

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING
POLYMERS OF 5,8-DI(PYRROL-2-YL)-2,3-DI(THIOPHEN-2-YL)
QUINOXALINE
AND ITS COPOLYMERS

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POLYMERS OF 5,8-DI(PYRROL-2-YL)-2,3-DI(THIOPHEN-2-YL)
QUINOXALINE AND ITS COPOLYMERS**

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ABSTRACT

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING POLYMERS OF 5,8-DI(PYRROL-2-YL)-2,3-DI(THIOPHEN-2-YL) QUINOXALINE AND ITS COPOLYMERS

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A novel electroactive monomer 5,8-Di(1H-pyrrol-2-yl)-2, 3-di(thiophen-2-yl) quinoxaline (PTQ) was successfully synthesized via Stille Coupling reaction between quinoxaline and pyrrole. Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) and Mass spectroscopy were used to characterize the monomer. The monomer was electrochemically polymerized in the presence of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in dichloromethane. Monomer reveals relatively low oxidation potential at +0.70V. Spectroelectrochemical behaviors and switching ability of homopolymer were investigated by UV-Vis spectroscopy and cyclic voltammetry. Two π - π^* transitions were observed at 400 nm and 815 nm with a low band gap, 1.0 eV. Polymer possesses 66% optical contrast in the Near IR region, which may be promising in NIR electrochromic device applications.

Spectroelectrochemical behaviors and switching ability of copolymers were investigated by UV-Vis spectroscopy and cyclic voltammetry. Copolymers of PTQ in the presence of BiEDOT and BEBT were synthesized via potentiodynamic method

in DCM/TBAP (0.1 M) solvent-electrolyte couple. P(PTQ-co-BiEDOT) reveals oxidation potential at +0.45V, whereas P(PTQ-co-BEBT) reveals oxidation potential at +0.70V. The spectroelectrochemical behavior of the P(PTQ-co-BiEDOT) and P(PTQ-co-BEBT) in comparison to homopolymer revealed solid evidence of copolymerization based upon the differences in the spectral signatures. Switching time of the polymers was evaluated by kinetic studies upon measuring the percent transmittance (%T) at the maximum contrast point.

Keywords: Electropolymerization; Conducting polymers; Electrochromic properties; Electrochromic devices; Copolymerization

ÖZ

5,8-Dİ(PİROL-2-İL)- 2,3-Dİ(TİYOFEN-2-İL) KUİNOKSALİNE İLETKEN POLİMERLERİNİN SENTEZİ, ELEKTROKROMİK ÖZELLİKLERİ VE KOPOLİMERLERİ

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Yeni elektroaktif monomer 5,8-Di(pirol-2il)-2,3-di(tiyofen-2-il) kuinoksaline, kuinoksaline ve pirol arasındaki Stille Coupling reaksiyonu ile başarı ile sentezlenmiştir. Nükleer magnetic rezonans (^1H NMR ve ^{13}C NMR) ve Kütle spektrometresi monomerin karakterizasyonu için kullanılmıştır. Monomer diklorometan içerisinde tetrabutilamonyum perklorat destek elektroliti varlığında elektrokimyasal olarak polymerleştirilmiştir. Monomer +0.70V'da nispeten düşük oksitlenme potansiyeli göstermiştir. Homopolimerin spektroeletrokimyasal özellikleri ve dönüşüm özellikleri UV-Vis spektroskopisi ve dönüşümlü voltametre ile incelenmiştir. 400 nm ve 815 nm'de iki π - π^* geçişi 1.0 eV düşük bant aralığı ile gözlemlenmiştir. Polimer, gelecekte Yakın Kızılötesi elektrokromik cihaz uygulamaları için ümit vaat edebilecek, Yakın Kızılötesi bölgesinde % 66 optik kontrasta sahiptir.

Kopolimerlerin spektroeletrokimyasal ve dönüşüm özellikleri UV-Vis spektroskopisi ve dönüşümlü voltametre ile incelenmiştir. BiEDOT ve BEBT varlığında PTQ kopolimerleri potansiyodinamik method ile DCM/TBAP (0.1M) çözücü-elektrolit çifti içerisinde sentezlenmiştir. P(PTQ-co-BiEDOT) +0.45V'da, oysa P(PTQ-co-BEBT) +0.70V'da oksitlenme potansiyeli göstermektedir. Spektroeletrokimyasal analizler sonucunda kopolimerlerin, homopolimerden de farklı bir elektrokromik özelliğe sahip olduğu gösterilmiştir. Polimerlerin tepki zamanı yüzde transmittans ölçümlerinin de yapıldığı kinetik çalışmalarla en yüksek kontrast noktasında incelenmiştir.

Anahtar sözcükler: Elektrokimyasal polimerleşme; iletken polimerler; elektrokromik özellikler; elektrokromik cihazlar; kopolimerizasyon

TO MY BELOVED FATHER AND MY MOTHER,

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ABBREVIATIONS

PTQ	5, 8-Di(1H-pyrrol-2-yl)-2,3-di(thiophen-2-yl) quinoxaline
DCM	Dichloromethane
TBAP	t-butylammonium perchlorate
BIEDOT	2,2'-bis(3,4-ethylenedioxythiophene)
BEBT	4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl- 2H-benzo [1,2,3] triazole
(Boc) ₂ O	Di- <i>tert</i> -butyl dicarbonate
DMAP	4-(dimethylamino) pyridine
ACN	Acetonitrile
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectrometer
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
CP	Conducting Polymers
ITO	Indium Tin Oxide

CHAPTER I

INTRODUCTION

1.1 Conducting Polymers

Polymers or commonly called “plastics” are known as insulators, this fact had changed almost 30 years ago with the partial oxidation of polyacetylene by Shirakawa, Mc Diarmid, and Heeger in 1977. They have received Nobel Prize in 2000 for the discovery and development of conducting polymers [1]. After this breakthrough, new organic polymers that can conduct electrical current have brought new scientific and technological interest.

Conductivity is satisfied with π -electrons in the polymer backbone. Conducting polymers called as synthetic metals, show electrical, electronic, magnetic and optical properties like a metal while almost keeping the simplicity of processibility like an ordinary polymer.

1.1.1 Historical Background

Since conventional polymers have striking chemical, mechanical and electrically insulating properties, they have been used for many applications [2]. The first conducting polymer was synthesized and published in 1862 by Letheby; "aniline black" was attained by the oxidation of aniline which was insoluble in water and soluble in common organic solvents but its electronic properties were not recognized [3]. Aniline black is used in printing industry [4].

Polymerization of acetylene was reported in 1958 by Natta and coworkers [5]. Due to polyacetylene's insolubility and fusibility problems, polymer did not attract much attention at that time. Following the discovery of the high conductivity property of poly(sulfurnitride) (SN)_x, a polymeric inorganic explosive, by MacDiarmid and others during 1960s, the idea that polymers could be good electrical conductors rose. The conductivity of (SN)_x at room temperature was in the order of 10³ S/cm [6]. To compare conductivities, copper has a conductivity of 1×10⁶ S/cm, and polyethylene, 10⁻¹⁴ S/cm (Figure 1.1). This confirmed the presence of highly conducting polymers and opened the way to the finding of a totally new class of conducting polymers even though its other properties such as its explosive nature disallowed its use as an important commercial polymer.

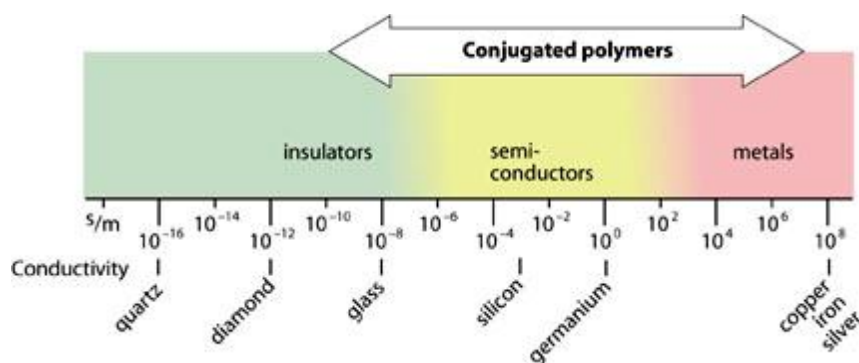


Figure.1. 1 Conductivities of some metals, semiconductors and insulators

At the end of the 1970s when Heeger and MacDiarmid discovered polyacetylene ((CH)_x) synthesized by Shirakawa's technique, modern period of conducting polymers began. Conductivity of polyacetylene increased 11 orders of magnitude due to charge-transfer oxidative doping with iodine [1]. Polyacetylene (PAC) has conjugated π -system structure enlarging over a large number of the chain-linked monomer units. Polyacetylene's high instability toward oxygen and water prevented it from being commercially important although it has a very high conductivity in the doped form [7]. After many studies to improve polyacetylene's properties, conjugated systems other than polyacetylene with other conjugated structures and heteroatomic molecules were examined (Figure 1.2).

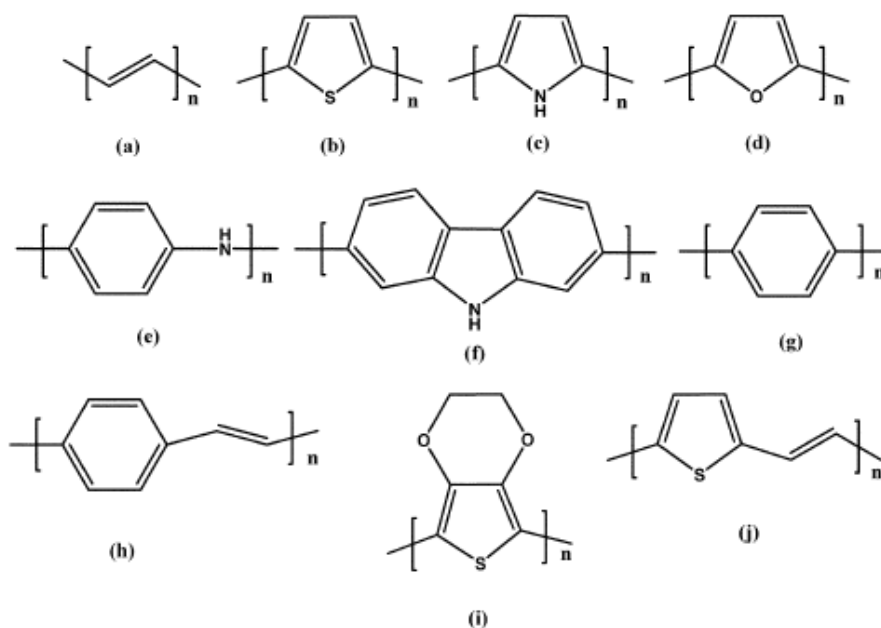


Figure.1. 2 Common conducting polymer structures: (a) polyacetylene, b)polythiophene, (c) polypyrrole, (d) polyfuran, (e) polyaniline, (f) polycarbazole (g) poly(p-phenylene), (h) poly(p-phenylenevinylene), (i) poly(3,4-ethylenedioxythiophene), (j) poly(thienylenevinylene)

Synthetic chemists were interested in synthesizing new conducting polymers with enhanced properties in the early 1980s. At this era, polypyrrole (PPy) was discovered via oxidative electropolymerization as a homogenous, free-standing film. Polypyrrole shows high conductivity (100 S/cm), flexible and stable to humidity and oxygen [8]. Additionally polythiophene [9], polyaniline [10], poly (p-phenylene) [11] and poly(p-phenylene vinylene) [12] and their derivatives such as poly(3,4-ethylenedioxythiophene) (PEDOT) were studied widely for their superior properties like low oxidation potential and ease of processability compared to PAc allocating for more variety of structures. Conductivities and stabilities of some of these polymers were given in Table 1.1. Even if highest conductivity was observed for polyacetylene, the stability and processability of heterocycles make them more functional.

Table1. 1 Conductivities and stabilities of some common conducting polymers

Polymer	Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Stability (doped state)	Processing Possibilities
Polyacetylene	10^3 - 10^5	Poor	Limited
Polyphenylene	10^3	Poor	Limited
PPS	10^2	Poor	Excellent
PPV	10^3	Poor	Limited
Polypyrroles	10^2	Good	Good
Polythiophenes	10^2	Good	Excellent
Polyaniline	10	Good	Good

Recently conjugated polymers are receiving interest since they are promising materials for electronic applications. Specially, conjugated polymers and π -conjugated oligomers [13] mainly used in organic-based transistors and integrated circuits [14, 15], photovoltaic devices [16] and organic-based light-emitting devices [17]. Actually, the development of polymer-based light emitting devices (LEDs) structures guided the enterprising of high-tech companies and academic institutes [18, 19].

