SELENOPHENE DERIVATIVES FOR ELECTROCHROMIC APPLICATIONS

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

SELENOPHENE DERIVATIVES FOR ELECTROCHROMIC APPLICATIONS

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A novel selenophene-based monomer; 1,4-di(selenophen-2-yl) benzene (DSB), synthesized via Stille coupling reaction of 1,4 dibromobenzene and tributyl (2-selenophenyl) stannane and corresponding conducting homopolymer (Poly (DSB)) was electrochemically synthesized in the presence of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) as the supporting electrolyte in dichloromethane. The resulting conducting polymer was characterized by Cyclic Voltammetry (CV), Fourier Transform Infra Red Spectrometry (FTIR) and Ultraviolet–Visible Spectrometry (UV-Vis Spectrometry). Spectroelectrochemistry analysis and kinetic studies of Poly (DSB) revealed π–π^* transition (λmax) at 340 nm with almost zero percent transmittance (ΔT%) concurrently with striking and rapid (0.6 s) absorbance change at near infrared region (1250 nm) with 35% percent transmittance, indicating that Poly (DSB) is a very suitable near infrared electrochromic material. Copolymer of selenophene with ethylenedioxythiophene (EDOT) was potentiostatically synthesized. Poly (selenophene-co-EDOT) was characterized by Cyclic Voltammetry, FTIR and UV-Vis Spectrometry. During spectroelectrochemistry studies, π–π^* transition (λmax) was observed at 555 nm with a switching time of 1.4 s and 39% transmittance. Polaron and bipolaron bands were observed at 851 nm and 1299 nm, respectively. Switching time at 1299 nm was 1.8 s with a percent transmittance of 72. Copolymer of DSB with EDOT (Poly (DSB-co-EDOT)) was synthesized and characterized. λmax, polaron and bipolaron bands were observed at 457 nm, 696 nm and 1251 nm, respectively. A rapid switching time (0.2 s) with 12% transmittance was observed at 696 nm. At the near infrared region (1251 nm), satisfactory percent transmittance (35%) and a moderate switching time (1.75 s) were observed.

Keywords: Conducting Polymer, Electrochromism, Electrochemical Polymerization

ÖZ

ELEKTROKROMİK UYGULAMALARDA KULLANILABİLİR SELENOFEN TÜREVLERİ

Aydemir, Kadir
Yüksek Lisans, Kimya Bölümü
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Yeni bir selenofen temelli monomer olan 1,4-di(selenofen-2-il) benzen (DSB), 1,4 dibromobenzen ve tributil (2- selenofenil)stannan'ın Stille birleştirme reaksiyonuyla sentezlenmiş ve Poly (DSB) elektrokimyasal polimerleştirmeyle tetrabütilamonyum hegzaflorofosfat(TBAPF$_6$) destek elektroliti ve diklorometan çözücüsü varlığında sentezlenmiştir. Oluşan iletken polimer Dönüşümlü Voltametre (CV), Fourier Dönüşüm Kızılötesi Spektroskopisi (FTIR) ve UV-Vis Spektroskopisi teknikleriyle karakterize edilmiştir. Poly (DSB) ile yapılan spektroelektrokimya ve kinetik çalışmaları π–π^* geçişini (λmax) 340 nm'de sıfıra yakın yüzde geçirgenlik farkı (ΔT%) ile tanımlamıştır. Yakın kızıl ötesi (1250 nm) absorplama değişimi ise %35 olarak bulunmuştur. Bu veriler homopolimerin yakın kızıl ötesi elektrokromik malzeme olarak kullanılmaya uygun olduğunu göstermektedir. Selenofen'in etilendioksitiyofen (EDOT) ile kopolimeri sentezlenmiştir. Kopolimer CV, FTIR and UV-VIS Spectroskopileriyle karakterize edilmiştir. Spektroelektrokimya çalışmalarında π–π^* *geçişi* (λmax) 555 nm'de, 1.4 s geçiş hızı ve %39 geçirgenlik farkı ile belirlenmiştir. Polaron ve bipolaron bantları ise sırasıyla 851 nm ve 1299 nm'de görülmüştür. 1299 nm'de dönüşüm hızı 1.8 s, geçirgenlik farkı ise %72 olarak saptanmıştır. DSB'nin EDOT ile kopolimeri (Poly (DSB-co-EDOT)) sentezlenmiş ve karakterize edilmiştir. λmax, polaron ve bipolaron bantları için sırasıyla 457 nm, 696 nm ve 1251 nm'de gözlenmiştir. 696 nm'de hızlı (0.2 s) bir dönüşüm gözlenmiştir. Bu dalga boyunda %12 geçirgenlik farkı tespit edilmiştir. Yakın kızıl ötesi bölgede (1251 nm), %35 geçirgenlik farkı ve 1.75 s'lik bir dönüşüm süresi gözlemlenmiştir.

Anahtar sözcükler: İletken Polimer, Elektrokromizm, Elektrokimyasal Polimerleştirme

TO MY BROTHER, BAHADIR AYDEMİR

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Words fail to express my eternal gratitude to my brother Bahadır AYDEMİR who always supported me throughout his life.

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LIST OF ABBREVIATIONS

DSB	1,4-di (selenophen-2-yl) benzene
Poly (DSB)	Poly (1,4-di(selenophen-2-yl) benzene)
EDOT	3,4-Ethylenedioxythiophene
Poly (DSB-co-EDOT)	Poly (1,4-di(selenophen-2-yl)benzene-co ethylenedioxythiophene)
Th	Thiophene
Py	Pyrrole
PEDOT	Poly (3,4-ethylenedioxythiophene)
ACN	Acetonitrile
PA	Polyaniline
PPP	Poly-p-phenylene
PPV	Poly-phenylene vinylene
PTFE	Poly-tetrafluoro ethylene (Teflon)
ACN	Acetonitrile
DCM	Dichloromethane
$TBAPF_6$	Tetrabutylammoniumhexafluorophosphate
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectrometer
CV	Cyclic Voltammetry
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

CHAPTER 1

INTRODUCTION

1.1. Conducting Polymers

Conducting polymers are organic materials that conduct electricity. They are also called “synthetic metals” due to their metal-like properties [1].

In 1977, three scientists, Alan MacDiarmid, Hideki Shirakawa and Alan Heeger increased the conductivity of pure polyacetylene by almost 10^{11} times by doping it with iodine [2]. They identified the main structure of conducting polymers as alternating single and double bonds between carbon atoms. Their experiments proved the need of “doping” the polymer through reducing it (giving electron to the polymer) or oxidizing (taking electrons from polymer) since without doping, conductivities of the polymers were very little due to the localization of the electrons on the backbone. They were the Chemistry Nobel Prize Laurates in 2000 due to their pioneering works on electrically conductive polymers. Many scientists from different academic backgrounds (chemistry, physics, material science, engineering) are interested in the field and still there is great interest in both academia and industry.

1.1.1. Historical Review of Conducting Polymers

In 1862, Letheby reported the first electrochemical synthesis of a conducting polymer. Anodic oxidation of aniline deposited a black polymer on electrode that is insoluble in common organic solvents and water [3]. In 1960s, a polymeric inorganic explosive, poly (sulfur nitride) $(SN)_{x,}$ stimulated the idea of using polymers as electrical conductors [4]. In 1970s, Heeger and MacDiarmid discovered 10^{11} S/cm increase in conductivity of polyacetylene by charge transfer oxidative doping with iodine [5]. However, low stability of doped polyacetylene against air and humidity was a limiting factor for applications. Attempts to produce stable polyacetylene decreased the conductivity [6]. New era of conducting polymers started with the synthesis of novel structures to improve polymer properties. Polyfuran [7], polypyrrole [8], poly (p-phenylene) [9], poly (p-phenylene vinylene) [10], polyfluorene [11], polyaniline [12], polythiophene [13] and polyselenophene [14] are some of these new materials (Figure 1.1).

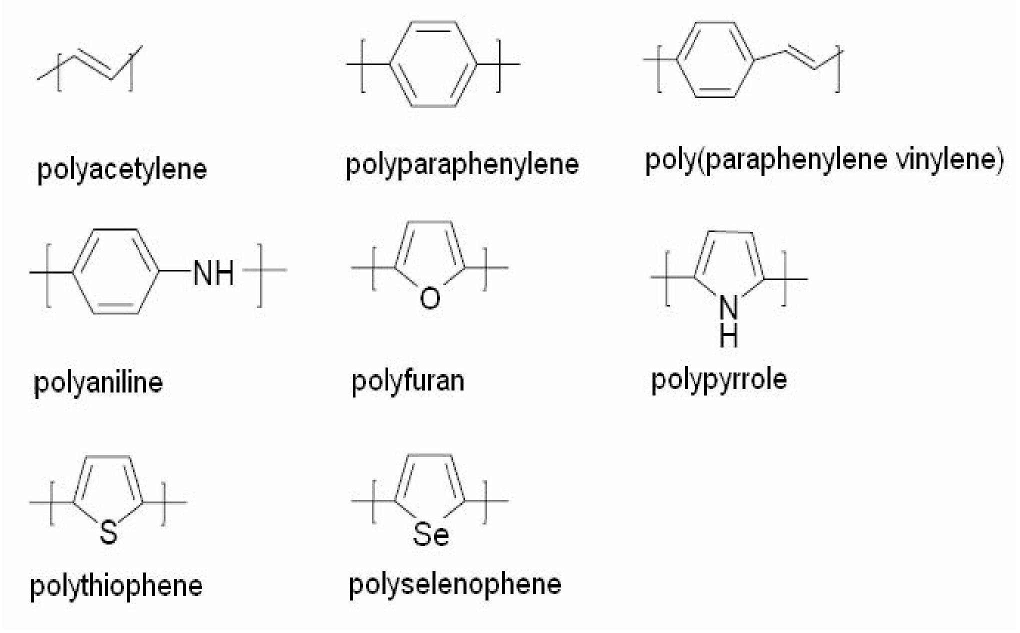


Figure 1.1 Some of the most common conducting polymers

Stabilities of these polymers are higher than polyacetylene and these polymers have structural versatility. Small modifications on backbones can improve physical and optical properties.

In 1979 oxidative electropolymerization of pyrrole yielded free standing films of polypyrrole with high conductivity (100S/cm) [15]. Although polypyrrole was stable against oxygen and water, its insolubility motivated scientists to move onto other heterocycles (thiophene, furan, pyrrole, carbazole and aniline).

Today, conducting polymers find various application areas due to their conductivity and electroactivity. More detailed discussion on the applications of conducting polymers can be found in Section 1.6.

1.1.2. Band Theory

Mobility of electrons through structure is a requirement for the electrical conductivity of a material. For this reason conducting polymers have both charge carriers and delocalized π orbital systems resulting from conjugation on their backbones. In most cases doping process adds charge carriers to the polymers and increases conductivity as in the case of doping polyacetylene with iodine.

Band theory explains the electronic structure and conduction mechanism of substances with the energy difference between unoccupied and occupied orbitals. Materials are classified as metals, semi-conductors and insulators according to these energy differences. In monomer structures, overlapping of neighbor atomic orbitals yield molecular orbitals. Energy levels of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) split with the combination of monomers. Insertion of more monomer units creates new energy levels and finally electronic structure of the polymer has two separated energy bands called conduction band (CB) and valence band (VB). Electrical properties of materials are determined by energy difference between conduction band and valence band namely, band gap (E_g) [16]. Band gap of insulators are greater than 3.0 eV. Typical band gap range for semiconductors is 0.5 to 3.0 eV and the range for metals is 0 to 0.5 eV. Insulators have very large band gaps which limits the conductivity to very low levels. High conductivity of metals is due to ease of movement of electrons through the material with the help of small band gap. Conductivity of a semiconductor is determined by the band gap and electron population distribution of each band. More electrons near the top of conduction band and the bottom of valence band increase conductivity. Band gap of linear π-conjugated systems is affected by chain length, bond length alternation, planarity, electron donor or acceptor substituents and the resonance stabilization energy of aromatic cycles [17]. UV-Vis spectroscopy can be used to estimate band gap of conducting polymers from the onset energy of π-π^* transition. Edge of the absorption band gives the energy required to promote an electron from valence band to the conduction band.

