SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING POLYMERS OF 1-(4-NITROPHENYL)-2,5-DI(2-THIENYL)-1H-PYRROLE AND THEIR USE IN ELECTROCHROMIC DEVICES

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ABSTRACT

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING POLYMERS OF 1-(4-NITROPHENYL)-2,5-DI(2-THIENYL)-1H-PYRROLE AND THEIR USE IN ELECTROCHROMIC DEVICES

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A new monomer; 1-(4-Nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole $SNSNO_2$ was synthesized through the Knorr-Paal condensation reaction of 1,4-di-2-thienyl-1,4-butanedione and p-nitroaniline. The chemical structure of monomer and polymer were characterized via Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Chemical polymerization produced a polymer which was completely soluble in organic solvents. Electrochemical behaviors of $SNSNO_2$ and $SNSNO_2$ in the presence of EDOT were studied by cyclic voltammetry (CV). The synthesis of homopolymer and copolymer were achieved via constant potential electrolysis. Both homopolymer P($SNSNO_2$) and copolymer P($SNSNO_2$-co-EDOT) were characterized by various techniques including cyclic voltammetry, FTIR, Scanning Electron Microscopy (SEM) 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 P($SNSNO_2$), P($SNSNO_2$-co-EDOT) 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 and high stabilities.

Keywords: 1-(4-Nitrophenyl)-2,5-di-2-thienyl-1*H*-pyrrole, Electrochromic polymers, Conducting polymers, Electropolymerization, Spectroelectrochemistry, Electrochromic Devices.

ÖZ

1-4-NİTROFENİL-2,5-Dİ(2-TİYENİL)-1H-PİROL'ÜN İLETKEN POLİMERLERİNİN SENTEZİ, ELEKTROKROMİK ÖZELLİKLERİ VE ELEKTROKROMİK CİHAZLARDA KULLANIMI

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Yeni bir monomer; 1-(4-nitrofenil)-2,5-di(2-tiyenil)-1H-pirol $SNSNO_2$, 1,4-di-2-tiyenil-1,4-bütandion ve *p*-nitroanilinin Knorr-Paal tepkimesi ile sentezlenmiştir. Monomerin kimyasal yapısı Nükleer Manyetik Rezonans Spektroskopisi (^{1}H-NMR ve ^{13}C-NMR) ve Fourier Transform İnfrared Spektroskopisi (FTIR) yöntemleri kullanılarak incelendi. Kimyasal polimerleşmeyle birçok organik çözücüde çözülebilen bir polimer elde edilmiştir. $SNSNO_2$'nin 3,4-etilendioksitiyofen (EDOT) ile kopolimerinin elektrokimyasal davranışları dönüşümlü voltametre ile araştırılmıştır. Homopolimerin ve kopolimerin sentezlenmesi sabit gerilim yöntemi kullanılarak gerçekleştirilmiştir. Gerek homopolimer $P(SNSNO_2)$ gerekse kopolimer $P(SNSNO_2$-co-EDOT) Dönüşümlü Voltametri (CV), Fourier Transform İnfrared Spektroskopisi (FTIR), Taramalı Elektron Mikroskopisi (SEM) ve UV-VIS Spektrofotometresi yöntemleri kullanılarak karakterize edilmiştir. Filmlerin iletkenlikleri dört-nokta tekniği ile belirlenmiştir. Polimerlerin elektrokromik özellikleri spektroelektrokimya, kolorimetre ve renk değiştirme analizleri ile tanımlanmıştır. Ek olarak, $P(SNSNO_2)$, $P(SNSNO_2$-co-EDOT) ve poli(3,4-etilendioksitiyofen) (PEDOT) kullanılarak elektrokromik cihazlar yapılmıştır. Cihazlar, iyi çevirme zamanlarının, uygun optik kontrastlarının ve yüksek dayanıklılıklarının olduğunu kanıtlamışlardır.

Anahtar Kelimeler: 1-(4-Nitrofenil)-2,5-di(2-tiyenil)-1H-pirol, Elektrokromik polimerler, İletken polimerler, Elektrokimyasal polimerleştirme, Spektroelektrokimya, Elektrokromik cihazlar

TO MY FAMILY

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ABBREVIATIONS

$SNSNO_2$	1-(4-Nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole
$P(SNSNO_2)$	Poly(1-(4-Nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole)
EDOT	3,4-Ethylenedioxythiophene
P($SNSNO_2$-co-EDOT)	Poly(1-(4-Nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole - co-ethylenedioxythiophene)
Th	Thiophene
Py	Pyrrole
PEDOT	Poly(3,4-ethylenedioxythiophene)
ACN	Acetonitrile
THF	Tetrahydrofuran
PMMA	Poly(methylmethacrylate)
PC	Propylene carbonate
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectrometer
CV	Cyclic Voltammetry
SEM	Scanning Electron Microscopy
GPC	Gel Permeation Chromatography
ECD	Electrochromic Device
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital

E_g	Band Gap Energy
CIE	La Commission Internationale de l'Eclairage
L a b	Luminance, hue, saturation
CP	Conducting Polymers
PA	Polyacetylene

CHAPTER I

INTRODUCTION

1.1. Conducting Polymers

All carbon based polymers were thought to be insulators about 30 years ago. However, in the last two decades an accelerated advancing field has developed on the basis of the ability of certain polymers to conduct charge. Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa were awarded with The Nobel Prize in Chemistry for their discovery and elaboration of electronically conducting polymers in 2000. The three conquerors authorized that polymer plastics can be made to conduct electricity if carbon atoms are linked via alternating single and double bonds, and electrons are either removed through oxidation or introduced through reduction.

The electrons in the bonds remain localized and cannot transmit an electric current, but when three scientists "doped" the material with strong electron acceptors such as iodine, the polymer began to behave as well as a metal, with conductivity 10^{11} times higher than pure polyacetylene (PA) [1,2].

Despite high conductivity of polyacetylene film in doped form, the material is unstable against oxygen or humidity. Synthetic works started in order to enhance the processability of PA by means of increasing its stability and solubility [3]. PA derivatives were also synthesized and tested. Unfortunately, the electrical conductivities of the PA derivatives were much lower than that of PA. Naturally, much work has been done to maturate durable and processable conducting polymer structures. Industrial, academic and government researchers have 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 most attention [4] due to higher environmental stability and structural versatility they possess. The electronic and electrochemical properties of these polymers can be devised by modifying the monomer structure [5]. Some examples of CPs are given in Figure 1.1.

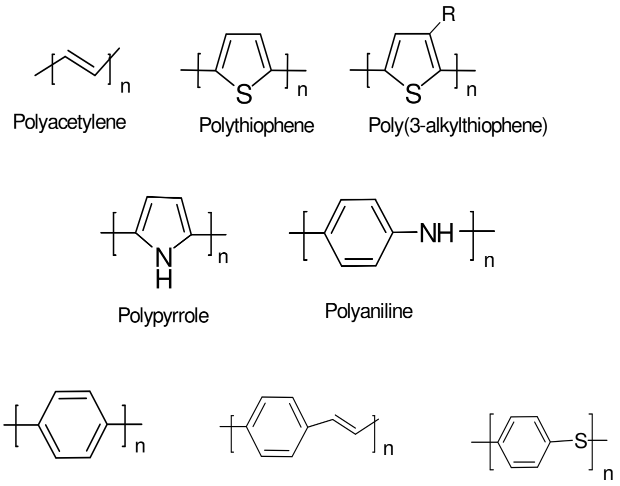


Figure 1-1. Structures of some common conducting polymers

In Table 1.1 conductivities and stabilities of some of these polymers were shown. Even if none have exhibited higher conductivity than polyacetylene, these polymers have been useful in designing new monomers functionalized with Th, Py, etc. that are soluble and stable. Introduction of various side groups, electron donating or withdrawing, to the polymer backbone, soluble derivatives can be obtained; in addition, the electronic structure of the material can be manipulated [6].

Table 1-1. Conductivities and stabilities of some common conducting polymers

Derivatives of	Conductivity (S/cm)	Stability (doped state)	Processing Possibilities
Polyacetylene	10^3-10^5	Poor	Limited
Polypyrrole	100	Good	Good
Polythiophene	100	Good	Excellent
Polyaniline	10	Good	Good
Polyphenylene	1000	Poor	Limited

1.2. Applications of Conducting Polymers

Conducting polymers achieved a new class of materials, demonstrating not only the conducting properties of metals, but also appealing the mechanical characteristics and processing advantages of polymers. The research on conducting polymers which are often referred to as "*synthetic metals*" has attracted the interest of thousands of scientists. Thus, this field has gradually become a science [7].

Materials now commercially available and real products on the markets include polymers as antistatic coatings in photographic films, electrode materials in capacitors and materials for through hole plating of printed circuit boards. Besides, various applications have been demonstrated and proposed for conjugated polymers. Some of the present and potential commercial applications of these systems are storage batteries, supercapacitors, electrolytic capacitors, fuel cells [8], sensors; biosensors and chemical sensors, ion-specific membranes, electrochromic displays, electromagnetic shutters, corrosion protection, transparent conductors, gas separation membranes, EMI shielding, conductive textiles, anti-static films and fibers, conductor/insulator shields, photoconductive switching, conductive adhesives and inks, non-linear optics [9], electroluminescence, electronic devices [10-12]

For such applications as switchable windows and mirrors, active advertising displays, and dynamic camouflage, electrochromic devices based on conducting polymers have become a recent focus of research. This is due in part to the fact that all electroactive and conducting polymers are potentially electrochromic materials, are more processable than inorganic electrochromic materials, and offer the advantage of a high degree of color tailorability [13]. The use of conducting polymers as potentially electrochromic materials is the most pertinent to the work in this thesis.

1.3. Electrical Conduction in Conducting Polymers

1.3.1. Band Theory

Materials can be classified into three categories according to their conductivity properties at room temperature: conductors, semiconductors and insulators. In polymeric materials conduction may be explained by using the band theory.

Band theory says that extended delocalized energy bands are formed by the overlapping of atomic orbitals and accordingly the conductivity depends on the relative population of each band and on the energy difference between bands. The electrical properties of direct-gap inorganic semiconductors are figured out by their electronic structures, and the electrons move within discrete energy states which are referred as bands.

Similarly, the bonding and antibonding π orbitals of the sp^2 hybridized π-electron materials such as polyenes generate energy bands that are fully occupied π band and empty π* band [14].

Neutral conjugated polymers are thought to be semiconductors. According to band theory, conjugated polymers generate two discrete energy bands, the highest occupied electronic levels that constitute the valence band (VB) and the lowest unoccupied levels that constitute the conduction band (CB). The difference between valence band and conduction band, or bandgap (Eg), between the VB and CB determines the intrinsic electrical properties of the material [15]. Various structural aspects such as chain length, bond length alternation, planarity, and the presence of electron-acceptor or electron donor substituents and the resonance stabilization energy of the aromatic cycles affect the HOMO–LUMO gap of a linear π-conjugated system [16]. Band gap refers to onset energy of the π-π* transition in neutral conjugated polymers. The band gap of a polymer can be estimated from the onset of absorption of the π to π* transition in the UV-VIS spectrum. Electrons must have certain energy to occupy a given band. Moving of electrons from the valence band to the conduction band requires extra energy. Moreover, the bands should be partially filled in order to have electrical conductance; because neither empty bands nor full ones can carry electricity. Metals have high conductivities due to presence of partially filled energy bands. (Fig 1.2)

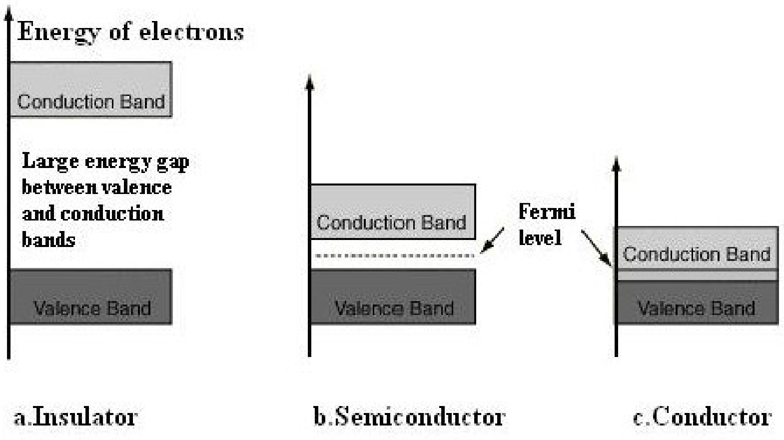


Figure 1-2. Band structures of insulator, semiconductor, conductor

The energy bands of insulators and semiconductors, however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap. In contrast, conjugated polymers have narrower band gaps, and doping can change their band structures by either taking electrons from the valence band (p doping) or adding electrons to the conduction band (n doping) [17].

1.3.2. Conduction Mechanism

1.3.2.1. Charge Carriers

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 [18].

Polaron is a radical cation (radical anion) that is partially delocalized over some polymer segment as a result of cleavage of a double bond in the polymer backbone by oxidation (reduction). The polaron has a spin of ½. A dication or a bipolaron has two charges associated with the localized polymer segment. Therefore, low oxidation produces polarons, and bipolarons are formed at higher oxidation potentials. Another charge defect is soliton, which can be classified into three categories: neutral soliton, positive soliton and negative soliton. It is interesting 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 1.3).

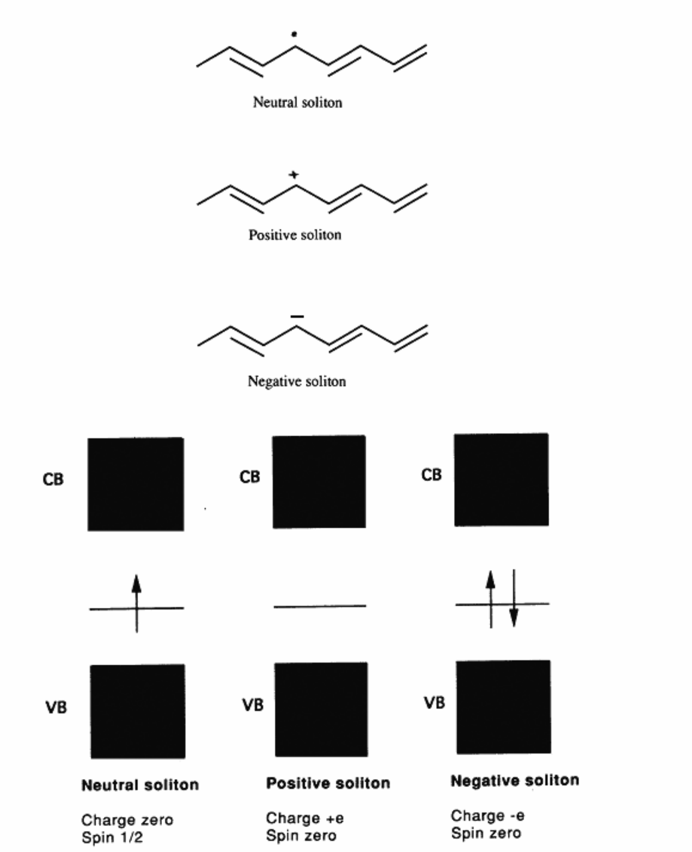
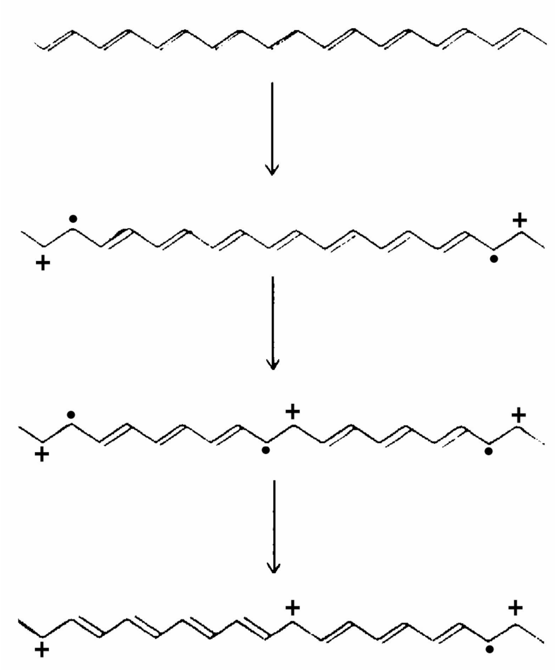


Figure 1-3. Soliton structures of polyacetylene

Polarons are the combination of a neutral and a charged soliton on the same polymer chain. Further oxidation causes more and more polarons to form and ultimately the unpaired electron of the polaron is removed, or two polarons can combine to form dications or bipolarons [19, 20].



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 π bond and a mobile bipolaron

Figure 1-4. Formation of polaron and bipolaron for polyacetylene

1.3.2.2. Doping

The conductivity of CPs is accomplished through simple chemical or electrochemical oxidation, or in some cases reduction, by a number of simple anionic or cationic species, called "dopants". That is to say, it is required to oxidize or reduce the polymeric backbone of these materials to introduce charge centers so that conductivity is fulfilled. The oxidation or reduction is performed by anions or cations, which are somewhat misnamed as "dopants". "Dopant" is a term borrowed from condensed matter physics.