1.2 Band Theory and Conduction Mechanism in Conducting Polymers

Materials are classified into three groups due to their room temperature conductivity properties: conductors, semiconductors and insulators. The electrical conductivity, σ , can be shown as the product of the carrier mobility, μ , its charge, q , and the number of carrier or the concentration, n .

$$\sigma = \mu q n$$

Conducting polymers possess high conductivity, approximately that of metals as a result of free movement of electrons throughout their structure. Conduction is created by the movement of charge carriers such as electrons and holes through a medium under influence of an electric field.

There are hardly any charge carriers in their neutral states. For this reason external doping must be done in order to create a semi-conductor. Via doping the polymer, electrical conductivity increases since number of charge carriers is increased. Mobility of the carriers along the conducting path affects the conductivity since it depends on the movement of the charges move inside the polymer structure. Mobility depends on the movement of electrical charges along the polymer chain, named as intra-chain movement, and also jumping from one chain to another, named as inter-chain movement. The intra-chain movement depends on the effective conjugation of the polymer, while the inter-chain hopping is determined by the stacking of the polymer molecules. In addition, mobility depends on the movement of electrical charges from particle to particle. As a result, mobility of the charges is associated with intra-chain, inter-chain, and inter-particle mobility.

1.2.1 Band Theory

Band theory is used to explain the electronic structure and conduction mechanism of materials. Electronically conducting polymers are widely conjugated molecules; it is believed that they acquire a spatially delocalized band-like electronic structure. In this theory, materials are classified as insulators, semiconductors, or metals depending on the relative separation of occupied and unoccupied energy states.

Upon electrochemical or photochemical doping process the excitation and/or removal or insertion of electrons in conjugated polymers require discussion of band theory. In conjugated polymers, the high degree of conjugation upon polymerization gives rise to two separate energy bands, the lowest energy containing the highest occupied molecular orbital (HOMO), also identified as the valence band (VB); and the highest energy containing the lowest unoccupied molecular orbital (LUMO),

identified as the conduction band (CB). The outermost shell of electrons in a material has the valence electrons and these can be located in the valence band that identifies their lowest energy states. An electron must obtain adequate energy to promote to the conduction band to satisfy the conduction in polymers. The energy difference between the valence band and the conduction band is known as the band gap (E_g) (Figure.1.3), and in neutral conjugated polymers refers to the onset energy of the π - π^* transition. The energy gap between the valence and conduction band of polymer is associated with the lowest allowed energy of its monomer units and to the bandwidth resulting from the overlap between the monomer orbital [20].

In their neutral form, conjugated polymers are semiconducting, but upon oxidation (p-doping) or reduction (n-doping), inter band transitions form between the valence and conduction bands, lowering the effective band gap, giving rise to the formation of charge carriers along the polymer backbone.

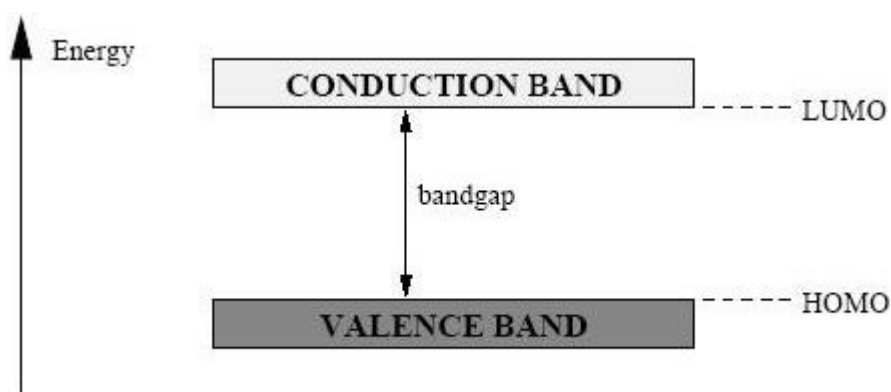


Figure.1. 3 Band structure in an electronically conducting polymer

The minimum energy needed to excite an electron to the conduction band from the valence band is the absorption band edge, which corresponds to the real energy gap between these two bands. Nevertheless, the absorption maximum is used occasionally and referred as the band gap. An additional way to determine the band gap is to compute the oxidation and reduction potentials of the polymer. The energy difference between these two provides the band gap [21].

The conductivity of the conjugated polymers could be maximized by minimizing the band gap. Most of the conducting polymers synthesized up to now have band gaps greater than 2 eV which makes them as mid to high band gap polymers. Those with lower than 1.5 eV are considered moderately low band gap materials. There exist few confirmed examples with band gaps below 0.8 eV.

The main difference between these materials is related with the gap between the valence and conduction bands. In metals, electrons can simply flow through the material since there is no energy gap between the valence and conduction bands. Insulators are illustrated by a comparatively large energy gap between the two bands which leads to the low conductivities observed in these substances. In semiconductors the valence band is separated from the conduction band by an energy gap varying from 1-4 eV (Figure.1.4). This range of energies associates to the visible spectrum and is correlated with electronic transitions [22]; therefore these materials often show intense color.

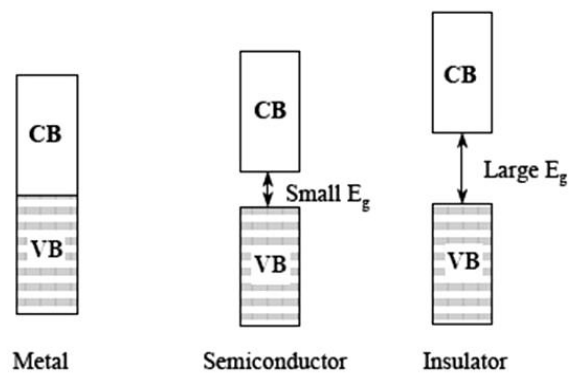


Figure.1. 4 Band structures of metal, semiconductor, insulator

The conjugated polymer's band structure is derived from the interaction of the π -orbitals of the repeating units throughout the chain [23]. This is represented in Figure 1.5. The electronic levels no longer have discrete energies but relatively display a one-dimensional band of allowed energies, as the number of repeating units become significant. Interactions between adjacent and piled π -electrons of conjugated polymers produce two and three-dimensional band structure [24].

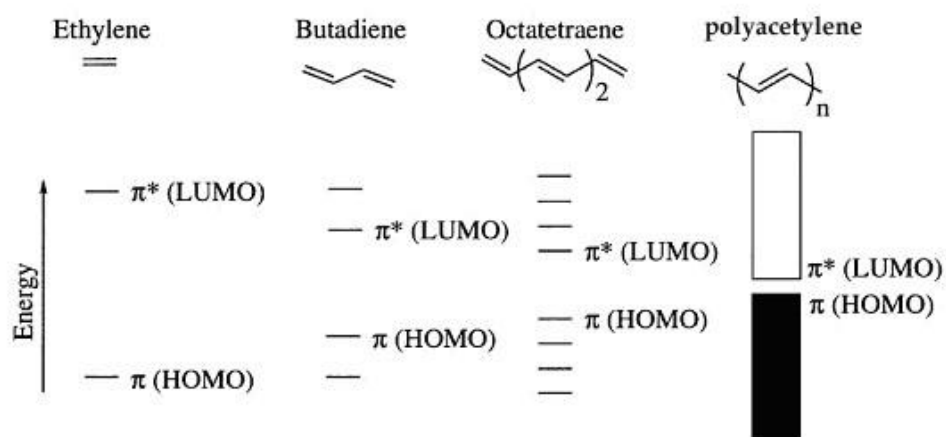


Figure.1. 5 Generation of bands in conjugated polymer systems

1.2.2 Conduction Mechanism

1.2.2.1 Charge Carriers

The mechanism of conductivity in conjugated polymers is created by the motion of charge defects within the conjugated structure. Positive charge carriers (p-type) and negative charge carriers (n-type) are the result of polymer oxidation and reduction correspondingly.

In a neutral conjugated polymer chain, the π -electrons are bound in the p orbitals giving increase to an alternation of single and double bonds. The conjugated polymer has typical semiconducting properties at this state.

In general, conduction is the movement of charge carriers (electrons, holes, polarons, solitons, etc.) through a medium under the influence of electric field. Therefore, the number and the mobility of charge carriers in the medium characterize the conductivity. As a result, positive or negative charges together with unpaired electrons are formed in the polymer chain.

When an electron is removed by oxidation from the π -system of polymers backbone an unpaired electron with spin $\frac{1}{2}$ (a free radical) and a spinless positive charge (cation) are produced. Polaron is created by the combination of the radical and cation to each other, which appears in the band structure as localized electronic states in the gap symmetrically, with the lower energy states. Further oxidation in the polymer with a loss of electron from either the polaron or the remaining neutral portion of the chain results in the formation of bipolarons. The energy states of bipolarons overlap which creates narrow bipolaron bands in the gap when high quantities of highly p-doped bipolarons are formed. However, the energy levels are below the conduction band when polymer is reduced (n-type) [25]. Both polarons and bipolarons can travel along the polymer chain in an electrical field.

Number of free charge carriers can be increased by doping. Charging the polymer film through chemical oxidation or reduction by dopant species involves chemical doping. The dopant stabilizes the charge of the polymer with its opposite charge. In most of the electrochemical systems, the polymer film can be reversibly doped-dedoped by oxidation and reduction [26]. The charge carriers alter the structures of the polymer and shorten the single bond and increase the length of the double bonds which results in quinoid character. This causes a reduced energy splitting between the HOMO and the LUMO levels, bringing these states closer inside the band gap (Figure 1.6).

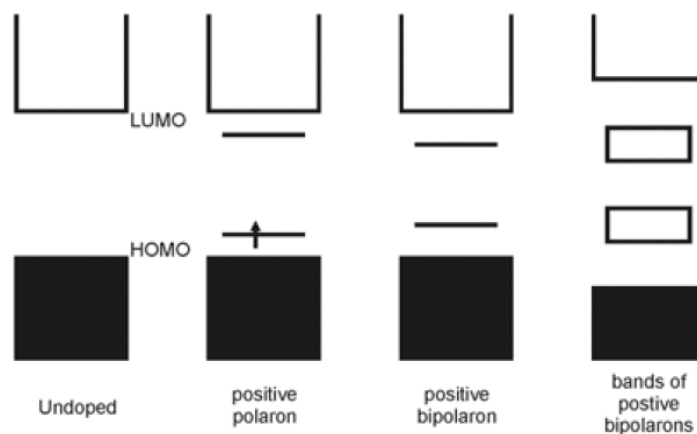


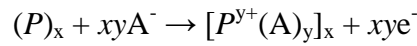
Figure.1. 6 Positive polaron and bipolaron in a conjugated polymer. Overlap between charge carriers at high doping levels results in the formation of bands.

1.2.2.2 Doping Concept

The unique and unifying theme which differentiates conducting polymers from all other types of polymers is the doping concept [2]. The conductivity of a conjugated polymer can be enhanced by orders of magnitude from insulating or semi-conducting (10^{-10} to 10^{-5} S.cm⁻¹) to metallic (1 to 10^4 S.cm⁻¹). The process which transforms the neutral polymer backbone to a charged π -conjugated system is known as “doping”. Doping of conducting polymers has been performed by redox processes involving the partial addition or removal of electrons to or from the π -system of the polymer backbone [26, 27]. This doping and dedoping process are usually reversible that do not change the chemical nature of the original polymer backbone. Oxidation or reduction can be utilized for changing the electronic structure of many conducting polymers. Basically, *p*-doping is defined as the oxidation of a neutral polymer by removing an electron from its valence band and *n*-doping is defined as reduction of a polymer by adding an electron to its conduction band. The requirement for strictly dry and oxygen-free conditions made the *p*-doping process more studied than *n*-

doping [28]. This study focuses mainly on *p*-doping effects; however *n*-doping process also exists in literature [28-31].

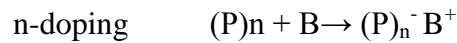
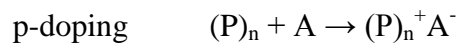
Electrical charge carriers are generated through doping of a conducting polymer. By adjusting the doping level carefully, conductivity between nondoped (insulating or semiconductor) and fully doped (conducting) form of the polymer can easily be obtained. The backbone of a conducting polymer consists of a delocalized π system in the doped state. In the nondoped state on the other hand, only after *p*-doping the polymer may have a conjugated backbone [32]. *p*-Doping takes electrons from the polymer system, creating positive charges on the polymer chain. When positioned in an electric field, these charges can move through the polymer chain, acting as charge carriers.



n-Doping in contrast, donates electrons to the polymer system as a result of reduction, producing negative charges on the polymer chain. These electrons function as current carriers and move in the polymer when positioned in an electric field.



Chemical doping is achieved on the polymer by either an electron acceptor, through oxidation (oxidant, A) or an electron donor, through reduction (reductant, B);



where A^- and B^+ are the doping ions. Chemical oxidation/reduction can arise by the exposure of the polymer to I_2 or AsF_5 vapors, $FeCl_3$ or $CuCl_2$. The doping level is determined by the vapor pressure of the dopant or its concentration, the temperature of the reaction, the doping time, and the type of the polymer.