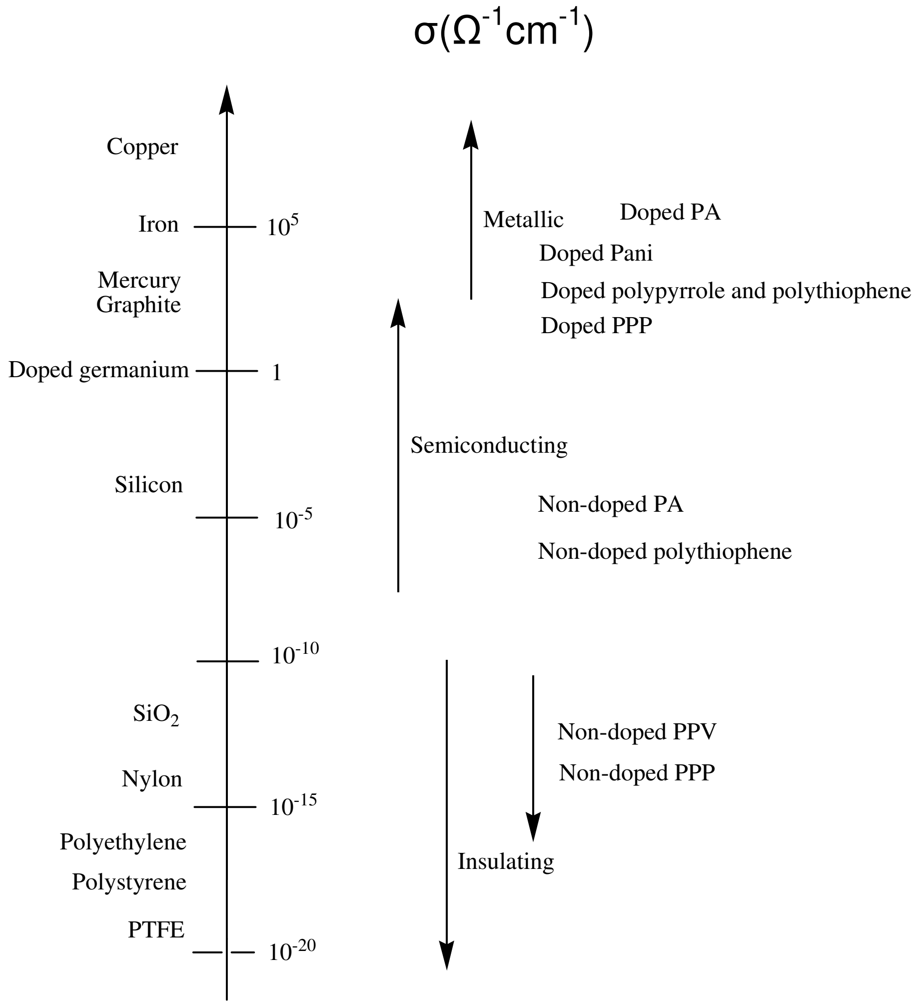
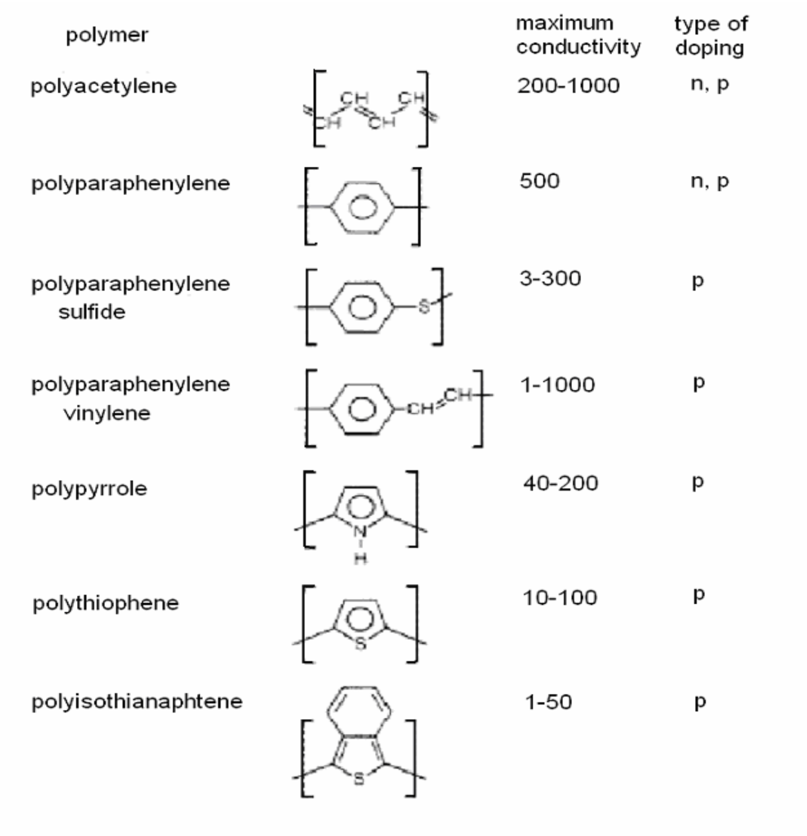


Figure 1.2 A comparison of the conductivities of some conjugated polymers with common materials [18]

1.2 Conduction Mechanism

1.2.1 Concept of Charge Carriers

Oxidation or reduction of a polymer creates defects on the structure such as radicals, cations and anions. Motion of these defects, namely charge carriers, forms the basis of the conduction mechanism on conducting polymers. P-type (positive) charge carriers are formed by oxidation of a conjugated polymer whereas reduction of the polymer yields n-type (negative) charge carriers. Mobility of the charge carriers and decrease in the band gap allow conjugated polymers act as semiconductors.



polymer		maximum conductivity	type of doping
polyacetylene		200-1000	n, p
polyparaphenylene		500	n, p
polyparaphenylene sulfide		3-300	p
polyparaphenylene vinylene		1-1000	p
polypyrrole		40-200	p
polythiophene		10-100	p
polyisothianaphtene		1-50	p

Figure 1.3 Conductivity and type of doping (n or p) for some important conjugated polymers [19]

Removal of an electron from the top of the valence band of a conjugated polymer forms a radical cation and addition of an electron to the conduction band results in a radical anion. Both structures are called polarons. Further removal or addition of electron leads to bipolaron states as given in Fig. 1.4. As the number of bipolarons increase in the polymer structure, new energy levels of the bipolaron states begin to overlap and form new energy bands near the valence band. Hence, conductivity increases due to the smaller band gap of the polymer.

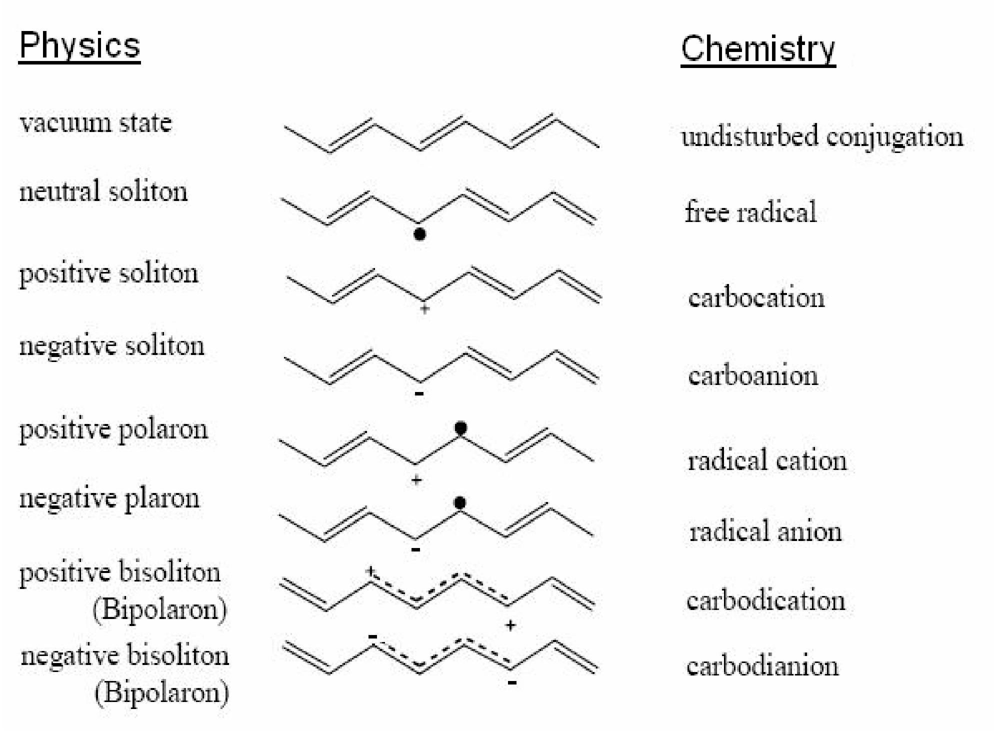


Figure 1.4 Structures and names of defects on a conjugated polymer [20]

1.2.2 Doping Process

Conductivities of conjugated polymers can be varied using a process called doping. Conductivity change can be of several orders of magnitude. A polymer can conduct electricity like a metal even if its undisturbed conjugation form is insulating. Doping process is defined as the formation of defects such as radicals, cations and anions (Fig 1.4.) on the polymer backbone. Chemical and electrochemical methods are used for doping the polymers. Oxidizing agents or reducing agents are used in chemical doping processes. Figure 1.5 illustrates doping and dedoping of well known polypyrrole.

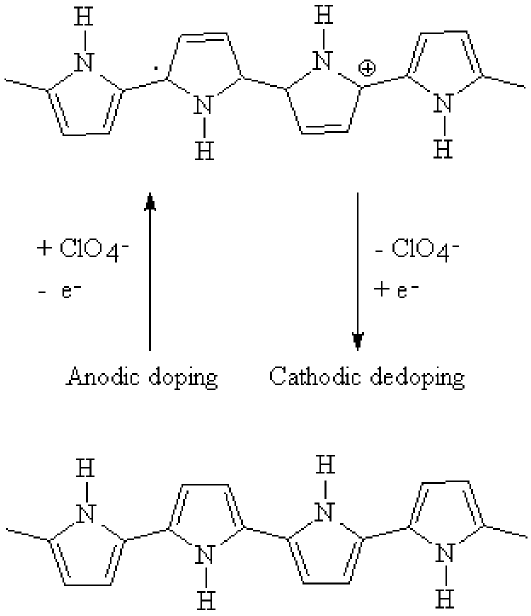


Figure 1.5 Doping and dedoping of polypyrrole using perchlorate as dopant.

Dopant counter ions such as perchlorate ion in polypyrrole are used for the stabilization of the p-doped form. There are two main ways for chemical doping. One of them is the use of gaseous agents such as I_2, AsF_3 and PF_3 and the second method is to react the polymer solution with $LiBH_4$ [21]. One major problem with chemical doping is the control of the degree of the doping process. Process results in either complete doping or in heterogeneous intermediate structures.

Electrodes take or give electrons to oxidize or reduce the polymer during electrochemical doping process. Moreover, counterions diffuse in and out of the polymer to maintain the electrical neutrality of the polymer. Electrochemical doping allows controlling level of doping through adjusting cell voltage at electrochemical equilibrium [22]. Doping level of conjugated polymers affect the conductivity of the polymers hence, different levels of conductivity can be achieved by adjusting the applied potential.

1.2.3 Hopping Process

Conductivity mechanism of conjugated polymers depends mainly on the mobility of the charge carriers. Doping process creates a great many of carriers, however their mobility determines the level of conductivity of the polymer [23]. There are three possibilities for the mobility of electrical charges on conducting polymers. Charges can move along the polymer backbone (intrachain movement), jump to neighbor polymers or variable range hopping can take place (interchain movement). Effective conjugation of the polymer determines the level of intrachain movement, while interchain movements are related to the stacking of the polymers. Temperature affects mechanism of variable range hopping in a manner which allows their characterization. Mott model states the conductivity as;

$$\sigma = \sigma_0 \exp [-(T_o/T)]^{\gamma} \qquad (1.1)$$

with T_0 is given by $T_0 = 1 / (k\xi N (E_F)$ where k is the Bolztmann's constant and $N (E_F)$ is the density of the states at the Fermi level, σ_0 is the conductivity at absolute zero (0 ^{0}K), T is the temperature and γ is a factor of the dimensionality (d) of the hopping process [24].

$$\gamma = 1/ (1 + d) \qquad (1.2)$$

Dimensionality of the hopping process of most polymers is 3-D, hence a linear log σ vs. $T^{-1/4}$ is an evidence of variable range hopping process [25].

1.3 Synthesis of Conducting Polymers

Chemical and electrochemical methods are widely used for synthesis of conducting polymers. Photochemical polymerization, plasma, pyrolysis, concentrated emulsion polymerization, inclusion polymerization, microwave initiation and solid state polymerization techniques are also used for these purposes [1].

1.3.1 Chemical Polymerization

Oxidative methods and catalytic Grignard reactions are used for the synthesis of conjugated polymers. Among these techniques, oxidative methods are the most used strategies due to their low cost and ease of application [26]. Polymers that are produced by oxidative chemicals such as $FeCl_3$ are in their doped and conducting state. These polymers are then treated with strong reducing agents such as ammonia or hydrazine to achieve neutral polymers. $FeCl_3$ is the most used oxidative reagent, some other transition metal chlorides are also used [27].

Chemical polymerization of unsubstituted heterocycles yield insoluble powders. However, substituted heterocycles could produce high quality polymer films. Oxidative chemical polymerization has the possibility of large scale applications with substituted heterocycles though in some cases poor-quality polymer films can be obtained. Lewis acids can limit the degree of polymerization because of the rigid character of oxidized polymers[28]. Moreover, oxidizing agents can cause overoxidation and decomposition of the polymers [29].

Catalytic Grignard reactions are generally used for the synthesis of thiophene-based polymers. For this purpose, 2,5 dibromothiophene derivatives are reacted with Mg in THF to produce corresponding -MgBr product. Addition of metal complex catalysts such as Ni(bipy)Cl_2 initiates self coupling reactions leading to polythiophene derivatives without unwanted $2,3'$ and $2,4'$ couplings [30]. Figure 1.6 illustrates chemical polymerizations of thiophene [31].

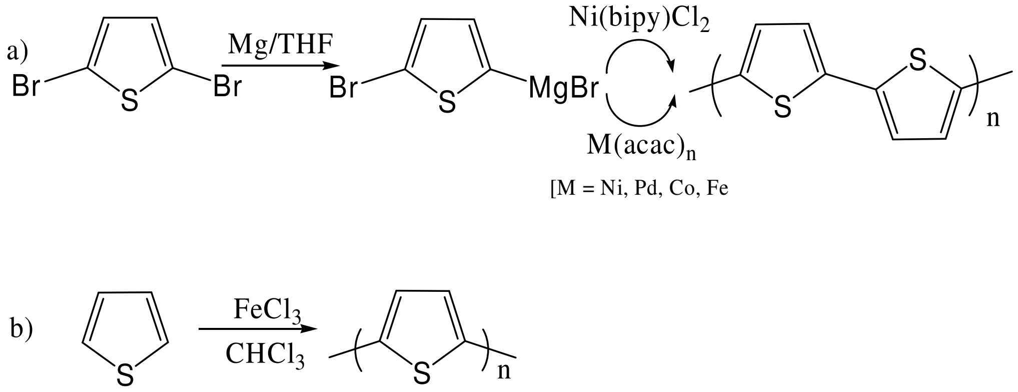


Figure 1.6 Synthesis of PTh via a) catalyzed Grignard reaction b) chemical oxidation

1.3.2 Electrochemical Polymerization

Electrochemical polymerization has several advantages over other techniques which make this approach a good choice for small scale synthesis and characterization of the polymers. These advantages are the following [32]:

i) Requirement of small amounts of monomer (typically 10 to 50 mg)
ii) Synthesis and characterization in relatively small time period
iii) In-situ analysis

iv) Ability to control film thickness, conductivity and morphology by varying applied potential, polymerization time and scan rate
v) Eliminating or decreasing side reactions by controlling applied potentials
vi) Simplicity of the technique
vii) In situ doping of the polymer as films form on electrode surface.

