SYNTHESIS OF CONDUCTING POLYMERS OF TEREPTHALIC ACID BIS-(2-THIOPHEN-3-YL-ETHYL)ESTER AND INVESTIGATION OF THEIR ELECTROCHROMIC PROPERTIES

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ABSTRACT

SYNTHESIS OF CONDUCTING POLYMERS OF TEREPTHALIC ACID BIS-(2-THIOPHEN-3-YL-ETHYL)ESTER AND INVESTIGATION OF THEIR ELECTROCHROMIC PROPERTIES

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Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester (TATE) was synthesized through the reaction of 2-thiophen-3-yl-ethanol and terepthaloyl chloride. Electrochemical behavior of the TATE and TATE in the presence of thiophene were studied by cyclic voltammetry (CV). The chemical structure of monomer is characterized via Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Homopolymer of TATE was synthesized by galvanostatic and potentiostatic methods, and copolymerization of TATE with thiophene was achieved via potentiostatic method. Both homopolymer (PTATE) and copolymer [P(TATE-co-Th)] were characterized by various techniques including cyclic voltammetry, FTIR, Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Thermal Gravimetry Analysis (TGA) and UV-VIS Spectrophotometer. Conductivities of samples were measured by four probe technique.

Electronic band gap of polymers measured as the onset of the π-π* transition using spectroelectrochemical analysis and colorimetry studies were investigated. Dual type polymer electrochromic devices (ECDs) based on PTATE, P(TATE-co-Th) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been constructed. Spectroelectrochemistry, switching ability and stability of the devices were investigated by UV-Vis Spectrophotometer and Cyclic Voltammetry.

Keywords: Electropolymerization, Electrochromic polymers, Conducting polymers, Electrochromic Devices, Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester

ÖZ

TEREFTALİK ASİT BİS-(2-TİYOFEN-3-İL-ETİL)ESTER' İN İLETKEN POLİMERLERİNİN SENTEZLENMESİ VE ELEKTROKROMİK ÖZELLİKLERİNİN İNCELENMESİ

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Tereftalik asit bis-(2-tiyofen-3-etil)ester (TATE), 2-tiyofen-3-ethanol ve tereftaloil klorür kullanılarak sentezlenmiştir. TATE'nin ve tiyofen ile kopolimerinin elektrokimyasal davranışı dönüşümlü voltametre vasıtasıyla araştırılmıştır. Monomerin kimyasal yapısı Nükleer Manyetik Rezonans Spektroskopisi (^{1}H-NMR ve ^{13}C-NMR) ve Fourier Transform İnfrared Spektroskopisi (FTIR) yöntemleri kullanılarak incelendi. TATE nin homopolimeri sabit gerilim ve sabit akım yöntemleri, tiyofenle kopolimeri sabit gerilim yöntemi kullanılarak sentezlenmiştir. Hem homopolimer (PTATE) hem kopolimer [P(TATE-co-Th)] Fourier Transform İnfrared Spektroskopisi (FTIR), Taramalı Elektron Mikroskopisi (SEM), ve UV-VIS Spektrofotometresi yöntemleri kullanılarak karakterize edilmiştir. Örneklerin ısıl analizleri DSC ve TGA ile incelenmiştir. Filmlerin iletkenlikleri dört-nokta tekniği ile belirlenmiştir. Filmlerin elektronik bant aralığı spektroelektrokimyasal yöntem kullanılarak belirlenmiş, kolorimetre analizleri yapılmıştır. Elektrokromik cihazlar, PTATE, P(TATE-co-Th) ve poli(3,4-etilendioksitiyofen) (PEDOT) kullanılarak yapılmıştır. Cihazların spektroelektrokimyasal özellikleri, renk değiştirme özelliği ve dayanıklılığı UV-Vis Spektrofotometresi ve dönüşümlü voltametre yöntemleri kullanılarak araştırıldı.

Anahtar Kelimeler: İletken polimerler, elektrokimyasal polimeştirme, elektrokromik özellikler, elektrokromik cihazlar, Tereftalik asit bis-(2-tiyofen-3-etil)ester

TO MY FAMILY

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ABBREVIATION

AN	Acetonitrile
BFEE	Boron flouride-ethyl ether
CPs	Conducting polymers
CV	Cyclic voltammetry
DSC	Differential scanning calorimetry
ECDs	Electrochromic devices
EDOT	3,4-Ethylenedioxythiophene
EPR	Electron paramagnetic resonance spectroscopy
FTIR	Fourier transform infrared spectrophotometer
HOMO	highest occupied molecular orbital
ITO	Tin doped indium oxide
LUMO	lowest unoccupied molecular orbital
NMR	Nuclear magnetic resonance
PA	Polyacetylene
PC	Propylene carbonate
PEDOT	Poly(3,4-ethylenedioxythiophene)
PMMA	Poly (methyl methacrylate)
PTATE	Poly (Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester)
P(TATE-co-Th)	Copolymer of TATE and Th
PTh	Polythiophene
RE	Reference electrode
SEM	Scanning electron microscope
TATE	Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester
TBAFB	Tetrabutylammonium tetrafluoroborate
TEA	Triethylamine

TGA	Thermal gravimetry analysis
Th	Thiophene
WE	Working electrode

CHAPTER I

INTRODUCTION

1.1. Conducting Polymers

Conducting polymers are organic materials that exhibit the conducting properties of metals while retaining the mechanical properties and processibility of polymers. They contain π- electron backbone responsible for their unusual electronic properties, and these properties make conducting polymers attract a great deal of attention and become a hot research area for many academic institutions. This research has supported the industrial development of conducting polymer compounds and provided the fundamental understanding of the chemistry, physics and materials science of these materials [1].

For the discovery and development of electrically conductive polymers, The Chemistry Nobel Prize in year 2000 was awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa. The first reports of high levels of conductivity in a polymer were seen in 1977 when it was found that polyacetylene become conducting when oxidized by suitable reagents [2,3]. Polyacetylene (PA) is the simplest form of conducting polymer that has the characteristic structure of a conjugated π system extending over a large number of the chain linked monomer units. The electrical conductivity of PA exhibited an increase of over seven orders of magnitude upon doping with iodine. This remarkable discovery stimulated the world wide efforts to develop new classes of CPs with properties similar to or better than those of PA [4]. CPs based on aromatic systems and heteroaromatic compounds such as aniline, pyrrole and thiophene have been developed. These polymers possess higher environmental stability and structural versatility. The electronic and electrochemical properties of these polymers can be manipulated by modification of the monomer structure [5]. Some examples of CPs are given in figure 1.1.

Due to their facile synthesis, good environmental stability and long term stability of electrical conductivity, conducting polymers replace metals and semiconductors in the electrical and electronics industry. Many important CPs can be prepared electrochemically as high quality conducting films that can extend their potential applications [6-9]. 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 [10,11]. Some of the applications are light emitting diodes [12,13], electrochromic devices [14-16], sensors [17], batteries [18] and enzyme immobilization [19].

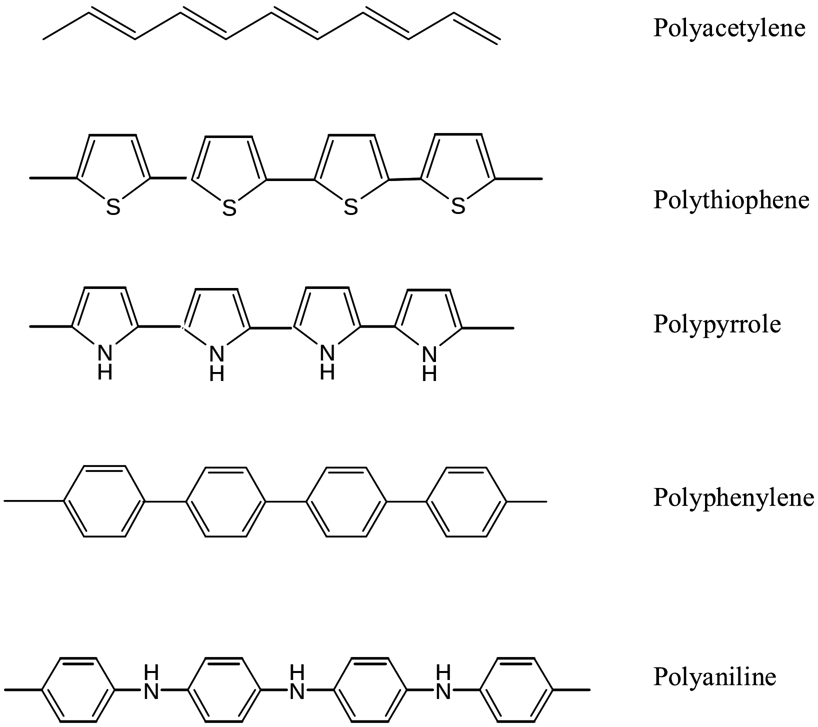


Figure 1.1 Chemical structures of some conducting polymers

1.2 Band Theory

Band theory is widely accepted in understanding the electrical behavior of conductors and semi conductors. When two *p* atomic orbitals are involved in forming a π bond, two π molecular orbitals are formed. One is a filled π orbital, and the other is an empty π anti bonding orbital. There is an energy difference between these two molecular orbitals. In the case of highly conjugated conducting polymers, the number of π bonding orbitals is large, the orbital energy spacing within them is very small. This provides nearly a continuom of orbitals resulting in valence and conduction bands. The valence band consists of filled π bonding orbitals and the conduction band consists of empty π anti bonding orbitals. The energy difference between these two band is called the band gap, which is the energy required to promote an electron from the valence band to conduction band. The band gap can be measured from the absorption band edge in the UV-vis spectrum of a conducting polymer.

According to band theory, metallic conductors have overlapping valence conduction bands, which means zero band gap. Electrons, the charge carriers of metals, can move freely within the crystal lattice of the metal, leading to metallic conductivity. On the other hand, insulators have a very large band gap. All electrons are confined to the valence band, no charge carriers are available for electrical charge flow, and therefore an electrical current can not go through an insulator.

The band gap of semiconductors lies between those of conductors and insulators, allowing some electrons to be promoted to the conduction band. In contrast to the empty conduction band of insulators, the conduction band of semiconductors is lightly populated at ambient temperature. This gives rise to charge carriers available in semiconductors. As the band gap becomes smaller, the number of charge carriers increses.

The electrical conductivity σ of a conducting polymer can be given by the following equation, where n is the total number of charge carriers, q is the charge on the carriers, and μ is the mobility of the carriers.

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

For most conducting polymers, there are very few charge carriers available in the neutral state. They usually behave as insulators or have a very low intrinsic conductivity. In order for a conducting polymer to be a semi-conductor, an external dopant has to be used like the usual practice in the semiconductor industry. In the above equation, another factor that affects the conductivity of a conducting polymer is μ, the mobility of charge carriers along the conducting path. When a conducting polymer conducts, the electrical charge travels through the polymer. The overall mobility of electrical charges is dependent on how easily the charges move inside the polymer. It depends on the movement of electrical charges along the polymer chain, called intra chain movement, and also jumping from one chain to another, called inter chain movement. Therefore, the overall mobility of charges is related to intra chain, inter chain, interparticle mobilities. Usually these factors convoluted together [20,21]. The conductivity ranges of material are given in figure 1.3.

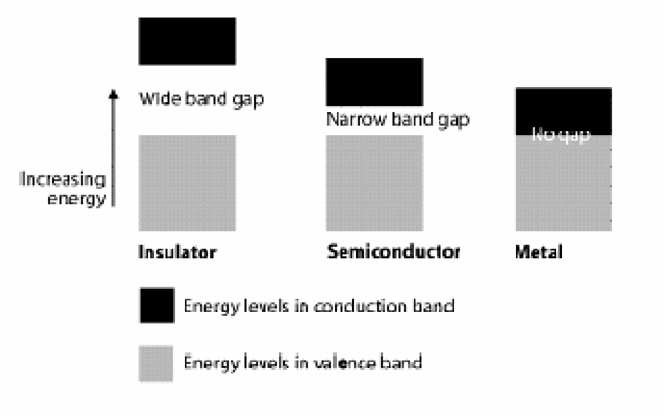


Figure 1.2 Schematic representations of band structures

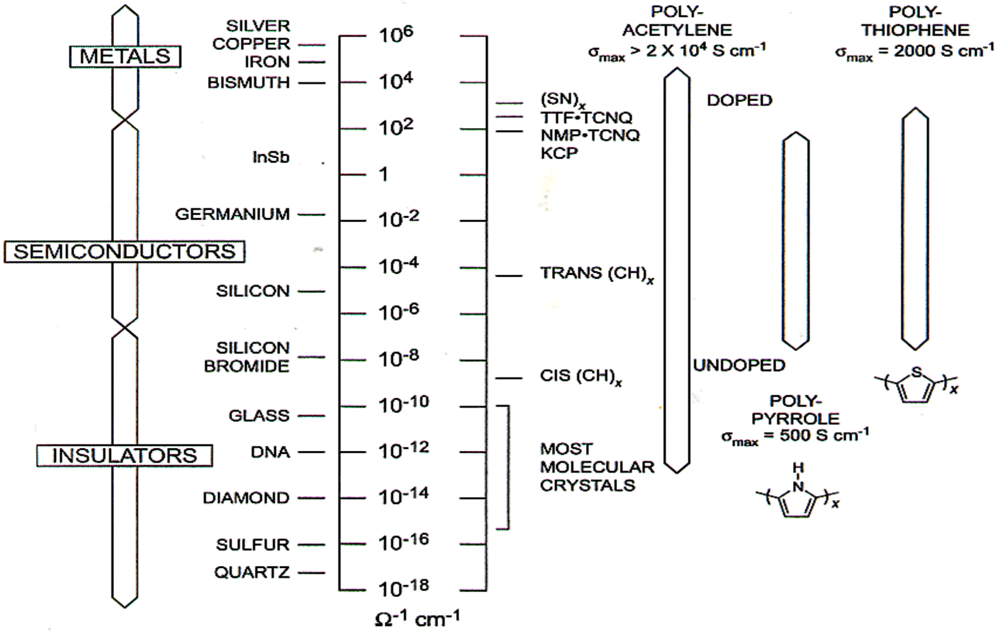


Figure 1.3 Conductivity range

1.3 Doping Process

It is well established that the electrical conduction properties of elemental semiconductors, such as Si, can be controlled by adding very small quantities of foreign atoms in the host semiconductor lattice. The host semiconductor can be made n type or p type depending on the nature of the added dopant ions. New dopant energy levels are introduced into the band gap and conduction is facilitated. The conductivity level attained depends strongly on the concentration of donor or acceptor species incorporated. Excess electrons or holes are generated in the material as a result of doping, so conductivity is enhanced. A similar terminology has been applied to conjugated polymers because of the π electron system allowing electron removal from or injection into the polymer. These materials may also be doped and indeed the conductivity level obtained depends on the doping level. However, the doping mechanism differs from that observed for elemental semiconductors. Doping levels attained in conjugated polymers are significant. Furthermore, there is charge transfer between the incorporated dopant atom and the polymer chain, hence the latter is partially oxidized or reduced. [20]

The partial oxidation of the polymer chains termed p- doping. The basic process involves removing electrons to form a positively charged repeat unit

$$—(P)x— + xyA- \rightarrow —[Py+(A)y]x— + xye-$$

where P presents the basic monomeric repeat unit in the polymer. Furthermore if the polymer chain is partially reduced, there is n type doping as follows

$$—(P)x— + xye- + xyM+ \rightarrow —[Py-(M+)y]x—$$

The extent of oxidation/reduction is called the “doping level”, and is generally measured as the proportion of dopant ions or molecules incorporated per monomer unit. Increased doping level leads to increased conductivity, via creation of more mobile charges [22].

