A NEW p AND n DOPABLE SELENOPHENE DERIVATIVE AND ITS ELECTROCHROMIC PROPERTIES

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A NEW p AND n DOPABLE SELENOPHENE DERIVATIVE AND ITS ELECTROCHROMIC PROPERTIES

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ABSTRACT

A NEW p AND n DOPABLE SELENOPHENE DERIVATIVE AND ITS ELECTROCHROMIC PROPERTIES

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May 2008, 73 pages

A novel electrically conducting polymer, poly(2-dodecyl-4,7-di(selenophen-2-yl)benzotriazole) (**Poly(SBT)**), containing selenophene as a strong donor and benzotriazole as a strong acceptor group was synthesized by electrochemical polymerization. Homopolymerization and copolymerization (in the presence of 3,4-ethylenedioxythiophene (EDOT)) was achieved in acetonitrile/ dichloromethane(95/5 v/v) with 0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The electrochemical and optical properties of homopolymer and copolymer were investigated by Cyclic voltammetry, UV-Vis, near IR Spectroscopy. Cyclic voltammetry and spectroelectrochemistry studies demonstrated that homopolymer can be reversibly reduced and oxidized (both n- and p-doped) between -1.9 V and 1.4 V, at a scan rate of 100 mV/s. Optical contrast was calculated as 32% and 56% with a switching time of 2.4 s and 0.4 s at 511 and 1200 nm respectively. Poly(SBT) exhibits a λmax value of 511nm and a band gap of 1.67eV.

Keywords: n and p-dopable conducting polymers, electrochromism, electrochemical polymerization, selenophene

ÖZ

YENİ p VE n KATKILANAN SELENOFEN TÜREVİ VE ELEKTROKROMİK ÖZELLİKLERİ

Ardahan, Gülben
Yüksek Lisans, Kimya Bölümü
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Mayıs 2008, 73 sayfa

Güçlü elektron verici selenofen ve güçlü elektron çekici benzotriazol içeren yeni iletken polimer, poly(2-dodecyl-4,7-di(selenophen-2-yl)benzotriazole) (**Poly(SBT)**), elektrokimyasal polymerleştirme ile sentezlenmiştir. Homopolimerizasyon ve kopolimerizasyon, tetrabütilamonyum hegzaflorofosfat (**TBAPF$_6$**) varlığında, asetonitril/diklorometan içinde gerçekleştirildi. Homopolimerlerin ve kopolimerlerin elektrokimyasal ve optik özellikleri Dönüşümlü voltametre, UV-Vis ve IR Spektroskopisi ile incelendi.Dönüşümlü Voltametre ve spektroelektrokimyasal çalışmalar, homopolimerlerin tarama hızı 100 mV/s de -1.9 V ile 1.4 V arasında tersinir biçimde indirgenebildiğini ve yükseltgenebildiğini kanıtlamaktadır. Optik kontrast 32% ve 56%, değişim zamanı ise 2.4 s and 0.4 s sırasıyla 511 and 1200 nm dalga boylarında hesaplanmıştır ve bant aralığı 1.67eV olarak bulunmuştur.

Anahtar sözcükler: n & p doplanabilen iletken polimerler, elektrokromizim, elektrokimyasal polimerleşme, selenofen

TO DEAR MY FATHER & MY MOTHER

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ABBREVIATIONS

SBT	2-Dodecyl-4,7-di(selenophen-2-yl)benzotriazole
Poly(SBT)	Poly(2-dodecyl-4,7-di(selenophen-2-l)benzotriazole)
EDOT	3,4-Ethylenedioxythiophene
PEDOT	Poly(3,4-ethylenedioxythiophene)
Poly(SBT-co-EDOT)	Poly(2-dodecyl-4,7-di(selenophen-2-l)benzotriazole-co-ethylenedioxythiophene)
PTh	Polythiophene
PPy	Polypyrrole
PPP	Poly(p-phenylene)
PPV	Poly(p-phenylene vinylene)
PPS	Poly(p-phenylene sulphide)
$TBAPF_6$	Tetrabutylammonium hexafluorophosphate
D	Donor
A	Acceptor
ITO	Tin doped indium oxide
DCM	Dichloromethane
THF	Tetrahydrofuran
ACN	Acetonitrile
R	Reduced form of the redox couple
O	Oxidized form of the redox couple
λ_{max}	Wave Length at Maximum Absorbance
$\Delta T\%$.	Percent tranmittance
i	Current
E	Potential
Epa	Polymer oxidation potentials
Epc	Polymer reduction potentials
NMR	Nuclear Magnetic Resonance
M	Molar Mass

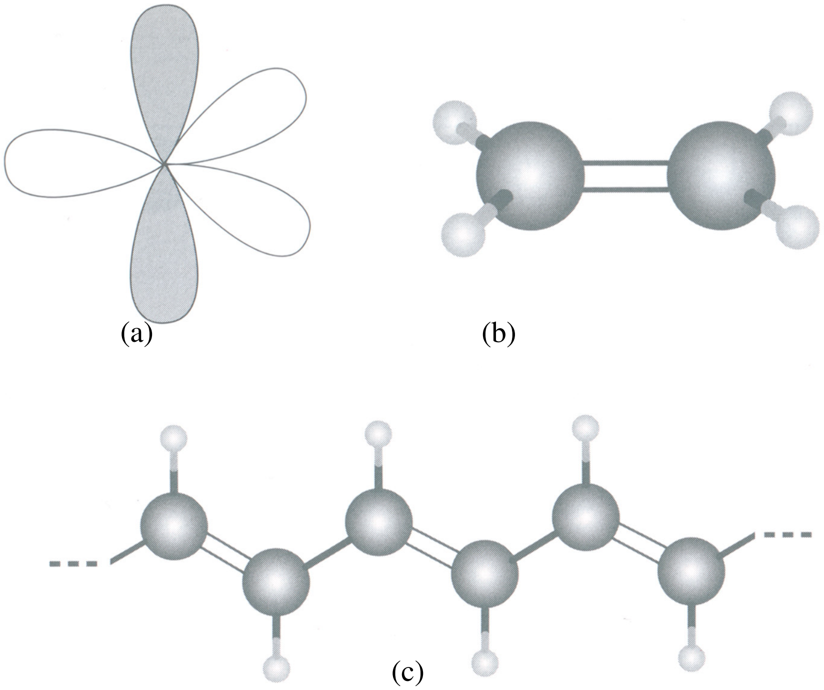
CV	Cyclic Voltammetry
ECD	Electrochromic Device
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
E_g	Band Gap Energy
CIE	La Commission Internationale de l’Eclairage
L a b	Luminance, hue, saturation

CHAPTER 1

INTRODUCTION

1.1 Conducting Polymers

Conducting polymers are organic materials possessing electric, electronic, magnetic and optical properties[1]. They also hold the mechanical properties of the conventional polymers. Therefore, they are called “synthetic metals”[2]. Conducting polymers have unusual electronic properties, such as low energy optical transition, low ionization potentials and high electron affinities which are caused by the delocalization. Electron delocalization is a consequence of presence of conjugated double bonds. In conjugated polymers, the backbones consist of sp^2 hybridized carbons. The $2p_z$ electron orbitals overlap along the backbone, which gives rise to the delocalization of the π-electron system[3](Figure1.1). Figure 1.2 demonstrates the structure of some conducting polymers. It is necessary to introduce mobile carries into double bond to make these polymers electrically conductive. This is achieved by oxidation or reduction reactions which is called doping. Dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymers can be achieved by the controlled addition of known, small (<10%) non-stoichiometric amounts of chemical species. This process can be called as p-doping or n-doping depending on the positive or negative sign of the injected charge in the polymer chain. Counter ions (anions or cations) named as ‘dopants’ are utilized to compensate the charges[4].


(a) (b)

(c)

Figure 1.1 (a) sp^2 hybrid orbitals, and the molecular structure of (b) ethylene and (c) polyacetylene

1.1.1 History of Conducting Polymers

Many conducting polymers were known in their nonconducting forms much before their conductivity. Polyaniline is one of the oldest conductive polymers known. It was first prepared by Letheby in 1862 by anodic oxidation of aniline in sulphuric acid. Although chemical oxidative polymerization of aniline was described by Letheby in 1862, its conductivity studied in more detail by Jozefowicz et al in 1967[5].

In 1976 Shrikawa and co-workers exposed free-standing films of polyacetylene to iodine vapors. Oxidation of this material with iodine results in a 10^8 fold increase in conductivity. This was one of the first known examples of a conductive organic polymer[6]. The high electrical conductivity discovered for these polymers in the 1970's accelerated their use. However, due to its high chemical instability in air and related factors, it has most recently confined to scientific aspects.

In the 1980's polyheterocycles (Figure 1.2) such as polythiophene (PTh), polyfuran, polypyrrole (PPy), poly(p-phenylene) (PPP), poly(p-phenylene vinylene) (PPV) and poly(p-phenylene sulfide) (PPS) were developed. Polyheterocycles were found to be much more air stable than polyacetylene however, their conductivities were not so high, typically about 10^3 Sm^{-1}.Derivatives were prepared by adding various side groups such as electron donating or withdrawing groups to the polymer backbone[7].

The importances of this class of materials were recently recognized by the world scientific community when MacDiarmid, Shirakawa and Heeger received the Nobel Prize in Chemistry in 2000 for their work in this field[8].

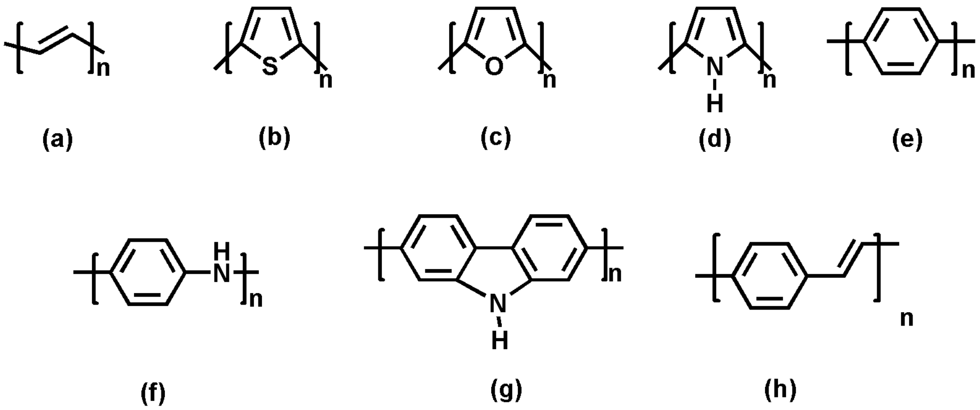


Figure 1.2 Common conducting polymer structures: (a) poly(acetylene), (b) poly(thiophene), (c) poly(furan), (d) poly(pyrrole), (e) poly(phenylene), (f) poly(aniline), (g) poly(carbazole), (h) poly(p-phenylene vinylene)

1.2 Band Theory and Conduction Mechanism in Conducting Polymers

1.2.1 Band Theory

Materials are devided into three groups according to their room temperature conductivity properties: conductors, semiconductors and insulators. A useful way to visualize the difference between them is to plot the available energy levels for electrons in the materials. The valence band is the highest energy band containing electrons and the conduction band is the next higher empty band. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is called bandgap[9] (Figure 1.3).

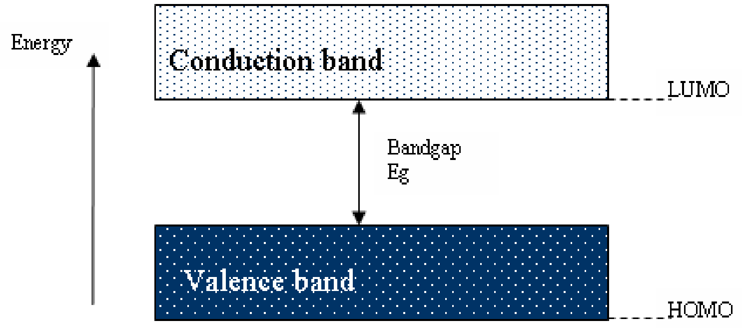


Figure 1.3 Energy levels for electrons in the materials

In conductive materials, the highest energy level of the valence electron and the lowest energy level of the conduction band are similar energy so there is no bandgap and electrons can easily pass from the valence band to the conductor band. If the energy levels are around 1.0 eV, then electrons can easily be excited from the valence band into conduction band by means such as thermal excitation, vibrational excitation, or excitation by photons;

the electrons are then mobile and the material is called a semiconductor. If the energy levels are large, e.g. 10.0 eV, the promotion of an electron to the conduction band has low probability at room temperature. Therefore, that kind of materials are termed as insulating materials[10] (1.4).

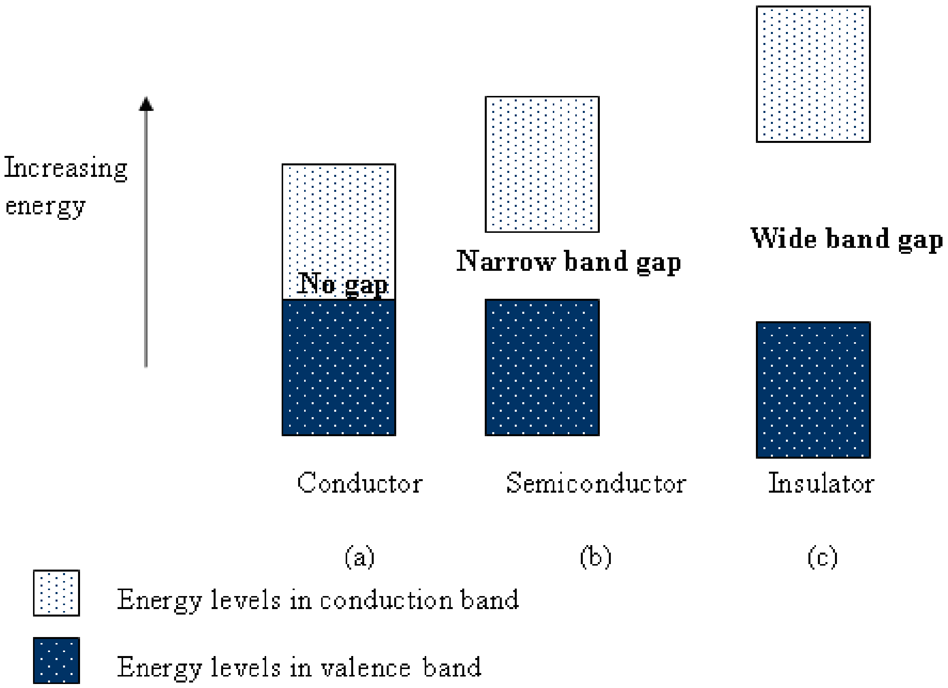


Figure 1.4 Band structures of (a) conductor, (b) semiconductor, (c) insulator

Neutral conjugated polymers are usually treated as semiconductors and their electronic energy levels can be described by using band theory. The π band is divided into π and π* bands in conjugated polymers, e.g. polyacetylene, $(\text{-CH=CH-})_n$. Since each band can contain two electrons per atom (spin up and spin down), the π band is filled, as a result π* band is empty. Chain length, bond length alternation, planarity, the presence of electron-acceptor or electron donor substituents and the resonance stabilization energy of the aromatic cycles are the main structural factors that affect the HOMO–LUMO gap of a linear π-conjugated system[11]. The band gap of a conjugated polymer can be approximated from the onset of absorption of the π to π* transition in the UV-VIS spectrum. As shown in the Figure 1.5 when the conjugation length increases along with an increase in the number of energy levels, the band gap decreases[12-13].

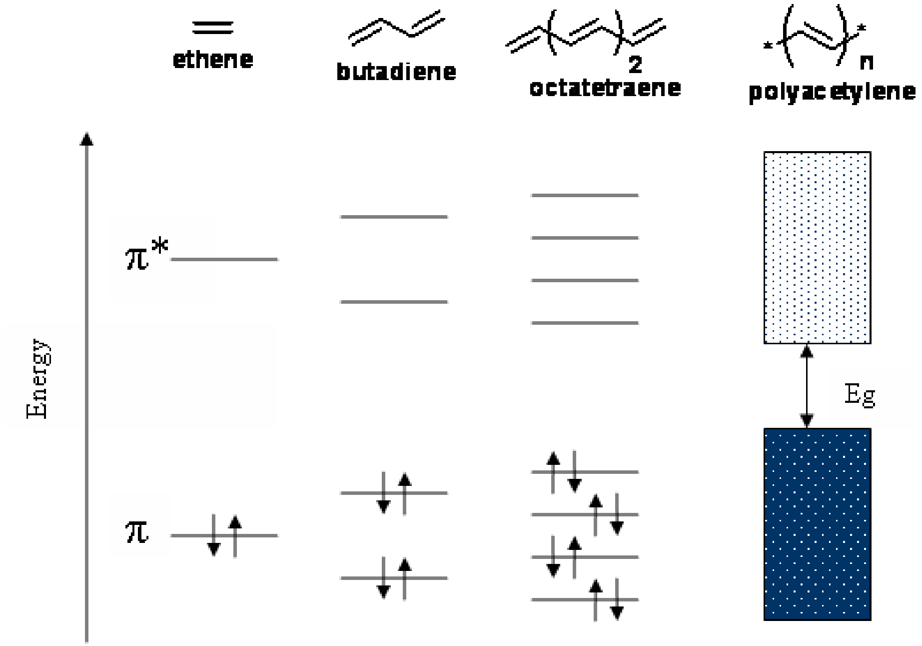


Figure 1.5 Generation of bands in conjugated polymer systems

Although conjugated polymers have narrower band gaps, they are not conductive. Therefore, the doping process is used to change the electronic structure by producing new states in the band gap and this makes them conducting[14]. Doping process can be classified into two groups; n-type doping and p-type doping.In n-type doping process an electron is added to the conduction band. This is also called reduction of conducting polymer chain. If the added material has more electrons in the valence shell than the host material, the result is a 'n-type semiconductor'. In n-type material, electron energy levels are near the top of the band gap so that they can be easily excited into the conduction band. In p-type doping process an electron is taken from the valence band. This is also called oxidation of conducting polymer chain. If the added material has fewer electrons than the host, it adds positive holes and the result is a 'p-type semiconductor'. In p-type material, extra holes in the band gap allow excitation of valence band electrons, leaving mobile holes in the valence band. As a result, as it is demonstrated in the Figure 1.6 the doping process modifies their electronic structure by producing new states in the band gap and makes them conducting[15].