1.3.2.1 Mechanism of Electrochemical Polymerization

Electrochemical polymerization mechanism of heterocycles is shown in Figure 1.7 with pyrrole as a specific example [33]. The first step consists of formation of the radical cation of the monomer through oxidation. At this stage high concentrations of radicals are found near electrode surface due to the fact that diffusion of the monomer is much slower than electron transfer reaction. As a second step, two of these radical cations can couple and lose two protons to rearomatize the system yielding a neutral dimer. Since oxidation of dimer is easier than its monomer, applied potential generates radical cations of the dimers. Further couplings of the dimer radical with monomer radical extend chain and repetitive additions produce polymer. As a second probability, monomer radical can couple with the neutral monomer. Loss of two protons yields a neutral dimer. Radical cation of dimer formed by oxidation of the neutral dimer reacts with a neutral monomer to yield a trimer. Polymer is obtained with repetition of these mechanisms.

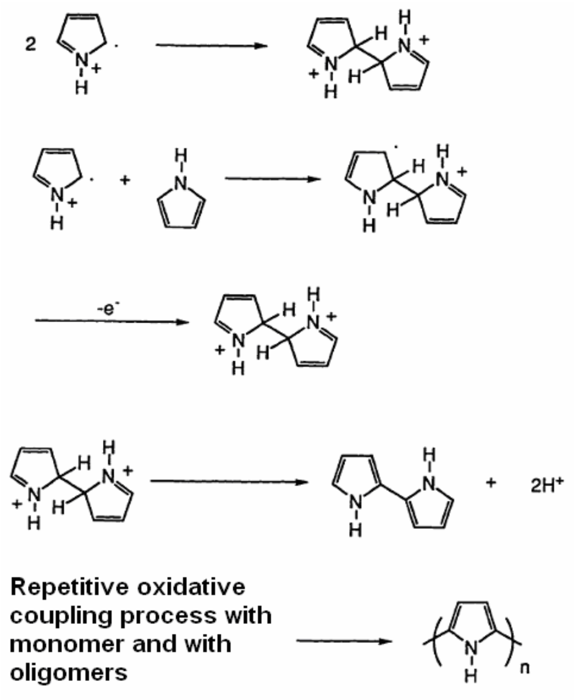


Figure 1.7 Electrochemical polymerization mechanism of pyrrole

1.3.2.2 Monomer Structure

Design of the monomer is one of the most important steps in conducting polymer research since structure of monomers determine conductivity, solubility, optical, electrochemical and mechanical properties of the polymers. Changes on the structure of the monomer such as addition of substituent groups can alter properties of the polymer.

Mechanical properties and processability are two big problems for most of the conducting polymers. Most of these polymers are insoluble in common solvents due to strong interchain forces. Hence, understanding of electronic interactions and characterization of these materials are difficult. Moreover, practical applications of insoluble polymers are limited [28]. Even tough thiophene and pyrrole received considerable attention due to their availability and low cost, both monomers can react from β positions which alter the conjugation. Figure 1.8 illustrates possible α – β couplings [34]. Such reactions decrease the conductivity of the polymer and increase band gap. One way to eliminate unwanted β couplings is to add substituents on 3 and 4 positions of the heterocycles. Nature of these substituents has a great influence on oxidation potential, band gap, mechanical and electronic properties of polymers. Electron donating substituents decrease the oxidation potential of polymers due to increased number of available electrons. Electron withdrawing groups increase oxidation potential by decreasing electron density on the polymer backbone [35]. Moreover, long alkyl or alkoxy chain substituents lead to soluble and processable polymers [36].

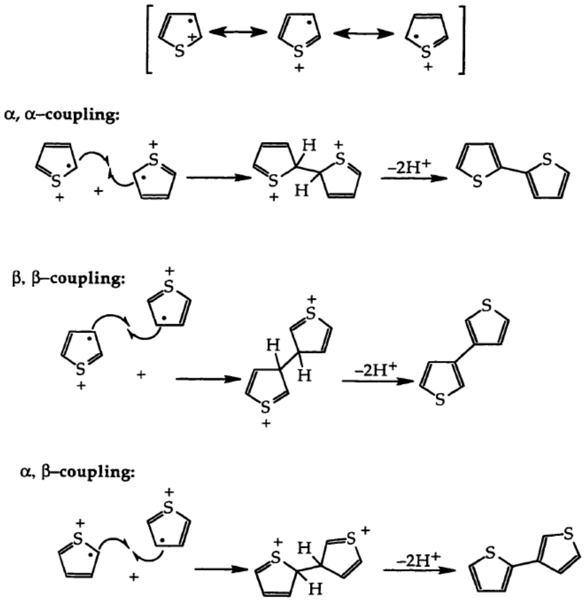


Figure 1.8 Possible α – β couplings during oxidative polymerization of thiophene

1.3.2.3 Effects of Electrolytic Media on Electrochemical Polymerization

Solvent, electrolyte, temperature and total amount of applied current are important parameters that can significantly affect the electrical properties and the morphology of the polymer.

For an appropriate polymerization media, solvent must have a high dielectric constant to dissociate supporting electrolyte. It should be stable enough at the applied potential range. Nitrile-based solvents have such properties; therefore they are the choice for most cases. Mechanism of oxidative electrochemical polymerization includes reactive radicals, thus, solvent should not have a nucleophilic character. Electrolytes should be electrochemically inactive and they should be non-nucleophilic. The electrolytes are also taking part in the doping of the polymers with the anion of the electrolyte. Tetraalkylammonium or lithium salts of perchlorates, hexafluorophosphates and tetrafluoroborates are generally preferred ones for the synthesis of conducting polymers [37]. The concentration of monomers is kept high (0.1M) in order to reduce side reactions of radical cations or oxidized polymer with nucleophiles in the media. When oxidation potential of monomer is low enough, number of side reactions decrease and millimolar concentrations of monomers can be used safely [38]. Electrochemical polymerizations are performed with inert electrodes such as gold, platinum, indium-thin-oxide (ITO) coated glass. Ag/Ag^+, Ag wire and saturated calomel electrode (SCE) can be used as reference electrodes.

1.4. Conducting Copolymers

Weaknesses in mechanical, physical and chemical properties of polymers can be eliminated through synthesis of block, graft and random copolymerization. Copolymerization process is basically integration of two or more different structures in a polymer chain. The usefulness of copolymerization technique is due to the different properties of the resulting materials than the corresponding homopolymers [39]. Concentration of monomer in the feed determines physical and chemical properties of copolymer. Hence, controlling concentrations of monomers can lead to copolymers with desired properties [40].

One widely used way to produce copolymers is to electropolymerize conducting material on an electrode that was previously coated with an insulating material. Another approach is to electropolymerize two electroactive monomers. 3,4-ethylenedioxythiophene (EDOT) is an ideal co-monomer for electrochromic applications thanks to its rapid switching time, stability, electron donor character and low oxidation potential of its polymer [41].

1.5. Characterization of Conducting Polymers

Highly conjugated structure in conducting polymers limits the solubility in common solvents. Thus, characterization of conducting polymers is harder than the conventional ones. Cyclic voltammetry is a powerful technique for understanding redox properties of conducting polymers. Structure confirmation, molecular motion and chain orientation of soluble polymers are examined by nuclear magnetic resonance. Molecular weight is determined via gel permeation chromatography (GPC). Differential scanning colorimeter and thermogravimetry analysis are used to determine glass, melting transitions and decomposition temperatures. Fourier transform infrared spectrometry (FTIR) is used to understand functional groups and doped ions in the polymer chain. X-ray photoelectron spectroscopy (XPS) can be used for structure analysis.

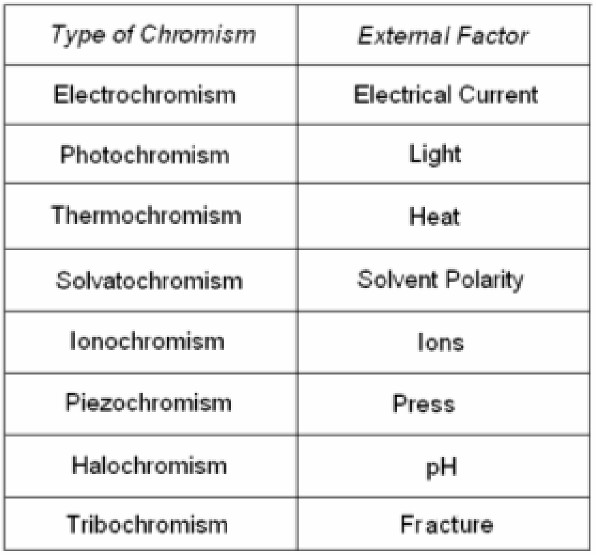
1.6. Applications of Conducting Polymers

Superior properties of conducting polymers such as high electrical conductivity, relatively low cost, flexibility, boundless diversity of the structures and properties explains the great efforts on conducting polymer application researches. A special application of conducting polymers uses neutral forms of these polymers. Field effect transistors [42] are one of such applications. Primary objective of these applications is to use semi-conducting and luminescent properties of conducting polymers. Another type of applications use doped or conducting forms of conducting polymers. Examples of such applications are electrode materials for capacitors and Electromagnetic Interference (EMI) shielding. A third type of application uses reversible changes such as color, conductivity, and volume in conducting polymers. Electrochromic devices (ECDs) [43], battery electrodes [44], sensors [45] are examples of such applications.

1.7. Chromism

Chromism is a reversible change in the color of a material. There are different types of chromism which are based on several factors of environment. Figure 1.9 illustrates common chromism types and related factors.

Table 1.1 Chromism types and related environmental factors



Type of Chromism	*External Factor*
Electrochromism	Electrical Current
Photochromism	Light
Thermochromism	Heat
Solvatochromism	Solvent Polarity
Ionochromism	Ions
Piezochromism	Press
Halochromism	pH
Tribochromism	Fracture

Chromism is based on energy change in π-π^* transition and conformational changes.

1.7.1 Electrochromism

Electrochromism is predominantly defined as the reversible optical change of a material observed upon alternation of the applied potential. Optical change can be between colors, or color(s) and a transparent state. Electrochromic materials that have more than two redox states can have several colors. Such materials are called as polyelectrochromic [46]. Metal complexes, metal oxides and conducting polymers are used as electrochromic materials. Conducting organic polymers are one of the leading options in the field of electrochromism due to their fast switching times, high optical contrasts and ease of processability [47-49].

Doping process causes structural changes on the polymer backbone. These changes decrease energies of electronic transitions compared with aromatic neutral forms. Electrochromism is based on such changes. Color changes are observed since most of the electronic transitions occur in the visible region. Doping and dedoping processes occur concurrently with a mass transport due to the motions of anions and cations in the polymer bulk. Color change kinetics are determined with the slower process [50].

1.7.1.1 Electrochromism in Near Infrared Region

Electrochromism is not only specific to visible region. Near-infrared (NIR), mid-infrared (mid-IR), ultraviolet (UV) and microwave active electrochromic materials are also available. Recent near-infrared active materials are transition metal complexes (such as WO_3), organic metal complexes (rutenium dendrimer) and organic polymers (selenophene and thiophene derivatives).

1.7.1.2 Applications of Near Infrared Active Electrochromic Materials

Recently near infrared active electrochromic materials found important applications in telecommunication windows where electro-optic switching in response to applied potential changes modulation of light transmission at near infrared region. Near infrared active devices, namely variable optical attenuators (VOA) have been employed to vary power [51, 52]. Moreover, near infrared active materials can be exploited for environmental control (decreasing heat loss) in buildings. Recently, there have been an interest in the near infrared electrochromic properties of transition metal oxides such as WO_3 and organic metal complex such as ruthenium dendrimer in the near infrared region [53-55]. Organic polymer based materials are also utilized as NIR active materials for electrochromic device applications [56, 57]

1.8 Spectroelectrochemistry

Spectroelectrochemistry is used to investigate electronic and optical structures of polymers and to monitor optical changes during electrochemical processes [58]. Polaron and bipolaron states can be examined using spectroelectrochemistry. Moreover, this method also allows calculation of the band gap.

1.9 Electrochromic Contrast and Switching Time

Electrochemical switching studies during repeated reduced and oxidized forms of polymers help to understand two important characteristics of electrochromic materials. Electrochromic contrast is the percent transmittance difference between the reduced and the oxidized states. Percent transmittance (ΔT %) is calculated at a specified wavelength where the polymers have the highest optical contrast [47].

Switching time is defined as the time required for the observation of optical changes for the reduced and oxidized forms of conducting polymers. Several factors such as morphology, accessibility of ions to electroactive sites and ionic conductivity of electrolytes affect switching time. Different ranges of switching times are necessary for applications. For instance, displays need very little switching times (milliseconds) and applications like office window coatings for heat control can tolerate up to several minutes.

1.10 Colorimetry

Electrochromic materials can possess different colors or tones of a color. Precise colors cannot be described with expressions. Hence, a color system is used for quantitative and objective reporting of colors. For this purpose, a device called colorimeter measures colors and gives a set of color coordinates. Color of a particular material can be located in CIE 1931 Lab color space (Figure 1.9).