Electrochemical doping allocates for better control of the doping level thus, it is considered as more preferable than chemical doping due to several advantages. Any doping level can be achieved by applying a constant potential over a length of time, and the level at which the polymer is doped is directly related to the voltage.

Conductivity of conducting polymers can be increased over eight or more orders of magnitude in the same material. Conducting polymer's doping level has an effect on the range of conductivity from insulator to metal (Figure 1.7)




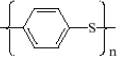
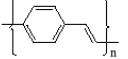
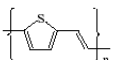




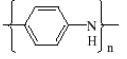
Polymer	Structure	Doping materials	$\Omega^{-1}\text{cm}^{-1}$
Polyacetylene	(CH) _n	I ₂ , Br ₂ , Li, Na, AsF ₅	10000
Polypyrrole		BF ₄ ⁻ , ClO ₄ ⁻	500-7500
Polythiophene		BF ₄ ⁻ , ClO ₄ ⁻	1000
Poly(3-alkylthiophene)		BF ₄ ⁻ , ClO ₄ ⁻	1000-10000
Polyphenylene sulfide		AsF ₅	500
Polyphenylenevinylene		AsF ₅	10000
Polythienylenevinylene		AsF ₅	2700
Polyphenylene		AsF ₅ , Li, Na	1000
Polyisothianaphthene		BF ₄ ⁻ , ClO ₄ ⁻	50
Polyazulene		BF ₄ ⁻ , ClO ₄ ⁻	1
Polyfuran		BF ₄ ⁻ , ClO ₄ ⁻	100
Polyaniline		HCl	200

Figure.1. 7 Conductivities of some conducting polymers with selected dopants

1.2.2.3 Hopping

Doping and hopping are the two important mechanisms of conduction process. Hopping is the motion of charges (intra-chain, inter-chain and interparticle) in a polymer matrix. The motion of the charge carrier through a single chain, the intra-chain movement, depends on the efficient conjugation, whereas the inter-chain movement, jumping from one chain to another, is determined by the piling of the polymer chains. The mobility depends on the movement of electrical charges from particle to particle also. Therefore, the mobility and the conductivity are verified both a macroscopic (inter-particle) and microscopic (intra- and inter-chain) level (Figure.1.8).

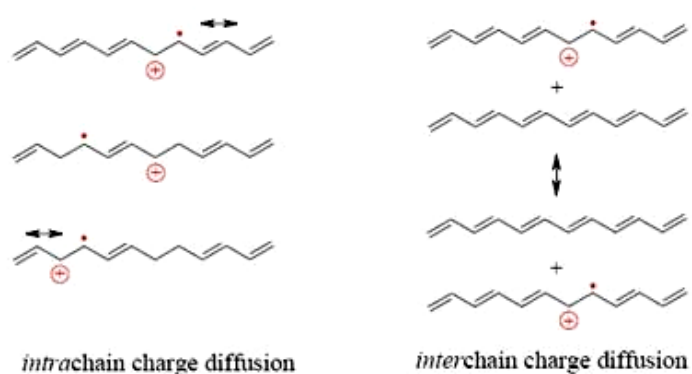


Figure.1. 8 Schematic representation of intrachain charge diffusion (left) and interchain charge diffusion (“hopping”, right) in polyacetylene.

1.3 Synthesis of Conducting Polymers

Although several methods for synthesizing conducting polymers are present, the most important method is the incorporation of extended π –electron conjugation.

Conducting polymers can be synthesized by one of the following techniques [33]:

1. Chemical polymerization
2. Electrochemical polymerization
3. Photochemical polymerization
4. Metathesis polymerization
5. Concentrated emulsion polymerization
6. Inclusion polymerization
7. Solid-state polymerization
8. Plasma polymerization
9. Pyrolysis
10. Soluble precursor polymer preparation

1.3.1 Chemical Polymerization

Chemical polymerization is the most useful technique for preparing conductive polymers in large amounts [34, 35]. In chemical polymerization, oxidative coupling of heterocyclic ring systems such as pyrrole, thiophene, indole, aniline, etc., using strong chemical oxidants such as ferric chloride, the most widely employed one, and iodine or ammonium persulfate [36].

Mostly, addition polymerization involves the repeated addition of an unsaturated monomer to an active center like a radical or an ion. The oxidants are capable of oxidizing the monomers in proper solution, creating chemically active cation radicals of the monomers used. Upon the attack of the oxidants, the cation radicals produced

and react with monomer molecules, giving in oligomers and then polymers. Chemical polymerization takes place in the bulk of the solution, and the consequent polymers precipitate since they are insoluble. Though, a fraction of conducting polymer can deposit impulsively on the surface of different materials dipped into the polymerization solution [37]. In Figure 1.9, oxidative polymerization of a heterocyclic compound with FeCl_3 is shown [38].

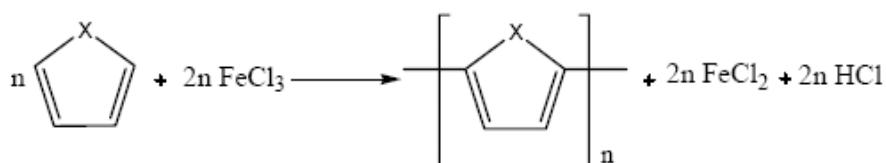


Figure.1. 9 Oxidative chemical polymerization of polyheterocycle in the presence of iron (III) chloride

1.3.2 Electrochemical Polymerization

Electrochemical synthesis of conducting polymers has many advantages compared to chemical synthesis including the in situ deposition of the polymer at the electrode surface. The thickness, morphology and degree of polymer doping by quantity of passed charge can be controlled. Additionally, the polymers are oxidized to their doped states simultaneously during the polymer growth.

Electrochemical polymerization is a simple technique that has been employed to control the oxidation potential for polymerization precisely and to explore the electronic properties of the resulting polymer. In general, oxidative coupling of monomers in a stepwise way to generate insoluble oligomers which precipitate onto the surface of working electrode can be defined as electrochemical polymerization.

Electrochemical syntheses of polyheterocycles have been succeeded by an anodic or a cathodic path (Figure 1.10).

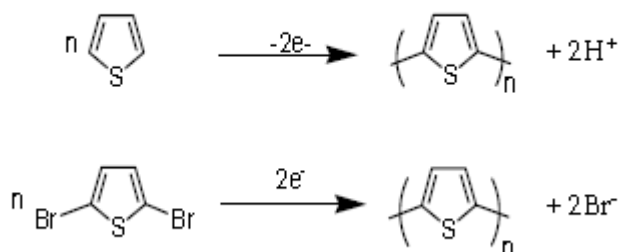


Figure.1. 10 Electrochemical synthetic routes to polythiophene

The major limitation of electroreduction method is that the insulating form of polymer passivates the activity of the electrode and limits attainable film thickness [39].

The polymers synthesized by electroreduction and chemical methods usually showed poorer properties compared to those synthesized by oxidative electrochemically prepared polymers. The advantages of oxidative electropolymerization are the followings compared with other chemical and electrochemical methods [40, 41]:

- Thickness of the film, morphology and conductivity can be simply controlled by the applied potential, time of the polymerization and the electrochemical potential scan rate. Reactions take place at room temperature.
- Investigation of in situ polymerization process and the properties of the resulting conducting polymer by electrochemical or spectroscopic techniques.
- A highly electrochemically active and conductive polymer film can be easily produced on an electrode, which can be directly used as an electrode in a battery or a sensor.

The electropolymerization conditions affect the structure and properties of the resulting polymers to a high level.

Via this method it is possible to produce homogeneous polymers and also the molecular weight distributions can be controlled. The solvent type, electrolyte system, monomer and electrodes choice and concentration strongly influence the properties of the final conducting polymer [42].

1.3.2.1 Mechanism of Electropolymerization

Oxidative electropolymerization of the heterocycle is accomplished in an inert organic solvent including supporting electrolyte [43]. Oxidation of the monomer to its radical cation is the first electrochemical step (E). High concentration of radicals is continuously upheld near the electrode surface since the electron-transfer reaction is much faster than the diffusion of the monomer from the bulk solution. In the radical-radical coupling, production of dihydro dimer dication is the second step which involves the coupling of two radicals leading to a dimer after loss of two protons and rearomatization. The driving force of the chemical step (C) is this rearomatization. The dimer, which is more easily oxidized than the monomer, comes about in its radical form and undergoes a further coupling with a monomeric radical due to the applied potential. The radical cation reacts with the monomer to produce a neutral dimer by the loss of another electron and two protons in a radical–monomer coupling mechanism. The oxidized dimer radical cation once more attacks a monomer to yield a trimer and the propagation continues to form polymer.

Electropolymerization proceeds until the oligomers become insoluble in the electrolytic medium and precipitates onto the electrode surface through successive electrochemical and chemical steps according to a general E(CE)_n scheme, [44,45].

The mechanism proposed for the electropolymerization of heterocycles by anodic coupling is shown in Figure 1.11.

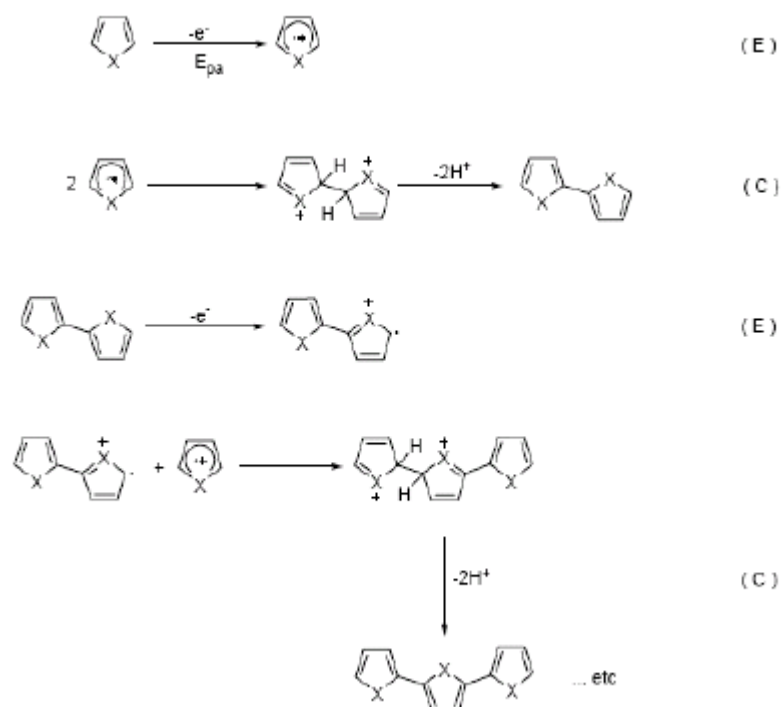


Figure.1. 11 Proposed mechanism (ECE) of the electrochemical polymerization of five membered aromatic heterocycles; where X = NH, S or O.

1.3.2.2 Effects of Electrolytic Medium

The type of solvent used, the nature of electrolyte employed, the amount of current or potential applied to the cell, and the temperature maintained during the course of the electrosynthesis affect the electrical properties and the morphology of the film.

The solvent must have two characteristics as an acceptable medium for polymerization. It must possess high dielectric constant to allow ionic conductivity and be stable over a broad potential range such that solvent redox processes do not interfere with electrochemical processes. The nucleophilicity of the solvent should be remained low since oxidative electrochemical polymerization includes the formation of radical cations. Polar aprotic solvents like acetonitrile or propylene carbonate have

large potential range, and high relative permittivities, which permit a good dissociation of the electrolyte and therefore a good ionic conductivity [46, 47].

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

The ionic conduction medium between the electrodes is generally satisfied with a supporting electrolyte which can be either liquid or solid. The polymer is doped by the electrolyte ions. The morphology and electrochemical properties of the conducting polymer were shown to be significantly affected by the electrolyte during polymerization [48]. The structure of the polymer is partially determined by the nature of the anion during the synthesis step. The nature of the cation in contrast, plays an essential role on the behavior of the polymer films during the charge-discharge processes. Conducting polymers are generally electrogenerated in the presence of lithium or tetraalkylammonium salts of either ClO_4^- or BF_4^- [49].

To evade competitive reactions of the oxidized polymer with nucleophiles in the medium, the monomer concentration is kept generally high (0.1 M or more). Oxidation potential of monomer affects the probability of the occurrence of these reactions. The occurrence of the competition decreases as the oxidation potential of the monomer decreases. Therefore, in order to achieve efficient polymerization, millimolar concentrations may be used [42].

1.3.2.3 Monomer Structure and Substituent Effect

New and novel structures of conducting polymers are designed to synthesize in order to increase the conjugation length and also the conductivity, processibility and solubility in certain solvents [50]. Many of these polymers have problems with processibility and mechanical properties. Interchain interactions in π -conjugated polymers are relatively strong as a result of electron transfer and coupling. It is usually difficult to characterize their structure, understand electronic interactions and

process them since these polymers are often insoluble in common organic solvents and infusible. This is a great limitation for their applications [51].

