

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING
POLYMERS OF SUCCINIC ACID BIS-(2-THIOPHEN-3-YL-ETHYL) ESTER
AND THEIR USE IN ELECTROCHROMIC DEVICES

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LALE SAÇAN

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Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Sciences.

Prof. Dr. Hüseyin İşçi
Head of the Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Sciences.

Prof. Dr. Levent Toppare
Supervisor

Examining Committee Members

Prof. Dr. Duygu Kısakürek (METU, CHEM) _____

Prof. Dr. Levent Toppare (METU, CHEM) _____

Prof. Dr. Erdal Bayramlı (METU, CHEM) _____

Prof. Dr. Mustafa Güllü (Ankara Unv., CHEM) _____

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ABSTRACT

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING POLYMERS OF SUCCINIC ACID BIS-(2-THIOPHEN-3-YL-ETHYL) ESTER AND THEIR USE IN ELECTROCHROMIC DEVICES

Saçan, Lale

M.Sc., Department of Chemistry

Supervisor: Prof. Dr. Levent Toppare

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A new monomer; succinic acid bis-(2-thiophen-3-yl-ethyl)ester (SATE) was synthesized through the esterification reaction of 2-thiophen-3-yl-ethanol and succinyl chloride. The chemical structure of monomer was characterized via Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Electrochemical behaviors of SATE alone and SATE in the presence of thiophene were studied by cyclic voltammetry (CV). The synthesis of homopolymer and copolymer were achieved via constant potential electrolysis. Both homopolymer (PSATE) and copolymer [P(SATE-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. The electrochromic properties of the polymers were investigated via spectroelectrochemistry, colorimetry and switching studies. In addition, dual type electrochromic devices (ECDs) composed of PSATE, P(SATE-

co-Th) and poly(3,4-ethylenedioxythiophene) (PEDOT) were constructed and evaluated. Spectroelectrochemistry, switching ability and stability of the devices were investigated by UV-Vis Spectrophotometer and Cyclic Voltammetry. They have shown to possess good switching times, reasonable contrasts, high stabilities and optical memories.

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

ÖZ

SÜKSİNİK ASİT BİS-(2-TİYOFEN-3-İL-ETİL)ESTER' İN İLETKEN POLİMERLERİNİN SENTEZİ, ELEKTROKROMİK ÖZELLİKLERİ VE ELEKTROKROMİK CİHAZLARDA KULLANIMI

Saçan, Lale

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Levent Toppare

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Yeni bir monomer; süksinik asit bis-(2-tiyofen-3-il-etil)ester (SATE), 2-tiyofen-3-ethanol ve süksinil klorürün esterleşme tepkimesi sonucu sentezlenmiştir. Monomerin kimyasal yapısı Nükleer Manyetik Rezonans Spektroskopisi ($^1\text{H-NMR}$ ve $^{13}\text{C-NMR}$) ve Fourier Transform İnfrared Spektroskopisi (FTIR) yöntemleri kullanılarak incelendi. SATE'nin ve tiyofen ile kopolimerinin elektrokimyasal davranışları dönüşümlü voltmetre vasıtasıyla araştırılmıştır. Homopolimerin ve kopolimerin sentezlenmesi sabit gerilim yöntemi kullanılarak gerçekleştirilmiştir. Gerek homopolimer (PSATE) gerekse kopolimer [P(SATE-co-Th)] Dönüşümlü Voltametri (CV), Fourier Transform İnfrared Spektroskopisi (FTIR), Taramalı Elektron Mikroskopisi (SEM), Termogravimetri (TGA), Diferansiyel Taramalı Kalorimetri (DSC) ve UV-VIS Spektrofotometresi yöntemleri kullanılarak karakterize edilmiştir. Filmlerin iletkenlikleri dört-nokta tekniği ile belirlenmiştir. Polimerlerin elektrokromik özellikleri spektroeletrokimya, kolorimetre ve renk

deęiřtirme analizleri ile tanımlanmıřtır. Ek olarak, PSATE, P(SATE-co-Th) ve poli(3,4-etilendioksitiyofen) (PEDOT) kullanılarak elektrokromik cihazlar yapılmıřtır. Cihazlar, iyi çevirme zamanlarının, uygun optik kontrastlarının, yüksek dayanıklılıklarının ve optik hafızalarının olduęunu kanıtlamıřlardır.

Anahtar Kelimeler: Süksinik asit bis-(2-tiyofen-3-il-etil)ester, Elektrokromik polimerler, İletken polimerler, Elektrokimyasal polimerleřtirme, Spektroelektrokimya, Elektrokromik cihazlar

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)
PSATE	Poly (Succinic acid bis-(2-thiophen-3-yl-ethyl)ester)
P(SATE-co-Th)	Copolymer of SATE and Th
PTh	Polythiophene
RE	Reference electrode
SATE	Succinic acid bis-(2-thiophen-3-yl-ethyl)ester
SEM	Scanning electron microscope
TBAFB	Tetrabutylammonium tetrafluoroborate
TEA	Triethylamine
TGA	Thermal gravimetry analysis
Th	Thiophene
WE	Working electrode

CHAPTER I

INTRODUCTION

1.1. Conducting Polymers

Electronically conducting polymers possess different properties related to their electrochemical behavior. The importance and the potentiality of this class of materials was recently recognized by the world scientific community when Shirakawa, Heeger and MacDiarmid (prominent scientists in conducting polymer science) were laureated in 2000 with the Nobel Price in Chemistry. Although these materials are known as new materials, the first work describing the synthesis of a conducting polymer was published in the 19th century. In that time, the “aniline black” was obtained as the product of the anodic oxidation of aniline and its electronic properties were not established. Despite this initial work, the discovery of conducting polymers as materials which present reasonable electrical conductivity is attributed to Shirakawa and co-workers, who obtained in 1974 an increase of twelve orders of magnitude in the conductivity of polyacetylene by “doping it” with electron acceptors (p-type dopants) which involved exposure of free-standing films of polyacetylene to vapors of chlorine, bromine, iodine, arsenic pentafluoride and sodium. A year later it was discovered that analogous effects may also be induced by electron donors (n-type doping). However, it turned out that, due to reactions involving counter ions of the dopants, its conductivity decreases with time. Also an “undoped” polyacetylene is unstable in the presence of oxygen, which initially acts as a dopant, but subsequent reactions, with the superoxide anions formed, destroy conjugation and cause degradation of the polymeric chains. Poor stability seems to limit the applicability of polyacetylene in commercial devices [1,2].

Much of the combined research efforts of industrial, academic and government researchers have been directed toward developing materials that are application stable in the conducting state, easily processable and relatively simple to produce at low cost. Of the many interesting conducting polymers that have been developed over the past 25 years, those based on resonance-stabilized aromatic molecules and heteroaromatic compounds such as polyanilines, polypyrroles and polythiophenes have attracted the most attention [3] due to higher environmental stability and structural versatility they possess. The electronic and electrochemical properties of these polymers can be manipulated by modification of the monomer structure [4]. Some examples of CPs are given in Figure 1.1.

Conducting polymers are frequently called “synthetic metals” because they present electric, electronic, magnetic and optical properties inherent to metals or semiconductors, while retaining some of the mechanical properties of conventional polymers [1]. The electrical conductivity results from the introduction of charge carriers (through doping) into the double bonds in the polymer backbone and from the ability of those charge carriers to move along the π -bonded “highway” [5].

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. Various methods, such as the introduction of alkyl groups into the main chain, the synthesis of soluble precursors, and the preparation of conducting polymer composites, blends, and 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].

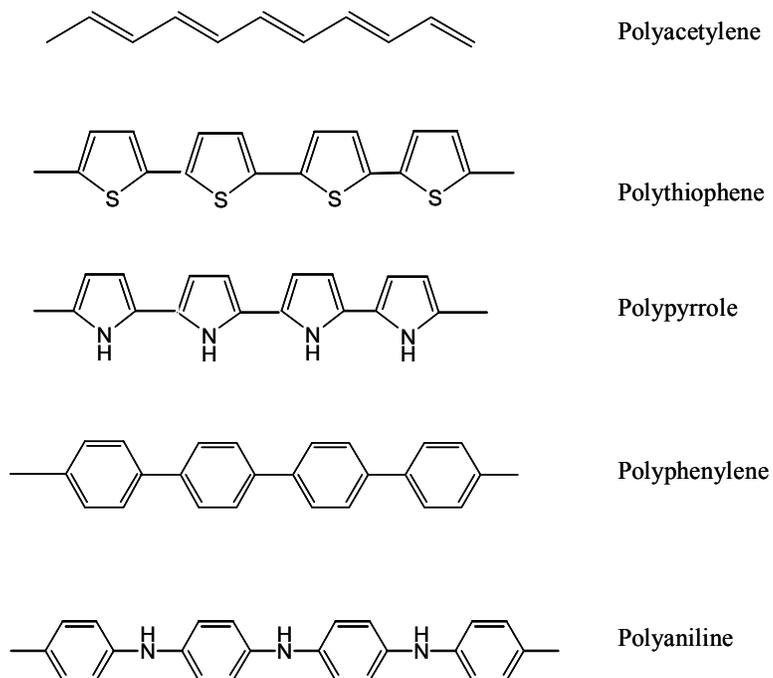


Figure 1.1 Chemical structures of some conducting polymers

1.2 Band Theory

The excitation and/or removal/insertion of electrons in conjugated polymers as a result of electrochemical or photochemical doping processes necessitate discussion of band theory. When two p atomic orbitals are involved in forming a π bond, two π molecular orbitals are formed one being filled π orbital with lower energy and the other empty π anti bonding orbital with higher energy. The magnitude of this energy difference is determined by the extent of orbital overlap. There is a energy spacing between the highest of the low energy molecular orbital (HOMO), also known as the valence band (VB); and the lowest of the high-energy molecular orbital (LUMO), known as the conduction band (CB) and this is called the band gap (E_g). The E_g of conjugated polymers can be approximated from the onset of the π - π^* transition in the UV-Vis spectrum. In their neutral form, conjugated polymers are semiconducting, but upon oxidation (p-doping) or reduction (n-doping), interband

transitions form between the VB and CB, lowering the effective band gap, and resulting in the formation of charge carriers along the polymer backbone.

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.

In semiconductors, valence band is filled and conduction band is empty. They are separated by a band gap, making conduction slightly more difficult. Introduction of dopants into semiconductor materials increases conductivity by producing states which lie loose to either the conduction or valence bands. The conduction band can be populated at the expense of the valence band by exciting electrons across the band gap either thermally or photochemically. In the case of highly conjugated conducting polymers, the difference between energy levels within these two sets of orbitals is so small that the bands may be regarded as continuous and the electron can take any energy within. Schematic representations of band structures are given in Figure 1.2.

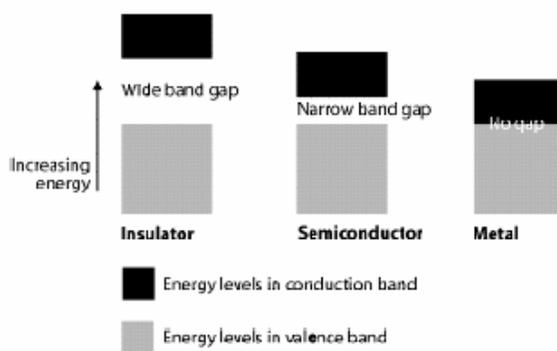


Figure 1.2 Schematic representations of band structures

The semi-conducting neutral polymer is converted into an ionic complex consisting of a polymeric cation (or anion) and a counter ion which is the reduced form of the oxidizing agent (or the oxidized form of the reducing agent). The use of

an oxidizing agent corresponds to p-type doping and that of a reducing agent to n-type doping.