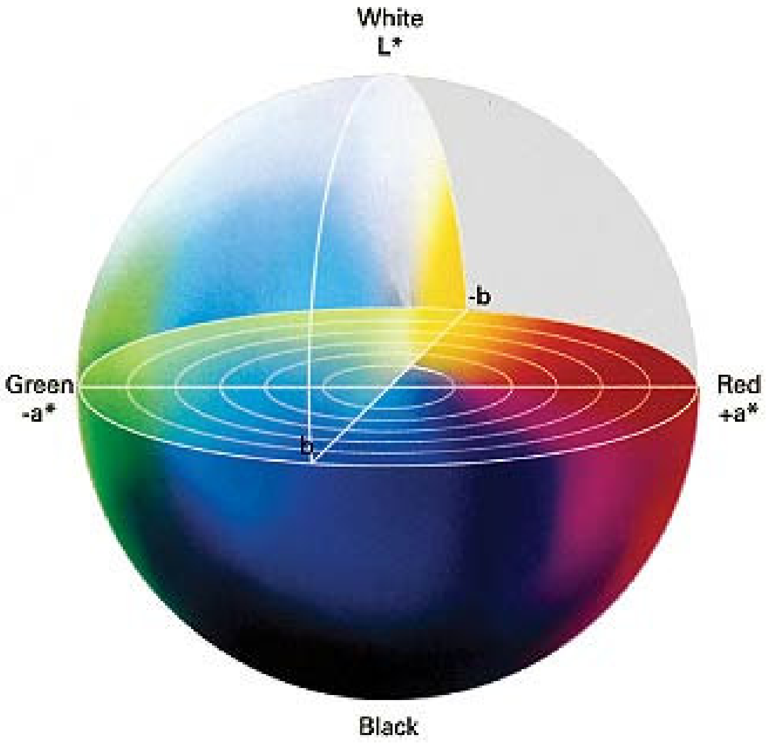


Figure 1.9 CIE LAB Color Space

In this color space, x, y and z-axis define hue (a), intensity (b) and luminance (L), respectively. These three values are obtained from colorimetry analysis. Hue is defined with “a” and corresponds to chromatic color or dominant wavelength, “b” refers to saturation (intensity of a color) and “L” corresponds to luminance or brightness. Yxy system is also used for reporting colors. This system is analogous to the Lab system. Y refers to luminance, x shows the redness of colors and y shows the amount of green in colors.

1.11 Aim of the Study

Aims of the studies were to get more information about selenophene derivatives and their electrochromic properties which are very limited in the literature, therefore, to synthesize a new selenophene derivative, 1,4-di(selenophen-2-yl)-benzene (DSB), electrochemically polymerize DSB monomer, electrochemically copolymerize selenophene and DSB with EDOT comonomer and to investigate electrochemical and electrochromic properties of homopolymers and copolymers.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

1,4 Dibromobutane (Aldrich), selenophene (Aldrich), tributyltin chloride (Aldrich), n-butyl lithium (Aldrich), dichlorobis (triphenyl phosphine)-palladium (II) (Aldrich), 3,4-ethylenedioxythiophene (EDOT) (Aldrich) were used as received. The electrolysis solvents; dichloromethane (DCM) (Merck) and acetonitrile (ACN) (Merck) were used without further purification. The supporting electrolyte $TBAPF_6$ (Aldrich) was used as received. Tetrahydrofuran (THF) (Merck) was distilled prior to use.

2.2 Equipment

2.2.1 Potentiostat

In the electrochemical polymerization, two potentiostats, A VoltaLab PST050 and a Solartron 1285, were used to apply the necessary potential. Potentiostats have the ability to keep the voltage difference between the working and reference electrodes at a constant desired value. This is especially important during the electrolysis in order to eliminate voltage drop in the electrolysis solution.

2.2.2 Electrolysis Cell

A one-compartment cell containing ITO coated glass working electrode, platinum wire counter electrode and a Ag wire pseudo-reference electrode was used during electrolysis.

2.2.3 Nuclear Magnetic Resonance (NMR)

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer at 400 MHz and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard.

2.2.4 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra of materials were recorded on Varian 1000 FTIR spectrometry, where samples were dispersed in KBr.

2.2.5 UV-VIS Spectrophotometer

Spectroelectrochemical and kinetic studies were carried out on Voltalab PST 50 potentiostat and Varian Cary 5000 UV–Vis-NIR spectrophotometer at a scan rate of 2000 nm/min.

2.2.6 Colorimetry Measurements

Colorimetry results were acquired by a Minolta CS-100A Chromameter with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

2.2.7 Mass Spectrometer

A 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system was used. The 70 eV EI mass spectra were recorded at a scan rate of 2 scans/s.

2.3 Procedure

2.3.1 Synthesis of Monomer

1,4-di (selenophene-2-yl)-benzene (DSB) monomer (2) was synthesized utilizing 1,4 dibromobenzene and tributyl (2-selenophenyl) stannane (1) via Stille coupling reaction as shown in Figure 2.1.

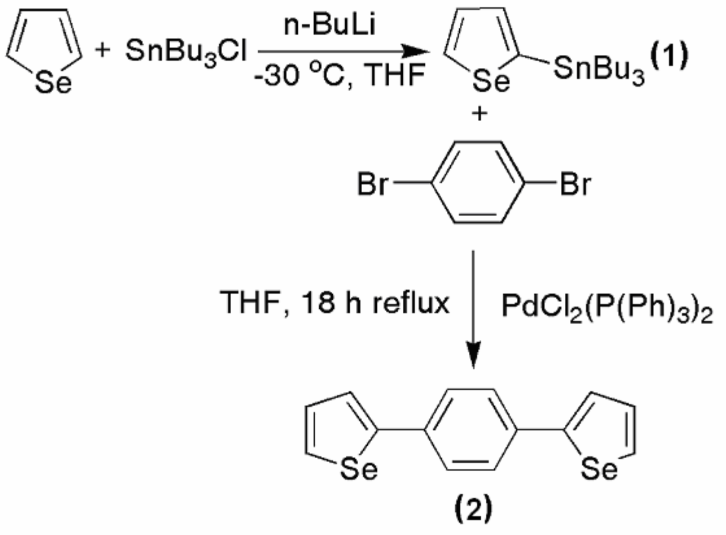


Figure 2.1 Synthetic route of 1,4-di (selenophene-2-yl)-benzene (DSB)

2.3.1.1 Synthesis of tributyl (2-selenophenyl)stannane (1)

Tributyl (2-selenophenyl) stannane was synthesized following the published procedures with some modifications [59, 60]. Selenophene (1 g, 7.64 mmol) was dissolved in anhydrous THF (10 ml) in argon atmosphere. Solution was cooled to -30 ^{0}C in ortho xylene – dry ice bath and subsequently n-butyllithium (1.76 ml of 2.0 M solution in hexane, 3.52 mmol) was added dropwise. Mixture was stirred at this temperature for 3.5 hours. Tributyltin chloride (1.3 g, 4 mmol) was added dropwise and stirred for another hour at this temperature. 20 ml of dichloromethane were added and the solution was extracted three times with saturated aqueous sodium carbonate. Organic phase was extracted two times with brine solution, dried over sodium sulfate and solvent was evaporated under vacuum. The residue was further purified by neutral alumina with petroleum ether as the eluent to yield colorless oil (0.72 g, 45%).

2.3.1.2 Synthesis of 1,4-di (selenophen-2-yl) benzene (2)

1,4 Dibromobenzene (236 mg, 1mmol), tributyl (2-selenophenyl) stannane (1.68 g, 4 mmol) and dichlorobis (triphenyl phosphine)-palladium (II) (50 mg, 0.045 mmol) were dissolved in anhydrous THF and refluxed for 18 hours under argon atmosphere. Solvent was evaporated under vacuum and the residue was purified by column chromatography (5:1 hexane: DCM as eluent) to yield yellow solid product (202 mg, 60%).

2.4 Synthesis of Conducting Polymers

2.4.1 Synthesis of Homopolymer of DSB

Poly (DSB) was achieved potentiodynamically in the potential range of -300 mV to 1300 mV at a scan rate of 100 mV/s in the presence of 50 mg of (2), $TBAPF_6$/DCM supporting electrolyte-solvent couple where indium tinoxide (ITO) coated glass was used as the working electrode. Poly (DSB) film was washed with DCM to remove unreacted monomer and excess $TBAPF_6$.

2.4.2 Synthesis of Copolymer of selenophene with 3,4-ethylenedioxy thiophene (EDOT)

The copolymer of EDOT with selenophene was synthesized via electrochemical oxidation on an ITO electrode using monomer mixtures with various feed ratios. Electrochemical polymerizations were carried out in a one compartment, three-electrode system in an ACN solution containing 0.1 M of $TBAPF_6$ as the supporting electrolyte via potentiostatic technique at 1.5 V potential applied for 1.5 minutes. Polymer films were washed with ACN in order to remove excess supporting electrolyte and unreacted monomers after the electrochemical polymerization.

2.4.3 Synthesis of Copolymer of DSB with 3,4-Ethylenedioxy thiophene (EDOT)

Copolymer of DSB (0.01 M) with 3,4-ethylenedioxythiophene (20 μL) was synthesized via potentiostatic polymerization with $TBAPF_6$ / DCM system at 1.3 V potential. Potential was applied for 1.5 minutes.

2.5 Characterization of Conducting Polymers

2.5.1 Cyclic Voltammetry (CV)

Cyclic Voltammetry is a powerful tool for investigation of reduction and oxidation processes. Hence, this technique is widely used for synthesis and characterizations of the conducting polymers. Cyclic voltammetry monitors current density as a function of applied potential which is linearly increased to a certain level and decreased to initial potential (Figure 2.2).

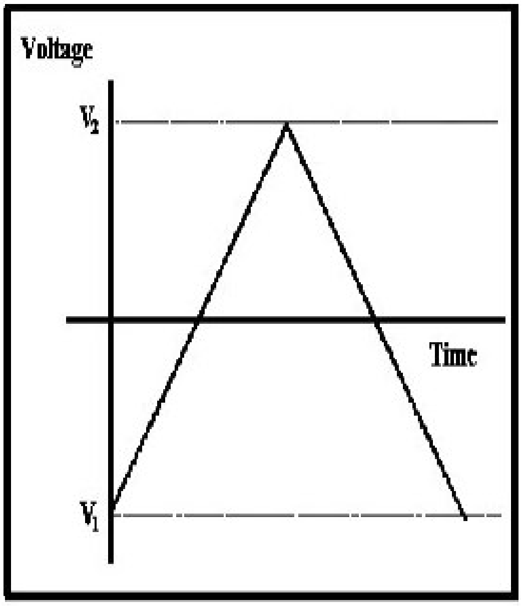


Figure 2.2 Triangular wave function

As the potential is increased, oxidation of the species near electrode surface is observed with the priority of more electron rich ones. A decrease on the potential reduces these oxidized materials. These two processes cause current response which is measured by CV. Figure 2.3 is a typical example of a reversible redox reaction in which oxidized material can be reduced to its original form through decreasing the potential.

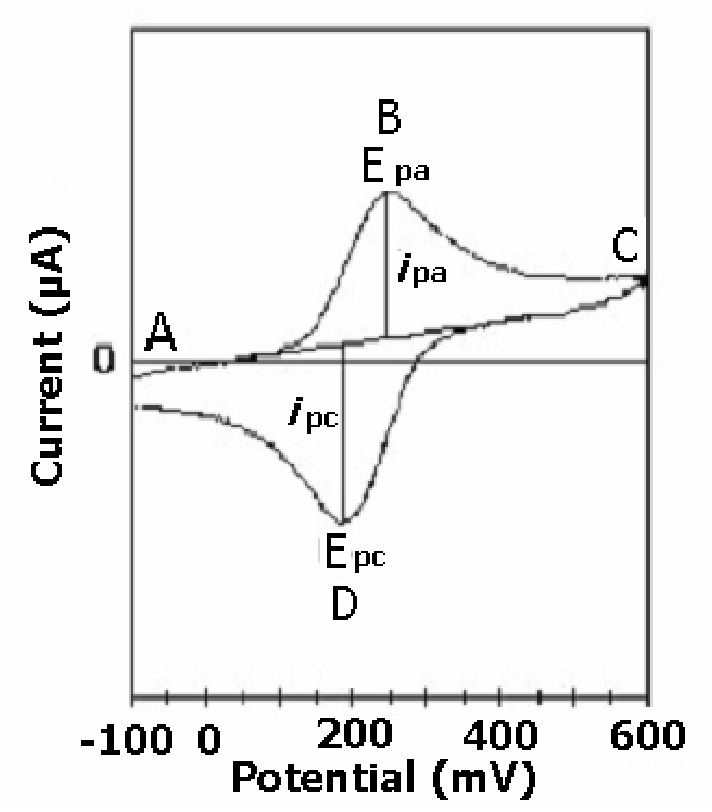


Figure 2.3 A cyclic voltammogram of a reversible redox reaction

Randles-Sevcik equation describes current as:

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}CV^{1/2} \qquad (2.1)$$

where n is the number of transferred electrons, A is the electrode surface area (cm^2), D is the diffusion constant (cm^2s^{-1}), C is the bulk concentration of the electroactive species (mol cm^{-3}) and V is the scan rate (V s^{-1}). Therefore, proportionality of the peak current to the square root of the scan rate is a good indication of a diffusion-controlled system.

Modified Randles-Sevcik equation describes current as:

$$ip = n^2 F 2\Gamma \nu /4RT \qquad (2.2)$$

where Γ is the concentration of surface bound electroactive centers (mol/cm^2) and F is Faradays constant (96,485 C/mol). In the systems that follow this equation, electroactive materials are adsorbed on the surface of the electrode, i.e. not diffusion-controlled. Therefore, a linear relation between current density and scan rate indicate non-diffusion controlled electroactivity.

A potentiostat, an XY recorder and a CV cell containing ITO coated glass working electrode, platinum wire counter electrode and a Ag wire pseudo-reference electrode are the components of a CV system. Potential was applied using a VoltaLab PST050 potentiostat.

2.5.2 Fourier Transform Infrared Spectrometry (FTIR)

FTIR spectra of the monomer, homopolymer and the copolymer samples were recorded on a Nicolet 510 FTIR spectrometer.

2.6 Electrochromic Properties of Conducting Polymers

2.6.1 Spectroelectrochemistry

Spectroelectrochemical analysis were performed to investigate the electronic structure of the polymers and to probe the optical changes on the materials as a result of reduction and oxidation of the polymer backbones.

Polymer films were potentiodynamically synthesized on indium tinoxide (ITO) coated glass slides with a sweeping potential between -0.3 and 1.3 V. Homopolymer synthesis was performed with 0.01 M solution of DSB monomer in $TBAPF_6$/DCM supporting electrolyte-solvent couple.

In situ spectroelectrochemical studies of copolymer films were performed with ITO coated glass slides that are previously coated with copolymer. The applied potential was switched between -0.3 V and +1.5 V using a square-wave potential step method coupled with optical spectroscopy.

Experimental setup of spectroelectrochemical analysis is shown in Figure 2.4. Previously polymer coated ITO-glass slides were used as working electrode where platinum wire and Ag wire were used as counter electrode and pseudo-reference electrode respectively. Potentiostat was used to apply potential with stepwise increase. UV-VIS spectra were obtained at each potential.

