SYNTHESIS AND CHARACTERIZATION OF THIOPHEN-3-YL-ACETIC ACID 4-PYRROL-1-YL-PHENYL ESTER AND ITS CONDUCTING POLYMERS

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF THIOPHEN-3-YL ACETIC ACID 4-PYRROL-1-YL PHENYL ESTER AND ITS CONDUCTING POLYMERS

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Thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE) monomer was synthesized by the reaction of thiophene acetic acid with thionyl chloride, and further reaction of thiophen-3-yl acetyl chloride with 4-pyrrol-1-yl phenol. Electrochemical behavior of this monomer (TAPE) was determined by cyclic voltammetry. Homopolymers were achieved both by using electrochemical and chemical polymerization techniques. Copolymers of TAPE in the presence of bithiophene and pyrrole were synthesized by potentiostatic electrochemical polymerization in acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB) solvent-electrolyte couple. The chemical structures were confirmed both by Nuclear Magnetic

Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA) were used to examine the thermal behavior of synthesized conducting homopolymers and copolymers. The morphologies of the films were investigated by Scanning Electron Microscope (SEM). Two-probe technique was used to measure the conductivities of the samples. Moreover, investigations of electrochromic and spectroelectrochemical properties of poly(TAPE) and TAPE/BiTh copolymer were done.

Keywords: Conducting copolymers, electrochromic properties

ÖZ

TİYOFEN-3-İL ASETİK ASİT 4-PİROL-1-İL FENİL ESTERİN VE İLETKEN POLİMERLERİNİN SENTEZİ

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Kasım 2003, 54 sayfa

3-tiyofen asetik asitin tiyonil klorür ile tepkimesinden oluşan tiyofen-3-il asetil klorürün tekrar 4-pirol-1-il-fenil ile tepkimesi sonucu, tiyofen-3-il asetik asit 4-pirol-1-il fenil ester (TAPE) monomeri elde edilmiştir. Bu monomerin elektrokimyasal davranışı dönüşümlü voltametri yöntemi ile incelenmiştir. Homopolimerler hem kimyasal hem de sabit potansiyel elektroliz yöntemleri ile elde edillmiştir. TAPE monomeri bitiyofen ve pirol varlığında asetonitriltetrabütilamonyum tetrafloroborat (TBAFB) çözücü-elektrolit ikilisinde sabit potansiyel elektroliz yöntemi ile polimerleştirilmiştir. Kimyasal yapı NMR ve FTIR ile tayin edilmiştir. Elde edilen polimerlerin ve kopolimerlerin termal davranışları DSC ve TGA yöntemleriyle belirlenmiştir. Filimlerin yüzeysel yapı analizleri SEM ile incelenmiştir. İletkenlik ölçümlerini yapmak için ise iki nokta tekniği kullanılmıştır. Bunlardan başka TAPE/BiTh kopolimerinin elektrokromik ve spektroelektrokimyasal özellikleri incelenmiştir.

Anahtar sözcükler: İletken kopolimerler; Electrokromik özellikler

TO MY FAMILY

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INTRODUCTION

1.1 Conducting polymers

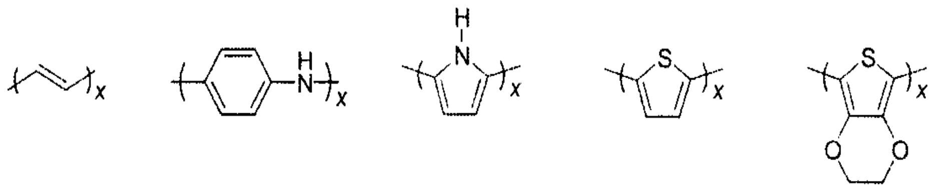
Conducting polymers (CPs) are organic materials possessing electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties and processability to a certain extent. The unique intrinsic property of these organic materials, which are generally comprised simply of C, H and simple heteroatom such as N and S, and the myriad of properties emanating from it, arise uniquely from Π-conjugation, which is the basic prerequisite for conduction in polymers.

Research on conducting polymers intensified soon after the discovery of poly(sulphur nitride) [$(SN)_x$] in 1975, which becomes superconducting at low temperatures [1]. Although conducting polymer complexes in the form of tetracyano and tetraoxalato-platinates, the Krogman salts charge transfer complexes [2] had been known earlier, the significance lies in the rediscovery of polyaniline (PA) in 1977 [3] by MacDiarmid and Heeger, University of Pennsylvania. They were able to enhance the electrical conductivity of PA (10^{-9} Scm^{-1}) by several orders by doping with oxidizing agents e.g. I_2 and AsF_5. Poly-paraphenylene (PPP) was synthesized by Ivory [4]. It forms highly conducting charge transfer complexes with both n and p type dopants. Doping with AsF_5 increases its conductivity. Theoretical models indicate that the charge transport in PPP is a polaron/bipolaron. PPS was non-rigid, but not fully carbon backbone linked to conducting polymer. Its discovery was particularly exciting since its property of solution processability opened the door for potentially obtaining commercially viable conducting plastics [5].

Polyacetylene was initially the most studied CP from both scientific and practical applications of point of view. However, due to its high chemical instability in air and related factors, interest in it has been recently confined to its scientific aspect.

Among polyheterocyclics, polypyrrole (PPy) has been investigated the most. The electrochemical oxidation of pyrrole in aqueous H_2SO_4 can be carried out on platinum electrode. The product is a conducting polymer known as 'Pyrrole Black' produced coherent films of PPy with a conductivity of 100 Scm^{-1} and exhibited excellent air stability. However, the main hindrance of its processability is in its insolubility in any organic solvents [6].

Polythiophene shows remarkable stability of both oxidized (p-doped) conducting form and its neutral (undoped) insulating form in both air and water.



(PA) (PAN) (PPy) (PTh) (PEDOT)

Figure 1.1: Structures of some common conducting polymers

It shows high doping level up to 50 % which may be attributed to the partially crystalline nature that has been confirmed by X-ray photoelectron spectroscopy studies [7]. Many other conducting polymers such as polyfuran, polyindole, polycarbazole, polyaniline etc. have also been synthesized. Chemical structures of some common conducting polymers are shown in Figure 1.1.

1.2 Applications of Conducting Polymers

Interest in conducting polymers is largely due to the wide range of possible applications because of their facile synthesis, good environmental stability and long term stability of electrical conductivity. However, they suffer from the fact that they are insoluble, show poor mechanical and physical properties, which limits their processability. Synthesis of substituted derivatives, composites, grafts and block copolymers were shown to be effective to overcome these problems [8-14]. These substituted derivatives have emerged as the materials to replace metals and semiconductors in the electrical and electronics industry, as well offering themselves as the materials for optoelectronic industry. Therefore, CPs have wide range of applications.

The electrical conductivity of conductive polymers makes them suitable candidates as cathodes in rechargeable batteries. The advantages of these materials offer many, such as ease of fabrication, processability, low cost and light weight. Research findings on a polyacetylene-lithium battery were published in 1981 [15]. Conductive polymer batteries have long life, are rechargeable and can produce current density up to 50 mA/cm^2 and energy density of 10 Watt-h/kg.

The polyanilines, polythiophene and polypyrrole are very useful materials for fabricating electrooptical display devices [16]. The systematic development of electro-optical polymer device structures for optical multichip modules and related components were presented by Lytel [17]. Polythiophenes show color change from red to blue on applying voltage. The changed color lasts for several hours, thus showing the possibility of being used as an optical memory element. Interestingly, polythiophene can also be conveniently used as the switching element because the switching time from red to blue is 80 msec. Similarly, three stable colors (yellow green, dark brown and blue) are observed for polypyrrole. The absorbance changes in these and a few other CPs such as 3-methyl thiophene [18], 3-4-dimethyl thiophene, thieno (2,3-C) pyrrole [19] and polyaniline [20] make them quite attractive for electrochromic applications. Conducting polymers like polyaniline and poltisothionapthene show a whole range colors as a result of their many protonation and oxidation forms [21]. The electrochromic properties of such polymers can be exploited to produce a number of different electrochromic devices, such as display and thermal smart windows. The smart windows absorb some of sunlight which changes color in response to sunlight or temperature changes, thus saving air conditioning cost.

In order to control air pollution and to detect combustible, toxic and noxious gases at low levels, tremendous efforts are being made towards the development of simple and inexpensive semiconducting gas sensors. However, semiconducting oxide film sensors generally operate efficiently only at 300 °C. In order to overcome this limitation, new materials are being developed. It is observed that vacuum deposited thin films of polyaniline exhibit excellent gas sensing properties. The electrical conductivity, optical absorption and electrical capacitance of the metal-polymer interface is strongly influenced by the presence of gas molecules. These results led to development of gas sensing elements for gases such as CO, NH_3, HCl and HCN. [22]

Thin-film polyaniline-based gas sensing elements [23] are inexpensive and operate at room temperatures with satisfactory selectivity for these gases.

1.3 Electrical conductivity in CPs

1.3.1 Band Theory

Materials in the world are classified to three broad categories according to their room temperature conductivity properties: Insulators, Semiconductors and Conductors. The electrical conductivity is dependent on a number of parameters such as number density of mobile charge carriers n, the carrier charge q, and the carrier mobility μ, which is given by the following formula:

$$\sigma = q\, n\, \mu$$

The conduction mechanism can be explained by band theory. The overlapping of individual molecular electronic states produces electronic bands. Valence electrons overlap to produce a valence band, while electronic levels immediately above these levels also coalesce to produce a conduction band. Between valence and conduction band, there exist an energy difference called band gap, which determines whether a material is insulator, semiconductor or conductor.

Electrons must have sufficient energy to promote itself to the conduction band, which will result in conduction. In conductive materials, the energies of highest energy level of valence band and of the lowest enery level of the conduction band are similar, which will lead to the promotion of electrons from valence band to the conduction band easily. The high conductivity of metals is the result of partially occupied valence band or zero band gap [24]. If there is small bandgap, electrons may be excited from the valence band to the conduction band by means of thermal excitation, vibrational excitation or excitation by photons. In this case , electrons are mobile and the material is termed as semiconductor. Existence of too large band gap will lead to some difficulties of promotion of electrons from the valence band to the conduction band. Compounds of such property are referred as insulators. Band structrure of a metal, a semiconductor and an insulator are shown in Figure 1.2.

