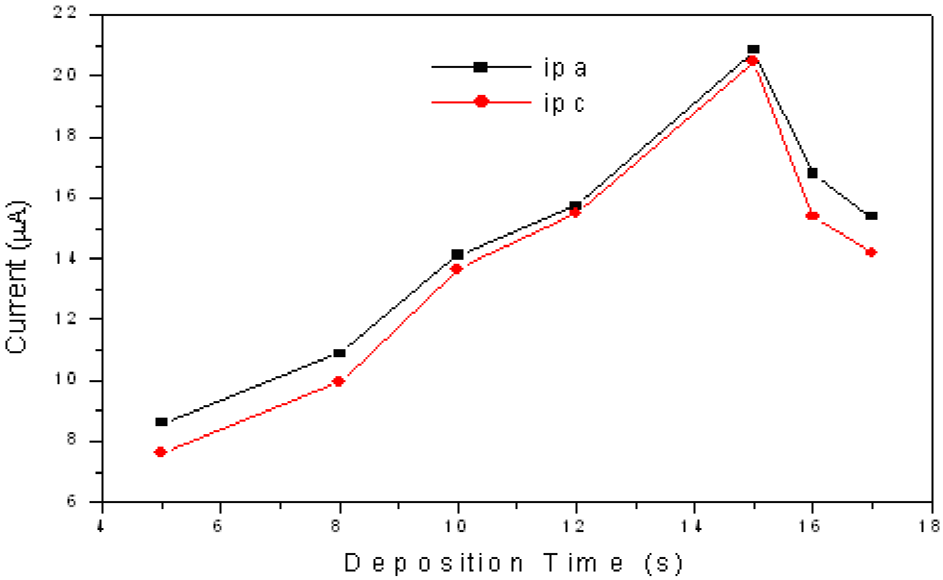


Figure 16. The effect of deposition time of poly(3HT-co-3MT)(1:1.5) at a Pt electrode on the electrocatalytic activity of the redox system of 2 mM $K_3Fe(CN)_6$ in 1 M KNO_3 solution, at a polymerization potential of 1.8 V

4.2 Voltammetric behavior of potassium ferricyanide at Pt electrode modified with the poly (3HT-co-3MT)

The electrocatalytic effect of the hompolymers (P3HT & P3MT) and the copolymer poly (3HT-co-3MT) (1:1.5) with the electropolymerization potential of 1.8 V and a deposition time of 15 sec were examined in Fig. 17.

As can be seen from Fig. 17 only P3MT and poly (3MT-co-3HT) catalyze the potassium ferricyanide redox system. A higher catalytic effect of poly(3HT-co-3MT) (1:1.5) with a reduction current of 20.45 μA was obtained as compared to P3MT with a reduction current of 3.55 μA and P3HT with no electrocatalytic effect as it can be seen from Fig. 17. This shows that copolymer of 3MT and 3HT catalyze better than pure P3MT.

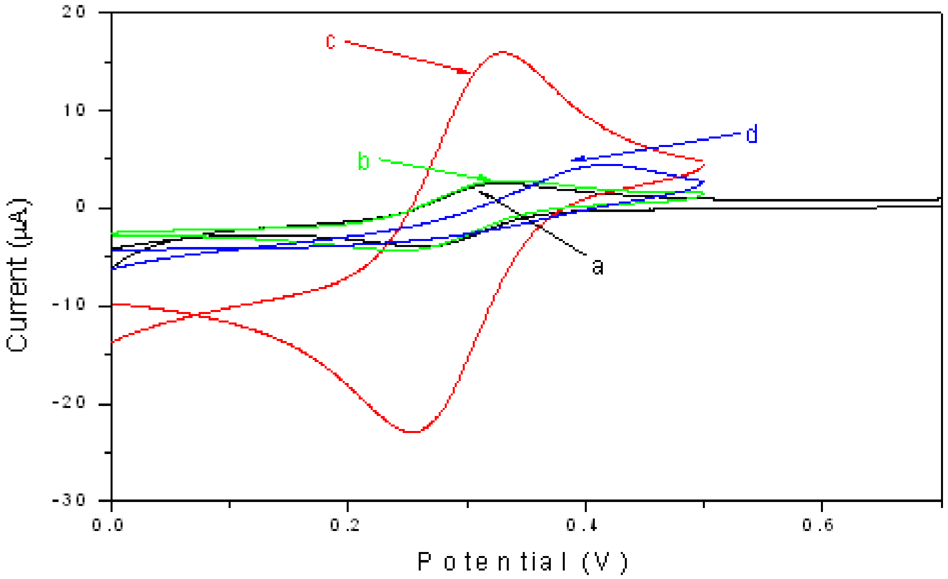


Figure 17. Cyclic voltammograms of 2 mM $K_3Fe(CN)_6$ in 1 M KNO_3 at Pt electrode modified with a) bare Pt b) P3MT c) poly(3HT-co-3MT) d) P3HT at a scan rate of 20 mV/s .

As can be seen from Fig. 19 the redox peak currents are linearly proportional to the square root of the scan rates therefore, the mass transport in the redox process was diffusion controlled. Thus the peak current (i_p) is consistent with the Randles sevcik equation ($i_p = 2.69 \times 10^5 n^{3/2} A D_O^{1/2} v^{1/2} C_O$), for a diffusion controlled redox system, where; A is the electrode area (cm^2), n is the number of electrons transferred, Co is the concentration (mol cm^{-3}) and v is the scan rate in V/s). The reduction peak potential was obtained at 259 mV and the oxidation peak potential was obtained at 327 mV, with a peak separation ΔE_P of 68 mV at poly(3MT–co-3HT) modified Pt electrode electro polymerized at a potential of 1.8 V and a deposition time of 15 sec at a scan rate of 20 mV/s. The magnitude of the reduction and oxidation currents was 20.81 µA and 20.45 µA.