In organic polymeric materials, conduction may occur through the movement of either the electrons or these ions. In each case, conductivity σ , is equal to the product of the carrier mobility μ , its charge q and the number of carriers or the concentration n , so that ;

$$\sigma = q n \mu$$

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.

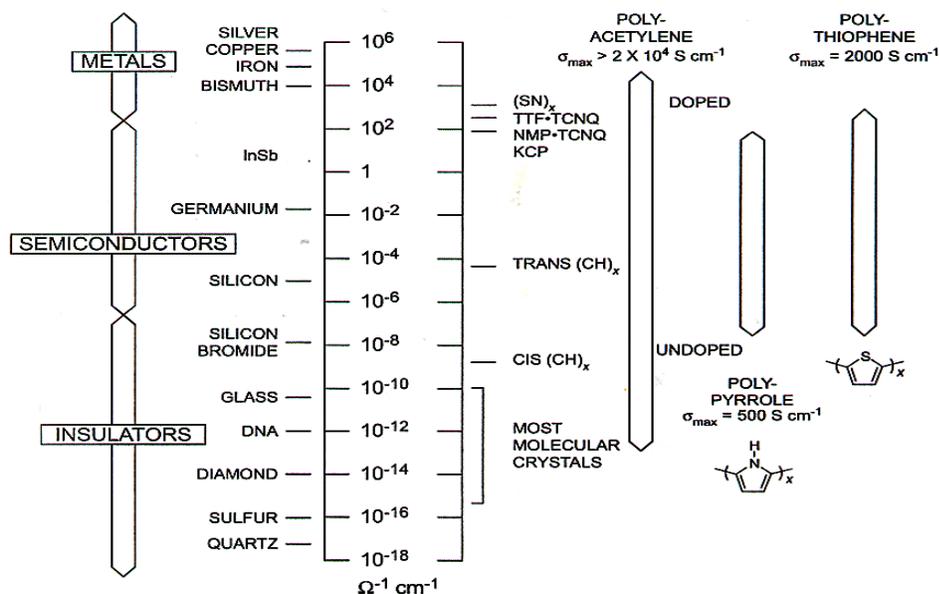


Figure 1.3 Conductivity range

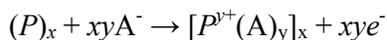
1.3 Doping Process

Conjugated organic polymers in their pure (undoped) state are best described as insulators. Due to the relatively large band gaps in conjugated polymers, the concentration of charge carriers at low temperatures is very low. Charge injection into conjugated, semiconducting macromolecular chains, “doping”, leads to the wide

variety of interesting and important phenomena which define the field of CPs. The doping process modifies the electronic structure, producing new electronic states in the band gap and causing the color changes and also generates high conductivities primarily by increasing the carrier concentration [20].

Doping is defined as the chemical oxidation of CPs by anions or reduction by cations and it is a reversible process which produces the original polymer with little or no degradation in the polymer backbone. 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. By controllably adjusting the doping level, conductivity anywhere between that of the non-doped (insulating or semiconductor) and that of the fully doped (conducting) form of the polymer is easily obtained. Doping is accomplished by chemical methods of direct exposure of the conjugated polymer to a charge transfer agent in the gas or solution phase, or by electrochemical oxidation or reduction. In the doped state, the backbone of a conducting polymer consists of a delocalized π system. In the undoped state, the polymer may have a conjugated backbone which is retained in a modified form after doping, or it may have a non-conjugated backbone which becomes truly conjugated only after p-doping [21].

p-Doping is the partial oxidation of the π backbone of an organic polymer. The basic process involves removing electrons to form a positively charged repeat unit



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



1.4 Hopping process

Carrier mobility is the main reason of electrical transport in conducting polymers. Mobility of the charge carriers can be restricted as the degree of overlapping decreases in molecular or atomic levels. As the electronic states become

increasingly localized, transport of the particle occurs through hopping process. 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 [22]. 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

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 a better understanding on the conduction mechanism of CPs [23].

A radical cation that is partially delocalized over some polymer segment as a result of break of a double bond in the polymer backbone by oxidation is called polaron. The polaron has a spin of $\frac{1}{2}$. A dication or a bipolaron has two charges associated with the localized polymer segment. Therefore, low oxidation yields polarons, and bipolarons are formed at higher oxidation potentials. Another charge defect is soliton, which is subdivided into three categories: neutral soliton, positive soliton and negative soliton. An interesting observation at this point is that charged solitons have no spin; however, neutral solitons have spin but no charge. Positively charged soliton is obtained by the insertion of acceptor band (p-type doping) or removal of an electron from localized state of a neutral soliton by oxidation. Negatively charged soliton is produced when an electron, donor band is inserted by reduction (Figure 1.4).

Polarons are obtained as a combination of a neutral and a charged soliton on the same polymer chain. Further oxidation causes more and more polarons to form

and eventually the unpaired electron of the polaron is removed, or two lone polarons can combine to form dications or bipolarons [24, 25].

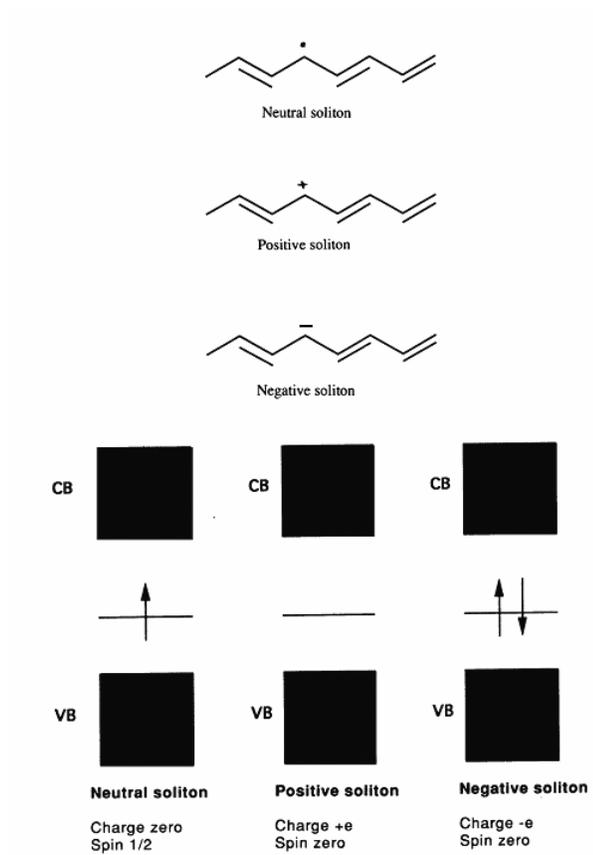


Figure 1.4 Soliton structures of polyacetylene

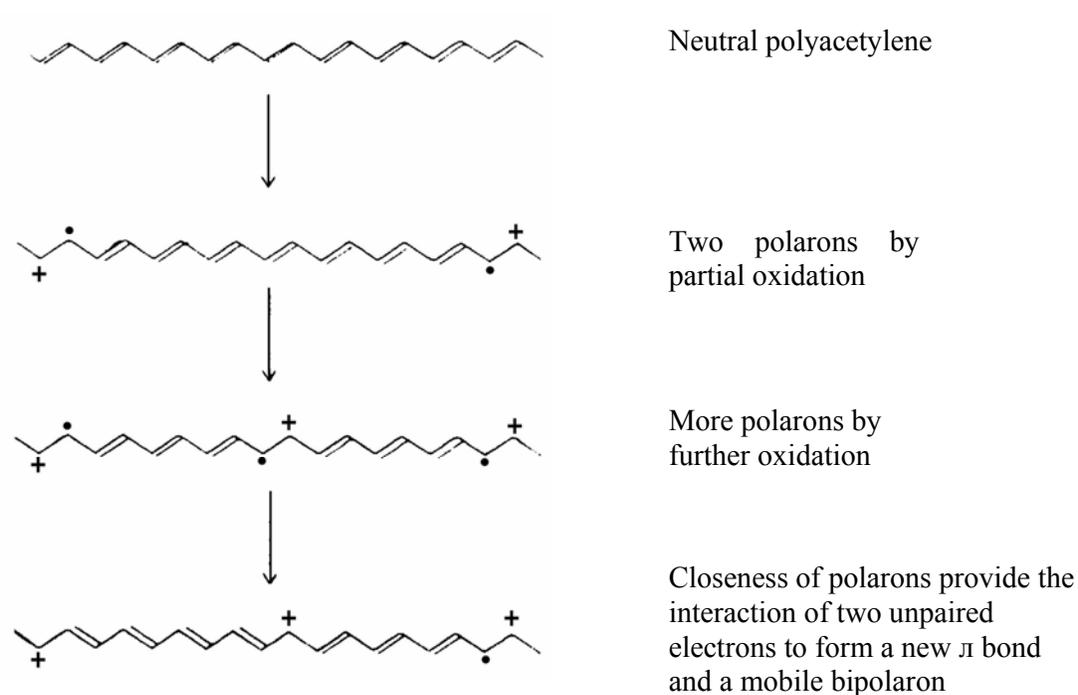


Figure 1.5 Formation of polaron and bipolaron for polyacetylene

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

Furthermore, they can be polymerized and then oxidized chemically or electrochemically. Since the electrochemical method is utilized in this study, the electrochemical polymerization will be discussed below.

Electropolymerization of molecules containing aromatic heterocyclic groups under oxidizing conditions that produces a positively charged polymer provides a unique and convenient method to synthesize smooth, free standing, electrically conducting polymer films on conductive substrates, and can easily be peeled off from

the electrode surface. There are many advantages of synthesizing conducting polymers electrochemically [27]:

- ☛ Simplicity
- ☛ Selectivity
- ☛ Reproducibility
- ☛ Easy control of the film thickness by the deposition charge
- ☛ Graft and block copolymers can be easily obtained
- ☛ It is possible to produce homogenous polymers
- ☛ Reactions are done at room temperature
- ☛ The polymer is directly obtained in the oxidized (doped) conducting form
- ☛ Films are directly deposited on the electrode surface
- ☛ Characterizations, such as CV, FTIR, spectroelectrochemistry, can be performed *in situ*

Electropolymerization is achieved by the electro-oxidation of the heterocycle in an inert organic solvent containing supporting electrolyte [28-30]. A schematic representation of the generally accepted mechanism for electropolymerization of five membered heterocycles is shown in Fig. 1.6. The initial electrochemical step (E) is 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 [31,32].

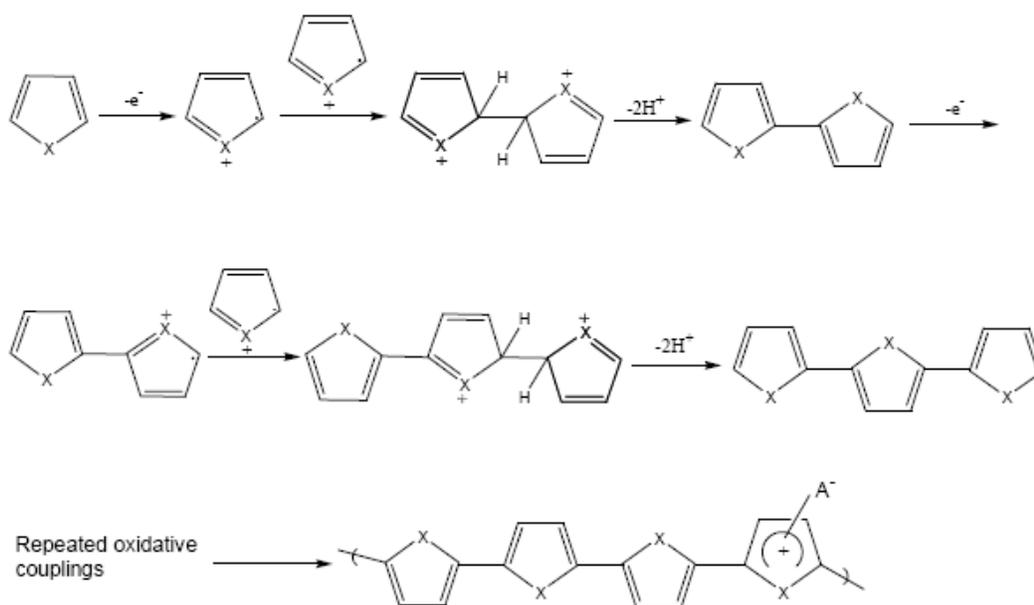


Figure 1.6 Electrochemical polymerization mechanisms of five-membered heterocycles

1.7 Electrochemical techniques

1.7.1 Constant Current Electrolysis (Galvanostatic)

Constant current electrolysis (CCE) is performed in a two electrode system, consisting of a working and a counter electrodes. The current is kept constant throughout the electrolysis and the potential is allowed to alter. The film thickness can be easily controlled by the inspection of the polymerization time. The increase in the resistance of the film may lead to a variation of potential which may cause all possible redox processes and make the nature of the generated species be unknown due to the side reactions. The complications may arise in the initiation and propagation steps [33] caused by inevitable involvement of species present in the system in addition to the monomer. In order to overcome these difficulties,

electrolyte or substrate can be added at the same rate as that of monomer consumption.