1.4 Hopping process

The conduction process is well described by a variable range of hopping process in which electrons are localized on individual monomer rings. The hopping process produces a generous supply of potential carriers. There are mainly three types of transport for the carrier mobility; single chain or intramolecular transport, interchain transport, interparticle transport. The intra chain movement depends on the effective conjugation of the polymer, while the inter chain jumping is determined by the stacking of the polymer molecules. The mobility also depends on the movement of electrical charges from particle to particle. These three show a resistive network determining the effective mobility of the carriers. Thus the mobility and therefore conductivity are determined on both a macroscopic (interparticle) and microscopic (intra and interchain) level.

1.5 Solitons, Polarons and Bipolarons

Increased doping level leads to increased conductivity, via creation of more mobile charges. At low doping levels, these charges self-localize and form the nonlinear configurations (solitons, polarons, and bipolarons). At higher doping levels, a transition to a degenerate Fermi sea is observed, with associated metallic behavior [23].

Polyacetylene is the only conjugated polymer to possess a degenerate ground-state. All other conjugated polymers possess non-degenerate ground states, and this affects the nature of charges which they can support [24].

Polyacetylene chains with odd number of carbon atoms have an unpaired electron (a neutral soliton). Upon oxidation or reduction, a radical cation or anion is generated which moves along a polymer chain by the mechanism shown in figure 1.4. Passing from one side of a soliton to another, the double bonds become gradually shorter, the single bonds gradually longer until they are equal in the center of soliton. In polyheterocycles there is an aromatic state and a quinoid state of higher energy. Oxidation of a polyheterocycle creates a radical cation called polaron. The polaron has a spin of ½. Further oxidation causes more and more polarons to form and eventually the unpaired electron of the polaron is removed, or two lose polarons can combine to form dications or bipolarons (figure 1.5). Unlike the solitons in polyacetylene, the two positive charges of the bipolarons stay associated and act as one charge carrier dispersed over many rings. Experimental results from electron paramagnetic resonance spectroscopy (EPR) support this mechanism showing neutral and heavily doped polymers have no unpaired electrons, but moderately doped polymers do exhibit an EPR signal and are paramagnetic [25].

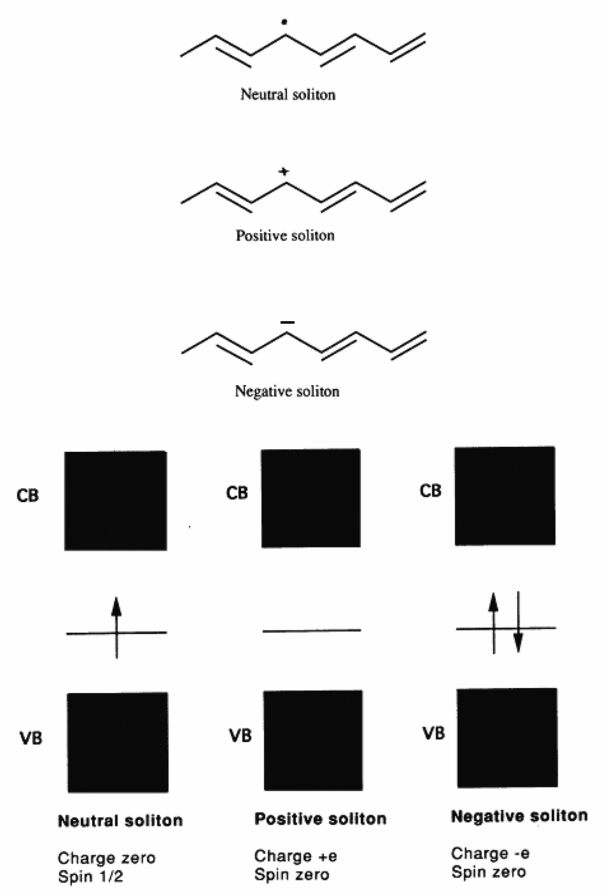
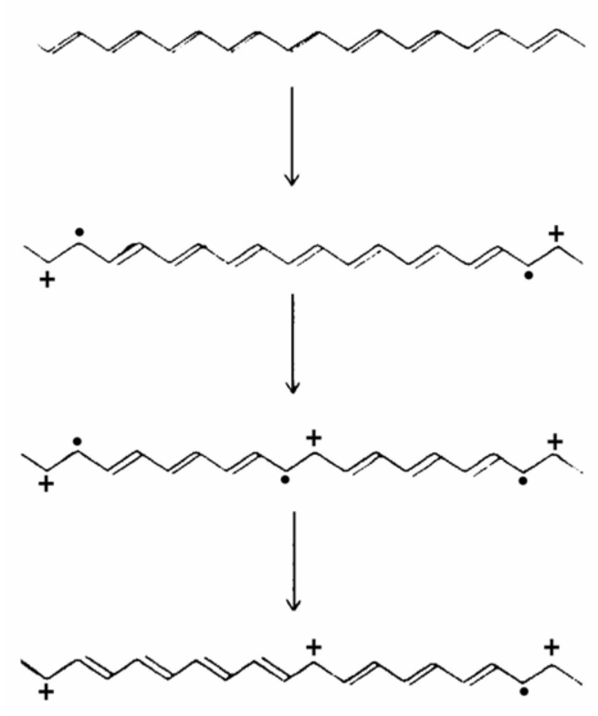


Figure 1.4 Soliton structures of polyacetylene



Neutral polyacetylene

Two polarons by partial oxidation

More polarons by further oxidation

Closeness of polarons provide the interaction of two unpaired electrons to form a new л bond and a mobile bipolaron

Figure 1.5 Formation of polaron and bipolaron for polyacetylene

1.6 Synthesis of Conducting Polymers

Conductive polymers may be synthesized by any one of the following techniques [26]:

- Electrochemical polymerization
- Chemical polymerization
- Photochemical polymerization
- Concentrated emulsion polymerization

1.7 Electrochemical Synthesis

Electrochemical synthesis of conducting polymers offers many advantages, including the in-situ deposition of the polymer at the electrode surface, and, hence, eliminating processibility problems and the control of the thickness, morphology and degree of polymer doping by the quantity of charge passed. In addition, the polymers are simultaneously oxidized to their doped conducting forms during polymer growth. Electropolymerization is achieved by the electro-oxidation of the heterocycle in an inert organic solvent containing supporting electrolyte [27-29]. A schematic of the generally accepted mechanism for electropolymerization of five membered heterocycles is shown in Fig. 1.6. The initial electrochemical step (E) is a one electron oxidation of the monomer to form its radical cation. A high concentration of these species is maintained at the anode surface because the rate of electron transfer greatly exceeds the monomer diffusion rate to the electrode surface. The second step, a chemical reaction (C), involves the spin-pairing of two radical cations to form a dihydro dimer dication, which subsequently undergoes the loss of two protons and rearomatization to form the dimer. Aromatization is the driving force of the chemical step (C). Coupling occurs primarily through the α-carbon atoms of the heterocyclic ring since these are the positions of highest unpaired electron π-spin density and hence reactivity. At the applied potential, the dimer, which is more easily oxidized than the monomer, exists in a radical cation form and undergoes further coupling reactions with other radical cations. This electropolymerization mechanism, according to the general scheme $E(CE)_n$, continues until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the anode surface [30,31].

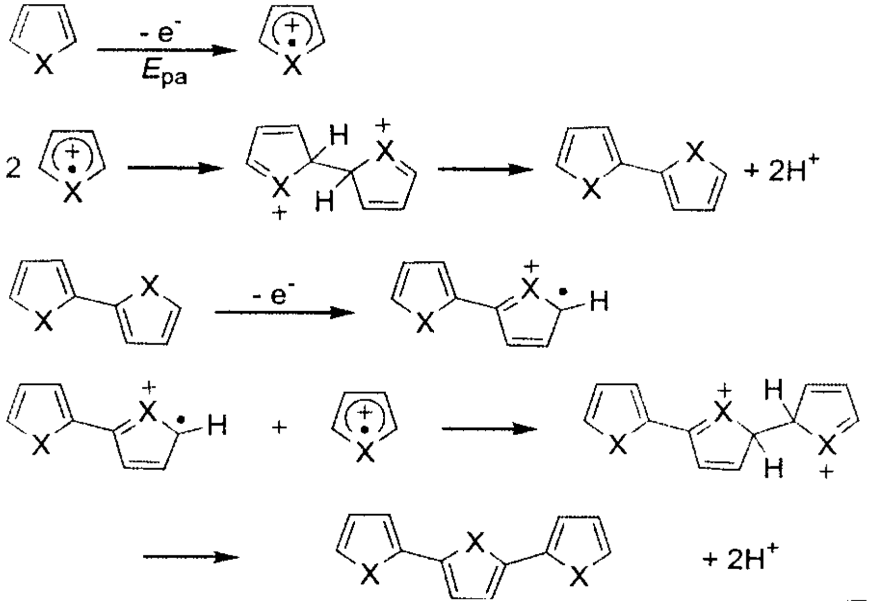


Figure 1.6 Electrochemical polymerization mechanism

1.8 Electrochemical techniques

1.8.1 Constant Current Electrolysis

Constant current electrolysis (CCE) is carried out in a cell containing two electrodes. Current is kept constant during the electrolysis and the potential is allowed to vary. It is simple in application but it has some disadvantages. The nature of the generated species may be unknown because of the variable potential. The involvement of species present in the system in addition to the monomer is generally inevitable; thus complications may arise in the initiation and propagation step [32].

1.8.2 Constant Potential Electrolysis

Constant potential electrolysis is carried out in a cell to maintain the potential on the working electrode and to prevent the excessive current flowing through reference electrode. The potential of the working electrode is adjusted to a desired value and kept constant while current is allowed to vary. The applied potential is determined by means of cyclic voltammetry. The voltage between the working and the reference electrode may be called the polymerization potential (E_{pot}). By keeping the potential constant, unwanted species can be eliminated [32].

1.8.3 Cyclic Voltammetry

Cyclic voltammetry method is used to find out the electrochemical behavior of electroactive species. In this method the voltage applied to the working electrode as a cyclic triangular wave and then current response is plotted as a function of applied potential by a recorder. A voltammogram of a material provides us to understand its electroactivity, redox potential, mechanism of the electrochemical reaction, it is reversible or irreversible and whether reaction products are further reduced or oxidized.

1.9 Electrochemical Polymerization in Lewis Acid

Intensive efforts in the area of the electrochemical synthesis of conducting polymers are to optimize the preparation by controlling the system and parameters. Boron flouride-ethyl ether (BFEE) is a promising system which has been used for electrochemical synthesis of some heterocyclics like thiophene, pyrrole and bithiophene. Electrochemical polymerization of thiophene in BFEE yields a free standing film with good mechanical properties [33]. High applied potentials support the degredation of the polymer and side reactions of the electrolytes and electrodes [34]. The significant decrease in the oxidation potential of benzene in the strong acid media can be rationalized in two ways: first, benzene forms a complex with the strong acid, thereby reducing the resonance stabilization of the aromatic ring and shifting the oxidation potential to less anodic potential. Second, the increased acidity of the solvent imparts a greater stability to the cation radical, which can promote the electrooxidative polymerization [35].

1.10 Electrochromism

An electrochromic material is the one that changes color reversibly by an electrochemical reaction, and the phenomenon is called electrochromism [36]. New electrochromic materials attract great interest, due to their rapid response times, long term stability, and high contrast [37, 38]. Conducting polymers represent an attractive class of electrochromic materials owing to their facile switching properties, processibility, and controllable optical properties [39-43].

The mechanism behind the electrochromic behavior is related to the doping of materials. In the neutral state, the color is determined by the band gap of the polymer. Upon doping (removal or addition of electrons), new electronic states are formed in the band gap, thus giving rise to optical absorptions at energies lower than the original band gap. The $\pi-\pi^*$ transition is the main electronic transition occurring in neutral polymers. Doping shifts the absorption towards the lower energies and the color contrast between doped and undoped forms of the polymer depends on the magnitude of the energy gap of the undoped polymer [44].

The incorporation of electron donating substituents onto a conjugated chain is a commonly employed strategy to decrease the polymers oxidation potential by raising the energy of the valence band electrons (HOMO of the conjugated chain). At the same time, there is a small perturbation on the energy of the conduction band (LUMO of the conjugated chain), which leads to a decrease in the polymer’s electronic band gap [45].

All conducting polymers are potentially electrochromic in thin film form, redox switching giving rise to new optical absorption bands in accompaniment with transfer of electron or counter ions [46].

Conjugated polymers with aromatic like structure are more promising as electrochromic materials when the p-doping process is involved, since n-doping is greatly affected by the nature of the cation in the charge balancing process; n-doped forms are also less stable than p-doped ones. Evolution of band structure can be seen in figure 1.7.

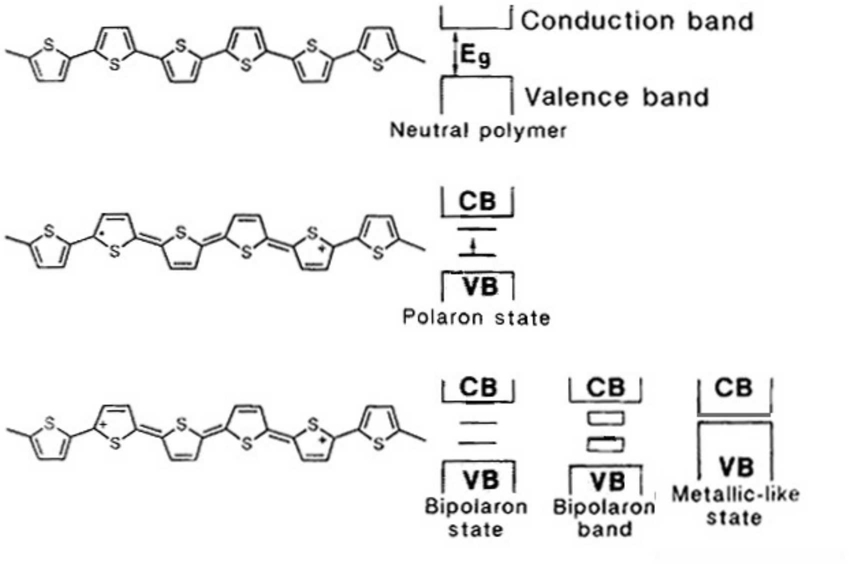


Figure 1.7 Evolution of electronic band structure with p-doping for conjugated polymer with non-degenerate ground state.