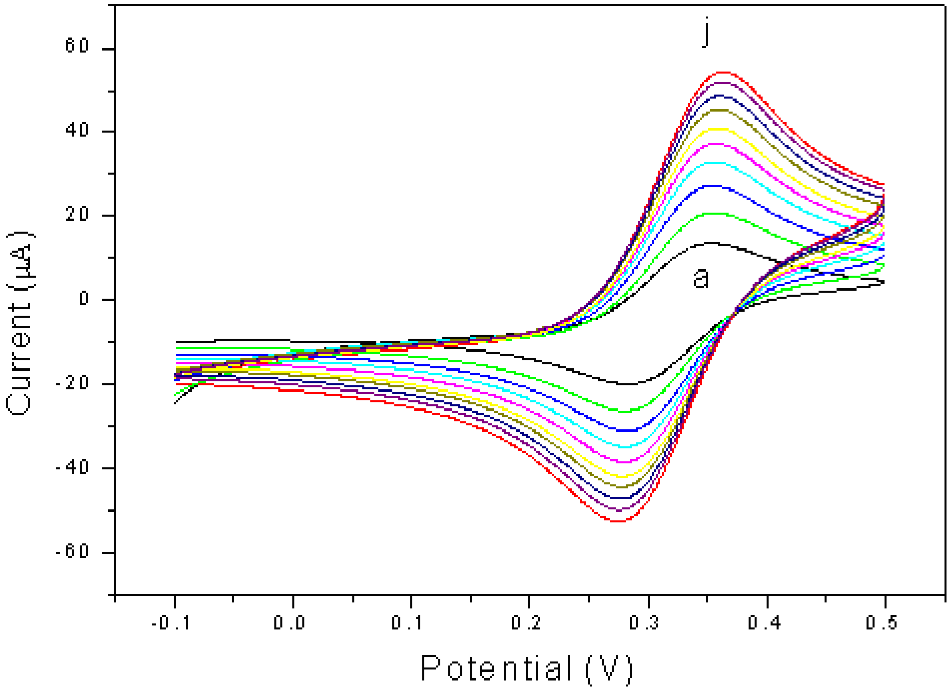


Figure 18. Cyclic voltammograms of 2 mM $K_3Fe(CN)_6$ in 1 M KNO_3 solution at a poly(3HT-co-3MT) modified Pt electrode, a) 20mV/s and j) 200 mV/s with 20 mV/s interval.

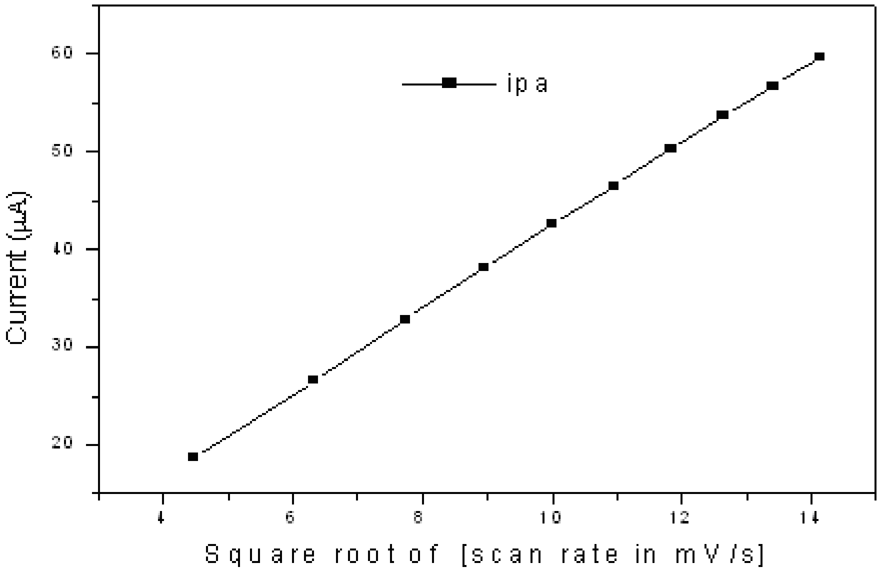


Figure 19. Peak current *versus* square root of scan rate from the cyclic voltammogram in Figure 18.

To examine the detection limit of the modified electrode, studies were made by varying the concentration of potassium ferricyanide and measuring the reduction peak current. A lower detection limit of 40 μM of potassium ferricyanide was obtained. From the calibration curve the variation of the reduction peak current with varying concentration showed a linear dependence in the concentration range between 0.04 mM to 0.20 mM as shown in Fig. 20.