Control of the electrical conductivity of a polymer over the range from insulating to highly conducting (metallic) state is possible. This process is referred as doping. The insulating neutral polymer is converted into an ionic complex which contains a polymer cation (or anion) and a counter which is the reduced form of the oxidizing agent (or the oxidized form of the reducing agent). In the solid state physics terminology, the use of an oxidizing agent corresponds to p-type (Fig. 1.5) doping and that of reducing agent to n-type doping [21].

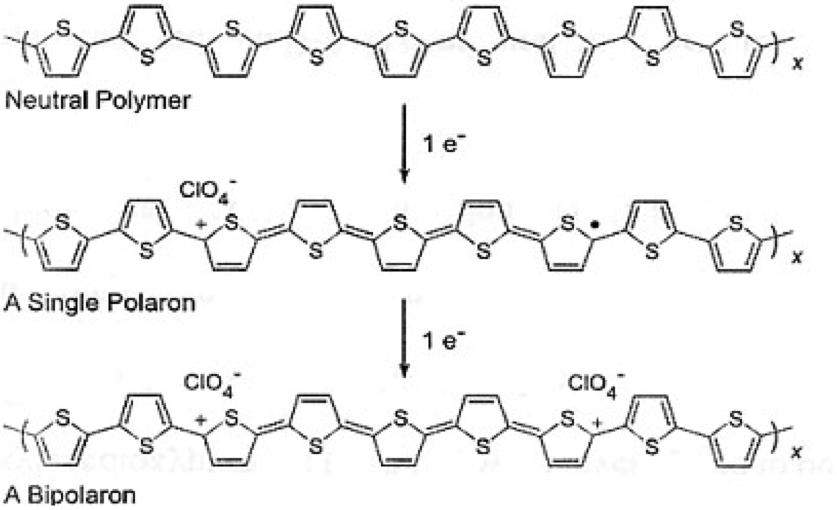


Figure 1-5. P-type doping of polythiophene

It is possible to carry out both doping and undoping processes, involving dopant counter ions which stabilize the doped state, either chemically and electrochemically [22].

Chemical doping involves charge-transfer redox chemistry:

(a) Oxidation (*p*-type doping)

$(\pi\text{-polymer})_n + 3/2\ ny\ (I_2) \rightarrow [(\pi\text{-polymer})^{+y}\ (I_3^-)_y]_n$ [2];

(b) Reduction (*n*-type doping)

$(\pi\text{-polymer})_n + [Na^+\ (\text{Napthtalide})^-]_y \rightarrow [(Na^+)_y\ (\pi\text{-polymer})^{-y}]_n + (\text{Naphth})^0$ [1]

Even though chemical doping is an efficient and straightforward process, it is typically difficult to control. Attempts to obtain intermediate doping levels often result in inhomogeneous doping. To solve this problem, electrochemical doping was invented [23].

It is easy to oxidize or reduce the polymer electrochemically by adjusting appropriate potential in an electrochemical cell. The charge on the polymer chain is then neutralized by the counter ion from the electrolyte solution [21].

Electrochemical doping is illustrated by the following examples:

(a) *p* type

$(\pi\text{-polymer})_n + [Li^+\ (BF_4^-)]_{\text{sol'n}} \rightarrow [(\pi\text{-polymer})^{+y}\ (BF_4^-)_y]_n + Li\ (\text{electrode})$;

(b) *n* type

$(\pi\text{-polymer})_n + [Li\ (\text{electrode})] \rightarrow [(Li^+)_y\ (\pi\text{-polymer})^{-y}]_n + [Li^+\ (BF_4^-)]_{\text{sol'n}}$ [18]

Doping at any level can be fulfilled by setting the electrochemical cell at a fixed applied voltage and simply waiting for the system to come to electrochemical equilibrium [24].

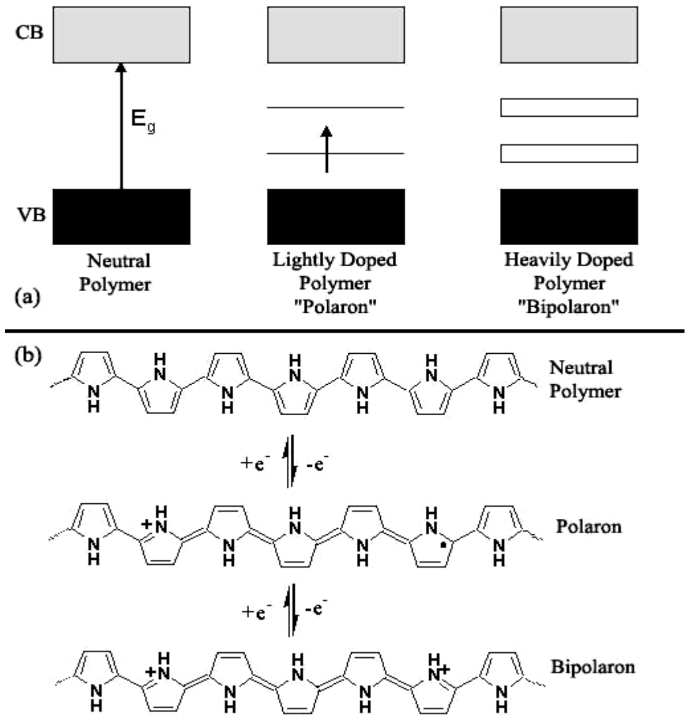


Figure 1-6. Charge carries in PPy and its corresponding energy bands in the mid gap

Conductivity of CPs can be tuned over eight or more orders of magnitude in the same material. The doping level of conducting polymers affects range of conductivity from insulator to metal. Fig 1.7 shows the typical conductivity ranges of the three most common conducting polymers (PA, PPy, PTh).

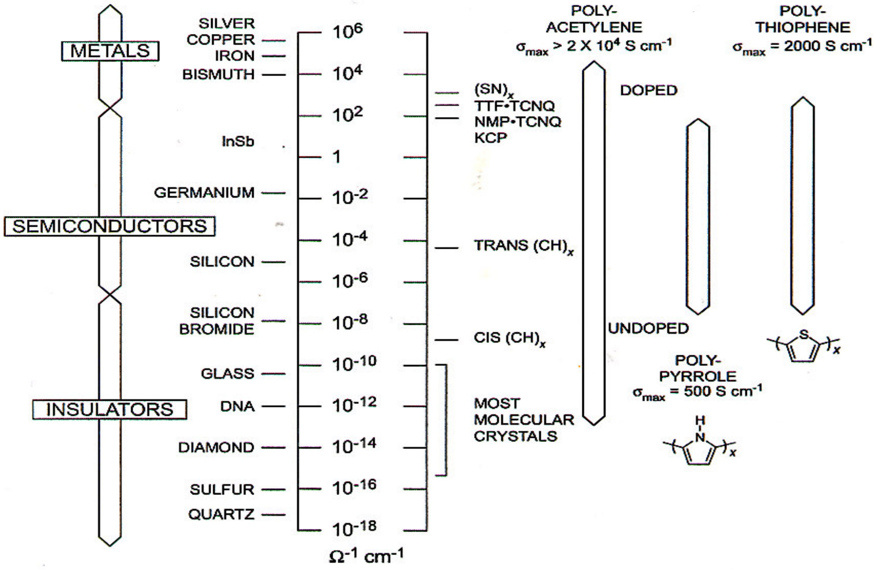


Figure 1-7. Conductivities of some metals, semiconductors and insulators

1.3.2.3. Hopping Process

The conduction process can be described with two important mechanisms, *doping* and *hopping*. Hopping is simply intra-chain, inter-chain and inter-particle motion of charges in a polymer matrix [25]. The intra-chain movement, motion of the charge carrier through a single chain, depends on the efficient conjugation. On the other hand, inter-chain movement, jumping from one chain to another, is determined by the piling of the polymer chains. The mobility also depends on the movement of electrical charges from particle to particle.

Variable range hopping process in which electrons are delocalized on monomer rings is a well described conductivity mechanism. This mechanism, which is known as hopping conduction, is observed in two well-known varieties, nearest neighbor hopping and variable range hopping. The latter conduction mechanism is distinguishable from other conduction mechanisms by its different temperature dependence:

$$\sigma = \sigma_0 \exp[-(T_o/T)^{\gamma}]$$

γ depends on the dimensionality of the hopping process [26].

To sum up, the mobility and therefore conductivity are determined on both a macroscopic (inter-particle) and microscopic (intra- and inter-chain) levels.

1.4. Synthesis of Conducting Polymers

Chemical and electrochemical polymerizations are widely employed techniques in the synthesis of conductive polymers. Other techniques used to synthesize conducting polymers include photochemical polymerization, metathesis polymerization, plasma, pyrolysis and solid state polymerizations [27].

1.4.1. Chemical Polymerization

In chemical polymerization, stoichiometric amount of oxidizing reagent is used to produce polymer that is in its doped or conducting form. Heterocyclic monomers are usually polymerized with $FeCl_3$ as the chemical oxidant [28, 29] although other oxidants can also be employed (Fig 1-8) [30]. Reduction to the neutral state is accomplished by the addition of a strong base such as ammonium hydroxide or hydrazine. Oxidative chemical polymerization is the least expensive, simple, and broadly used technique in the synthesis of conducting polymers [31].

Chemical synthesis provides the advantage of mass production at low cost. However, products are generally in powder form ultimately decreasing the intrinsic properties of the materials obtained such as having very low conductivity. Besides, there is also an abundance of side reactions occurring during chemical oxidation polymerization of heterocycles including formation of coupling defects along the backbone [32].

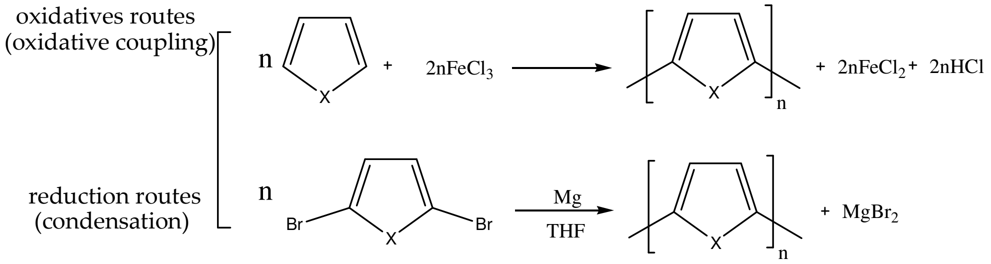


Figure 1-8. Chemical synthetic routes of polyheterocycles

1.4.2. Electrochemical Polymerization

Electrochemical polymerization is a convenient technique when a polymer film with controlled thickness is desired. Electrochemical oxidation of various resonance stabilized aromatic molecules, such as pyrrole, thiophene, aniline, furan etc., produce electronically conductive polymers. The polymerization is believed to involve either radical-cation/radical cation coupling or reaction of a radical cation with a neutral monomer (Figure 1.10) [33-34]. The mechanism of electropolymerization of the five membered heterocycle, with radical-cation/radical-cation coupling and resonance stabilization after removal of an electron are shown in the following figures.

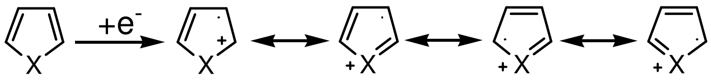


Figure 1-9. Resonance stabilization of a five membered heterocyclic compound upon formation of radical-cation where X = N-H, S, O

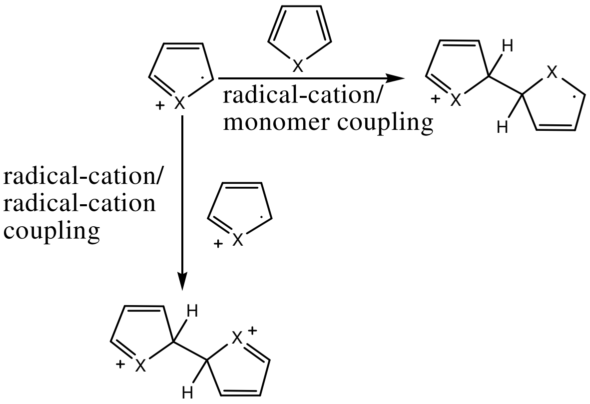


Figure 1-10. Radical-cation/monomer and radical-cation/radical cation coupling where X = N-H, S, O

Upon release of two protons and re-aromatization, a dimer forms. The dimer (and succeeding oligomers) is more easily oxidized than the monomer and the resulting dimer radical cation undergoes further coupling reactions, proton loss and re-aromatization. Electropolymerization advances through successive electrochemical and chemical steps according to a general ECE (E for electrochemical, C for chemical) scheme (Fig1-10), until the oligomers become insoluble in the electrolyte solution and precipitate onto the electrode surface [35].

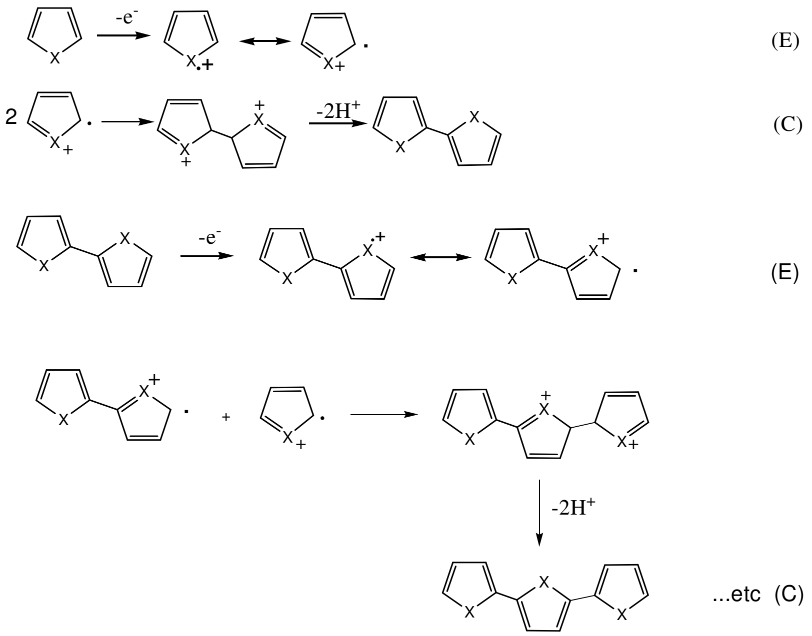


Figure 1-11. ECE Mechanism

Polymer oxidation occurs concurrently with electro-deposition; because conjugated oligomers are oxidized at less positive potentials than their corresponding monomer.

In the oxidized state, conducting polymers are p-doped and have delocalized π-band structure; the charge on the chain is balanced with counter anions. After reduction, counter anion leaves or cation of the electrolyte enters, electronic conjugation is removed and polymer is in insulating form (Figure 1.12).

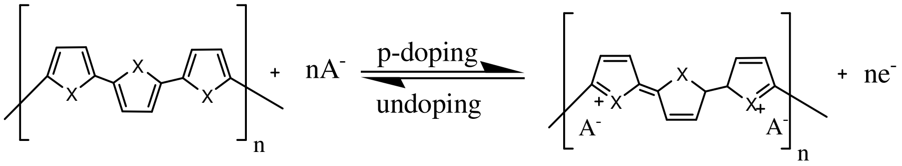


Figure 1-12. Undoping, p-doping in a conducting polymer

There is a general belief that oxidative coupling takes place at sites on the heterocyclic ring where a high spin density resides for the radical cation. For thiophene, pyrrole, and furan, the highest spin densities have been measured at the 2- and 5-positions, also referred to as the α positions [36, 37]. The 3- and 4-positions (referred to as the β positions) have also measurable spin densities, therefore some coupling reactions may occur at these positions. Different coupling situations for the electrochemical polymerization of pyrrole are shown in Figure 1.13. However, α-β and β-β coupling generally brings irregular backbones and poor electronic properties. The introduction of various alkyl and alkoxy groups can eliminate these chain imperfections.

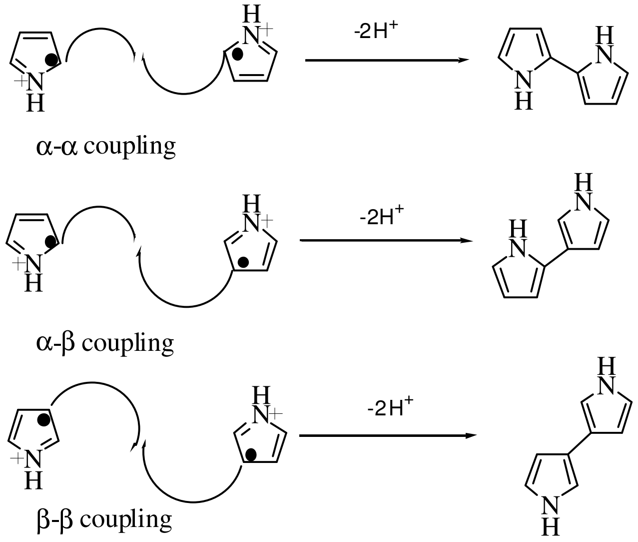


Figure 1-13. Coupling reactions of pyrrole during oxidative polymerization.