Short electrochromic response time, long switching life and optical memory are the most important requisites for electrochromic materials in device tecnology. Electrochromic response time is the time the polymer takes in response to the potential pulse to go one color state to the other. Switching life is related to the ratio of the reduction to the oxidation charges involved in the electrochromic process. The optical memory is the persistence of the colored state even when the driving voltage is removed [47].

Tin doped indium oxide (ITO) is routinely used as an electrode in electrochromic applications due to its unique combination of properties including optical transparency, low electrical resistance and excellent surface adhesion.

1.10.1 Spectroelectrochemistry

Spectroelectrochemistry plays a key role in probing the electronic structure of conducting polymers as well as in examining the optical changes that occur upon doping. It provides information about the material's band gap and intraband states created upon doping. In addition it gives some insight into a polymer color through the location of the absorption maxima and the ratio of peak intensities if the material shows fine structure on the main π-π* peak.

1.10.2 Colorimetry

Colorimetry is a quantitative analytical tool that has proven an effective objective method to compare and evaluate the optical responses of electrochromic polymers and devices. There are three attributes that are used to describe the color: hue, saturation and brightness. Hue represents the wavelength of maximum contrast (dominant wavelength) and is commonly referred to as color. Saturation takes into consideration the purity (intensity) of a certain color, whereas the third attribute, brightness, deals with the luminance of the material, which is the transmittance of light through a sample as seen by the human eye.

A commonly used scale that numerically defines colors has been established in 1931 by The Commission Internationale de l'Eclairge (CIE system). This method takes into consideration the response of a standard observer to various color stimuli, the nature of the light source, and the light reflected by the object under study. These functions are used to calculate tristimulus values (XYZ) that define the CIE color spaces [48].

Figure 1.8 shows the color space used to determine the color of the copolymers. On this chart, x-axis corresponds to *a*, which is hue, y-axis corresponds to *b* which is intensity and z-axis corresponds to *L*, luminance.

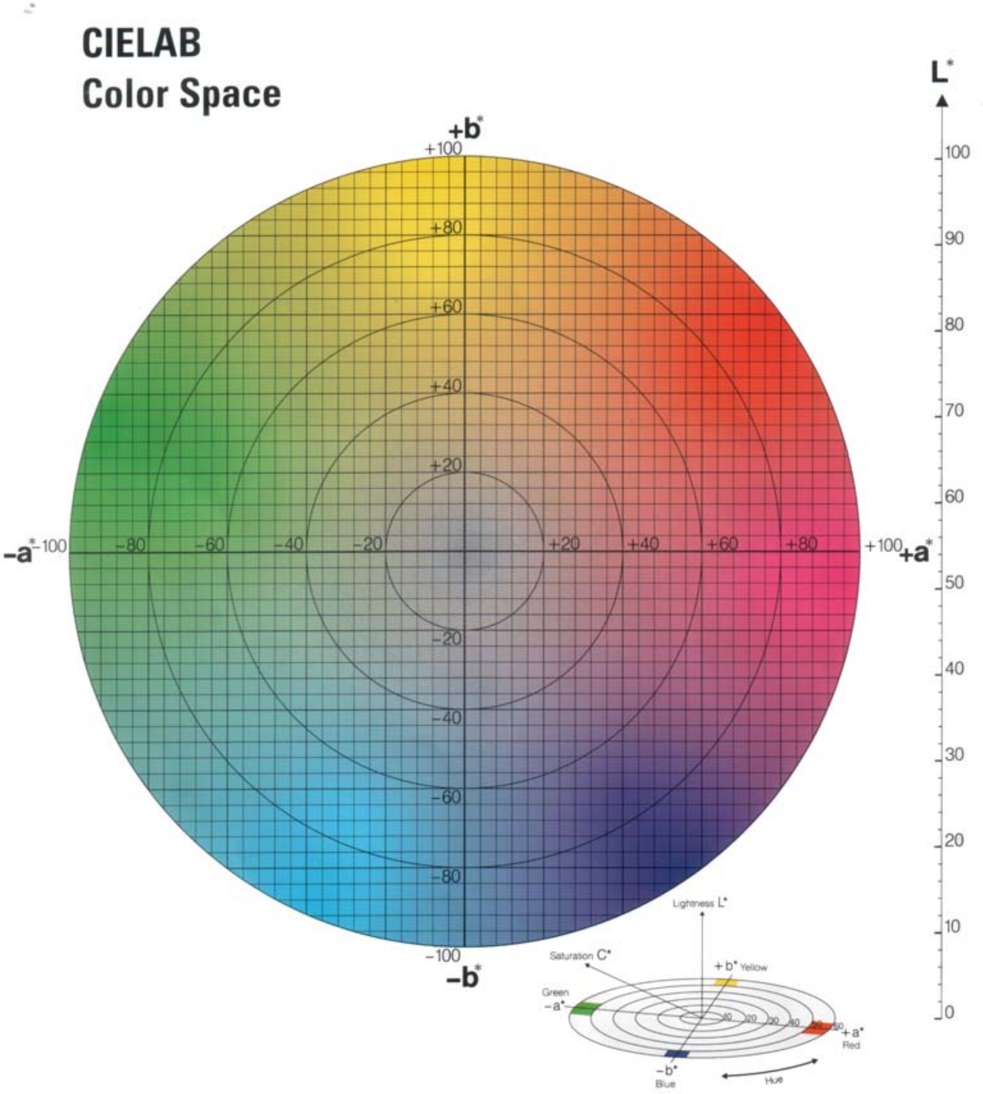


Figure 1.8 CIELAB color space

1.10.3 Switching

For electrochromic applications, the ability of a polymer to switch rapidly and to exhibit a striking color change is important. Color contrast is the difference between the absorptions between the pristine, completely doped polymer. The response time of a polymer is defined as the time needed to switch between the two extreme redox states of the active polymer layer. Electrochromic switching studies can monitor these types of properties. In order to study the switching time, polymer was connected to a power supply that applies a square-wave potential, allowing for potential period and amplitude control. The potential is set at an initial potential for a set period of time, and is stepped to a second potential for a set period of time, before being switched back to the initial potential again. During the experiment, the % transmittance (%T) at λ_{max} of the polymer is measured using a UV-Vis-NIR spectrophotometer [21, 47].

1.11 ECDs

An electrochromic device is essentially a rechargeable battery in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a charge balancing suitable electrode, and the color changes occur by charging and discharging the electrochemical cell with applied potential [36]. Electrochromic devices take part in various applications, such as display panels [49], camouflage materials [50], variable reflectance mirrors [51] and variable transmissive windows [52].

A dual type electrochromic device consists of two thin polymer films deposited on transparent indium tin oxide coated glass (ITO), and separated by a viscous gel electrolyte based on supporting electrolyte dissolved in an acetonitrile/propylene carbonate swollen poly(methyl methacrylate) matrix. The device construction is carried out with one polymer oxidatively doped while the other is neutral, and both films are simultaneously in either their transmissive or absorptive states. As such, the device is observed as bleached or colored. Application of a voltage neutralizes the doped polymer with concurrent oxidation of the complementary polymer, inducing color formation, or bleaching. The ability to match the number of redox sites in each film enhances the contrast of a device, as the extremes of absorption and transmission can be attained. Cathodically coloring polymer is the one that passes from an almost transparent state to a highly colored state upon reduction of the p-doped form, while an anodically coloring polymer is highly transmissive neutral and absorbs visible light in the oxidatively doped state. An ideal cathodically coloring material has a band gap around 1.8-2.2 eV (550-650 nm) in order for the π- π * transition to occur in the visible region where the human eye is highly sensitive. In addition, it should undergo large optical changes when switched between neutral and doped states. Some of the most promising conducting polymers for use in ECDs are based on poly(3,4-ethylenedioxythiophene) and its derivatives, as they exhibit high electrochromic contrasts, low oxidation potentials and high conductivity, as well as good electrochemical and thermal stability [53].

An high performance electrochromic device should have; high electrochromic efficiency, expressed in $cm^2 C^{-1}$ and related to the injected charge in the material to change its color; short electronic response time; good stability; optical memory, defined as the color stability under open circuit potential conditions; optical contrast, also called write-erase efficiency; color uniformity [54].

1.12 Aims of the work

Aim of this work is fist to synthesize terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester (TATE); second, to perform electrochemical polymerization of TATE and its copolymer with thiophene. Third characterization of the polymer films with various techniques. Then, investigation of electrochromic and spectroelectrochemical properties of polymers. Finally, examination of their use in an electrochromic devices.

CHAPTER II

EXPERIMENTAL

2.1 Materials

2-thiophen-3-yl-ethanol (Aldrich), terepthaloyl chloride (Aldrich), triethylamine (TEA) (Merck), dichloromethane (DM) (Merck), methanol (Merck), acetonitrile (AN) and borontrifluoride ethylether (Aldrich) were used without further purification. Thiophene (Aldrich) was distilled before use. Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich) was used as received. Propylene carbonate (PC) and poly(methyl metacrylate) (PMMA), were purchased from Aldrich and used without further purification. 3,4-Ethylenedioxythiophene (EDOT), was purchased from Aldrich and used as received.

2.2 Instrumentation

2.2.1 Potentiostat

Wenking POS 73 and Solatron 1285 potentiostats were used to supply a constant potential in electrochemical syntheses. Electrochemical polymerization is carried out in a three electrode system containing working electrode (WE), reference electrode (RE) and counter electrode. The major current passes through the CE and WE. Potential of working electrode is adjusted at a level with respect to fixed reference electrode. The potential between WE and CE is equal to input potential that can be controlled externally. The current can be controlled by measuring the voltage drop across a small resistance.

2.2.2 Galvanostat

Galvanostat controls the current and keep it constant throughout the experiment while the potential is monitored as a function of time by two electrode system, consisting of a working and a counter electrode. The film thickness can be easily controlled by the checking the polymerization time.

2.2.3 Cyclic Voltammetry System

Cyclic voltammetry system is a convenient way of analyzing the electroactivity of polymers and obtaining the oxidation-reduction peak potentials of the monomers. Cyclic voltammetry method consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current at the working electrode. Experiments were carried out in a three electrode cell consisting of Pt wire as the counter, silver electrode as the reference, ITO coated glass as the working electrode. Solatron 1285 potentiostat/galvanostat was used for the cyclic voltammetry experiments.

2.2.4 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.

2.2.5 Nuclear Magnetic Resonance Spectrometer (NMR)

1H-NMR and ^{13}C-NMR spectra of monomer were investigated on a Bruker-Instrument-NMR Spectrometer (DPX-400) instrument. $CDCl_3$ was used as solvent.

2.2.6 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra of the samples were recorded on a Nicolet 510 FTIR spectrometer for the detection of functional groups. Samples were prepared by forming KBr pellets.

2.2.7 Thermal Analysis

Thermal analyses were carried out by Du Pont 2000 instrument. Both Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA) experiments were performed by heating rate of 10 ^{o}C/min under N_2 atmosphere.

2.2.8 Scanning Electron Microscope (SEM)

Surface morphologies were inspected by JEOL JSM-6400 scanning electron microscope.

2.2.9 UV-VIS Spectrophotometer

Spectroelectrochemical studies, electrochromic properties and characteristics of the polymers and devices were investigated by Agilent 8453 UV-Vis spectrophotometer.

2.2.10 Colorimetry Measurements

Colorimetry measurements were obtained by a Coloreye XTH Spectrophotometer (GretagMacbeth).

2.2.11 Four-Probe Conductivity Measurements

Among available conductivity techniques, four probe method is more advantageous for measuring electrical properties of conducting polymers. This technique eliminates errors caused by contact resistance, since the two contacts measuring the voltage drop are different from the contacts applying the current across the sample.

Figure 2.1 shows the simplest form of a four-point probe measurement setup. A row of pointed electrodes touches the surface of a polymer film taped or spin cast on an insulating substrate. A known current *I* is injected at the electrode 1 and is collected at the electrode 4, while the potential difference ΔV between contacts 2 and 3 is measured. Conductivity is calculated from the following equation:

$$\sigma = \ln 2 / (\pi R t)$$

where R is the resistance of the sample, and t is the thickness.

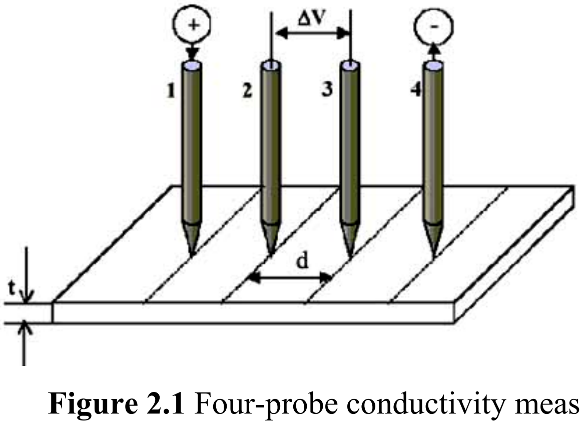


Figure 2.1 Four-probe conductivity measurement

2.3 Procedure

2.3.1 Preparation of Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester (TATE)

2-Thiophen-3-yl-ethanol (1.12 mL, 0.001 mol) was dissolved in 10 mL dichloromethane containing 1.11 mL (0.008 mol) triethylamine (TEA). To this solution terepthaloyl chloride (0.81 g, 0.004 mol) in 10 mL of dichloromethane were added dropwise in 0.5 h, by cooling in ice bath and nitrogen atmosphere. The esterification was carried out for overnight at 0 °C. Then the solution was washed with HCl 1% solution (three times) and water (three times). The organic layer was dried over Na_2SO_4 and the solvent was removed via rotaevaporatory. Twice recrystalization from ethanol provided 1.1 g of white crystals (yield 71%). Route for synthesis is shown in figure 2.2.