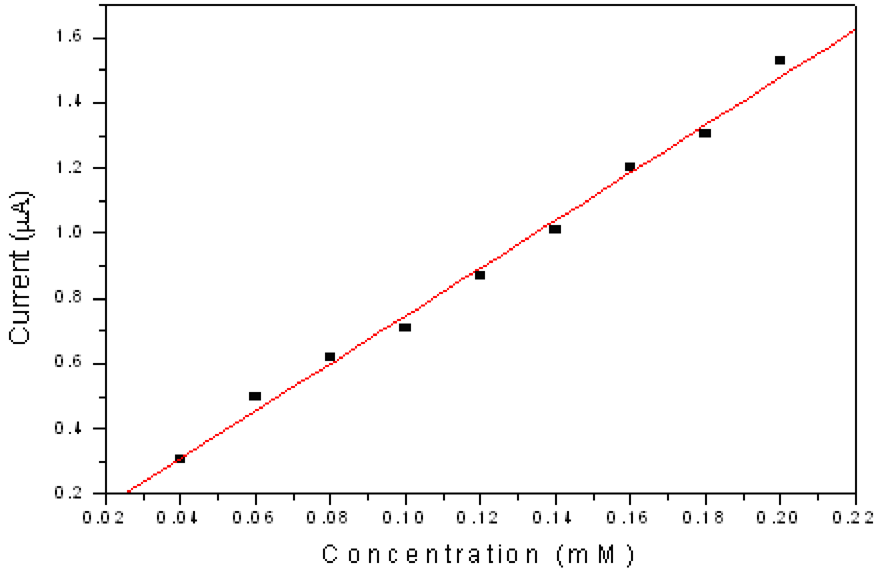


Figure 20. Effect of concentration of $K_3Fe(CN)_6$ on its reduction peak current at poly(3HT-co-3MT) modified Pt electrode, at a scan rate of 20 mV/s.

4.3 Electrochemical Behaviors of Catechol and Hydroquinone at a Poly(3MT-co-3HT) Modified Pt Electrode

One of the redox systems most often used in the investigation of electrocatalysis at conducting polymer electrodes is the hydroquinone/benzoquinone redox couple (HQ/BQ). The well studied quasireversible redox transition between HQ and BQ implies the transfer of two electrons and two protons, in acidic aqueous solutions. However, at high pH, and in non aqueous solutions, intermediate products like anion radicals, are known to form during the electrochemical oxidation or reduction. Cooper and Hall [26] found the reduction of BQ proceeds nearly reversibly with $2e^-$ transfer at stationary polyaniline electrodes in the low pH region, whereas the transfer of the second electron is prevented at rotating disc electrode by the loss of intermediate from the surface before it can migrate into the polymer film. The authors concluded that, at stationary electrode, the reaction product is stabilized by the possible formation of the charge compensating complex between BQ anion radical and the polymer. At higher pH, the reaction occurs on the outside of PANI film, because of the slow charge transfer through the polymer film.

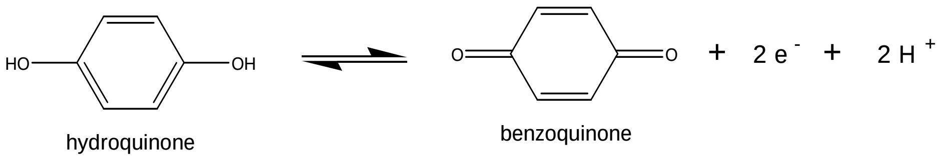
Measuring the secretion of neurotransmitters such as catechol and catecholamine has been considered to be of great importance to probe the brain chemistry.

For both hydroquinone and catechol the working solution were prepared by appropriate dilution of the corresponding stock solutions with 0.1 M phosphate buffer and phosphoric acid in order to obtain the appropriate pH which is 0.5 based on previous studies which shows that the maximum current response was obtained at a pH of 0.5 for both catechol and hydroquinone [27].

As can be seen from the cyclic voltammograms (CV) of 2 mM hydroquinone, at bare pt electrode the anodic peak and the cathodic peak of hydroquinone appeared at 591 mV and 363 mV respectively, with the separation between oxidation peak and reduction peak potentials (ΔE_P) of 228 mV. The large ΔE_P indicates that hydroquinone exhibits an irreversible electrochemical behavior at bare Pt electrode at that condition.

The oxidation peak current of hydroquinone at poly(3HT-co-3MT) modified Pt electrode greatly increased, compared with that at bare Pt electrode (Fig. 21a), and the anodic peak and the cathodic peak potential appeared at 495 mV and 450 mV, respectively, with a peak separation (ΔE_p) of 45 mV. This small ΔE_p indicates that the oxidation and reduction potentials of hydroquinone at poly(3MT-co-3HT) modified Pt electrode are becoming closer and the electrochemical reversibility of hydroquinone at the modified Pt electrode is much improved.

The ΔE_p of 45 mV was consistent with the literature value of 46 mV at which hydroquinone undergoes oxidation to the corresponding benzoquinone by a transfer of two electrons and two protons in acidic media [28, 29] as shown in Equation 1. The stability of poly(3MT-co-3HT) modified electrode towards detection of hydroquinone was examined by scanning for eight repetitive cycles (Fig. 19a), where no change in the current response was observed.



(1)

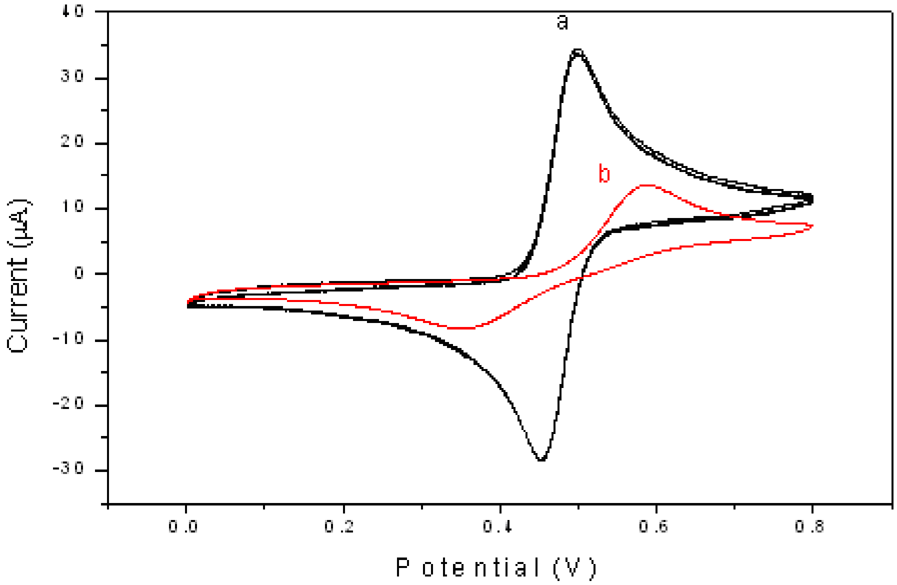
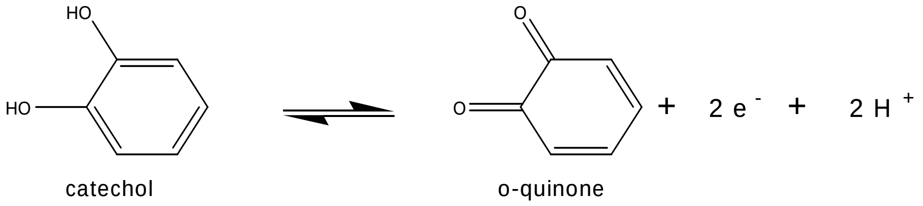