Electrochemical synthesis is simple, selective and a reproducible method. It has the advantage of producing the material on an electrode. Furthermore; the method allows easy control of the film thickness by the deposition charge. Anodic coupling consists of oxidation of the monomer into a polymer accompanied with proton elimination. Anodic coupling is preferred because it uses the unmodified monomer and the resultant polymer, being more easily oxidized (doped), is produced in the conductive state and therefore, allows the continuous deposition of the material up to considerable thickness.

The type of solvent, electrolyte system, choice and concentration of monomer and electrodes strongly affect the properties of the final conducting polymer [38].

1.4.2.1. Effect of Electrolytic Medium

Since the electrochemical polymerization reaction advances via radical cation intermediates, the choice of appropriate solvent and electrolyte is essential. The solvent to be used in the electrochemical polymerization should have sufficiently high dielectric constant so that ionic conductivity of the medium is fulfilled. The solvent should dissolve and dissociate the supporting electrolyte and should have potential range to oxidize or reduce polymer. Nitriles are favored due to their widest range in both oxidation and reduction with a high dielectric constant (ε= 37 for ACN) [38].

The criteria of the choice of electrolyte are the solubility and degree of dissociation and its nucleophilicity. The nature of electrolyte used significantly affects the morphology of the resulting film [39]. Supporting electrolyte used in electrochemical polymerization serves for two purposes [21]:

a) It makes electrolytic bath solution conducting.
b) It dopes the polymer by allowing one of its ions to couple with monomer unit.

Salts of perchlorates, tetrafluoroborates and hexafluorophosphates are broadly used supporting electrolytes for the synthesis of conducting polymers.

Inert materials are used in electrochemical polymerization as electrodes such as platinum, gold, carbon electrodes and indium-tin-oxide (ITO). Saturated calomel electrode (SCE), Ag/Ag^+ and Ag/AgCl electrodes can be used as reference electrodes.

1.5. Conducting Copolymers, Composites and Blends

Conducting polymers are promising materials due to their ease of synthesis, good environmental stability, and long term stability of electrical conductivity; however, there are several drawbacks restricting their processing and applications for practical use. The π-electron system along the polymer backbone leads to rigidity and crosslinking. The crosslinking in the polymer chain makes it insoluble, hard, brittle and therefore, poorly processable. These films also have a variety of conductivity values depending on the electrolysis conditions. In order to obtain a material suitable for applications in various technological fields certain limitations need to be overcome [40]

The mechanical properties of these polymers can be advanced through the production of polymer composites, graft and block copolymers [41,42]. Electrochemical synthesis of copolymer films from pyrrole and substituted pyrroles [42,43] pyrrole and thiophene [44], bithiophene [45] and other combination of aromatic compounds [46] have been reported in the literature. The strong electron donor properties of EDOT represent an interesting tool for the molecular engineering of the band gap of π-conjugated systems. One of the simplest ways to take advantage of these properties is to associate EDOT with electron withdrawing groups by synthesizing copolymers [47].

Those materials can be prepared either chemically or electrochemically. In electrochemical synthesis three methods can be employed. One of which is to copolymerize the monomer with another monomer. The second method uses an electrolyte solution that contains both the monomer and the host polymer. Third one is the polymerization of the conducting component on electrode previously coated with the insulating host polymer.

When an electrically conducting phase is dispersed with a sufficient quantity in a polymeric resin, a conductive composite is formed. The unique properties of such composites make them technologically superior to alternative materials [48]. Structural and electrical properties can be improved by the preparation of composite materials containing a conducting polymer composed of a nonconducting polymer such as poly(vinyl chloride) (PVC) poly(vinyl alcohol) (PVA) and natural rubber [49-50].

1.6. Characterization of Conducting Polymers

A variety of analytical techniques can be utilized to characterize conducting polymers. Many examples exist in literature, some of which include; cyclic voltammetry for understanding reduction-oxidation behavior of conducting polymers, optoelectronic characterization for examination of π to π^* transitions, nuclear magnetic resonance and FTIR for structure confirmation, gel permeation chromatography for molecular weight determination, differential scanning calorimetry and thermogravimetry analysis for evidence of glass and melting transitions and decomposition temperatures.

1.7. Electrochromism

Electrochromism can be defined as the capability of a material to alter its optical properties within the whole electromagnetic spectrum under an applied voltage, such as in the visible region (400-800 nm) and in the near-infrared (NIR) region (e.g., 1000-2000 nm) [51].

There is a vast number of chemical species possessing electrochromic properties. Viologens [52], transition metal oxides, most famously tungsten trioxide (WO_3)

systems [53-55], prussian blue systems [56], phthalocyanines [57, 58], and conducting polymers [3] are widely utilized electrochromic materials.

Conducting polymers attract more attention than inorganic materials due to their advantages over inorganic compounds, such as fast switching ability, high coloration efficiency, fine tuning of the band gap through chemical structure modification and multiple colors within the same material [59].

Electrochromism arises from the energy difference between the π-bonding orbitals and the π*-antibonding orbitals that lies within the visible region. The optical properties of these materials can be adjusted by controlled doping (and/or dedoping).

The doping process (e.g: 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 leads to the color changes. As doping level is increased; the bipolaron states overlap in bipolaron bands, the bipolaron bands may appear with valence and conduction bands. Evolutions of band structure and color changes are given in Figure 1.14.

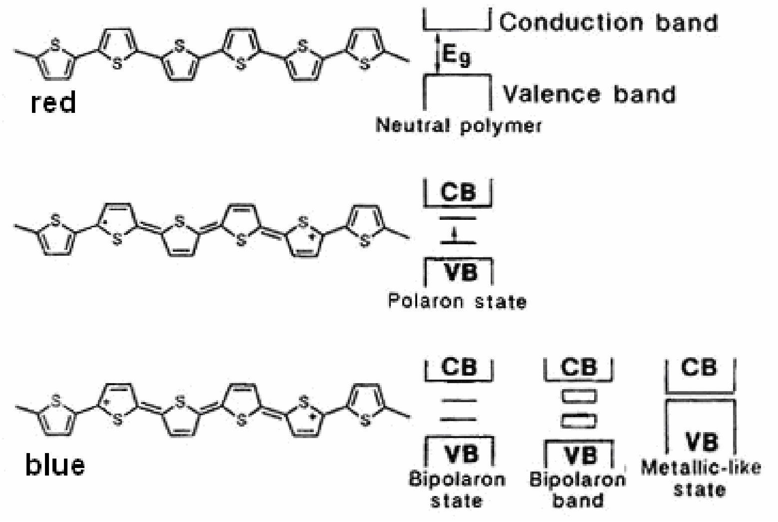


Figure 1-14. Evolution of electronic band structure with p-doping for conjugated polymer with non-degenerate ground state.

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 (Eg) 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 [60]. Eg 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. This slower process controls the color variation kinetics in polymer films [61].

The introduction of electron donating substituents into a conjugated chain is a widely utilized approach 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 [62].

1.7.1. Types of Electrochromic Materials

Three main types of electrochromic materials in terms of their electronically accessible optical states are reported in the literature.

The first type consists of materials with at least one colored and one bleached state. These materials are especially useful for absorption/transmission-type device applications such as smart windows and optical shutters. Typical examples of this area are metal oxides, viologens, and polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT). A second class of materials consists of electrochromes with two discrete colored states. These electrochromic materials lack a transmissive state but are useful for display-type applications where different colors are desired in different redox states. Polythiophene is a good example of this type, where the thin films of this polymer switch from red to blue upon oxidation. A third class includes the growing interest in the electrochromic field, where more than two color states are accessible depending on the redox state of the material [63].

Window applications are the most prominent uses for electrochromic polymers. A device can be cycled between transparent and tinted states through the use of a polymer with transmissive and absorptive color states. As the palette of obtainable colors in electrochromic polymers advances, these materials become more suitable for display technology [64]. Even though electrochromic materials find spread usage in the area of smart windows, displays, and storage devices; they are also employed in the construction of devices that operate in the infrared and microwave regions, as well in key components (i.e., variable optical attenuators) in telecommunications that operate in the NIR region (e.g., around 1310 and 1550 nm) [51].

1.7.2. Spectroelectrochemistry

Spectroelectrochemistry is a technique that examines electronic and optical changes of conducting polymers that occur upon doping. It provides information about electronic band gap intraband states formed upon doping.

In their neutral state, conducting polymers are in insulating regime with a band gap, Eg, between the valence band (HOMO) and the conduction band (LUMO). Upon oxidizing or doping, the band structure of the polymer is modified, in other words lower energy intraband transitions occurred as well as charged carriers (polarons and bipolarons) are created, as a consequence the conductivity is increased. Spectroelectrochemistry is crucially important in determination of π to π^*, polaronic and bipolaronic transitions in addition to calculation of band gap energy.

1.8. Electrochromic Devices (ECD)

Electrochromic displays are typically constructed by combining an electrode covered with a thin layer of electrochromic materials, transparent solid polymer electrolytes and a complimentary electrochromic material as a counter electrode. If the back of the counter electrode is covered with a reflective material it will act as an electrochromic mirror [21].

There is one to one analogy between the electrochromic devices and batteries. Electrochromic devices consist of at least one transparent electrode in electromagnetic spectrum with electrochemically reversible cathode material (which colors upon being oxidized) and anode material (which colors upon being reduced) and ion-conducting electrolyte.

One of the electrodes is oxidized, while the other is being reduced upon externally applied potential, leading to a device switching between combination of the neutral color of one film and the oxidized color of the other film, and vice versa [65].

The conductive electrolyte must not only provide physical separation between cathode and anode, a source of cations and anions to balance redox reactions, but also be transparent in the given region of the spectrum. The ion conducting electrolyte (gel electrolyte) is usually an inorganic salt dissolved in a solvent such as propylene carbonate with a stiffener polymer poly(methylmethacrylate) [66]

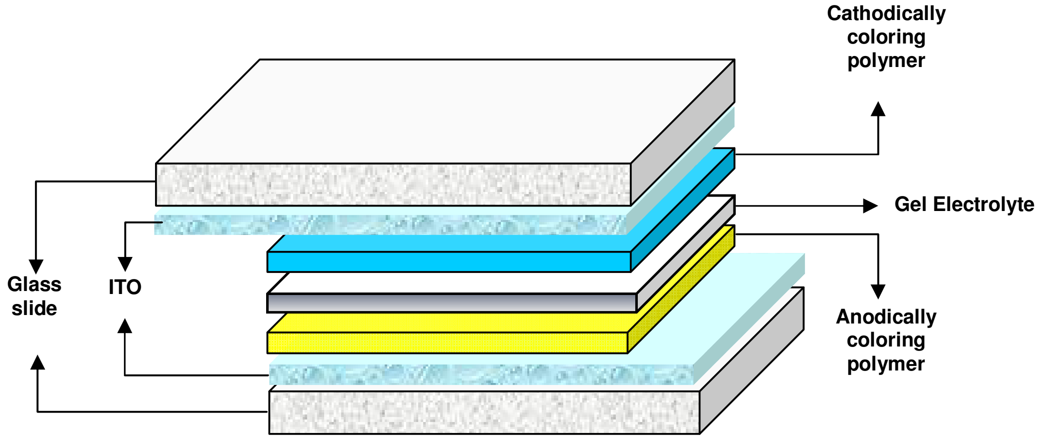


Figure 1-15. Schematic representation of ECDs

The preconditions for high performance electrochromic devices are: a) high electrochromic efficiency, expressed in $cm^2 C^{-1}$ and related to the injected charge in the material to change its color; b) short response time; c) good stability; d) optical memory, defined as the color stability under open circuit potential conditions; e) optical contrast, also called write-erase efficiency, and f) color uniformity [61].

1.9. Characteristics of Electrochromic Device

1.9.1. Electrochromic Contrast and Switching Speed

Optical contrast is an essential parameter to evaluate an electrochromic material. It is frequently reported as percent transmittance change (Δ%T) between the two colored redox states at a specific wavelength where the highest contrast is monitored. Switching speed is the time required for the coloring/bleaching process of an electrochromic material. The switching speed of electrochromic material is dependent on ionic conductivity of the electrolyte, ion diffusion in thin films, magnitude of the applied potential, film thickness and morphology of the film [63].

1.9.2. Open Circuit Memory and Stability

Open Circuit Memory is defined as the time the material retains its absorption state after the electrical field is removed. Electrochromic stability is usually associated with electrochemical stability since the degradation of the active redox couple results in the loss of electrochromic contrast and hence the performance of the electrochromic material [63].

1.9.3. Colorimetry

The colors of the electrochromic materials were defined scientifically by achieving colorimetry measurements. Colorimetry is defined as the measurement of color. The measurement of color allows colored objects to be described, ordered and compared. CIE system was employed as a quantitative scale to define colors. 1976 CIE *L a b* system of colorimetry established by The Commission Internationale de l'Eclairage (International Commission on Illumination) is used for an objective description of the color of the ECDs, where *L* corresponds to brightness or luminance, *a* refers to hue, dominant wavelength, or chromatic color, and *b* known as the saturation, chroma, tone, or purity [61, 64].

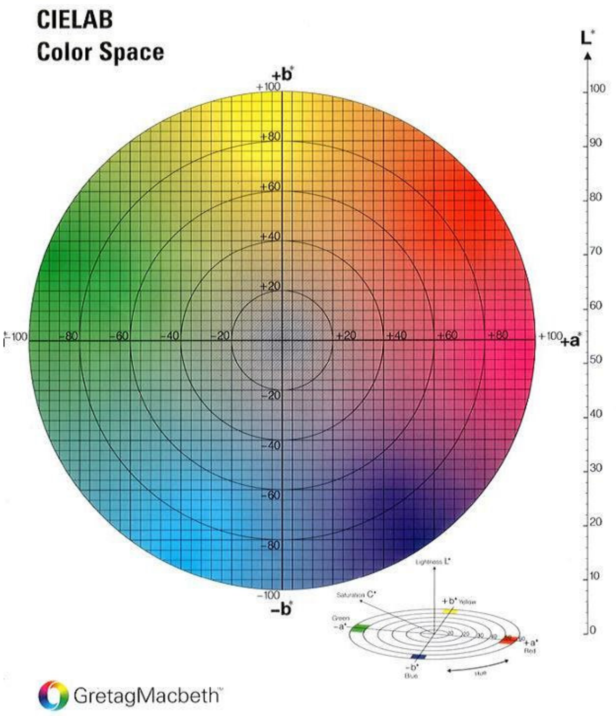


Figure 1-16. CIELAB color space

1.10. Objectives of the Study

- ✓ To synthesize the target monomer; 1-(4-Nitrophenyl)-2,5-di(2-thienyl)-1H-pyrrole ($SNSNO_2$)
- ✓ To perform the chemical polymerization of $SNSNO_2$
- ✓ To perform the potentiostatic polymerization of $SNSNO_2$
- ✓ To achieve the potentiostatic polymerization of $SNSNO_2$ in the presence of EDOT to obtain the conducting copolymers with better mechanical and physical properties
- ✓ To characterize conducting poly($SNSNO_2$) and poly($SNSNO_2$-co-EDOT) with common characterization techniques
- ✓ To investigate electrochromic and spectroelectrochemical properties of homopolymer and copolymer

CHAPTER II

EXPERIMENTAL

2.1. Materials

$AlCl_3$ (Merck), succinyl chloride (Aldrich), p-nitroaniline (Merck), NaOH (Merck), dichloromethane (Sigma-Aldrich), toluene (Merck), acetonitrile (ACN) (Merck), methanol (Merck), $LiClO_4$ (Aldrich), $NaClO_4$ (Aldrich), poly(methylmethacrylate) (PMMA) (Aldrich), propylene carbonate (PC) (Aldrich) were used without further purification. Thiophene (Aldrich) was distilled before use. Ferric chloride (Aldrich), 3,4-ethylenedioxythiophene (EDOT) (Aldrich), *p*-toluene sulfonic acid (PTSA) (Sigma) and nitromethane (Aldrich) were used as received.

2.2. Instrumentation

2.2.1. Nuclear Magnetic Resonance (NMR) Spectrometer

^1H-NMR and ^{13}C-NMR spectra of the monomer and the chemically produced polymer of $SNSNO_2$ 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.

2.2.2. Fourier Transform Infrared (FTIR) Spectrometer

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

2.2.3. Scanning Electron Microscope (SEM)

JEOL JSM-6400 scanning electron microscope was used to analyze the surface morphologies of the polymer films.

2.2.4. Gel Permeation Chromatography (GPC)

GPC (PL220) was employed for the determination of molecular weight of insulating precursor polymer.

2.2.5. UV-VIS Spectrophotometer

Varian Cary 5000 UV-Vis-NIR spectrophotometer and Agilent 8453 UV-Vis spectrophotometer were used in order to perform the spectroelectrochemical studies of the polymer and copolymer and the characterization of their devices.

2.2.6. Colorimetry Measurements

Colorimetry measurements were fulfilled via Minolta CS-100 spectrophotometer.

2.2.7. Potentiostat

Wenking POS 73 and Solartron 1285 potentiostats were employed to supply a constant potential in electrochemical synthesis. Electrochemical polymerization is achieved 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 passing 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.