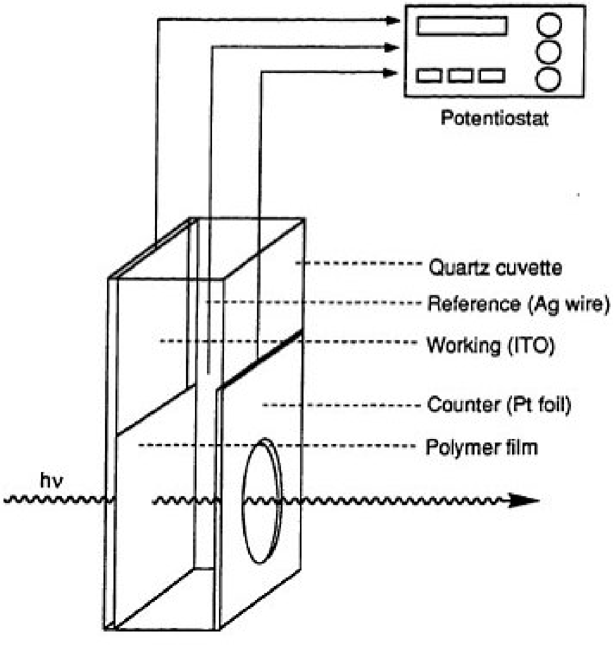


Figure 2.4 Spectroelectrochemical analysis experimental setup

2.6.2 Kinetic Studies

Kinetic studies provide valuable information about the capacity of electrochromic materials to perform for particular application. Long term absorbance changes, switching time and stability of a material can be determined through this method with the application of square wave potentials and monitoring the absorbance changes with optical spectroscopy (Figure 2.5). Percent transmittance difference (ΔT %) is used for reporting optical contrast. Switching time is reported as the time required to the change in absorption from maximum point to the lowest.

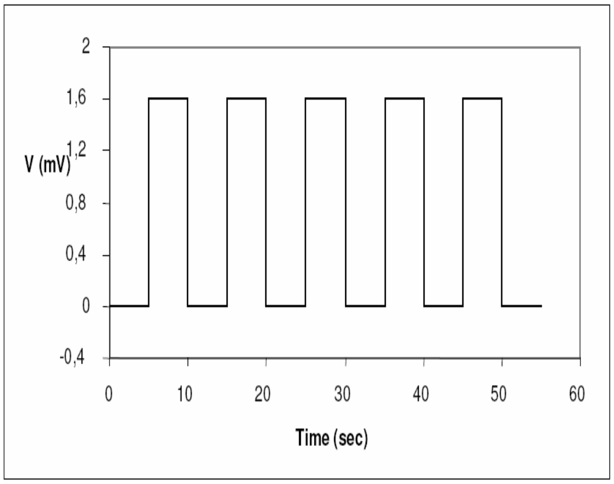


Figure 2.5 Square wave voltammetry

Kinetic studies for homopolymer and copolymers were performed with 5 second residence times at -0.3 and 1.5 V.

2.6.3.0 Colorimetry Studies

Colorimetry studies of the polymers were performed with their fully reduced and oxidized states. Colors of the homopolymer and copolymers were given in Y, x and y values.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization with ^{1}H-NMR and 13C-NMR Spectroscopy

^{1}H-NMR and ^{13}C-NMR spectra of the tributyl (2-selenophenyl)stannane (1) precursor and monomer were investigated with $CDCl_3$ as the solvent and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard.

Tributyl (2-selenophenyl)stannane is a colorless oil; ^{1}H-NMR spectrum (Fig. 3.1): $C_{16}H_{30}SeSn$, ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): δ 8.25 (d, 1 H) , 7.4 (m, 2 H) , 1.5 (m, 6 H) , 1.27 (m, 6H) , 1.02 (t, 6H), 0.81 (t, 9H).

^{13}C-NMR spectrum of tributyl (2-selenophenyl)stannane (Fig. 3.2): $C_{16}H_{30}SeSn$, ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): δ 11.19, 13.68, 27.32, 29.13, 130.55, 135.29, 137.81, 143.57.

Yellow powder; ^{1}H-NMR spectrum of monomer (Fig. 3.3): $C_{14}H_{10}Se_2$, ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25 (t, J = 3.9 Hz, 2 H, selenophene), 7.42 (d, J = 3.5 Hz, 2 H, selenophene), 7.48 (s, 4 H), δ 7.88 (d, J = 5.4 Hz, 2 H, selenophene).

^{13}C-NMR spectrum of the monomer $C_{14}H_{10}Se_2$, ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 125.29, 126.79, 129.70, 130.12, 130.24, 130.73

Due to insolubility of the polymer, NMR spectroscopy could not be used for polymer characterization.

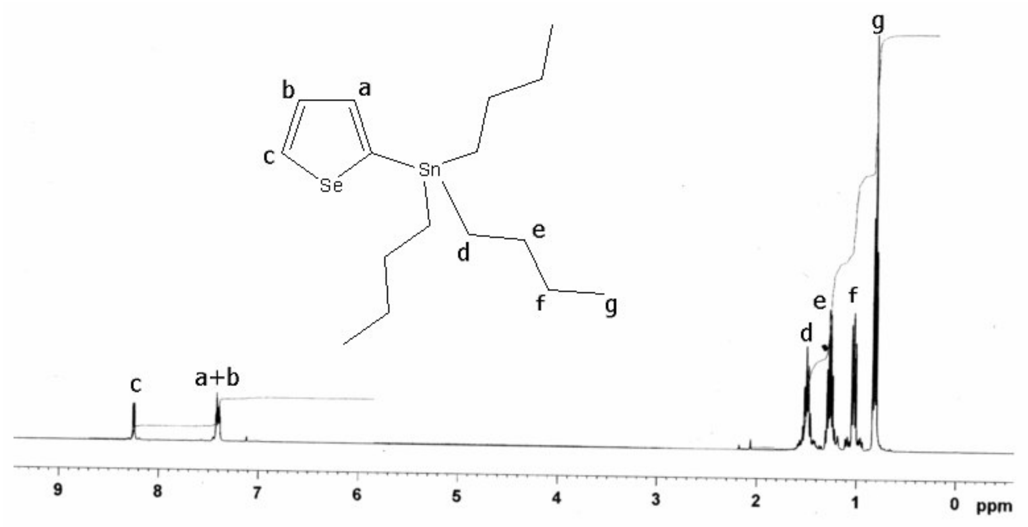


Figure 3.1 ^{1}H-NMR spectrum of tributyl (2-selenophenyl)stannane

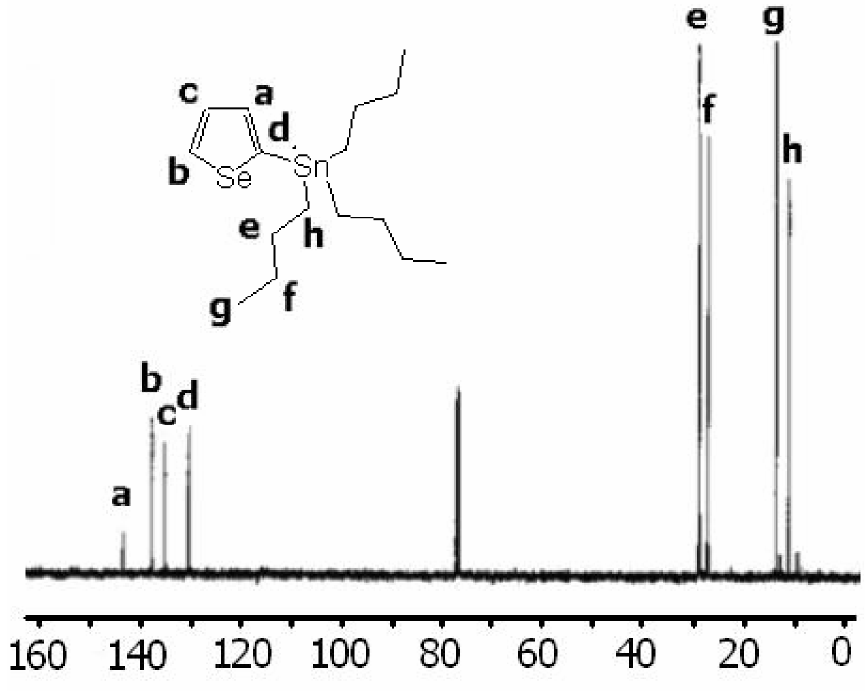


Figure 3.2 ^{13}C-NMR spectrum of tributyl (2-selenophenyl)stannane

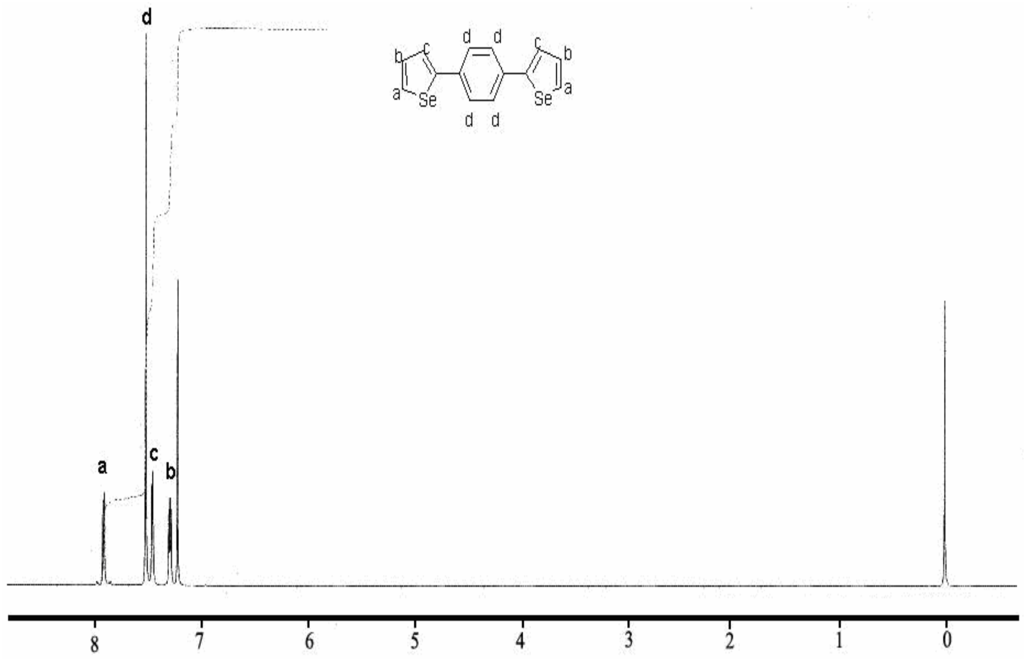


Figure 3.3 ^{1}H-NMR spectrum of the monomer

3.2 FTIR Spectra

FTIR spectrum of DSB monomer (Fig. 3.4) showed the following absorption bands: 3051 cm^{-1} (aromatic C-H), 1635 cm^{-1} , 1496 cm^{-1} (aromatic C=C streching), 933 cm^{-1}, 817 cm^{-1}, 690 cm^{-1} (C–H in plane bending of benzene and thiophene), 1112 cm^{-1} (C-Se stretching).

In the FTIR spectrum of Poly (DSB) (Fig. 3.5), in addition to the characteristic peaks of the monomer, the bands at 933 cm^{-1}, 817 cm^{-1} and 690 cm^{-1} corresponding to the out of plain C-H vibration of the monomer were almost disappeared. The wide band at 1644 cm^{-1} proves the formation of polyconjugation. The peaks at 795 cm^{-1} showed incorporation of the PF_6^- ions (dopant ion) into the polymer film during doping process. Hence, the results depict successful polymerization of the monomer.

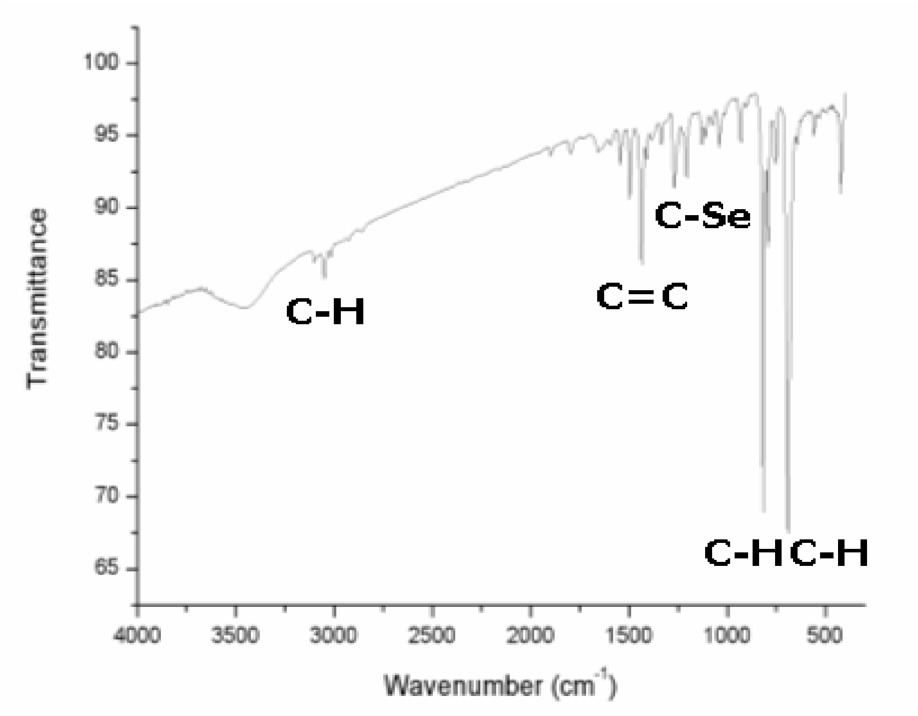


Figure 3.4 FTIR spectrum of DSB

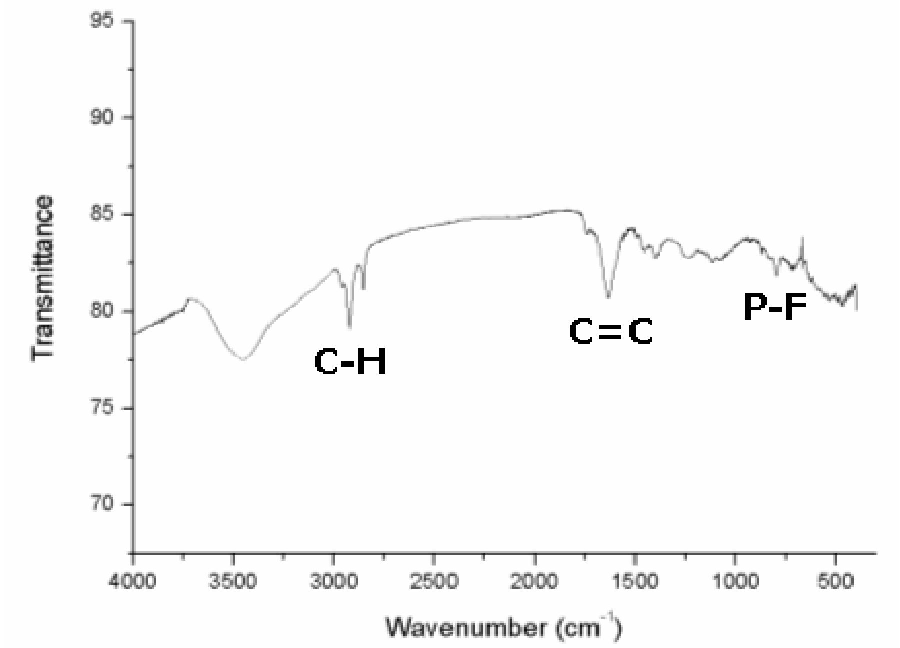


Figure 3.5 FTIR spectrum of Poly (DSB)

3.3 Cyclic Voltammograms

DSB monomer was homopolymerized by oxidative polymerization in $TBAPF_6$/DCM supporting electrolyte-solvent couple where indium tinoxide (ITO) coated glass was used as the working electrode. Cyclic voltammogram of electropolymerization is illustrated in Figure 3.6.