Figure 21. Cyclic voltammogram of 2 mM hydroquinone a) at poly(3HT-co-3MT) modified Pt electrode b) at bare Pt electrode at pH = 0.5 phosphoric acid solution, at a scan rate of 20 mV/s.

The cyclic voltammogram of 2 mM catechol at a Pt electrode modified with poly(3MT-co-3HT) is also compared with that of bare Pt electrode at a scan rate of 20 mV/s in 0.1 M phosphate buffer (pH 0.5) (Fig. 22). At a bare Pt electrode, the anodic peak potential and the cathodic peak potential of catechol were 676 mV and 483 mV, respectively, with ΔE_p of catechol being 193 mV. At poly(3MT-co-3HT) modified Pt electrode, the oxidation peak current of catechol greatly increased and the anodic peak and the cathodic peak potentials appeared at 602 mV and 547 mV, respectively, with ΔE_p of catechol at poly(3MT-co-3HT) Pt electrode being 55 mV. This result indicates that the oxidation peak current of catechol at the poly(3MT-co-3HT) modified Pt electrode is significantly enhanced and the oxidation potential of catechol at poly(3MT-co-3HT) modified Pt is much lowered. The ΔE_p value of 55 mV obtained was consistent with the literature value of 57 mV at which catechol undergo oxidation to the corresponding o-quinone by a transfer of two electrons and two protons in acidic media [28, 29, 30] as shown in Equation 2. Similar stability behavior of the poly(3MT-co-3HT) modified Pt electrode like that of hydroquinone was observed with eight repetitive cycles as shown Fig. 22a.



(2)

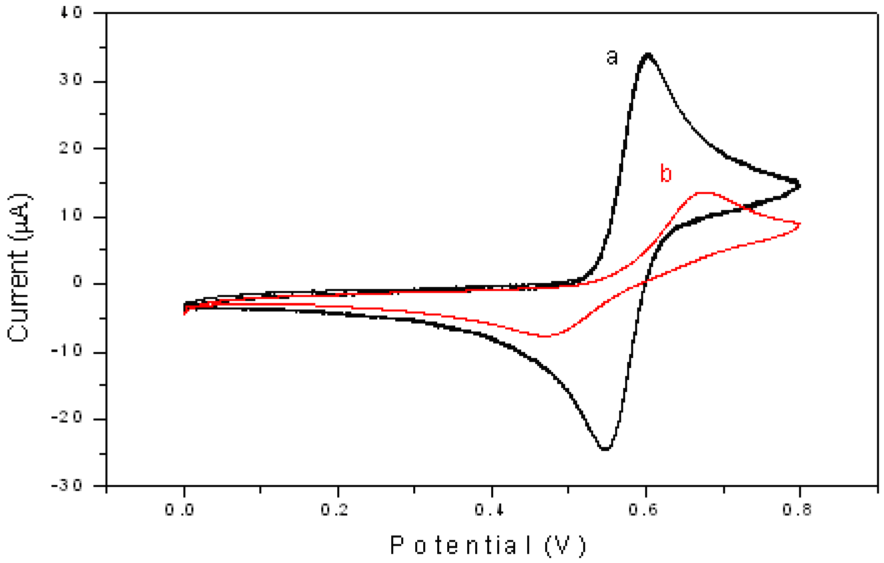


Figure 22. Cyclic voltammogram of 2 mM catechol a) at poly(3HT-co-3MT) modified Pt electrode b) at bare Pt electrode at pH = 0.5 phosphoric acid solution, at a scan rate of 20 mV/s.

Hydroquinone (1,4-dihydroxybenzene) and catechol (1,2-dihydroxybenzene) are phenolic compounds and often coexist as isomers in environmental samples. Simultaneous determination of hydroquinone and catechol levels is of great importance because of their coexistence in environmental samples as environmental pollutants with high toxicity. Most established common methods for the determination of catechol and hydroquinone are performed after previous separation [28]. Disadvantages of the separation are operating complexity, time wastage and reagent consumption. Thus, it is necessary to develop a new method with possibility of the simultaneous determination without previous separations of these compounds.

The cyclic voltammogram of equimolar mixture of catechol and of hydroquinone at bare Pt electrode and at poly(3MT-co-3HT) modified Pt electrode at a scan rate of 20 mV/s in 0.1M phosphate buffer solution (pH 0.5) shown in Fig. 23.