To overcome these limitations substitution can be used which is a tool for the design of conducting polymers for different applications. The position and character of the side chain will manipulate properties like solubility, band gap, ionic conductivity, morphology and miscibility with other substances [52].

Electron density of the ring is significantly affected by the electronic effects due to electron withdrawing and electron donating substituents. The oxidation potentials of electron withdrawing groups such as cyano, aldehydes and nitro substituted monomers are higher than the non-substituted ones, and they cannot be polymerized electrochemically. Whereas monomers substituted with electron donating groups have lower oxidation potentials due to the stabilization of the radical cation formed upon oxidation.

Substituents affect the band gap, oxidation potential of the monomers and polymers and their optical absorption. Electron donating groups raise the valence band or HOMO level and hence lower the band gap. This can be exemplified by comparing the band gaps of polythiophene (2.0 eV) and poly(3,4-ethylenedioxythiophene) (PEDOT) (1.6 eV) [53].

Non- α,α' -linkages (e.g. α,β' and β,β' couplings (Figure 1.12)) can take place to variable extents, causing breaks in the conjugation and consequently reduction in the film conductivity. The monomer is protected against β coupling via attachment of various alkyl and alkoxy groups at 3 or 4 positions [54].

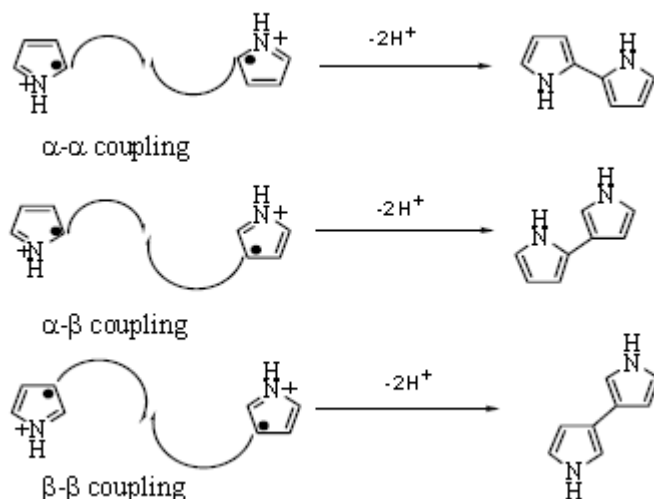


Figure.1. 12 Potential coupling reactions for pyrrole during oxidative polymerization

1.4 Conducting Copolymers

Thanks to their conductivities, stability against environmental conditions and ease in preparation, conducting polymers are very promising materials. On the other hand, they have poor mechanical properties; they are often insoluble, non-melting, and thus not processible. A variety of methods like the grafting alkyl groups into the main chain, the synthesis of soluble precursors and preparation of conducting polymer composites, blends and copolymers used to improve mechanical properties [55].

Syntheses of conducting copolymers are revealed to be an effective way to compensate the deficiencies of conducting polymers. Conducting copolymers can be synthesized by polymerization of two monomers with different properties than their corresponding homopolymers [56,57]. Most widely used methods of copolymerization are either electrochemical polymerization of the conducting component on an electrode previously coated with the insulating polymer or electrochemical polymerization of the two electroactive monomers. 3,4-Ethylenedioxythiophene (EDOT) is mainly used for the synthesis of a copolymer for

the reason that it is superior to its parent, polythiophene, in many ways vital for organic electrochromic materials [58]. The resultant copolymer may reveal improved electrochemical and optical properties than its homopolymers. Copolymers from pyrrole, pyrrole derivatives, thiophene, bithiophene and other combination of aromatic compounds had been reported [59-63].

1.5 Characterization of Conducting Polymers

Usual techniques for polymer characterization cannot be applied to all conductive polymers, since the highly conjugated backbone leads to insolubility in common solvents. Conducting polymers can be characterized by cyclic voltammetry technique that shows the oxidation and reduction potentials and the degree of reversibility of the electrode reaction [64]. FTIR and NMR spectroscopy have found wide applications in the structural characterization of polymeric materials. Structural information can be provided by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (cross-section of surface) (TEM) and atomic force microscopy also. Morphology of conducting polymer film can be described by scanning electron microscopy [65].

1.6 Applications of Conducting Polymers

Conducting polymers, which exhibit novel properties, have several applications in many areas. Conjugated polymers are employed as semiconductors in electronic devices such as light emitting diodes (LED) [66], field effect transistors (FET) [67, 69], nonlinear optical (NLO) devices, photovoltaic cells, solar cells, chemical, biochemical and thermal sensors. In the doped state, conjugated polymers are used as electrostatic dissipation materials, electromagnetic shielding materials and electronic conductors. Additionally, construction of electrochromic devices, battery electrodes and biosensors are possible due to the reversible switching between their neutral and doped states. The polymer goes through color, conductivity and volume changes upon switching between the two states. Applications that utilize these properties

include battery electrodes, mechanical actuators, sensors, drug delivery and electrochromics [69, 70].

1.7 Chromism

One of the characteristic of conducting polymers is the chromic behavior. Chromism is a reversible change in a substance's color resulting from a process caused by some form of incentive. There are many types of chromism reported in the literature for conducting polymers such as thermochromism, solvatochromism, piezochromism, ionochromism. These different chromic behaviors created from conformational modification and the energy change in π - π^* transition band gap induced by the subsequent environmental changes such as temperature, solvent power, pressure, ion strength, and applied potential, respectively [71].

1.7.1 Electrochromism

Electrochromism is the reversible and visible change in transmittance and/or reflectance that is related with an electrochemically stimulated oxidation–reduction reaction. An electrochromic material can be defined as a material that changes color in a steady but reversible manner by an electrochemical reaction. Color changes are generally between the two colored states or between a colored and a transparent state, where the chromophore absorbs either in the UV or visible region. The electrochromic material may exhibit several colors and be termed as multielectrochromic when more than two redox states are electrochemically available [72].

The doping process of a conducting polymer backbone structure alters to a doped state with more quinoidal structure. This change in structure is along with a change in the electronic transition from a higher energy to a lower energy. These transitions are positioned in the visible region mainly, with a transformation from a more optical transparent to a more optically opaque material or vice versa showing a color change [73].

Figure 1.13 shows the general characteristics of the doping- induced electronic structure and the corresponding optical-absorption bands of non-degenerate ground-state polymers. In the neutral state the polymer exhibits one transition from the valence to the conduction band (π - π^*). The polaron is the expected state when the system is slightly doped. There is a lowering of the corresponding antibonding level in the conduction band, and two intragap states are introduced (Figure 1.13 (b)). Therefore, the signature of a polaron is the two low energy transitions [74]. Further oxidation of polymer creates the bipolaron state. Since the bipolaron levels are unoccupied, only transitions from the valence band can occur (Figure 1.13 (c)).

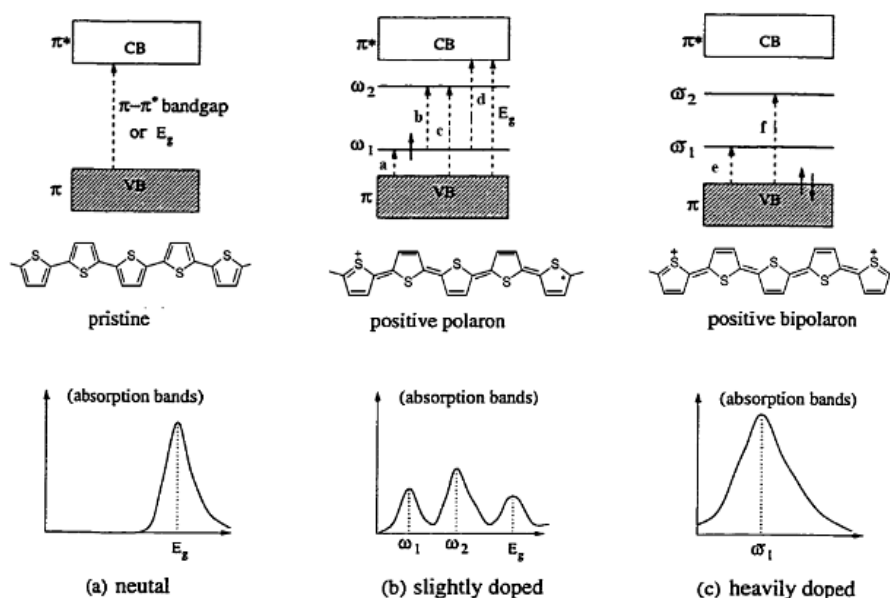


Figure.1. 13 Polaron and bipolaron in non-degenerate ground state polymers: band diagrams for neutral (a), positive polaron (b) and positive bipolaron (c)

The color exhibited by the polymer is closely associated with the band gap. Tuning of color states is possible by appropriate choice of monomer. This is a major advantage of using conducting polymers for electrochromic applications. Subtle modifications to the monomer can considerably modify spectral properties [75].

The ideal electrochromic polymer should have a high contrast between its states, with a short switching time. It should also be stable and maintain the color after the current has been switched off.

1.7.2 Types of Electrochromic Materials

There are three main types of electrochromic materials. First group of these materials are soluble in the electrolysis solution at both redox states, the second group are soluble in either reduced or oxidized state and a thin film forms on the electrode surface following electron transfer, and the third group including conducting polymers have both solid redox states and are studied in thin solid forms on the electrodes [75].

Due to their ease in the synthesis and environmental stability, polythiophenes [76] are widely used as electrochromic materials. Polypyrrole, (PPy), another class of organic electrochromic materials, has lower oxidation potential than PTh and its color alters between yellow, red and blue upon undoping and doping.

Viologens [77], transition metal oxides, most famously tungsten trioxide (WO_3) systems [78-81], Prussian blue systems [82], phthalocyanines [83,84], and conducting polymers [24] are among the most widely utilized electrochromic materials. These are some of the examples of many chemical species that possess electrochromic properties.

1.7.3 Spectroelectrochemistry

In order to investigate the electronic structure of the polymers, along with the optical changes arising from during redox switching which are important for electrochromic applications, optoelectrochemical analyses were carried out [85]. It offers information on the material's band gap and interband states produced upon doping. In addition it gives some information about the color through the location of the

absorption maxima and the ratio of peak intensities if the material shows fine structure on the main π - π^* peak.

1.8 Electrochromic Contrast and Switching Speed

Electrochromic contrast is one of the important parameters for evaluating an electrochromic material. Electrochromic switching studies are carried out to observe absorbance alterations with time through repeated potential stepping between reduced and oxidized states to obtain an insight about the optical contrast. It is often reported as a percent transmittance change (ΔT %) at specified wavelength where the electrochromic material has the highest optical contrast [86].

Switching time is the time required to switch between bleached and colored states. The switching speed of electrochromic materials is affected by factors such as the morphology of the film, the ionic conductivity of the electrolyte, and accessibility of the ions to the electroactive sites.

1.9 Colorimetry

When light hits our eyes, it is absorbed by photoreceptors called the rods and cones on the retina and transformed into nerve signals translated into a perception of color by the brain. Many of the existing color systems have three coordinates because humans have a three-dimensional color space. Three pixels with red, green and blue (RGB) color are used to span color space in electrochromic materials. The RGB color system is practical for forming a display; however it is actually not a good description of the full color space accessible with human eyes.

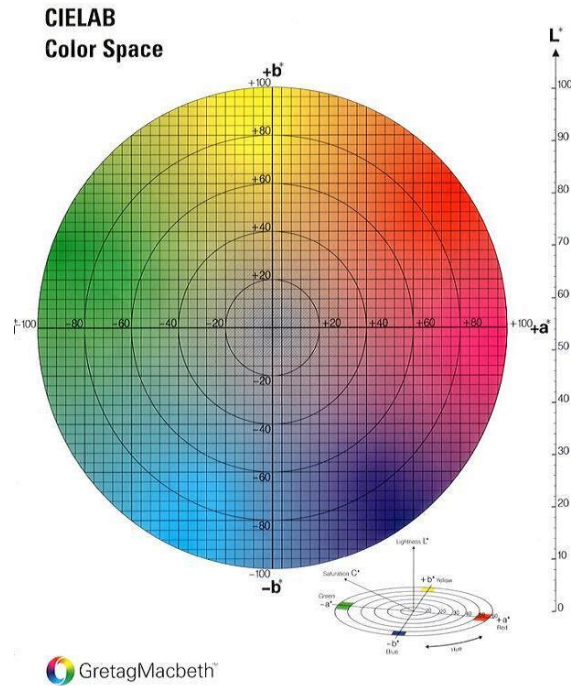


Figure.1. 14 CIE LAB color space

In 1931, the International Commission on Illumination (Commission Internationale de l'Eclairage, CIE) developed a model defining colors by three coordinates by X , Y and Z , corresponding to different biological receptors in the human eye (Figure 1.14) The model was improved in 1976 to be able to further adapt, to the way the human eye perceives colors, by introducing the CIE L , a , b color system, where the nonlinear behavior of the eye is considered. In the CIE L , a , b system the color is represented by L , a and b coordinates. L gives the luminance (lightness), while a refers to hue, dominant wavelength, or chromatic color, and b known as the saturation, chroma, tone, or purity (Figure 1.15). L has values from 0 (dark) to 100 (light), a ranges from -128 (green) to 127 (red) and b from -128 (blue) to 127 (yellow) [25].