By comparing the conductivities of CPs, one can gain a better idea about their place among the three broad conductivity classifications or materials, which is shown in Figure 1.3. In this figure, conductivities are given in Siemens/cm. The conductivity is generally denoted with σ, which is the reciprocal of the resistivity. ρ is used to denote resistivity. It is defined as the potential drop across a given distance in a cross section of a material in question of a given area, when a given current passes through this section;ρ = (ΔE/distance)/ (I/Area)

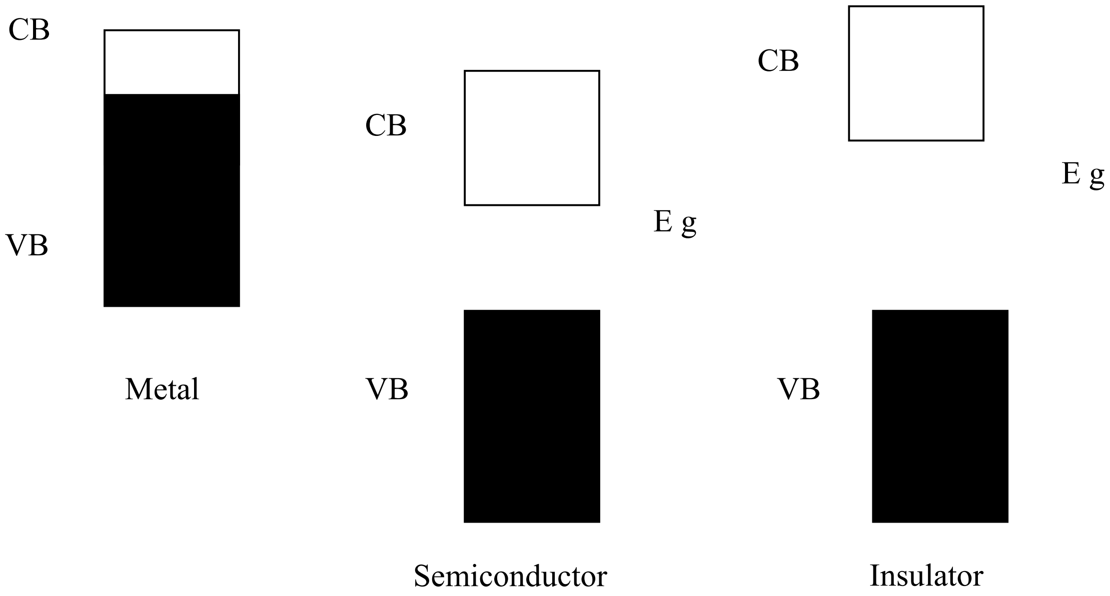


Figure 1.2: Schematic representation of band structure of metal, semiconductor and insulator (Dark regions represent the valence band and white regions stand for conduction band)

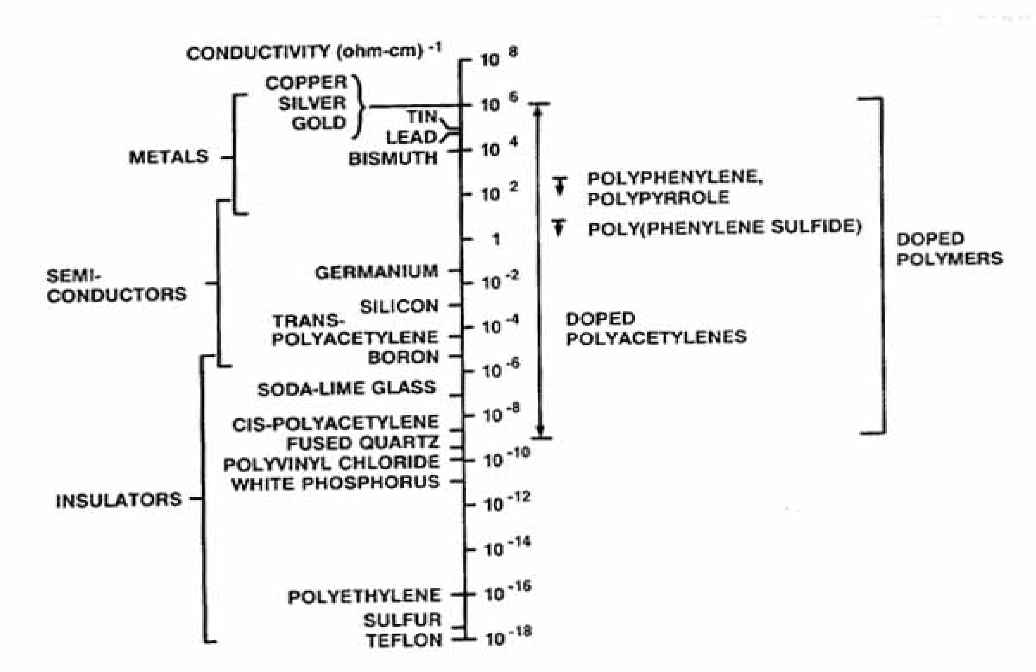


Figure 1.3: Comparison of conductivities

1.3.2 Doping

The semiconductor band structure of CPs permits electronic excitation or electron removal /addition, which results in properties of CP of interest. Excitation of electrons form valence band to the conduction band yields typical excited state properties such as photoluminescence and nonlinear optical properties.

Chemical and electrochemical oxidation of CP leads to the presence of charges on CPs, which is strongly delocalized over several monomer units in the polymer. It is also possible that these charges cause a relaxation of geometry of the polymer to a more energetically favored conformation. By donation of a charge to the conduction band, the CPs can be reduced.

The conductivity of a polymer can be increased several-fold by doping it with oxidative/reductive substitutents or by donor/ acceptor radicals. Shirakawa and Ikeda [25] discovered that doping of polyacetylene with metallic regimes increases its conductivity by 9-13 orders of magnitude. Doping is accomplished by chemical methods of direct exposure of the conjugate polymer to a charge transfer agent in the gas or solution phase, or by electrochemical oxidation or reduction. Doping is defined as the chemical oxidation of the CPs by anions or its reduction by cations. The associated anions/ cations are referred as dopants. A CP in its undoped state is termed pristine. The doping is usually quantitative and the carrier concentration is directly proportional to the dopant concentration. Doping of conductive polymer involves random dispersion or aggregation of dopants in molar concentrations in the disordered structure of, polarons and bipolaron in the polymer chain [26]. The extent of oxidation/reduction is called doping level, which is generally measured as the proportion of dopant ions or molecules incorporated per monomer unit. Increased doping level leads to higher conductivity by the creation of more mobile charges.

The maximum doping levels are different for different CPs and different dopants. Doping agents are either strong reducing agents or strong oxidizing agents. The nature of dopants plays an important role in the stability of conductive polymers. For example, perchloric acid doped polyacetylene is not sensitive to water and oxygen. Similarly, electrochemical doping of polyacetylene with sodium fluoride makes it more resistant to oxygen.

1.3.3 Charge Defects in Conjugated Polymers

The Band Theory is not sufficient to explain the electrical conduction behavior of CPs. The concept of solitons, polarons and bipolarons has been proposed to get better understanding on the conduction mechanism of CPs [21].

When polymers are doped, conjugational defects e.g. solitons, polarons and bipolarons are formed in the polymer chain. Oxidation of the polymer breaks one double bond leaving a radical and a positive charge on the polymer chain, which is referred as polaron. Another charge defect is soliton, which is subdivided into three categories: Neutral soliton, positive soliton and negative soliton. In neutral soliton, energy level is singly occupied and therefore, the spin has the value of ½. Neutral solitons have spin but no charge. The positively soliton is obtained by the insertion of acceptor band (p-type doping) or electrochemical oxidation, where an electron is removed. By the insertion of donor band, an electron is added, which results in the generation of negatively charged soliton Figure 1.4.

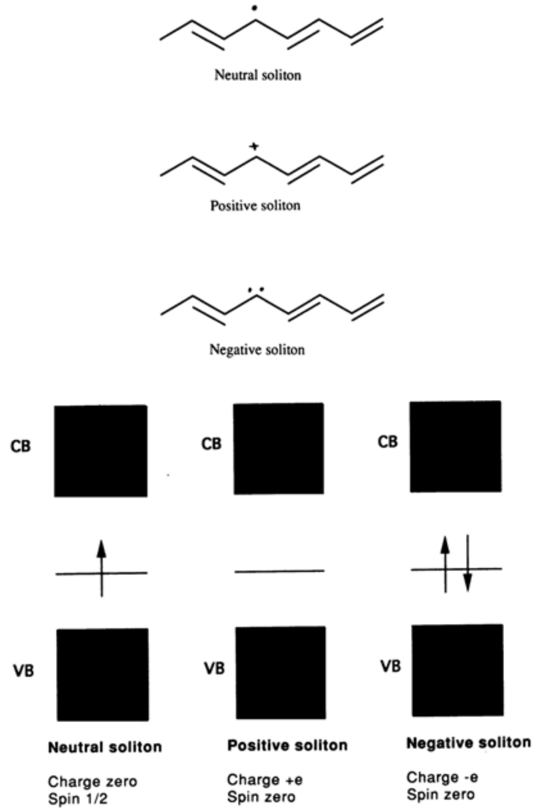


Figure 1.4: Soliton structures of polyacetylene

Polarons are obtained as a combination of a neutral and a charged soliton on the same polymer chain with a minimum energy configuration. Unlike solitons, polarons must overcome an energy barrier before it can move. It undergoes a hopping process both along the chain and between the chains. Polaronic defects can be delocalized over approximately five ring units in the chain. Polarons converge into bipolarons when the concentration of polarons gets high enough for the polarons to feel each other, i.e., the radical cations spread out through adjacent Π structure across about 8 bond lengths make contact with another radical cation. The combinations of these two radicals generate a new Π bond, which is more stable than two polarons at the same distance apart Figure 1.5.

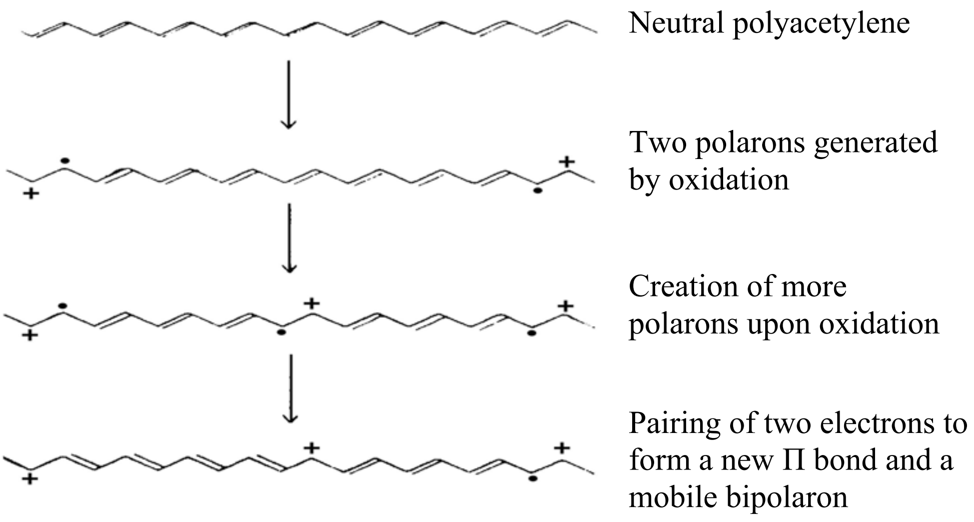


Figure 1.5: Schematic representation of polaron and bipolaron formation in polyacetylene

Upon increasing oxidation level, the polarons get closer to each other to form Π bonds and the remaining positive charges achieve high mobility along the chain [27]. At this point, remarkable increase is observed in the conductivity.

1.4 Synthesis of Conducting Polymers

Conducting polymers can be synthesized by both chemical and electrochemical polymerization techniques. Other than these two techniques, synthesis of CPs via photochemical polymerization, metathesis polymerization, solid state polymerization and plasma pyrolysis are also possible.

1.4.1 Chemical Polymerization

Among all the above categories, chemical polymerization [28-31] is the most useful technique for preparing large amounts of conductive polymers, since it is performed without electrodes [19, 32]. Chemical polymerization (oxidative coupling) is followed by the oxidation of monomers to a radical cation and their coupling to form dications and repetition of this process generate a polymer. All the classes of conjugated polymers can be synthesized by this technique.

In this method, a stoichiometric amount of oxidizing agent is used to form the polymer in its doped form. Heterocyclic monomers are usually polymerized with $FeCl_3$ as the oxidant [33-34]. Reduction to the neutral state is accomplished by addition of a strong base such as ammonium hydroxide or hydrazine.