Hydroquinone and catechol at poly(3MT-co-3HT) modified Pt electrode yielded two well-defined oxidation peaks, at potentials of 500 mV and 598 mV, respectively with 98 mV separation between the corresponding anodic peaks of hydroquinone and catechol (Fig. 23a). The oxidation peak currents also increased remarkably at poly(3MT-co-3HT) modified Pt electrode. The modified electrode was stable for simultaneous detection of hydroquinone and catechol for eight repetitive cycles as shown in Fig. 23a. In addition to this using poly(3MT-co-3HT) modified Pt electrode, there was no shift in redox potentials of catechol and hydroquinone whether they are detected alone or in the presence of the other (simultaneously) (Fig. 24). So this shows that poly(3MT-co-3HT) modified Pt electrode is highly sensitive and selective for simultaneous detection of catechol and hydroquinone. The increase in anodic current responses and the lowering in separation peak potential (ΔE_p) of both hydroquinone and catechol arise from electrochemical modification of Pt electrode with poly(3MT-co-3HT).

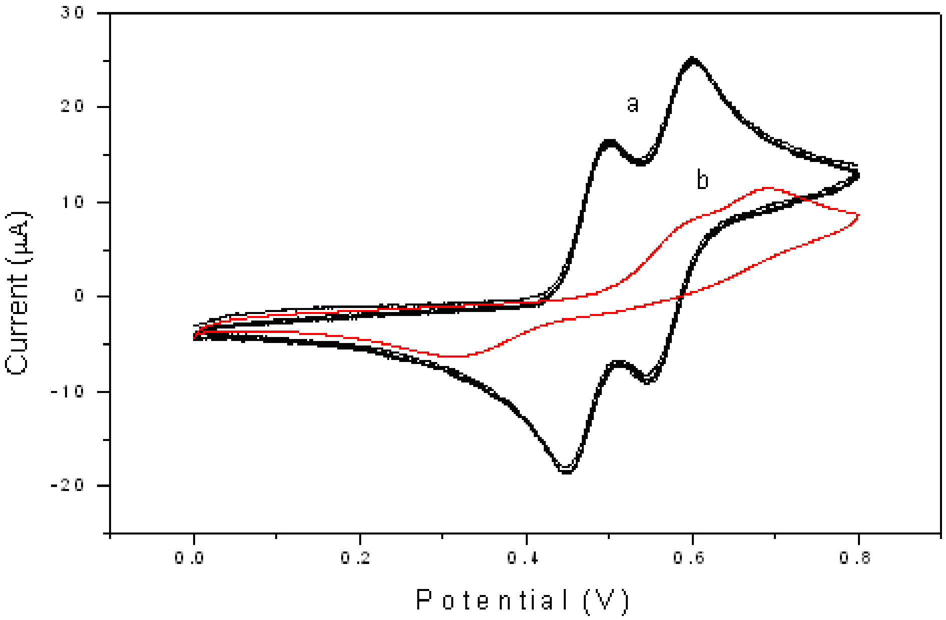


Figure 23. Cyclic voltammogram of equimolar of 2 mM catechol and hydroquinone a) at poly(3HT-co-3MT) modified Pt electrode b) at bare Pt electrode at pH = 0.5 phosphoric acid solution, at a scan rate of 20 mV/s.

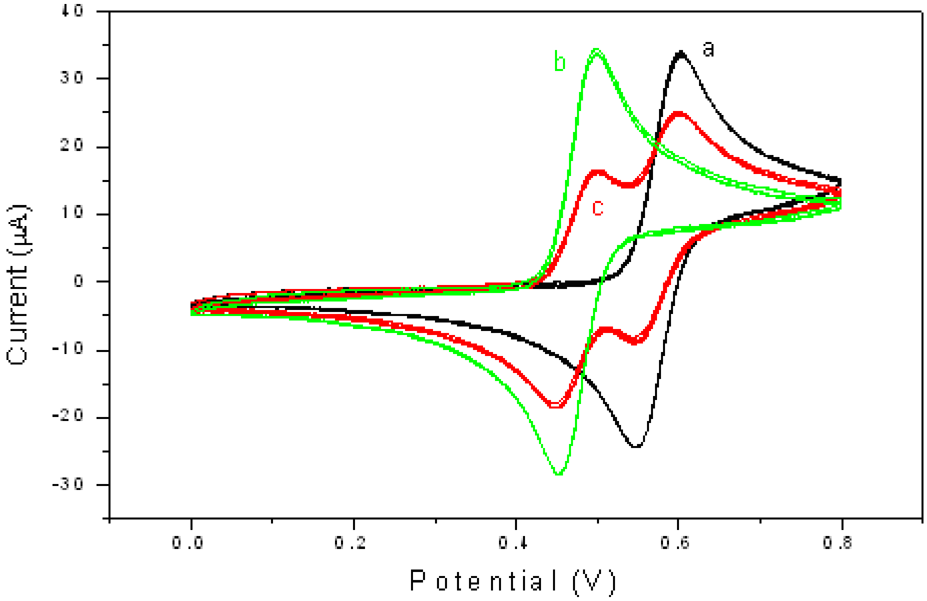


Figure 24. Cyclic voltammograms of catechol and hydroquinone a) catechol (2 mM) alone b) hydroquinone (2 mM) alone, c) equimolar(2Mm) mixtures at poly(3HT-co-3MT) modified Pt electrode in 0.3 M phosphoric acid pH = 0.5.

To study the electrochemical behaviour of the system in the simultaneous determination of catechol and hydroquinone, the effect of scan rate on the oxidation peak currents and peak potentials of both catechol and hydroquinone were examined using cyclic voltammetry at poly(3MT-co-3HT) modified platinum electrode in a solution containing equimolar concentrations (2 mM) of both analytes (Fig. 25).