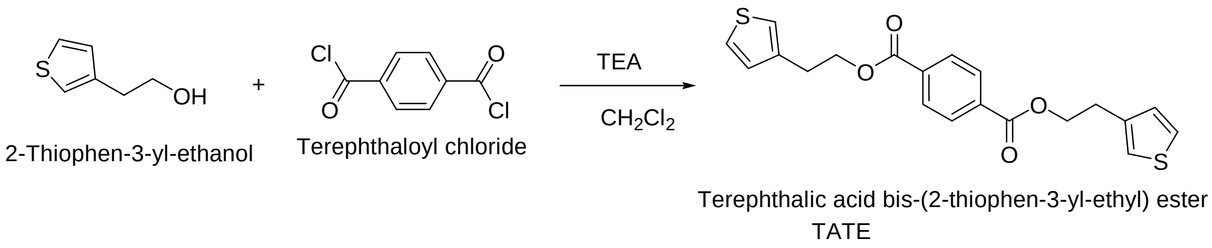


Figure 2.2 Synthesis route of TATE

2.3.2 Synthesis of Homopolymer of TATE

Homopolymerization of TATE was achieved via constant potential electrolysis in a one compartment cell. 0.01 M TATE dissolved in DM/BFEE (8:2, v/v) solvent mixture and 0.1 M TBAFB used as the supporting electrolyte. Electrolysis performed at

1.6 V. Working and counter electrodes were Pt foils and the reference electrode was Ag/Ag^+. Films were washed several times to remove the unreacted monomer and TBAFB.

2.3.3 Synthesis of Copolymer of TATE with Thiophene

For the copolymerization of TATE with thiophene, constant potential electrolysis was carried out in DM/BFEE (8:2, v/v) solution composed of 0.01 M TATE, 0.1 M TBAFB, 15µL thiophene at 1.6 V in a one compartment cell where the working and counter electrodes were Pt and the reference electrode was Ag/Ag^+. Films were washed several times to remove the unreacted monomer and TBAFB.

2.3.4 Galvanostatical Polymerization of TATE

For the constant current electrolysis, 50 mg of TATE and 0.1 M TBAFB were dissolved in 15 mL of dichloromethane. Electrolysis was carried out in one-compartment cell equipped with Pt working and counter electrodes. Electrolysis was performed by passing constant current of 20 mA at 0 ^oC. Polymer film obtained was washed with dichloromethane several times to remove unreacted monomer.

2.3.4 Potentiodynamic Study of Polymers

Oxidation/reduction behavior of homopolymer of TATE (PTATE) was investigated by cyclic voltammetry using TBAFB (0.1 M) as the supporting electrolyte in DM/BFEE solvent mixture (8:2, v/v). Experiments were carried out sweeping the potential between -0.5 V and +1.6 V. Solution was containing 0.01 M TATE. For the investigation of copolymer, same conditions were used and the solution contained 5µL thiophene.

2.3.5 In-situ Electrochemical Polymerization

Measurements were carried out by Agilent UV-Vis spectrophotometer by using a three electrode cell. A silver wire was used as the pseudo reference electrode and a Pt wire was used as the counter electrode.

In-situ electrochemical polymerization of TATE and copolymerization of TATE with thiophene was investigated by UV-Vis spectrophotometer. PTATE was coated on ITO glass electrode by applying +1.4 V to AN/BFEE mixture (8:2, v/v) solution consisting of 0.01 M TATE and 0.1 M TBAFB; P(TATE-co-Th) was coated by applying +1.4 V to same solution containing 5 μL thiophene additionally. While coating the electrodes spectroelectrochemical series were taken at every 20 second time interval.

2.3.6 Spectroelectrochemical Studies

Spectroelectrochemical analyses of the homopolymer and copolymer were studied by depositing the samples as thin films potentiodynamically sweeping between -0.5 V and + 1.6 V for homopolymer and copolymer on ITO-coated glass slides in DM/BFEE mixture (8:2, v/v) solution consisting of 0.01 M TATE and 0.1 M TBAFB. Different potentials from fully reduced states of polymer to fully oxidized states are applied to coated ITO slides in a monomer free (0.1 M) TBAFB/AN solvent electrolyte couple, while spectroelectrochemical series are taken at the same time.

2.3.7 Switching Properties of Polymers

In order to study switching properties of polymers, square-wave potential applied by Solatron 1285 potentiostat/galvanostat to control the potential period. By this technique, the voltage was switched between 0.0 V and +1.6 V with a residence time of 5 seconds as shown in figure 2.3. After coating the polymers on ITO electrode, they were switched by potential square wave in (0.1 M) TBAFB/AN solvent electrolyte couple while monitoring the percent transmittance during doping and dedoping process at the maximum absorbtion wavelength.

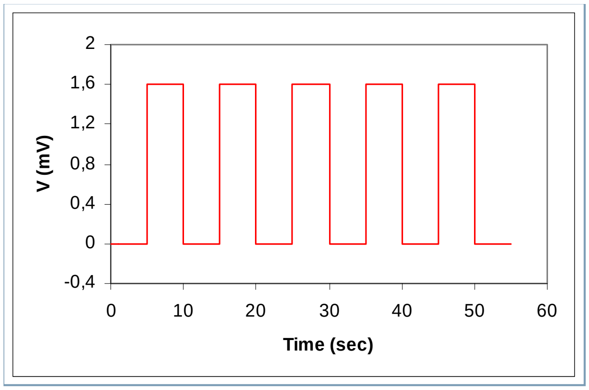


Figure 2.3 Square wave voltammetry

2.3.8 Colorimetry Studies of Polymers

Colorimetry method allows for accurate reporting a quantitative measure of the color and graphically representing the track of doping-induced color changes of an electrochromic material or device. There are three attributes that are used to describe the color: hue, saturation and brightness.

Colorimetry studies were performed in UV cuvette in monomer free solution of TBAFB(0.1 M)/AN after the synthesis of film on ITO in DM/BFEE (8:2, v/v) solvent mixture containing 0.01 M TATE and 0.1 M TBAFB.

2.3.9 Electrochromic Device (ECD) Construction

In order to construct ECD's first polymers were coated on ITO-glass electrode potentiodynamically. A three-electrode cell containing an ITO-coated glass slide as the working electrode, a platinum flag as the counter electrode, and a silver wire as the pseudo-reference electrode were used for electrodeposition of polymer films. Electrochemistry experiments were carried out using a Solatron 1285 model potentiostat/galvanostat. Poly(3,4-ethylenedioxythiophene) (PEDOT) films were deposited on ITO from a 0.1 M monomer solution in (0.1 M) TBAFB/AN electrolyte-solvent couple potentiodynamically sweeping between -0.7 V and +1.8 V. PTATE was coated on ITO electrode via cyclic voltammetry, scanning between -0.5 V and +1.6 V in DM/BFEE (8:2, v/v) solution containing 0.01 M TATE and 0.1 M TBAFB. P(TATE-co-Th) was prepared in the same solution that contains 5 μL thiophene sweeping between -0.5 V and +1.6 V. In order to improve the optical stability during redox process, it is important to equilibrate the charge on the electrodes [55]. Polymer coated electrodes were removed from polymerization medium and placed in monomer free AN solution containing (0.1 M) TBAFB. Cathodically coloring film which is PEDOT was fully reduced by polarizing to -1.0 V, anodically coloring films were fully oxidized by polarizing to +1.6 V in the monomer free solution. Finally, electrochromic devices were constructed by sandwiching the gel electrolyte between conducting polymer deposited ITO's. Schematic representation of devices is given in figure 2.4.

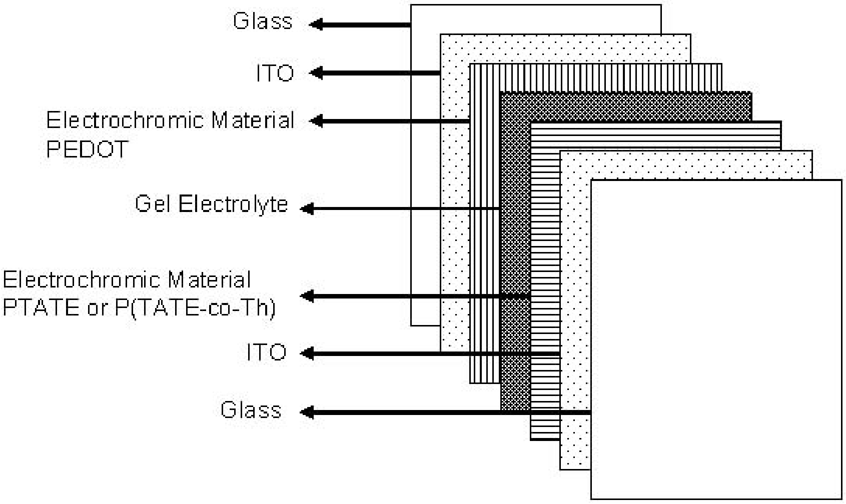


Figure 2.4 Schematic representation of devices

2.3.10 Gel Electrolyte Preparation

Gel electrolyte which is a highly transparent and conductive gel based on PMMA and TBAFB was plasticized by PC and AN was used as the solvent. The composition of the casting solution by weight ratio of ACN:PC:PMMA:TBAFB was 70:20:7:3. Initially, electrolyte salt dissolved in AN, and PMMA was added to the solution. This polymeric component is not easily dissolved, so vigorous stirring and mild heating (60 °C) for a period of about two hours is required. When all of the PMMA has dissolved, PC was introduced to the reaction medium. The gel was stirred and heated on a hot plate for about two more hours until it reached a honey-like consistency and started to stick to the container walls.

2.3.11 Spectroelectrochemistry study of devices

The characterization of the devices, optical properties was carried out using a Agilent 8453 UV-Vis spectrophotometer. A device without the electrochromic polymer layer, but otherwise with the same assembly, was used as a reference. In order to apply voltage across the device, the counter and the reference leads are connected to one another.

Spectroelectrochemistry analysis was obtained by sequentially stepping the applied potential. The device constructed by using PTATE as the anodically and PEDOT as the cathodically coloring material (PTATE/PEDOT device) switched at voltages varying between -0.2 V and + 1.6 V while measuring the absorbance as a function of wavelength.

Spectroelectrochemical study of P(TATE-co-Th)/PEDOT device was carried out varying the voltage between 0.0 V and + 1.5 V and absorbance was measured as a function of wavelength.

2.3.12 Switching properties of devices

Switching properties of devices were investigated by application of potential square wave technique (2.3.7) with a residence time of 5 seconds between 0.0 V and +1.6 V for PTATE/PEDOT device, between 0.0 V and +1.6 V for P(TATE-co-Th)/PEDOT device.

2.3.13 Stability of devices

Stability of devices were tested by cyclic voltammetry technique via repeatedly sweeping between -0.5 V and +1.6 V; 0.0 V and +1.7 V for PTATE/PEDOT and P(TATE-co-Th)/PEDOT devices respectively with a scan rate of 500 mV/s.

2.3.14 Open Circuit Memory Studies

After setting the device in one color state and removing the applied voltage, it should retain that color with no further current required; thus giving the device an open circuit memory. To test this property potential applied to devices for one second for each 200 seconds time intervals while monitoring the percent transmittance change at fixed wavelength. Memory effect of PTATE/PEDOT device tested at 0.0 V and +1.6 V at 620 nm , P(TATE-co-Th)/PEDOT device tested at 0.0 V and +1.6 V at 640 nm.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Characterization of monomer by ^{1}H-NMR and ^{13}C- NMR Spectroscopy

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

^{1}H NMR ($CDCl_3$) spectrum for the monomer (δ, ppm) (Figure 3.1): 8 (s, 4H) from benzene ring, 6.95-7.3 (m, 6H) from 2,4,5 positions of thiophene ring, 4.5(t, 4H) from $COOCH_2$, 3.1 (t, 4H) from thiophene-CH_2.

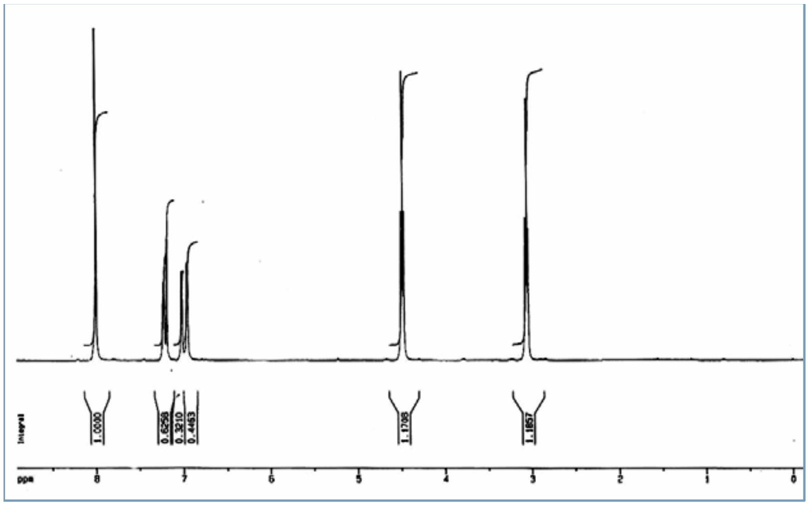


Figure 3.1 ^{1}H-NMR spectrum of the monomer

^{13}C-NMR ($CDCl_3$) spectrum for the monomer (δ, ppm)(Figure 3.2): 166 from CO; 122,126,128,138 from thiophene ring; 129, 134 from benzene ring; 65 from CH_2-O-; 30 from CH_2.

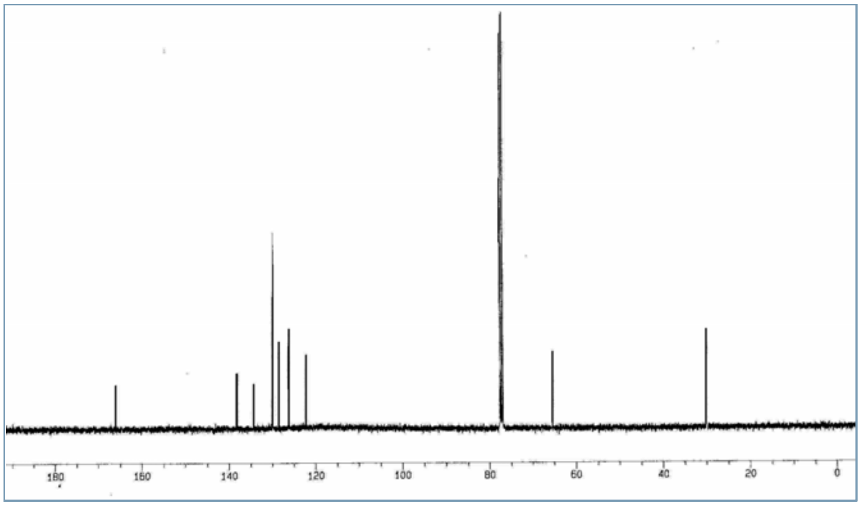


Figure 3.2 ^{13}C-NMR spectrum of the monomer

3.2. FTIR Spectra

In FTIR spectrum of monomer (Figure 3.3) the absorption bands at 780 cm^{-1} and 3093 cm^{-1} arised from thienylene C-H$_{\alpha}$ stretching modes. The bands related to the carbonyl group observed at about 1713 cm^{-1}and C-O-C stretching was at 1271 cm^{-1} respectively. Also the peak at 833 cm^{-1} was related to β-hydrogen in the thiophene ring. The peaks at 2952 cm^{-1} and 2870 cm^{-1} belong to aliphatic C-H group.