2.2.8. Cyclic Voltammetry (CV)

Cyclic voltammetry is a convenient technique that determines the oxidation-reduction peak potentials of the monomers and the electroactivity of polymers.

The CV system consists of a potentiostat, a function generator, an XY recorder, and a cyclic voltammetry cell. Function generator or wave generator applies a triangular wave potential to the cell so that the working electrode potential is swept linearly through the voltammetry wave (Figure 2.1). During these scans, potential-time response and current (I) versus potential (V) curves are recorded.

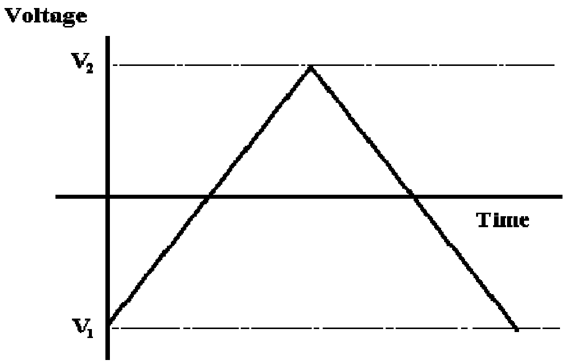


Figure 2-1. Triangular wave function

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is indicated in Figure 2.2. Solution contains only a single electrochemical reactant. The forward scan produces a current peak for any analyte that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will reach a potential that will reoxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak.

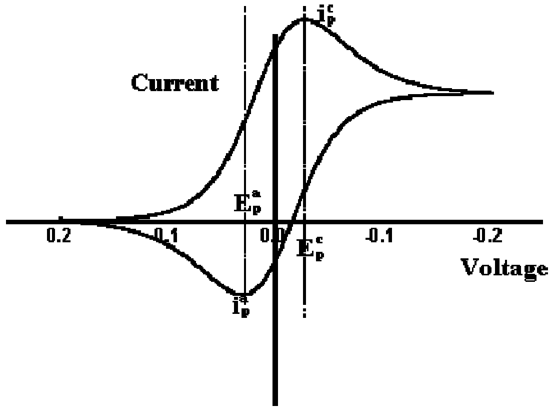


Figure 2-2. A cyclic voltammogram for a reversible redox reaction

The peak current, i_p, is described by the Randles-Sevcik equation:

$$i_p=(2.69x10^5)\ n^{3/2}\ A\ C\ D^{1/2}\ v^{1/2}$$

where n is the number of moles of electrons transferred in the reaction, A is the area of the electrode, C is the analyte concentration (in moles/cm^3), D is the diffusion coefficient, and v is the scan rate of the applied potential.

Cyclic voltammetry experiments were carried out at room temperature and under nitrogen atmosphere in a three electrode cell (Figure 2-3) consisting of platinum (Pt) wire as the counter, silver (Ag) wire as the reference, ITO (indium doped tin oxide) coated glass as the working electrode. ACN was utilized as solvent in all experiments $LiClO_4$ (0.1 M)/$NaClO_4$ (0.1 M) salts were used as supporting electrolytes. Bank Wenking POS2 and Solartron 1285 potentiostat/galvanostat were employed for electrochemical studies.

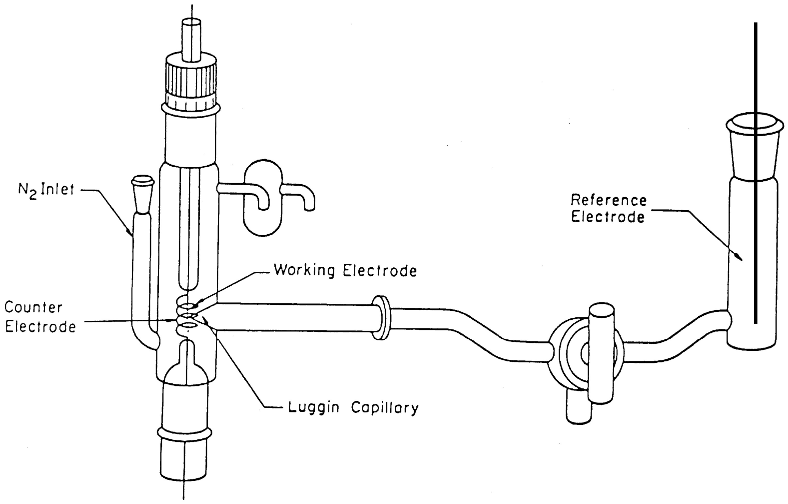


Figure 2-3. Cyclic voltammetry cell

2.2.9. Electrolysis Cell

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

2.2.10. Four-Probe Conductivity Measurements

Four probe method was preferred to measure electrical properties of conducting polymers due to its advantage over two probe technique. Elimination of errors caused by contact resistance is possible with this method. A simple four-probe measurement setup is demonstrated in Figure 2-4. Four equally spaced osmium tips touch the surface of polymer film taped on an insulating substrate. A known steady current is passed through the electrodes 1 and 4 and measured while the potential drop (ΔV) between contacts 2 and 3 assessed.

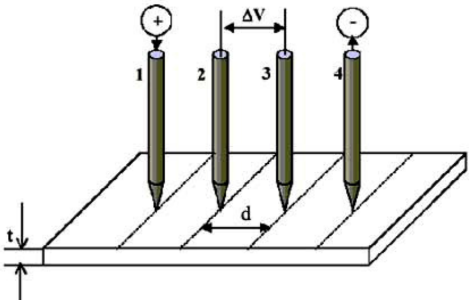


Figure 2-4. Four-probe conductivity measurement

Conductivity is calculated from the following equation,

$$\sigma = \frac{\ln 2}{\pi R t}$$

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

2.3. Procedure

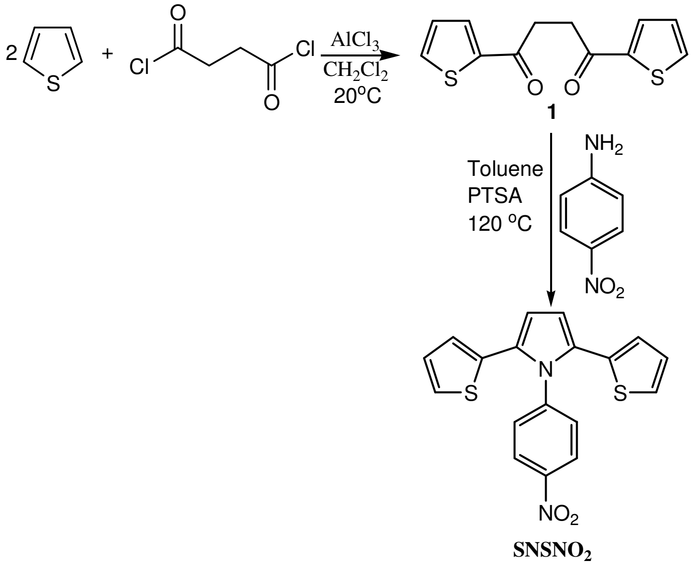
2.3.1. Synthesis of Monomer

2.3.1.1. Synthesis of 1,4-di(2-thienyl)-1,4-butanedione

The starting material, 1,4-di(2-thienyl)-1,4-butanedione, was synthesized according to a literature method [67-73]. To a suspension of $AlCl_3$ (16 g, 0.12 mol) in CH_2Cl_2 (15 ml), a solution of thiophene (9.61 ml, 0.12 mol) and succinyl chloride (5.51 ml, 0.05 mol) in CH_2Cl_2 was added dropwise [74]. The red mixture was stirred at room temperature CH_2Cl_2 for 4 h. This was then poured into ice and concentrated HCl (5 ml) mixture. After stirring, the dark green organic phase was separated; this phase was washed with concentrated $NaHCO_3$ solution and brine solution, respectively and then dried over $MgSO_4$. After evaporation of the solvent a blue green solid remained and suspended in ethanol. Filtration and washing with absolute ethanol yielded the 1,4-bis(2-thienyl)butane-1,4-dione. The synthetic route of 1,4-di(2-thienyl)-1,4-butanedione is shown in Scheme 1.

2.3.1.2. Synthesis of 1-(4-Nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole Monomer

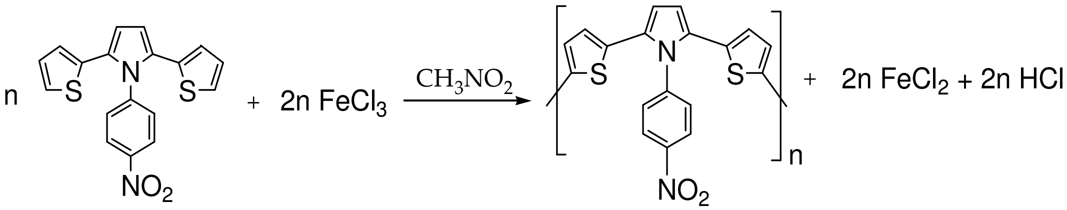
The monomer 1-(4-nitrophenyl)-2,5-di(2-thienyl)-1H-pyrrole was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and 4-nitroaniline in the presence of catalytical amount of para-toluene-sulfonic acid (PTSA) [75]. A round bottom flask equipped with an argon inlet and mechanical stirrer was charged with 1,4-di(2-thienyl)-1,4-butanedione (1.25 g, 5mmol), 4-nitro-aniline (0.97g, 7mmol), para-toluenesulfonic acid (PTSA) (0.1 g, 0,58 mmol) and toluene (20ml). This mixture was refluxed for 24 hours under argon. Afterwards, toluene was evaporated and 1-(4-nitrophenyl)-2,5-di(2-thienyl)-1H-pyrrole was obtained via column chromatography. Elution with dichloromethane of SiO_2 flash column afforded the desired compound at the solvent front. The synthetic route of the monomer is shown in Scheme 1.



Scheme 2-1. Synthetic route of 1-(4-nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole SNSNO$_2$

2.3.2. Chemical Polymerization of SNSNO$_2$ with Ferric Chloride

A typical chemical polymerization of SNSNO$_2$ was achieved using iron(III) chloride as the oxidant. To carry out the oxidative polymerization, SNSNO$_2$ (1x10^{-3} M) was dissolved under a blanket of nitrogen in nitromethane (15 mL). A solution of iron(III) chloride (2 x10^{-3} M) in nitromethane (5 mL) was dropwise added to the monomer solution. The reaction was carried out for 5 min with constant stirring. The dark blue oxidized polymer was first washed with methanol, filtered, compensated with 30% NaOH, and dried under vacuum for ^{1}H- NMR analyses. Scheme.2-2 shows the chemical polymerization of SNSNO$_2$.



Scheme 2-2. Oxidative chemical polymerization of $SNSNO_2$

2.4. Gel Permeation Chromatography (GPC)

For molecular weight determination, the chemically synthesized $P(SNSNO_2)$ was dissolved in tetrahydrofuran (THF) and GPC studies were fulfilled. Molecular weights were determined on the basis of polystyrene standards.

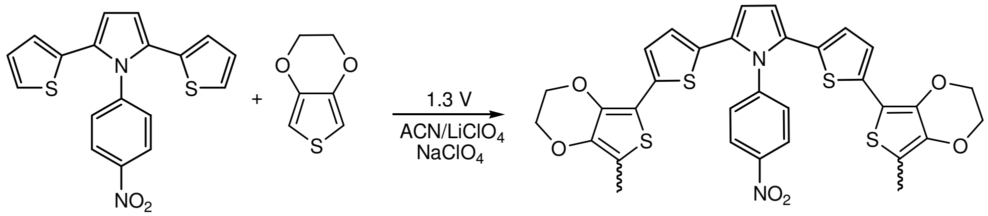
2.5. Electrochemical Synthesis of $P(SNSNO_2)$ and $P(SNSNO_2$-co-EDOT)

2.5.1. Synthesis of Homopolymer of $SNSNO_2$

CV was utilized in order to investigate the electroactivity of the polymers and to accomplish the oxidation-reduction peak potentials of the polymer. The measurements were achieved at room temperature under nitrogen atmosphere by using $NaClO_4$ (0.1 M) and $LiClO_4$ (0.1 M) / ACN solvent-electrolyte couple. The working and counter electrodes were Pt wires and the reference electrode was a Ag wire electrode. A background voltammogram was taken to discard the impurity effects before the addition of substrate. Experiments were carried out sweeping the potential between 0.40 V and 0.98 V with 500 mV/sec scan rate in the presence of 50 mg $SNSNO_2$.

2.5.2. Synthesis of Copolymer SNSNO$_2$ with 3,4-Ethylenedioxythiophene P(SNSNO$_2$-co-EDOT)

EDOT was used as the comonomer for the synthesis of conducting copolymer of SNSNO$_2$. SNSNO$_2$ (50 mg) was dissolved in 5 ml of ACN and 2 μL of EDOT were introduced into the single compartment electrolysis cell. NaClO$_4$ (0.1 M) and LiClO$_4$ (0.1 M) were used as the supporting electrolyte. The working and counter electrodes were Pt wires and the reference electrode was Ag wire electrode. A constant potential of 1.3 V was applied for 10 min under inert atmosphere. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomers. Scheme 2-3 shows copolymerization reaction.



Scheme 2-3. Copolymerization Reaction of SNSNO$_2$ with EDOT

2.6. Electrochromic Properties of Polymers

2.6.1. Spectroelectrochemistry

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques that can be operated at the same time. Compared to common electrochemical methods, it can provide information on both electrochemical response and accompanying optical characteristics of all states of the electrochemical reaction. It is essential to gather information in-situ, during electrochemical process.

Potentiodynamic deposition of homopolymer film on indium tin oxide (ITO) coated glass slides were performed sweeping the potential between 0.40 V and 0.98 V with 500 mV/sec scan rate in the presence of 50 mg $SNSNO_2$ and ACN/ $NaClO_4/LiClO_4$ (0.1 M) solvent-electrolyte couple.

For the investigation of copolymer, 2 μL EDOT and 50 mg $SNSNO_2$ were used in ACN/ $NaClO_4/LiClO_4$ (0.1 M) solvent-electrolyte couple. Constant potential of 1.3 V was applied for 10 min under the inert atmosphere. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomers.

2.6.2. Switching Properties of Polymers

For electrochromic applications, the significant point is the ability of a polymer to switch rapidly and exhibit a striking color change. Electrochromic switching studies can monitor these types of properties. A square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry was used to investigate switching times and contrast in these polymers. In this double potential step experiment, the potential was set at an initial potential for a set period of time, and was stepped to a second potential for a set period of time, before being switched back to the initial potential again.

In order to study switching properties of polymers, homopolymer and copolymer were deposited on ITO-coated glass slides as in the form of thin films. After coating the polymers on ITO electrode, a potential square wave was applied in the monomer free ACN/ $NaClO_4/LiClO_4$ (0.1 M) solution while recording the percent transmittance between its neutral and doped states at a fixed maximum absorption wavelength.

Switching properties of polymer films were investigated by application of potential square wave technique with a residence time of 5 seconds between 0.2 V and 1.0 V for the homopolymer, between -0.6 V and 1.0 V for the copolymer.

2.6.3. 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. Following the syntheses of P(SNSNO$_2$) and P(SNSNO$_2$-co-EDOT) films on ITO electrodes, they were placed into monomer-free solutions containing ACN/ NaClO$_4$/LiClO$_4$ (0.1 M) solution. Three attributes of color; hue (a), saturation (b) and luminance (L) were measured.

2.7. Electrochromic Device (ECD) Construction

The construction of a transmissive type ECD consists of two thin polymer films deposited on transparent indium tin oxide coated glass (ITO), and separated by a viscous gel electrolyte. Polymer films used to assemble a device will be obtained by constant potential oxidative polymerization.

2.7.1. P(SNSNO$_2$) /PEDOT Electrochromic Device

Cathodically coloring polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was electrochemically deposited onto the ITO-coated glass from a 0.01 M solution of EDOT in NaClO$_4$ (0.1 M) and LiClO$_4$ (0.1 M)/ACN solvent-electrolyte couple at +1.5

V versus Ag/Ag$^+$. The anodically coloring homopolymer, P(SNSNO$_2$) was potentiodynamically deposited onto the ITO-coated glass sweeping between 0.40 V and 0.98 V in the presence of 0.01 M SNSNO$_2$ in ACN/NaClO$_4$/LiClO$_4$ (0.1 M) solvent-electrolyte couple.

Before the device construction, it is important to balance the charge capacities of the electrochromic layers. Otherwise, it would result in incomplete electrochromic reaction and residual charges will remain during the coloring/bleaching processes, which would lead to residual coloration of the ECD in the bleached state. To minimize the effect of charge imbalances in ECD, we matched the redox charges of the two complementary polymer films by chronocoulometry and provided a balanced number of redox sides for switching.

The gel electrolyte was spread on the polymer-coated sides of the electrodes (one doped, the other neutral) and the electrodes were sandwiched under atmospheric conditions.

2.7.2. P(SNSNO$_2$-co-EDOT) / PEDOT Device

For the investigation of copolymer, 2 μL EDOT and 50 mg SNSNO$_2$ were used in ACN/ NaClO$_4$/LiClO$_4$ (0.1 M) solvent-electrolyte couple. A constant potential of 1.3 V was applied for 10 min under the inert atmosphere. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomers.