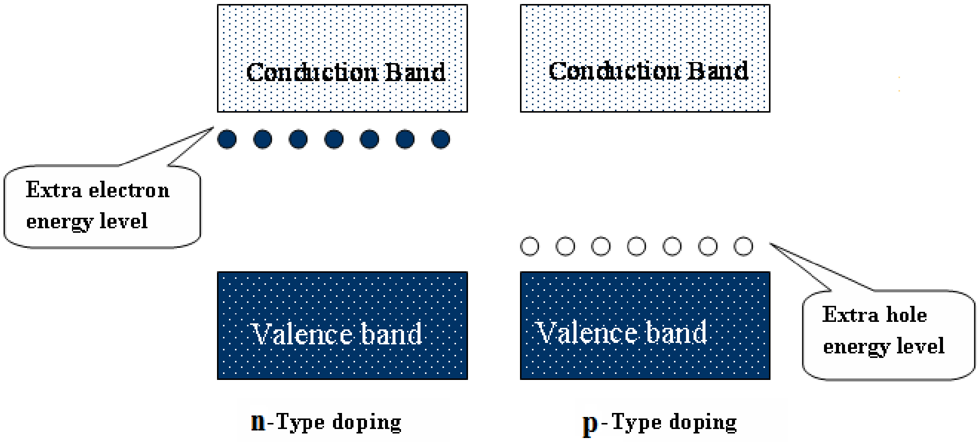


Figure 1.6 Semiconductor bands for n-type semiconductor and p-type semiconductor

1.2.2 Conduction Mechanism

1.2.2.1 Charge Carriers

Since polymers are doped, conjugational defects occurs in the polymer chain. These defects in the polymer act as the charge carriers which can be radicals, anions, cations or combinations of these. These combinations are termed solitons, polarons, and bipolarons[16].

Soliton is classified in three categories: Neutral soliton, positive soliton and negative soliton. In neutral soliton, energy level is singly occupied and therefore, the spin value is ½. Although neutral solitons have spin, they have no charge. Removal of an electron which is called electrochemical oxidation results in the generation of the positive soliton (p-type doping). The negative soliton is obtained by an addition of an electron (n-type doping)[17] (Figure 1.7).

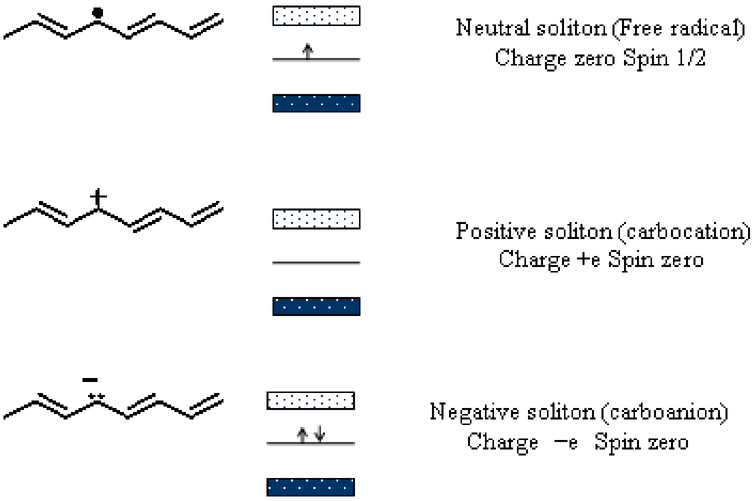


Figure 1.7 Soliton structures of polyacetylene

Polarons are the combination of neutral and charged soliton on the same polymer chain and they have two types: positively charged polaron and negatively charged polaron[18]. Positively charged polaron is obtained after removing an electron from valence band (Figure 1.8.b). The oxidation of the polymer breaks one double bond leaving a radical and positive charge on the polymer chain (radical cation). Negatively charged polaron is obtained after addition of an electron to the conducting band. (Figure 1.9.b) The reduction of polymer also breaks one double bond leaving a radical and negative charge on the polymer chain (radical anion). Further oxidation (reduction) of the polymer results in polarons in the same chain called bipolarons (Figure 1.8c,1.9c). When a great many bipolarons are formed (highly p-doped), their energy states overlap at the edges which creates narrow bipolaron bands in the gap. Both polarons and bipolarons are mobile and can move along the polymer chain in an electrical field and hence conduct electrical current. Figures 1.8(c) and 1.9(c) show these charges[19].

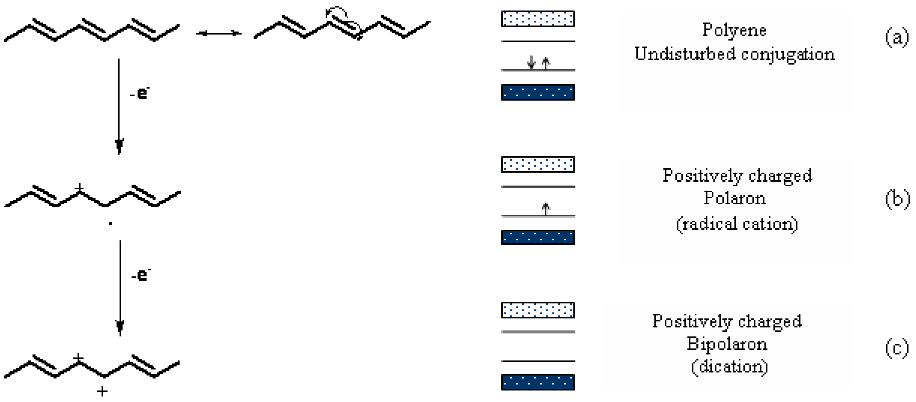


Figure 1.8 A schematic description of the formation of positively charged polaron and bipolaron pair

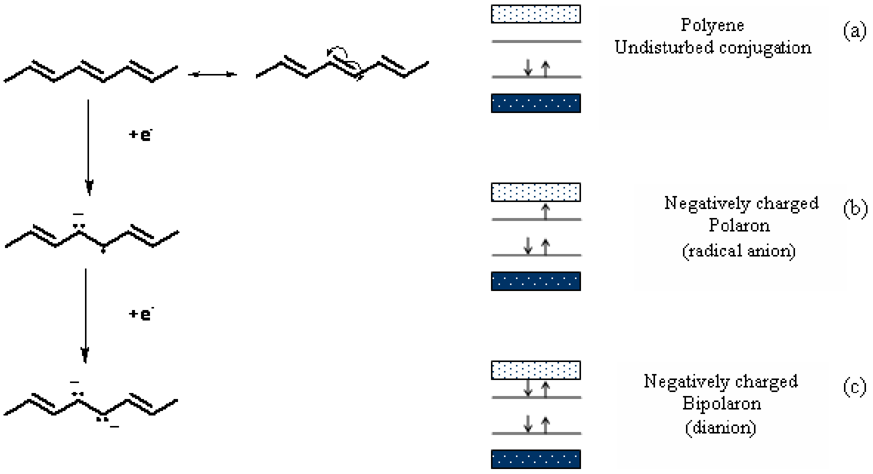


Figure 1.9 A schematic description of the formation of negatively charged polaron and bipolaron pair on a trans-polyacetylene chain upon n-doping.

1.2.2.2 Doping Process of Conducting Polymers

To control the electrical conductivity of a polymer over the range from insulating to highly conducting (metallic) state is possible. This process is called doping[20]. Different conductivity levels between the undoped (insulation and semiconducting) and fully doped (highly conducting) form can be easily obtained by adjusting the doping level (Figure 1.10)[21].

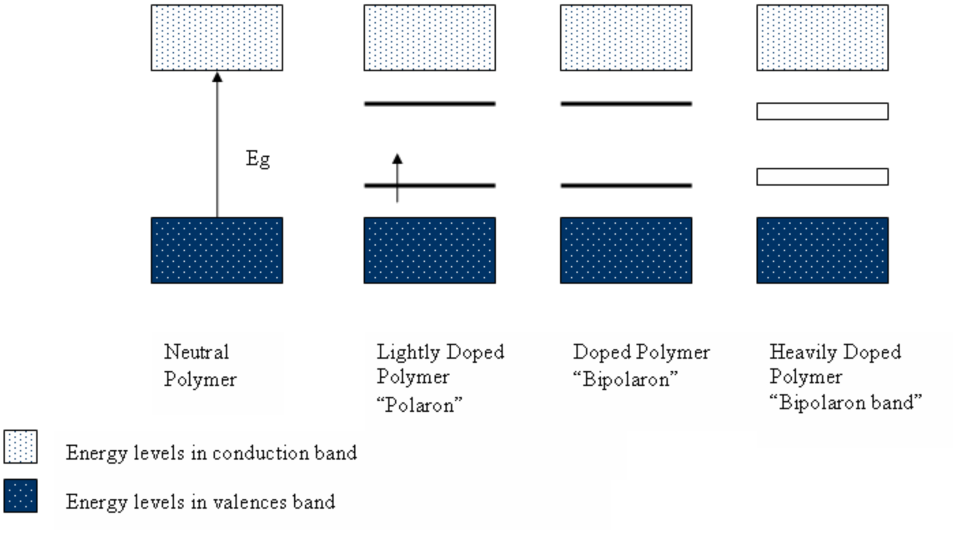


Figure 1.10 Caption band model of (a) non-doped , (b) slightly doped, (c) doped and (d) heavily doped conducting polymers

Doping of conducting polymers has been achieved by redox processes. This process consist of partial addition (reduction) or removal (oxidation) of electrons to or from the π-system of the polymer backbone. It is known that doping and dedoping are generally reversible and do not change the chemical nature of the original backbone (Figure 1.11). Both doping and undoping processes involve dopant counterions which stabilize the doped state[22].

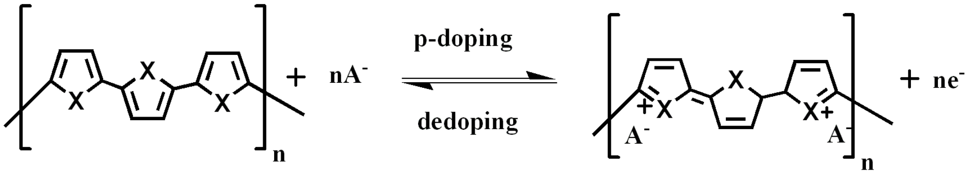


Figure 1.11 Caption reversible doping-dedoping process of polyheterocycles

Conducting polymers can be doped either by chemical or electrochemical means. Chemical doping is done by reacting the polymer with suitable oxidizing or reducing agents(doping agents or dopants) which can be neutral molecules, compounds or inorganic salts. Organic dopants or polymeric dopants and the nature of dopants affect the stability of conducting polymers[23]. Chemical doping can be performed either by reaction with $FeCl_3$ in aqueous solution or by reaction with gaseous species, such as AsF_3, F_3, or I_2 [24]. The chemical reaction describing the oxidative p-doping of a polymer with I_2 can be shown as[25]:

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

For n-type doping of a polymer to be performed with sodium naphthalide (Na^+Npt^-) in tetrahydrofuran solution:

$$(\pi\text{-polymer})_n + yn[\mathrm{Na}^+\ \text{Napthtalid}^-] \longrightarrow [(\mathrm{Na}^+)_y\ (\pi\text{-polymer})^{-y}]_n + yn(\text{Napthtalid})^0$$

where n is the number of polymers; and y is amount of charge transfer from a polymer chain to counter ions.

Chemical doping is an efficient and straightforward process, however it is typically difficult to control. Attempts to obtain intermediate doping levels often causes inhomogeneous doping. This problem was solved by electrochemical doping which is performed by biasing the polymer film in a suitable solution to an appropriate potential[26].

If a positive potential is applied to a conducting polymer, for instance to the one immobilized on an inert electrode, the dopant anion moves in from the solution into the CP towards delocalized charge site on the CP hence anionic doping occurs. This anionic doping is called p-type doping[27].

$$(\pi\text{-polymer})_n + ny[Li^+(BF_4)^-]_{soln} \longrightarrow [(\pi\text{-polymer})^{+y}(BF_4)_y^-]_n + ny\,Li\ (electrode)$$

Similarly, when a negative potential is applied in solution to a CP immobilized on an electrode, a cation would move in from the solution into the polymer. This would be called cationic or n-type doping.

$$(\pi\text{-polymer})_n + ny[Li(electrode)] \longrightarrow [(Li^+)_y(\pi\text{-polymer})^{-y}]_n + ny[Li^+(BF_4)^-]_{soln}$$

The doping level which affects the conductivitiy of the polymer is determined by the voltage between the reference electrode and the working electrode. Figure 1.12 illustrates the range of conductivities in CPs and their comparison with other materials. The magnitude of this change varies with doping levels, which can be controlled by the applied potential in the case of electrochemical doping[23].

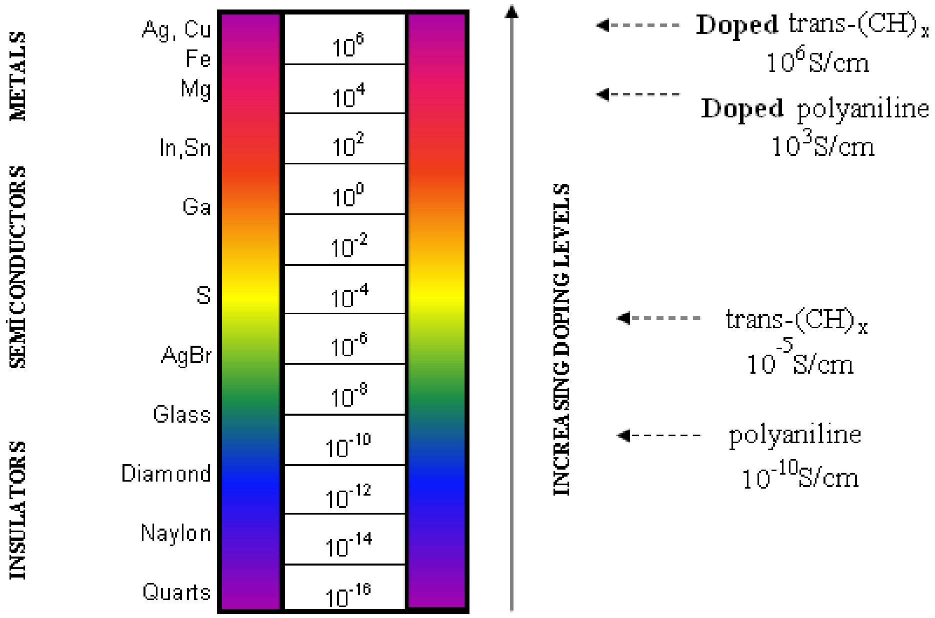


Figure 1.12 Conductivity of polymers

1.2.2.3 Hopping

Doping and hopping are the two important mechanisms to define the conduction process. Hopping can be simply described as intra-chain, inter-chain and interparticle motion of charges in a polymer matrix. The intra-chain movement is defined as motion of the charge carrier through a single chain and this motion depends on the efficient conjugation. On the other hand, the inter-chain movement which is hopping from one chain to another is determined by the piling of the polymer chains. The movement of electrical charges from particle to particle affects the mobility. As a consequence, the mobility and hence, conductivity depends on both a macroscopic (inter-particle) and microscopic (intra- and inter-chain) levels[28](Figure1.13).

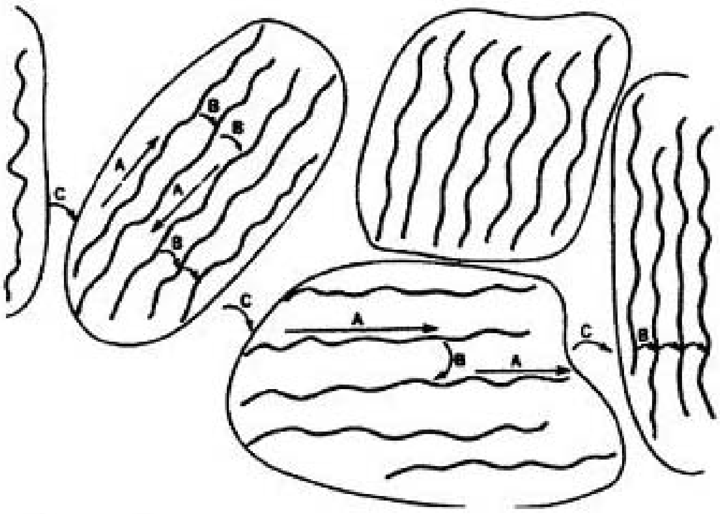


Figure 1.13 Conductivity network of a conducting polymer with A indicating intra-chain transport of charge, B indicating inter-chain transport, C indicating inter-particle transport, and arrows showing path of a charge carrier migrating through the material

1.3 Synthesis of Conducting Polymers

Conductive polymers are synthesized by photochemical polymerization, metathesis polymerization, plasma, pyrolysis, solid state polymerizations chemical or electrochemical polymerization techniques, however, chemical and electrochemical polymerization are the widely used ones[29].