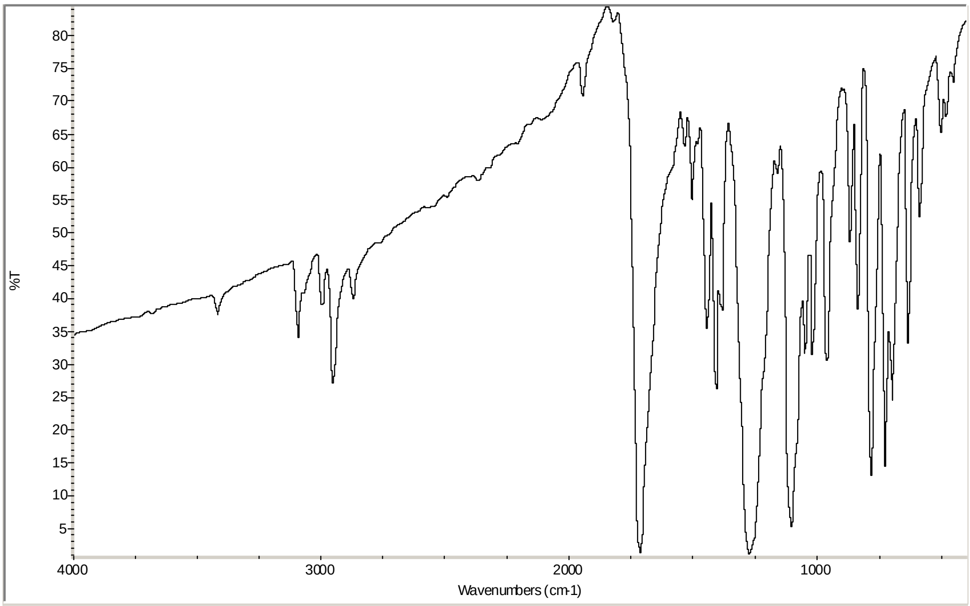


Figure 3.3 FTIR spectrum of the monomer

After the galvanostatic polymerization of TATE, the disappearance of peak at 3093 cm^{-1} and decreasing the intensity of peak at 780 cm^{-1} is an evidence of the polymerization from 2,5 position of thiophene ring (Figure 3.4). The shoulder occurring at around 1643 cm^{-1} indicates the conjugation and is a proof of polymerization. The sharp peaks in FTIR spectrum of pure monomer between 1410 and 1460 cm^{-1} became broader, which is also the evidence of conjugation. The peak appeared at 1078 cm^{-1} in figure 3.4 shows the presence of the dopant ion which is BF_4^-. The peaks at 1270 cm^{-1} and 1719 cm^{-1} appeared in spectrum means that carbonyl group exist after polymerization.

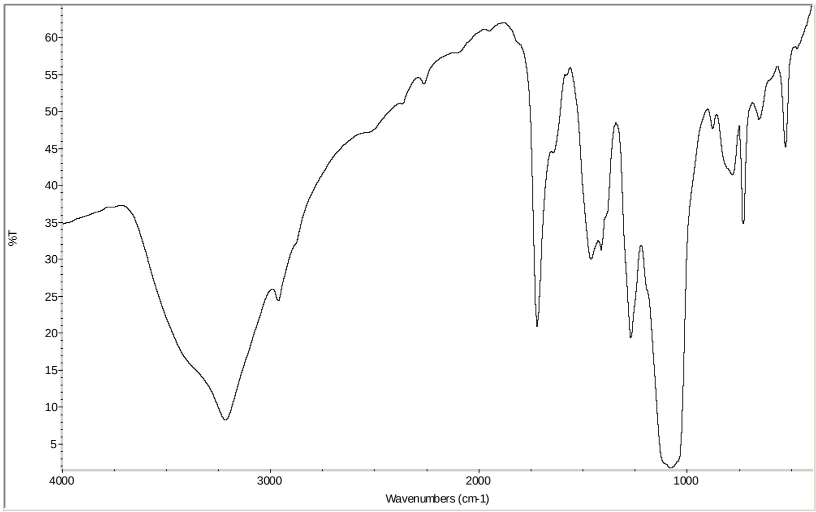


Figure 3.4 FTIR spectrum of the galvanostatically polymerized homopolymer

After the potentiostatic polymerization of TATE, the disappereance of peak at 780 cm^{-1} is an evidence of the polymerization from 2,5 positions of thiophene ring (Figure 3.5). The shoulder occuring at around 1636 cm^{-1} indicates the conjugation and is also a proof of polymerization. The peaks at 1718 cm^{-1} and 1269 cm^{-1} remained in spectrum revealing the presence of carbonyl group and C-O-C after polymerization. The peak appeared at 1086 cm^{-1} shows the presence of the dopant ion (BF_4^-).

FTIR spectrum of P(TATE-co-Th) showed the characteristic absorbtions . The peaks at 1733 cm^{-1} and 1270 cm^{-1} belonging to the carbonyl group and C-O-C moiety respectively remained unperturbed (Figure 3.6). The peak appeared at 1083 cm^{-1} shows the presence of the dopant ion (BF_4^-).

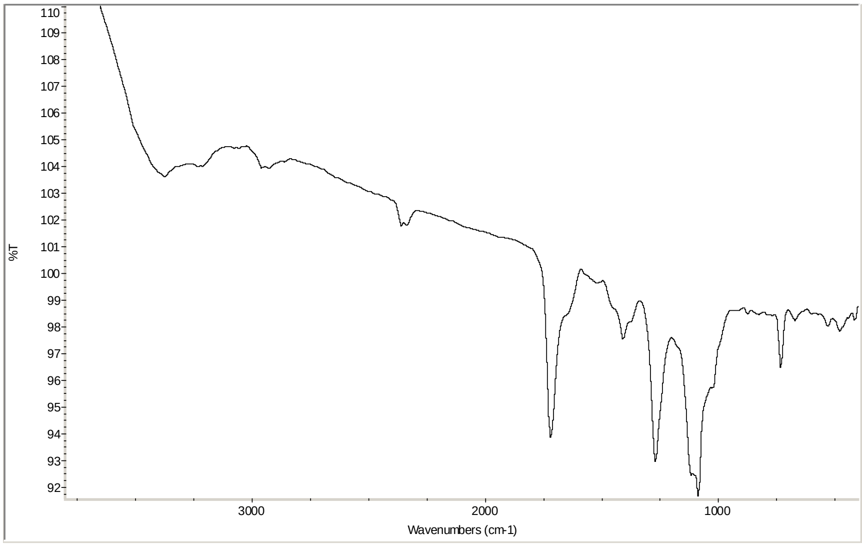


Figure 3.5 FTIR spectrum of the potentiostatically polymerized homopolymer

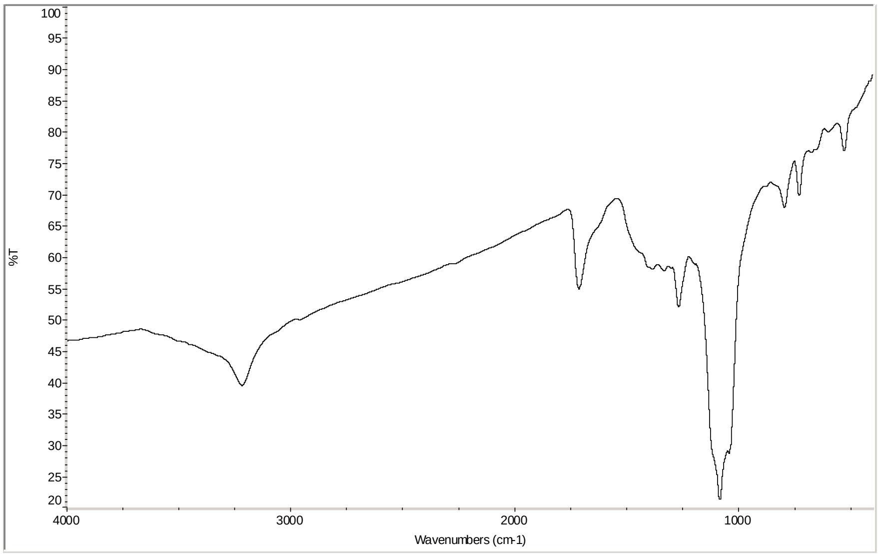


Figure 3.6 FTIR spectrum of the copolymer

3.3. Cyclic Voltammograms

Electrochemical behavior of TATE was examined by cyclic voltammetry. Upon sequential cycles, there was a gradual film formation, indicated by the continuous increase in the current intensity, which shows the electroactivity of TATE. An oxidation peak appeared at + 1.0 V and a reduction peak appeared at + 0.3 V in the cyclic voltammogram of TATE, as shown in figure 3.7 (a).

The potential values in cyclic voltammogram of TATE in the presence of thiophene was found to be + 1.0 V as the oxidation and + 0.4 V as the reduction peaks, which are different from those of both the monomer and the pure polythiophene in terms of current increments [Figure 3.7 (b)].

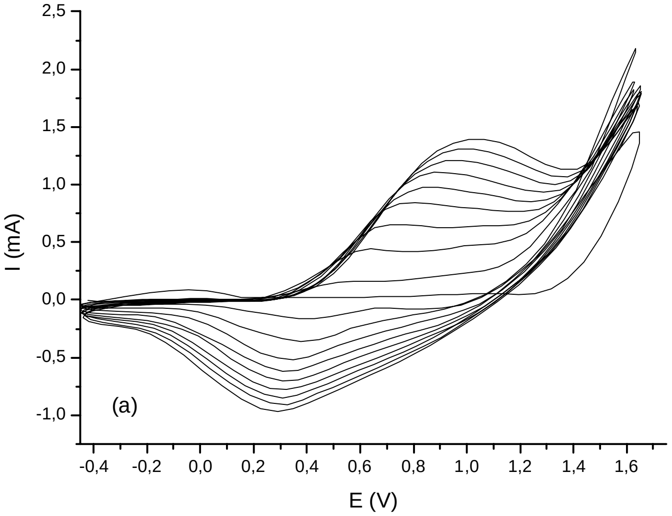


Figure 3.7 (a) Cyclic voltammogram of TATE

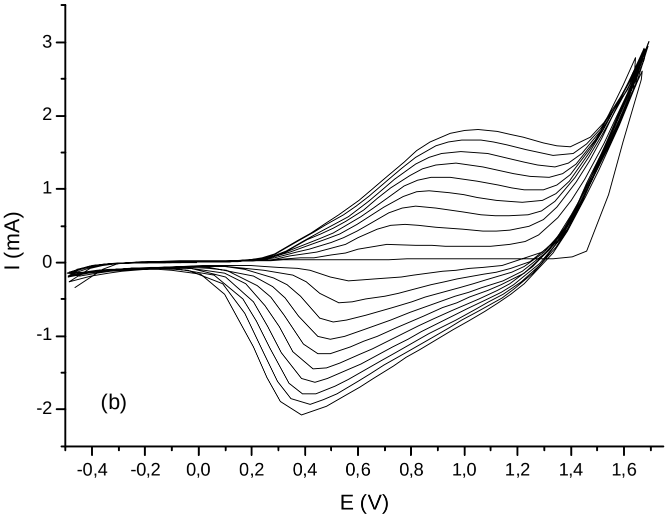


Figure 3.7 (b) Cyclic voltammogram of TATE/Th

3.4. Thermal Behaviour of Samples

DSC thermograms were examined in the range 30 to 500 ^{o}C at a heating rate of 10 ^{o}C/min. DSC thermogram of TATE exhibits two thermal events; a melting temperature at 111^{o}C and decomposition at 336 ^{o}C [Figure 3.8 (a)]. As shown in figure 3.8 (b), TGA curve of TATE showed single weight loss at 342^{o}C. DSC thermogram of PTATE exhibits a transition starting from 80 ^{o}C with a peak at 120 ^{o}C [Figure 3.8 (c)]. The TGA curve for homopolymer revealed two transitions at 81 ^{o}C and 412 ^{o}C, which can be attributed to the removal of solvent and decomposition respectively [Figure 3.8 (d)]. The char residue of PTATE was 49 % after 630 ^{o}C. However, 2 % of TATE remained after 530 ^{o}C. In the case of copolymer, DSC thermogram revealed a thermal event at 122 ^{o}C [Figure 3.8 (e)]. The thermogravimetry scan showed weight loss at 82 ^{o}C due to entrapped solvent and monomer, at 235 ^{o}C due to the removal of dopant ion and at 407 ^{o}C due to decomposition [Figure 3.8 (f)].