Monomer oxidation potential was determined as irreversible at +1.1 V. Consecutive cycles decreased the intensity of this peak, the polymer revealed two oxidation peaks at +0.95 V, +0.25 V and two reduction peaks at +0.7 V, +0.05 V respectively. Continuous increase in the current density of the peaks with repeating cycles showed the formation of conductive film.

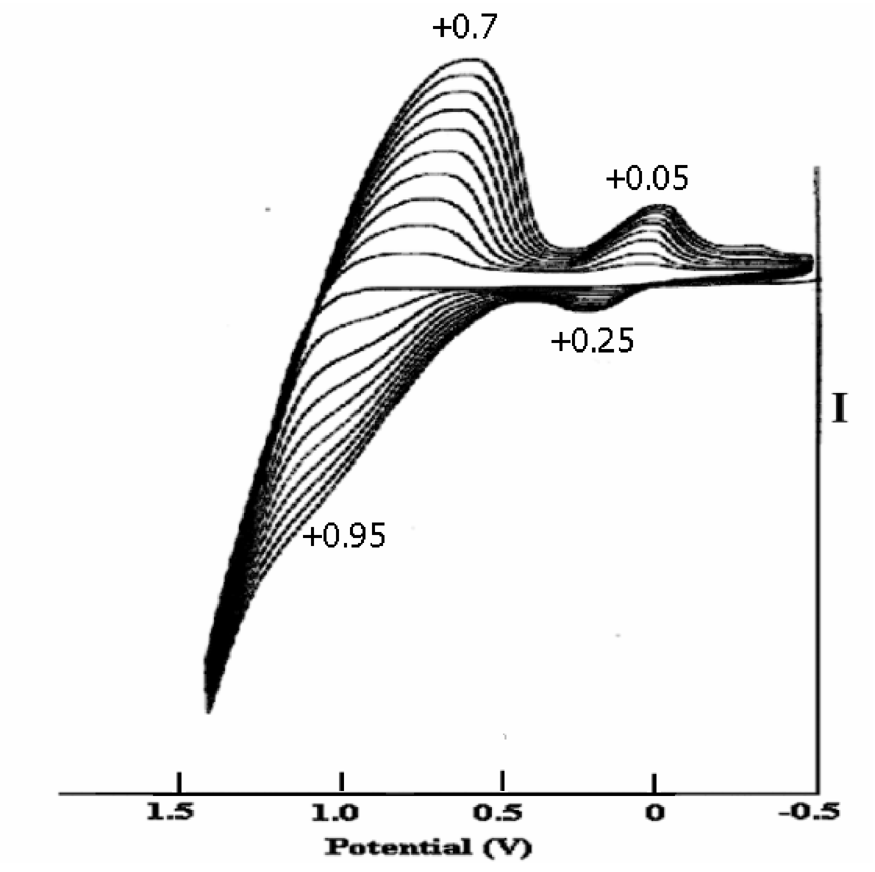


Figure 3.6 Cyclic Voltammogram of Poly (DSB)

3.4 Mass Spectroscopy

In the mass spectrum of DSB monomer (Figure3.7), monomer molecular weights with all of the stable Selenium isotopes (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, and ^{80}Se) can be seen. Average molecular weight of the monomer was calculated as 336.1 g/mole which supported purposed structure of the monomer.

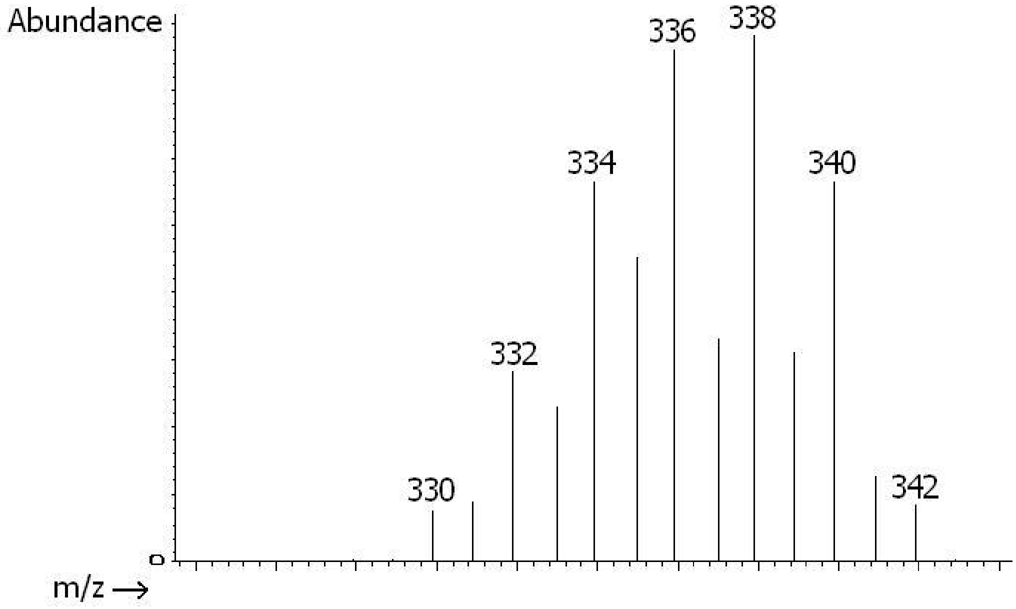


Figure 3.7 Mass Spectrum of Poly (DSB)

3.5 Electrochromic Properties of Conducting Polymers

3.5.1 Spectroelectrochemical Studies

Spectroelectrochemical analyses highlight optical changes and electronic transitions by applying different potentials to polymer coated ITO glass slide electrodes. Key electronic properties of Poly (DSB), Poly (selenophene-co-EDOT) and Poly (DSB-co-EDOT) such as the band gap (E_g) and intergap states that appear on doping were demonstrated. Poly (DSB) film was potentiodynamically synthesized on ITO electrode in the presence of 0.01 M DSB, while the potential was swept between -0.5 V and 1.3 V in $TBAPF_6$/DCM. The electrochemical and electrochromic properties of the polymer film were studied with a monomer free medium. A π–π^* transition was observed at 340 nm and the band gap (Eg) was calculated as 1.85 eV (Fig. 3.8). The absorption at the near infrared region drastically increased upon applied potential was incrementally increased between -0.3 V and 1.0 V. The polaron band (radical cation) and the bipolaron band (dication) were observed at 608 nm and 1250 nm, respectively.

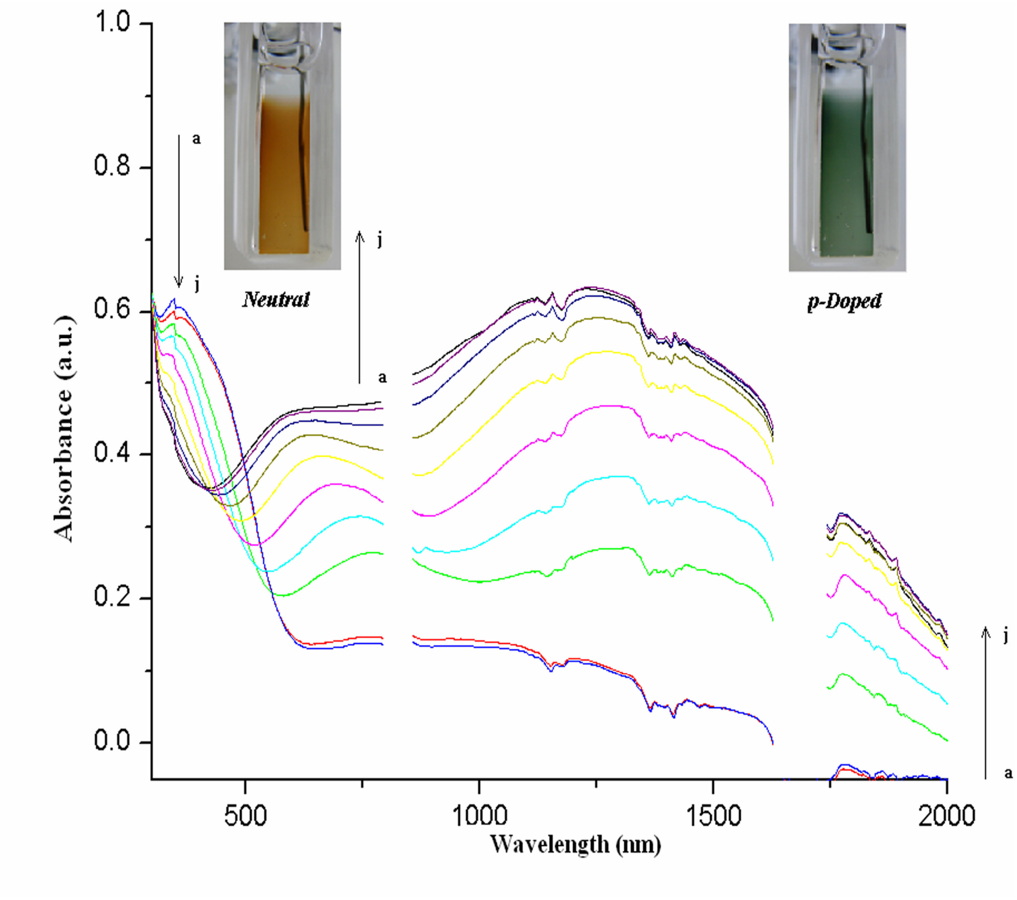


Figure 3.8 Spectroelectrochemistry of Poly (DSB) film on an ITO coated glass slide in monomer-free 0.1 M TBAPF$_6$/DCM solution where (a) -0.3, (b) 0.0, (c) 0.3, (d) 0.4, (e) 0.5, (f) 0.6, (g) 0.7, (h) 0.8, (i) 0.9, (j) 1.0 V vs Ag wire

In the spectra there are two cuts at specific wavelenghts due to the lamp and grating changings of the UV-VIS spectrophotometry that result in big jumps. These jumps are not related to the character of the material. Therefore, spectroelectrochemistry results are reported by cutting the jumping points.

Copolymer of selenophene with EDOT was electrosynthesized onto ITO-coated glass slides under constant potential conditions (at 1.5 V). Figure

3.9 shows UV-Vis-NIR absorption spectra of the copolymer under different applied potentials. At -0.3 V, the copolymer is undoped and in neutral state. The optical spectrum shows an absorption band with a maximum at 555 nm, corresponding to the conjugated π-π* transition and the film is revealing blue color. The onset energy for the π-π* transition which is called electronic band gap (E_g), was found to be 1.5 eV. Two new absorption bands appear at longer wavelengths with increase in the applied potential. The peak at 851 nm corresponds to the absorption by polarons, and the other peak at 1299 nm is due to the bipolarons. The copolymer switches from a violet reduced state to a blue oxidized state.