1.7.2 Constant Potential Electrolysis (Potentiostatic)

Constant potential electrolysis is carried out in a three compartment cell to maintain the potential on the working electrode and to prevent the excessive current flowing through reference electrode all which ensures effective potential control and maximize the reproducibility of the polymerization process.. The potential of the working electrode with respect to a reference is adjusted and kept constant while current is allowed to vary. Cyclic voltammetry is used in the determination of the applied potential. The voltage between the working and the reference electrodes may be called the polymerization potential (E_{pot}). By keeping the potential constant, unwanted species can be eliminated [33] and the initiation proceeds only through monomer.

1.7.3 Cyclic Voltammetry

Cyclic voltammetry is a very popular technique, in which a potential is linearly scanned up to a switching potential and then reversed to its initial value [34]. A number of electrochemical studies favor cyclic voltammetry since this method not only illustrates the formation of conducting polymers, but also indicates the potential range of its charging and discharging [35]. The applied voltage to the working electrode is in the form of triangular wave form and the current response is plotted as a function of applied potential by a recorder. This method provides useful information on the mechanism of the electrochemical reactions, reversibility of electron transfer (if it is reversible or irreversible), whether the reaction products are further reduced or oxidized, and the growth rate of conducting polymers. The increase in current with each cycle of multisweep voltammogram is a direct measure of the increase in the surface of the redox-active polymer and, thus, a convenient measure of relative growth rates.

1.8 Electrochemical Polymerization in Lewis Acid

There are some intensive efforts in the area of the electrochemical synthesis of conducting polymers to optimize the preparation by controlling the system and parameters. Borontrifluoride ethyl ether (BFEE) is a promising system which has been used for electrochemical polymerization of some heterocyclics like thiophene, pyrrole and bithiophene. Electrochemical polymerization of thiophene in BFEE yields a free standing film with good mechanical properties [36]. High applied potentials cause the degradation of the polymer and side reactions of the electrolytes and electrodes [37]. 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 [38].

1.9 Factors Affecting The Electropolymerization

Electropolymerization is affected by many parameters such as nature and concentration of the electrolyte, solvent, temperature, nature and shape of the electrodes, the electrochemical method used and the cell geometry.

The nature and the concentration of the dopant which represents about 7-25% of the weight of the polymer film for polythiophene affects the physical characteristics and morphology of a polymer. Supporting electrolyte used in electrochemical polymerization serves two purposes. Not only it makes electrolytic bath solution conducting, but also it dopes the polymer by allowing one of its ions to couple with monomer unit [39]. The choice of an electrolyte is made by considering some parameters such as its solubility, nucleophilicity, size, acidity and oxidation potential. 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. The electrolyte concentration is also important although the effect is not entirely

understood. The polymers of the highest conductivity are produced when elevated concentrations of electrolyte are used [40]. In addition to these, the counterion should be stable both chemically and electrochemically; otherwise, breakdown products can interfere in the polymerization process [41].

Solvent with high dielectric constant is required to ensure the ionic conductivity of the electrolytic medium and a good electrochemical resistance against decomposition at potentials required to oxidize the monomer. In addition, it should be capable of dissolving monomer and counterion at appropriate concentrations. Furthermore, the solvents must have poor nucleophilic character since more nucleophilic solvents are likely to attack the free radical intermediates. Aprotic solvents appear to be the best for PTh and PPy synthesis. Among these solvents, acetonitrile is the most commonly used. The basicity of the solvent is the principal factor affecting the selectivity in polymer formation. On the other hand, the solvent polarity affects the strength of the interactions between the solvent and the electrolyte anions.

Temperature is the other parameter that should be taken into consideration during electropolymerization since it has a substantial influence on the kinetics of polymerization as well as on the conductivity, redox properties and mechanical characteristics of the films [42]. It should be noted that as the temperature increases, a decrease in the redox properties is observed. 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. At higher temperatures, side-reactions such as solvent discharge and nucleophilic attacks on polymeric radicals cause the formation of more structural defects, resulting in lower conducting films. However, films with more rugged appearance and poorer adhesion are obtained at lower temperatures than those obtained at higher temperatures [43].

It is necessary to use inert electrodes, such as Pt, Au and ITO in order to avoid concurrent oxidation or reduction with the aromatic monomer [44] since the polymerization proceeds via oxidation and reduction reactions. Saturated calomel electrode (SCE), Ag/Ag⁺ and Ag/AgCl electrodes can be used as the reference electrode [39].

The choice of the electrochemical method has an influence on the morphology, appearance and adhesion of the polymer [45]. When a constant current or potential technique is used, a non-adhesive dendrite type polymer film is obtained with poor homogeneity and some electrolyte remains between the electrode surface and the polymer. On the other hand, films obtained potentiodynamically are shiny black, very adhesive, and have a smooth and homogeneous surface.

1.10 Electrochromism & Spectroelectrochemistry

Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation-reduction reaction [46]. An electrochromic material is the one that exhibits diverse variation of color and high contrast ratio depending upon oxidation state. Color changes are commonly between a transparent (“bleached”) state and a colored state or between two colored states. Where more than two redox states are electrochemically accessible in a given electrolyte solution, the electrochromic material may exhibit several colors and be termed as multicolor-electrochromic [47].

Electrochromism results from the energy difference between the π -bonding orbitals (conduction band) and the π^* -antibonding orbitals (valence band) that lies within the visible region. The optical properties of these materials can be tuned by controlled doping (and/or dedoping). The doping process (oxidation) introduces new electronic states in the band gap with a decrease in the intensity of the π -to- π^* transition and the formation of lower energy transitions causing the color changes. As doping level increases the bipolaron states overlap in bipolaron bands, the bipolaron bands may emerge with valence and conduction bands. Evolution of band structure can be seen in Figure 1.7. The π - π^* transition is the main electronic transition occurring in neutral polymers. In the neutral state, the color is determined by the band gap of the polymer. The color contrast between doped and undoped forms of the polymer depends on the magnitude of the energy gap of the undoped polymer [48]. E_g is related to the mean conjugation length of the polymer, different polymerization routes and different experimental conditions such as current density,

starting molecule concentration, electrolytic medium and temperature. Simultaneous to doping-undoping process, a mass transport takes place into the polymer bulk due to the counter-ion motion inside the films. The slower process controls the color variation kinetics in polymer films [1].

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 [49].

Electrochromic polymers which exhibit short response time, long switching life with high chromatic contrast, good optical memory and chemical stability are ideal candidates for device applications. Electrochromic response time is the time the polymer takes in response to the potential pulse to go from one color state to another. Switching life is related to the ratio of the reduction charges to the oxidation ones involved in the electrochromic process. The optical memory is the persistence of the colored state even when the driving voltage is removed [50].

Electrochromic techniques are readily employed in a multitude of applications such as controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear for the military, controllable aircraft canopies, glare-reduction systems for offices and “smart windows” for use in cars and in buildings [51-53].

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.

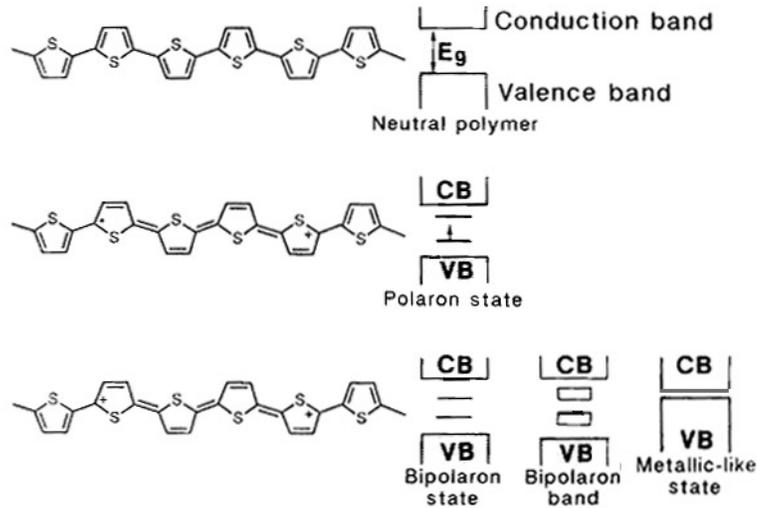


Figure 1.7 Evolution of electronic band structure with p-doping for conjugated polymer with non-degenerate ground state.

1.11 Colorimetry

For an objective description of color, a color system established by The Commission Internationale de l’Eclairage (International Commission on Illumination) which is known as the CIE system of colorimetry was used. There are three attributes to describe a color, where “L” corresponds to brightness which deals with the luminance of the material and is the transmittance of light through a sample as seen by the human eye, “a” refers to hue which represents the wavelength of maximum contrast (dominant wavelength) and is commonly referred to as color and “b” known as the saturation which takes into consideration the purity (intensity) of a certain color.

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

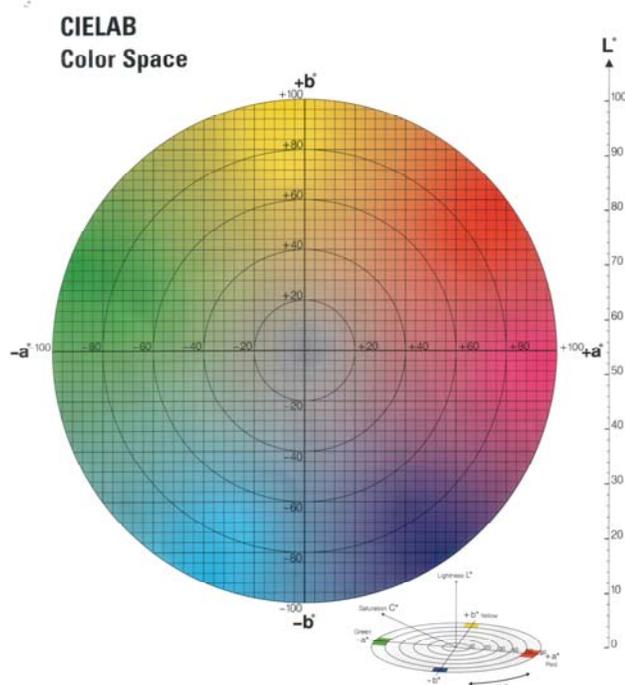


Figure 1.8 CIELAB color space

1.12 Switching

For electrochromic applications, the most important characteristics are the response time needed to switch between the two extreme redox states of the active polymer layer and the optic contrast which can be defined as the percent transmittance difference between the redox states. The ability to switch rapidly and to exhibit a striking color change is required for a polymer for use in display applications.