This method has the advantage of low-cost production. By this method, one obtains the products in powder form, which decreases the inherent properties of materials such as conductivity. During the chemical polymerization of heterocycles, there are many side reactions taking place.

1.4.2 Electrochemical Polymerization

Electrochemical anodic oxidation is the most widely used technique to prepare polyheterocyclics of high conductivity. It is an efficient method to synthesize smooth polymer films on conductive substrates. Polymer films can be obtained on the electrode surface and can be easily peeled off from the surface to yield free-standing, electrically conducting films, which are homogenous.

Applied potential, supporting electrolyte, solvent medium, temperature and type of electrode [35] are the most important factors affecting electrochemical polymerization. This technique offers the advantage of accurate control of oxidation potential at which the polymerization takes place and thickness of the films. Thus, it is possible to produce a variety of different conducting polymers prepared from the same monomer by simply varying specific electrochemical parameters.

Moreover, electrolysis can be carried out at room temperature. It is a rapid, simple, selective and reproducible technique.

Besides its advantages, electrochemical polymerization technique has some drawbacks. Products are insoluble films, which makes it difficult to modify the primary structure. Characterization of electrochemically prepared films is impossible by the most standard techniques for molecular weight and structure determination.

1.5 Electrochemical Techniques

Two methods can be used for preparative-scale electrolysis: constant current and constant potential electrolysis.

1.5.1 Constant Current Electrolysis (Galvanostatic)

In this technique, two electrodes are used, which are counter and working electrodes. A direct current of fixed magnetitude is passed between the anode and cathode for the necessary time. The disadvantage of this technique is that some unwanted species are formed during the course of polymerization.

1.5.2 Constant Potential Electrolysis (Potentiostatic)

Constant potential electrolysis consists simply of an experiment in which electrochemical reaction is allowed to proceed to completion at an electrode whose potential is held constant. By keeping the potential at the desired value, unwanted side reactions can be avoided.

It is carried out in a three-electrode system (working, counter and reference electrodes), which ensures effective potential control and maximize the reproducibility of the polymerization process. The positioning of the auxiliary electrode is critical since it determines the electrical field generated, which can influence the quality of the polymer. The nature of the polymer is affected by the geometry of the electrodes as well as the distance between them. Isothermal conditions must be maintained since slight changes in temperature may result in undesired side-reactions such as the reaction of oxygen in medium with the radicals [36].

1.6 Cyclic Voltammetry

Cyclic Voltametry is a simple method, which is capable of providing a great deal of useful information about the electrochemical behavior with little experimental effort. The applied voltage to the working electrode is in the form of triangular wave function and the current response is plotted as a function of applied potential by a recorder.

The shape of cyclic voltammogram is highly dependent on the relative rates of electron transfer, mass transport and any chemical reactions taking place at the electrode surface, which permits us to deduce a great deal about electroactivity of materials, redox potentials, and mechanism of electrochemical reaction and reversibility of an electron transfer.

1.7 Mechanism of Electrochemical Reaction for Heterocyclic Monomers

Electrochemical polymerization is achieved by placing the monomer in a suitable solvent-electrolyte medium and applying a mild potential. There are many mechanisms of polyheterocyclics proposed by many scientists [37].

The polymer chains consist of linked aromatic units which in the case of pyrrole and thiophene are primarily 2,5-coupled. The first step of electrochemical polymerization process involves the removal of an electron from a monomer unit to form a radical action at the suitable electrode potential. Then, there exist two possible pathways. First one is the coupling of radical cation with monomer to generate a radical cation dimer, which loses another electron before losing two protons to form neutral dimer [38]. The second pathway includes the coupling of two radical cations to form a neutral dimer [39-41]. This process is followed by the oxidation of one monomer unit of dimmer. The dimer radical cation will continue to undergo further coupling with monomer radical cation to generate trimer, tetramer, etc. Consequently, the polymerization proceeds through successive electrochemical and chemical steps until oligomer become insoluble in the medium and polymer film deposits on the electrode surface. Generation of the monomer radical cation is slow since monomer has a higher oxidation potential than that of dimers and oligomers. However, the radical-radical coupling, deprotonation and subsequent constitutes the fast steps [42]. The proposed mechanism for heterocyles is shown in Figure 1.6.

1.8 Electrolytic Conditions

The physical properties of polymers synthesized by electrochemical polymerization technique is affected by many parameters such as solvent, electrolyte, temperature, nature of electrode potential, concentration of monomer and oxidation potential.

The electropolymerization reaction is sensitive to nucleophilicity of the environment in the region near the electrode surface since the reaction proceeds via radical cation intermediates, which limits the choice of solvent and electrolyte. Therefore, many studies have been performed in aprotic solvents, which are poor nucleophiles. Acetonitrile is most commonly used solvent. By the choice of electrolyte salt, the solubility, degree of dissociation and nucleophilicity should be considered. Most of the salts used are tetraalkylammonium salts since they are soluble in aprotic solvents, have high degree of dissociation and a wide potential window.

Selection of electrode is important for electrochemical polymerization. Since the polymerization proceeds via oxidation and reduction reactions, the electrode should not be oxidized or reduces. Electrodes like Pt, Au, ITO, stainless steel and SnO_2 substrates are suitable. As reference electrode saturated calomel electrode (SCE), Ag/Ag^{+1} and Ag/AgCl electrodes can be used.

The electrolysis potential should be also carefully controlled since high potentials may lead to the breakdown of electrolytes [43].

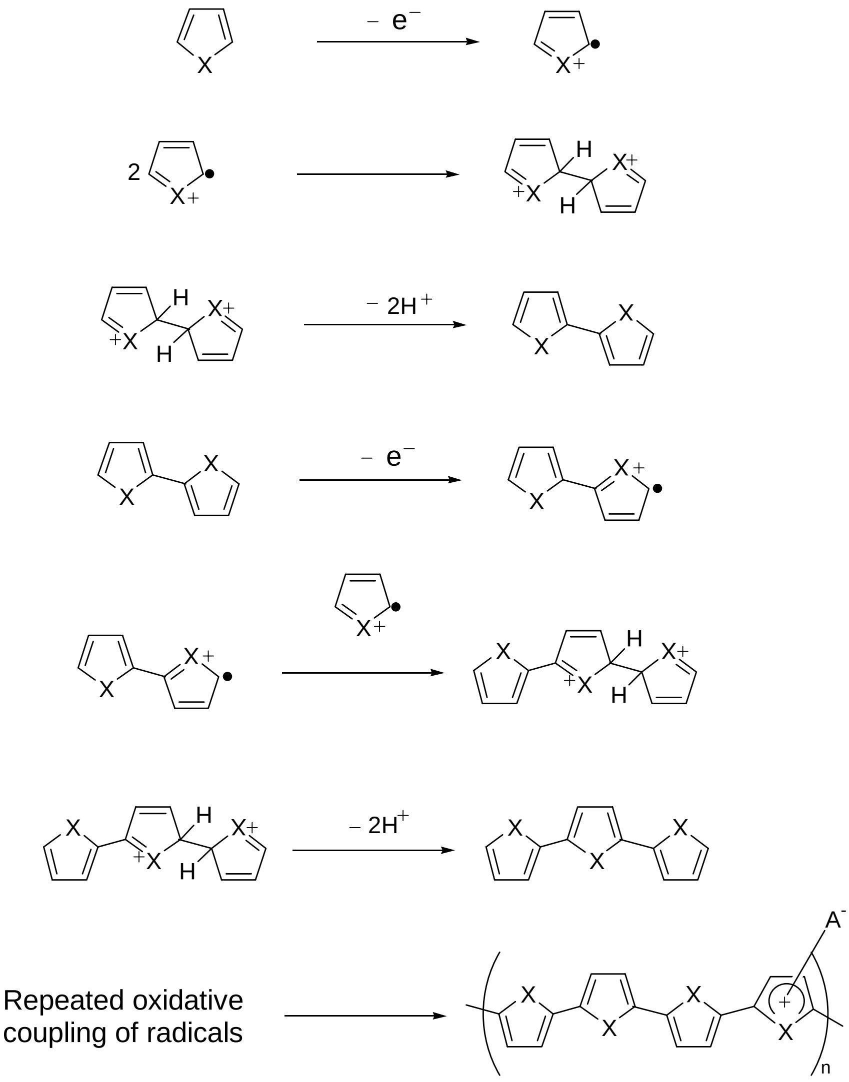


Figure 1.6: Electrochemical polymerization mechanism proposed for heterocycles

One should also pay attention to the temperature during electrochemical polymerization. With increasing temperature, it is possible that the conductivity and yield decreases. Temperature promotes termination step and therefore, oligomers with small conjugation length are formed instead of being deposited as an insoluble polymer at the electrode surface [44].

1.9 Electrochromism of Conducting Polymers

Conducting polymers represents an attractive class of electrochromic materials owing due to their facile switching properties, processibility, and controllable optical properties [45-47]. An electrochromic material is one that changes color in a persistent but reversible manner by an electrochemical reaction. Conjugated polymers can be repeatedly driven from insulating to conductive states electrochemically with high contrast in colour, which makes them promising materials for electrochromic device technology [47].

The color change is due to the electrochemical p-doping-undoping process. Upon switching of conjugated polymers between insulating and conductive states, color change is observed. The oxidation-reduction reaction involves ion transport into or out of the polymer matrix to balance the electronic charge.

Conjugated polymers have an electronic band structure. The energy gap between the highest occupied Π electron band and the lowest unoccupied band determines the intrinsic properties of the polymer. Observation of color change upon doping is due to the modification of the band structure of polymer. Charge is created upon this process, which is followed by the generation defects. These defects are responsible for the creation new electronic states in the gap, which causes color changes. As doping level increases the bipolaron states overlap in bipolaron bands, the bipolaron bands may emerge with valence and conduction bands (Figure 1.7).

Doping shifts the absorption towards the lower energies, and the color contrast between doped and undoped forms of the polymer depends on the magnetitude of the energy gap of the undoped polymer.

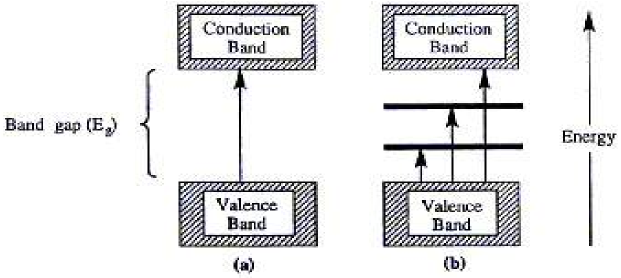


Figure 1.7: Schematic representation of conduction and valence bands of (a) undoped (b) doped form of a polymer

A great variety of color contrast can be achieved by using conducting polymers. E_g is related to the mean conjugation length of the polymer and different polymerization routes and different experimental conditions such as current density, starting molecule concentration, electrolytic medium, and temperature.

UV-visible spectroscopy provides a method for comparing the conductivity of conducting polymer thin films as there is a direct relationship between conductivity and tail of the absorbance in the near-infrared (NIR) corresponding to the transitions associated with the charge carriers as reported previously for PPy [48-50].

1.10 Aim of the study

The aim of this study is to synthesize thiophen-3-yl acetic acid 4-pyrrol-1-yl phenyl ester (TAPE) monomer, its conducting polymers both by using chemical and electrochemical polymerization techniques, to characterize the monomer and polymers by common characterization techniques and to investigate electrochromic and spectroelectrochemical properties of TAPE/BiTh copolymer.