Cathodically coloring polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was electrochemically deposited onto the ITO-coated glass from a 0.01 M solution of EDOT in NaClO$_4$ (0.1 M) and LiClO$_4$ (0.1 M)/ACN solvent-electrolyte couple at +1.5 V versus Ag/Ag$^+$. The film was fully reduced by polarizing to -1.5 V vs Ag/Ag$^+$ in the monomer free solution. The gel electrolyte was spread on the polymer-coated sides of the electrodes (one doped, the other neutral) and the electrodes were sandwiched under atmospheric conditions.

2.7.3. Preparation of the Gel Electrolyte

Gel electrolyte was prepared by using $NaClO_4$:$LiClO_4$: ACN: PMMA: PC in the ratio of 1.5:1.5:70:7:20 by weight. After $NaClO_4/LiClO_4$ was dissolved in AN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating was required. Propylene carbonate (PC), as a plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced.

2.8. Characterization of Electrochromic Devices

2.8.1. Spectroelectrochemistry Studies of Electrochromic Devices

Agilent 8453 UV-Vis spectrophotometer were used in order to characterize the optical properties of electrochromic devices (ECDs). During spectroscopic studies a device having no active polymer layer, was used as the reference. Applied potentials were delivered via potentiostat where the counter and the reference electrodes were shortcut and working electrode was connected to anodically coloring polymer layer. Spectroelectrochemical studies of electrochromic devices were recorded under sequential variation of applied potentials between ultimate operation conditions, while measuring the absorbance as a function of wavelength.

Spectroelectrochemical UV-Vis transmittance of electrochromic device of $P(SNSNO_2)$/PEDOT was measured under miscellaneous applied potentials between -0.8 V and +1.6 V while measuring the absorbance as a function of wavelength.

Spectroelectrochemical study of P($SNSNO_2$-co-EDOT) / PEDOT device was carried out varying the voltage between -2.0 V to 2.2 V and absorbance was measured as a function of wavelength.

2.8.2. Switching Properties of Electrochromic Devices

Potential square wave technique, similar to described procedure in section 2.6.2 was applied to determine switching properties of ECDs, where the applied potentials and wavelength of inspection were determined according to spectroelectrochemistry studies.

Potential square wave technique was employed to determine switching properties of ECDs between -0.8 V and +1.6 V with a residence time of 5 s for P($SNSNO_2$)/PEDOT device and between -2.0 V to 2.2 V with a residence time of 5 s for P($SNSNO_2$-co-EDOT) / PEDOT device.

2.8.3. Stability of the Electrochromic Devices

The stability of the devices was evaluated via CV studies by continuous sweeping of the applied potential across the device up to 500 cycles.

P($SNSNO_2$)/PEDOT device repeatedly switched up to 500 cycles with CV sweeping voltage of -0.8 V and +1.6 V range with 500 mV/s scan rate under atmospheric conditions. P($SNSNO_2$-co-EDOT)/PEDOT device were repeatedly switched up to 500 cycles with CV voltage of -2.0 V and + 2.2 V.

2.8.4. Colorimetry Studies of ECDs

The colors of polymer films and devices were determined by the Coloreye XTH spectrophotometer (GretagMacbeth) at the reduced and oxidized states of P($SNSNO_2$)/PEDOT and P($SNSNO_2$-co-EDOT]/PEDOT devices.

CHAPTER III

RESULTS AND DISCUSSION

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

^{1}H-NMR and ^{13}C-NMR spectra of monomer and ^{1}H-NMR of polymer were investigated in $CDCl_3$ and chemical shifts (δ) are given relative to tetramethylsilane as the internal standard.

Pale orange crystals; mp 188 °C; ^{1}H-NMR spectrum of monomer (Fig. 3.1.): $C_{18}H_{12}N_2O_2S_2$, δ_H ($CDCl_3$): 6.46 (s, 2H, pyrrolyl), 6.47 (dd, 2H, d, *J* = 1.00 Hz, 3.60 Hz), 3-thienyl, 6.77 (dd, 2H, *J* =3.60 Hz, 4.98 Hz), 4-thienyl, (7.05 dd, 2H, *J* = 1.0 Hz, 4.98 Hz), 5-thienyl, 7.30 (dd, 2H, *J* =2.20 Hz, 9.18 Hz) phenyl, 8.13 (dd, 2H, *J* = 2.20 Hz, 9.18 Hz, phenyl).

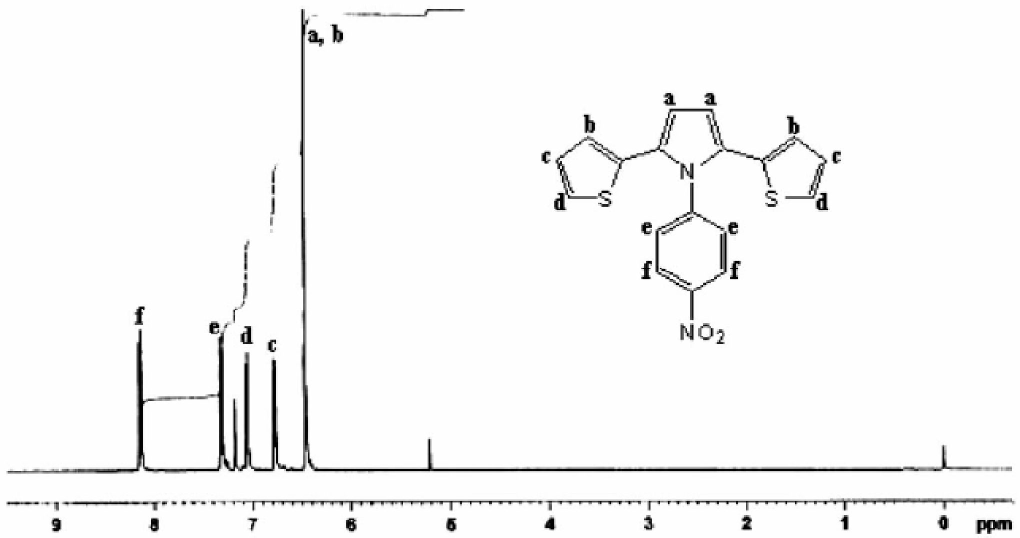


Figure 3-1. ^{1}H-NMR spectrum of the monomer

^{13}C-NMR spectrum of the monomer $C_{18}H_{12}N_2O_2S_2$ (Fig. 3.2.): ^{13}C-NMR (δ,ppm): Ca: 111.5, Cb: 124.3, Cc: 133.8, Cd: 129.7, Ce: 130.1, Cf: 127.2, Cg: 147.3, Ch: 125.7, Ci: 125.2, Cj: 147.3

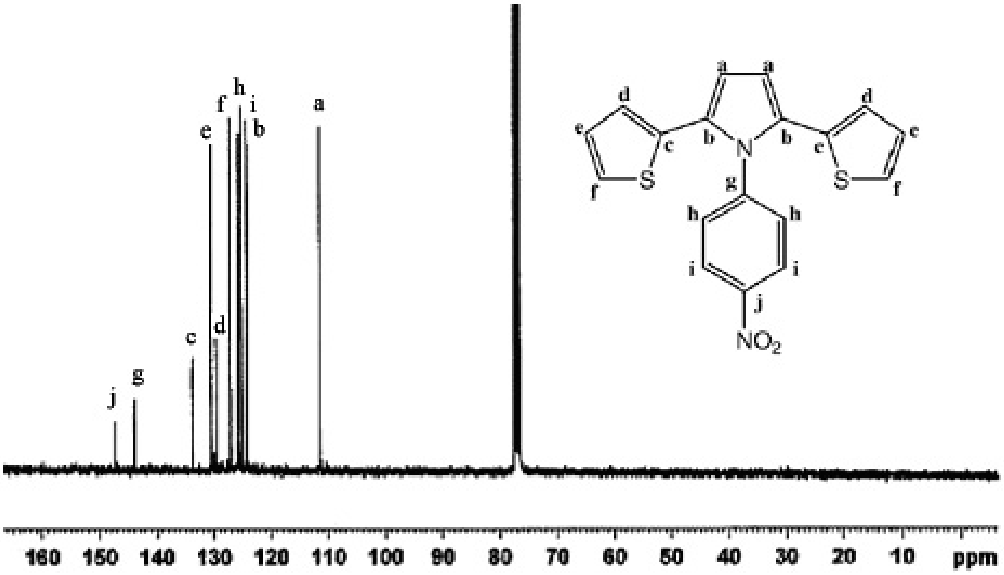


Figure 3-2. ^{13}C-NMR spectrum of the monomer

^{1}H-NMR spectrum of chemically synthesized polymer (Fig. 3.3): δ_H ($CDCl_3$): 6.3–6.5 2H, broad s, pyrrolyl, 6.50–6.75 2H, s, 3-thienyl, 6.75–7.00 2H, broad s, 4-thienyl, 7.10–7.50 2H, broad s, phenyl, 8.20–8.40 2H, broad s, phenyl.

Broadening of the peaks and the tremendous decrease in the intensity of 5-thienyl (H_d) proton confirm the polymerization through the thiophene moiety of the monomer.

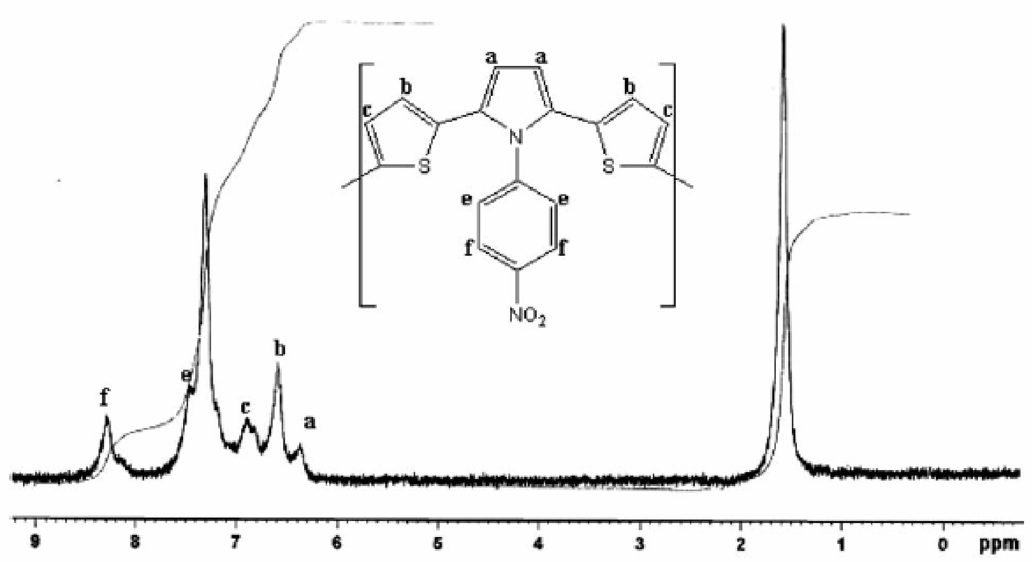


Figure 3-3. ^{1}H-NMR spectrum of the chemically synthesized P(SNSNO$_2$)

3.2. FTIR Spectra

FTIR spectrum of the SNSNO$_2$ (Fig 3-4) shows the following absorption peaks: 3103 cm^{-1} aromatic C–H stretching, 1521 cm^{-1} asymmetric Ar-NO$_2$ stretching, 1349 cm^{-1} symmetric Ar-NO$_2$ stretching, 840 cm^{-1} C–N stretching for Ar-NO$_2$, 3020 cm^{-1} C–H$_\alpha$ stretching of thiophene., 1494–1340 cm^{-1} aromatic C=C, C–N stretching due to pyrrole and benzene, 1035 cm^{-1} C–H in plane bending of benzene, 774 cm^{-1} C–H$_\alpha$ out of plane bending of thiophene.

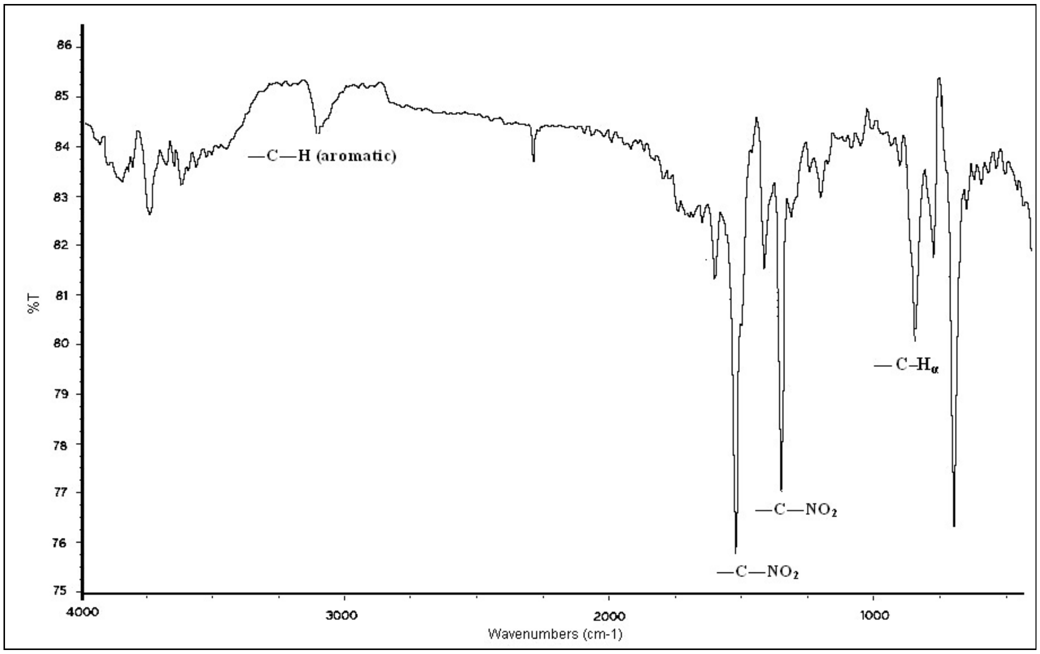


Figure 3-4. FTIR spectrum of SNSNO$_2$

Most of the characteristic peaks of the monomer SNSNO$_2$ remained unperturbed upon electrochemical polymerization. The intensity absorption bands of the monomer at 3020 cm^{-1} and 774 cm^{-1} arising from C–H$_{\alpha}$ stretching of thiophene moiety, respectively, disappeared completely. This is an evidence of the polymerization from 2, 5 positions of thiophene moiety of the monomer. Whereas, two new bands related to C–H$_{\beta}$ out-of plane bending of 2, 5 disubstituted thiophene and C–S stretching appeared at 779 and 632 cm^{-1}, respectively. The broad band observed at around 1649 cm^{-1} proves the presence of polyconjugation. The strong absorption peaks at 1113, 1087 and 620 cm^{-1} were attributed to the incorporation ClO$_4^-$ ions into the polymer film during doping process. The baseline shift in FTIR spectrum also implies the conducting polymer formation. Results of the FTIR studies clearly indicated the polymerization of the monomer. (Fig 3-5)

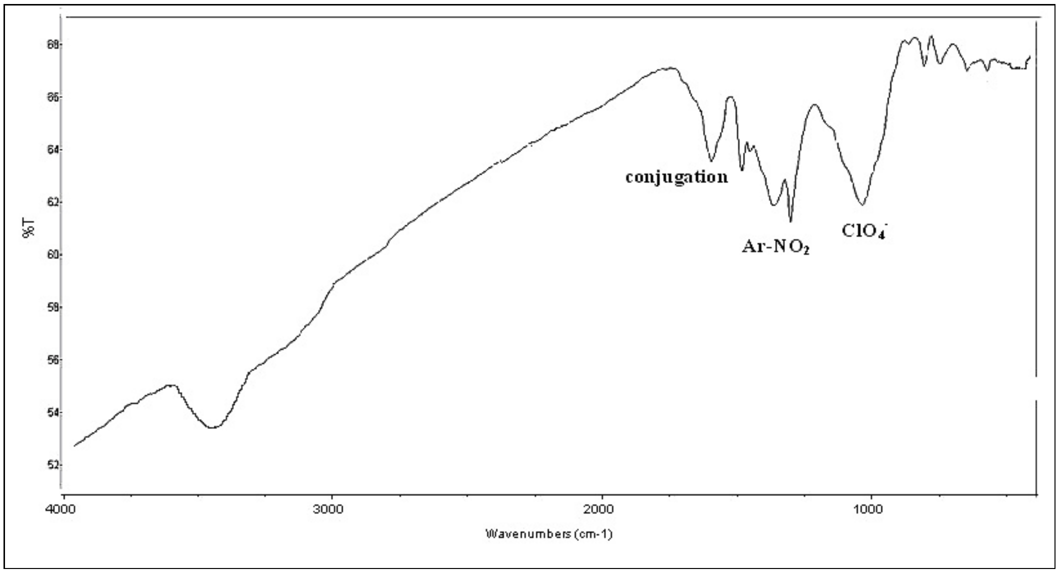


Figure 3-5. FTIR Spectrum of electrochemically synthesized P(SNSNO$_2$)

FTIR spectrum (Fig. 3.6) of electrochemically synthesized P(SNSNO$_2$-co-EDOT) showed the characteristic peaks of the monomer. The peak at 1518 cm^{-1} was due to conjugated cyclic C-N stretching, the peak at 1354 cm^{-1} was due to pyrrole-benzene stretching. The strong peak at 1342 cm^{-1} was Ar-NO$_2$ stretching. The peaks related to C–H$_{\alpha}$ stretching of thiophene disappeared completely. On the other hand, evolution of new peaks was observed at 2925 and 2870 cm^{-1}, which are attributed to the aromatic ethylene group belonging to EDOT. The strong absorption peaks at 1113, 1087 and 630 cm^{-1} are attributed to the incorporation ClO$_4^-$ ions into the polymer film during doping process. The baseline shift in FTIR spectrum also implies the conducting polymer formation. Results of the FTIR studies clearly indicated the copolymerization was successfully achieved.