1.3.1 Chemical Polymerization

The synthesis of pristine polymers which exhibit metallic character upon doping can be accomplished by two common chemical methods; the oxidation of monomers in the presence of an excess metal chloride ($FeCl_3$)

and catalytic Grignard coupling of 2,5-dihalothiophenes especially with nickel catalysts[30].

In the first method ammonium peroxidisulfate (APS), ferric ions, permanganate or bichromate anions, or hydrogen peroxide are used as the oxidizing agent, however, the most widely employed oxidizing agent has been $FeCl_3$[31]. These oxidants are able to produce chemically active cation radicals of the monomers in appropriate solution. After the cation radicals are formed by the attack of the oxidants, the cation radicals react with the monomer to form oligomers and then polymers. Chemical polymerization occurs in the bulk of the solution, and the resulting polymers precipitate as insoluble solids. However, conducting polymer can be obtained spontaneously on the surface of several materials, immersed into the solution [32]. In Figure 1.14 oxidative polymerization with $FeCl_3$ of a five membered heterocyclic compound is shown.

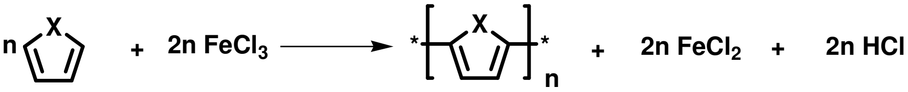


Figure 1.14 Oxidative chemical polymerization of heterocyclic compound in the presence of iron (III) chloride

As mentioned above in the second method metal-catalyzed coupling of 2,5-dihaloheterocycle take places. For instance, the controlled chemical synthesis of polyheterocycle is performed by metal-catalyzed coupling of 2,5-dibromoheterocycle (Figure 1.15). In order to replace either 2- or 5- bromo substituent with –MgBr, the dibromoheterocycle substrate is reacted with Mg in THF. Self coupling is then performed by Ni(bipy)Cl_2, finaly the condensation reactions occur without undesirable 2,3' and 2,4'-couplings[33].

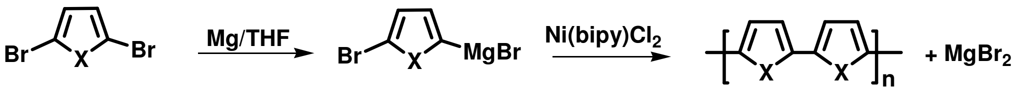


Figure 1.15 Reductive chemical polymerization of heterocyclic compound in the presence of Mg

Moreover, polymers synthesized by a chemical procedure are in their insulating form and they can be doped by chemical or electrochemical techniques to obtain their conducting form.

While chemical methods for the synthesis of conducting polymers have the advantages of speed, low cost, and freedom from the restrictions of electrodes, there are many problems that are inherent to chemical polymerizations. For instance, it is believed that the oxidized form of the synthesized polymer is more rigid than the neutral form and the oxidized form can precipitate from the polymerization medium which limits the degree of polymerization. If the strong oxidizing agents are used in this polymerization, over oxidation and decomposition can also occur. In contrast, polymers generated electrochemically are in their oxidized, conducting state. The thickness and morphology of the polymer film can be controlled during the electrolysis process[31].

1.3.2 Electrochemical Polymerization

Electrochemical polymerization have been carried out by two ways: anodic and cathodic routes [32] (Figure 1.16).

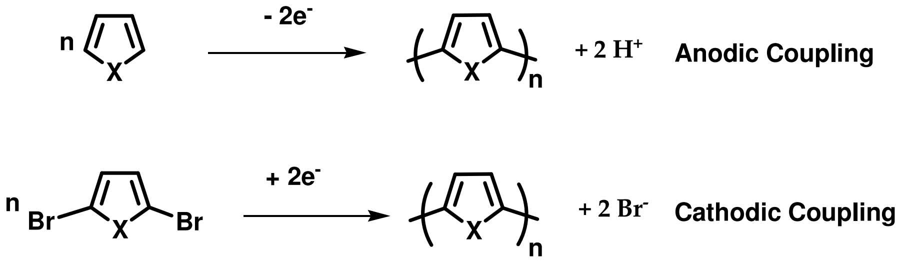


Figure 1.16 Electrochemical synthetic routes to poly(heterocyclic) compound

Anodic coupling includes oxidation of the monomer into a polymer by the elimination of proton. Anodic coupling is preferred due to the use of the unmodified monomer and easy doping process of the resultant polymer[34].

Oxidative electropolymerization has several advantages such as being simple, reproducible and selective. In addition, in electrochemical synthesis, polymers are deposited on the electrode surface as a film and the thickness of the film can be controlled by the deposition charge. Polymerization is performed at room temperature and to obtain homogenous polymers is possible. Furthermore, doping of the polymer can be accomplished simultaneously with the desired ion and copolymers can easily be obtained. When the electroreduction method is considered, it has a major disadvantage where the polymer is in its insulating form which results in the passivation of the electrode limiting the thickness of the polymer film[35].

1.3.2.1 Mechanism of Electrochemical Polymerization of Heterocyclics

The proposed mechanism for the electrochemical oxidative polymerization of a heterocycle is demonstrated in Figure 1.17. In the first step, the heterocyclic monomer is oxidized by the removal of one of the electron from the lone pair to produce a radical cation and resonance stabilization is the driving force for the removal of the electron as illustrated in Figures 1.17a and 1.17b . In the second step, coupling may proceed by two different ways: the combination of two radical cations to produce a dimeric heterocyclic dication (Figure 1.17c) and electrophilic addition of radical cation to heterocyclic monomer followed by oxidation to a dimeric heterocyclic dication (Figure 1.17d). In the third step, two protons are eliminated to get the aromatic character again (Figure 1.17e). The resultant dimer radical cation undergoes further coupling reactions, proton loss and re-aromatization again (Figure 1.17f). Electropolymerization proceeds through further electrochemical and chemical steps until the insoluble oligomers collected on the electrode surface[36].

When the oxidation of oligomer and monomer are compared, it is known that oligomer is more easily oxidized than the monomer. During the oxidation of polymer, electro deposition occurs at the same time.

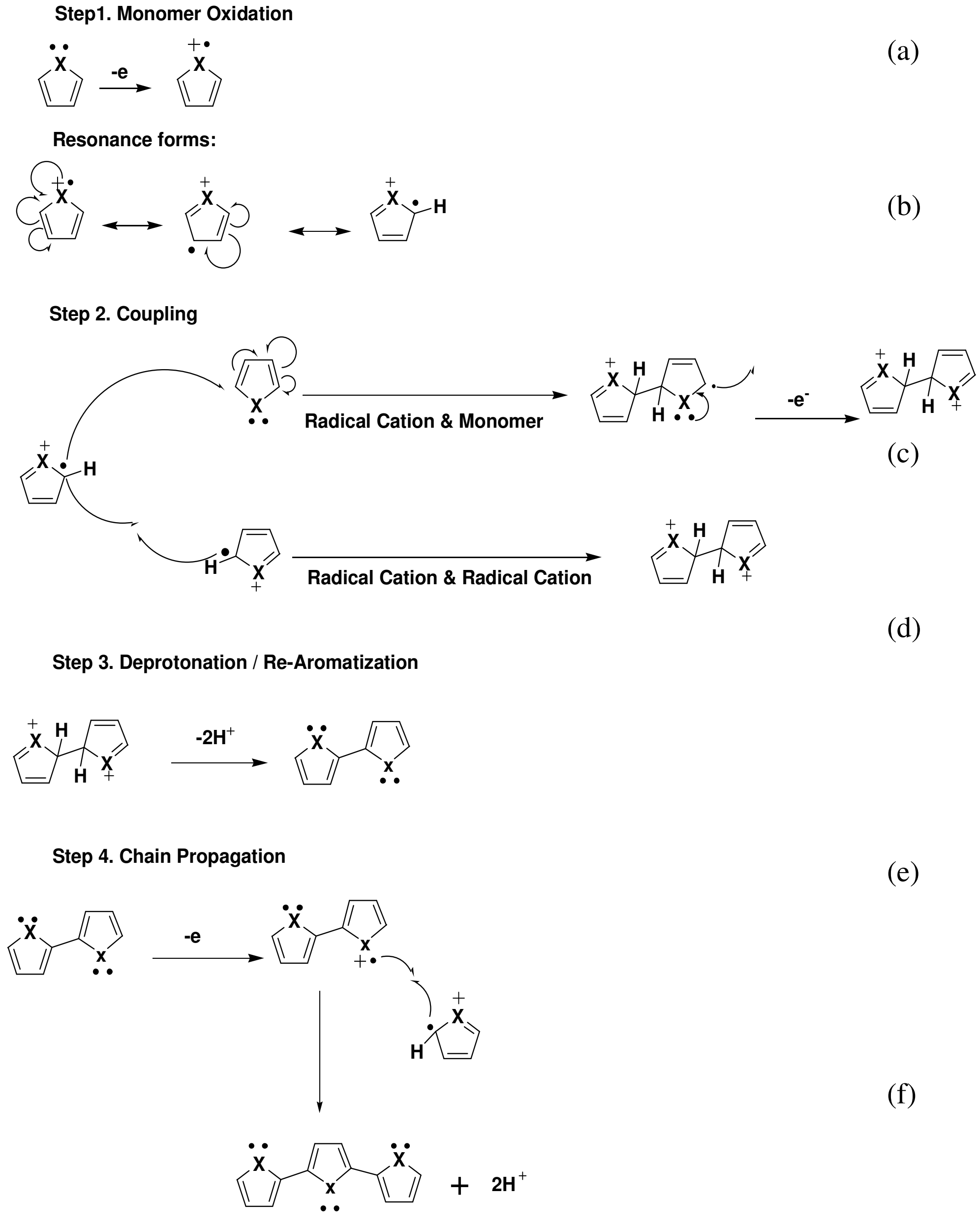


Figure 1.17 Proposed mechanism for electropolymerization of a five membered heterocyclic compound, where X = N-H, S, O, Se

As a result, p-doped conducting polymers which have delocalized π-band structure are obtained. Typically one electron is removed from the polymeric backbone for every three-four monomer units to form polar structures, responsible for inherent conductivity and the charge on the chain is balanced with counter anions (Figure 1.11)[37]. On the other hand, during the reduction process counter anions leave the polymer. Hence, while the oxidized form of polymer is conducting, the reduced form of polymer is insulating.

1.3.2.2 Electrolytic Medium

The properties of the conducting polymer film depends on the several parameters such as the type of solvent, electrolyte system, choice and concentration of monomer, electrodes, the amount of current or potential applied to the cell and the temperature maintained during the electrosynthesis[38].

The solvent used for the polymerization must have certain properties. The first one is that it must have a high dielectric constant to allow ionic conductivity. The second property is the stability of the solvent within the applied potential during the polymerization. Otherwise, the solvent redox process can interfere with the electrochemical process occurring during polymerization. The third one is that the nucleophilicity of the solvent must be low since oxidative electrochemical polymerization includes the formation of the radical cations and if the nucleophilicity in not low, solvent can easily react with the radicals formed during the polymerization process. For instance, polar aprotic solvents like acetonitrile or propylene carbonate have wide potential ranges, and high relative permittivities, which allow a good dissociation of the electrolyte and a good ionic conductivity[39]

Supporting electrolyte is used to provide electrical conductivity. During the polymerization, doping is performed by one of its ions. The type of the electrolyte directly affects the morphology and electrochemical properties of the conducting polymer. While the nature of the anion used plays an important role during the synthesis step, the nature of the cation has an important effect on the polymer film during the charge-discharge processes. Lithium or tetraalkyamonium salts of ClO_4^- or BF_4^- are the most used supporting electrolytes[40-41]

The monomer concentration is another important parameter for the polymerization. In order to prevent the competitive reactions of the radical cations and of the oxidized polymer with nucleophiles high monomer concentration (0.1 M or more) is used. Oxidation potential of monomer plays an important role on the probability of these reactions and a decrease in the oxidation potential of monomer results in a decrease in the probability of occurrence of these competition reactions. Therefore, even millimolar concentrations can be used to carry out an efficient polymerization[42].

The other parameter that affects the polymerization is the electrodes. In electrochemical polymerization working electrodes are made of inert materials such as platinum and gold or optically transparent electrodes such as indium-tin-oxide (ITO) coated glass. Saturated calomel electrode (SCE), Ag/Ag+ and Ag/AgCl electrodes are used as the reference electrodes.

1.4 Low Band Gap Polymer

In recent years the design and synthesis of low band gap polymers have been an area of intense interest since the band gap of polymer determines the intrinsic electrical and optical properties in doped state and their ability to be both p- and n- type doped[43],[44,45]. Moreover, lower oxidation potential engenders high quality polymer films during electropolymerization due to minimized harmful effects of high potentials such as degradation of the polymer films as they form[46]. Several ways have been developed to synthesize low band gap polymers[47]. One of the most successful approaches is the application of an alternating sequence of donor-acceptor(D-A) units in the π-conjugated polymer chain[48]. Alternating electron releasing and withdrawing units will consequently increase the HOMO level or lower the LUMO level which in return increase the possibility of having metallic conduction[49-50]. Figure1.18

includes representation of donor acceptor moieties.

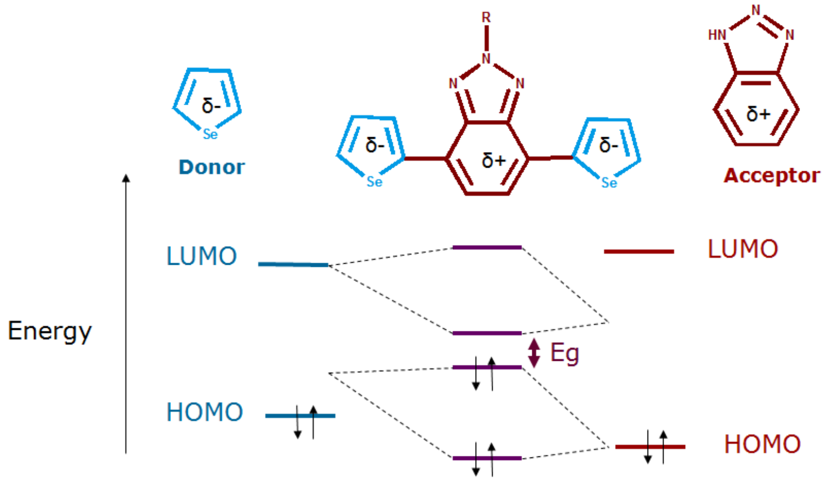


Figure 1.18 Hybridization of the energy levels of donor unit and acceptor unit leads to a donor-acceptor monomer

1.5 Application of Conducting Polymers

In recent years, application of conducting polymers has been studied extensively due to the high electronic conductivity, flexibility and the plasticity. When neutral form of these polymers is doped, they gain conductivity. The color change between these two states is observed, and due to that property they are widely used in electrochromic devices (ECDs) or smart windows. Other properties of the conducting polymers also enable their use as active components in batteries, biosensors, drug-releasing agent, gas separation membranes, electrochemical capacitors and electromagnetic radiation shielding transistors[51-52] (Figure 1.19).

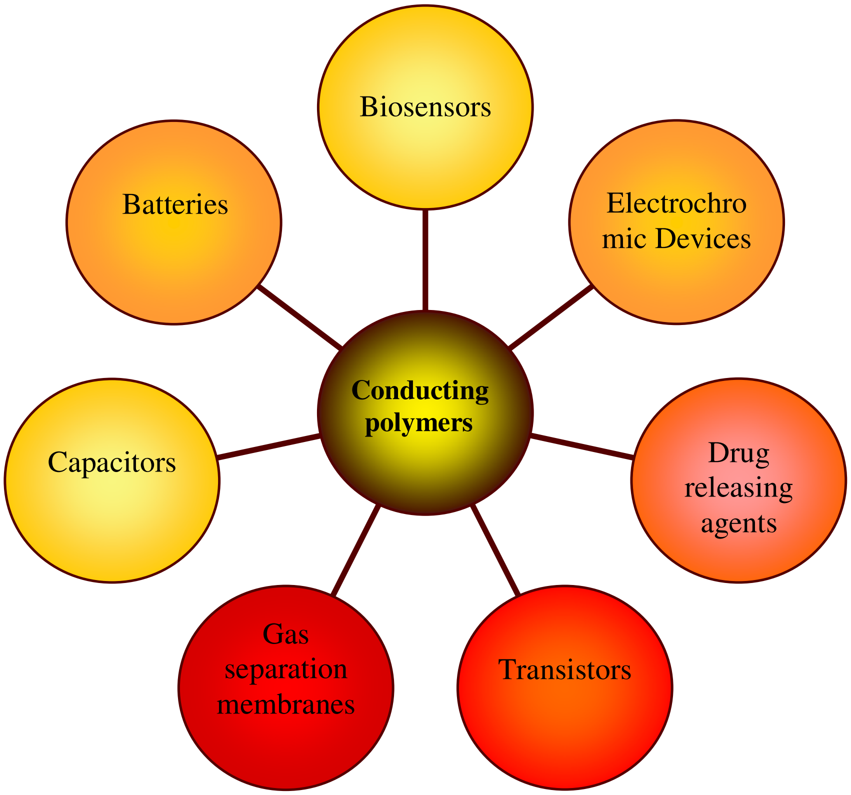


Figure 1.19 Applications of conducting polymers

1.6 Electrochromism

Electrochromism is the reversible and visible change in transmittance and /or reflectance that is associated with an electrochemically induced oxidation-reduction reaction. It is generated by the formation of the different visible region electronic absorption bands in the visible region. Switching between these bands bring about transparent and colored state. In some cases materials can have more than two electrochemically available redox states thus, material can exhibit several colors. This material is called as polyelectrochromic or said to possess multicolor-electrochromism[53-54]. Several materials exhibit electrochromism and there are some important groups of compounds having that properties. They can be classified as Prussian blue systems, viologens(1,1'-disubstituted-4,4'-bipyridinium salts), conducting polymers, transition metal and lanthanide coordination complexes and metallopolymers, and metal phthalocyanines[55].