CHAPTER II

EXPERIMENTAL

2.1 Materials

4-pyrrol-1-yl phenol (Aldrich), 3-thiophene acetic acid (Aldrich), thionyl chloride (Aldrich), pyrrole (Aldrich), 2,2’-bithiophene (Aldrich), triethylamine (TEA) (Merck), dichloromethane (DCM) (Merck), methanol (Merck), acetonitrile (ACN) (Merck), tetrachloromethane (Riedel-de-Haen) and nitromethane (Aldrich) were used without further purification. Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich) and ferric chloride (Aldrich) were used as received.

2.2 Instrumentation

2.2.1 Potentiostat

A Wenking POS 73 Potentiostat was used for the supply of a constant potential in the electrochemical polymerization. By this device, one can maintain the voltage difference between the working and reference electrodes at a constant desired value during electrolysis.

2.2.2 Cyclic Voltammetry System

Electroactivity of materials were examined by cyclic voltammetry. The cell of cyclic voltammetry system consists of a platinum bead working electrode of 1 cm length, a platinum spiral counter electrode made from 3 cm wire, and Ag/Ag^+ reference electrode. The cell had a total volume of about 20 mL. Voltage was provided by Wenking POS 2 potentiostat, and voltammograms were obtained by the help of an X-Y recorder.

2.2.3 Electrolysis Cell

Electrolysis were performed in a one-compartment cell with two platinum (Pt) foil electrodes as working and counter electrodes and a silver (Ag) wire as the reference electrode.

2.2.4 Nuclear Magnetic Resonance (NMR)

^1H-NMR and ^{13}C-NMR spectra were investigated on a Bruker-Instrument-NMR Spectrometer (DP-400) instrument.

2.2.5 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra of the monomer (TAPE), polymer (polyTAPE) and copolymers were recorded on a Nicolet 510 FTIR spectrometer.

2.2.6 UV-VIS Spectrophotometer

Spectroelectrochemical studies were carried on a HP8453A UV-VIS spectrophotometer.

2.2.7 Differential Scanning Calorimetry (DSC)

Thermal analysis was performed on a Du Pont 2000 instrument.

2.2.8 Thermal Gravimetry Analysis (TGA)

A Perkin Elmer TGA instrument was used to examine the thermogravimetry analysis; weight loss was followed upon heating.

2.2.9 Scanning Electron Microscope (SEM)

Surface Morphologies of polymer and copolymer films were examined by JEOL JSM-6400 scanning electron microscope.

2.2.10 Two-Probe Conductivity Measurements

Conductivity measurements were carried out by two-probe technique.

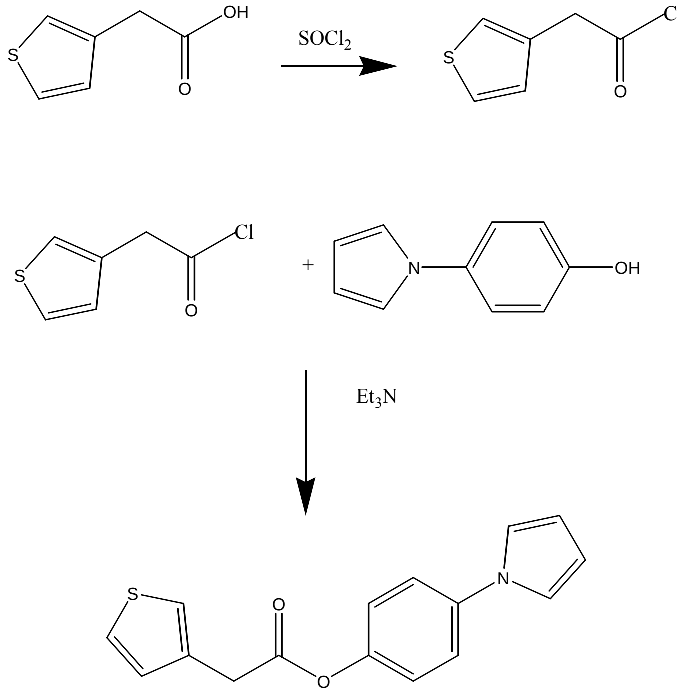
2.2.11 Colorimetry Measurements

Colorimerty measurements were done with a Coloreye XTH Spectrophotometer (GretagMacbeth).

2.3 Procedure

2.3.1 Synthesis of Monomer

3-thiophene acetic acid (0.007 mole, 1.02 g) was dissolved in 10 mL dichloromethane and further reacted with excess thionyl chloride (0.014 mole, 1.02 mL), where thionyl chloride was added dropwise by cooling in ice bath (0 °C). The chlorination reaction was carried out for over night at room temperature, which yields 3-chloro acetic acid as product of 1.04 g solid (yield 92 %). 4-pyrrol-1-yl-phenol (0.0065 mole, 1.03 g) was dissolved in 10 mL DCM and cooled to 0 °C. Later, triethylamine (TEA) (0.008 mole, 1.1 mL) was added. The esterification reaction was started with the addition of this mixture to the product obtained in first step. This reaction was let to stand overnight at room temperature. The product was dissolved in 50 mL DCM and extracted with NaOH (10 % v/v) twice. The organic layer was dried over $CaCl_2$ and the solvent was removed by rotaevaporatory. The final product was of 1.0 g solid (yield: 54 %). The schematic representation of synthesis procedure is given in Scheme 2.1.



Scheme 2.1 Synthesis route of TAPE monomer

2.3.2 Synthesis of Copolymers of TAPE with Bithiophene

The potentiostatical polymerization of TAPE with bithiophene was carried out in a one-compartment cell with two platinum foils as the working and counter electrodes and Ag/Ag^{+1} as the reference electrode. 35 mg of TAPE and 35 mg bithiophene were dissolved in 20 mL ACN. Tetrabutylammonium fluoroborate (TBAFB; 0.1 M) was used as the supporting electrolyte. Electrolysis was performed at 1.4 V and it was allowed to proceed until black polymer films are formed (1hr). After electrolysis, films are washed with ACN several times to remove unreacted monomer.

2.3.3 Synthesis of Copolymers of TAPE with Pyrrole

The potentiostatical polymerization of TAPE with pyrrole was carried out in a one-compartment cell with two platinum foils as working and counter electrodes and Ag wire as the reference electrode. Firstly, 100 mg monomer was dissolved in 20 mL ACN and 0.1 M TBAFB was used as supporting electrolyte. Electrochemical polymerization was started by applying of 1.2 V vs Ag wire reference electrode. After 5 minutes, 30 μL pyrrole were introduced to electrolysis medium. After electrolysis, films were washed several times with ACN to hinder the presence of unreacted monomer.

2.3.4.Homopolymerization of TAPE

Homopolymerization of TAPE was achieved potentiostatically. Homopolymerization of TAPE was carried out in the presence of 100 mg monomer dissolved in 20 mL ACN and 0.1 M. TBAFB supporting electrolyte. The polymerization reaction was allowed to proceed at 1.5 V for 2 hr. ACN was used to wash the films after electrolysis.

2.3.5 Chemical Polymerization of TAPE with Ferric Chloride

Homopolymerization of TAPE was also achieved by chemical polymerization. To carry out the oxidative polymerization of TAPE, monomer ($3.53\text{x}10^{-4}$ mole, 0.1 g) was dissolved in 5 mL CCl_4 at 0 °C $FeCl_3 \cdot 6H_2O$ ($14.12\text{x}10^{-4}$ mole, 0.38 g) was dissolved in 15 mL CH_3NO_2, which was later added to the monomer solution dropwise. The reaction was carried out for 24 h with constant stirring. Methanol was used as the nonsolvent and a black solid product was obtained after filtration. Resultant product was insoluble and infusible.

2.3.6. Electrochromic Studies and Spectroelectrochemistry

To carry out spectroelectrochemical and electrochromic studies, copolymer films were synthesized on indium tin oxide (ITO) coated glass in a strong Lewis acid, boron fluoride-ethyl ether BF_3Et_2O (BFEE) by potentiostatic methods. Copolymer films deposited on ITO-coated glass were used both for spectroelectrochemistry and electrochromic measurements in TBAFB (0.1M)/ACN with a silver wire as the reference electrode and a Pt wire as the auxiliary electrode. Films were deposited on ITO coated glass and dried under atmospheric conditions.

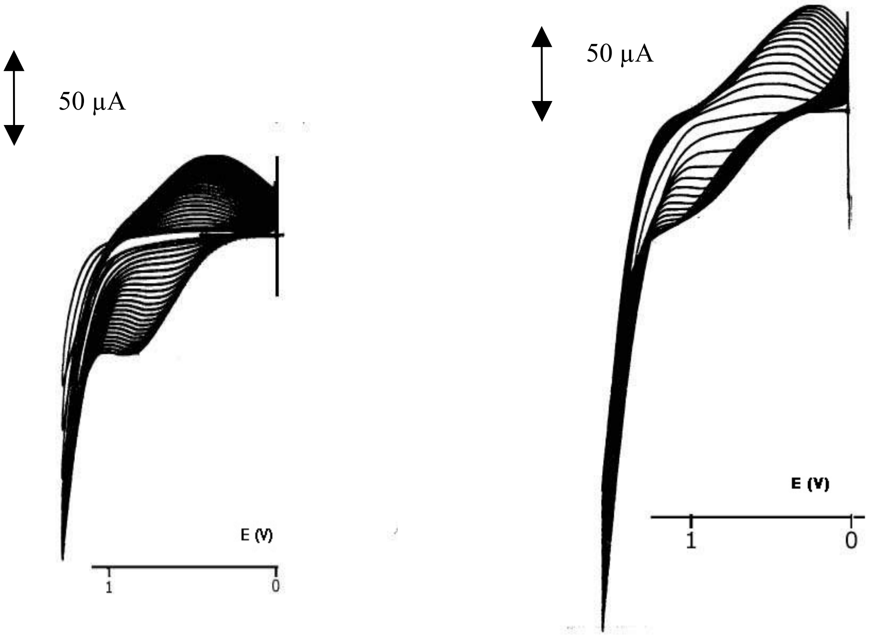
CHAPTER III

RESULTS AND DISCUSSION

3.1. Cyclic Voltammetry

The oxidation/reduction behavior of monomer (TAPE), TAPE in the presence of bithiophene and pyrrole was investigated by cyclic voltammetry. Cyclic voltammetry measurements were done in ACN-TBAFB solvent-electrolyte couple at room temperature.