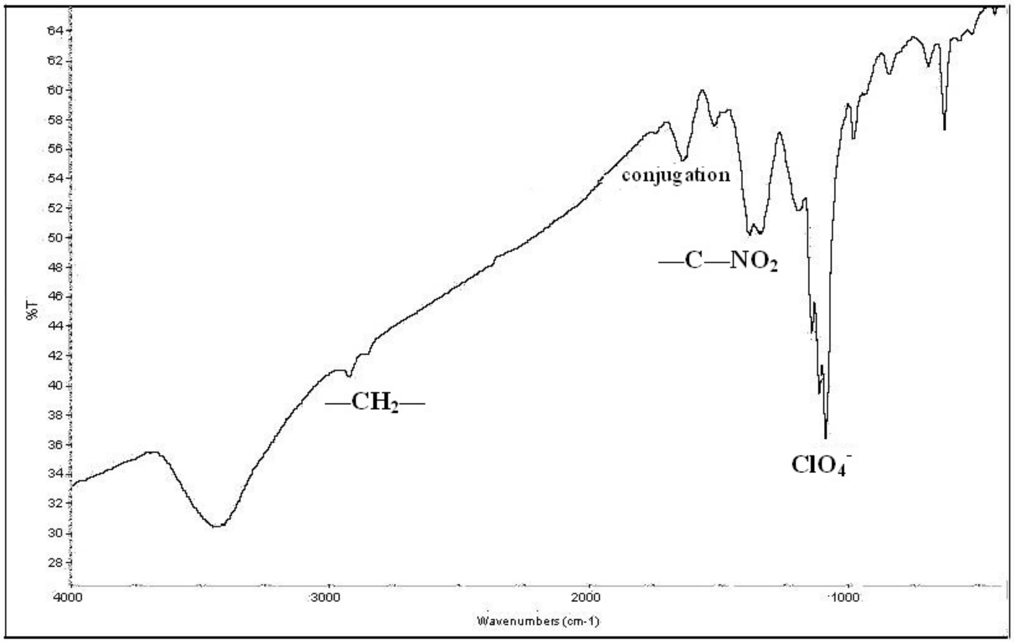


Figure 3-6. FTIR Spectrum of electrochemically synthesized P(SNSNO$_2$-co-EDOT)

3.3. Cyclic Voltammograms

Cyclic voltammetry experiments were carried out in ACN/NaClO$_4$/LiClO$_4$ solvent electrolyte system on bare Pt electrode with a 500 mV/s scan rate. When the range between -0.3 V and +1.3 V was swept, electroactivity increased with increasing scan number. Homopolymer of SNSNO$_2$ in acetonitrile indicated two oxidation peaks at 0.88 V and 1.11 V and a reduction peak at 0.66 V, which implied the electroactivity of P(SNSNO$_2$) (Fig 3-7). This process promotes an electrochromic change of the film to a yellow-orange color, while a greenish cloud is formed around the electrode due to the partial dissolution of neutral linear oligomers of low molecular weight present as the reduced P(SNSNO$_2$).

Potentials more positive than 0.98 V promoted lower adherence of deposits, due to the oxidation and degradative crosslinking of polymer at 1.11 V anodic peak. On the other hand, potentials lower than 0.88 V seemed to be useful in obtaining insoluble, adherent and electroactive films. Under these conditions, the monomer gives a polymer, which is subsequently oxidized at the same potential to produce polarons balanced with ClO_4^- counterions. Further reduction of this polymer at 0.4 V peak involves the neutralization of polarons with loss of ClO_4^- and the resulting short linear species are dissolved. Hence, in order to obtain uniform, adherent and dark-blue deposit of oxidized P(SNSNO$_2$), potential was swept between 0.4 V and 0.98 V.

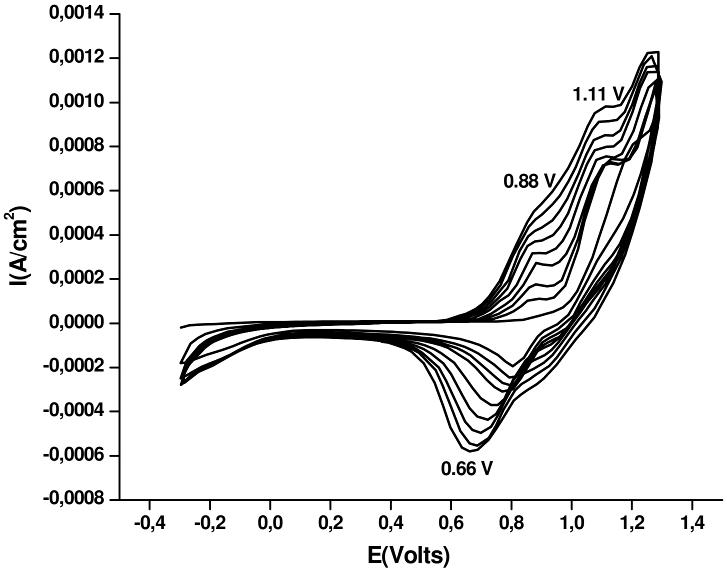


Figure 3-7. Cyclic voltammogram of SNSNO$_2$

As for the copolymer, EDOT was used as the comonomer. EDOT is a popular choice as a substituted monomer since it produces a low band gap polymer with high stability and good conductivity [76]. EDOT can give rise to noncovalent intramolecular interactions with adjacent thiophenic units and thus induce self-rigidification of the π-conjugated system in which it is incorporated [77–79].

CV of copolymer (Fig 3-8b) does not have a single oxidation potential instead, there is a range between -0.3 V and 1.13 V due to the oxidation of both EDOT and $SNSNO_2$. The reduction peak at 0.1 V is very different from those of both PEDOT and $P(SNSNO_2)$. This indicates that the peak is due to the reduction of copolymer. The other reduction peak at -0.70 V signals the reduction of the PEDOT part of the copolymer. (Fig 3-8.a)

The redox behavior and the increments between concentric cycles of $SNSNO_2$ in the presence of EDOT were completely different than that of $P(SNSNO_2)$ and PEDOT at 500 mV/s scan rate. This is an indication of formation of a copolymer between $SNSNO_2$ and EDOT.

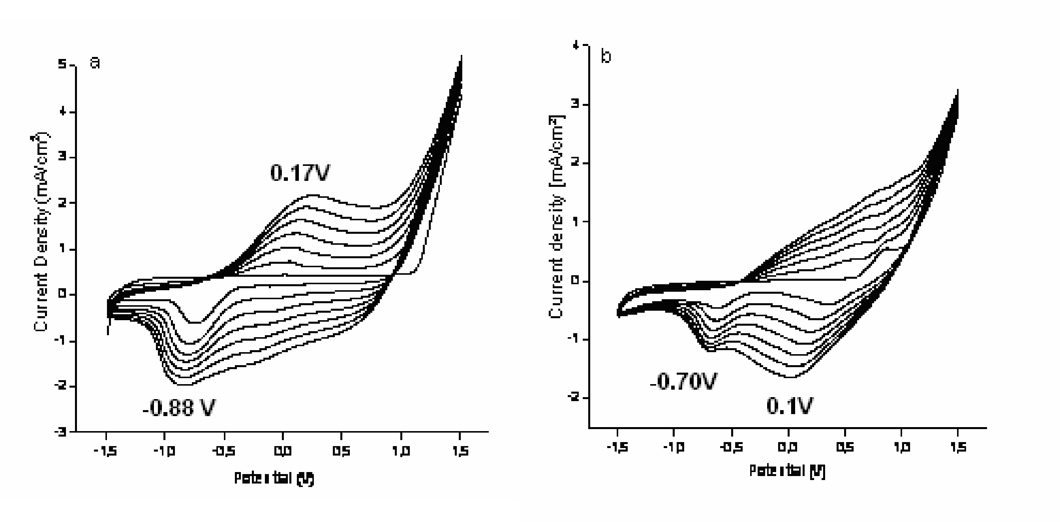


Figure 3-8. Cyclic Voltammograms of (a) pure EDOT, (b) $SNSNO_2$ in the presence of EDOT, $P(SNSNO_2\text{-co-EDOT})$.

3.4. Conductivities

Four probe technique was employed to measure the conductivities of electrochemically and chemically prepared $SNSNO_2$. Table 3.1 shows the conductivity results. It is observed that the conductivity increased 1 order of magnitude upon copolymerization due to increase in conjugation through $SNSNO_2$ and EDOT.

The difference between the conductivities of chemical and electrochemical polymers is due to the different dopant anions on the polymer chains. The chemical polymer has both Cl^- and $FeCl_4^-$; thus shows lower conductivity; whereas the electrochemical polymer has only ClO_4^- dopant.

Table 3-1. Conductivities of $P(SNSNO_2)$ and $P(SNSNO_2$-co-EDOT)

Sample	**Conductivity ($S.cm^{-1}$)**	
	Chemical polymer	**Electrochemical Polymer**
$P(SNSNO_2)$	$4.0x10^{-5}$	$6.0x10^{-4}$
$P(SNSNO_2$-co-EDOT)	$2.5x10^{-3}$	
PEDOT	$1.0\ x10^{-2}$	

3.5. Morphologies of Films

SEM imaging is a good way of obtaining surface morphologies of conducting polymers. SEM micrographs of $P(SNSNO_2)$, $P(SNSNO_2$-co-EDOT) and PEDOT show the excellence of film forming ability of the polymers. All polymers exhibited homogeneous and compact structure. Wrinkled structures were observed on the solution side of P(SNSNO$_2$) film (Fig. 3.9 a); while solution side of P(SNSNO$_2$-co-EDOT) (Fig. 3.9 c) indicated spongelike structures and PEDOT revealed globules.

When SEM micrograph of copolymer (Fig. 3.9 c) is compared to those of PEDOT and P(SNSNO$_2$), very different morphologies can be seen, implying copolymerization reaction has occurred.

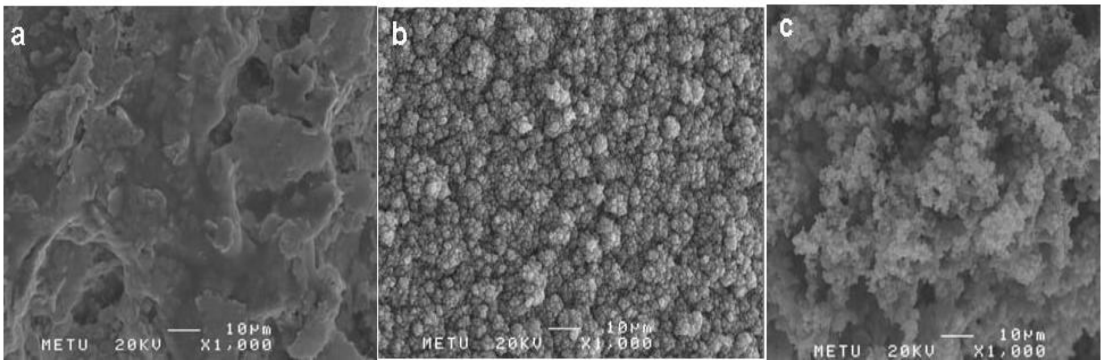


Figure 3-9. SEM micrographs of (a) solution side of P(SNSNO$_2$) (b) solution side of PEDOT (c) solution side of P(SNSNO$_2$-co-EDOT)

3.6. Gel Permeation Chromatography (GPC)

GPC is the best and exact way of measuring molecular weights of polymers. The weight average and number average molecular weight of chemically synthesized P(SNSNO$_2$) were determined by GPC in THF solution. The polydispersity (M_w/M_n) of P(SNSNO$_2$) was found as 1.20. The number of repeating unit was determined as 18. The results of GPC studies are given in the following Table 3-2.

Table 3-2. GPC Results

	Chemical polymer
M_o	352 g/mol
M_n	$6.6x10^3$ g/mol
M_w	$7.9x10^3$ g/mol
PD	1.20

3.7. Inspection of Electrochromic Properties of Polymers

3.7.1. Spectroelectrochemistry

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques that can be operated simultaneously. It provides information on both electrochemical response and accompanying optical characteristics of all states of the electrochemical reaction. It also provides information on the properties of conjugated polymers, such as band gap (E_g) and the intergap states that appear upon doping. P($SNSNO_2$) film was potentiodynamically synthesized on ITO electrode in the presence of 0.01 M $SNSNO_2$, sweeping the potential between 0.40 V and 0.98 V with 500 mV/sec scan rate using ACN/ $NaClO_4$/$LiClO_4$ (0.1 M) solvent-electrolyte couple.

The spectroelectrochemical and electrochromic properties of the resultant homopolymer were studied by applying potentials ranging between +0.2 V and +1.0 V in monomer free ACN/$NaClO_4$/$LiClO_4$ (0.1 M) medium. At the neutral state λ_{max} value due to the π-π^* transition of the homopolymer was found to be 400 nm and E_g was calculated as 2.15 eV. Upon applied voltage, reduction in the intensity of the π-π^* transitions and formation of charge carrier bands were observed. Thus, appearance of peaks around 635 nm and 860 nm could be attributed to the evolution of polaron and bipolaron bands respectively (Fig 3.10).

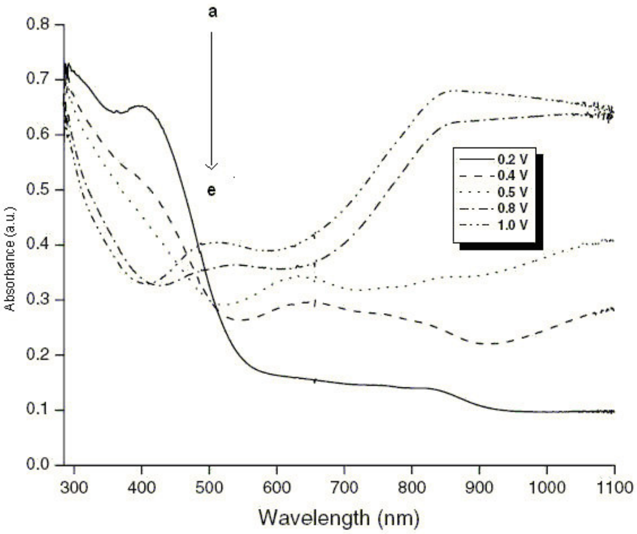


Figure 3-10. 2D Spectroelectrochemical spectrum of P(SNSNO$_2$) with applied potentials between 0.2 V and 1.0 V in ACN/NaClO$_4$/LiClO$_4$ (0.1 M), a) 0.2 V, (b) 0.4 V, (c) 0.5 V, (d) 0.8 V, (e) 1.0 V.

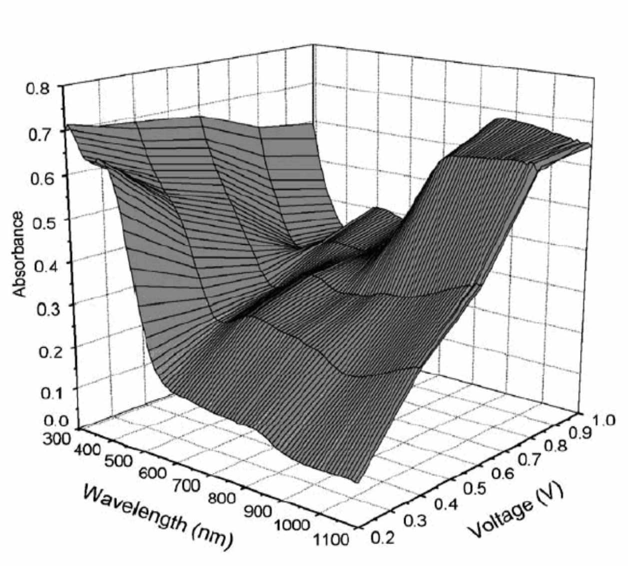


Figure 3-11. 3D Spectroelectrochemical spectrum of P($SNSNO_2$) with applied potentials between 0.2V and 1.0 V in ACN/$NaClO_4$/$LiClO_4$ (0.1M)

P($SNSNO_2$-co-EDOT) film was potentiostatically synthesized at 1.3 V on ITO electrode. Electrolysis solution was composed of 50 mg $SNSNO_2$, 2 μL EDOT and ACN/$LiClO_4$/$NaClO_4$(0.1M). The spectroelectrochemical and electrochromic properties of the resultant copolymer were studied by applying potentials ranging between -0.6 V and +1.0 V in monomer free ACN/$LiClO_4$/$NaClO_4$ (0.1 M) medium. At the neutral state λ_{max} value due to the π-π* transition of the copolymer was found to be 544 nm and Eg was calculated as 1.7 eV. Upon applied voltage, reduction in the intensity of the π-π* transitions and formation of charge carrier bands were observed. Thus, appearance of peaks around 815 nm and >1040 nm could be attributed to the evolution of polaron and bipolaron bands respectively (Fig3.12).