1.6.1 Types of Electrochromic Materials

There are three main types of electrochromic materials in terms of their electronically accessible optical states. The first type contains materials that have at least one colored and one transparent (bleached) states. That kind of materials is useful for the construction of the Smart Windows and Optical Shutters. Metal oxides, viologens and polymers such as PEDOT are the examples of that type of materials. The second types of materials have two distinctive colored states. Although these materials do not have the transmissive state, they are utilized for display type applications where different colors are necessary in different redox states. Polythiophene is one of the examples of this type of materials which switches from red to blue upon oxidation. The third types of materials have more than two colored states depending on the redox state of the material[56].

1.6.2 Conducting Polymers as Electrochromic Materials

Electrochromism in conjugated polymers occurs through changes in the conjugated polymer's π electronic character accompanied by reversible insertion and extraction of ions through the polymer film upon electrochemical oxidation and reduction. In their neutral (insulating) states, these polymers have energy gap (Eg) between the valence band (HOMO) and the conducting band (LUMO) and exhibit semiconducting behaviour[54]. When the electrochemical doping occurs, the band structure of the neutral polymer is changed, hence, new intraband transitions having lower energy and charged carriers (polarons and bipolarons) which cause increase in conductivity and optical modulation are generated[57].

Figure1.20 shows the general features of the doping- induced electronic structure and the corresponding optical-absorption bands of nondegenerate ground-state polymers. In the neutral state the polymer shows only one transition from the valence band to the conduction band (π-π*). The energy level difference between these two levels is equal to the band gap (Eg) (Figure 1.20(a)).

When the system is lightly doped, the expected state is the polaron. This cause the formation of the state which has a higher energy than the valence band. In addition, lowering of the corresponding antibonding level in the conduction band is occurred so two new intragap states are formed. Normally four new transitions are expected, however two of them occur since the oscilator strength of transitions a and b are much greater than the transitions c and d (Figure 1.20 (b)). Hence, two low energy transitions is the significant property of the polaron [58]. In addition, bipolaron state is formed by further oxidation and only transitions from the valence band can occur if the bipolaron levels are not occupied. Transition e is much greater than f for bipolaron, therefore one low energy transition is expected[59].

When the polymer is doped, shift of the optical absorption occurs towards the higher wavelengths i.e. lower energy part of the spectrum. Band gap energy of the polymer determines the color change or the optical contrast between redox states. When Eg of the thin film of the polymer is greater than 3 eV (~400 nm) or equal to and less than 1.5 eV (~800 nm), they are colorless and transparent. When the Eg of the polymer between 1.5 eV and 3.0 eV it has a distinct color [34].

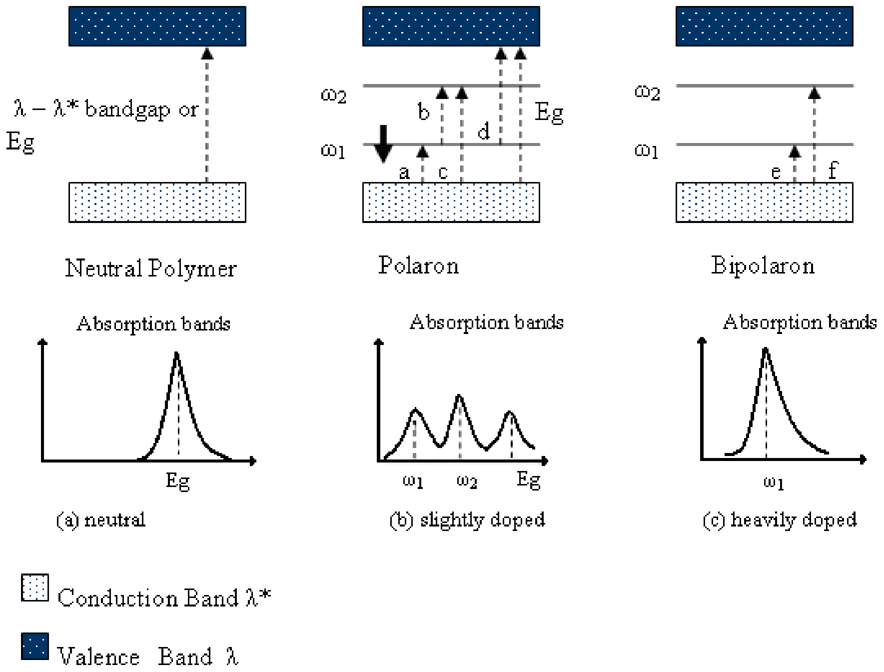


Figure 1.20 Polaron and bipolarons in non-degenerate ground state polymers: band diagrams for neutral (left), positive polaron (center) and positive bipolaron (right)

1.7 Experimental Methods for Studying Electrochromic Polymers

Conducting polymers are coated onto the working electrode. Working electrode substrates are generally made of glass or a flexible plastic, e.g. poly(ethylene terephthalate) (PET), sheet coated with an optically transparent electrically conducting film, e.g. tin doped indium oxide (ITO), antimony doped tin oxide, or fluorine-doped tin oxide[60]. After the material is collected onto the substrate, it is placed in a monomer free electrolyte, and spectroelectrochemistry, optical contrast, switching speed and colorimetry of the material are investigated.

1.7.1 Spectroelectrochemistry

In their neutral state, conducting polymers are in insulating regime and has a band gap, Eg, which is the energy between the valence band (HOMO) and the conduction band (LUMO). When the polymer is oxidized or doped, lower energy band transitions and charged carriers (polarons and bipolarons) are created, thus the band structure of the polymer is changed. As a result of this change, conductivity of the polymer is increased. Calculation of band gap energy, determination of π to π*, polaronic and bipolaronic transitions are performed with the help of the spectroelectrochemistry[56] .

1.7.2 Electrochromic Contrast

The most important factor utilized to evaluate an electrochromic material is electrochromic contrast. Electrochromic contrast is generally measured at a specified wavelength where the electrochromic material has the highest percent transmittance change (Δ%T) [56].

1.7.3 Switching Speed

The time required between the colored state and the transmittance state of the electrochromic material is the switching speed. This parameter is important for applications such as a dynamic display or a switchable mirror. There are several parameters that affect the switching speed of the electrochromic materials. This can be listed as the ionic conductivity of the electrolyte, accessibility of the ions to the electroactive site (ion diffusion in the thin films) magnitude of the applied potential, film thickness, and morphology of the thin film [56].

1.7.4 Stability

Electrochromic stability is usually related with the electrochemical stability since loss of the electrochromic contast is caused by the degradation of the active redox couple, and as a result this affects the performance of the a electrochromic material. There are some several degradation paths such as irreversible oxidation or the reduction at extreme potentials, loss of the electrode or the electrolyte, side reaction due to the presence of water or oxygen in the cell, and heat release due to the resistive parts in the system [56].

1.7.5 Colorimetry

The colorimetry analysis is based on a mathematical representation of a color, CIE (Commission Internationale de l'Eclairage) Yxy or L a b color space In the three- dimensional Yxy color space, Y(L) represents the luminance (brightness) of a color and the two dimensional xy (ab) chromaticity diagram represents the hue (dominant wavelength) and saturation level of white and/or black). The CIE system of colorimetry is based on a standard observer i.e. sense like a human eye. Thus, colorimetriy analysis is used to make a precise and accurate description of color. Figure 1.21 shows the CIE color space[61].

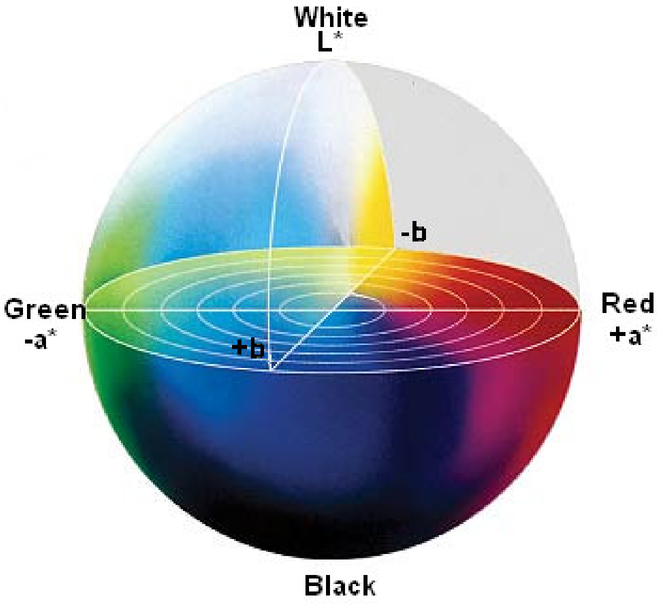


Figure 1.21 CIE Lab color space

1.8 Selenophene

The search for organic conducting polymers started in the 1970s and up to date largely focused on polyfuran[62], polythiophene[63], polypyrole[64] and their functional derivatives. Relatively little work was conducted on selenium-containing analogues [65]. In comparison, the differences in the chemistry of selenium versus sulfur includes the increased metallic character and decreased electronegativity of the heteroatom. Hence, selenophene has a lower oxidation potential and higher electron donating character than sulfur analog[66]. Lower oxidation potential engenders high quality polymer films during electropolymerization due to minimized harmful effects of high potentials such as degradation of the polymer films as they form[67].

1.9 Aims of the Work

Aims of the work are:

1.To synthesize a monomer containing electron-rich selenophene and electron deficient benzotriazole units where electron withdrawing imine (C=N) group exhibits a π-deficient nature[68]

2.Examine the electrochromic properties of the homopolymer and copolymer.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

1,2,3-Benzotriazole (Aldrich), bromododecane (Aldrich), potassium tert-butoxide (Aldrich), bromine (Aldrich), selenophene(Aldrich), tributyltin chloride(Aldrich), n-butyl lithium(Aldrich), dichlorobis(triphenyl phosphine)-palladium(II) (Aldrich), 3,4-ethylenedioxythiophene (EDOT) (Aldrich), $TBAPF_6$ (Aldrich) were used as received. The Solvents; dichloromethane(DCM) (Merck), and acetonitrile(ACN) (Merck), chloroform($CHCl_3$) (Riedel de Haën), Methanol (Merck), HBr (Merck), hexane (Riedel de Haën), petroleum ether(Merck) were used without further purification. Tetrahydrofuran(THF) (Merck) was distilled prior to use.

2.2 Equipment

2.2.1 Nuclear Magnetic Resonance (NMR) Spectrometer

^1H-NMR and ^{13}C-NMR spectra of the monomer was investigated 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 Mass Spectroscopy

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.

2.2.3 Potentiostat

A potentiostat is an electronic device that keeps voltage differences between the working and reference electrodes at a constant value despite the changes in the current passing through the electrolytic cell. Electrolysis was performed by using Wenking Pos 73 potentiostat was utilized to supply the polymerization potential. For determining the electrochromic properties of the polymers, Solatron 1285 and Volta Lab® PST050 potentiostats were used.

2.2.4 Cyclic voltammetry Cell

Potentiodynamic electrochemical polymerization and cyclic voltammetry studies were performed in a three-electrode cell consisting of Pt bead working electrode 1 cm in length, a platinum spiral counter electrode (3 cm), and a Ag wire as the pseudo reference electrode under argon atmosphere. The total volume of cell was about 15 mL(Figure 2.1).

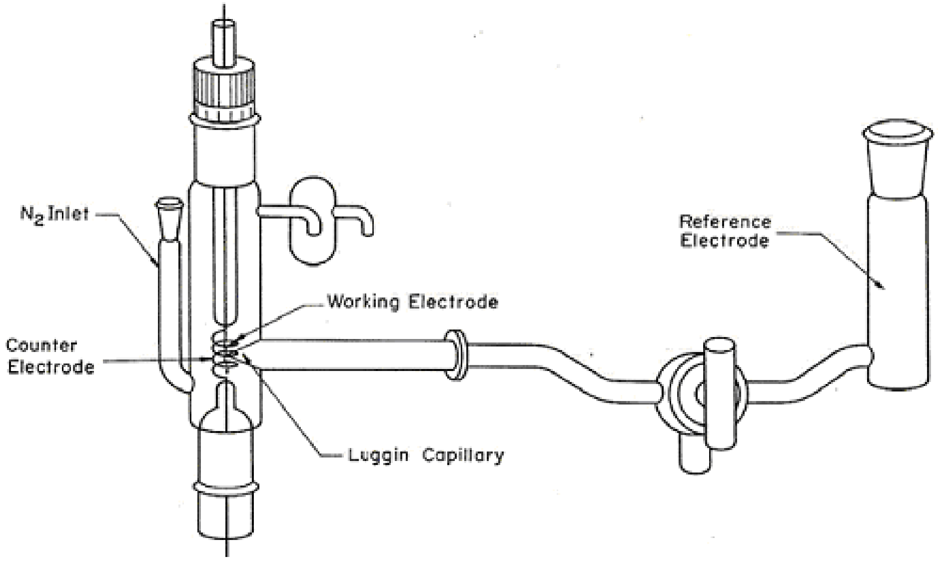


Figure 2.1 Cyclic voltammetry cell

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 measurements were made by a Konica Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE. During measurement, samples were placed in a light booth system where it was illuminated from behind by a D65 light source.

2.3 Procedure

2.3.1 Synthesis of monomer

2.3.1.1 Synthesis of 2-dodecylbenzotriazole

The synthesis of 2-dodecylbenzotriazole was performed according to methodology described in literature[69]. 1,2,3-benzotriazole (5.0g, 42mmol) was dissolved in methanol (50 mL) together with potassium tert-butoxide(5.0 g, 44 mmol). Bromododecane (12.2 g, 49mmol) was added drop wise to mixture. The reaction was refluxed for 12 h and monitored by TLC. After removal of the solvent by evaporation, the residue was washed with H_2O and extracted with $CHCl_3$. The organic extract was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on a SiO_2 column to obtain 2-dodecylbenzotriazole; Yield: 3.73 g, 31%, colorless oil, Rf (3:2 hexane: $CHCl_3$) 0.29

2.3.1.2 Synthesis of 4,7-dibromo-2-dodecylbenzotriazole

The synthesis of 4,7-dibromo-2-dodecylbenzotriazole was achieved as described in literature[69]. 2-Dodecylbenzotriazole (4.8g, 16.8mmol) and an aqueous HBr solution (5.8 M, 15 ml) were added to a flask, and the mixture was stirred for 1 h at 100°C. Bromine (5.9 g, 36 mmol) was added, and the mixture was stirred for 12 h at 135^{o}C and monitored by TLC. After the mixture was cooled to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic extract was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography on a SiO_2 column to obtain 4,7-dibromo-2-dodecylbenzotriazole; Yield: 4.0 g, 55%, white solid, Rf (1:1 hexane: $CHCl_3$) 0.33.

2.3.1.3 Synthesis of tributyl(2-selenophenyl)stannane

Stanylation of selenophene was achieved in one step according to a previously reported method[46]. Selenophene (1 g, 7.64 mmol) was dissolved in anhydrous THF (10 ml) in argon atmosphere. Solution was cooled to -30 ^{o}C in orthoxylene - liquid nitrogen 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. The organic extract was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residue was further purified by neutral alumina with petroleum ether as eluent to yield colorless oil (0.72 g, 45%).