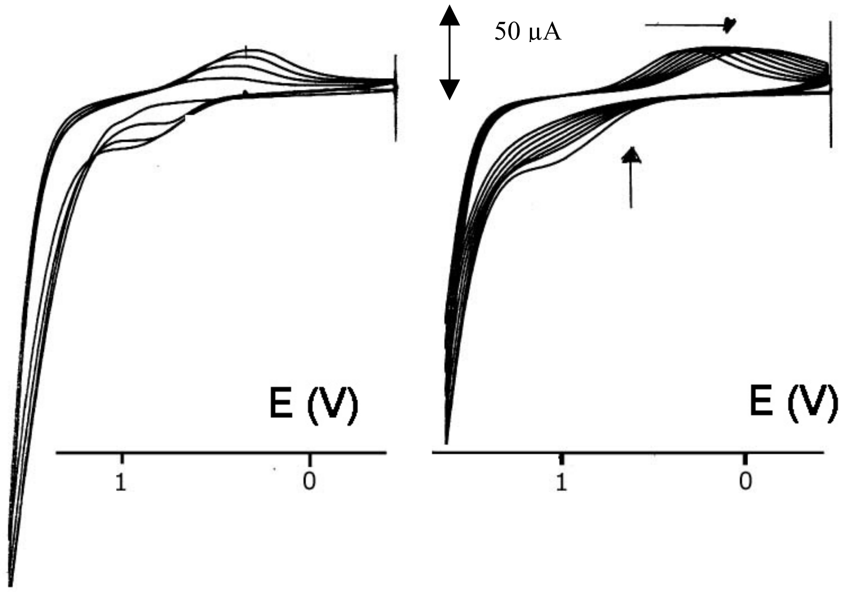
Cyclic voltammogram of homopolymer of TAPE in acetonitrile showed an oxidation peak at 0.8 V and a reduction peak at 0.4 V implying that TAPE is an electroactive substance. Several cyclic voltammograms were taken by application of different potentials. When the regions from 0 V to 1.3 V (Figure 3.1a) and to 1.5 V (Figure 3.1b) were studied, it is seen that the electroactivity increases with increasing scan number.



(a) (b)

Figure 3.1: Cyclic Voltammograms of TAPE in scan range (a) 0-1.3 V (b) 0-1.5 V

Cyclic voltammograms from -0.5 V to 1.7 V showed both an oxidation and reduction peak, which increases in height during the first six runs (Figure 3.2a). However, after the sixth run the disappearance of the oxidation peak and a shift for the reduction peak were observed (Figure 3.2b).

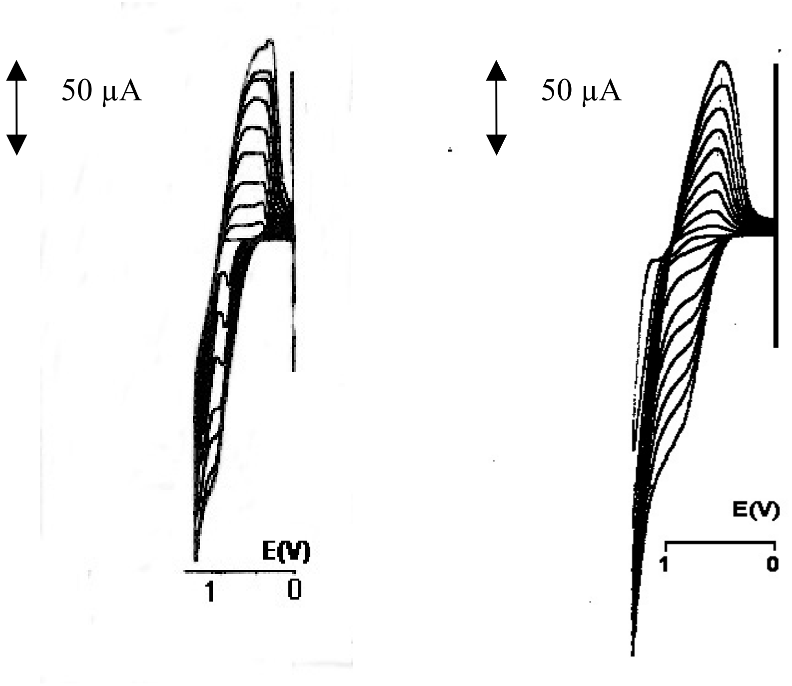


(a) **(b)**

Figure 3.2: Cyclic Voltammograms of TAPE in scan range (-0.5-1.7 V) (a) first six runs (b) after the sixth run

To determine the route of polymerization, oxidation/reduction behavior of starting materials namely 4-pyrrol-1-yl phenol and thiophen-3-yl acetic acid were investigated. It was observed that thiophen-3-yl acetic acid (Appendix A) has an oxidation peak at 1.9 V. On the other hand, 4-pyrrol-1-yl phenol (Appendix A) revealed oxidation and reduction peaks at 0.5 V and 0.4 V respectively. This implies that homopolymerization goes from the pyrrole moiety of TAPE since the applied voltage is only enough for generation of pyrrole radical cation. Since the applied voltage was increased, overoxidation of pyrrole unit takes place yielding a decrease in electroactivity after the sixth run for TAPE when a potential of 1.7 V is applied (Figure 3.2b).

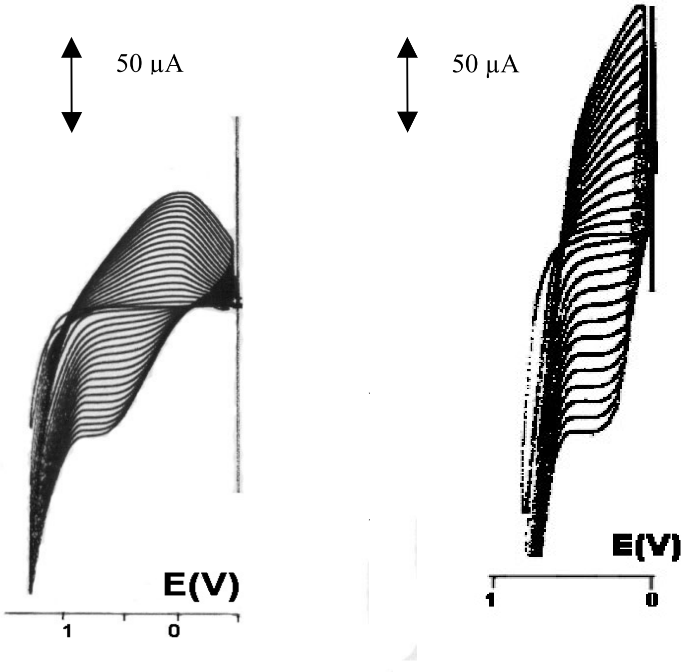
After the addition of bithiophene to the solution, an oxidation peak at 0.7 V and a reduction peak at 0.6 V were observed revealing an increase in height with increasing scan number (Figure 3.3b) This redox behavior is completely different than that of pure polybithiophene, which has oxidation and reduction peaks at 1.25 V and 0.5 V respectively (Figure 3.3a). This huge difference in CVs may indicate an interaction between TAPE and bithiophene, possibly a copolymer formation. BiTh was preferred instead of thiophene since lower potential is required for its oxidation, which enabled the polymerization to be performed under milder conditions that will decrease the probability of overoxidizing the monomer during the polymerization.



(a) **(b)**

Figure 3.3: Cyclic Voltammograms for (a) BiTh (b) TAPE/BiTh

CV of TAPE in the presence of pyrrole revealed an oxidation peak at 0.6 V and a reduction peak at 0.1 V (Figure 3.4a). Addition of pyrrole to the reaction medium made also a significant difference compared to that of poly(TAPE) (Figure3.1a) and pure polypyrrole (Figure 3.4b) cyclic voltammogram. The above argument about a possible interaction between TAPE and pyrrole may also be valid in this case.

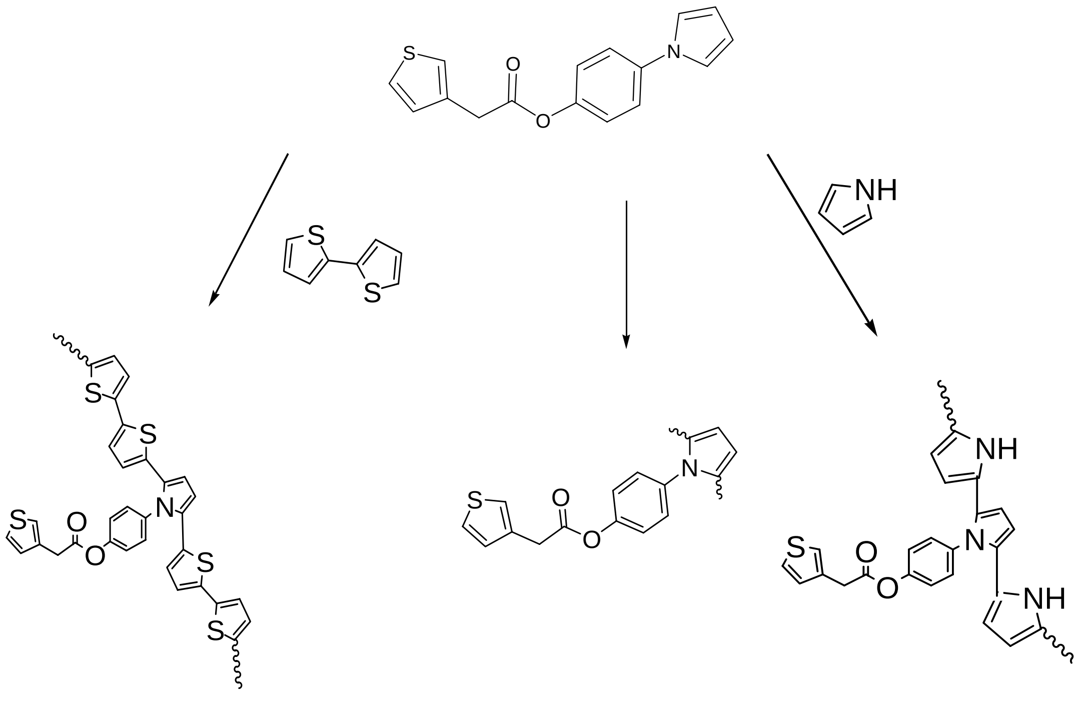


(a) (b)

Figure 3.4: Cyclic Voltammograms for (a) TAPE/Py (b) Py

3.2. Characterization

Homopolymers of TAPE were synthesized both by electrochemical and chemical polymerization methods successfully. Moreover, electrochemical polymerizations of TAPE in the presence of bithiophene and pyrrole were tried, and both of them were successful in ACN/ TBAFB solvent-electrolyte couple (Scheme3.1).



Scheme 3.1: Synthesis route for conducting poly(TAPE) and copolymers of TAPE with bithiophene and pyrrole

3.2.1 NMR

NMR spectra of monomer were taken by using $CDCl_3$ as the solvent and chemical shifts (б) are given relative to tetramethylsilane as the internal standard.

^{1}H-NMR spectrum of monomer (Figure 3.5): ^{1}H-NMR (б, ppm): 7.0 (m, 2H) and 6.2 (m, 2H) from pyrrole ring, 7.2 (m, 2H) and 7.3 (m, 2H) from benzene ring, 6.8 (m, 1H), 6.85 (m, 1H) and 7.1 (m, 1H) from thiophene ring and 3.9 (s, 2H) from CO-CH_2.

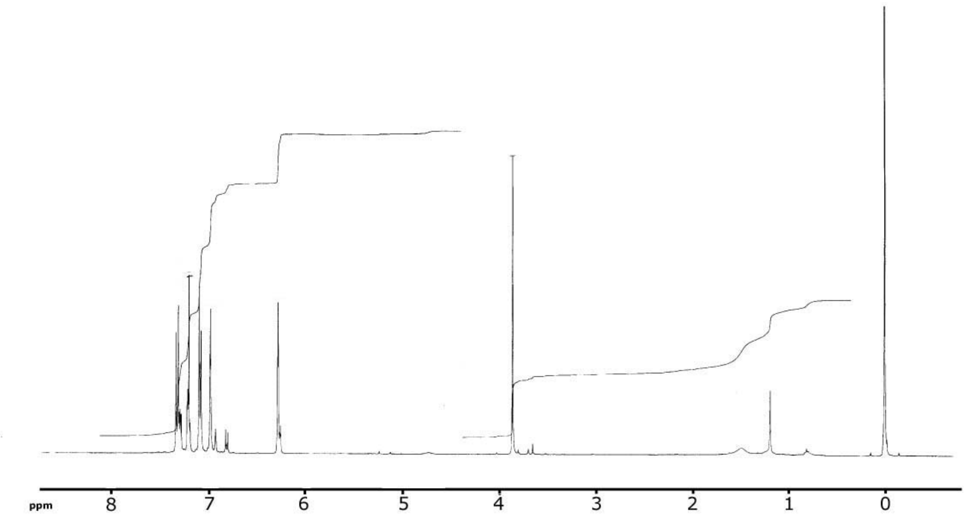


Figure3.5: ^{1}H-NMR spectrum of the monomer

^{13}C-NMR spectrum of the monomer (Figure 3.6): ^{13}C-NMR (б,ppm): 168 from CO, 122, 121 from benzene ring, 118, 109 from pyrrole ring,127, 131 from thiophene ring, 34 from the aliphatic group and 100 due to CCl_4 added to decrease the concentration of the sample.