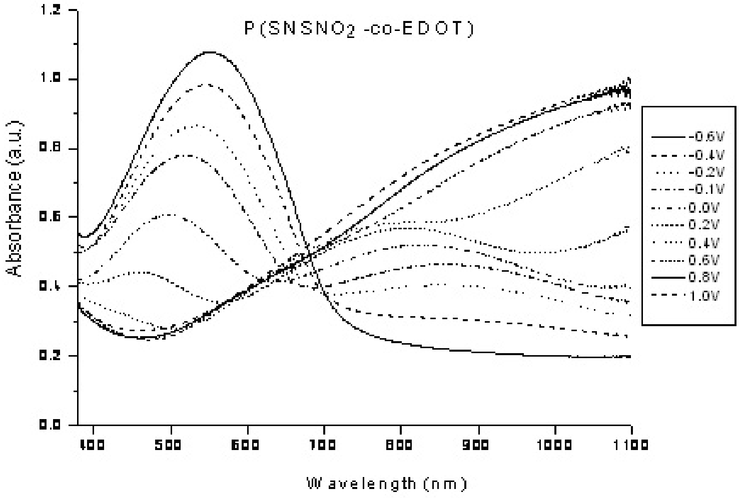


Figure 3-12. 2D Spectroelectrochemical spectrum of P(SNSNO$_2$-co-EDOT) with applied potentials between -0.6 and +1.0 V in in ACN/NaClO$_4$/LiClO$_4$ (0.1 M), a) -0.6 V, (b) -0.4 V, (c) -0.2 V, (d) -0.1 V, (e) 0.0 V (f) 0.2V (g)+0.4V (h) +0.6V (i) +0.8V (j)1.0 V

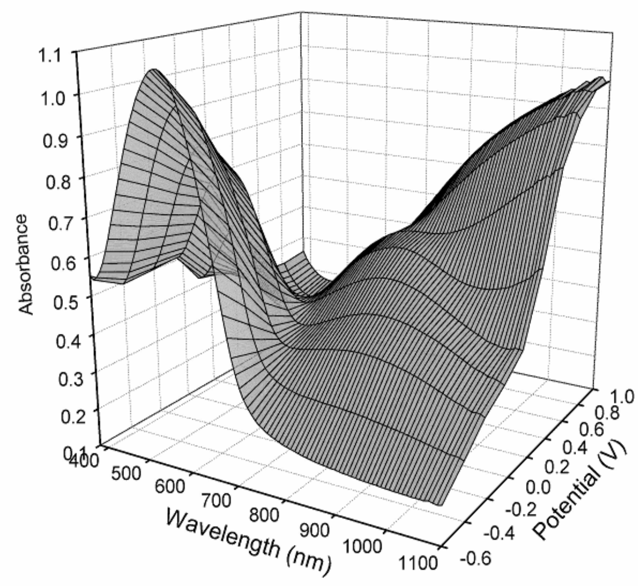


Figure 3-13. 3D Spectroelectrochemical spectrum of P(SNSNO$_2$-co-EDOT) with applied potentials between -0.6 and +1.0 V in ACN/NaClO$_4$/LiClO$_4$ (0.1M)

Table 3.3 is a good summary of comparison of the homopolymer, copolymer and PEDOT. λ_{max} value of the copolymer is between those of the PEDOT and the homopolymer. As seen from the table, introduction of EDOT to the polymer chain leaded to a noteworthy decrease in the band gap. These numerical values also support the copolymerization phenomena.

Table 3-3. Comparison of homopolymer, copolymer and PEDOT in terms of Eg and λ_{max} values

	Homopolymer	Copolymer	PEDOT
λ_{max}	400 nm	544 nm	600 nm
Eg	2.15 eV	1.7 eV	1.6 eV

3.7.2. Electrochromic Switching

For electrochromic applications, the ability of a polymer to switch rapidly and exhibit a striking color change is important. Electrochromic switching studies can monitor these types of properties. A square wave potential step method (Fig 3-14) coupled with optical spectroscopy known as chronoabsorptometry was used to probe switching times and contrast in these polymers. In this double potential step experiment, the potential was set at an initial potential for a set period of time, and was stepped to a second potential for a set period of time, before being switched back to the initial potential again.

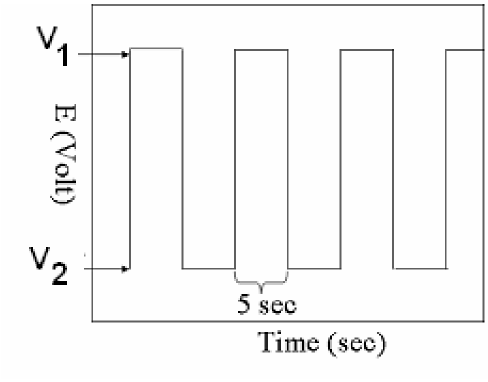


Figure 3-14. Square wave potential step method

The experiments carried out by spectroelectrochemistry showed the ability of P(SNSNO$_2$) to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. During the experiment, the % transmittance (%T) at 400 and 860 nm of the polymer was measured using a UV-Vis spectrophotometer. The polymer film was synthesized on ITO-coated glass slides.

The %T was then monitored at λ_{max} while the polymer was switched from +0.2 V to +1.0 V. The contrast was measured as the difference between %T in the reduced and oxidized forms and noted as 13 and 23 %T for 400 and 860nm respectively. As seen in Figure 3.15, homopolymer has reasonable stability and switching time (2 sec.).

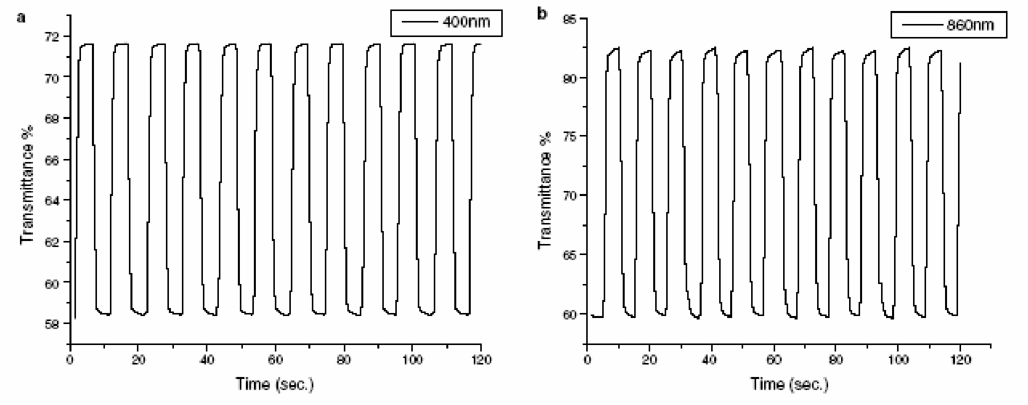


Figure 3-15. Electrochromic switching, optical absorbance change monitored at (a)400 nm and (b)800 nm for P(SNSNO$_2$) between 0.0 V and 1.0 V

Experiments for P(SNSNO$_2$-co-EDOT) were carried out at 544 nm while switching the potential between -0.6 V and +1.0 V with a residence time of 5 seconds. The contrast was measured as the difference between %T in the reduced and oxidized forms and noted as 42 %T. As seen in Figure 3.16, copolymer has a reasonable stability and switching time of 1.2 sec.

The optical contrast of the homopolymer at its λ_{max} was 13 %. The copolymerization with EDOT increased the optical contrast from 13 % to 42 %.

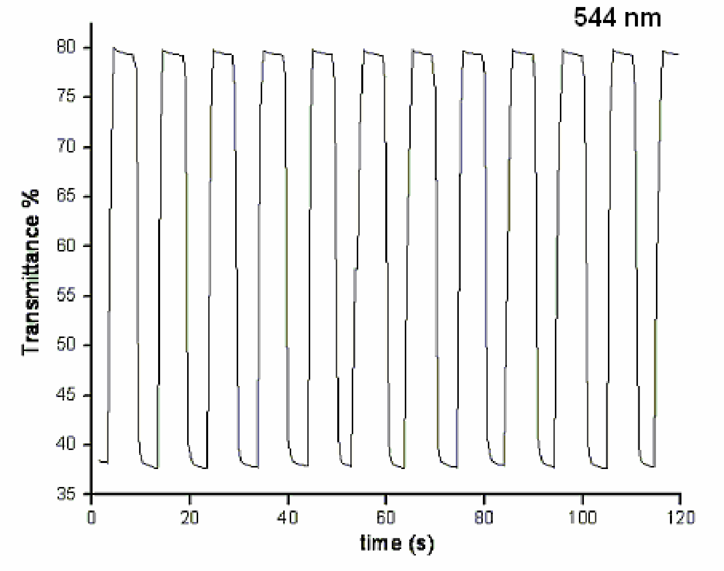


Figure 3-16. Electrochromic switching, optical absorbance change monitored at 550 nm for P(SNSNO$_2$-co-EDOT) between -0.6 V and 1.0 V

Table 3.4 is a comparison of homopolymer and copolymer in terms of switching time and optical contrast. Introduction of EDOT to the polymer chain led to a tremendous decrease in the switching time and an increase in the optical contrast

Table 3-4. Comparison table of homopolymer and copolymer in terms of Switching Time and Optical Contrast values

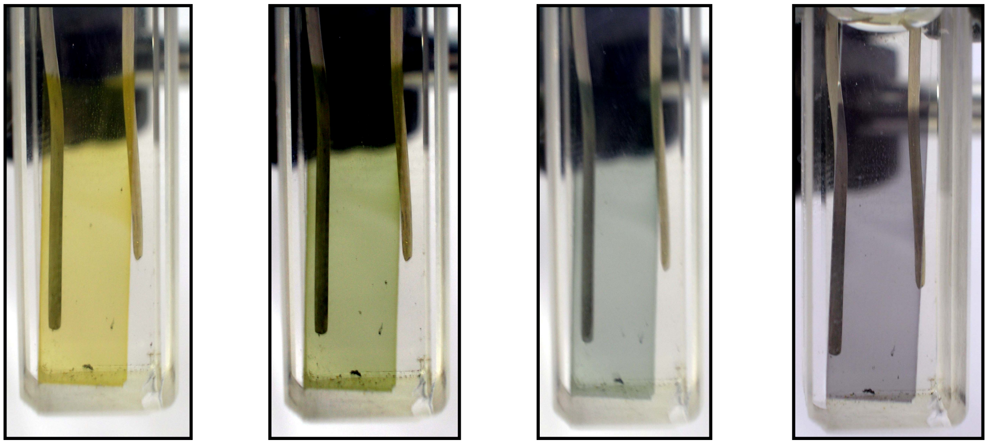
	Switching Time	**Optical Contrast**
Homopolymer	2 sec	13 %
Copolymer	1.2 sec	42 %

3.7.3. Colorimetry Studies

The colors of the electrochromic materials were defined accurately by performing colorimetry measurements. CIE system was used as a quantitative scale to define and compare colors. Three attributes of color; hue (a), saturation (b) and luminance (L) were measured and recorded. The P(SNSNO$_2$) film shows different colors in the fully reduced state (0.2V), half reduced state (0.4 V), half oxidized state (0.6 V) and fully oxidized state (1.0 V). They are given in Table 3.5.

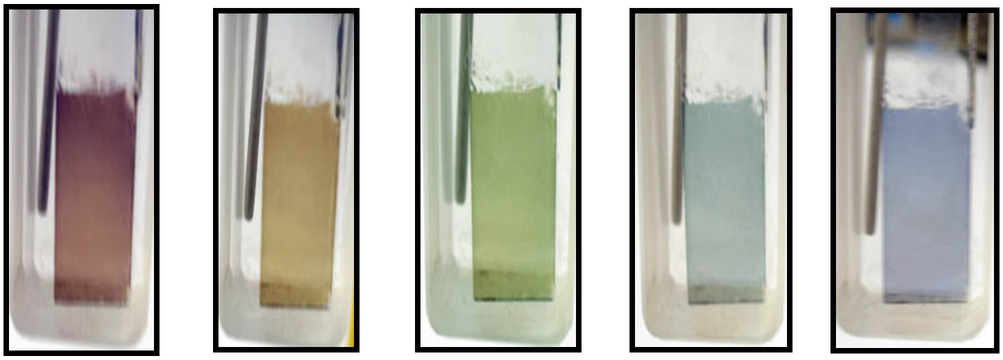
P(SNSNO$_2$-co-EDOT) film coated on ITO electrode exhibited five different colors. L a b values of the films were measured at the fully oxidized and the fully reduced states in addition to states in between and the results were collected in Table 3.6.

Table 3-5. Colors and corresponding L, a, b values of the P($SNSNO_2$) film at different applied potentials in ACN/$NaClO_4$/$LiClO_4$ (0.1 M)



0.2 V	**0.4V**	**0.6V**	**1.0V**
L:78	L:66	L:70	L:59
a:-5	a:-9	a:-3	a:11
b:39	b:26	b:3	b:-12

Table 3-6. Colors and corresponding L, a, b values of the P($SNSNO_2$-co-EDOT) film at different applied potentials in ACN/$NaClO_4$/$LiClO_4$ (0.1 M)



-0.6 V	**-0.1V**	**0.3V**	**0.6V**	**1.1V**
L:47	L:62	L:72	L:72	L:63
a:19	a:2	a:-14	a:-7	a:-1
b:12	b:29	b:36	b:-2	b:-26

3.8. Characterization of Electrochromic Devices

3.8.1. Spectroelectrochemistry

ECDs were constructed with the following configuration;

ITO/ P(SNSNO$_2$) | | gel electrolyte | | PEDOT/ITO

Their characteristics were investigated. For constructing the electrochromic device, the anodically coloring polymer film P(SNSNO$_2$) was fully reduced and the cathodically coloring polymer (PEDOT) was fully oxidized. Upon application of a voltage, one of the polymer films was oxidized, whereas the other was neutralized, resulting in a color change.

Spectroelectrochemistry experiments were performed to investigate the changes of the electronic transitions of the ECD, with the increase in applied potential. Figure 3-17 represents the absorption spectrum of the ECD, recorded by application of different voltages between -0.8 V and 1.6 V. At -0.8 V, the homopolymer layer was in its neutral state, where the absorption at 400 nm was due to π-π^* transition of the homopolymer. At this potential, PEDOT was in oxidized state showing no pronounced absorption at the UV-Vis region of the spectrum, thus the color of the device was yellow. As the applied potential was increased the homopolymer layer started to get oxidized, and a decrease in the intensity of the absorption was observed. Meanwhile, PEDOT layer was in its reduced state, which was followed by the appearance of the new absorption at 600 nm and dominated the color of the device was blue.

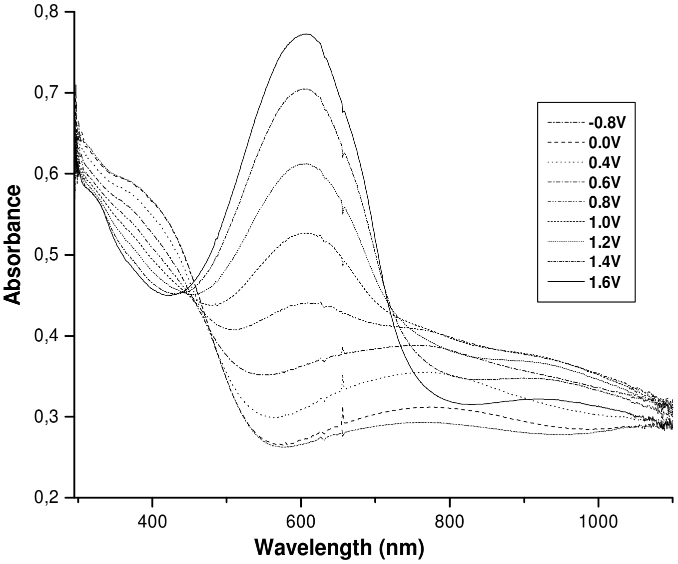


Figure 3-17. 2D Spectroelectrochemical spectrum of the P(SNSNO$_2$)/PEDOT ECD with applied potentials between -0.8 and +1.6 V

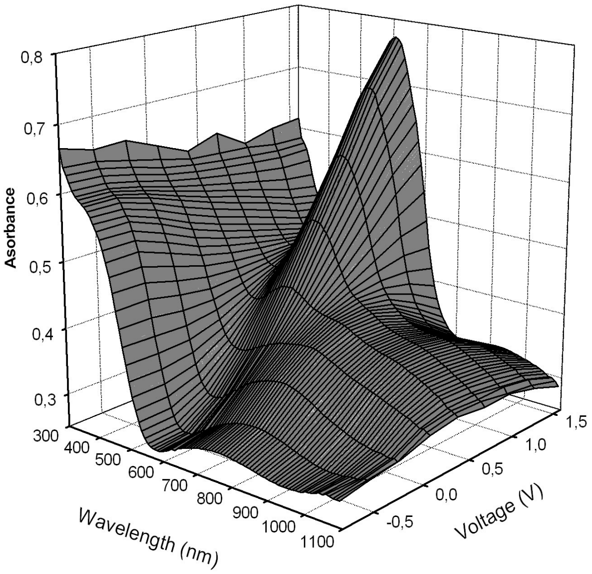


Figure 3-18. 3D Spectroelectrochemical spectrum of the P(SNSNO$_2$)/PEDOT ECD with applied potentials between -0.8 and +1.6 V

The same configuration was used to assemble ECD of the copolymer. The anodically coloring polymer film P($SNSNO_2$-co-EDOT) was fully reduced and the cathodically coloring polymer (PEDOT) was fully oxidized prior to construction of electrochromic devices (ECD). Optoelectrochemical spectra of the dual type ECD as a function of applied potential (from -2.0 V to 2.2 V) are given in Figure 3-19. Maximum absorption at 510 nm revealing reddish brown color was observed due to π-π^* transition upon application of positive voltages. At that state, PEDOT did not reveal an obvious absorption at the UV-Vis region of the spectrum and device revealed light brown color. At moderate potentials device have good transparency and colors of the device are green and grey at -0.7 V and 0.4 V respectively. When the applied potential decreased, due to reduction of PEDOT layer, blue color became dominant and a new absorption observed at 610 nm.