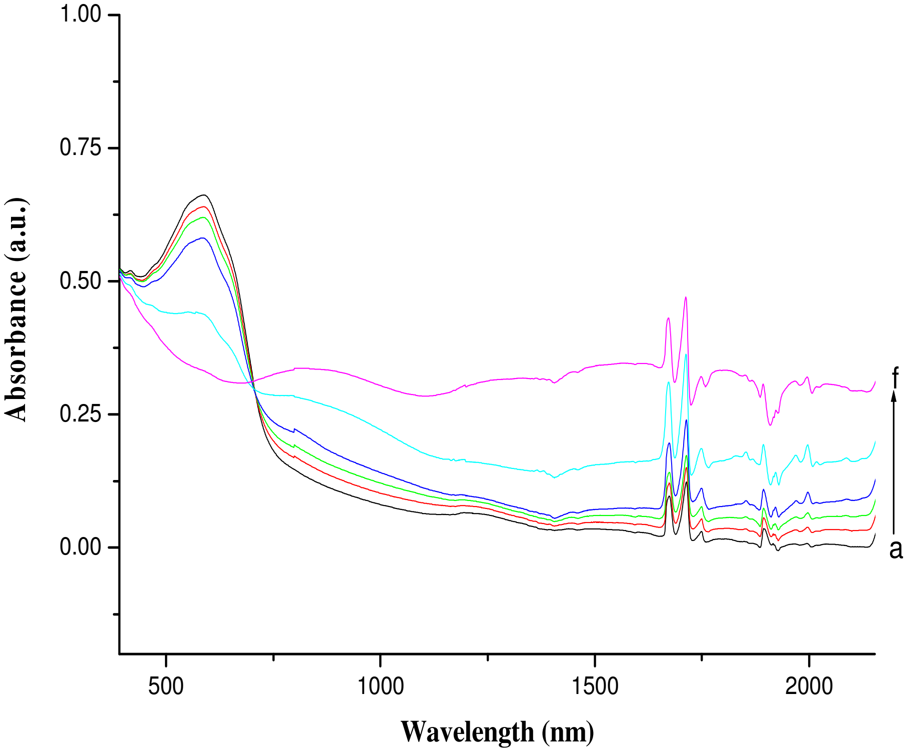


Figure 3.9 Spectroelectrochemistry of Poly (selenophene-co-EDOT) film on an ITO coated glass slide in monomer-free 0.1 M $TBAPF_6$/ACN solution where (a) -0.3, (b) 0.3, (c) 0.6, (d) 0.9, (e) 1.2, (f) 1.5 V vs Ag wire

Copolymer of DSB with EDOT was synthesized onto ITO-coated glass slides similar to the copolymer of selenophene with EDOT. Poly (DSB-co-EDOT). Constant potential of 1.3 V was applied for 1.5 minutes and spectroelectrochemical analysis of the copolymer yielded the spectra shown in Figure 3.10. π-π* transition was observed at 457 nm and band gap calculated from the onset of the π-π* transition was found as 1.57 eV. Polaron and bipolaron bands were observed at 696 and 1251 nm, respectively.

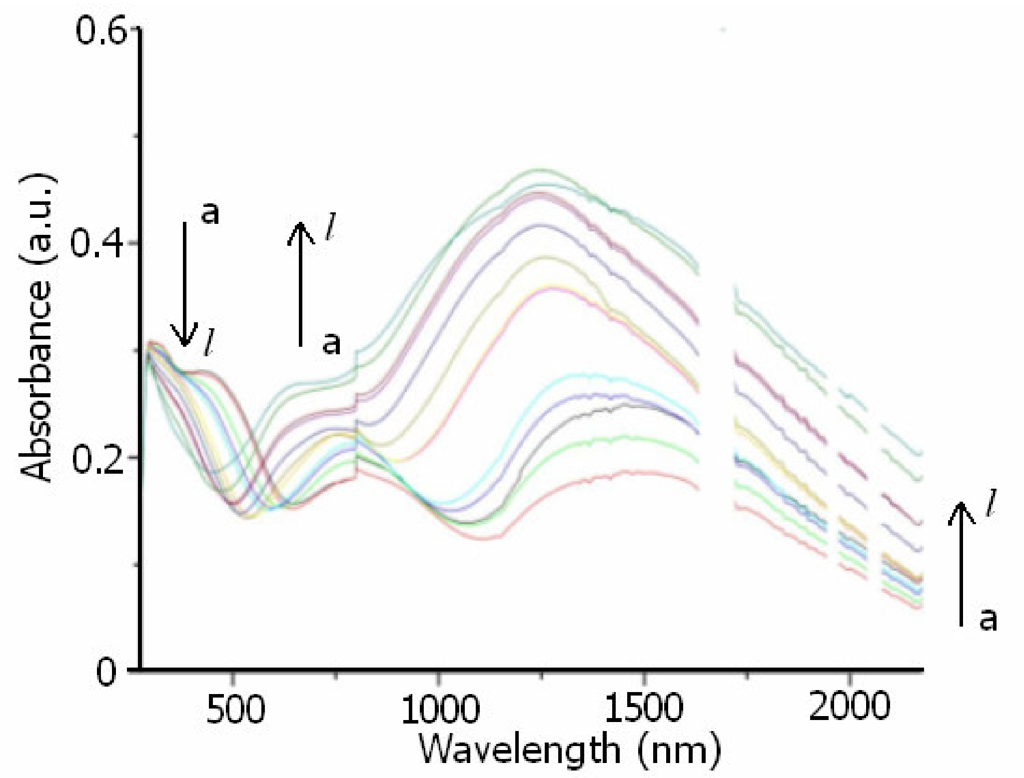


Figure 3.10 Spectroelectrochemistry of Poly (DSB-co-EDOT) film on an ITO coated glass slide in monomer-free 0.1 M TBAPF$_6$/DCM solution where (a) -0.5, (b) -0.3, (c) -0.1, (d) 0.1, (e) 0.3, (f) 0.5, (g) 0.6, (h) 0.8, (i) 0.9, (j) 1.0, (k) 1.2, (l) 1.4V vs Ag wire electrode

3.5.2 Kinetic Studies

Electrochromic switching studies are employed to determine the ability of the polymer to switch rapidly and exhibit striking color change. Chronoabsorptometry is a square-wave potential step method coupled with UV-Vis spectroscopy. It is used to investigate switching time and contrast of the polymer. The Poly (DSB) films synthesized on ITO-coated glass as described previously, were switched while the potential was stepped between -0.3 and 1.0 V with a switching time of 5 s (Fig. 3.11). From these experiments the contrast value was measured as the difference between the transmittance in the reduced and oxidized forms (ΔT %) and found to be 0.2% at 340 nm. At 1250 nm a percent transmittance of 35% with a switching time of 0.6 s was observed. A very low contrast in the visible region with a satisfactory contrast in the NIR region indicates its potential application as a near infrared active electrochromic material. Many polymers have shown to have NIR activity but polymers with such a small contrast in the visible region are limited in the literature [61].

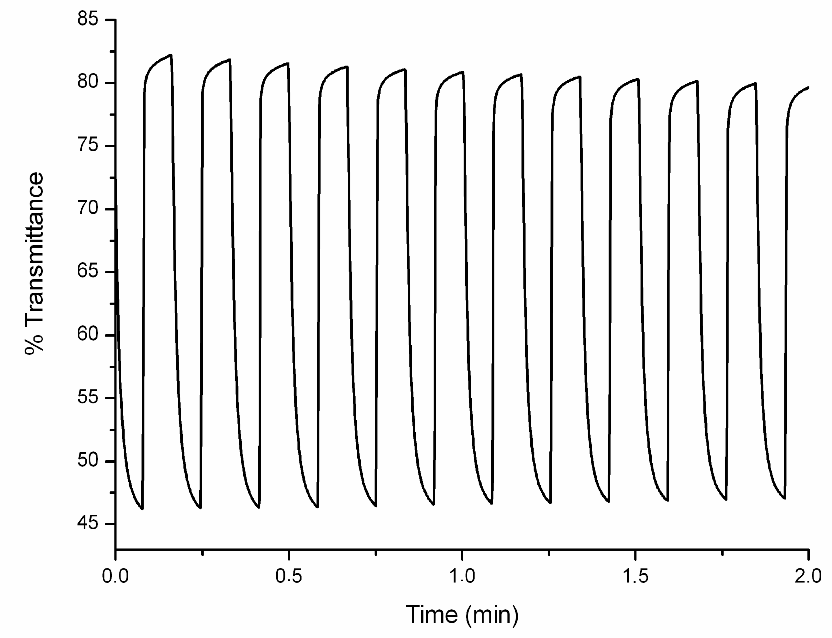


Figure 3.11 Electrochromic switching and optical absorbance change monitored at 1250 nm for Poly (DSB) in 0.1 M $TBAPF_6$/ACN

The copolymer of selenophene with EDOT was deposited on ITO-coated glass as described above and the transmittance was monitored at 555 nm and 1299 nm as the potential was switched between -0.3 V and +1.5 V using a square-wave potential step method coupled with optical spectroscopy (Fig 3.12). The response time that needed to perform switching between the two colored states was found to be 1.8 s at 555 nm and 1.4 s at 1299 nm. The optical contrasts for the copolymer were calculated as 39% at 555 nm and 72% at 1299 nm.

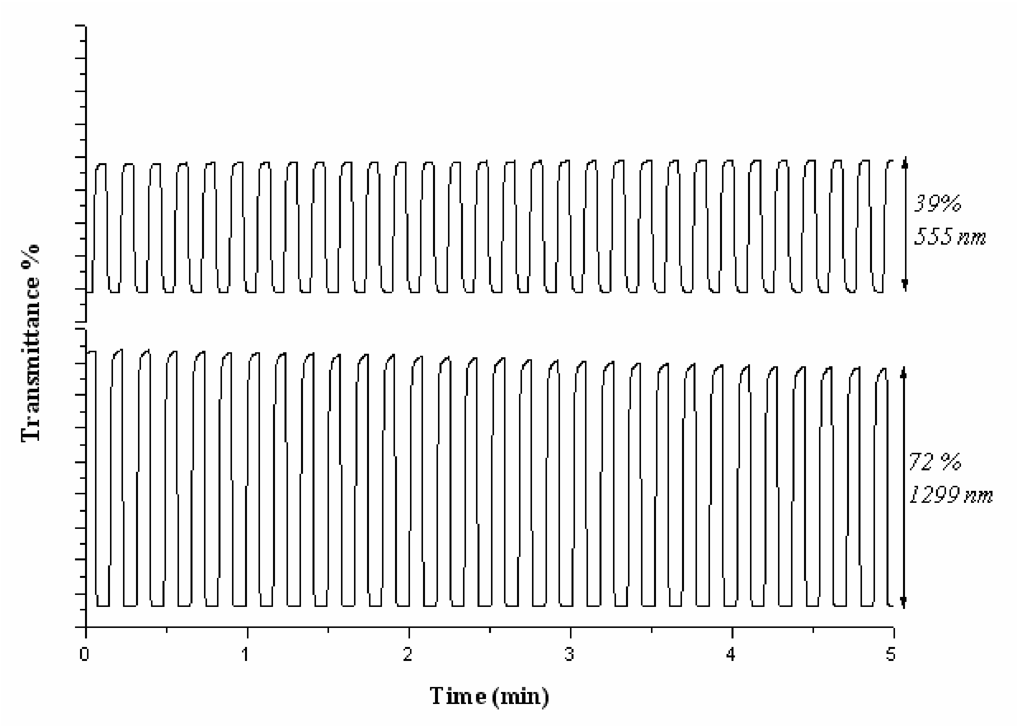


Figure 3.12 Change in optical absorbance at 555 nm and 1299 nm for Poly (selenophene-co-EDOT)

The copolymer of DSB with EDOT was deposited on ITO-coated glass and the transmittance change was monitored at 696 nm (Fig 3.13) and 1251 nm (Fig 3.14) with potential switch between -0.3 V and +1.2 V. The response times were found to be 0.2 s at 696 nm and 1.75 s at 1251 nm. The optical contrasts for the copolymer were calculated as 12% at 696 nm and 35% at 1251 nm.

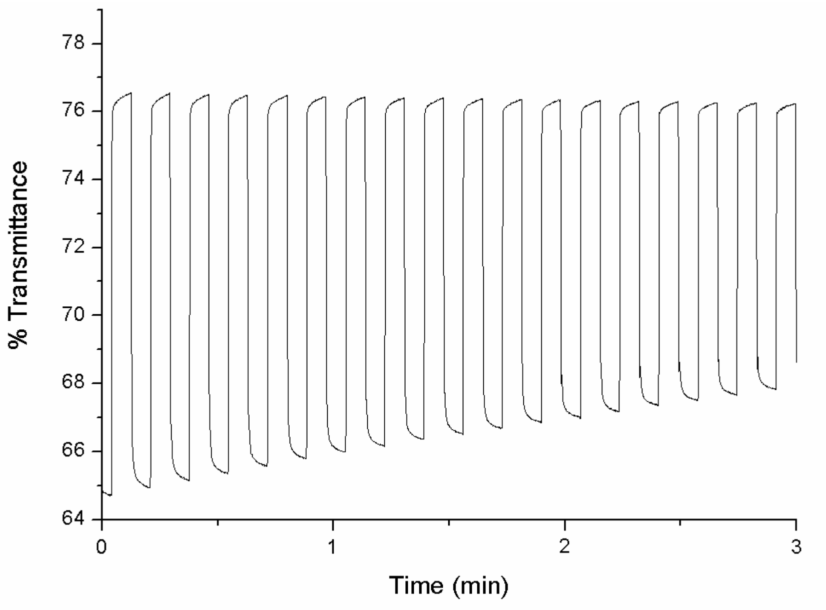


Figure 3.13 Change in optical absorbance at 696 nm for Poly (DSB-co-EDOT)

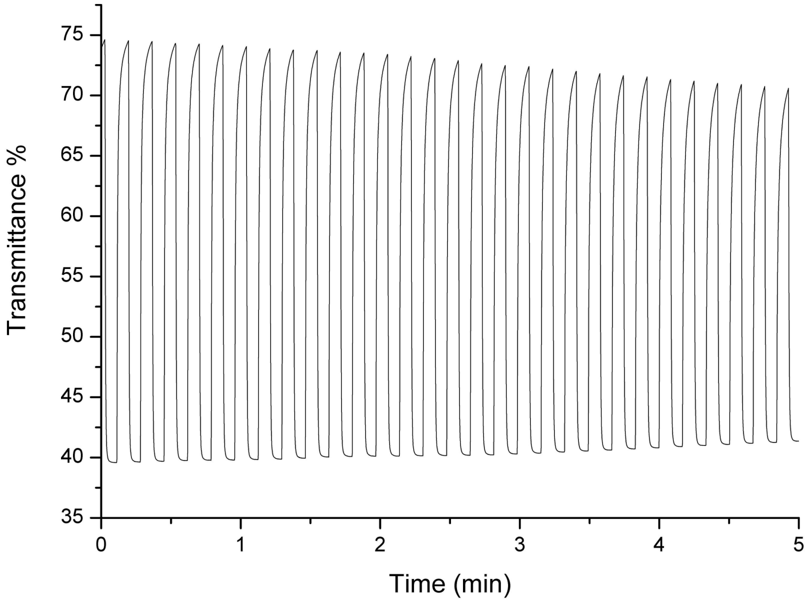


Figure 3.14 Electrochromic switching and optical absorbance change monitored at 1251 nm for Poly (DSB-co-EDOT) in 0.1 M $TBAPF_6$/ACN

Kinetic studies revealed the potential of selenophene derivatives as electrochromic materials when compared with thiophene and pyrrole derivatives [62-65].