It was found that the change in redox peak potentials of both catechol and hydroquinone and the separation between the redox peak potentials of the two were insignificant with varying the scan rate from 20 mV/s to 200 mV/s, which suggests that the redox processes of catechol and hydroquinone are diffusion controlled. It was also found that the oxidation peak currents of both catechol and hydroquinone were directly proportional to the square root of the scan rate between 20 mV/s and 200 mV/s as shown in Figure 26. This is consistent with Randles Sevcik equation indicating that the electrochemical process is diffusion controlled.

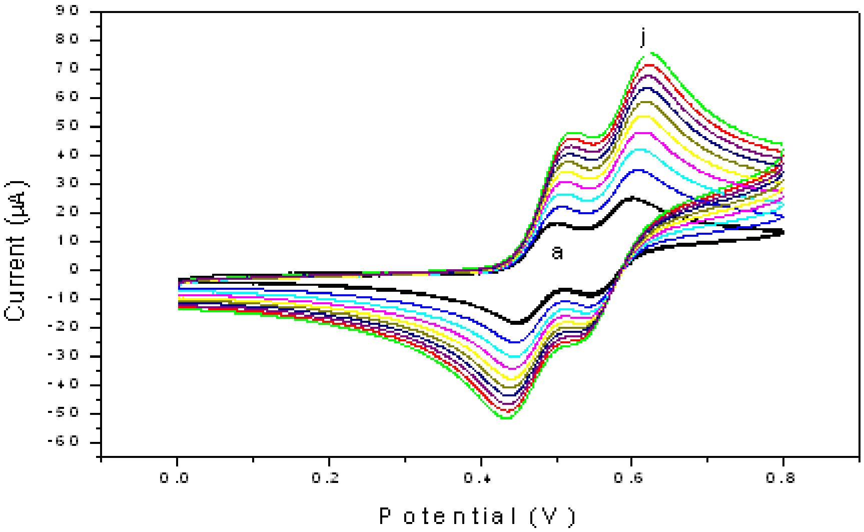


Figure 25. Cyclic voltammograms of equimolar (2 mM) mixtures of catechol and hydroquinone at different scan rates, (a) 20 mV/s and (j) 200 mV/s with 20 mV/s interval.

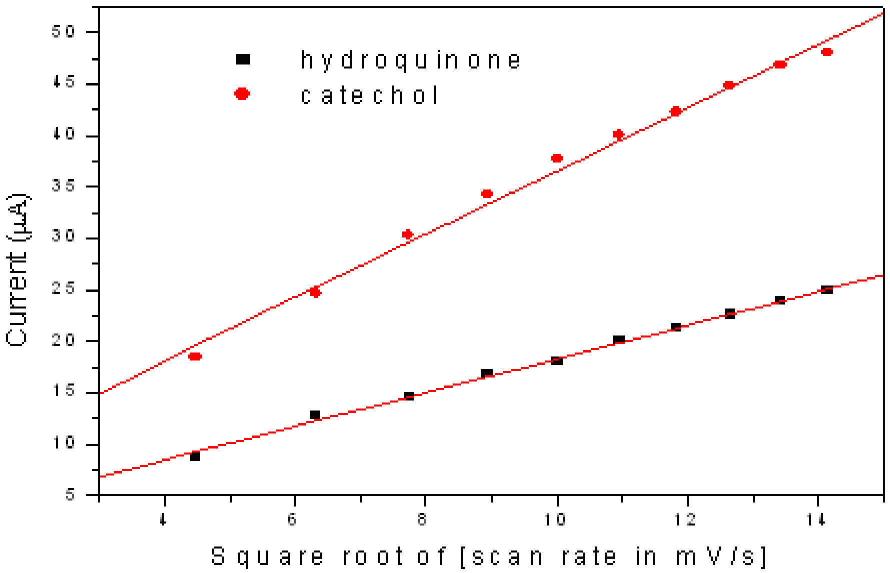


Figure 26.The effect of scan rate on the oxidation currents of equimolar (2 mM) mixtures of catechol and hydroquinone at different scan rates.

To examine the detection limit of the modified electrode in the case of hydroquinone and cathecol a more selective and sensitive methods known as differential pulse voltammetry was used. The parameters used for DPV were at a scan rate of 20 mV/s pulse amplitude of 50 mV, pulse width of 50 ms and pulse period of 200 ms. Under these optimized conditions, the calibration plots for hydroquinone and cathecol are obtained using DPV at poly (3MT-co-3HT) modified Pt electrode (Fig. 27 – 30).

As it can be shown from Fig. 28, a lower detection limit of 20 µM of both hydroquinone and catechol was obtained. From the calibration curve the variation of the reduction peak current with varying concentration showed a linear dependence in the concentration range between 0.02 mM to 0.2 mM for both hydroquinone and catechol.