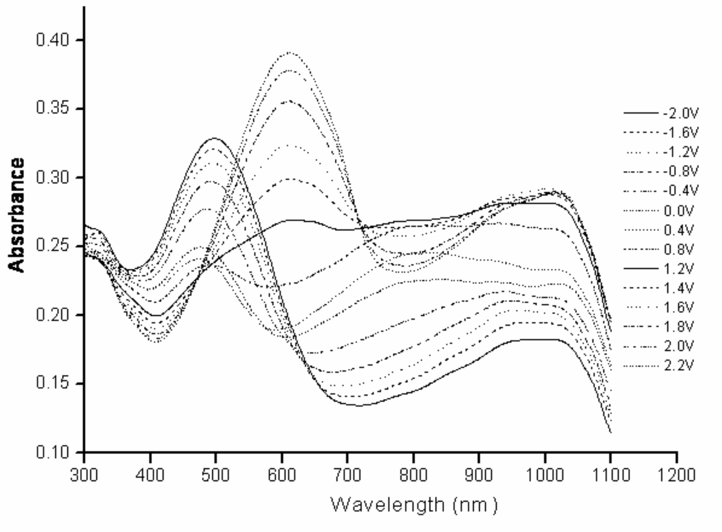


Figure 3-19. 2D Spectroelectrochemical spectrum of the P($SNSNO_2$-co-EDOT)/PEDOT ECD with applied potentials between -2.0 and +2.2 V

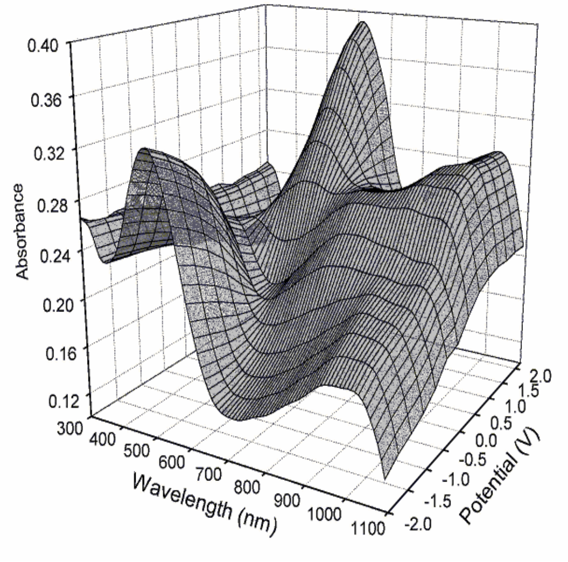


Figure 3-20. 3D Spectroelectrochemical spectrum of the device with applied potentials between -2.0 and +2.2 V

3.8.2. Colorimetry Studies of ECDs

L, a, b values of the ECDs were measured at the fully oxidized and the fully reduced states of devices and the results were recorded. The P(SNSNO$_2$)/PEDOT ECD was yellow at -0.8 V when the P(SNSNO$_2$) layer was in its reduced and PEDOT was in its oxidized state. Blue color was observed at 1.6 V when PEDOT was in its reduced state and P(SNSNO$_2$) layer in its oxidized state. At 0.5 V intermediate state was observed. L, a, b values of P(SNSNO$_2$)/PEDOT ECD are given in Table 3.7.A

The P(SNSNO$_2$-co-EDOT)/PEDOT ECD was light blue at -2.0 V when the P(SNSNO$_2$-co-EDOT) layer was in its oxidized and PEDOT was in its reduced state (blue). Reddish brown color was observed at 2.2 V when PEDOT was in its oxidized state (transparent) and P(SNSNO$_2$-co-EDOT) layer in its reduced state. At -0.7V and

0.4V intermediate states were observed. L, a, b values of P(SNSNO$_2$-co-EDOT) ECD are given in Table 3.7.B.

Table 3-7.

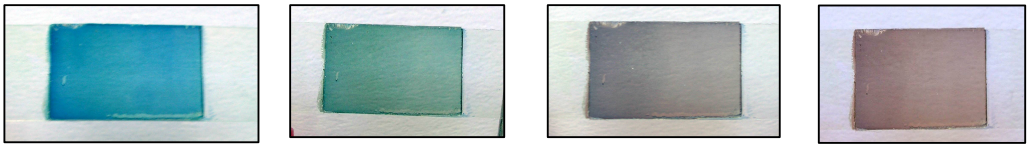
A. L, a, b Values of P(SNSNO$_2$)/PEDOT ECDs

B. L, a, b Values of P(SNSNO$_2$-co-EDOT)/PEDOT ECDs

A

-0.8 V	**0.5 V**	**1.6 V**
L:55	L:25	L: 39
a: 2	a: -2	a: -1
b:20	b:23	b:-16

B



-2.0 V	**-0.7 V**	**0.4 V**	**2.2 V**
L:51	L:68	L: 66	L:49
a:-21	a: -16	a: 0	a: 9
b:-28	b: 0	b: 3	b: 2

3.8.3. Switching of ECDs

The kinetics of color changes within devices were investigated performing fast in situ spectral scans while applying potential step in square wave form. This technique provides information about the kinetics of color-switching.

To investigate switching characteristics of the P(SNSNO$_2$)/PEDOT ECD, the transmission and the response time at the maximum contrast wavelength were monitored during repeated redox stepping experiments. For the device, maximum contrast (%T) at 600 nm was measured as 30 % by stepping potential between -0.8 V and + 1.6 V with a switching time of 5 s (Fig 3. 21).

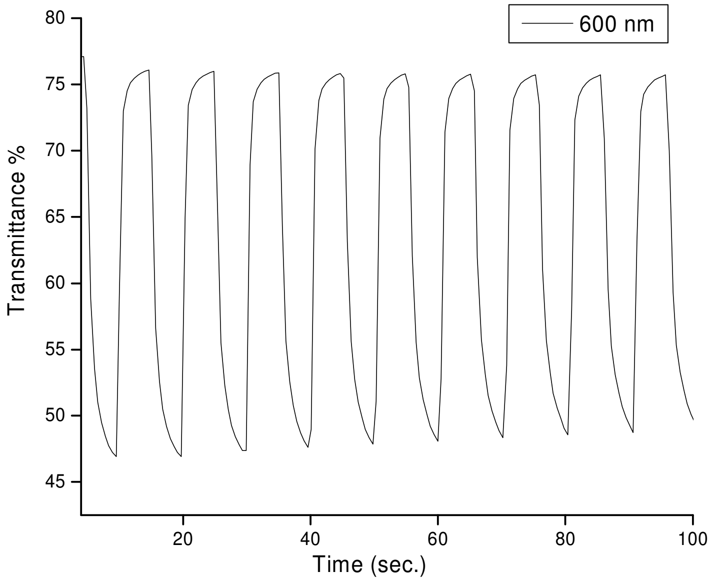


Figure 3-21. Electrochromic switching, optical absorbance change monitored at 600 nm for P(SNSNO$_2$)/PEDOT device between -0.8 and +1.6V .

Switching properties and optical contrast (ΔT %) of P(SNSNO$_2$-co-EDOT)/PEDOT device at the wavelength of maximum contrast (650 nm) were measured (Fig 3. 22). Switching square wave potentials between –2.0 and +2.2 V with a residence time of 5 s, the optical contrast (ΔT %) at 650 nm was found as 23% and it was calculated that the ECD switches rapidly in about 1.2 s to reach the total transmission change. The P(SNSNO$_2$-co-EDOT)/PEDOT showed a more steady graph when compared to that of P(SNSNO$_2$)/PEDOT.

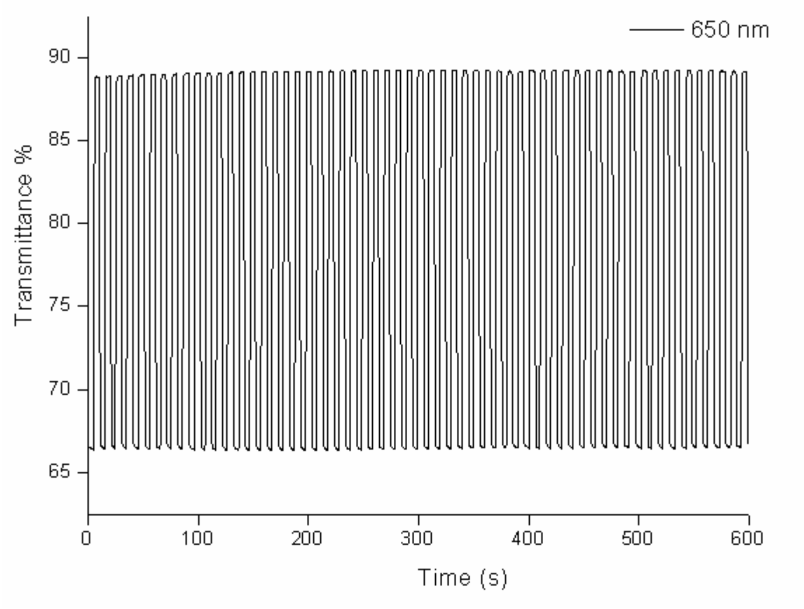


Figure 3-22. Electrochromic switching, optical absorbance change monitored at 650 nm for P(SNSNO$_2$-co-EDOT)/PEDOT device between -2.0 and +2.2 V .

3.8.4. Stability of the Electrochromic Device

Redox stability is a significant requirement for production of reliable electrochromic devices with long lifetimes. Main reasons for device failure are high applied voltages and environmental conditions. Cyclic voltammetry was employed by monitoring current alterations to visualize the long term stability of the P(SNSNO$_2$)/PEDOT ECD (Fig 3.23). The voltage was continuously swept between -0.8 V and 1.6 V with 500 mV/s scan rate. After 500 cycles, % 78 of initial electroactivity was almost maintained proving that ECD has reasonable environmental and redox stability.

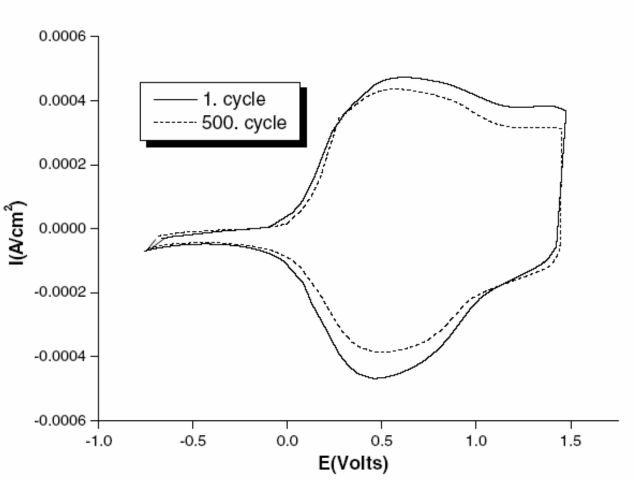


Figure 3-23. Cyclic voltammogram of the P(SNSNO$_2$)/PEDOT device as a function of repeated scans 500 mV/s after 1st cycle plain, after 500 cycles dash.

The stability measuments for P(SNSNO$_2$-co-EDOT)/PEDOT device were also carried out by cyclic voltammetry. The device was subjected to -2.0 V and +2.2 V with 500 mV/s scan rate under atmospheric conditions. The results (Fig. 3.24) show that P(SNSNO$_2$-co-EDOT/PEDOT ECD could be repeatedly switched up to 500 cycles retaining % 83 of its electroactivity.

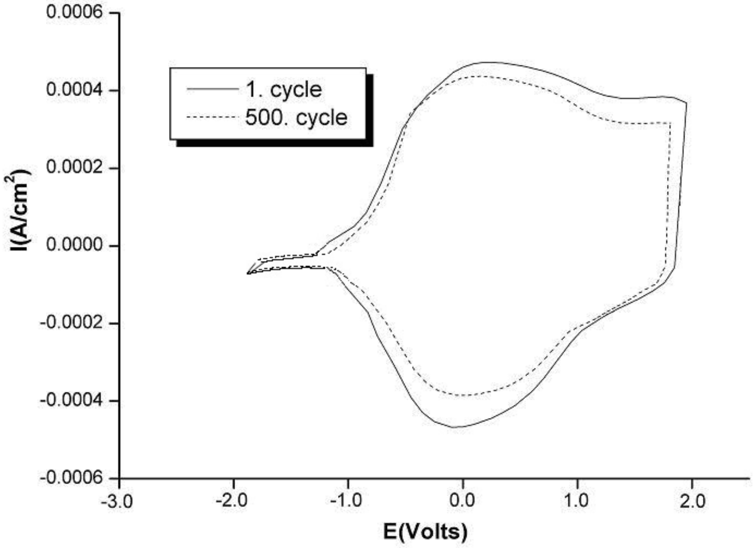


Figure 3-24. Cyclic voltammogram of the P(SNSNO$_2$-co-EDOT)/PEDOT device as a function of repeated scans 500 mV/s after 1st cycle plain, after 500 cycles dash.

CHAPTER IV

CONCLUSION

Synthesis of a novel full conjugated monomer, 1-(4-nitrophenyl)-2,5-di-2-thienyl-1H-pyrrole $SNSNO_2$ was successfully accomplished. Oxidative polymerization was achieved via both electrochemical and chemical methods.

Insolubility is the major limitation of conducting polymers. Synthesis of soluble conducting polymers enables direct application of these polymers to any substrate using conventional printing techniques. In this study, we synthesized a polymer which is completely soluble in common organic solvents. This work is a nice contribution to the area of soluble conducting polymers. Soluble $P(SNSNO_2)$ obtained by chemical polymerization method was characterized by ^{1}H-NMR and GPC. Conducting copolymer of $SNSNO_2$ with EDOT was synthesized electrochemically. Cyclic voltammetry studies revealed the electroactivity of $SNSNO_2$. The copolymer, $P(SNSNO_2$-co-EDOT) revealed different redox behavior than that of the monomer and EDOT. Copolymerization was also proved by FTIR, conductivity and SEM studies. The polymers were found to have reasonable conductivities.

The copolymer produced a stronger free standing film compared that of homopolymer. EDOT in the copolymer chain gave rise to noncovalent intramolecular interactions with adjacent thiophenic units and thus induced self-rigidification of the π-conjugated system.

Spectroelectrochemical analyses revealed that P(SNSNO$_2$) and P(SNSNO$_2$-co-EDOT) can be switched between their fully oxidized and fully reduced states with distinct color alterations. Spectroelectrochemistry experiments showed that π-π^* transition occurs at 400 nm with a band gap 2.15 eV for P(SNSNO$_2$). On the other hand λ_{max} for P(SNSNO$_2$-co-EDOT) was found as 544 nm and the band gap was calculated as 1.7 eV. We showed the effect of EDOT on Eg upon copolymerization. Electrochromic investigations showed that both P(SNSNO$_2$) and P(SNSNO$_2$-co-EDOT) were found to be multichromic materials.

Dual-type P(SNSNO$_2$)/PEDOT and P(SNSNO$_2$-co-EDOT)/PEDOT electrochromic devices were assembled with a configuration: ITO coated glass/anodically coloring polymer || gel electrolyte|| cathodically coloring polymer (PEDOT)/ITO coated glass. The color of P(SNSNO$_2$) device changed between yellow, green and blue upon applied potential, while color of P(SNSNO$_2$-co-EDOT) device can be changed between reddish brown, green, gray and blue. Spectroelectrochemistry, electrochromic switching and open circuit stability of the devices were studied. ECDs were found to have reasonable switching times and contrasts. Considering these results, P(SNSNO$_2$) and P(SNSNO$_2$-co-EDOT) are promising candidates for electrochromic layers in ECDs.

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