1.13 ECDs

An ECD is a design in which a gel electrolyte based on supporting electrolyte is sandwiched between reversibly switchable CPs such that one CP is anodically coloring while the other is cathodically coloring, allowing the device to switch

between highly transmissive and absorptive states with the applied potential of a few volts [48].

In order to maintain a balanced number of redox sites for switching, the redox charges of the two complementary polymer films were matched by chronocoulometry. Before constructing the ECD, the anodically coloring polymer film was fully reduced and the cathodically coloring polymer film was fully oxidized. Upon application of voltage, the neutral polymer will be oxidized, whereas the other will be reduced, thus will result in the color change. Schematic representation of devices is given in Figure 1.9.

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. Poly(isothianaphthene) (PITN) was reported as the first example of a low band gap, cathodically coloring CP [54]. For a number of synthetic and electrochemical reasons, PITN has not found a high level of applicability in ECDs. Since its discovery in the late 80s, PEDOT and its derivatives have proven to be outstanding polymers for use in ECDs for its high electrochromic contrast, high conductivity, low oxidation potentials, high stability in the doped form and low band gap ($E_g = 1.6$ eV, 775 nm) which allows the polymer to be almost transparent in the doped state and blue in the neutral state [55,56].

Ideally, an anodically coloring CP is chosen to have a high band gap (E_g) ≥ 3.0 eV (< 410 nm) with π to π^* electronic transitions extending from the high-energy end of the visible spectrum into the ultraviolet region. In its reduced form, the polymer is transmissive to a major portion of the visible spectrum. This anodically coloring behavior is observed for many of the common conjugated polymers, including poly(*p*-phenylene), polypyrrole, and poly(*p*-phenylene vinylene) [48].

A high performance electrochromic device should have; high electrochromic efficiency, expressed in $\text{cm}^2 \text{C}^{-1}$ 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 [1].

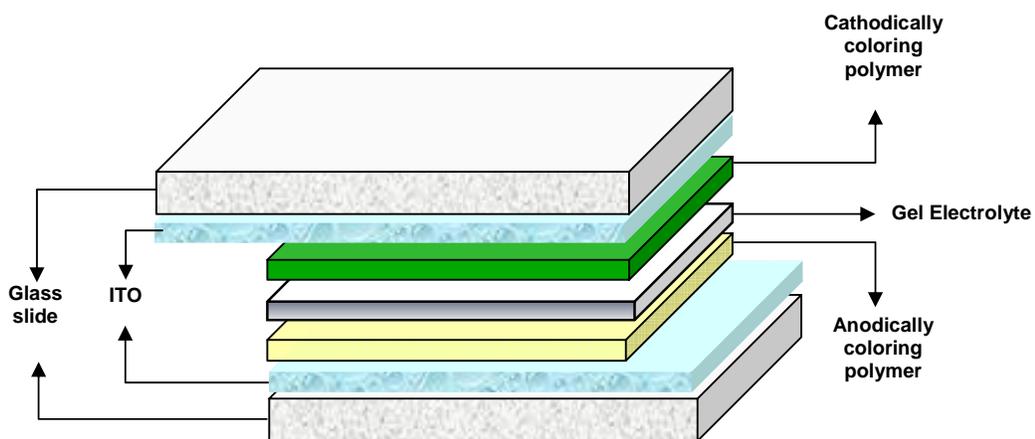


Figure 1.9 Schematic representation of ECDs

1.14 Aims of the work

Aim of this work is to synthesize succinic acid bis-(2-thiophen-3-yl-ethyl)ester (SATE), perform electrochemical polymerization of SATE and its copolymer with thiophene, characterize the resultant products with various techniques, investigate their spectroelectrochemical and electrochromic behaviors and lastly examine their use in electrochromic devices.

CHAPTER II

EXPERIMENTAL

2.1 Chemicals

2-thiophen-3-yl-ethanol (Aldrich), succinyl 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 (CE). The major current passes through the CE and WE. Electrochemical reactions occur at working electrode.

Potentiostat controls the voltage difference between a working electrode (WE) and a reference electrode (RE) by injecting current into the cell through the counter electrode (CE) minimizing the effect of IR drop by positioning reference

electrode close to the working electrode. To compensate the changes in potential of working electrode, potentiostat continuously checks the potential of working electrode measured with respect to reference electrode, and changes the potential difference in between to maintain the desired potential value that was set.

2.2.2 Cyclic Voltammetry System

Cyclic voltammetry system is a convenient way of obtaining the oxidation-reduction peak potentials of the substrates such as monomers and to analyze the electroactivity of polymers. It is carried out by sweeping the potential of stationary electrode from the initial potential E_1 to the final potential E_2 , and the direction of voltage scan is reversed when E_2 is reached. The sweeping is done by applying a triangular voltage wave form to the electrode. Either a single cycle or more can be carried out. The cell consists of ITO coated glass working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode. The volume of the cell is about 15 mL and its geometry is given in Figure 2.1. CV experiments were carried out by a Solatron 1285 potentiostat/galvanostat. XY recorder was used to obtain the voltammograms.

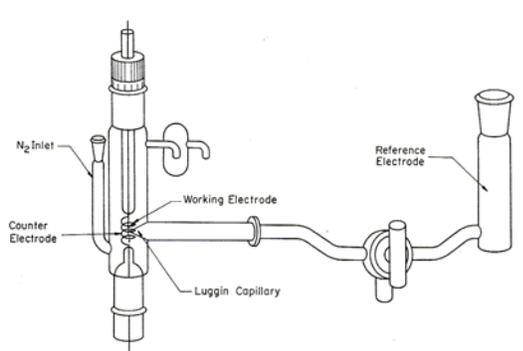


Figure 2.1 Cyclic Voltammetry Cell

2.2.3 Electrolysis Cell

The electrolysis were performed in a one-compartment cell which has suitable inlets for passing N_2 gas through the solution equipped with two platinum

(Pt) foil electrodes as the working and counter electrodes and a silver (Ag) wire as the reference electrode.

2.2.4 Nuclear Magnetic Resonance Spectrometer (NMR)

NMR Spectra of the monomer were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) with CDCl_3 as the solvent and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard.

2.2.5 Fourier Transform Infrared Spectrometer (FTIR)

All the monomer and copolymer samples were transformed into KBr pellets and all the spectra were recorded by using a Nicolet 510 FT-IR spectrometer in order to detect the functional groups present in the polymers.

2.2.6 Thermal Analyses

Thermal analyses were carried out by using Du Pont 2000 Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analyser (TGA) with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under N_2 atmosphere.

2.2.7 Scanning Electron Microscope (SEM)

Surface morphologies of conducting polymer films were inspected by a JEOL JSM-6400 scanning electron microscope.

2.2.8 Four-Probe Conductivity Measurements

Among available conductivity techniques, four probe method is more reliable and rapid one to measure the electrical properties of conducting polymers since it

eliminates the errors caused by contact resistance with the contacts measuring the voltage drop different from the contacts applying the current across the sample.

In four-probe technique, four equally spaced osmium tips were placed on a head which was lowered to the sample till the probes touch the sample. 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. The simplest form of a four-point probe measurement setup is shown in Figure 2.2. Conductivity is calculated from the following equation:

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

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

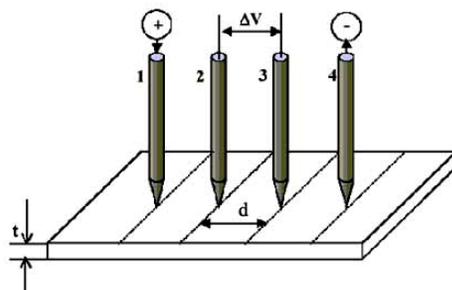


Figure 2.2 Schematic representation of the four-probe device

2.2.9 UV-Vis Spectrophotometer

Spectroelectrochemical and kinetic studies of the polymers and the devices were recorded by Agilent 8453 UV-Vis spectrophotometer.

2.2.10 Colorimetry Measurements

Colorimetry measurements were performed by using the Coloreye XTH Spectrophotometer (GretagMacbeth).

2.3 Procedure

2.3.1 Synthesis of succinic acid bis-(2-thiophen-3-yl-ethyl)ester (SATE)

2-Thiophen-3-yl-ethanol (1.12 mL (0.01 mol)) was dissolved in 10 mL dichloromethane containing 1.11 mL (0.008 mol) triethylamine (TEA). To this solution, succinyl chloride (0.44 mL, 0.004 mol) in 10 mL of dichloromethane was added dropwise in 0.5 h, by cooling in ice bath under nitrogen atmosphere. The esterification was carried out for over night at 0 °C. Then the solution was washed with HCl 1% solution (three times) and water (three times). The organic layer was dried over Na₂SO₄ and the solvent was removed via rotaevaporatory. Twice recrystallization from ethanol provided 1.1 g of white crystals (yield 71 %). Route for synthesis is shown in Figure 2.3.

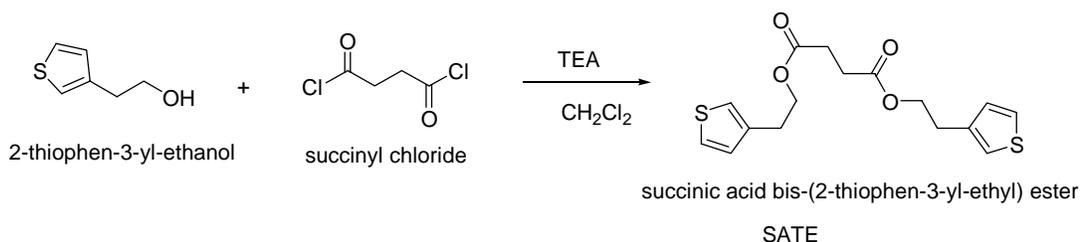


Figure 2.3 Synthesis route of SATE.

2.3.2 Synthesis of Homopolymer of SATE

Synthesis of homopolymer of SATE was achieved via constant potential electrolysis. Experiment was carried out in a one compartment cell in the presence of ACN/BFEE solvent mixture (10:2, v/v), 0.01 M SATE and TBAFB (0.1 M) as the supporting electrolyte, equipped with Pt working and counter electrodes and a Ag/Ag⁺ reference electrode by the application of 1.6 V for 30 min at room temperature under inert atmosphere. The free standing films were washed with ACN several times to remove unreacted monomer and TBAFB.

2.3.3 Synthesis of Copolymer of SATE with Thiophene

For the synthesis of the conducting copolymer of SATE with thiophene, constant potential electrolysis was carried out in ACN/BFEE (10:2, v/v) solvent mixture composed of 0.01 M SATE, 0.1 M TBAFB and 30 μL thiophene at 1.6 V in one compartment cell where the working and counter electrodes were Pt and the reference electrode was Ag/Ag^+ . Films were washed with ACN several times to remove unreacted monomer and TBAFB.

2.3.4 Potentiodynamic Study of Polymers

Oxidation/reduction behaviors of SATE and its copolymer with thiophene were investigated by cyclic voltammetry (CV) in ACN:BFEE (10:2 v/v) solvent mixture in the presence of 0.1 M TBAFB as the supporting electrolyte and 0.01 M SATE, where additional 4 μL thiophene was also present for the investigation of copolymer. The measurements were performed in a three electrode cell consisting of Pt wire as the counter, Ag/Ag^+ as the reference, Pt-foil as the working electrode sweeping between 0 and +1.7 V for the investigation of the polymers.