2.3.1.4 Synthesis of 2-dodecyl-4,7-di(selenophen-2-yl)benzotriazole

4,7-Dibromo-2-dodecylbenzotriazole (445 mg, 1mmol), and tributyl(2-selenophenyl)stannane(1.68 g, 4mmol) were dissolved in anhydrous THF (100ml), the solution was purged with argon for 30 min. and dichlorobis(triphenyl phosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature under argon atmosphere. The mixture was refluxed for 18 hours under argon atmosphere. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on a SiO_2

column to obtain 2-dodecyl-4,7-di(selenophen-2-yl)benzotriazole; Yield: 78 mg 63%, yellow solid, Rf (2:1 hexane: $CHCl_3$) 0.45,

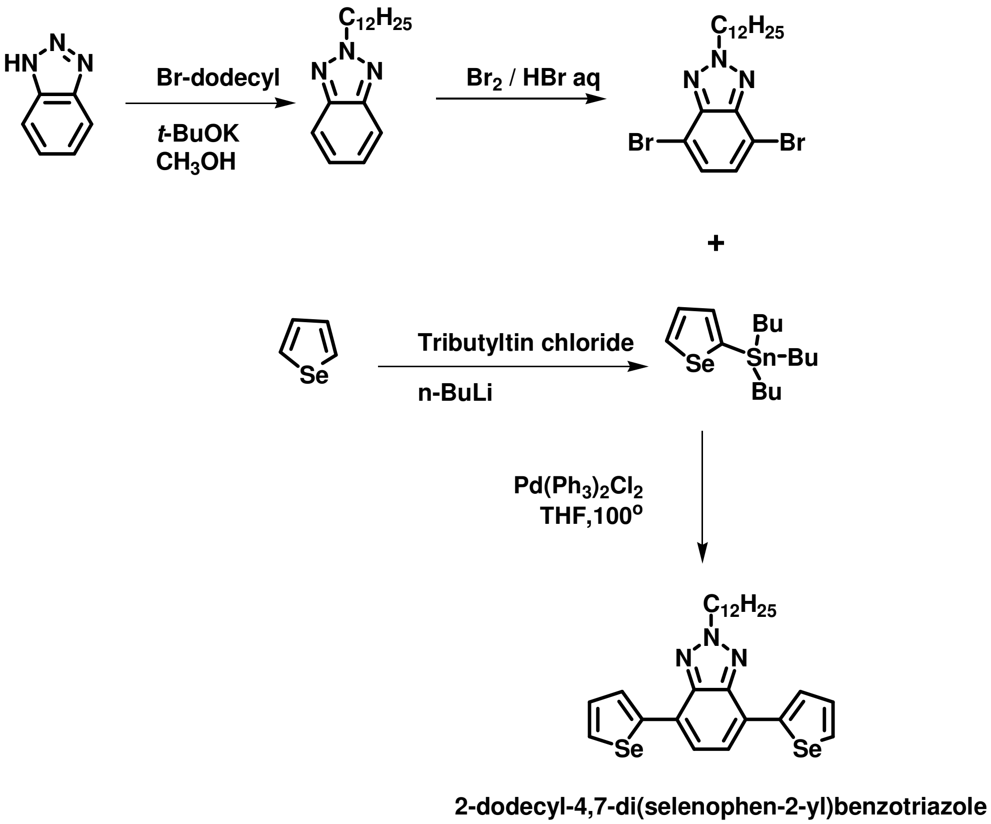


Figure 2.2 Synthetic route of 2-dodecyl-4,7-di(selenophen-2-yl)benzotriazole (SBT)

2.4 Synthesis of Conducting Polymers

2.4.1 Electrochemical Polymerization

2.4.1.1 Synthesis of Homopolymer of SBT

Polymerization of SBT was performed in the presence of 0.01M SBT, 0.1 M $TBAPF_6$ in acetonitrile/ dichloromethane(95/5 v/v) in a three-electrode cell equipped with Pt counter electrode and a Ag wire pseudo reference electrode. Polymer films were grafted on Pt foil or an ITO glass working electrode by potentiodynamic scanning wherein the potential was cycled between -0.4V and +1.4 V with 100 mV/sec scan rate. The free standing film was washed with ACN to remove unreacted monomer and excess $TBAPF_6$ after the electrolysis.

2.4.1.2 Synthesis of Copolymer of SBT with 3,4-Ethylenedioxythiophene (EDOT)

For the synthesis of conducting copolymer Poly(SBT-co-EDOT), EDOT was used as the comonomer (Figure 2.3). 1 mg of SBT was dissolved in 0.1 M TBAPC in 95:5 ACN:DCM and 0.2 μL of EDOT were introduced into a single compartment electrolysis cell. A three-electrode cell assembly was used where the working electrode was a platinum flake, the counter electrode was a platinum wire. Ag/Ag+ wire was used as the reference electrode.

The copolymer was potentiodynamically synthesized by sweeping the potential between -0.3V and +1.4 V with 500 mV/sec scan rate. The free standing film was washed with ACN in order to remove excess $TBAPF_6$ and unreacted monomer after the electrolysis.

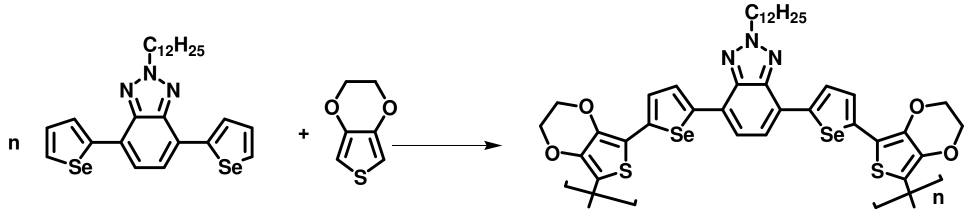


Figure 2.3 Copolymerization of SBT with EDOT

2.5 Characterization of Conducting Polymers

2.5.1 Cyclic Voltammetry (CV)

Cyclic voltammetry is a convenient technique, since it provides a fast and simple method for initial characterization of a redox-active system. In addition to providing an estimate of the redox potential, it can also provide information about the rate of electron transfer between the electrode and the analyte, and the stability of the analyte in the electrolyzed oxidation states (e.g., whether or not they undergo any chemical reaction).

In cyclic voltammetry, the potential is applied between the reference electrode and the working electrode. Complex wave form composed of two isosceles triangles (Figure 2.4) and the current is measured between the working electrode and the counter electrode. This data is then plotted as current (i) vs. potential (E) as shown in Figure 2.5.

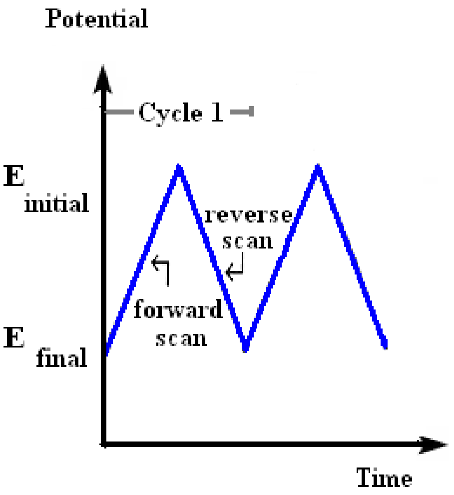


Figure 2.4 Triangular wave function

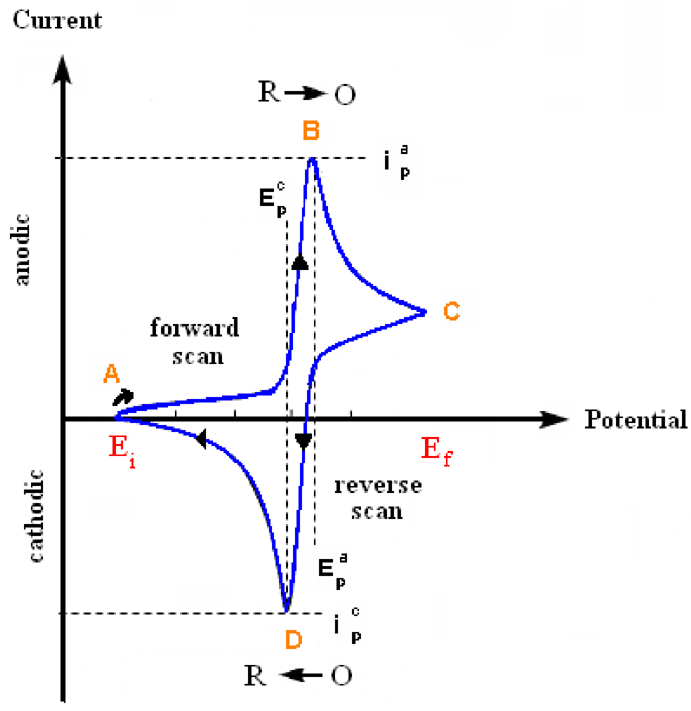


Figure 2.5 A cyclic voltammogram for a reversible redox reaction

The basic shape of the current response for a cyclic voltammetry experiment is shown above. At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidized form (point A). As the redox potential is approached, there is a net anodic current which increases exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidized to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface. The anodic current decrease rapidly (B-C) until the concentration of the monomer at the electrode surface approach zero, causing the current peak C, and then decay as the solution surrounding the electrode is depleted of monomer. Monomer oxidation is immediately followed by chemical coupling that affords oligomers in the vicinity of the electrode. Once these oligomers reach certain length, they precipitate onto electrode surface. At this point, a net reduction of O to R occurs which causes a cathodic current which eventually produces a peak shaped response (point D).

This oxidation peak will usually have a similar shape to the reduction peak. The peak current, ip, is described by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C V^{1/2}$$

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/cm3), D is the diffusion coefficient, and v is the scan rate of the applied potential.

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 grafted on ITO coated glass slides by potentiodynamic scanning wherein the potential was cycled between -0.4V and +1.4 V with 100 mV/sec scan rate. The free standing film was washed with ACN to remove unreacted monomer and excess $TBAPF_6$ after the electrolysis. In situ spectroelectrochemical studies of polymer films were investigated using a square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry in a monomer free solution.

Experimental setup of spectroelectrochemical analysis is shown in Figure 2.6. Polymer coated ITO-glass slides were used as the working electrode where platinum wire and Ag/Ag^+ were used as the counter electrode and reference electrodes respectively. Potentiostat was used to apply potential with stepwise increase. UV-VIS spectra were obtained at each potential.

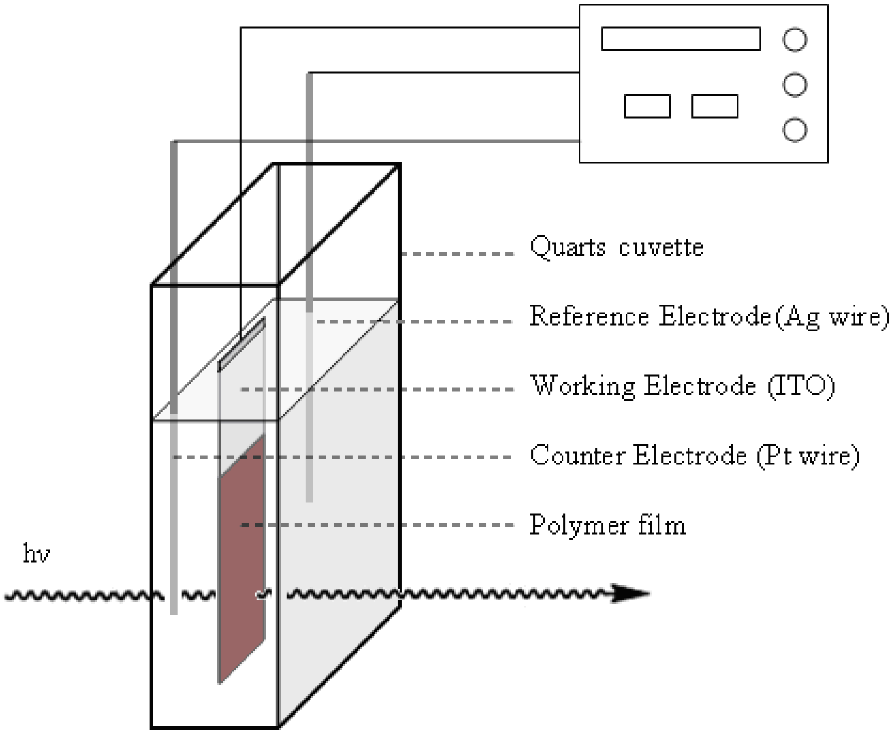


Figure 2.6 Spectroelectrochemical analysis experimental setup

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 2.7). Change in percent transmittance (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.

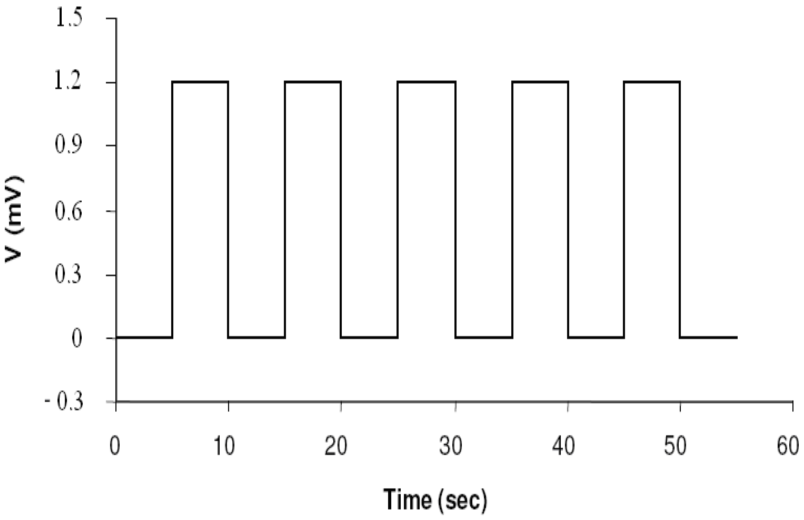


Figure 2.7 Square wave voltammetry

2.6.3 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 Monomer Synthesis

The synthesis of 2-dodecylbenzotriazole was performed according to methodology described in literature[70]. The mechanism for this reaction is shown in the following Figure 3.1. In the first step, benzotriazole, weak acid, can be converted to potassium benzotriazole by potassium tert-butoxide . The benzotriazole anion acts a strong nucleophile and it reacts with an bromododecile as alkyl halide by an SN2 mechanism to give an 2-dodecylbenzotriazole.

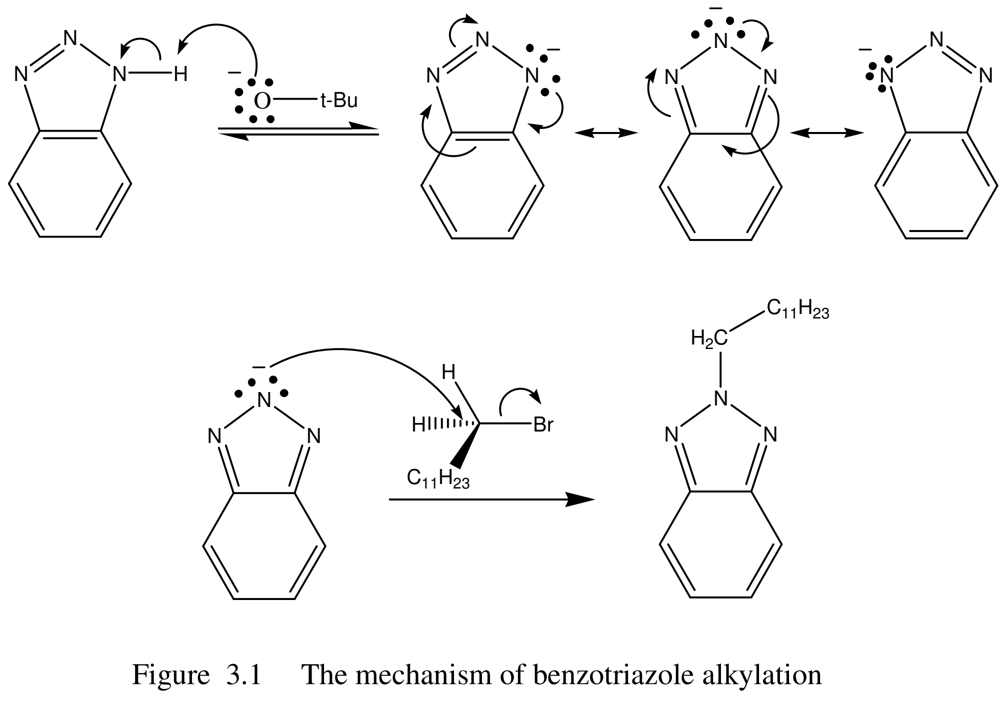


Figure 3.1 The mechanism of benzotriazole alkylation

Bromination of 2-dodecylbenzotriazole was carried out according to previously reported methods which is a type of electrophilic aromatic substitution[70]. In the first step of the reaction mechanism for this reaction, the electron-rich aromatic ring attacks to the electrophile to form positively-charged sigma complex which is unstable, owing both to the positive charge on the molecule and to the temporary loss of aromaticity. However, the sigma complex is partially stabilized by resonance, which allows the positive charge to be distributed over other carbon atoms. In the second stage of the reaction, a Lewis base donates electrons to the hydrogen atom at the point of electrophilic attack, and the electrons shared by the hydrogen return to the π system, restoring aromaticity and reaction is faster in polar solvents because solvation stabilizes the transition state (Figure 3.2).