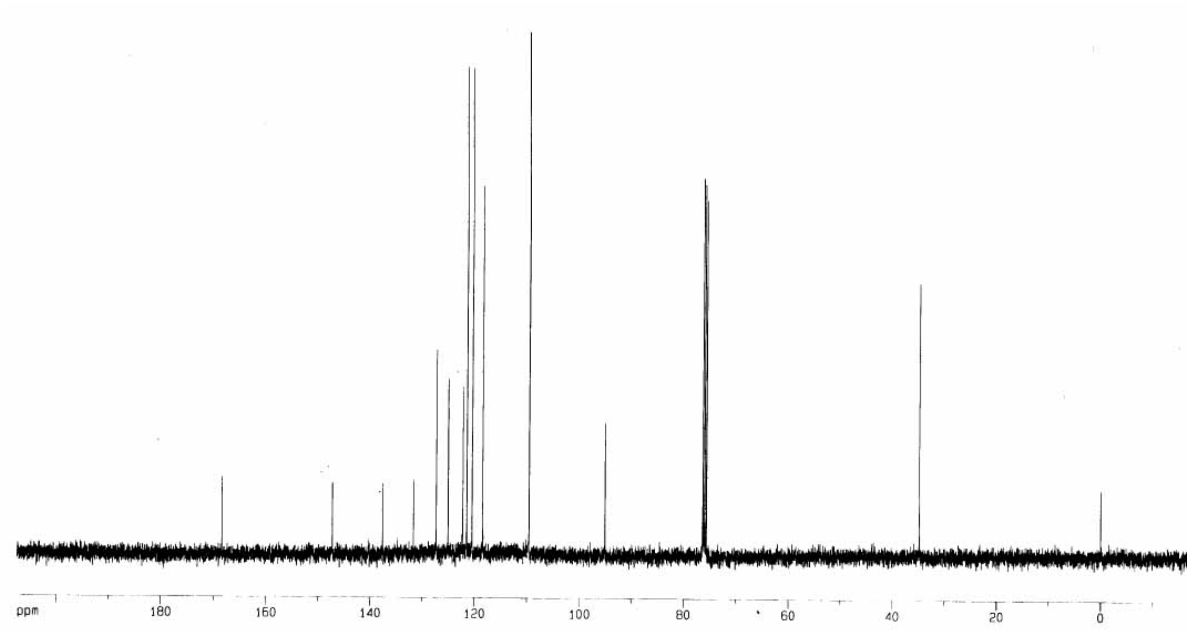


Figure 3.6: ^{13}C-NMR spectrum of the monomer

3.2.2 FTIR

FTIR spectrum of monomer (Figure 3.7) exhibits some characteristic features of N-substituted pyrroles. The absorption bands at 720, 3157 and 3131 are due to the in phase cis out-of-plane movement of HC=CH; bands at 1012 and 1071 cm^{-1} correspond to C-H strecthings of N-substituted pyrroles [51,55]. The intense peak at 1753 cm^{-1} may be attributed to the C=O stretching vibrations and C-O-C stretching vibrations are observed in the region of 1100-1204 cm^{-1}. The absorption band at 699 and 1548 cm^{-1} indicates the presence of benzene ring. Absorption bands in the region of 808-857 cm^{-1} may be due to the thiophene moiety.

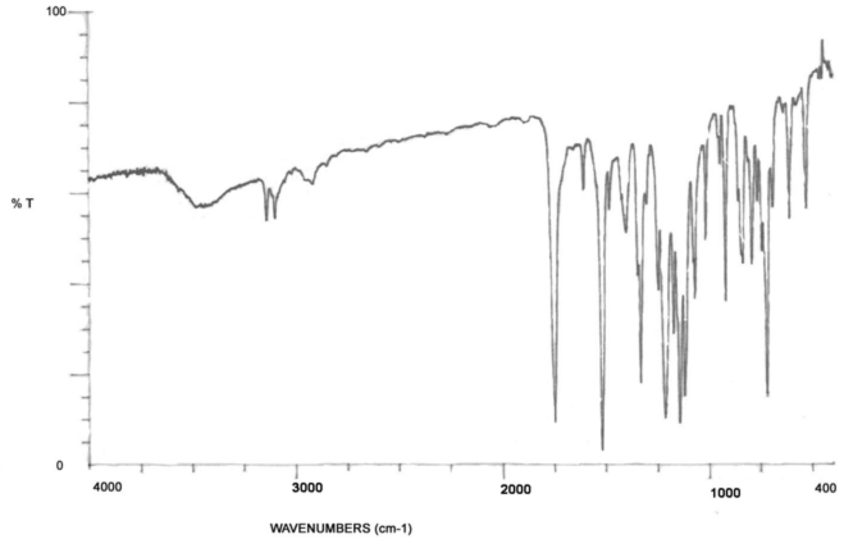


Figure 3.7: FTIR spectrum of monomer

After homopolymerization of TAPE, band at 720 cm^{-1} due to out-of-plane bending or ring bending disappears. This is a characteristic feature of poly(N-substituted pyrrole)s [56]. On the other hand, an absorption peak at 840 cm^{-1} was observed. The presence of C=O group and benzene ring was confirmed by the presence of absorption bands at 1750 cm^{-1} and 1598 cm^{-1} respectively. Moreover, the shoulder at 1040 cm^{-1} reveals that dopant ion is present in the structure, which confirms that polymerization reaction took place (Appendix B).

After chemical polymerization of TAPE, a new band appears at 1616 cm^{-1} indicating the conjugation [57] in addition to characteristic bands of TAPE monomer. Besides, chemically synthesized poly(TAPE) was insoluble in common solvents such as ACN and DCM, in which the monomer was soluble. This may also indicate that chemical polymerization of TAPE was achieved.

FTIR spectrum of electrochemically synthesized copolymer of TAPE/BiTh (Appendix B) shows the presence of carbonyl group at 1753 cm^{-1}, and benzene ring was observed at 1548 cm^{-1}. Incorporation of tetrafluoroborate ions in the structure may be inferred by the presence of strong absorption peak at 1080 cm^{-1}. Other than these, ester groups were also observed. These results indicate that copolymers of TAPE with bithiophene were achieved because carbonyl functionality and benzene ring exist only in the monomer.

The characteristic functional groups of monomer were also present in FTIR spectrum of copolymer of TAPE with pyrrrole. No absorption bands are observed at 730, 3140, 1012 and 1071 cm^{-1}, which can be used as an evidence for the polymerization from 2, 5 positions of pyrrole ring [57].

3.2.3 Thermal Analysis

Thermal analysis of monomer and homopolymers were investigated by DSC in the range 30 ° C to 425 °C at a heating rate of 10 °C/min under N_2 atmosphere.

DSC thermogram of the monomer shows a sharp melting point at 88.5 °C. It is stable up to 210 °C and it begins to decompose at 210 ° C (Figure 3.8).

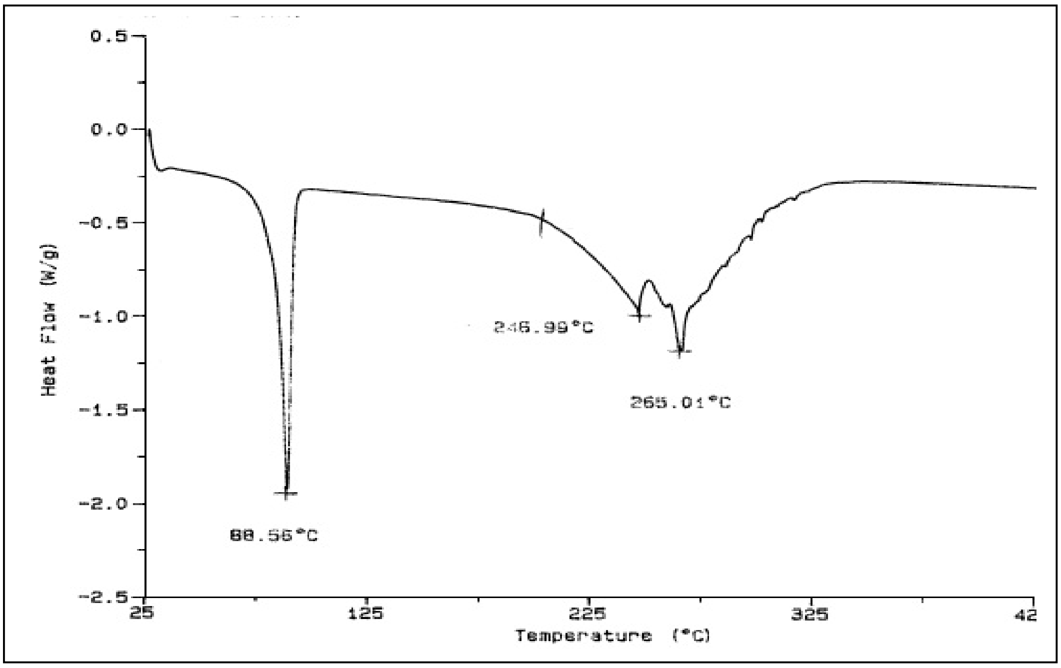


Figure 3.8: DSC thermogram of monomer

In DSC thermogram of homopolymer, there are two endothermic transitions at 65 °C and 86 °C due to removal of the solvent, ACN, and an endothermic transition at 383 °C corresponding to the decomposition of homopolymer (Figure 3.9). A broad shoulder starting at 190 °C was observed, which may be due to the formation of dopant based fragments. Upon heating, dopant fragments such as BF_3, BF_2 and HF are formed [58]. Moreover, this broad shoulder may also include the removal of low molecular weight species from the matrix.

TGA thermogram of homopolymer, poly(TAPE) showed weight loss at 193°C, which is due to the removal of dopant ion. Moreover, at 381 °C weight loss due to the decomposition of homopolymer was observed. The char residue is 47.71 % after heating to 830 °C (Figure 3.10). TGA thermogram of chemically synthesized poly(TAPE) revealed decomposition at 362 °C and upon heating to 830 °C, 18.29 % of the sample remained.