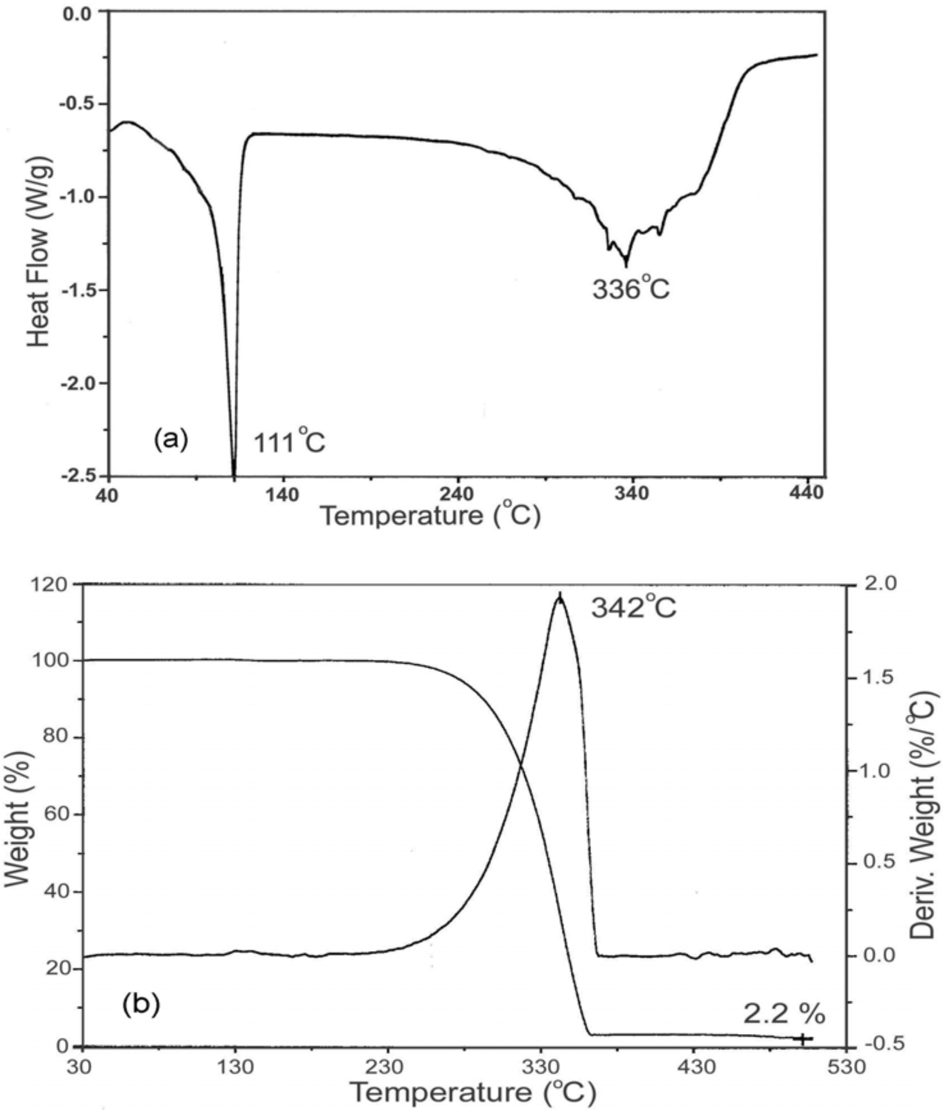


Figure 3.8 (a) DSC thermogram of TATE (b) TGA thermogram of TATE

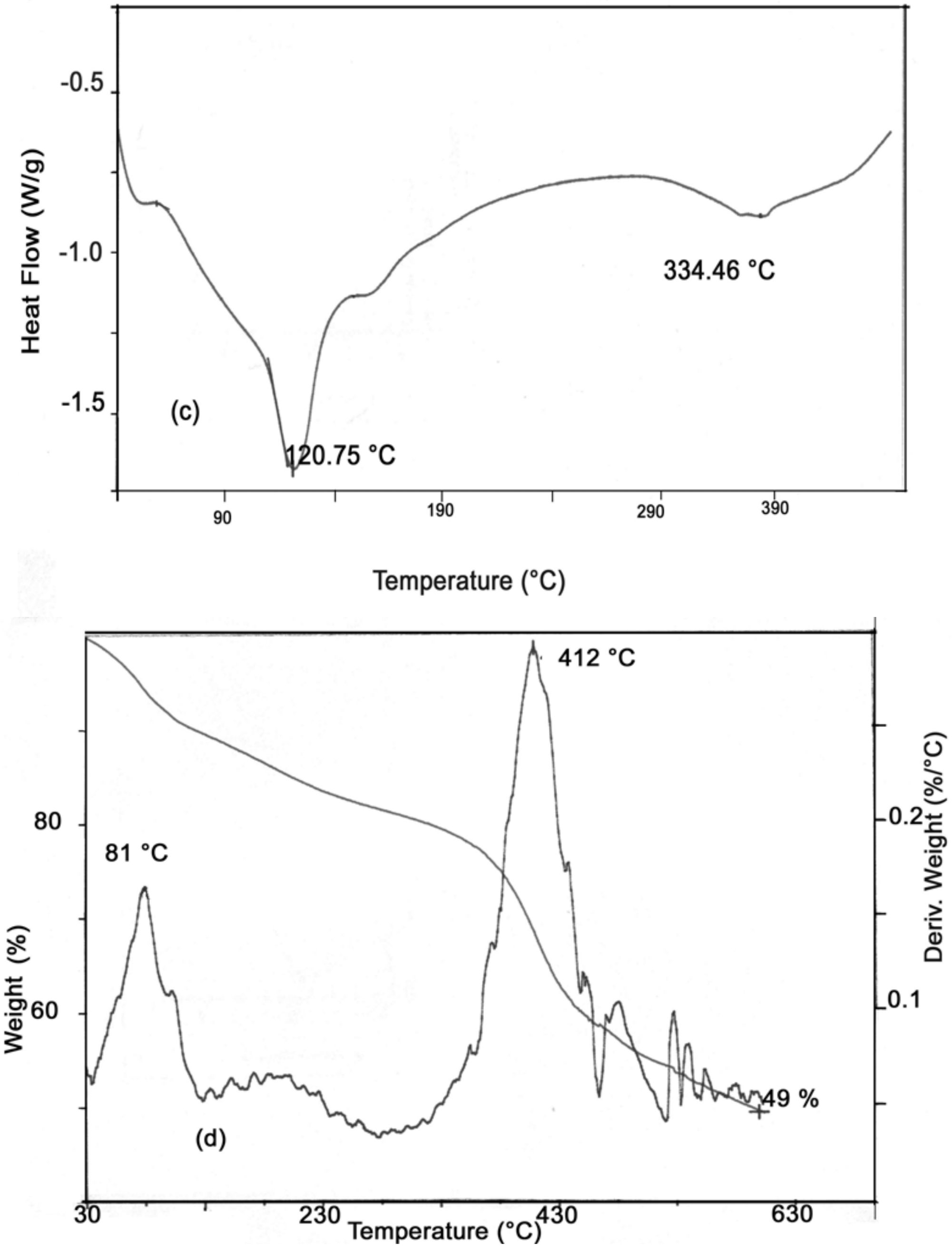


Figure 3.8 (c) DSC thermogram of PTATE (d) TGA thermogram of PTATE

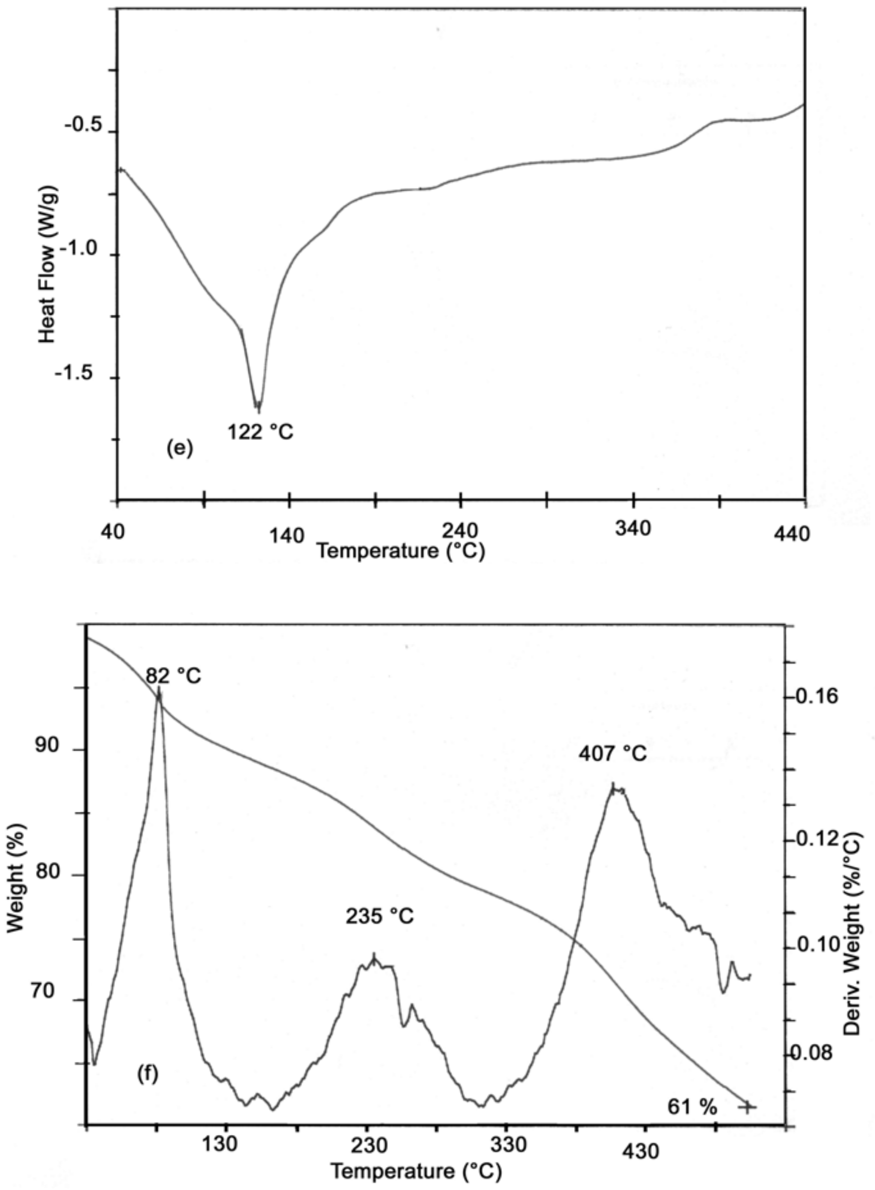


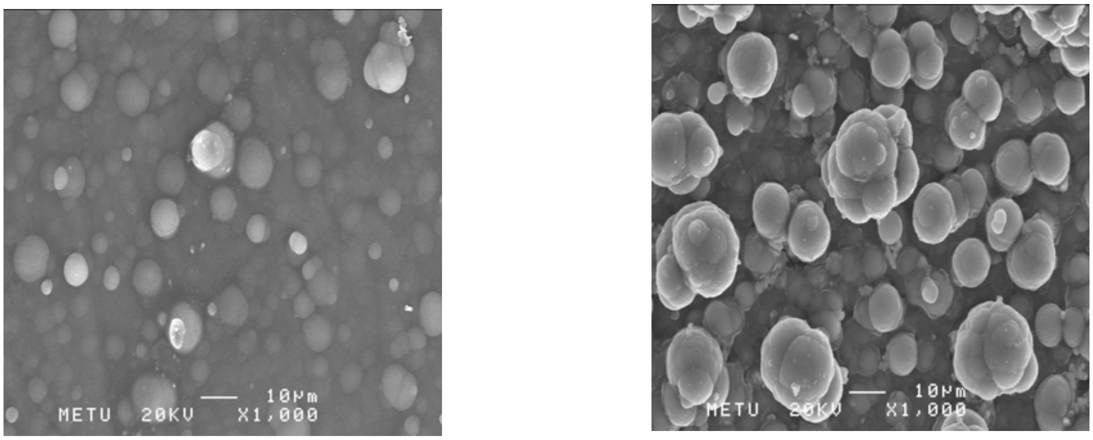
Figure 3.8 (e)DSC thermogram of P(TATE-co-Th) (f) TGA thermogram of P(TATE-co-Th)

3.5. Conductivities

The conductivity of PTATE was measured as 4×10^{-5} S/cm according to four probe technique. For the copolymer with thiophene this value was determined to be 4×10^{-3} S/cm. By the help of copolymerization conductivity increased as 10^2, which is a siginificant increase.

3.6. Morphologies of films

SEM micrograph of solution side of PTATE film shows globular structure [Figure 3.9 (a)] and the electrode side is rough. As far as the SEM micrographs of P(TATE-co-Th) are concerned, both the solution and electrode side morphologies are significantly different from that of pure polythiophene and PTATE [Figure 3.9 (b)]. Solution side of P(TATE-co-Th) reveal big droplets whereas it is cauliflower-like structure in pristine PTh case.



(a) (b)

Figure 3.9 SEM micrographs of (a) solution side of PTATE and (b) solution side of P(TATE-co-Th).

3.7. Investigation of Electrochromic Properties of Polymers

3.7.1 In-situ Electrochemical Polymerization

In-situ electrochemical polymerization of TATE and copolymerization of TATE with thiophene was investigated by UV-Vis spectrophotometer by applying +1.4 V in BFEE:AN-TBAFB system at every 20 second time intervals [Figures 3.10 (a) and (b)]. There was a gradual increase in the peak intensity at around 550 nm and 900 nm for PTATE and at around 590 nm and 900 nm for P(TATE-co-Th) revealing the formation of the charge carriers.

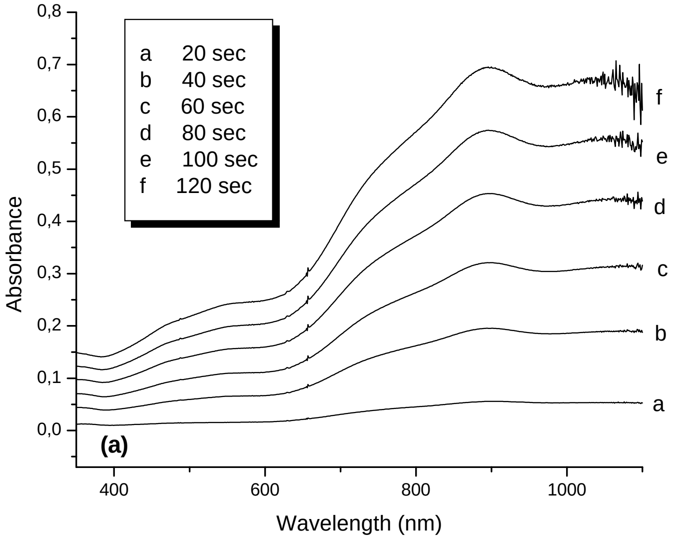


Figure 3.10 In-situ electrochemical polymerization of (a) PTATE

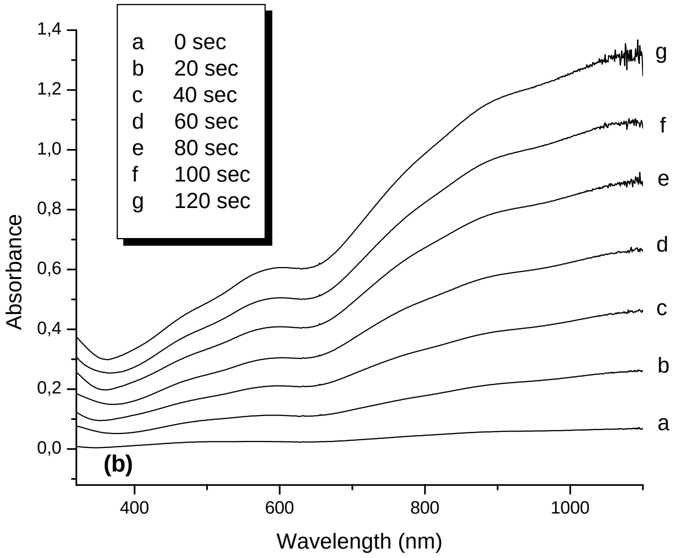


Figure 3.10 In-situ electrochemical polymerization of (b) (PTATE-co-Th)

3.7.2 Spectroelectrochemistry

Spectroelectrochemical analyses of the PTATE and P(TATE-co-Th) were studied in order to elucidate electronic transitions upon doping and dedoping of the polymer. Figures 3.11 (a) and (b) show series of optoelectrochemical spectra of PTATE and P(TATE-co-Th) respectively. The observed band gap was found to be 2.17 eV and 2.00 eV and λ_{max} values were 420 nm and 438 nm for PTATE and its copolymer, when taken at the onset of the π- -π* transition. The similar spectroscopic behavior obtained for these two polymers brings out the dominance of the TATE units in the resultant copolymer. Stepwise oxidation of polymers shows reduction in absorbance throughout the visible region as the color changes from yellow to blue. Upon applied potential, reduction in the intensity of π- -π* transitions and formation of charge carrier band was observed. The absorptions observed at 730 nm and 775 nm were attributed to polarons, at 1000 nm and 900 nm were attributed to bipolarons for PTATE and P(TATE-co-Th) respectively.