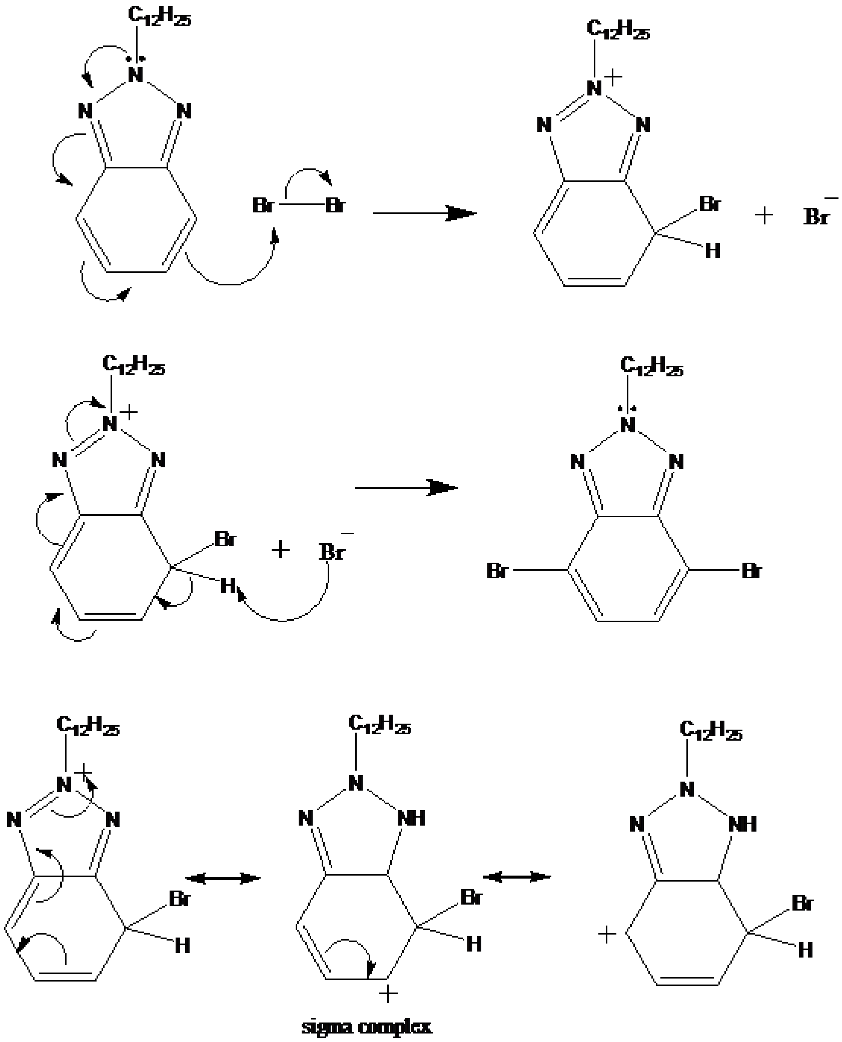


Figure 3.2 The mechanism of electrophilic aromatic substitution of 2-dodecylbenzotriazole

Monomer SBT was generated through Stille reaction of 4,7-dibromo-2-dodecylbenzotriazole with tributyl(2-selenophenyl)stannane and tributyl stannyl group was located on the electron rich, selenophene, unit whereas the bromo substituent was located on the electron-deficient, benzotriazole. The reaction mechanism involved the donation of electrons from the electron rich carbon-metal bond, tributyl(2-selenophenyl)stannane, to the π-electron acceptor, 4,7-dibromo-2-dodecylbenzotriazole, this resulted in the formation of symmetrical 2-dodecyl-4,7-di(selenophen-2-yl)benzotriazole (SBT)[71]. Palladium was used as a catalyzer and the mechanism for this reaction is shown in the following scheme (Figure 3.3)[72.]

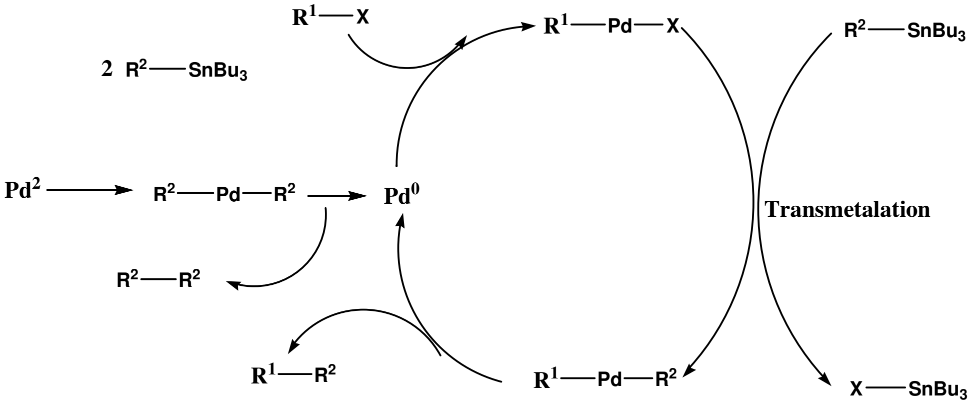


Figure 3.3 The mechanism of Stille Reaction

3.2 Monomer Characterization by ^{1}H-NMR and ^{13}C- NMR Spectroscopy

^{1}H-NMR (400MHz) and ^{13}C-NMR (100MHz) spectra of 2-dodecylbenzotriazole, 4,7-dibromo-2-dodecylbenzotriazole and SBT were investigated in $CDCl_3$. Tetramethylsilane (TMS) was used as the internal standard and chemical shifts (δ) are given relative to TMS.

^{1}H-NMR spectrum of 2-dodecylbenzotriazole (Figure 3.4): $C_{18}H_{29}N_3$, δ ($CDCl_3$): 7.76 (2H, m, benzotriazolyl-Hb), 7.26 (2H, m, benzotriazolyl-Ha), 4.62 (2H, t, J=7.1Hz, dodecanyl-Hc), 2.22 (2H, t, J=6.5Hz, dodecanyl-Hd), 1.25-1.15 (18H, m, dodecanyl-He), 0.78 (3H, t, J=6.0 Hz, dodecanyl-Hf) ^{13}C-NMR spectrum of 2-dodecylbenzotriazole (Figure 3.5): ^{13}C-NMR (δ,ppm):

144.3, 126.1, 117.9, 56.6, 31.8, 30.0, 29.5, 29.4, 29.3, 29.3, 29.0, 26.5, 22.6, 14.0.

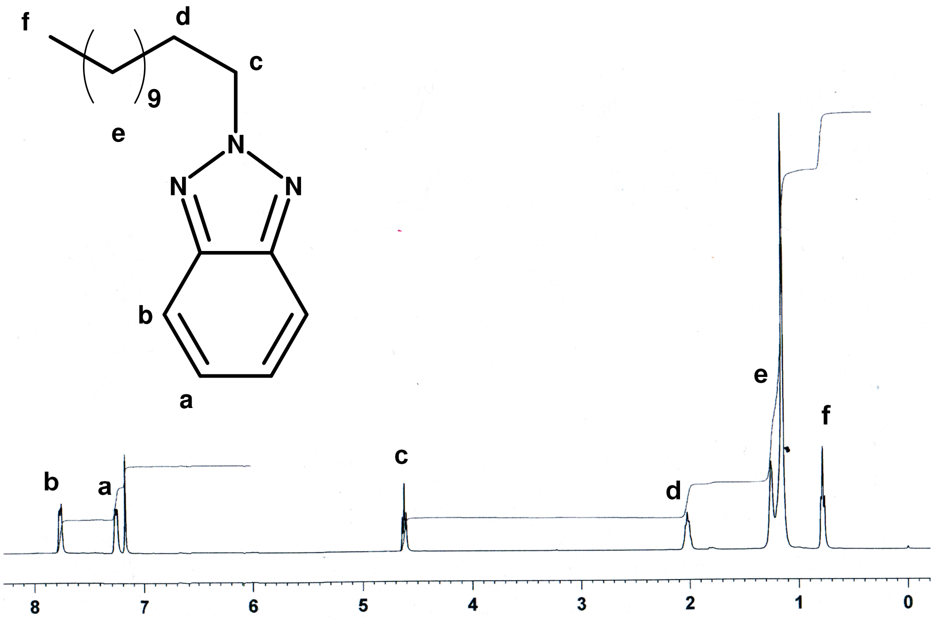


Figure 3.4 ^{1}H-NMR spectrum of 2-dodecylbenzotriazole

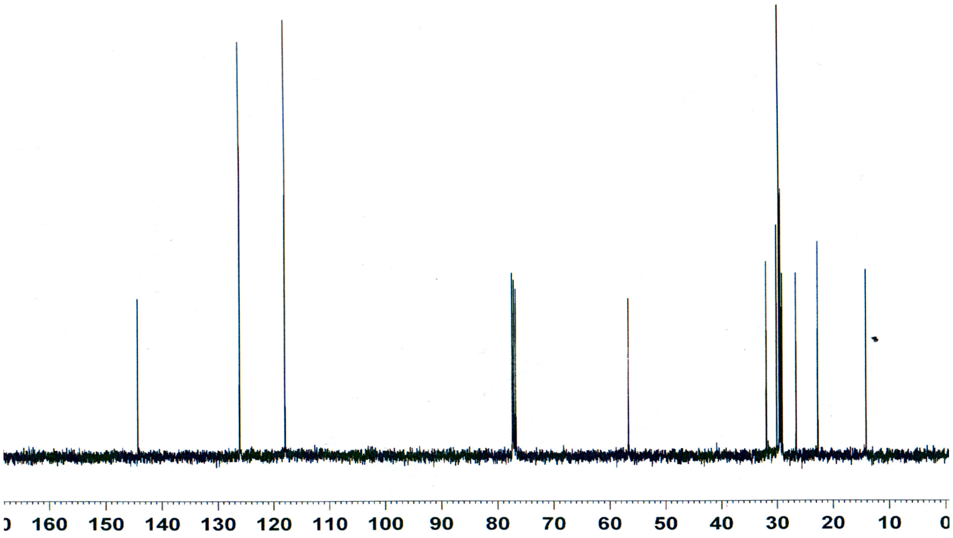


Figure 3.5 ^{13}C-NMR spectrum of 2-dodecylbenzotriazole

^{1}H-NMR spectrum of 4,7-dibromo-2-dodecylbenzotriazole(Figure 3.6): $C_{18}H_{27}Br_2N_3$, δ ($CDCl_3$): 7.36 (2H, s, benzotriazolyl-Ha), 4.70 (2H, t, J=7.0 Hz, dodecanyl-Hb), 2.00 (2H, m, dodecanyl-Hc), 1.28-1.12 (18H, m, dodecanyl-Hd), 0.80 (3H, t, J=6.9 Hz, dodecanyl-He). ^{13}C-NMR spectrum of 4,7-dibromo-2-dodecylbenzotriazole(Figure 3.7): ^{13}C-NMR (δ,ppm): 143.7, 129.4, 109.9, 57.4, 31.8, 30.1, 29.5, 29.4, 29.3, 28.9, 26.4, 22.6, 14.0, 0.99.

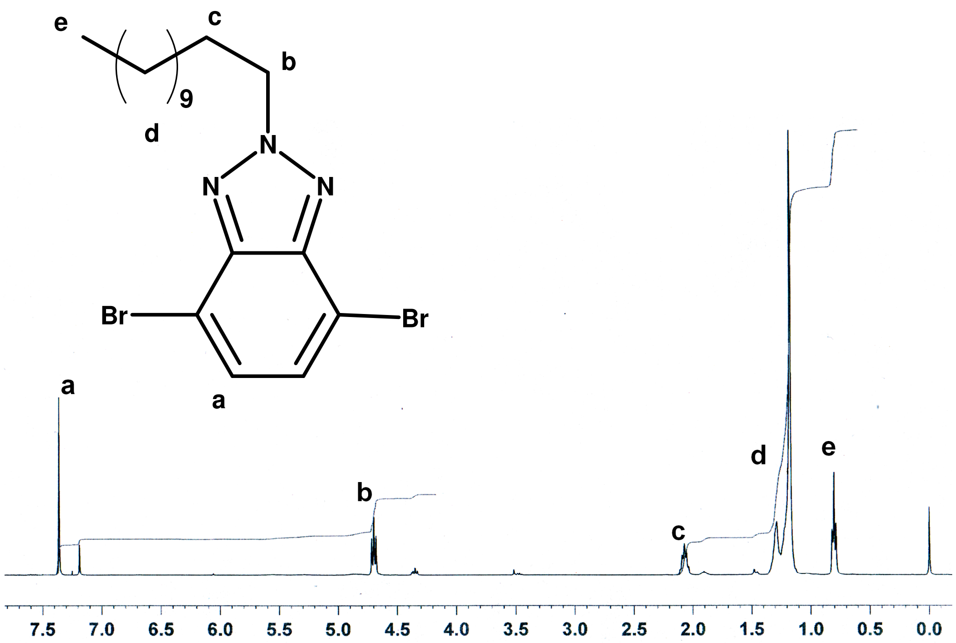


Figure 3.6 ^{1}H-NMR spectrum of 4,7-dibromo-2-dodecylbenzotriazole

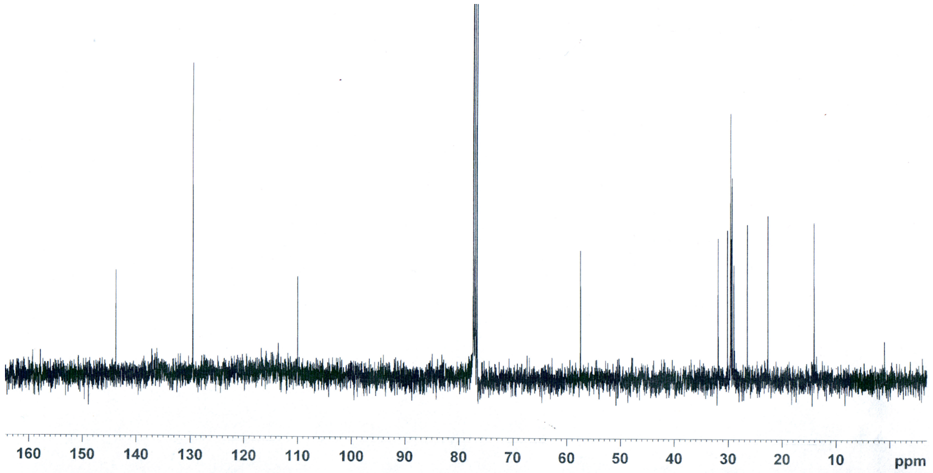


Figure 3.7 ^{13}C-NMR spectrum of 4,7-dibromo-2-dodecylbenzotriazole

^{1}H-NMR spectrum of SBT (Figure 3.8): $C_{26}H_{33}N_3Se_2$, δ_H ($CDCl_3$): δ 8.12 (2H, d, J=3.6 Hz, selenophenyl-Ha), 8.01 (2H, d, J=5.5 Hz, selenophenyl-Hc), 7.52 (2H, s, benzotriazolyl-Hd), 7.35 (2H, d-d, J=3.8-1.5 Hz, selenophenyl-Hb), 4.74 (2H, t, J=7.1 Hz, dodecanyl-He), 2.16-2.09 (2H, m, dodecanyl-Hf), 1.37-1.18 (18H, m, dodecanyl-Hh), 0.81 (3H, t, J=6.9 Hz, dodecanyl-Hg).^{13}C-NMR spectrum of the SBT (Figure 3.9): ^{13}C-NMR (δ,ppm): 143.3, 140.1, 129.5, 128.6, 126.3, 123.6, 121.1, 55.0, 30.0, 28.1, 27.7, 27.7, 27.6, 27.4, 27.2, 24.7, 20.8, 12.2;

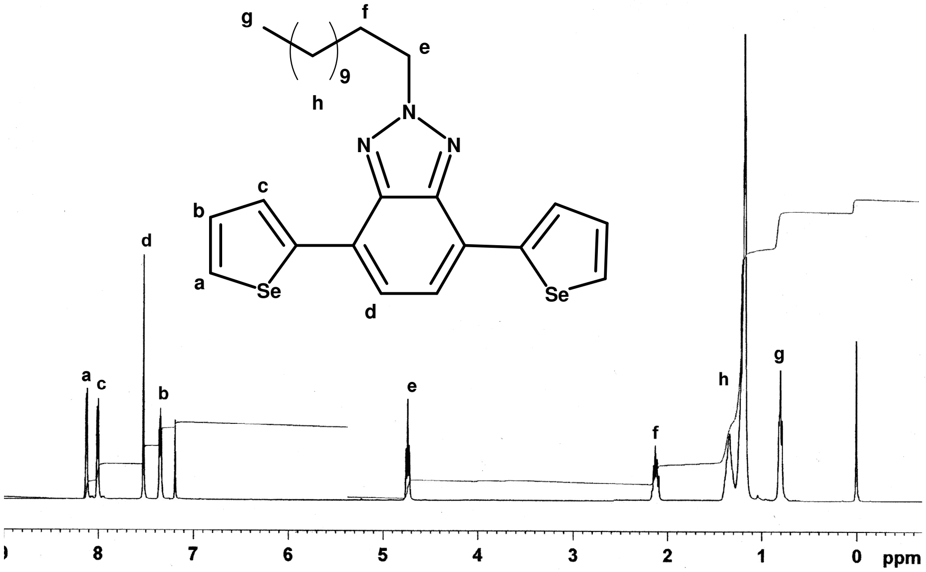


Figure 3.8 ^{1}H-NMR spectrum of SBT

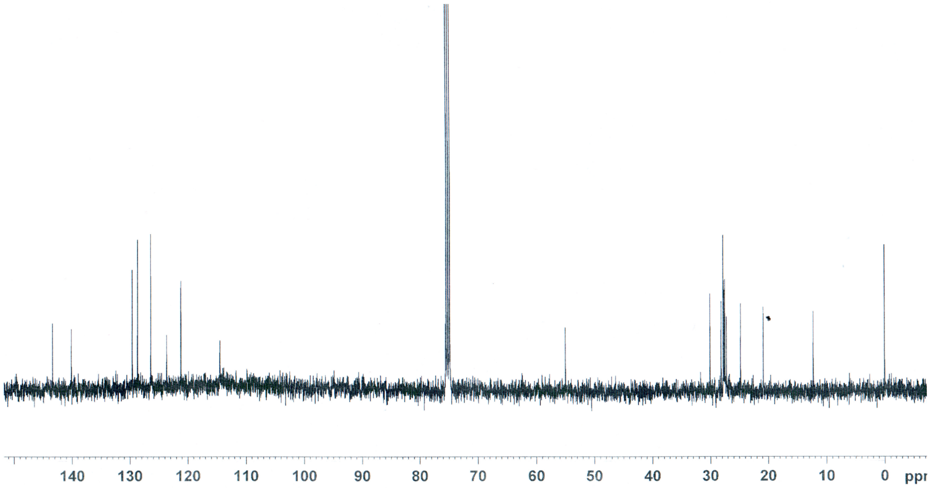


Figure 3.9 ^{13}C-NMR spectrum of SBT

3.4 Monomer Characterization by Mass Spectroscopy

Mass spectroscopy analysis determined molecular weight of SBT as 545.1 g/mole where theoretical calculation gives 545.5 g/mole which supports proposed structure(Figure 3.10).