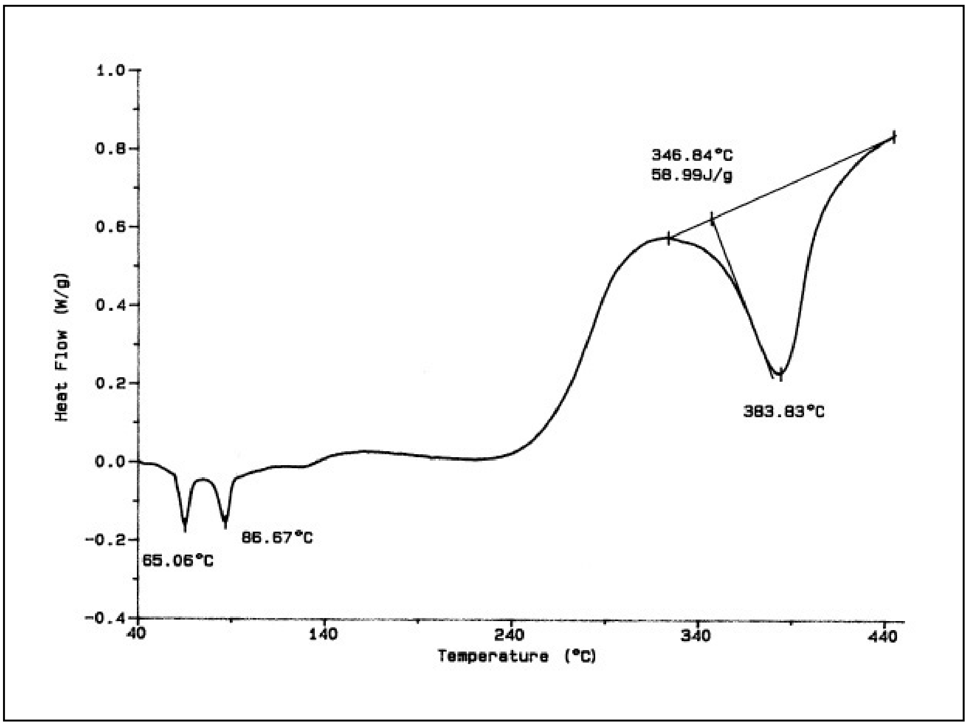


Figure 3.9: DSC Thermogram of homopolymer

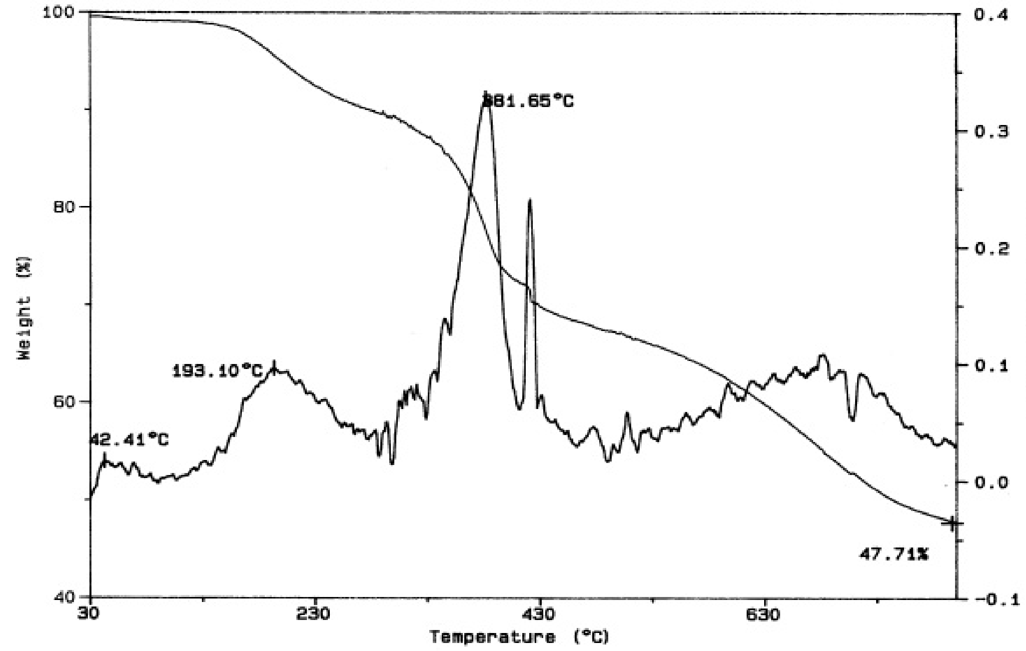


Figure 3.10: TGA Thermogram of homopolymer

For copolymer of TAPE with bithiophene, DSC thermogram revealed several endothermic transitions at 109 °C, 182 °C, 303 °C and 378 °C. The first transition may be attributed to the removal of solvent from the matrix, the second one is due to removal of tetrafluoroborate ions from the system, and last two transitions show the decomposition of the copolymer (Figure 3.11).

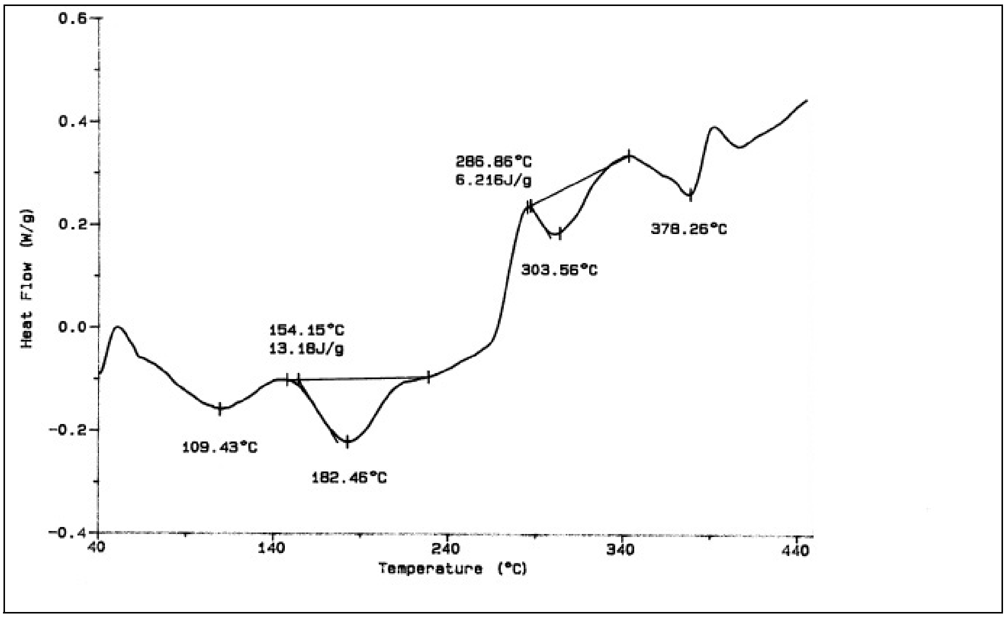


Figure 3.11: DSC Thermogram of TAPE/BiTh copolymer

TGA thermogram of TAPE/BiTh copolymer exhibited two transitions at 138°C and 374 °C, the first one may be due to removal of solvent or low molecular weight species from the matrix. The second transition is due to the decomposition of copolymer. 31.43 % of the sample remained after heating to 830 °C.

In the case of TAPE/Py copolymer, TGA thermogram showed decomposition at 390 °C. The char residue is 38.67 % after heating to 830 °C

3.2.4. Conductivity Measurements

Electrical conductivity measurements of copolymers were carried out by using two-probe technique. The conductivity of the homopolymer was measured via two-probe technique because of the poor quality of the films, which is in accordance with the literature. It has already been shown that N-substituted pyrrole monomers yield poor quality of electrically conducting polymer films when the substituent is ethyl or larger [59, 60]. Conductivity values of the samples are given in Table 3.1.

Table 3.1: Conductivities of poly(TAPE), poly(TAPE-co-BiTh),poly(TAPE-co-Py)

Sample	**Conductivity (S/cm)**
Poly(TAPE)	$2x10^{-10}$
Poly(TAPE-co-BiTh)	$1x10^{-6}$
Poly(TAPE-co-Py)	$5x10^{-6}$

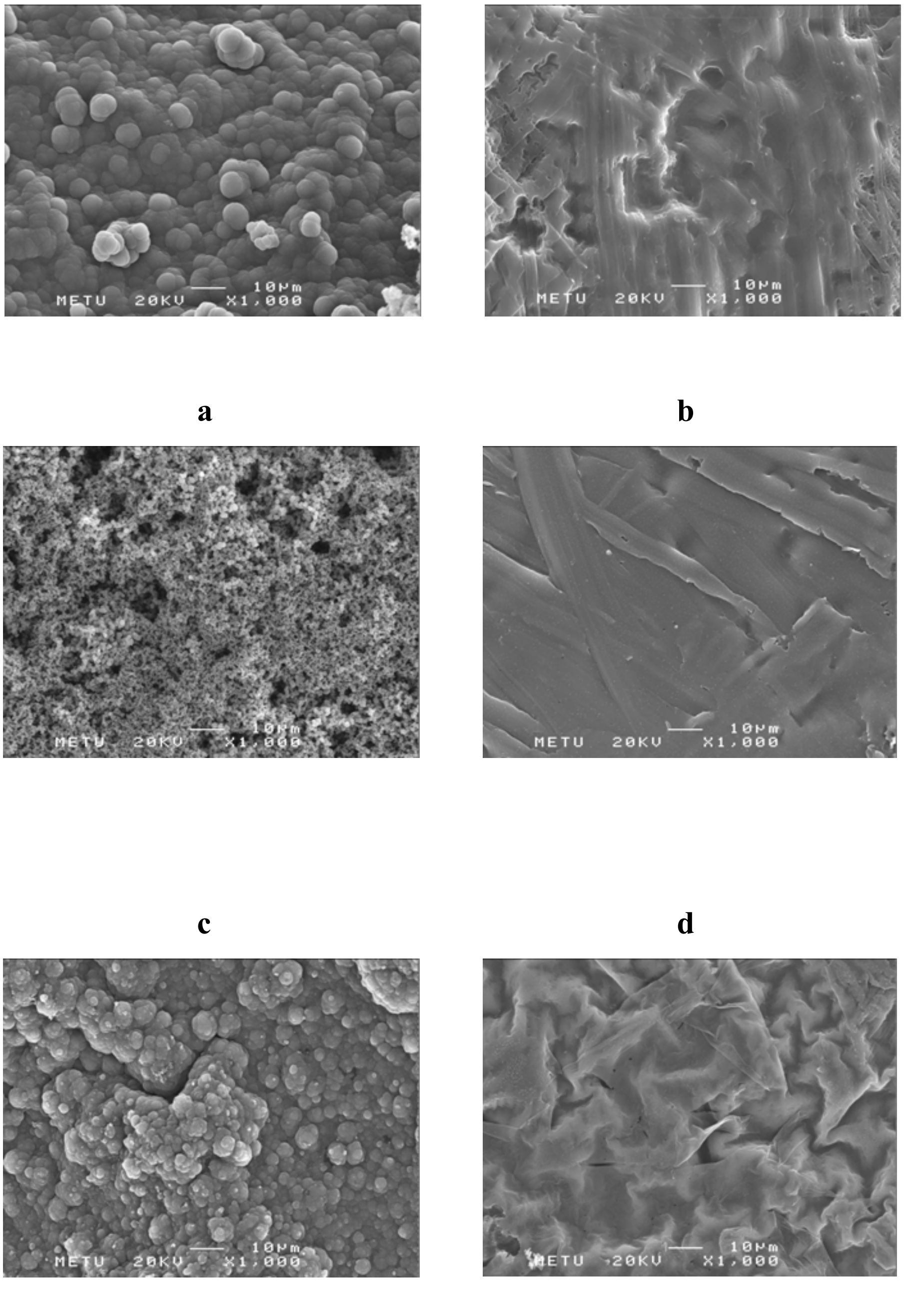
The order of magnititude of the conductivity of homopolymer was found as $2x10^{-10}$ S/cm. The best films were obtained from the polymerization of TAPE with Py, the conductivity of which was measured as $5x10^{-6}$ S/cm. The conductivity of both and electrode sides of poly(TAPE-co-Py) were in the same order of magnetitute, which reveals the homogeneity of the films. The conductivity of poly(TAPE-co-BiTh) was measured as $1x10^{-6}$. The low conductivities are in agreement with the previous results reported in the literature for poly(N-substituted pyrrole)s and its copolymers [56, 61, 62].The conductivity of homopolymer is improved by introduction of pyrrole and bithiophene to the matrix. The conductivity results of homopolymers and copolymers of TAPE may be used as evidence that polymers grow from the pyrrole moiety of the monomer.