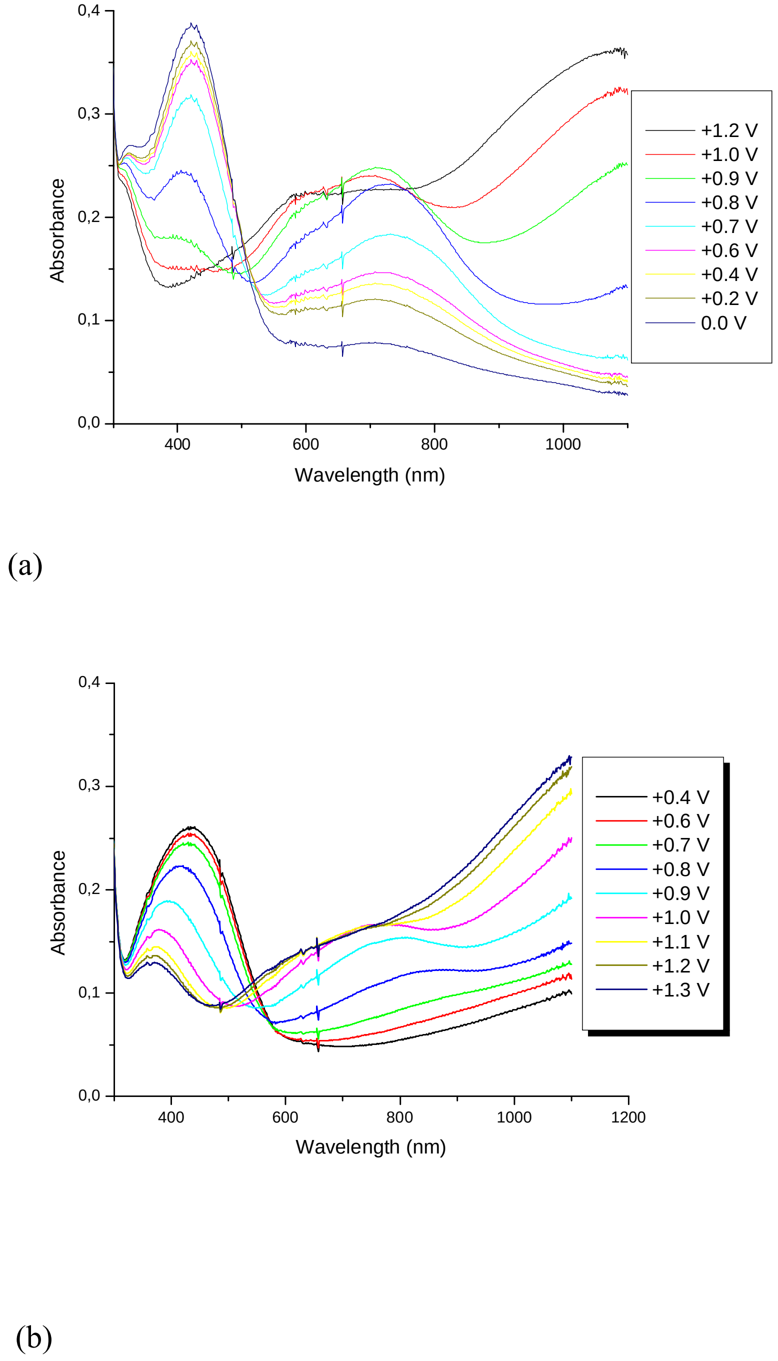


Figure 3.11 Spectroelectrochemistry of (a) PTATE (b) P(TATE-co-Th)

3.7.3 Electrochromic switching

The experiments were carried out by spectroelectrochemistry showed the ability of PTATE and its copolymer to switch between its neutral and doped states with a change in transmittance in a fixed wavelength. The results were displayed in Figures 3.12 (a) and (b) for a switching time of 5 s. It is seen that the contrast is significantly higher for the PTATE. The contrast of PTATE was measured as 43.1 % at fixed wavelength which was 1000 nm and switching time was 2.2 s [Figure 3.12 (a)]. For P(TATE-co-Th) the contrast measured at 900 nm was 20 %. Copolymer production decreased the switching time to 1.2 s [Figure 3.12 (b)].

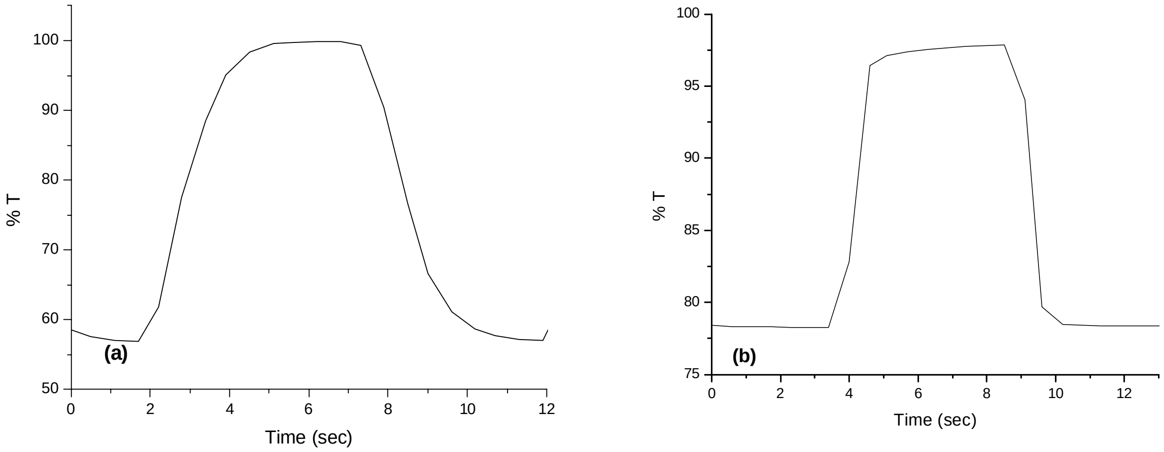


Figure 3.12 Electrochromic switching of (a) PTATE (b) P(TATE-co-Th)

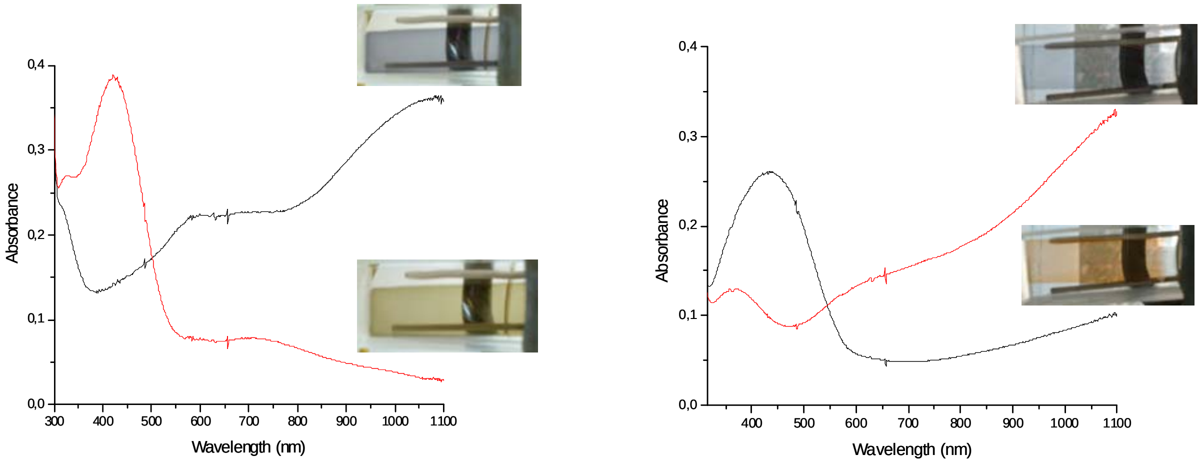
3.7.4 Colorimetry

PTATE film was blue in its oxidized state and yellow in its reduced state. P(TATE-co-Th) film was blue in its oxidized state and orange in its reduced state. L*a*b values of the films were measured at the fully reduced and fully oxidized states and the data is given in Table 1. This variation in color as well as band gap values, points to the formation of a new copolymer.

Table 3.1 Electrochromic Properties of Polymers

Polymers	λmax (nm)	L	a	b	Eg (eV)
PTh	495	ox : 57 red: 51	ox : -7 red: 52	ox : -2 red: 46	1.92
PTATE	420	ox : 67 red: 67	ox : -4 red: -3	ox : 21 red: -2	2.17
PTATE-co-Th	475	ox : 69 red: 69	ox : -5 red: 5	ox : 23 red: -2	2.00

Fully oxidized and fully reduced states of PTATE and P(TATE-co-Th) and the colors in that states are given in figures 3.13 (a) and (b).



(a) (b)

Figure 3.13 Extreme states of (a) PATE (b) P(TATE-co-Th)

3.8. Characterization of Electrochromic Devices

PTATE, P(TATE-co-Th) and PEDOT (structures shown in figure 3.14) were coated onto ITO-coated glass slides potentiodynamically. Once the PTATE film was fully oxidized and reduced back to the neutral state, the color changed from blue to yellow. P(TATE-co-Th) film was blue in its oxidized state and orange in its neutral state. PEDOT was transparent sky blue color in its oxidized state, deep blue in its neutral state. Two dual electrochromic devices, namely PTATE/ PEDOT and P(TATE-co-Th)/ PEDOT were constructed with these polymers.

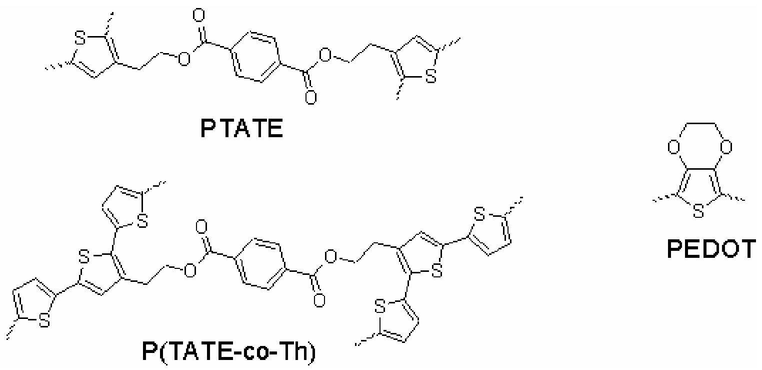
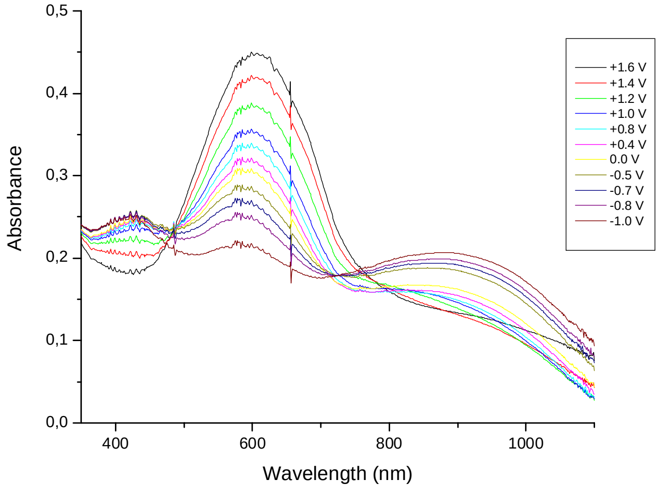


Figure 3.14 Structures of Polymers

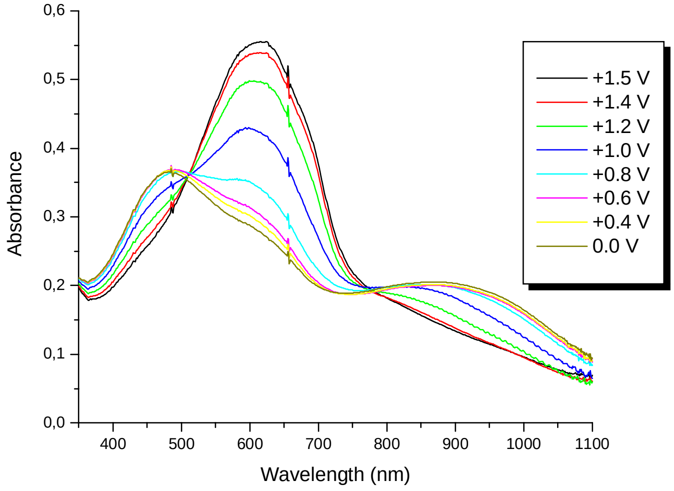
3.8.1 Spectroelectrochemistry

Spectroelectrochemical study of PTATE/PEDOT device at voltages varying between -0.2 V and + 1.6 V are shown in figure 3.15 (a). When negative potential was applied to PTATE layer, due to π-π* transition there was a maximum absorption at 420 nm revealing the yellow color. In that state PEDOT layer was in transparent blue color and device revealed yellow color. When the applied potential increased, due to reduction of PEDOT layer, blue color became dominant and maximum absorption observed at 620 nm.

Spectroelectrochemical study of P(TATE-co-Th)/PEDOT device was carried out varying the voltage between 0.0 V and + 1.5 V (figure 3.15 (b)). At 0.0 V, when the PEDOT layer was in oxidized form and reveals the transparent sky blue color, P(TATE-co-Th) layer reveals the orange color. λmax value due to π-π* transition was observed at 450 nm in that state. As the applied potential increased, especially beginning from + 0.8 V, PEDOT layer become dominant, λmax value was observed at 640 nm and color of device was revealed as blue.