1.10 Donor Acceptor Theory

For commercial applications of conducting polymers, they must possess properties like high optical contrast (%T), short response time, and good optical memory [87]. Most of the conducting polymers have considerably high band gaps. To eliminate these problems and obtaining conducting polymers with better optical properties is the aim of research groups. In order to enhance these properties, designing alternative monomer structures is one of the ways.

The donor-acceptor theory is one of the ways used for lowering the band gap [88]. Increasing the double-bond character between the repeating units of a conjugated polymer, which results in the reduction of bond length alternation, leads to a low band gap. Since mesomeric effects can be observed between the units, the interactions between the donor (D) and acceptor (A) groups may also give rise to an increased double bond character. Thus, alternating donor and acceptor units are expected to produce a lower band gap in conjugated polymers [89].

Polypyrrole can easily be synthesized chemically or electrochemically and has a wide range of optoelectronic properties available through alkyl and alkoxy substitution which gives it an extensive value as an electrochromic material. The pristine polypyrrole however, has electrochromic properties of low quality. It has a high band gap. Since it switches between dark colors its optical contrast is low with a moderate switching time in the visible region [90]. The number of functionalized polypyrrole derivatives is quite low, [91-97] though numerous studies have been conducted on pristine polypyrrole [98, 99].

There are quite low monomers bearing pyrrole as a donor group. In order to improve the pyrrole's fundamental properties and obtain an electroactive monomer possessing superior spectroelectrochemical behaviors pyrrole is a great candidate as a donor group.

1.11 Aim of the Work

Aims of this work are;

- ✓ To synthesize the target monomer 5, 8-Di(1H-pyrrol-2-yl)-2,3-di(thiophen-2-yl) quinoxaline (PTQ).
- ✓ To polymerize PTQ and characterize its electrical and optical properties.
- ✓ To electrochemically polymerize and copolymerize PTQ with two comonomers BiEDOT & BEBT
- ✓ To examine the electrochromic properties of the homopolymer and copolymers

CHAPTER II

EXPERIMENTAL

2.1 Materials

Benzothiadiazole, hydrobromic acid, bromine, sodium borohydride, ditertbutyl dicarbonate, 2,2,6,6 tetramethyl piperidine, acetone, ethanol, pyrrole, succinyl chloride, *n*-butyl lithium, 4-(dimethylamino)pyridine and tributyltin chloride were obtained from Aldrich Chemicals. Dry tetrahydrofuran (THF) (Acros) were used without further purification. The electrolysis solvents, acetonitrile (ACN) and dichloromethane (DCM) (Merck) were used without further purification. The supporting electrolyte, t-butylammonium perchlorate (TBAP) (Aldrich) was used as received.

2.2 Instrumentation

2.2.1 Potentiostat

A VoltaLab PST050 potentiostat in a three-electrode cell consisting of platinum wire or Indium Tin Oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode, and an Ag wire as the pseudo reference electrode were used to provide constant potential in the electrochemical polymerization. Measurements were performed at room temperature under nitrogen atmosphere. This device can attain to keep the voltage difference between the working and reference electrodes at a constant desired value during the electrolysis and compensates for the voltage drop in the electrolysis solution.

2.2.2 Cyclic Voltammetry System

Cyclic voltammetry measurements were achieved by cycling the potential of the working electrode with respect to a reference electrode and measuring the resulting current. The potential is linearly scanned up to a switching potential and then reversed to its initial value in this technique (Figure 2.1). The current response is observed as a function of the applied potential.

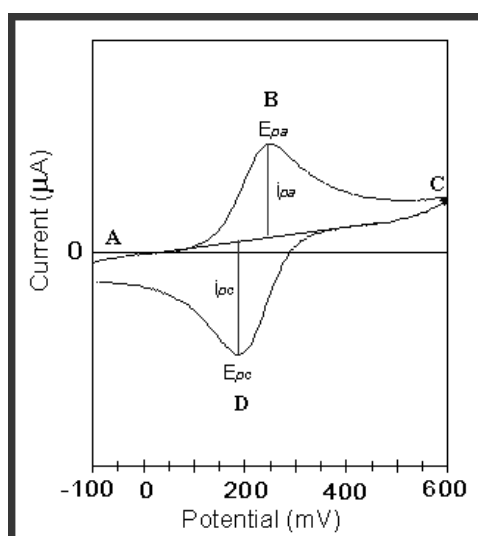


Figure.2. 1 Cyclic voltammogram for a reversible redox reaction

Diffusing species are easily oxidized and react near the electrode surface as the potential is increased. When the direction of the scan is reversed, the oxidized species near the electrode surface are reduced, and again a current response is measured.

The peak current i_p 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 electrons, A is the surface area of the electrode (cm^2), D is the diffusion constant (cm^2/s), C is the bulk concentration of electroactive species

(mol/cm³), and V is the scan rate (V/s). Consequently, for a diffusion-controlled system, the peak current is proportional to the square root of the scan rate.

The cyclic voltammetry system consists of a potentiostat, an XY recorder and a CV cell. The cyclic voltammetry cell consists of a platinum bead working electrode of 1 cm in length, a platinum spiral counter electrode (3 cm) wire, and a Ag wire reference electrode. The total volume of cell was about 15 mL. The VoltaLab PST050 potentiostat was used to provide voltage. An X-Y recorder was used to obtain the voltammograms.

2.2.3 Conductivity Measurements

Conductivity of polymer films are performed with four probe conductivity measurements on the free standing films. For measuring electrical properties of conducting polymers this method has several advantages. Firstly, the four probe technique reduces the errors caused by contact resistance, while two contacts measuring the voltage drop are different from the contacts applying the current across the sample. Secondly, this method allows conductivity measurements over a wide range of applied currents.

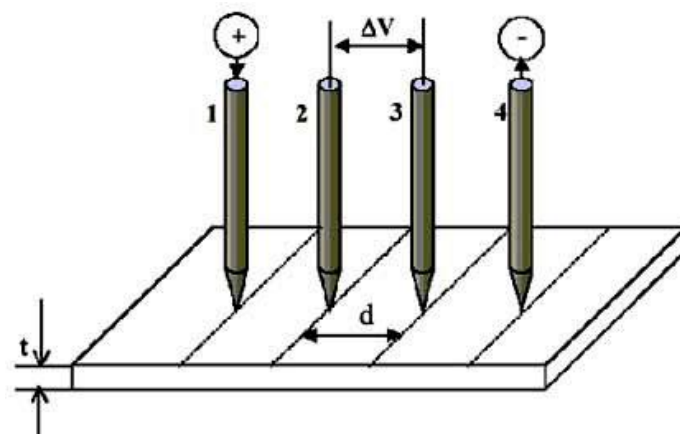


Figure.2. 2 Four-probe conductivity measurement setup

The four osmium probes are brought into line in a collinear geometry. A row of pointed electrodes touches the surface of a polymer film taped on an insulating substrate (Fig.2.3). A known amount of current is introduced at electrode 1 and collected at electrode 4, while the potential difference ΔV between contacts 2 and 3 is measured. The four probe method allows for the contact points to be easily relocated in various area of the film, therefore allowing several conductivity measurements on the same sample. Conductivity is calculated from the following equation,

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

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

2.2.4 Other Equipments

UV-Vis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. Colorimetry measurements were done via a Conica Minolta CS-100 spectrophotometer. A Bruker-Instrument-NMR Spectrometer (DPX-400) was used to record ^1H and ^{13}C NMR spectra in CDCl_3 . Chemical shifts were given in ppm relative to tetramethylsilane as the internal standard. High resolution mass spectrometry was performed with a Thermo Scientific LTQ-Orbitrap Mass Spectrometer operating with a (+) mode.

2.3 Procedure

2.3.1 Synthesis of monomer

2.3.1.1 Synthesis of 4,7-Dibromobenzo[1,2,5]thiadiazole (2)

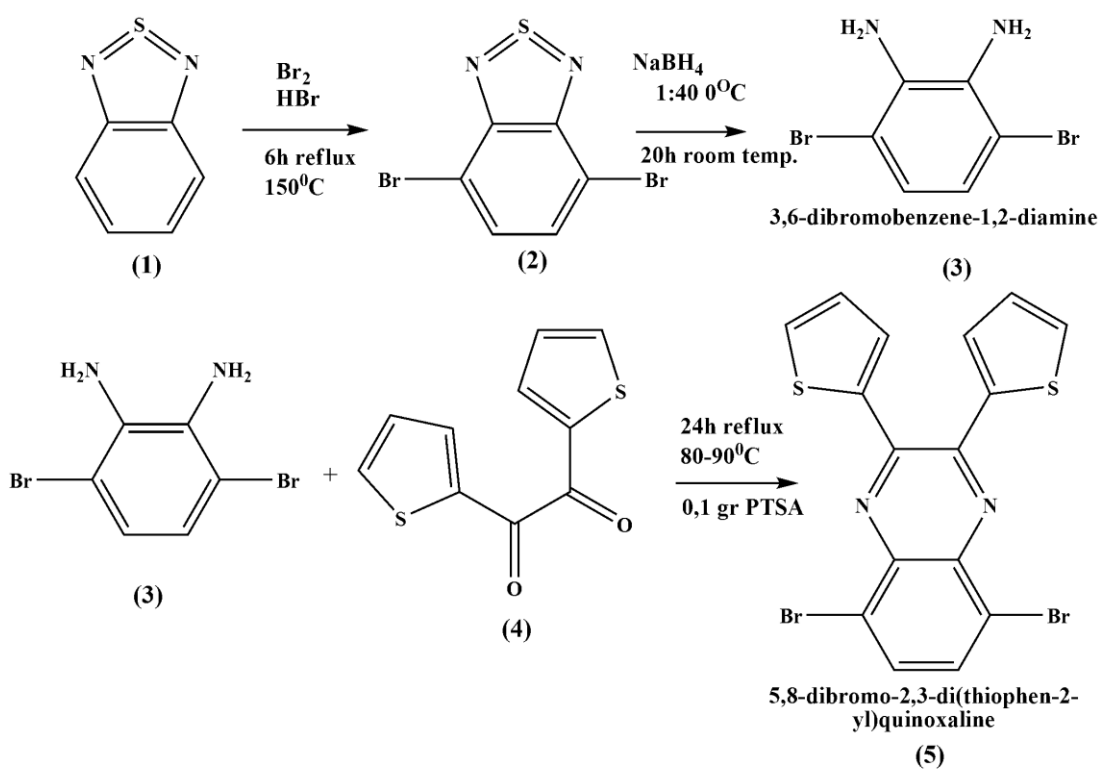
4,7-Dibromobenzo[1,2,5]thiadiazole (2) was synthesized according to the procedure in literature [100]. Mixture of 5.5 mL bromine and 50 mL of HBr were slowly added into benzothiadiazole (1) (5 g, 0.037 mol) dissolved in 75 mL HBr and refluxed at 150°C for 6 hours. After cooling, saturated NaHSO₃ solution was added to remove excess bromine. The solution was filtered by suction filtration; the residue was washed with water and cold ether. Light yellow solid (8.3 g, 0.028 mol) was obtained after drying the product. The synthetic route is shown in Scheme 2.1.

2.3.1.2 Synthesis of 3,6-dibromo-1,2-phenylenediamine (3)

4,7-Dibromobenzo[1,2,5]thiadiazole (5.1 g) was added into 170 mL ethanol and 12.2 g NaBH₄ was slowly added to solution at 0°C. After the addition of NaBH₄, the solution was stirred mixed at room temperature for 20 hours [101]. Solvent was evaporated under vacuum and the residue was treated with water and extracted with ether twice. The combined organic layers were washed with brine and dried over MgSO₄. After removal of the solvent under vacuum, the product (Scheme 2.1) was obtained as a white solid (4.5g, 0.017mol).

2.3.1.3 Synthesis of 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline (5)

The condensation reaction of 3,6-dibromo-1,2-phenylenediamine (3) (1g, 0.003 mol) and 1,2-di(thiophen-2-yl)ethane-1,2-dione (4) (0.85 g, 0.004 mol) in 50 mL ethanol at 90°C for 24 hours with 0.1 g PTSA [102] resulted in yellow solid product (1.8 g, 0.004 mol) after cooling to 0°C filtered and washed with ethanol [101] (Scheme 2.1).