3.2.5 Morphologies of Polymer Films

Surface morphologies of homopolymers and copolymers were investigated by Scanning Electron Microscope. SEM micrographs of solution sides and electrode sides differ from each other significantly. Some globule like droplets were observed on the solution side of poly(TAPE) film (Figure 3.12 a). On the other hand, electrode side of poly(TAPE) film has flat-plain structure with some cracks (Figure 3.12 b).

As far as SEM micrographs of copolymers of TAPE with BiTh are concerned, solution sides of copolymer films differ from those of pure polybithiophene considerably. This may be used as an evidence of the presence of an interaction of monomer (TAPE) with bithiophene. The surface of solution side of pure polybithiophene has a sponge like structure. The solution side of TAPE/BiTh films shows granular-like structure, whereas its electrode side is smooth (Figure 3.12 c and d).

In SEM micrographs the solution side of SEM micrographs of BF_4^- doped copolymers of TAPE with Py, a significant difference of morphology were observed compared to the cauliflower structure of pure Py, which might be arising from the copolymerization of TAPE with Py. The solution side of the polymer shows globule like droplets, which are significantly smaller than those of the solution side of poly(TAPE), which excludes the probability of synthesis pure poly(TAPE) (Figure 3.12 d and e).



a b

c d

e f

Figure 3.12: SEM Micrographs of a) solution side of poly(TAPE) b) electrode side of poly(TAPE) c) solution side of poly(TAPE-co-BiTh) d)

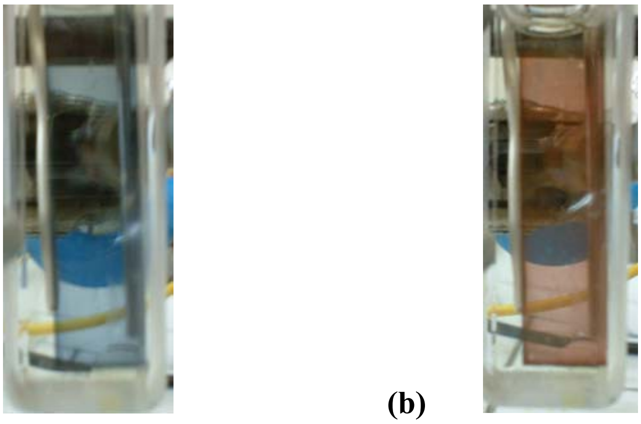
electrode side of poly(TAPE-co-BiTh) e) solution side of poly(TAPE-co-Py) f) electrode side of poly(TAPE-co-Py)

3.3 Electrochromic Properties

The electrochemical switching of the copolymer of TAPE with bithiophene was studied. The potentiodynamic electrochemical polymerization of TAPE with bithiophene was carried out in boron fluoride-ethyl ether (BFEE). The copolymer film was coated to an ITO electrode by application of +1.4 V vs. Ag/Ag$^+$ reference electrode. The same experiment was also carried out in ACN, where we obtained films of poor quality and inhomogeneous films on ITO electrode.

The electrochromism, optoelectrochemical analysis switching studies were performed in ACN /TBAFB (0.1M) solvent-electrolyte couple since polymer films redox cycled in BFEE exhibit ill-defined redox responses [63] and ACN is easier to handle compared to BFEE from the point of practical purposes.

Upon switching of copolymer film between -1.4 and + 1.4 V, transparent pale blue and brownish colors were observed for oxidized and reduced states respectively (Figure 3.13).



(a) **(b)**

Figure 3. 13: TAPE/BiTh films (a) fully oxidized state (b) fully reduced state

The color coordinates (L, a, b values) are given in Table 3.2. L is the relative luminance, and a,b-values are the x,y-coordinates of the chromaticity diagram. By increasing the positive applied potential, the polymer was oxidized and the x,y- coordinates decrease in value.

Table 3.2: λ_{max}, E_g, L, a and b values of poly(BiTh) and poly(TAPE-co-BiTh)

Polymer	**Λ_{max} (nm)**	**E_g (eV)**	**Color (red)**	**Color(ox)**	**L**	**a**	**b**
Poly(2,2'bithiophene)	480	1.1-1.2	Orange red	blue	(ox) 77	-11	-30
					(red) 60	10	22
Poly(TAPE-co-2,2'-bithiophene)	410	1.99	brownish	Pale blue	(ox) 84	5	-7
					(red)72	14	23

Optoelectochemical analysis was performed to clarify the electronic structure of the copolymer and to determine its optical behavior upon switching. To carry out optoelectrochemical analysis, the film deposited onto ITO coated glass was placed in a UV cuvette for spectroelectrochemistry experiment after being washed with an electrolyte solution, which does not contain any monomer. By application of a potential ranging from 0.0 V to 1.3 V, a series of UV-VIS spectra were collected (Figure 3.14). To determine the reversibility of the film, another series of potential ranging from 1.3 V to 0.0 V was applied. The λ_{max} value for the $\Pi \rightarrow \Pi^*$ transition in the completely reduced state of poly(TAPE-co-BiTh) was found to be 410 nm. The electronic band gap is defined as the onset energy for the $\Pi \rightarrow \Pi^*$ transition and it was determined as 1.99 eV for the copolymer. On the other hand, pure poly(BiTh) has a peak absorbance at 480 nm and has a band gap of 1.1-1.2 eV [64].

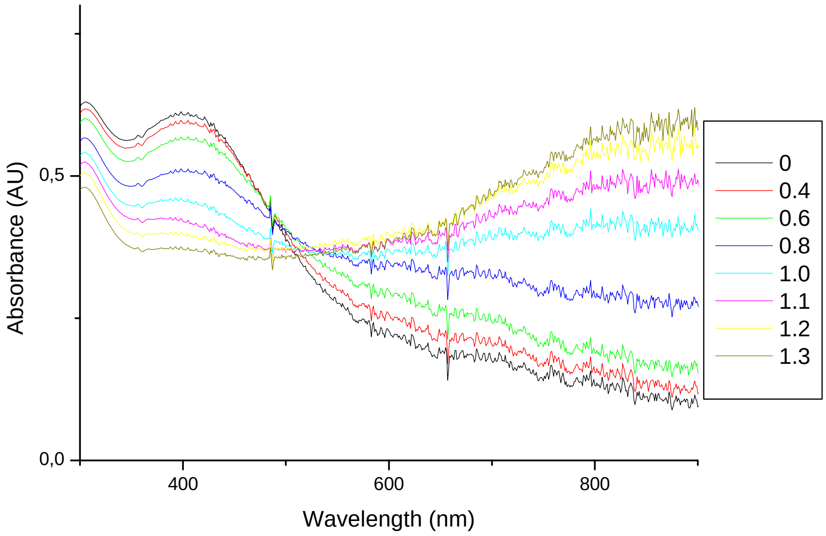


Figure 3.14: Optoelectrochemical Spectrum of poly(TAPE-co-BiTh) at applied potentials between 0.0 and +1.3 V (0.0 V, +0.4 V, +0.6 V, +0.8 V, +1.0 V, +1.2 V, +1.3 V

CHAPTER IV

CONCLUSION

Thiophen-3-yl-acetic acid 4-pyrrol-1-yl phenyl ester (TAPE) monomer was synthesized from 3-thiophene acetic acid and 4-pyrrol-1-yl phenol. The synthesis of both homopolymers and copolymers of TAPE with Py and BiTh were accomplished achieved by using ACN/TBAFB solvent-electrolyte couple by constant potential electrolysis. Chemical polymerization of TAPE was performed by the controlled addition of $FeCl_3$ at low temperature.

Electrochemical behavior of TAPE monomer was investigated by cyclic voltammetry. Cyclic voltammogram of TAPE in ACN/ TBAFB system revealed first an increase in peak intensities with increasing scan number, and then loss of electroactivity was observed. Morover, redox behavior of TAPE in the presence of Py and BiTh was studied. TAPE/BiTh showed different redox behavior from that of pure polybithiophene and poly(TAPE) which indicates the copolymer formation. This observation is also true for TAPE/Py system.

FTIR analyses also support the TAPE/Py and TAPE/BiTh copolymer formation. The morphology study of the polymer films made also a positive contribution to the above argument.

Furthermore, TAPE was polymerized with BiTh in BFEE to yield homogenous polymer films. Results of optoelectrochemical analysis and electrochromic studies have shown that poly(TAPE-co-BiTh) exhibits different electronic and electrochromic properties as compared to pure poly(BiTh).

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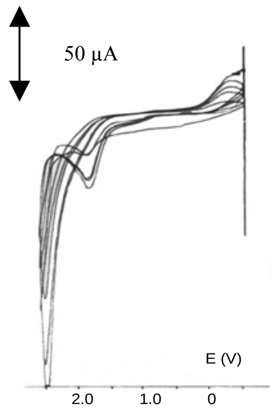
APPENDIX A

Cyclic Voltammograms of Starting Materials



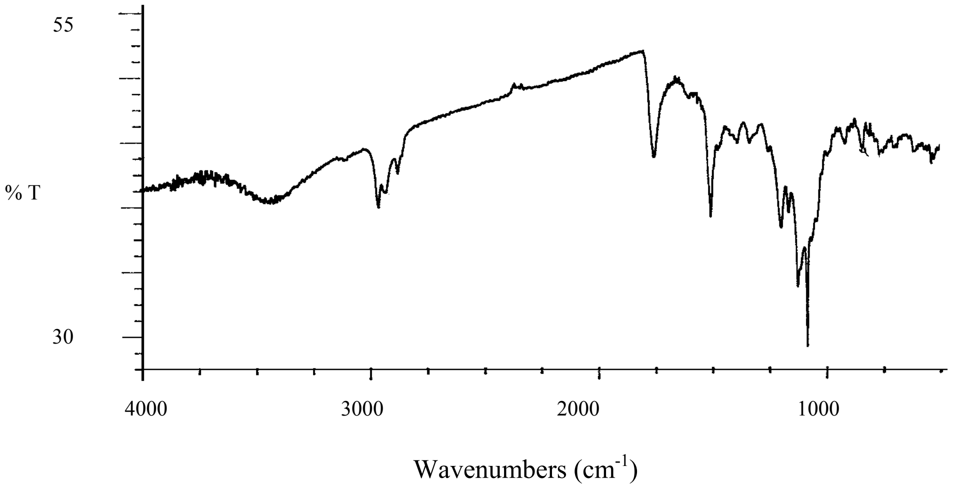
3-thiophene acetic acid

4-pyrrole-1-yl phenol

APPENDIX B

FTIR Spectra of Polymers

1. FTIR Spectrum of Poly(TAPE)



2. FTIR Spectrum of Poly(TAPE-co-BiTh)