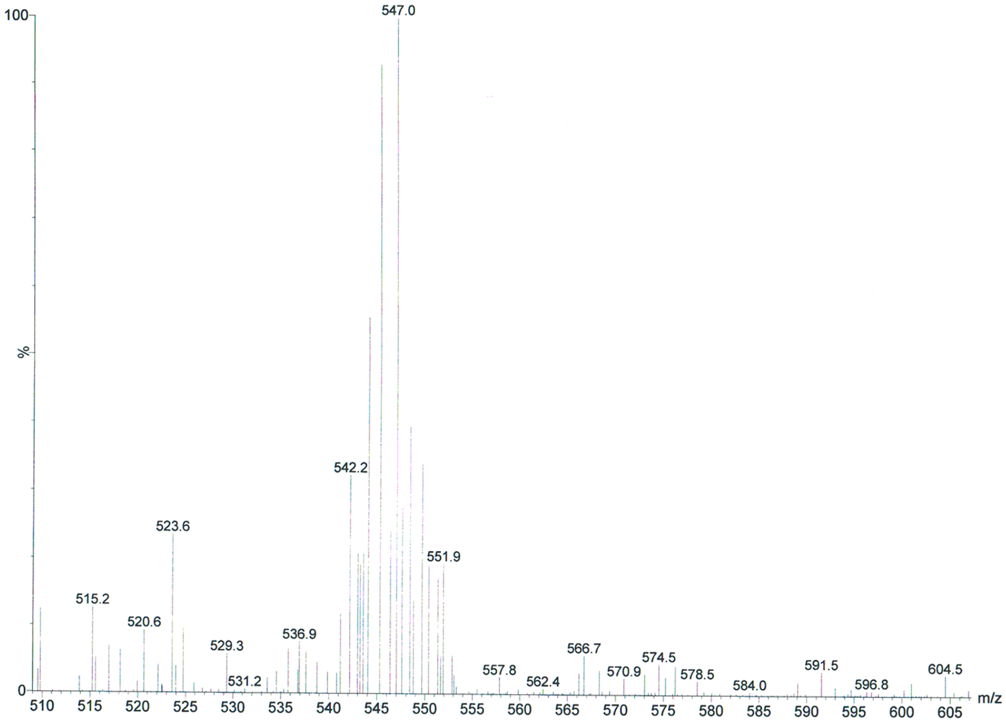


Figure 3.10 Mass spectrum of SBT

3.5 Cyclic Voltammograms

With cyclic voltammetry the accessibility of the redox sites of the polymer can be investigated. For this purpose the electrochemical behavior of SBT (0.01M) was examined in acetonitrile dichloromethane (95:5) system and during the measurements 0.1M $TBAPF_6$ was used as the supporting electrolyte. Figure 3.11 shows the first 8 scans for the anodic electropolymerization of a solution of SBT on an ITO electrode at 100 mV/s where the potential was scanned between -0.4 and 1.4 V. An irreversible oxidation peak of monomer was observed at 1.2 V and its intensity increase on consecutive cycles. As seen in the Figure 3.11 during the consecutive cycles poly(SBT) revealed an oxidation peak at 1.0 V and a reduction peak at 0.8 V and also a gradual increase was observed in the current density. Free standing conducting polymer films were synthesized and the film was washed with ACN several times in order to remove the unreacted monomer.

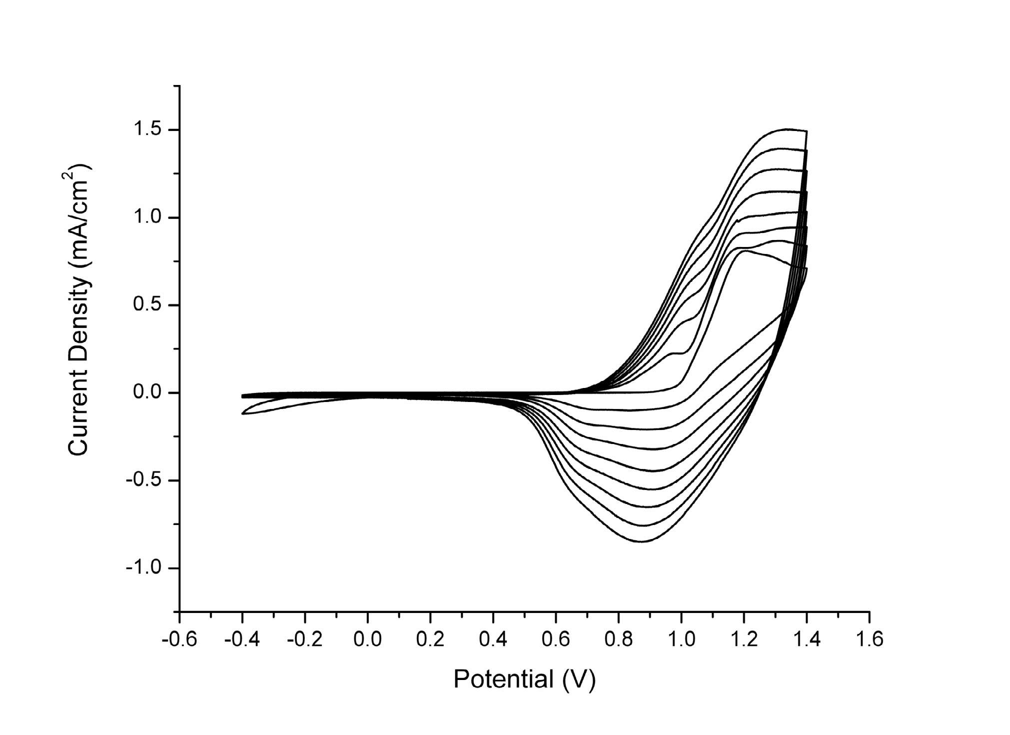


Figure 3.11 Cyclic Voltammogram of Poly(SBT)

The n-doping property of the polymer was investigated using CV in a monomer free solution. The polymer deposited on ITO can reversibly be reduced and oxidized between -1.9V and +1.4 V versus Ag wire pseudo-reference electrode in $TBAPF_6$/ACN. The cyclic voltammogram of poly(SBT) is shown in Figure 3.12. A redox couple with an oxidation potential of -1.3 and a reduction potential of -1.7 V was observed which are important indications for an n-dopable character of the film. Further supporting data on n-doping properties of the polymer was provided with spectroelectrochemistry. The scan rate dependence of the polymer films were also investigated. The current was found to scale proportionally with the scan rate indicating the adherence of the polymers to the electroactive surface and charge transfer process was not dominated by diffusion effects[73].

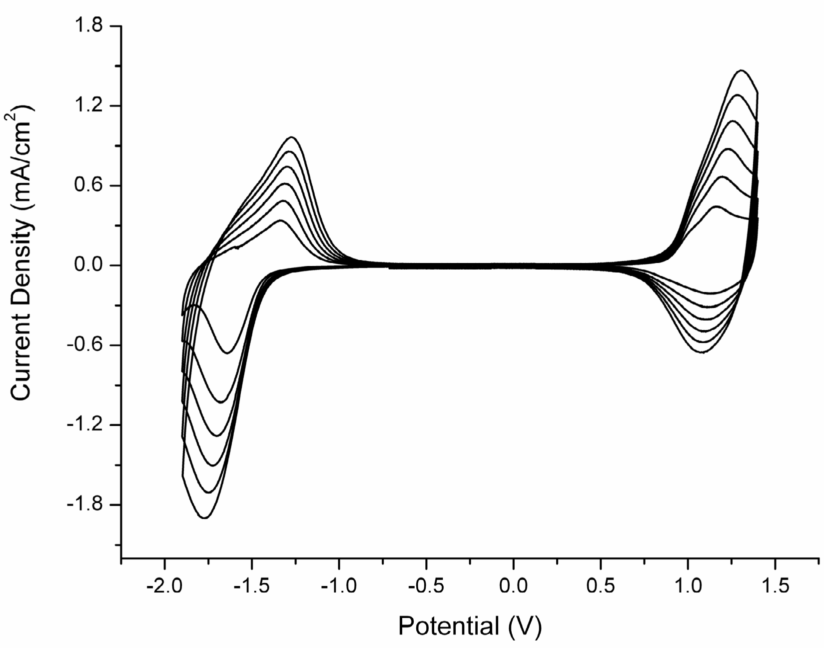


Figure 3.12 Scan rate dependence of poly(SBT)

For the synthesis of conducting copolymer, poly(SBT-co-EDOT), EDOT was used as the comonomer. Copolymer was synthesized with a [EDOT]/[SBT] molar ratios of 2. A similar oxidative electrochemical copolymerization procedure was carried out in the presence $TBAPF_6$ in acetonitrile /dichloromethane (95/5 v/v) via cyclic voltammetry at a scan rate of 100mV/s. The cyclic voltammogram of copolymer is shown in Figure 3.13. A nonwell-defined redox couple with an oxidation of 0.74 V and a reduction potentials of 0.54 V vs same reference electrode were observed which demonstrate that there was a drastic change in the voltammogram, the oxidation potential of the material were different than those of SBT and pristine EDOT, which , in fact, could be interpreted as the formation of copolymer.

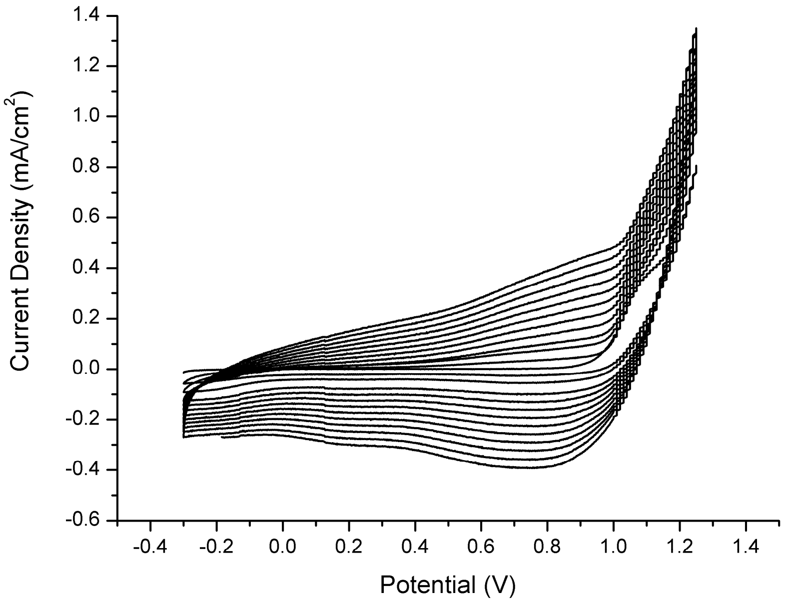


Figure 3.13 Cyclic voltammogram of Poly(SBT-co-EDOT)

3.6 Investigation of Electrochromic Properties of Polymers

3.6.1 Spectroelectrochemistry

In order to investigate the spectroelectrochemistry of the poly(SBT), ITO-coated glass was used to deposit the polymer film. Potentiostatic electrochemical polymerization of SBT (0.01M) was carried out in the presence of 0.1 M $TBAPF_6$ / 95:5 ACN:DCM. After deposition, polymer film coated ITO was inverstigated by UV-Vis Spectroscopy in the monomer free electrolytic system by switching the applied potential between 0 V and 1.4 V with incremental increase. Figure 3.14 shows the spectroelectrochemistry of poly(SBT), monitored while the polymer was sequentially stepped between its fully oxidized and fully reduced forms. Dedoped polymer have two distinct absorption bands, as expected from a donor acceptor type polymer[74], centered at 483 nm and 511nm. The band gap, onset of the π→π* transition for the conjugated backbone, of the neutral polymer is calculated 1.67eV at 511nm. Upon comparisons of neutral dedoped polyselenophene film with poly(SBT), poly(SBT) exhibits lower optical band gap than the other selenophene-containing polymers reported so far[75].

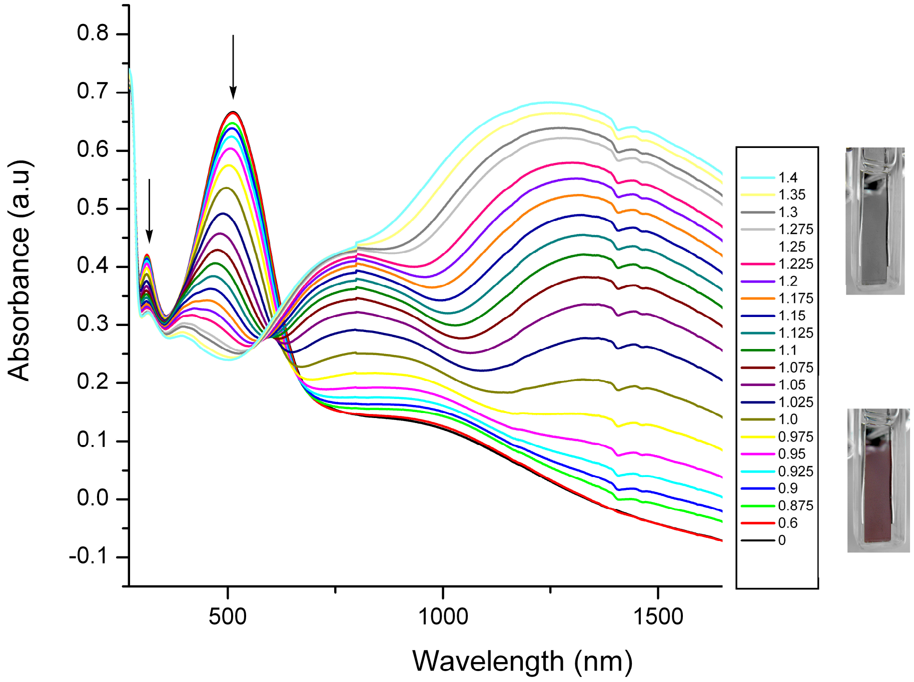


Figure 3.14 Spectroelectrochemical spectra of poly(SBT) with applied potentials between 0 V and + 1.4 V in ACN/ TBAPF$_6$ (0.1 M)

As shown in Figure 3.15 when the applied potential was stepwise, evolution of polaron charge carriers signatured by peaks at around 800 nm and 1200 nm are observed because transition occured through both path a and path b. Also a decrease was observed in the intensity of the π-π* transitions. When further oxidation was performed, absorbtion at longer wavelengths (1200nm) became more intense due to the formation of bipolaron charge carriers.

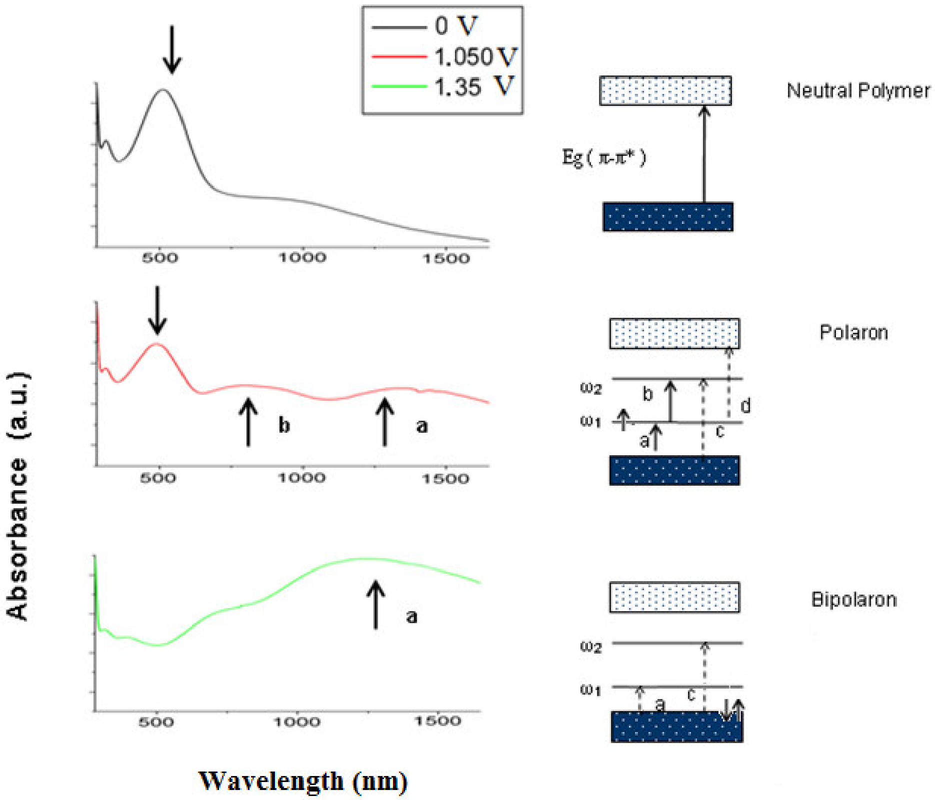


Figure 3.15 Polaron and bipolarons in non-degenerate ground state poly(SBT): band diagrams for (a) neutral , (b) polaron and (c) bipolaron

Moreover, Spectroelectroelectrochemistry studies were performed in order to prove the n-type doping process of a conjugated polymer system since formation of a redox couple at a negative potential in cyclic volatammetry is not adequate information. A drastic change in the NIR region was known to be one of the most important proofs of true n-type doping process[76]. As shown in Figure 3.16, the optical spectrum of poly(SBT) reveals the changes associated with a transmissive light blue color. Hence, it can be concluded that poly(SBT) is a true n-type dopable polymer[77].