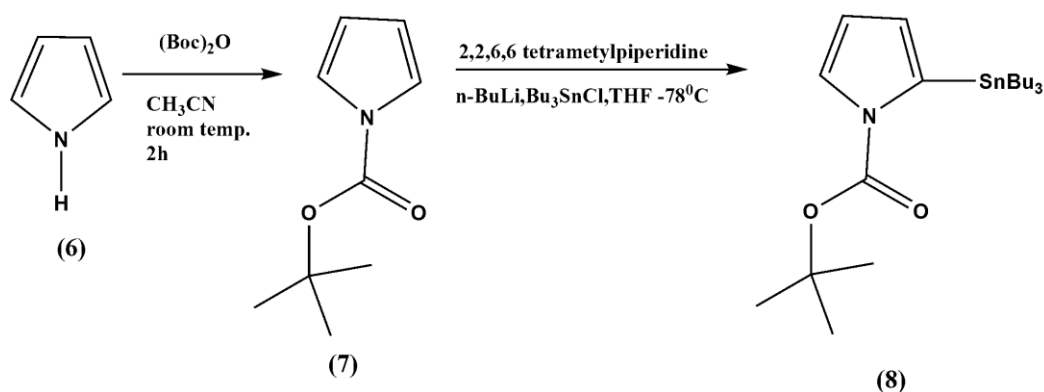
Scheme 2.1 Synthesis of 5, 8-dibromo-2, 3-di (thiophen-2-yl) quinoxaline

2.3.1.4 Synthesis of *tert*-butyl pyrrole-carboxylate (7)

To a solution of pyrrole (6) (2.0 g, 0.03 mol) in acetonitrile (30 mL), di-*tert*-butyl dicarbonate, (Boc)₂O, (7.8 g, 0.036 mol) and 4-(dimethylamino)pyridine, DMAP, (0.5 g, 0.004 mol) were added under argon (Scheme 2.2). The mixture was stirred for two hours at room temperature. *Tert*-butyl pyrrole-1-carboxylate (4.73 g) of was obtained as a colorless liquid after column chromatography (Al₂O₃, hexane) [102].

2.3.1.5 Synthesis of *N*-(*tert*-butoxycarbonyl)-2-(tributylstannyl)pyrrole (8)

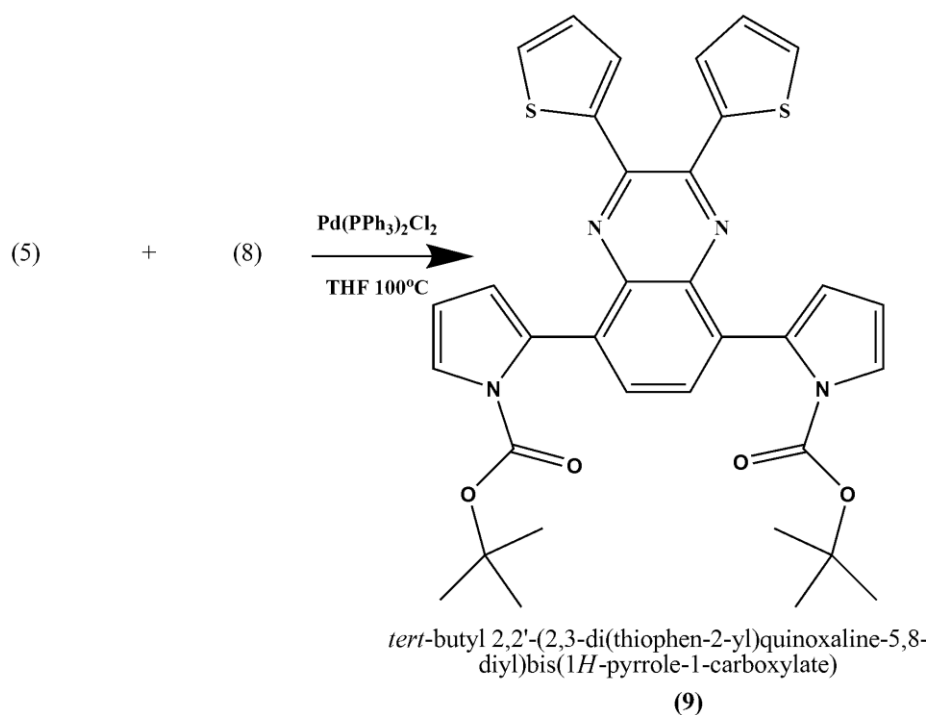
2,2,6,6-Tetramethylpiperidine (2.79 g, 0.02 mol) in dry THF (50mL) was cooled to -78°C (acetone / liquid nitrogen bath) and 18 mL of a 1.6 N solution of *n*BuLi (21.5 mmol) in hexane were added dropwise. The reaction mixture was warmed to 0°C for 30 minutes and cooled again to -78°C. *Tert*-butyl pyrrole-1-carboxylate (3 g, 0.018 mol) in dry THF (40 mL) was dropwise added at this temperature. A solution of Bu₃SnCl (7.5 mL, 0.023 mol) in dry THF (40 mL) was dropwise added. The mixture was warmed to room temperature slowly and stirred overnight at this temperature (Scheme 2.2). THF was removed under reduced pressure, crude product was extracted with water and diethyl ether (50:50 mL).The organic layer was dried over (Na₂SO₄) and the solvent was evaporated. Column chromatography on neutral alumina resulted of *N*-(*tert*-butoxycarbonyl)-2-(tributylstannyl)pyrrole as a light yellow oil with 75% yield (6.18g) [102].



Scheme 2.2 Synthesis of N-(tert-butoxycarbonyl)-2-(tributylstannyl)pyrrole

2.3.1.6 Synthesis of tert-butyl-2,2'-(2,3-di(thiophen-2-yl) quinoxaline-5,8-diyl) bis(1H-pyrrole-1-carboxylate) (9)

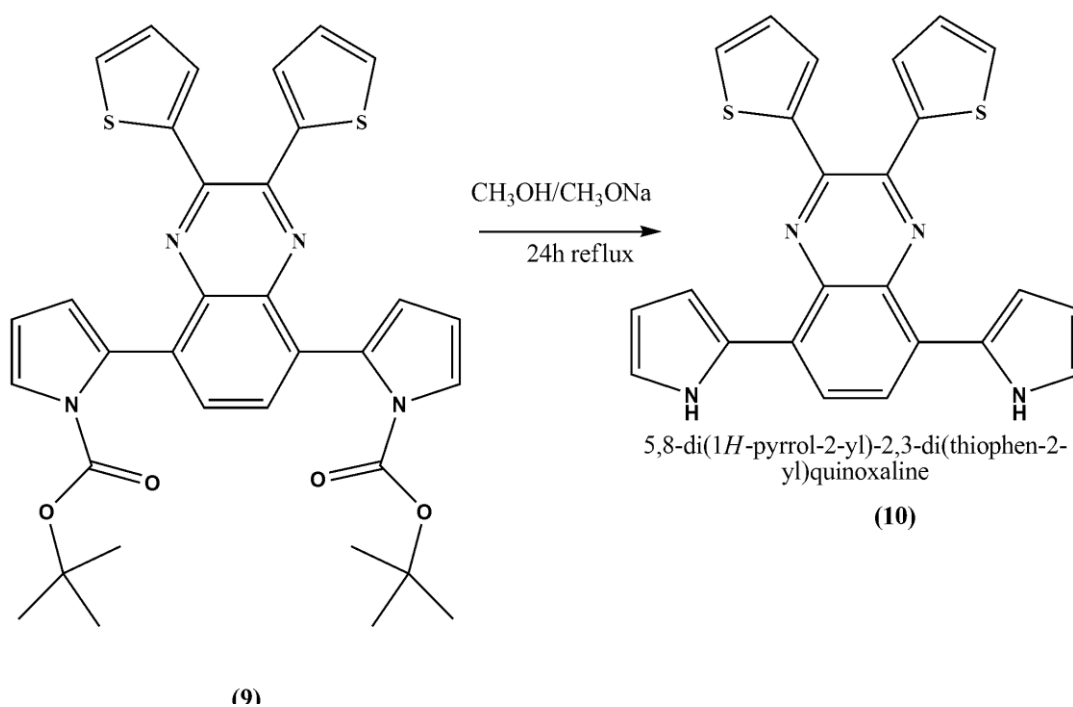
5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline (200 mg, 0.446 mmol), and *N*-(*tert*butoxycarbonyl)- 2-(tributylstannyl)pyrrole (1.0 g, 0.002 mol) were dissolved in anhydrous THF (100 mL) and purged with argon for 30 min. Dichlorobis(triphenyl phosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature under argon atmosphere (Scheme 2.3). The mixture was refluxed for 3 days. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on neutral alumina (DCM:hexane, 2:1 v/v) to obtain *tert*-butyl-2,2'-(2,3-di(thiophen-2-yl)quinoxaline-5,8-diyl)bis(1H-pyrrole-1- carboxylate (190 mg (68%)) as yellow solid.



Scheme 2.3 Synthesis of *tert*-butyl-2,2'-(2,3-di(thiophen-2-yl) quinoxaline-5,8-diyl) bis(1*H*-pyrrole-1-carboxylate)

2.3.1.7 Synthesis of 5,8-di (1*H*-pyrrol-2-yl) - 2,3-di(thiophen-2-yl) quinoxaline (PTQ) (10)

Tert-butyl-2,2'-(2,3-di(thiophen-2-yl) quinoxaline- 5,8-diyl) bis (1*H*-pyrrole-1-carboxylate (350 mg, 0.560 mmol) was dissolved in methanol (50 mL). Sodium (120 mg, 5.2 mmol) were added and the reaction mixture was heated under reflux for 24 h (Scheme 2.4). The solvent was evaporated and the residue was treated with water and extracted with dichloromethane. The organic extracts were dried over MgSO₄, the solvent was evaporated and the residue chromatographed on a column with silica gel using hexane–dichloromethane (2:1 v/v) as eluent. In the second fraction 200 mg (84 %) of the product was isolated as dark red solid.



Scheme 2.4 Synthesis of 5,8-Di (1*H*-pyrrol-2-yl) - 2,3-di(thiophen-2-yl) quinoxaline (PTQ)

2.4 Electrochemical Polymerization of Homopolymer and Copolymers

2.4.1 Electrochemical Synthesis of Homopolymer-PTQ

Electrochemical polymerization of PTQ was performed using TBAP as the supporting electrolyte (0.1M) in DCM. A background voltammogram was run to ensure that no impurity was present before the addition of substrate. The electrolysis solution contained 0.050 M PTQ. Experiments were carried out sweeping the potential between -0.5 V and +1.1 V with 100 mV/sec scan rate and the free standing film that formed was washed with DCM to remove unreacted monomer and excess electrolyte after electrolysis.

2.4.2 Electrochemical Synthesis of Copolymers P(PTQ-co-BiEDOT) & P(PTQ-co-BEBT)

For the synthesis of conducting copolymers P(PTQ-co-BiEDOT) and P(PTQ-co-BEBT), 2,2'-bis(3,4-ethylenedioxythiophene) (BiEDOT) and 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole (BEBT) were used as the comonomers. PTQ (0.050 M) was dissolved in DCM and BiEDOT (0.020 M) and BEBT (0.020 M) was introduced into single compartment electrolysis cell separately to obtain copolymers. TBAP (0.1 M) was used as the supporting electrolyte. The potentiodynamic polymerization was carried out by sweeping the potential between -0.5 V and +1.1 V with 100 mV/sec scan rate. After electrolysis, the film was washed with DCM to remove the supporting electrolyte and the unreacted monomers.

2.5 Electrochromic Properties of PTQ and Its Copolymers

2.5.1 Spectroelectrochemical Studies

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques operated at the same time.

Compared to common electrochemical methods, it can provide information on both electrochemical response and accompanying optical characteristics of all states from an electrochemical reaction. It is essential to gather in-situ information, during electrochemical processes. For the investigation of homopolymer and copolymers, films were potentiodynamically deposited on indium tin oxide (ITO) coated glass slide, via sweeping the potential between -0.5 V and 1.1 V in the presence of PTQ

and TBAP in DCM. The polymer films were reduced, washed with electrolyte solution to remove unreacted monomer and comonomer.

For the spectroelectrochemical studies, the polymer film coated ITO was placed in a cuvette equipped with a reference electrode (Ag wire) and a Pt wire counter electrode. Different potentials in a range (from fully reduced states of polymers to fully oxidized states) were applied to the coated ITO glass slides in a monomer free solution. The types and concentrations of electrolytes were the same as those in electrolysis solutions. The results were then recorded as a graph of the extent of absorption versus wavelength.