2.3.5 Spectroelectrochemical Analyses

Spectroelectrochemical studies of the polymers were carried out by Agilent UV-Vis spectrophotometer in a UV-cuvette as a single compartment three electrode cell equipped with ITO-coated glass slide as working, Pt wire as the counter and Ag/Ag^+ wire as the pseudo reference electrodes. Thin films of the samples were deposited on ITO-coated glass slides potentiodynamically and potentiostatically for homopolymer and copolymer, respectively, in ACN:BFEE (10:2 v/v) solution consisting of 0.01 M SATE and 0.1 M TBAFB, where additional 4 μL thiophene was also present for the investigation of copolymer. Following the deposition of films on ITO slides, a background measurement, using a blank ITO slide, and then sample measurements, using coated ITO slides, were carried out in monomer-free,

ACN/BFEE/TBAFB (0.1 M) solution sweeping from 0.0 to +1.2 V and from +0.2 to +1.2 V for homopolymer and copolymer, respectively, at the same time.

2.3.6 Switching Analyses

In order to get information about the potentials to be applied for a full switch and the wavelength of maximum contrast, spectroelectrochemistry results should be taken into account. A square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry was applied to evaluate the response time and the optical contrast. By this technique, polymers coated on ITO slides were switched in monomer-free, ACN/BFEE/TBAFB (0.1 M) solution between the potentials of fully oxidized and reduced states for a residence time of 5 seconds cycling 15 times at 421 nm for the homopolymer and 120 times at 456 nm for the copolymer while monitoring the percent transmittance as a function of time.

2.3.7 Colorimetry Analyses

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. After synthesizing PSATE and P(SATE-co-Th) films on ITO electrodes, they were placed into monomer-free solutions containing ACN/BFEE/TBAFB (0.1 M) solution. Three attributes of color; hue (a), saturation (b) and luminance (L) were measured.

2.3.8 Electrochromic Device (ECD) Construction

Polymers were coated on ITO-glass electrode by Solatron 1285 model potentiostat/galvanostat, in order to construct ECD's. A three-electrode cell containing an ITO-coated glass slide as the working electrode, a platinum flake as the counter electrode, and a silver wire as the pseudo-reference electrode was used for electrodeposition of the polymer films. Poly (3,4-ethylenedioxythiophene)

(PEDOT) was potentiostatically deposited on ITO working electrode by applying +1.5 V in ACN/TBAFB (0.1 M) solvent-electrolyte system. P(SATE) film was deposited on ITO-glass electrode via cyclic voltammetry, scanning between 0.0 V and 1.6 V in ACN:BFEE (10:2 v/v) solution, containing 0.01 M SATE and 0.1 M TBAFB. P(SATE-co-Th) film was prepared potentiostatically at 1.6 V in the same solution that contains additional 4 μ L thiophene. In order to improve the optical stability during redox process and minimize the effect of charge imbalances which may lead to residual coloration of the ECD, it is important to equilibrate the charge on the electrodes. The redox charges of the two complementary polymer films were matched by chronocoulometry and a balanced number of redox sites was provided for switching. The electrodes were arranged by doping one of the polymers while leaving the other in neutral form, placing them in a position to face each other and sandwiching the gel electrolyte in between to provide ion exchange. When the excess ACN is evaporated, the gel electrolyte seals itself and the construction is not ruined.

2.3.8.1 Gel Electrolyte Preparation

Gel electrolyte which is a highly transparent and conductive gel was prepared by using TBAFB:ACN:PMMA:PC in the ratio of 3:70:7:20 by weight. Initially, electrolyte salt was dissolved in ACN, and then PMMA was added to the solution with vigorous stirring at mild temperature (60 °C) for a period of two hours in order to dissolve. When all of the PMMA was dissolved and homogeneity of the solution was achieved, PC, as a plasticizer, was introduced into 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.

2.3.8.2 Spectroelectrochemical studies of devices

The characterization of the devices' optical properties was carried out using a HP8453A UV-Vis spectrophotometer. A device without the electrochromic polymer layer, but otherwise with the same assembly, was used as reference. In order to apply

voltage across the device, the counter and the reference leads are connected to one another.

Spectroelectrochemistry analyses were obtained by sequentially stepping the potentials. The devices were constructed by using PSATE and P(SATE-co-Th) as the anodically and PEDOT as the cathodically coloring materials (PSATE/PEDOT and P(SATE-co-Th) devices) switching at voltages varying between 0.0 V and + 1.9 V for homopolymer and 0.0 V and + 1.8 V for copolymer while measuring the absorbance as a function of wavelength.

2.3.8.3 Switching studies of devices

Switching properties of the devices were investigated by application of potential square wave technique (2.3.6) with a residence time of 5 seconds between 0.0 V and +1.9 V for PSATE/PEDOT device, between 0.0 V and +1.8 V for P(SATE-co- Th)/PEDOT device. The experiments were carried out at 618 and 632 nm for PSATE/PEDOT and P(SATE-co-Th)/PEDOT devices, respectively, where the maximum transmittance difference between redox states were observed in the visible region.

2.3.8.4 Stability of the devices

Cyclic voltammetry technique was used for the stability experiments of the devices via repeatedly sweeping between 0.0 V and +1.9 V; 0.0 V and +1.8 V for PSATE/PEDOT and P(SATE-co-Th)/PEDOT devices, respectively, with a scan rate of 500 mV/s.

2.3.8.5 Open Circuit Memory Studies

Color persistence of an induced state after the applied potential is turned off is required for a device to possess a good open circuit memory. To test this property, potential was applied to the devices for one second for each 100 seconds time

intervals while monitoring the percent transmittance change at a fixed wavelength. Memory effect of the devices were tested at 0.0 V and +1.9 V at 618 nm for PSATE/PEDOT device and at 0.0 V and +1.8 V at 630 nm for P(SATE-co-Th)/PEDOT device.

CHAPTER III

RESULTS AND DISCUSSION

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

$^1\text{H-NMR}$ (CDCl_3) spectrum for the monomer (δ , ppm) (Figure 3.1): 6.91-7.2 (m, 6H) from 2,4,5 positions of thiophene ring, 4.24 (t, 4H) from COOCH_2 , 2.85 (t, 4H) from thiophene- CH_2 , 2.52 (s, 4H) from CO-CH_2 .

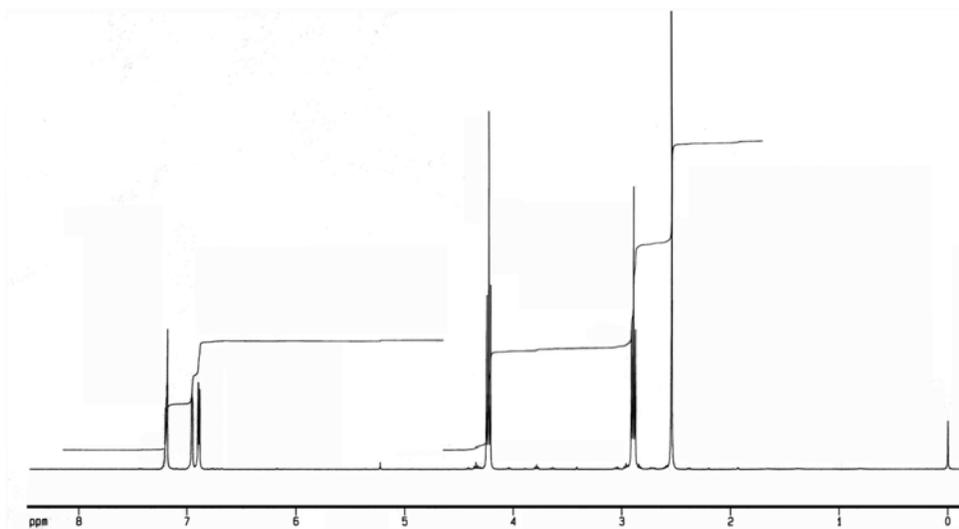


Figure 3.1 $^1\text{H-NMR}$ spectrum of the monomer

$^{13}\text{C-NMR}$ (CDCl_3) spectrum for the monomer (δ , ppm) (Figure 3.2): 172.6 (CO); 122.1, 126.3, 128.4, 137.9 (thiophene ring); 65.3 ($\text{CH}_2\text{-O}$); 29.5 (CH_2).

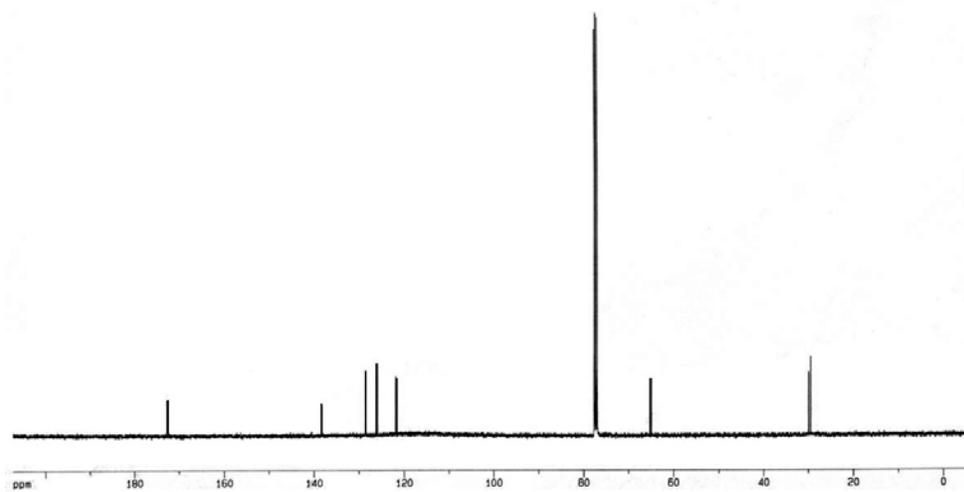


Figure 3.2 ^{13}C NMR spectrum of the monomer

3.2 FTIR Spectra

In the FTIR spectrum of the monomer (Figure 3.3), the absorption bands at 793 and 3094 cm^{-1} arose from thiophene out of plane C-H_α and aromatic C-H stretching modes, respectively. The bands related to the carbonyl group and C-O-C stretching were observed at about 1718 and $1070\text{-}1290\text{ cm}^{-1}$, respectively. Also the peak at 834 cm^{-1} was related to thiophene out of plane C-H_β stretching. The peaks at 2898 cm^{-1} and 2960 cm^{-1} were related to aliphatic C-H group.

Most of the characteristic peaks of the monomer, SATE, were present upon the potentiostatic homopolymerization, especially the bands related to the carbonyl group and C-O-C stretching. The disappearance of the peaks at 793 and 3094 cm^{-1} with the evolution of a new absorption peak at 820 cm^{-1} related to 2,3,5-trisubstituted thiophene is an evidence of the polymerization from 2, 5 positions of thiophene ring (Figure 3.3). Presence of the peaks at 1083 cm^{-1} and the shoulder at around 1643 cm^{-1} is due to presence of the dopant ion (BF_4^-) and the polyconjugation, respectively, all which could be considered as a proof of polymerization.

Similarly, the characteristic absorptions of the SATE are also observed in the FTIR spectrum of P(SATE-co-Th) . The peaks which belong to carbonyl group and

C-O-C moiety remained in the spectrum signifying the formation of polymerization (Figure 3.3). The peak appeared at 1084 cm^{-1} shows presence of dopant ion (BF_4^-).