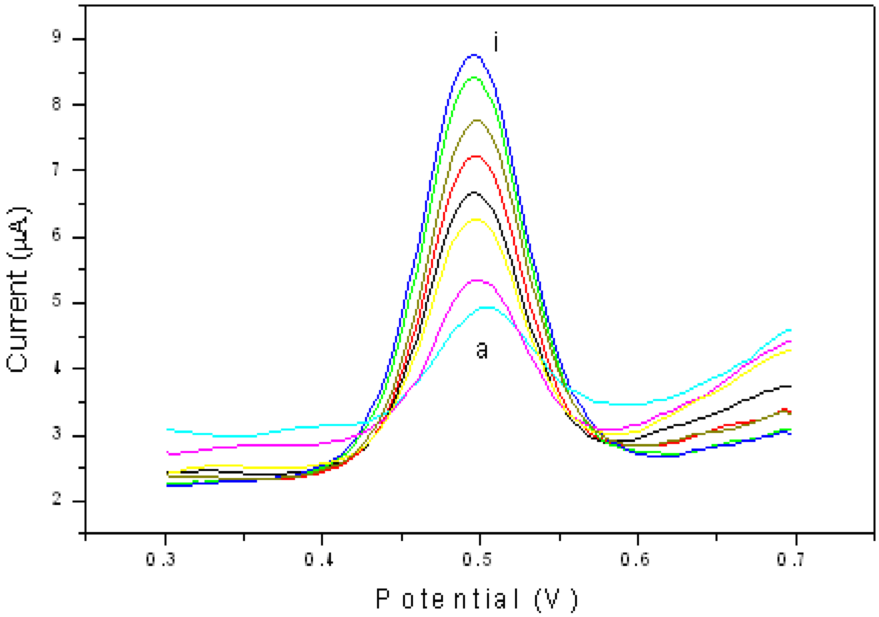


Figure 27. DPV of hydroquinone at a) 0.02 mM, to i) 0.2 mM varying concentration at poly(3HT-co-3MT) modified Pt electrode in pH = 0.5 phospheric acid solution.

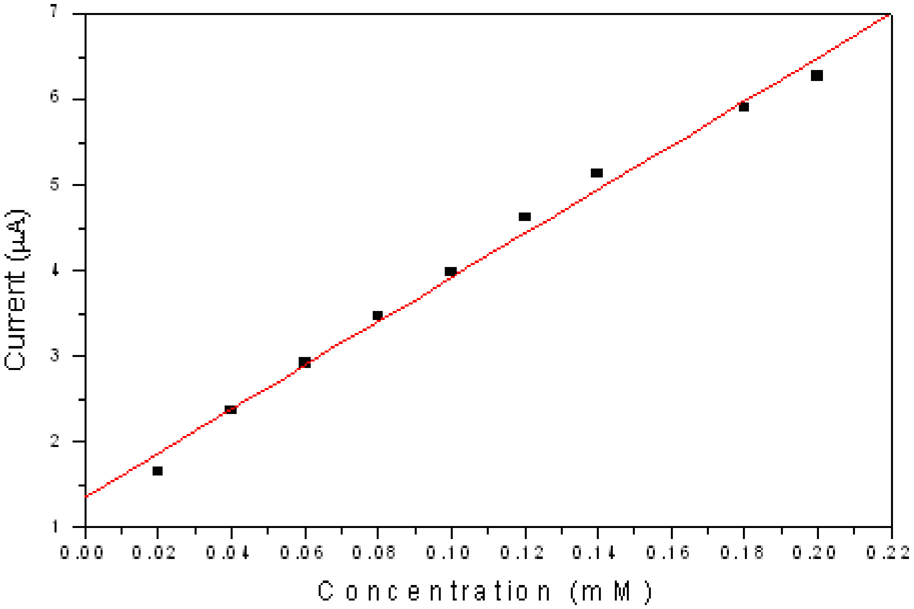


Figure 28. The calibration curve for hydroquinone from the DPV in Fig. 27 in the range of 20 µM to 0.2 mM.

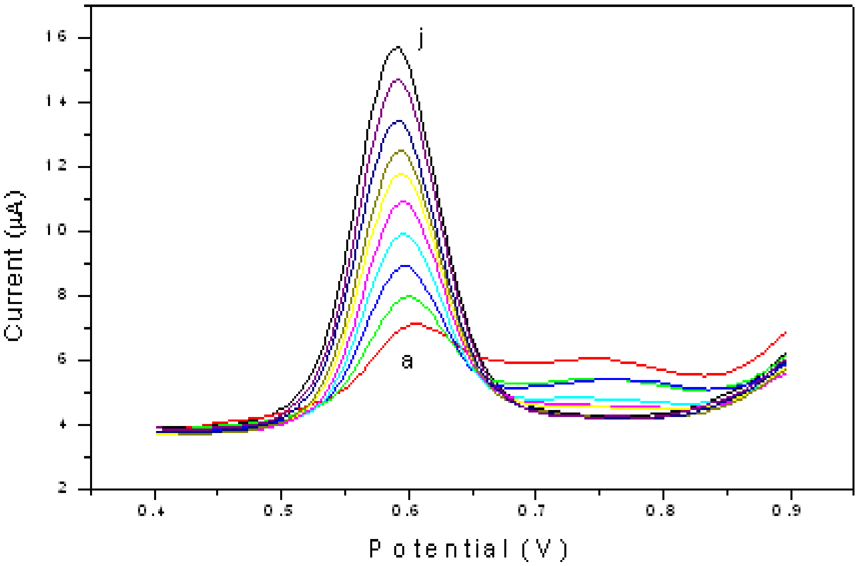


Figure 29. DPV of catechol at a) 0.02mM, to J) 0.2 mM varying concentration at poly(3HT-co-3MT) modified Pt electrode in pH = 0.5 phospheric acid solution.