2.5.2 Switching Studies

A remarkable color change and the switching ability between the two colored states of the polymer are crucially important for electrochromic applications. Long term switching studies were carried out to monitor absorbance changes with time during repeated potential stepping between bleached and colored states to obtain an insight about the optical contrast (Figure. 2.3). A square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry was used to probe switching times and contrast in these polymers. In this double potential step experiment, the potential was set at an initial potential for a set period of time, and was stepped to a second potential for a set period of time, before being switched back to the initial potential again. Electrochromic contrast is often reported as percent transmittance change (T %) at a specified wavelength where the material has the highest optical contrast.

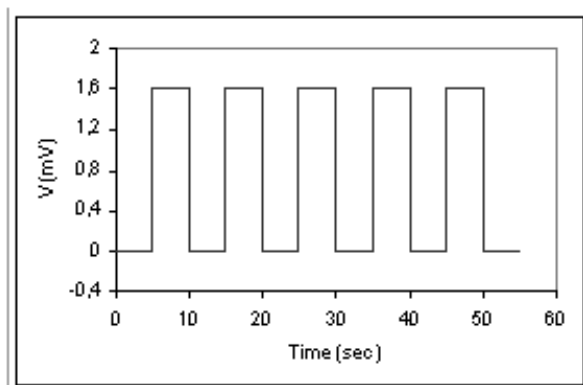


Figure.2. 3 Square wave voltammetry

In order to study switching properties, homopolymer and copolymers were deposited on ITO-coated glass slides in the form of thin films. After coating the polymers on ITO electrode, a potential square wave was applied in the monomer free solution while recording the percent transmittance between its neutral and doped states at a fixed maximum absorption wavelength. Switching properties of polymer films were investigated using potential square wave technique with a residence time of 5 seconds between -0.5 V and 1.1 V.

2.5.3 Colorimetry

The quantitative measure of the colors and graphically representing the track of doping-induced color changes of the electrochromic materials were defined accurately by performing colorimetry measurements. The Commission Internationale de l'Eclairage (CIE) system was employed as the quantitative scale to define and compare colors. The identifications of the colors; Y_{xy} values, were measured at the fully oxidized and reduced states of the homopolymer and copolymer.

2.5.4 Coloration Efficiency

Coloration efficiency (CE), provides information on the contrast ratio obtained for a certain amount of charge introduced in the material is a major electrochromic material characteristic. CE (η) is defined as the relation between the injected/ejected charge as a function of electrode area (Q_d) and the change in optical density, ΔOD , at a specific dominant wavelength (λ_{max}) [103].

CHAPTER III

RESULTS&DISCUSSION

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

^1H NMR and ^{13}C NMR spectra of monomer were taken on a Bruker-Instrument-NMR Spectrometer (DPX-400) monomer with CDCl_3 as the solvent and chemical shifts (δ) are given relative to tetramethylsilane as the internal standard.

Tert-butyl- 2,2'- (2,3-di(thiophen-2-yl) quinoxaline- 5,8-diyl) bis (1H-pyrrole-1-carboxylate as yellow solid. ^1H NMR (400 MHz, CDCl_3) δ = 0,98 (s, 18H), 6.27 (t, 2 H, J = 6.4 Hz) , 6.31 (q, 2H, J = 1.6 Hz.), 6.87 (dd, 2 H, J = 5.0, 1.2 Hz.), 7.28 (d, 2H, J = 3.6 Hz), 7.34 (d, 2H, J = 4.0 Hz), 7.48 (q, 2H, J = 2 Hz), 7.64 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ =27.78, 83.42, 110.77, 115.68, 123.45, 127.67, 128.90, 129.51, 129.71, 131.53, 133.59, 139.21, 142.68, 145.01, 149.80 (Figure.3.1).

5,8-Di(1H-pyrrol-2-yl)-2,3-di(thiophen-2-yl)quinoxaline (PTQ) as dark red solid. ^1H NMR (400 MHz, CDCl_3) δ = 6.27 (m, 2H), 6.80 (m, 2H), 6.95 (m, 2H), 7.03 (dd, 2H, J = 5.0-1.2 Hz), 7.30(d, 2H, J = 4.8 Hz), 7.50 (d, 2H, J = 4,5 Hz), 7.94 (s, 2H), 11.65 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 108.06, 109.59, 120.07, 126.13, 126.34, 128.45, 129.27, 129.66, 130.84, 137.18, 141.90, 144.07 (Figure.3.2).

The new peak formed at 11.65 ppm and loss of the peaks belong to t-BOC group proves that deprotection reaction was successful.

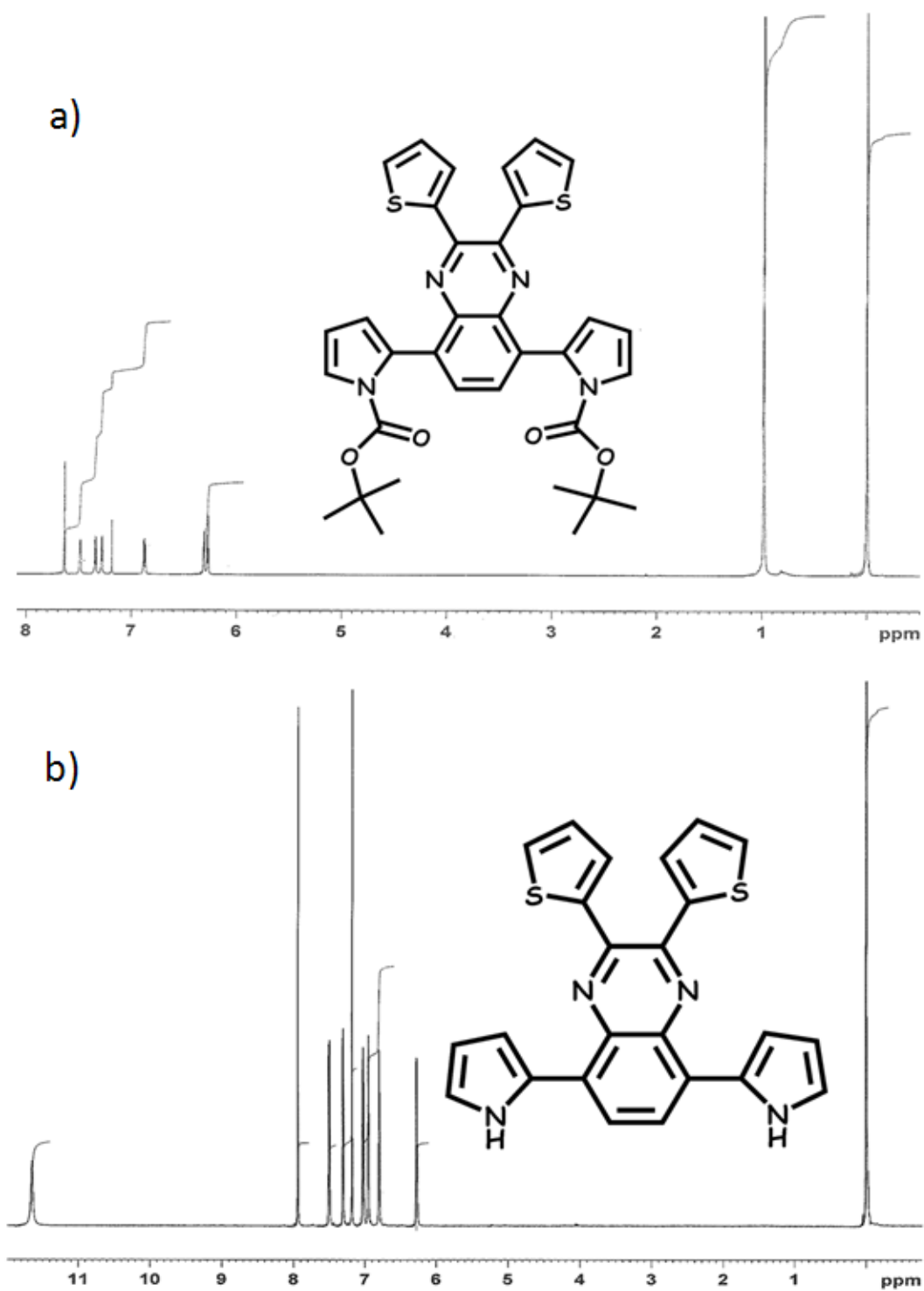


Figure.3. 1 (a) ^1H spectrum of tert-butyl- 2,2'- (2,3-di(thiophen-2-yl) quinoxaline-5,8-diyl) bis (1H-pyrrole-1- carboxylate) **(b)** ^1H spectrum of 5,8-di(1H-pyrrol-2-yl)-2,3-di(thiophen-2-yl)quinoxaline (PTQ)

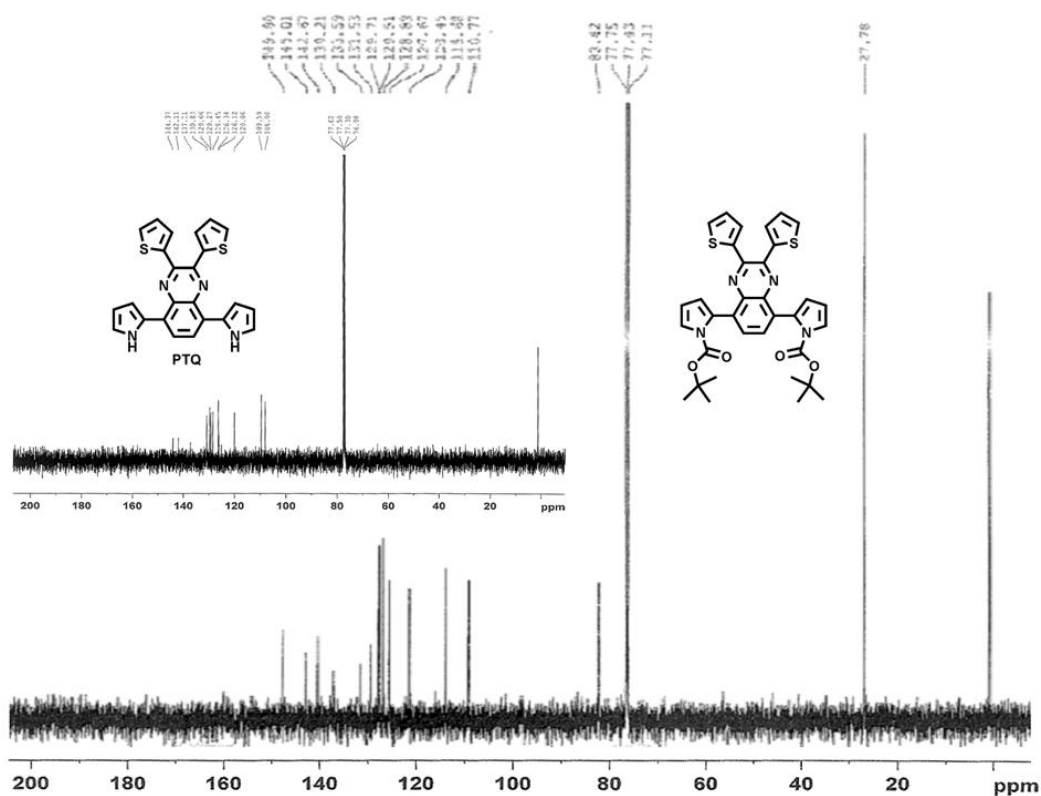


Figure.3. 2 ^{13}C -NMR spectrum of the tert-butyl- 2,2'- (2,3-di(thiophen-2-yl) quinoxaline- 5,8-diyl) bis (1H-pyrrole-1- carboxylate) and 5,8-di(1H-pyrrol-2-yl)- 2,3-di (thiophen-2-yl)quinoxaline (PTQ)

3.2 High Resolution Mass Spectrometry

High Resolution Mass Spectrometry (HRMS) results; calculated PTQ $C_{24}H_{16}N_4S_2$ (m/z) 424.08, found 425.09.