3.5.3 Scan rate dependence

Investigation of peak current intensity with respect to scan rate indicates whether the process is controlled by diffusion or not [53, 54].
The current response of Poly (DSB) was directly proportional to the scan rate with a potential range between 0.3 V and 1.4 V, indicating the non-diffusion controlled character of the polymerization (Fig. 3.15b).

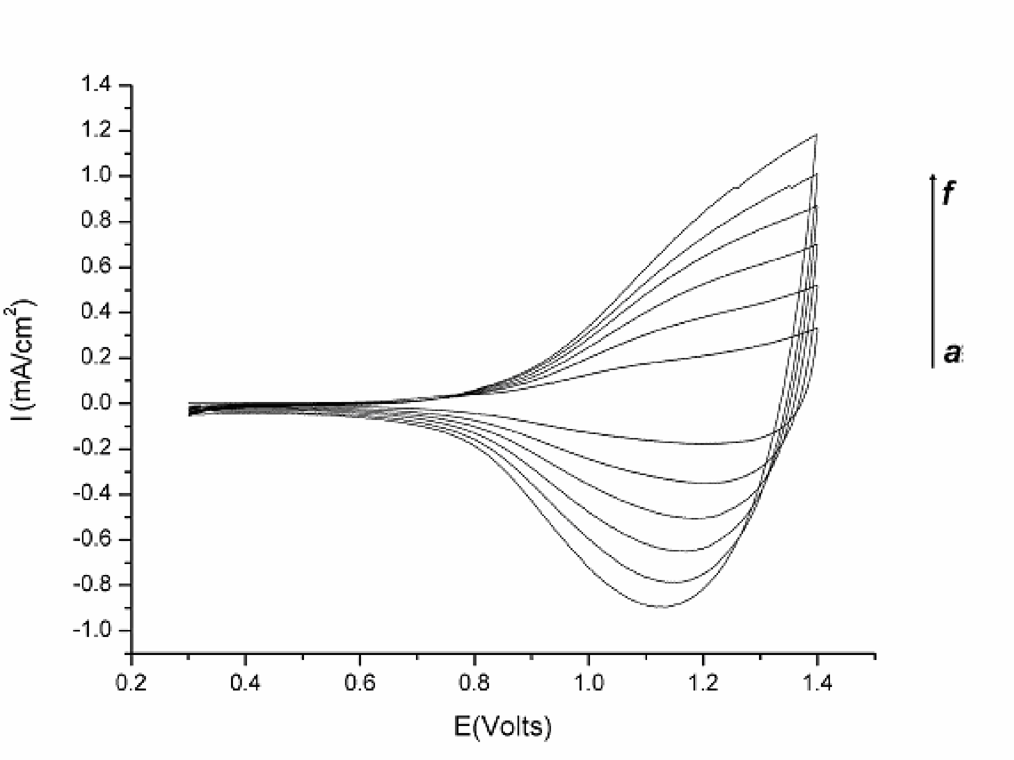


Fig 3.15a Cyclic Voltammograms of Poly (DSB) at different scan rates (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, (f) 300 mV/s.

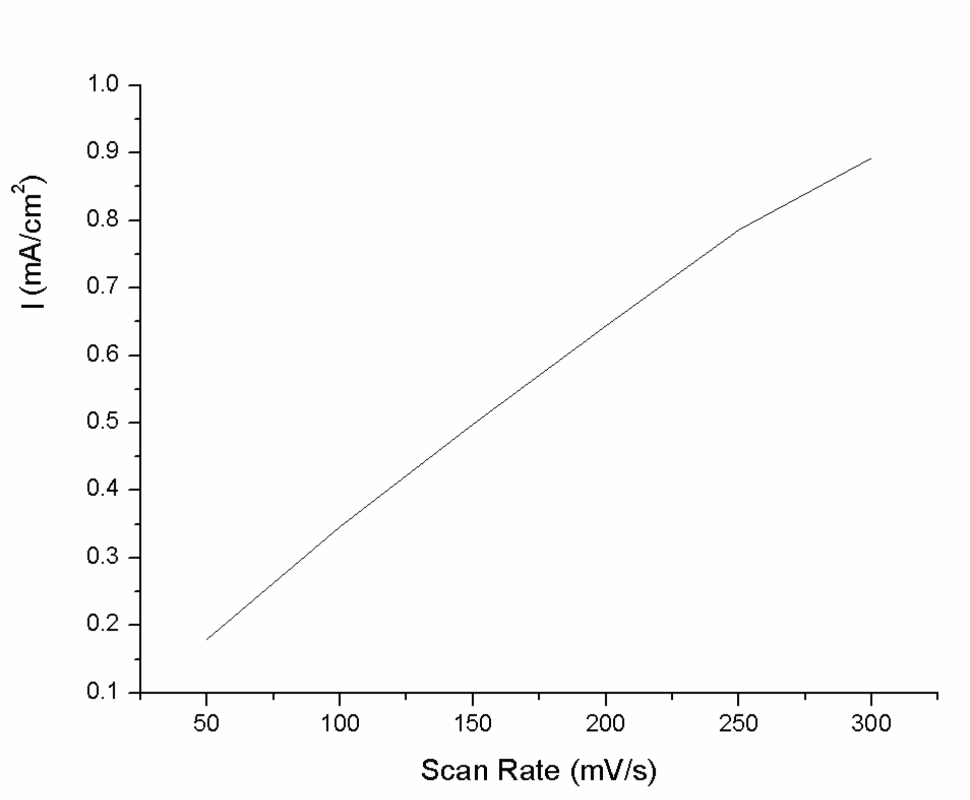


Fig 3.15b Scan rate dependence of Poly (DSB) in TBAPF$_6$/DCM (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, (f) 300 mV/s scan rates.

The scan rate dependence of the anodic and cathodic peak currents shows a linear dependence on scan rate as illustrated in Figure 3.16b for Poly (selenophene-co-EDOT). This linear dependence demonstrates that the redox process is controlled by the polymer film adsorption on the ITO electrode, not diffusion controlled.

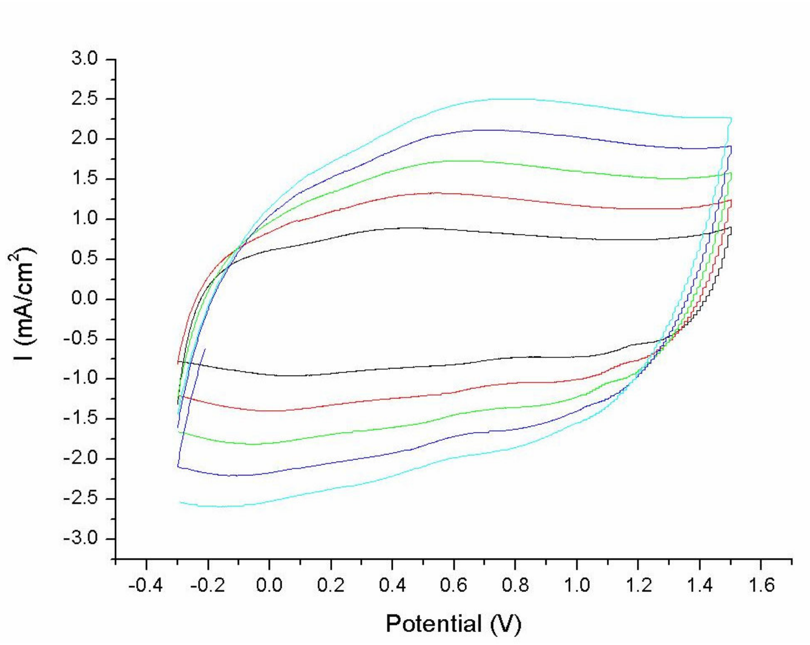


Fig 3.16a Cyclic Voltammograms of Poly (selenophene-co-EDOT) at different scan rates (a) 100, (b) 150, (c) 200, (d) 250, (e) 300 mV/s

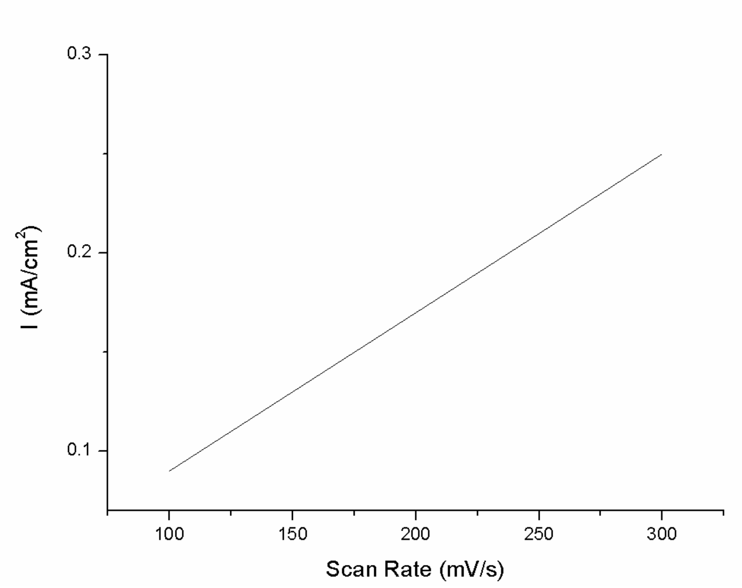


Fig 3.16b Scan rate dependence of Poly (selenophene-co-EDOT) in TBAPF$_6$/ACN

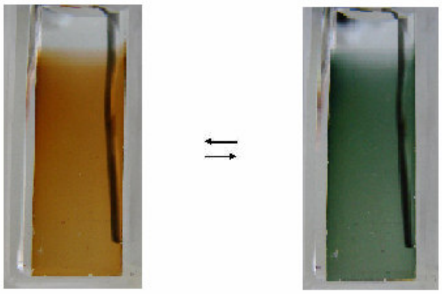
(a) 100, (b) 150, (c) 200, (d) 250, (e) 300 mV/s scan rates.

3.5.4 Colorimetry Studies

The reduced state (-0.3 V) color of Poly (DSB), orange-yellow, changed to green upon oxidation (1.0 V). Figure 3.17 illustrates the Y, x and y values and the images of the polymer.

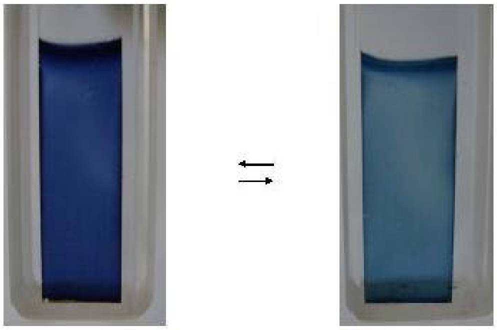
Copolymer of selenophene and EDOT changed its color from blue to violet at reduced and oxidized states, respectively (Figure 3.18).

Copolymer of DSB and EDOT was dark orange at the reduced state (-0.3 V) and green at oxidized state (1.2 V) (Figure 3.19).



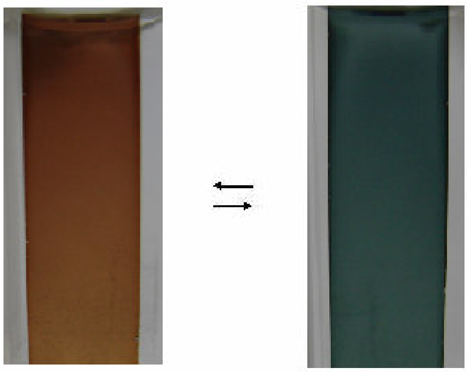
(-0.3 V)	(1.0 V)
Y= 526	Y= 428
x= 0.410	x= 0.300
y= 0.413	y= 0.361

Figure 3.17 Electrochromic properties of Poly (DSB)



(-0.3 V)	(1.5 V)
Y= 373	Y= 743
x= 0.257	x= 0.275
y= 0.289	y= 0.322

Figure 3.18 Electrochromic properties of Poly (selenophene-co-EDOT)



(-0.3 V)	(1.3 V)
Y= 461	Y= 466
x= 0.357	x= 0.279
y= 0.389	y= 0.345

Figure 3.19 Electrochromic properties of Poly (DSB-co-EDOT)

CHAPTER IV

CONCLUSION

A new conjugated monomer, 1,4-di (selenophene-2-yl)-benzene, was synthesized in high purity and characterized by spectral methods (^{1}H NMR, ^{13}C NMR and FTIR). Corresponding conjugated homopolymer, Poly (selenophene-co-EDOT) and Poly (DSB-co-EDOT) were synthesized via oxidative electrochemical polymerization. Characterization of the polymers was performed by FTIR, spectroelectrochemical analysis, electrochromic switching and colorimetry studies.

Spectroelectrochemistry experiments of the homopolymer demonstrated π-π^* transition, polaron and bipolaron band formations at 340 nm, 608 nm and 1250 nm respectively. Band gap was calculated as 1.85 eV. Furthermore, % ΔT at 340 nm was found as 0.2% and 35% at 1240 nm with a switching time of 0.6 s. Considering these results, we can conclude that Poly (DSB) is a promising candidate for near infrared applications.

π-π^* transition, polaron and bipolaron bands of Poly (selenophene-co-EDOT) were observed at 555, 851 and 1299 nm. Band gap of the copolymer was calculated as 1.5 eV. Kinetic studies revealed 39% and 72% percent transmittance at 555 and 1299 nm, respectively. Switching times were 1.8 s at 555 nm and 1.4 s at 1299 nm.

Synthesis and characterization of the Poly (DSB-co-EDOT) was also successfully accomplished. Percent transmittance was monitored at 696 nm and 1251 nm with response times of 0.2 s at 696 nm and 1.75 s at 1251 nm.

The optical contrasts for the copolymer were calculated as 15% at 696 nm and 38% at 1251 nm.

Homopolymer of selenophene does not form high-quality films. Hence, optical properties could not be studied. We managed to form high quality films and studied optical properties through synthesis of a derivative of Poly (selenophene) (DSB) and copolymerization (Poly (selenophene-co-EDOT), Poly (DSB-co-EDOT)). All of these studies indicate the potential of selenophene derivatives for electrochromic applications.

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