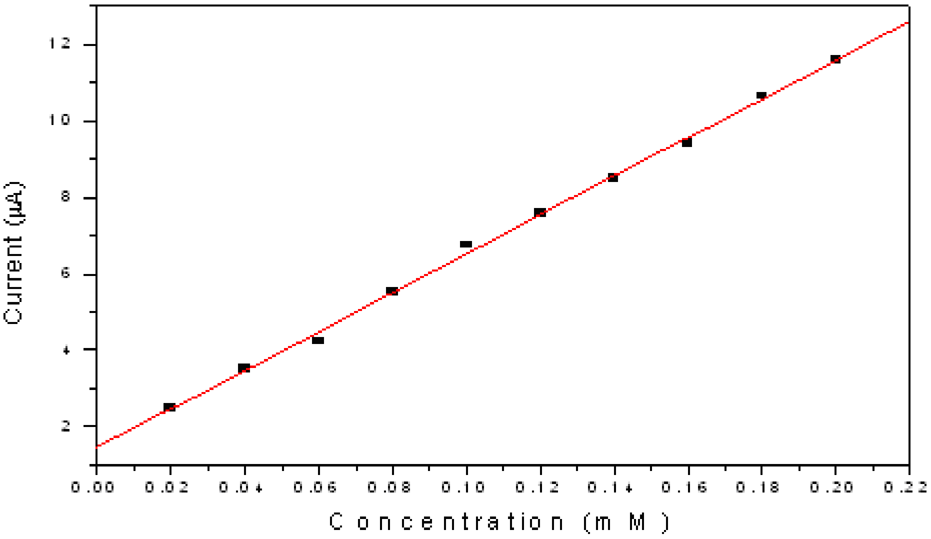


Figure 30. The calibration curve for catechol from the DPV in Fig. 29 in the range of 20 μM to 0.2 mM.

5.CONCLUSION

In this study electrochemical characterization of both P3HT and P3MT with respect to Pt, GC and Au electrodes were made. The possibility of copolymer formation was also shown between P3HT and P3MT. The optimum copolymer ratio, polymerazation potential and deposition time that are required to obtain the best electrocatalytic effect was also demonstrated using various redox species. The detection limits for poly(3HT-co-3MT) modified Pt electrode were also shown for these redox species. Therefore, this work establishes and demonstrates an approach for the development of voltammetric sensor based on the copolymer of 3HT and 3MT.

6. REFERENCES

1. Teketel Yohannes, *All-Solid-State Photoelectrochemical Solar Energy Conversion,* (1997), PhD thesis, AAU, Ethiopia.
2. C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, and A.G. MacDiarmid, *Phys. Rev. Lett*, **39** (1977) 1098.
3. A. O. Patil, *Electrically Conducting Polymers* **325**(2000) 300.
4. M. Gerard, A. Chaubey , B. D. Malhotra, *Biosensors and Bioelectronics* **17** (2002) 345
5. Teketel Yohannes, J. C. Carlberg, O. Inganas, and T. Solomon, *Synth.Met*., **88** (1997) 15.
6. D. Bouchta, N. Izaoumen, H. Zejli, M. El Kauoutit, K. R. Temsamani, *Biosensors and Bioelectronics* **20** (2005) 2228
7. N.F Atta, I. Marawi , K. L. Petticrew , H. Zimmer , H.B. Mark, Jr. , A. Galal *J. Electroanal. Chem.* **408** (1996) 47
8. M. Depaoli, G. Casalbore, E. Girotto, and W. Gazotti, *Electrochimica Acta.*, **44** (1999) 2983.
9. Malinauskas, *Synth., Met.,* **107** (1999) 75.

10. A. Kros, Stephan W. F. M. van Hövell, Nico A. J. M. Sommerdijk, and J. M. Nolte Roeland, *Adv. Mater.*, **20** (2001)1550.

11. M. Onoda, Y. Oshiyuki kato, H. Shonaka and K. Tada, *Electrical Engineering in Japan.*, **149** (2004) 120.

12. P. Roy, M. Sudan, S. Takeyoshi, O.Gil, P. A. Fujishima, and T. Ohsakaa, *Electroanalysis.,* **16** (2004)1777.

13. G. Yu and A. J. Heeger, *J. Appl. Phys*., **78** (1995) 4510.

14. P. Tuyen E. Nguyen U. Rammelt,W. Plieth, *J. Solid State Electrochem.,***7** (2003) 497.

15. Teketel Yohannes, T. Solomon, and O. Inganas, *Synth. Met*., **82** (1996) 215.

16. Teketel Yohannes and O. Inganas, *Solar Materials and Solar Cells*, **51** (1998) 193.

17. Teketel Yohannes and O. Inganas, *Synth. Met.,***107** (1999) 97.

18. S. Lupu, C. Mihail, L. Pigani, R. Seeeber, N. Totir, and C. Zanardi, *Electrochemistry Communication.,* **4** (2004) 753.

19. G. Zotti, S. Zecchin, G. Schiavon, and L. Bert, *Micromol. Chem.Phys.,* **203** (2002) 1958.

20. B. Sean, M. Ann Wilson, N. Dyer, Emmanuel and I. Antony G. *Microchem. Acta.,* **43** (2003) 123.

21. P. Rajiv, R. C. Srivastava, P. C. Pandey, *J. Solid State Electrochem.*, **6** (2002) 203.

22. M. A. Vorotyntsev and J. Heinze *Electrochimica Acta.,* **46** (2001) 3309.

23. P. Chandrasekhar, *Conducting Polymers Fundamentals and Applications: A Practical Approach,* Kluwer academic publisher, (2002).

24. H. A.M. van Mullekoma, J. A.J.M. Vekemansb, E. E. Havingab, and E.W. Meijerb, *Materials Science and Engineering*, **32** (2001) 40.

25. G. Gustafsson, O. Inganas and J. O.Nilsson, , *Synth. Met.,* **26** (1988) 297.

26. A. Malinauskas, *Synth. Met.,* **107** (1999) 75.

27. Getachew Adem, *Electrochemical Synthesis and characterization of polymers and copolymers of 3-Hexylthiophene, 3-Methylthiophene, and 3-octylthiophene*, (2005), Msc. thesis, AAU, Ethiopia.

28. Q. Honglani, and C. Zhang, *Electroanalysis,* **17** (2004) 120.

29. M. B.Smith and j. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure, 5th Edition,* John wiley and Sons, INC, NewYork, 2001, p.1511.

30. M. Zen and P. J. Chen, *Electroanalysis,* **10** (1998) 12.