(a)



(b)

Figure 3.15 Spectroelectrochemistry Study of (a) PTATE/PEDOT device (b) P(TATE-co-Th)/PEDOT device

3.8.2 Switching

To investigate switching characteristics of the ECDs, the transmission and the response time at the maximum contrast wavelength monitored during repeated redox stepping experiments. For PTATE/PEDOT device, maximum contrast (%ΔT) was measured as 12.9 and switching time was less than 2 seconds (Figure 3.16 (a)) by stepping potential between 0.0 V and + 1.6 V with a residence time of 5 s. For the case of P(TATE-co-Th)/PEDOT device, switching time and %ΔT values were measured as less than 1.1 s and 20.9 respectively (Figure 3.16 (b)) while stepping the potential between 0.0 V and + 1.6 V. Consequently, copolymerization procedure in device processing not only decreases the response time, but also increases the %ΔT.

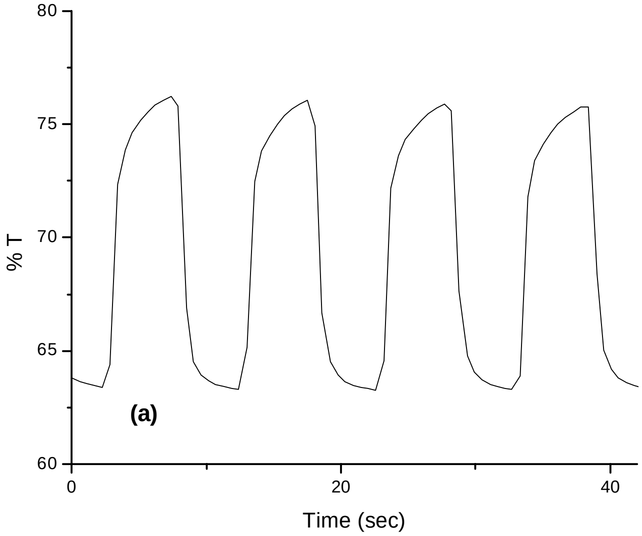


Figure 3.16 Electrochromic transmittance changes during redox switching of (a) PTATE/PEDOT device

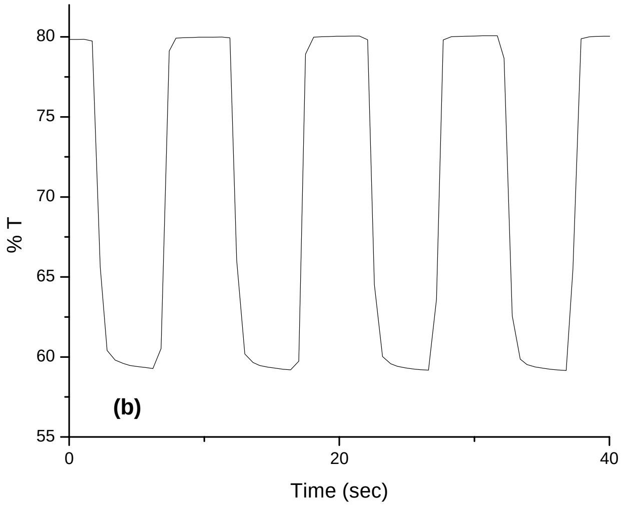
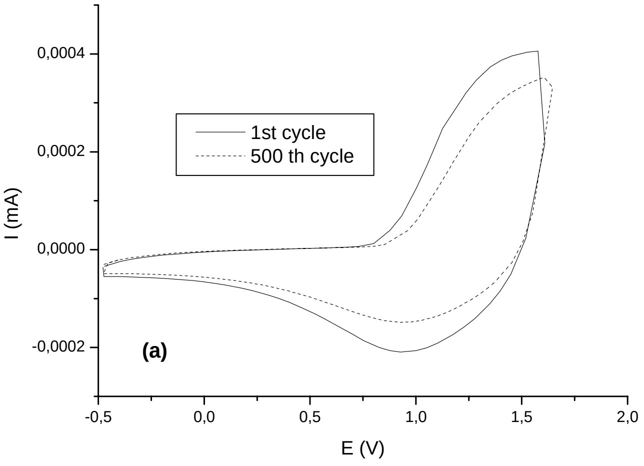


Figure 3.16 Electrochromic transmittance changes during redox switching of (b) P(TATE-co-Th)/PEDOT device

3.8.3 Stability

To test the stability of devices, potential between -0.5V and +1.6 V, 0.0 V and +1.7 V for PTATE/PEDOT and P(TATE-co-Th)/PEDOT devices respectively sweeped repeatedly with a scan rate of 500 mV/s. Between 1^{st} and 500^{th} cycles only limited decrease in the current response was observed (figures 3.17 (a),(b)), which show that ECD's have good environmental and redox stability.



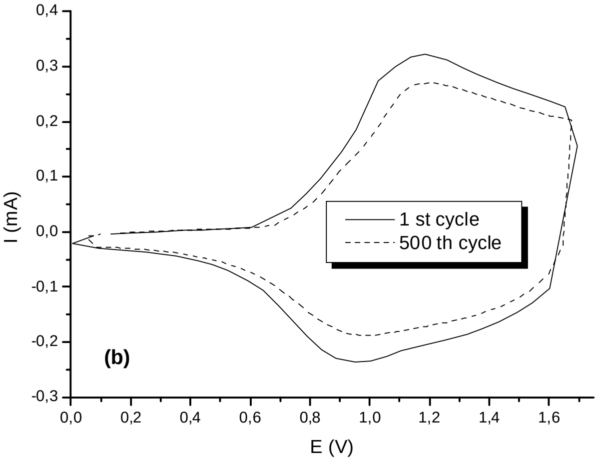


Figure 3.17 Switching stability of (a) PTATE/PEDOT device (b) P(TATE-co-Th)/PEDOT device

3.8.4 Memory Effect

Figures 3.18 (a) and (b) show the variation of the transmittance (%T) of 620 nm for yellow and blue states of PTATE/PEDOT device and 640 nm for blue and orange states of P(TATE-co-Th)/PEDOT device. We applied a pulse (0.0 V or + 1.6 V) for 1 second and held the cell in an open-circuit condition for 200 seconds while the transmittance was monitored as a function of time. We observe that the transmittance of the yellow state of the PTATE/PEDOT device is highly stable at 620 nm while blue state exhibits a 11 %T loss and at 640 nm the transmittance of the orange state of the P(TATE-co-Th)/PEDOT device is highly stable while blue state exhibits a 8 %T loss.

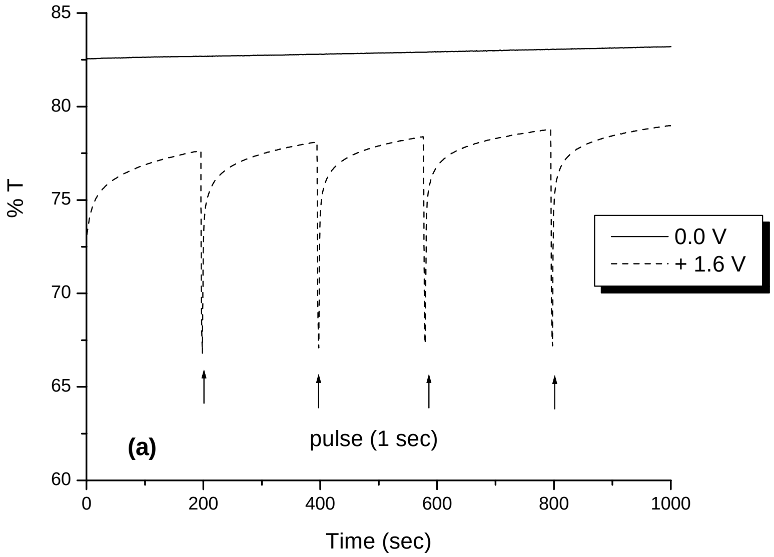


Figure 3.18 Open circuit memory of (a) PTATE/PEDOT device

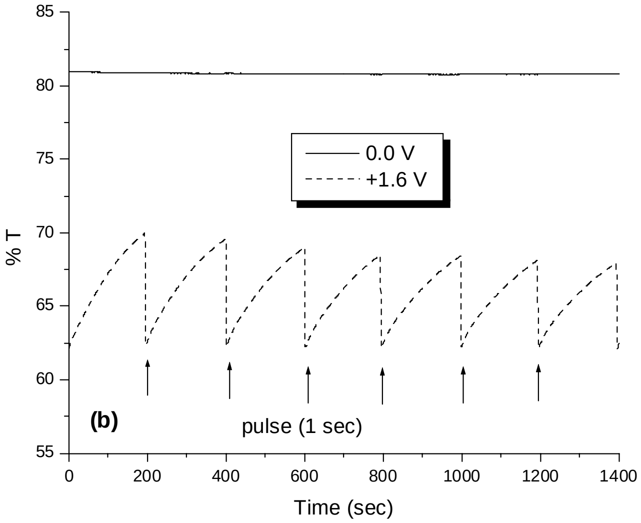
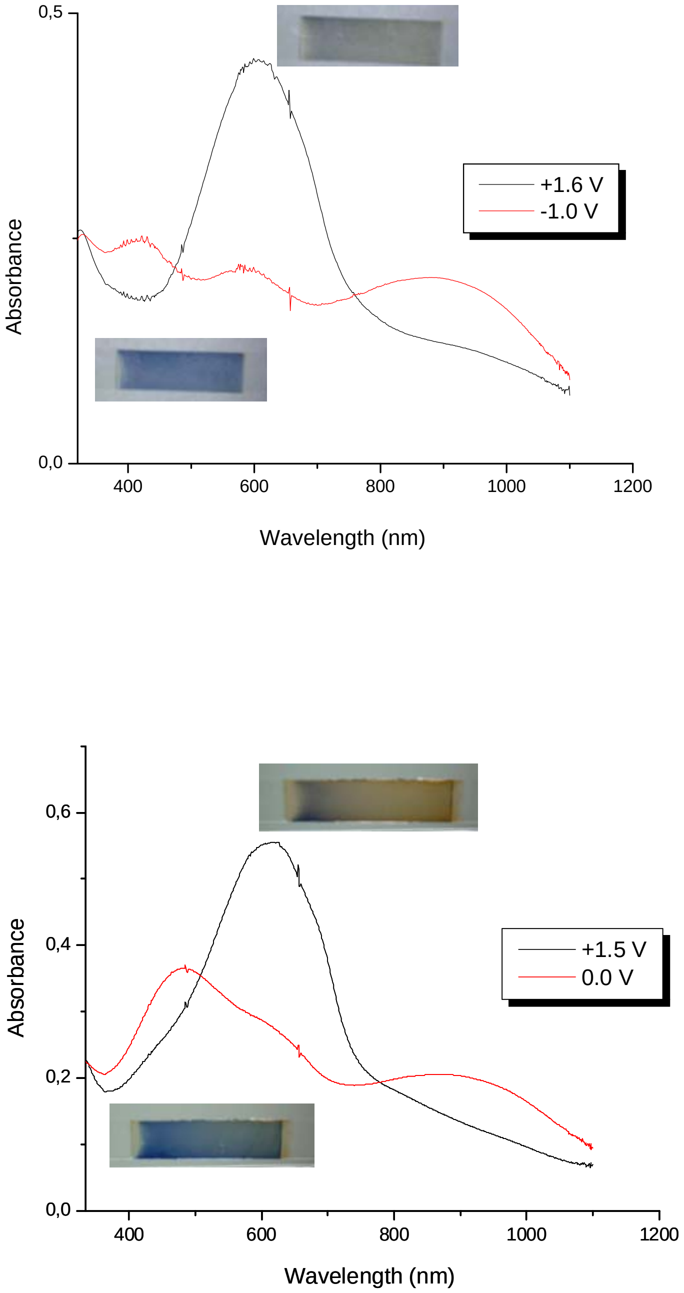


Figure 3.18 Open circuit memory of (b) P(TATE-co-Th)/PEDOT device

3.8.5 Colorimetry

The colorimetry data of the devices are given below. The L a b values were measured in their fully oxidized state, and fully reduced state. Extreme states of devices were given in figure 3.19 and electrochromic properties of devices were given in table 3.2



(a)

(b)

Figure 3.19 Extreme states of (a) PATE/PEDOT (b) P(TATE-co-Th)/PEDOT

Table 3.2 Electrochromic Properties of Devices

Electrochromic Devices	color (ox)	Color (neut)	L	a	b
PTATE/PEDOT	blue	yellow	55	-2	3
			38	-1	-24
P(TATE-co-Th)/PEDOT	intense blue	orange	36	6	26
			20	7	-34

ox: oxidized state

neut: neutral state

CHAPTER IV

CONCLUSIONS

Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester (TATE) was synthesized successfully through the reaction of 2-thiophen-3-yl-ethanol and terepthaloyl chloride. Homopolymer of TATE was synthesized through galvanostatic and potentiostatic methods. DM/TBAFB was used as the solvent electrolyte couple for the galvanostatic polymerization and DM/BFEE /TBAFB solvent mixture electrolyte couple was used for the potentiostatic homopolymerization. Copolymer of TATE with thiophene was achieved by using DM/BFEE/TBAFB solvent mixture electrolyte couple potentiostatically.

Cyclic voltammetry studies show the electroactivity of TATE. Cyclic voltammetry was also used to investigate the oxidation/reduction behavior of TATE in the presence of thiophene. Difference in cyclic voltammograms shows the interaction between Th and the Th moieties of the monomer.

The polymers were characterized by several techniques including FTIR, TGA, DSC, SEM, and conductivity measurements. The proof of copolymerization was evident in terms of FTIR results as the characteristic peaks can be seen. Also the morphologies of the films verify this result. The thermal behavior revealed the formation of thermally stable polymers. Spectroelectrochemistry results showed that both homopolymer and copolymer can be switched between their fully oxidized and fully reduced states.

Polymers were appropriate for construction of devices due to their distinctive colors, and good switching properties.

Dual type electrochromic devices were constructed by using PEDOT as cathodically coloring material and the polymers as anodically coloring materials. Devices exhibited reversible color change between the two states, reasonable stabilities, and good optical memory in their reduced state.

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LIST OF PUBLICATION

1. Y. Coskun, A. Cirpan, L. Toppare “Conducting Polymers of Terepthalic acid bis-(2-thiophen-3-yl-ethyl) ester and Their Electrochromic Properties” *Polymer* (In Press 2004)

2. Y. Coskun, A. Cirpan, L. Toppare “Construction of Electrochromic Devices Using Thiophene Based Conducting Polymer” *J. Mater. Sci.* (Submitted 2004)