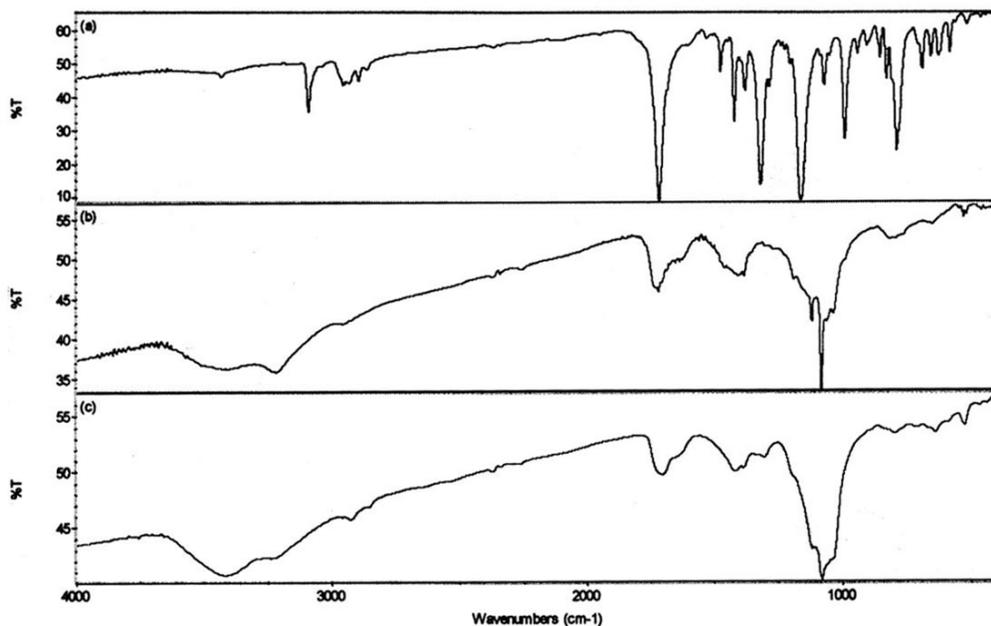


Figure 3.3 FTIR spectrum of (a) SATE, (b) PSATE, (c) P(SATE-co-Th)

3.3 Cyclic Voltammograms

Electrochemical polymerization and study of electroactivity under redox reactions was performed via cyclic voltammetry. As reflected in the voltammogram (Figure 3.4) of SATE which was recorded in the absence of BFEE, SATE did not reveal electroactivity upon repetitive cycles. However, addition of 2 mL BFEE into the same electrolytic system resulted in continuous electroactivity (Figure 3.5) with a gradual increase in the current intensity with increasing scan number. This was attributed to the fact that BFEE facilitates electrochemical polymerization by lowering the aromatic resonance energy and promoting the abstraction of an electron from the α -position of heterocycle ring [57]. As seen in Figure 3.5, PSATE revealed an oxidation peak at +0.9 V and a reduction peak at +0.7 V vs Ag/Ag^+ .

In the case of addition of thiophene into the same electrolytic system, a voltammogram (Figure 3.6) which is different from those of both the homopolymer and the pure polythiophene, in terms of oxidation-reduction potentials and peak increments has been observed which could serve as an indication of copolymer formation.

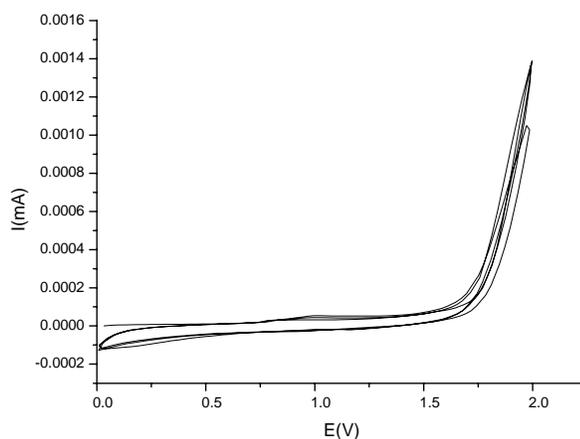


Figure 3.4 Cyclic voltammogram of SATE in the absence of BFEE.

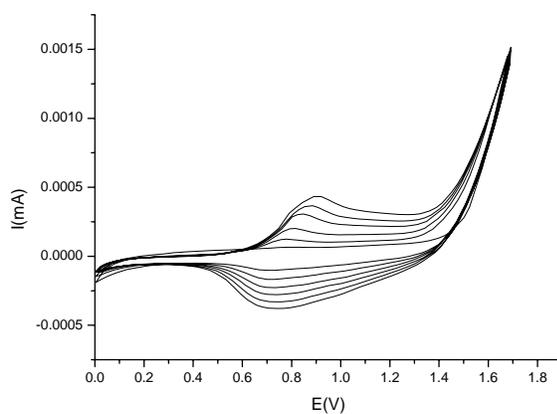


Figure 3.5 Cyclic voltammogram of SATE in the presence of BFEE.

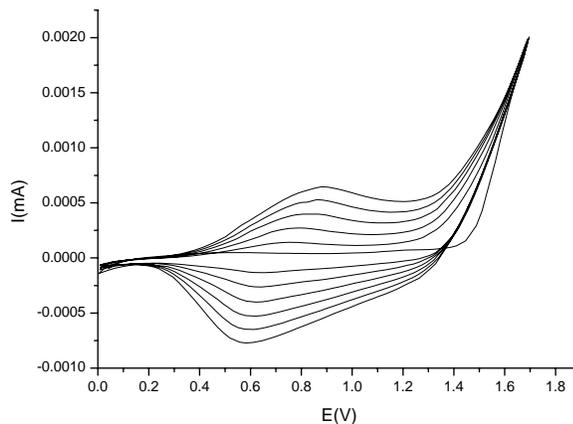


Figure 3.6 Cyclic voltammogram of P(SATE-co-Th) in the presence of BFEE.

3.4 Thermal Analyses

DSC thermograms were examined in the range 30 to 500 °C at a heating rate of 10 °C/min. DSC thermogram of SATE showed a sharp melting point at 86 °C and onset of its decomposition was 285.0 °C (Figure 3.7 (a)). The thermogravimetry scan of the monomer showed single weight loss starting from 230 °C and reached its maximum at 313 °C where the remaining residue was less than 4.6 % after 400 °C (Figure 3.7 (b)). DSC thermogram of PSATE exhibited a shoulder at 84 °C which may be due to evolution of water, entrapped solvent and monomer followed with a peak at 114 °C that can be attributed to the removal of dopant based fragments such as BF₂, BF, HF [58] and another thermal event at 240 °C due to the thermal degradation of the polymer (Figure 3.8). In the case of copolymer, DSC thermogram revealed a shoulder at 77 °C with a peak at 135 °C (Figure 3.9) which may be associated with the same events discussed in the homopolymer case. Thermal degradation was detected at 267 °C.

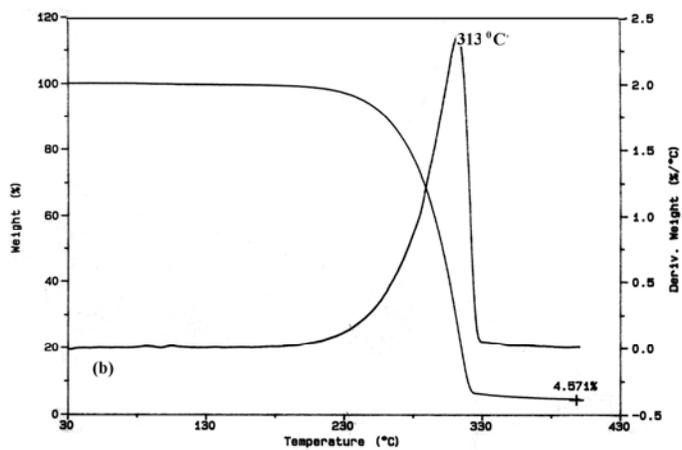
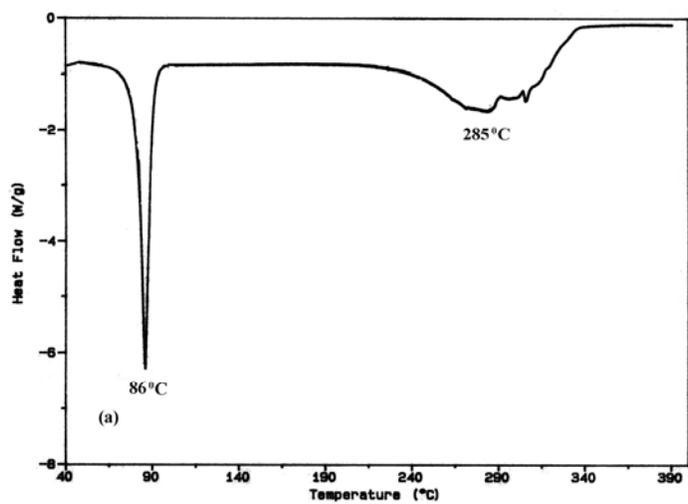


Figure 3.7 (a) DSC thermogram of SATE (b) TGA thermogram of SATE.

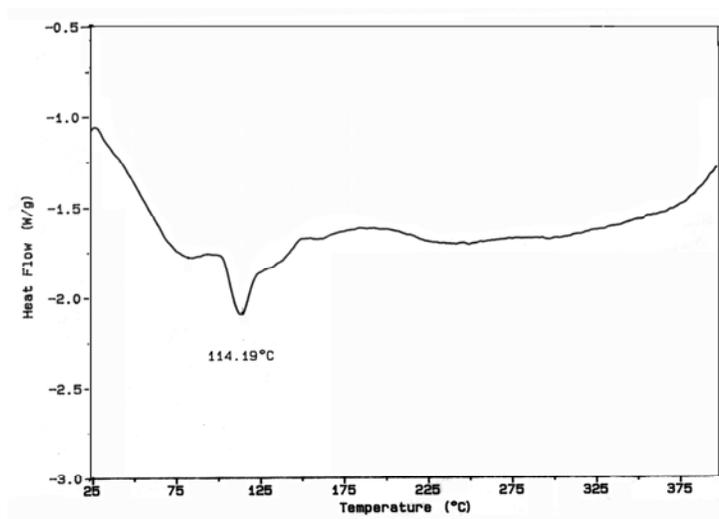


Figure 3.8 DSC thermogram of PSATE.

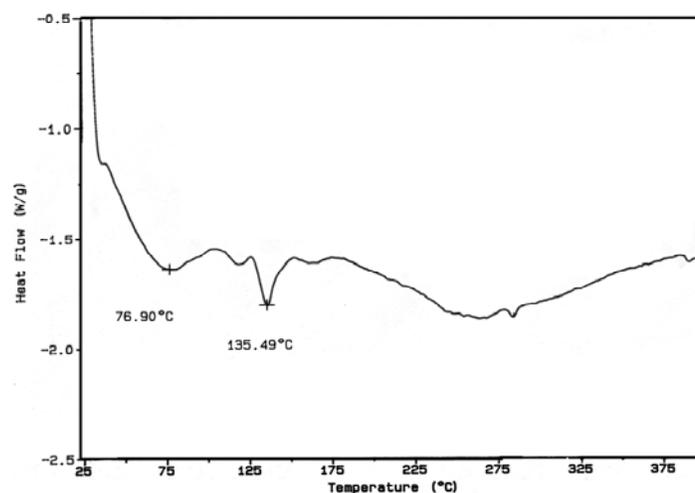


Figure 3.9 DSC thermogram P(SATE-co-Th).

3.5 Morphologies of the films

SEM micrographs of PSATE imply that the synthesized monomer is good in polymer film forming, exhibiting homogeneous and compact structure (Figure 3.10 (a)). The copolymer P(SATE-co-Th) (Figure 3.10 (b)) reveals droplets on the surface which is quite different from the homopolymer and pure polythiophene cauliflower morphology.