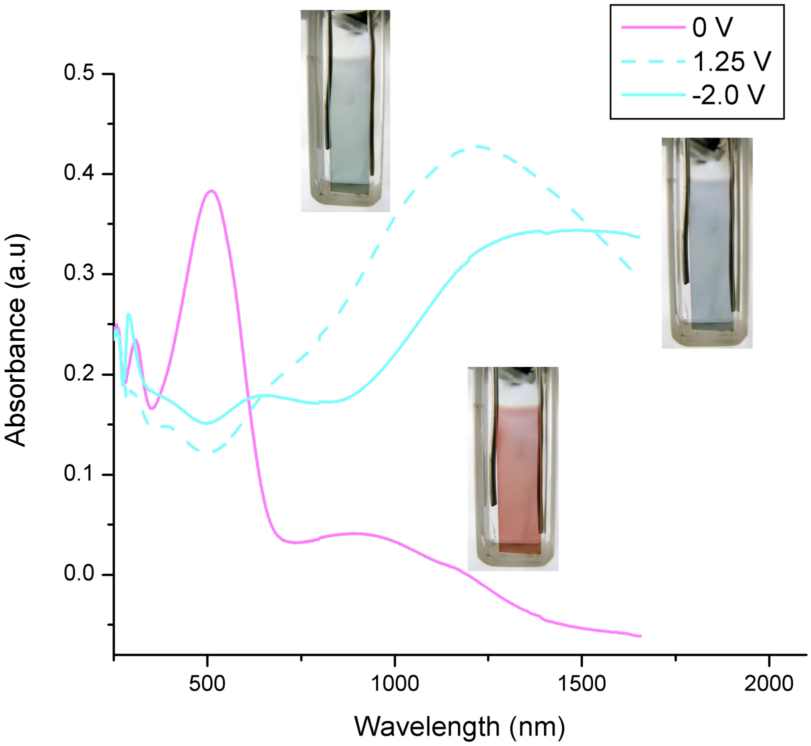


Figure 3.16 Spectroelectrochemical spectra of poly(SBT) at applied potentials of (a) 1.25 V (b) 0V (c)-2.0 V in ACN/ $TBAPF_6$ (0.1 M)

In order to investigate the spectroelectrochemistry of the copolymer of SBT with EDOT, ITO-coated glass was used to deposit the copolymer film. Potentiostatic electrochemical polymerization of SBT with EDOT was carried out in the presence of 0.1 M TBAPF$_6$ / 95:5 ACN:DCM. Spectroelectrohemical properties were studied in the monomer free solution. The λ_{max} value for the π-π^* transitions in the neutral state of copolymer was found to be 560 nm. This gave the copolymer a purple color which is significantly different from the pure poly(EDOT) and poly(SBT). The electronic band gap was found to be 1.54 eV. When the applied voltage increased, the evolution of a new absorption band at 860 nm was obtained due to evolution of charge carriers, polarons (Figure3.17). In addition, a gradual decrease in the intensity of the bands at λ_{max} was observed. At 1.05 V copolymer was fully oxidized and the color of the copolymer turned to light blue with an absorption beyond 1400 nm (bipolaron).

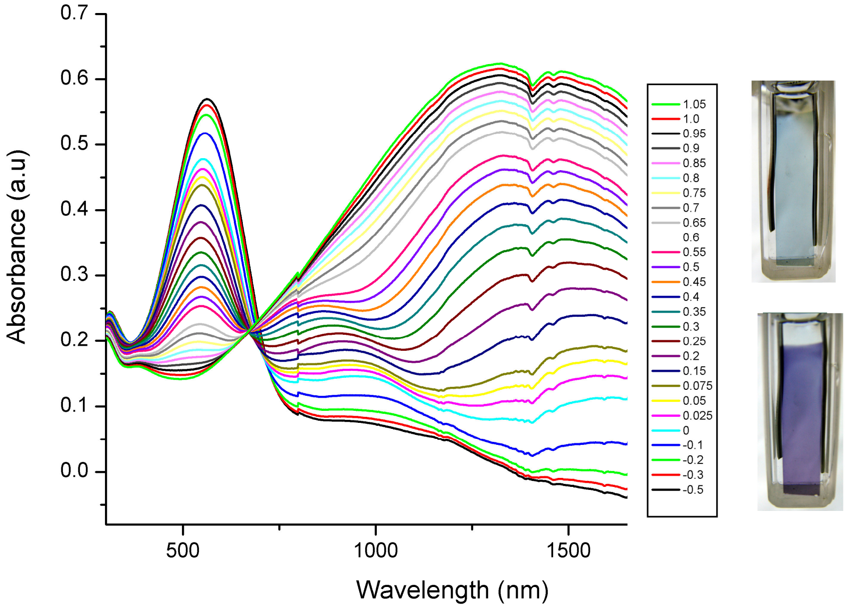


Figure 3.17 Spectroelectrochemical spectra of poly(SBT-co-EDOT) with applied potentials between -0.5 V and +1.05 V in ACN/TBAPF$_6$ (0.1 M)

3.6.2 Electrochromic Switching

The optical switching studies were investigated using a square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry in a monomer free solution. The percent transmittance versus time was monitored at λ_{max} while the polymer on ITO coated glass slides was repeatly switched between the reduced (0V) and oxidized (1.2V) states for a residence time of 5s. The optical contrast was measured as the difference in % transmittance between neutral and oxidized forms and noted as ΔT%. Figure 3.18 reveals the electrochromic switching properties of poly(SBT). The optical contrast for poly(SBT) is 32% at 511 nm and 56 % at 1200 nm.

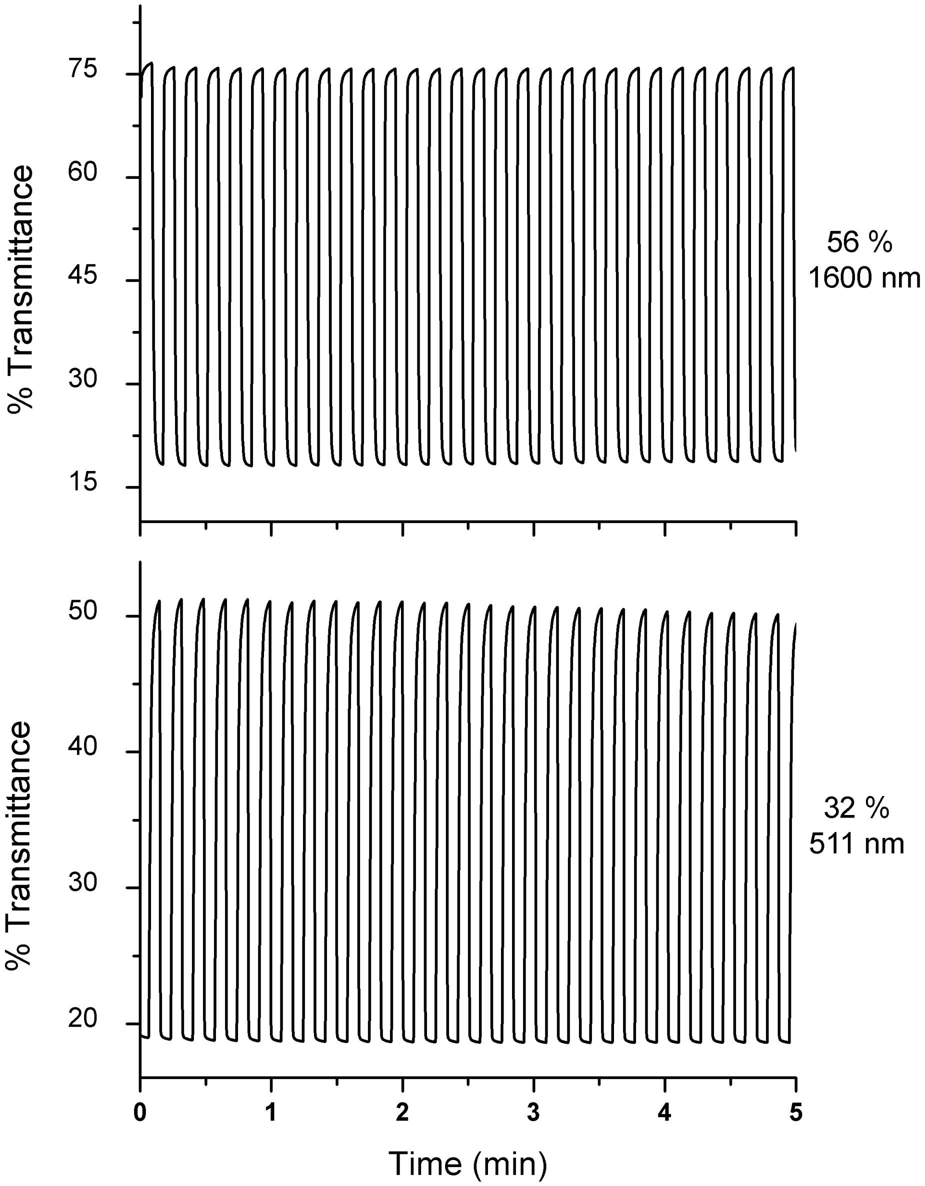


Figure 3.18 Electrochromic switching, optical absorbance monitored for poly(SBT) in the presence of 0.1 M $TBAPF_6$/ACN

Switching time is an important parameter for a polymer since it indicates how fast ions move to into the polymer chains during doping process[78.] The switching time was determined by monitoring the absorption intensity at 511nm and 1200 nm while switching the applied voltage between 0V and 1.2V . The homopolymer revealed switching times of 2.4s and 0.4s at 511 nm and 1200nm respectively. Morever, copolymerization studies show that copolymer has fast switching times (0.48, 0.42s) and high optical contasts (42%, 68%) at 560 nm and 1400nm respectively (Figure3.19). As evident from the results of the kinetic studies, copolymer exhibited a better optical contrast than the homopolymer.

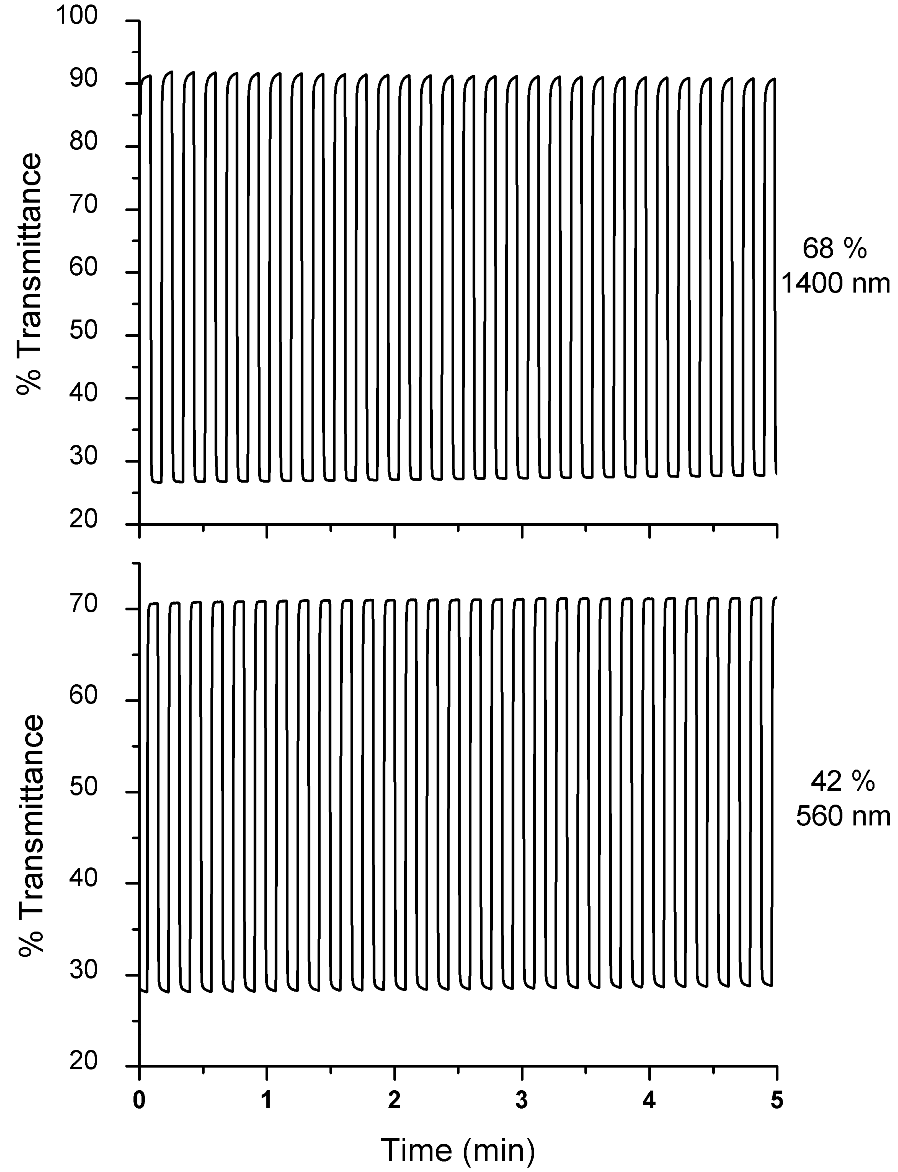
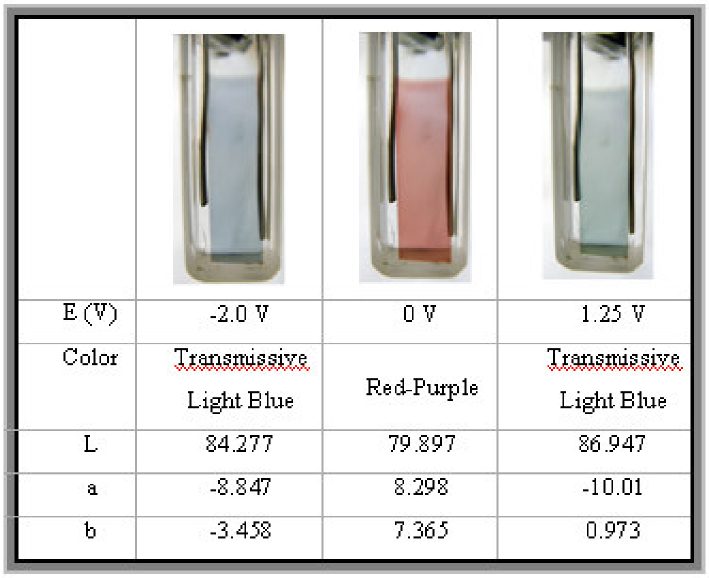


Figure 3.19 Electrochromic switching, optical absorbance monitored for poly(SBT-co-EDOT) in the presence of 0.1 M $TBAPF_6$/ACN

3.6.3 Colorimetry of Polymers

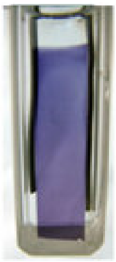
Colorimetry is used to measure the color with an objective and quantitative practice, which can allow for matching the colors in electrochromic devices. Color is made up of three attributes; hue, saturation, and luminance, and color systems, such as CIE, are used as a quantitative scale to define and compare colors. The three identifications of the colors (L,a,b) for homopolymer and copolymer were measured and summarized in table1 and table 2 respectively.

Table 3.1 Electrochromic properties of poly(SBT)



E (V)	-2.0 V	0 V	1.25 V
Color	Transmissive Light Blue	Red-Purple	Transmissive Light Blue
L	84.277	79.897	86.947
a	-8.847	8.298	-10.01
b	-3.458	7.365	0.973

Table 3.2 Electrochromic properties of poly(SBT-co-EDOT)

		
E (V)	-0.5 V	1.05 V
Color	Purple	Transmissive Light Blue
L	61.912	79.328
a	4.581	-7.982
b	-10.93	0.891

CHAPTER 4

CONCLUSIONS

A donor acceptor polymer was prepared via applying Pd-catalyzed Stille coupling methodology. Use of selenophene as the electron-rich unit and benzotriazole as the electron deficient unit results in reducing the electronic band gap of the polymer significantly. The electrochemically active polymer can be both p and n- doped. Through cyclic voltammetry, the polymer oxidation (Epa) and reduction (Epc) potentials for p-doping process were observed at 1.0 and 0.8 V, respectively, at a scan rate of 100 mV/s. Via spectroelectrochemistry studies of the polymer, two π-π^* transitions, polaron, and bipolaron band formations were obtained at 483, 511, 800, and 1200nm, respectively. Moreover, we have demonstrated that the tunable electrochromic copolymers can be switched easily between purple neutral state to a light blue oxidized state.

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