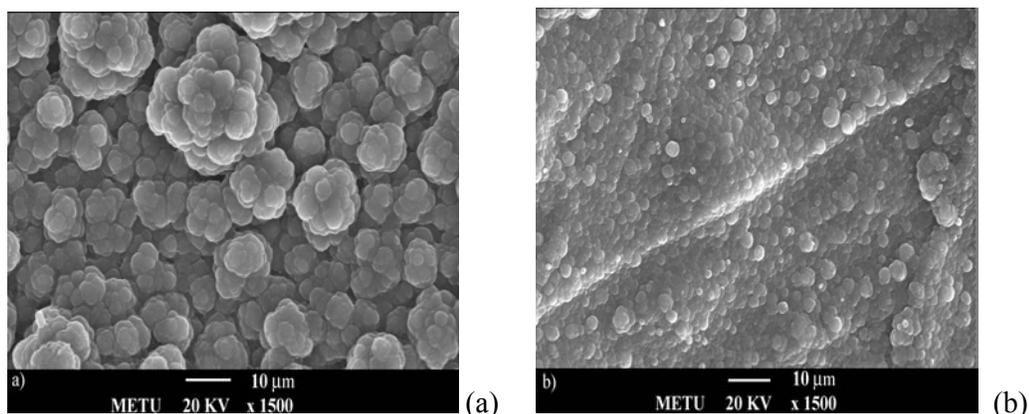


Figure 3.10 SEM micrographs of (a) solution side of PSATE and (b) solution side of P(SATE-co-Th)

3.6 Conductivity Measurements

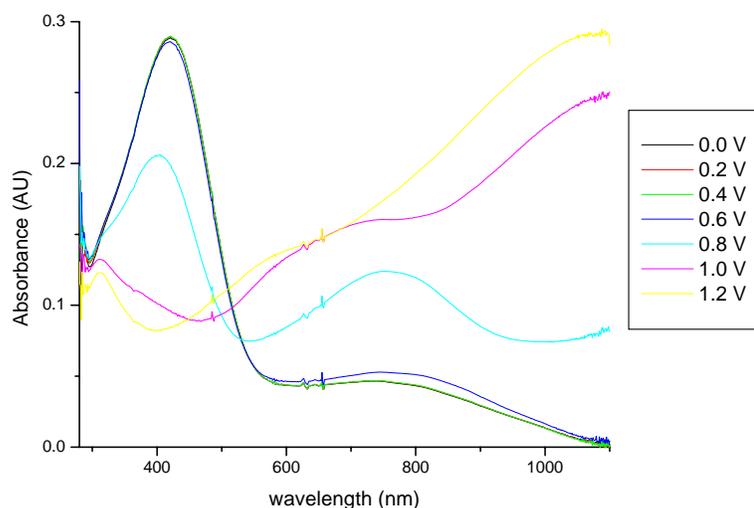
Electrical conductivity measurements were carried out by using the standard four-probe technique. Conductivities of PSATE and P(SATE-co-Th) were determined as 2×10^{-4} and 6×10^{-2} S/cm, respectively. These results show that copolymer production resulted in an increase of 3×10^2 orders of magnitude in the conductivity.

3.7 Investigation of Electrochromic Properties of Polymers

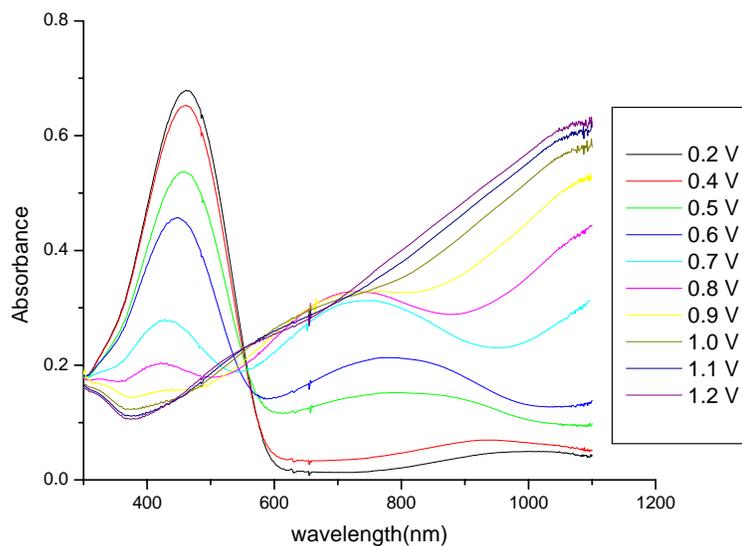
3.7.1 Spectroelectrochemistry

Spectroelectrochemical analyses were performed to investigate properties of conducting polymers related to electronic structure and optical behavior upon redox switching. Figure 3.11 (a) and (b) show series of optoelectrochemical spectra of PSATE and P(SATE-co-Th), monitored while the polymers were sequentially stepped between their fully reduced and oxidized forms. The electronic band gap, defined as the onset of the π -to- π^* transition, was determined as 2.19 eV and 2.12 eV and λ_{\max} values were 421 and 456 nm, causing the films to appear in yellow and in orange for PSATE and P(SATE-co-Th), respectively. Upon stepwise increase in the applied potential and doping, lower energy transitions emerged while the absorbance

due to the π -to- π^* transition was diminished. This is typically associated with the evolution of a new absorption band; the polaron charge carrier bands along the polymer backbone, signatred by the peaks at 760 and 732 nm for PSATE and P(SATE-co-Th), respectively, causing the films both to appear in blue. At higher doping levels, peak intensities decrease in favor of much broader absorptions attributed to bipolar formation and extend into the near-IR region of the spectrum. The spectroelectrochemistry results show that upon doping-dedoping processes, PSATE changes color reversibly between yellow and blue whereas P(SATE-co-Th) does between orange and blue which differs from PTh, indicating the formation of copolymer again. P(SATE-co-Th) also shows a useful electrochromic behavior in that the orange color which is observed in the fully reduced form changes to green at mildly oxidizing potentials (0.6-0.8 V) and then to blue at higher potentials which could be termed as multicolor-electrochromism.



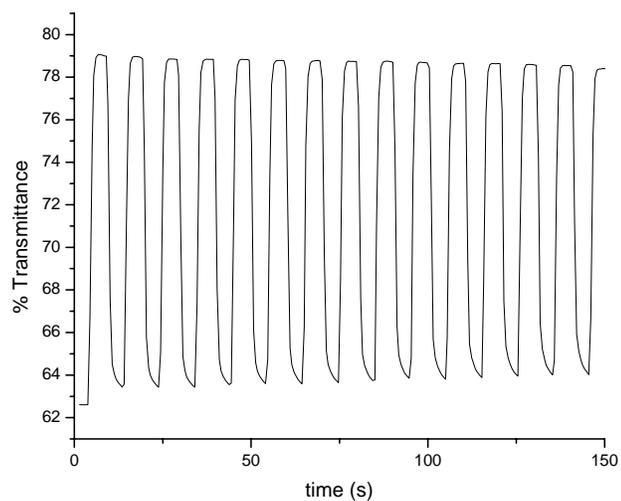
(a)



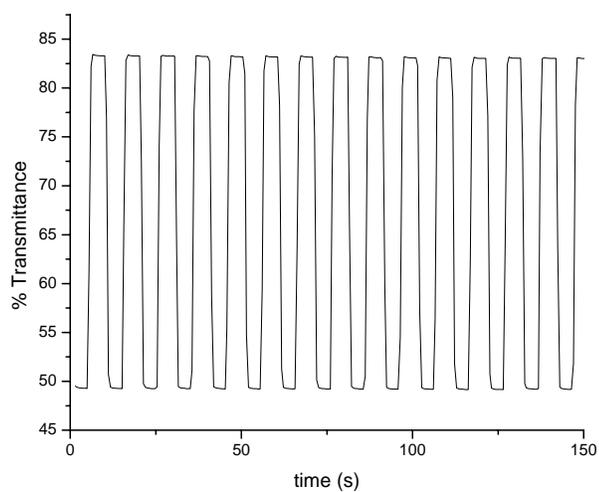
(b)
Figure 3.11 Spectroelectrochemistry of (a) PSATE (b) P(SATE-co-Th)

3.7.2 Electrochromic switching

Electrochromic switching studies are carried out to investigate the ability of a polymer to give a short response time, exhibit a striking color change and maintain a high stability upon repeated cycles which are important for electrochromic applications. The contrast, measured as the difference in % T between reduced and oxidized forms is determined as 16 and 33.7 % and the response time is noted as 2.3 s and 1.5 s for PSATE and P(SATE-co-Th), respectively (Figure 3.12). These results show that copolymer has a shorter response time, higher contrast and higher stability.



(a)



(b)

Figure 3.12 Dynamic electrochromic study of (a) PSATE (b) P(SATE-co-Th)

3.7.3 Colorimetry

PSATE was blue in its oxidized state and yellow in its reduced state. P(SATE-co-Th) film was blue in its oxidized state, yellow in its intermediate state, and orange in its

reduced state. L*a*b values of the films were measured at the fully oxidized and the fully reduced states and the results were recorded in Table 3.1.

Table 3.1 Electrochromic Properties of Polymers

Polymer	λ_{\max} (nm)	color (ox)	color (int)	color (red)	L (ox)	a (red)	b (red)	Eg (eV)
					54	-2	1	2.19
PSATE	421	blue		yellow	64	-6	23	
P(SATE-co- Th)	456	blue	green	orange	40 (ox) 45 (int) 45 (red)	-2 0 40	1 27 51	2.16

3.8 Characterization of Electrochromic Devices

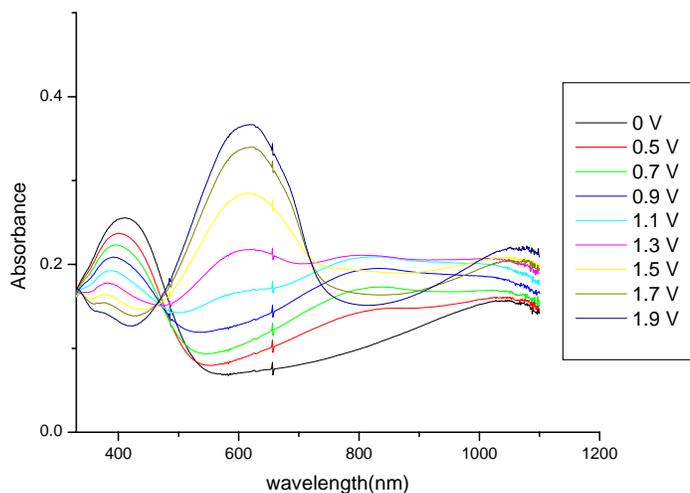
Following the deposition of PSATE and P(SATE-co-Th) layers as the anodically coloring polymers and PEDOT as the cathodically coloring polymer on ITO's, dual type electrochromic devices (ECDs) were constructed with one polymer oxidatively doped while the other is neutral by placing them in a position to face each other and sandwiching a gel media in between. Reversal of the bias potential oxidizes the neutral polymer with concurrent reduction (charge neutralization) of the oxidized polymer.

3.8.1 Spectroelectrochemistry of ECDs

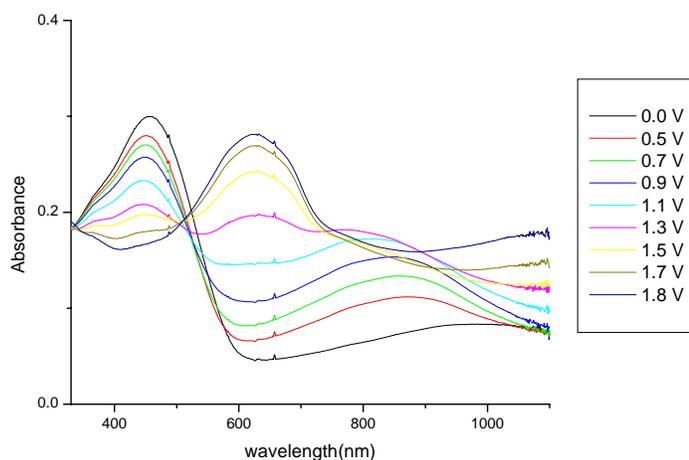
Optoelectrochemical studies of the ECDs were performed to evaluate the useful potential range and the wavelength of maximum color contrast both of which

are very important for electrochromic applications. Figure 3.13 (a) shows the absorbance spectra of PSATE/PEDOT device in the UV-Vis-NIR region in yellow and blue states. The potential range of 0.0-1.9 V was sufficient to cause a perceptible optical contrast (yellow to blue) in a reversible way. At 0.0 V, the anodically coloring polymer dominated in the device revealing maximum absorption at 411 nm with a yellow color due to π - π^* transitions of the electrochromic layers. At this potential, the PEDOT layer was in its oxidized state, exhibiting a transmissive sky blue color. Upon application of further positive potentials, PSATE layer started to get oxidized resulting in a decrease in the intensity of the peak and development of a second absorption at around 800 nm due to formation of charge carrier bands. Further increase lead to the evolution of a new peak at 618 nm due to reduction of PEDOT. At -1.9 V, PEDOT layer was in its most reduced state dominating in the device with a blue color. Thus, upon varying the applied potential from 0.0 V to -1.9 V, the color alternation from yellow to blue was observed.

Similar behavior was observed for P(SATE-co-Th)/PEDOT device, which showed maximum absorption at 456 nm with orange color at 0.0 V due to P(SATE-co-Th) layer. Upon stepwise increase in the applied potential from 0.0 V to -1.8 V, charge carrier band formation and color change from orange to blue were observed. At -1.8 V, PEDOT layer was in its reduced state revealing the π - π^* transition at 632 nm (Figure 3.13 (b)).



(a)



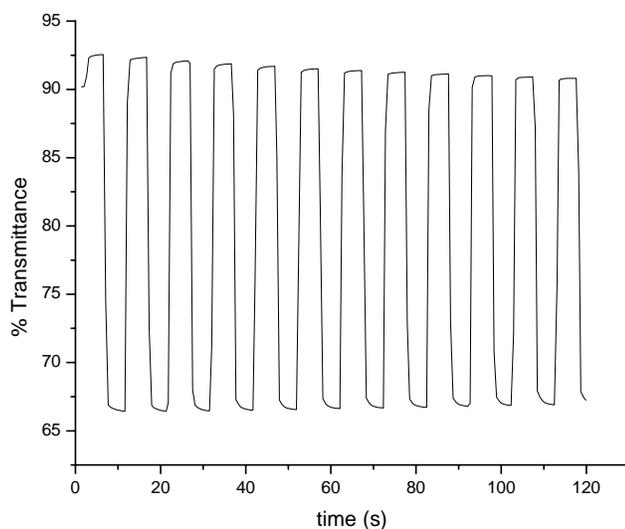
(b)

Figure 3.13 Optoelectrochemical spectrum of (a) PSATE/PEDOT ECD
(b) P(SATE-co-Th)/PEDOT ECD

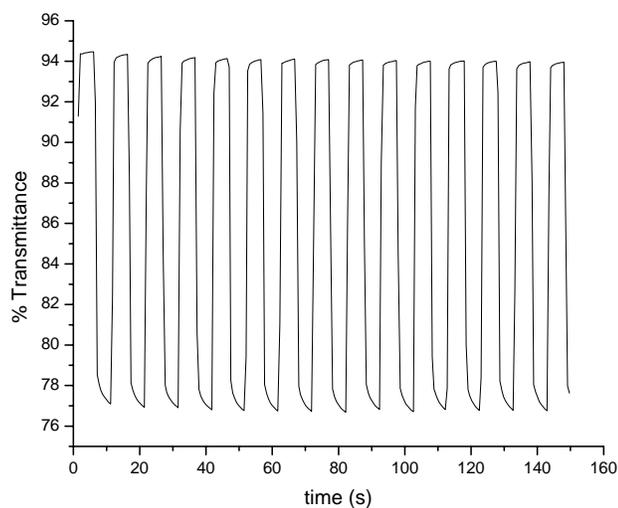
3.8.2. Switching of ECDs

To probe switching characteristics of the ECDs, the transmission and the switching response time at the wavelength of maximum contrast were monitored during repeated redox stepping experiments. For PSATE/PEDOT device, maximum contrast ($\% \Delta T$) was measured as 24.6 and switching time as 2 seconds (Figure 3.14

(a)) by stepping the potential between 0.0 V and + 1.9 V with a residence time of 5 s at 618 nm. For the case of P(SATE-co-Th)/PEDOT device, switching time and $\% \Delta T$ values were measured as 1.5 s and 16.9 respectively (Figure 3.14 (b)) while stepping the potential between 0.0 V and + 1.8 V at 632 nm.



(a)

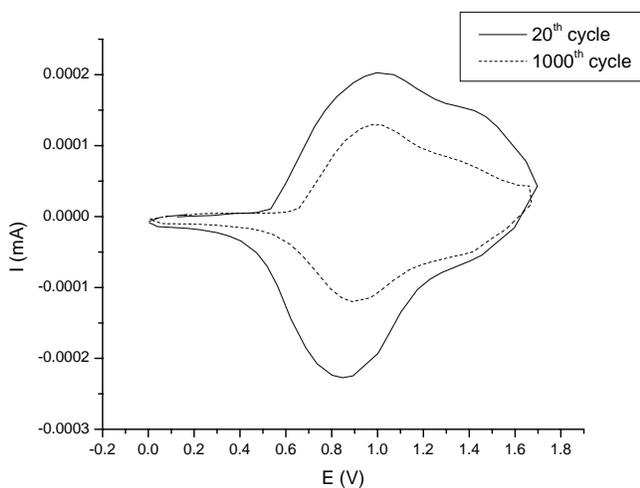


(b)

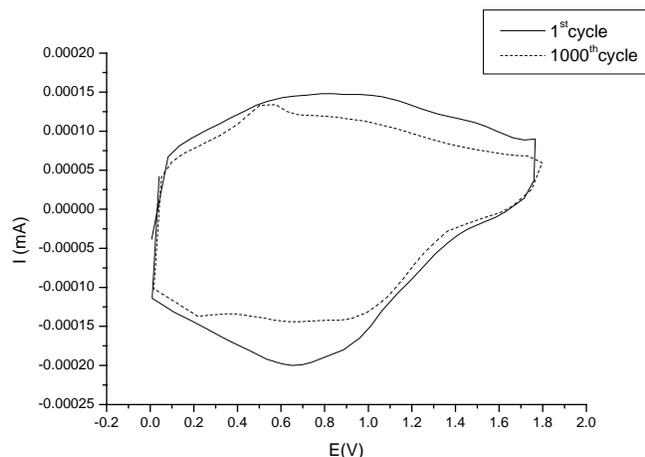
Figure 3.14 Electrochromic switching of (a) PSATE/PEDOT, (b) P(SATE-co-Th)/PEDOT

3.8.3 Stability of ECDs

Cyclic voltammetry method was used to test the long-term stability of the devices by sweeping repeatedly between 0.0 and ± 1.9 V, 0.0 and ± 1.8 V for PSATE/PEDOT and P(SATE-co-Th)/PEDOT devices, respectively, with a scan rate of 500 mV/s. When cycled 1000 times, PSATE/PEDOT device was able to retain 63% of its electroactivity with an unperturbed color change (Figure 3.15 (a)). In the case of P(SATE-co-Th)/PEDOT device, the ability to retain its electroactivity after the 1000th cycle was measured as % 79 (Figure 3.15 (b)) all which show that both ECDs have good environmental and redox stability.



(a)

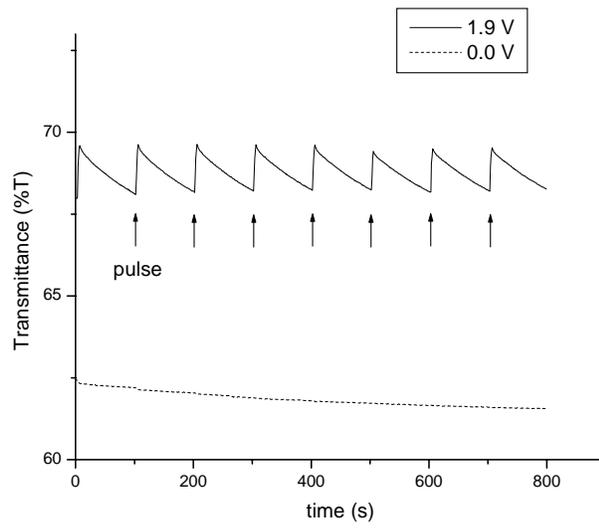


(b)

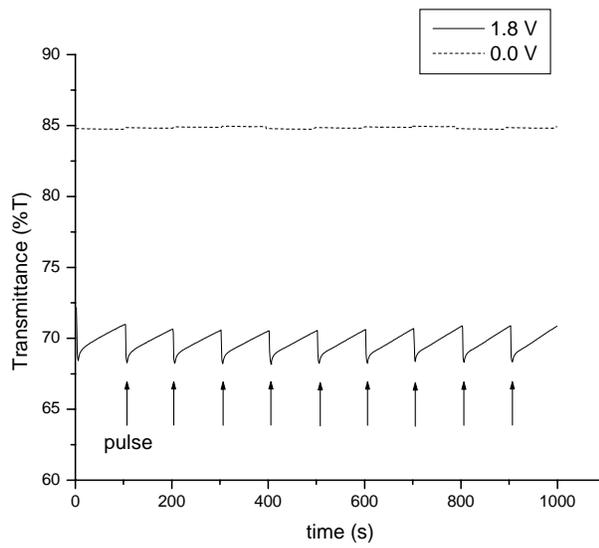
Figure 3.15 Stability test of (a) PSATE/PEDOT, (b) P(SATE-co-Th)/PEDOT via cyclic voltammetry with a scan rate of 500 mV/s.

3.8.4 Open Circuit Memory of ECDs

The variation of transmittance (%T) of PSATE/PEDOT device for yellow (0.0 V) and blue colored (1.9 V) states at 411 nm and P(SATE-co-Th)/PEDOT device for orange (0.0 V) and blue colored (1.8 V) states at 632 nm as a function of time is shown in Figures 3.16 (a) and (b) when a pulse is applied for 1 second and the circuit is disconnected for 100 seconds. We observe that both devices show quite good optical memories in reduced states with almost zero transmittance change and in oxidized states with 1.5 % and 2.5 % transmittance change for PSATE/PEDOT and P(SATE-co-Th)/PEDOT devices respectively.



(a)



(b)

Figure 3.16 Open circuit memory of (a) PSATE/PEDOT, (b) P(SATE-co-Th)/PEDOT

3.8.5 Colorimetry

Colorimetry analyses of the ECDs were performed by using the same procedure and instrument as described in part 3.7.3. Electrochromic properties of the devices were given in Table 3.2.

Table 3.2 Electrochromic Properties of Devices

Electrochromic Devices	color (ox)	Color (neut)	L	a	b
PSATE/PEDOT	blue	yellow	54	-5	24
			31	0	-29
P(TATE-co-Th)/PEDOT	blue	orange	39	11	28
			33	-4	5

CHAPTER IV

CONCLUSIONS

In the present work, a new monomer, succinic acid bis-(2-thiophen-3-yl-ethyl)ester (SATE) was synthesized successfully through the esterification reaction of 2-thiophen-3-yl-ethanol and succinyl chloride. Electrochemical polymerization of SATE and its copolymer with thiophene were achieved in ACN/BFEE solvent mixture using TBAFB as the supporting electrolyte. Cyclic voltammetry studies showed the presence of electroactivity and the oxidation/reduction behavior of SATE.

The resultant free standing, stable and electrically conducting films were characterized by several techniques. Copolymerization was proved by the characteristic peaks in FTIR spectra and morphologies in SEM micrographs. The polymers were found to have reasonable conductivities and stable thermal behavior. Spectroelectrochemistry results showed that both homopolymer and copolymer can be switched between their fully oxidized and fully reduced states with distinct color changes.

In the second part of the study, dual-type complementary colored polymer ECDs made up of PSATE/PEDOT and P(SATE-co-Th)/PEDOT were constructed and their characteristics were examined. Devices exhibited reversible color change between the two states, reasonable stabilities, and good optical memories in their reduced state.

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