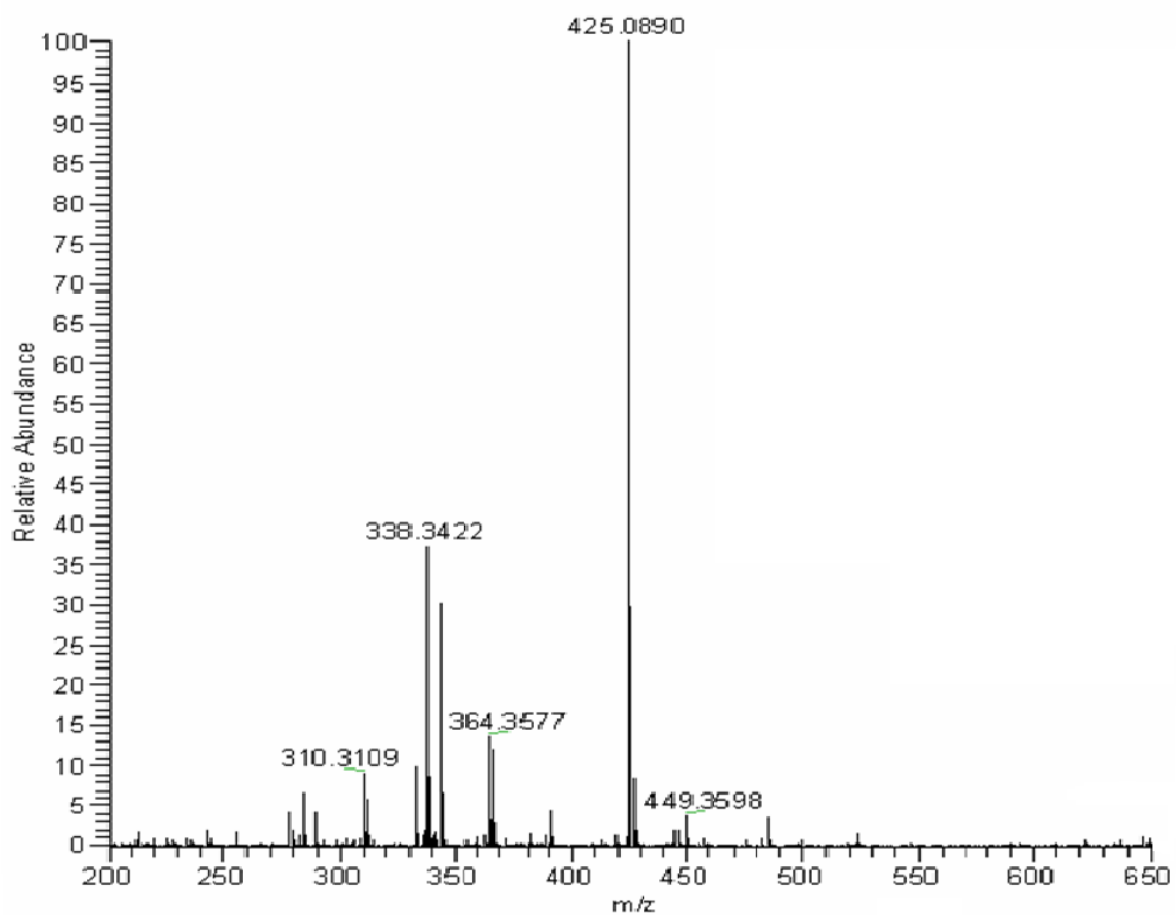


Figure.3. 3 HRMS results for monomer PTQ

3.3 Electrochemical Synthesis of Polymers

3.3.1 Electrochemical Synthesis of Homopolymer P(PTQ)

For monitoring electrochromic characteristics of homopolymer, electropolymerization on ITO was performed with 0.1 M TBAP supporting electrolyte and 0.050 M PTQ in DCM. Multiple scan voltammetry was used via applying potentials between -0.5 V and +1.1 V at a scan rate of 100 mV/s.

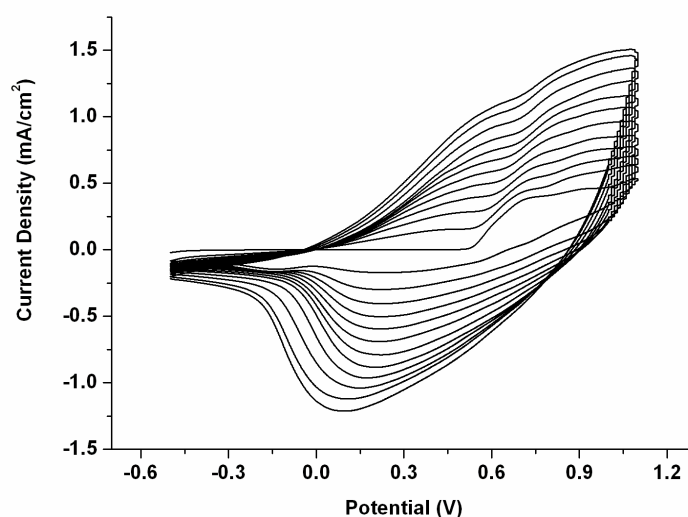


Figure.3. 4 Repeated potential scan electropolymerization of PTQ at 100 mVs^{-1} in 0.1 M TBAP/ CH_2Cl_2 on an ITO electrode

The monomer oxidation potential was observed at +0.70 V. After the first cycle, polymer's oxidation peak was observed at +0.55 V together with its reduction peak

at +0.10 V (Figure.3.4). Upon consecutive cycles, there was a gradual increase in the current intensity indicating continuous film formation.

Current response versus scan rate represents a linear relation which proves that the P(PTQ) film was electroactive and well adhered to the ITO electrode (Figure.3.5). Additionally, linear relation between anodic peak currents and scan rate indicated that electrochemical processes are not diffusion controlled and are reversible [104].

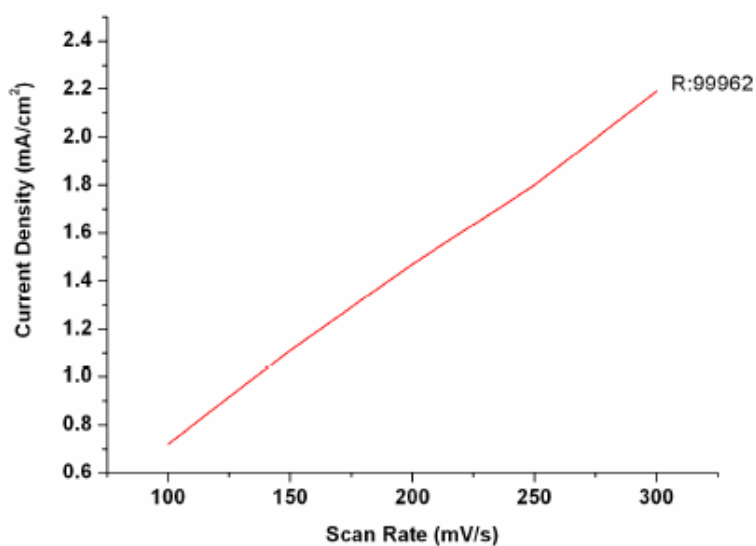
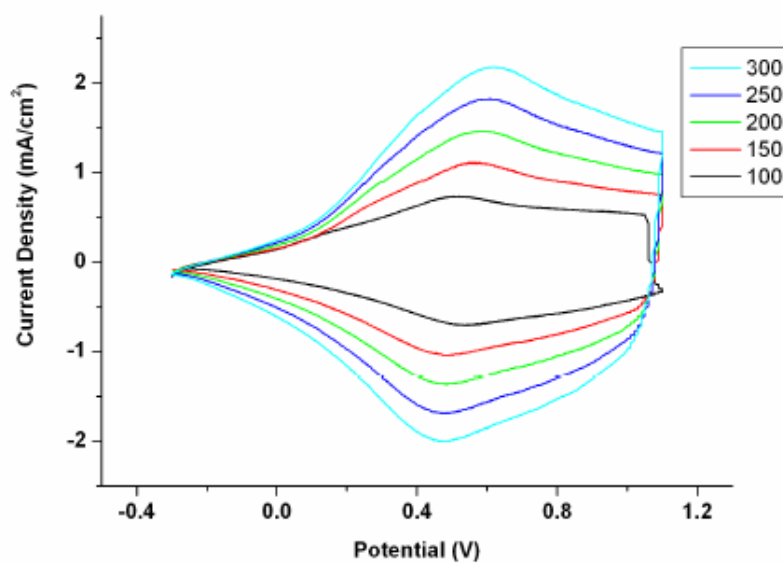


Figure.3. 5 a) Scan rate dependence of P(PTQ) in TBAP/DCM (a) 100, (b)150, (c)200, (d) 250, (e) 300 mV/s. b) Linear relation between current density and scan rate

3.3.2 Electrochemical Synthesis of Copolymers P(PTQ-co-BiEDOT) & P(PTQ-co-BEBT)

Copolymerization was done to improve the optical properties of homopolymer P(PTQ). Oxidation potentials of the two monomers should be close to each other, to achieve an effective copolymerization reaction electrochemically. BiEDOT was chosen due to its oxidation potential, its advanced optical and mechanical properties [105] like EDOT. On the other hand, BEBT was shown to have superior properties over EDOT [106].

Electrochemical copolymerizations of PTQ with BiEDOT and BEBT were explored by cyclic voltammetry in 0.1 M TBAP/DCM.

The oxidation reduction behavior and the increments between following cycles of two copolymers are completely different from those of PTQ, BiEDOT and BEBT. P(PTQ-co-BiEDOT) has an oxidation potential at +0.45 V and a reduction potential at -0.2 V (Figure.3.6 (a)), whereas P(PTQ-co-BEBT) has an oxidation potential at +0.70 V and a reduction potential at +0.30 V (Figure.3.7 (a)). The broad, oxidation peak, during the second voltammetric cycle can be attributed to the oligomeric species (dimers, trimers etc.) with variable chain lengths. When CV's of copolymers are compared with the voltammogram of pure BiEDOT and BEBT (Figure.3.6, Figure.3.7 (b)), the redox peaks are not at the same potentials.

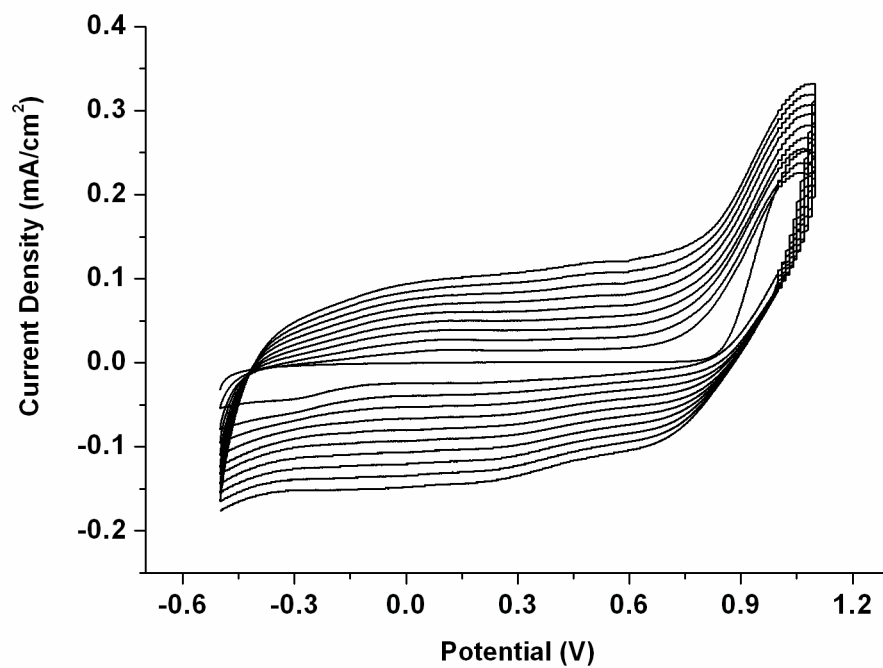
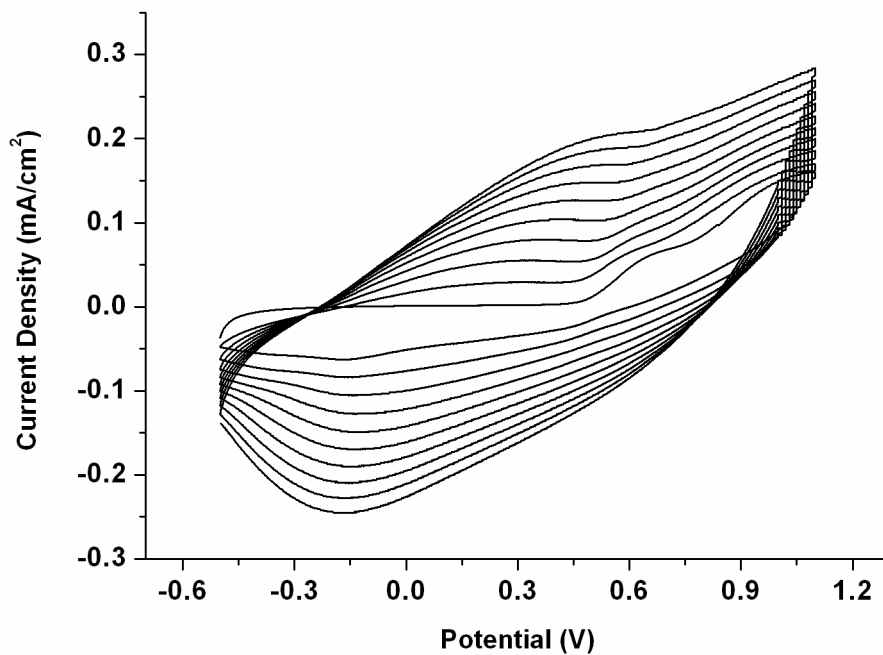


Figure.3. 6 Cyclic voltammograms of (a) P(PTP-co-BiEDOT),
(b) pure P(BiEDOT)

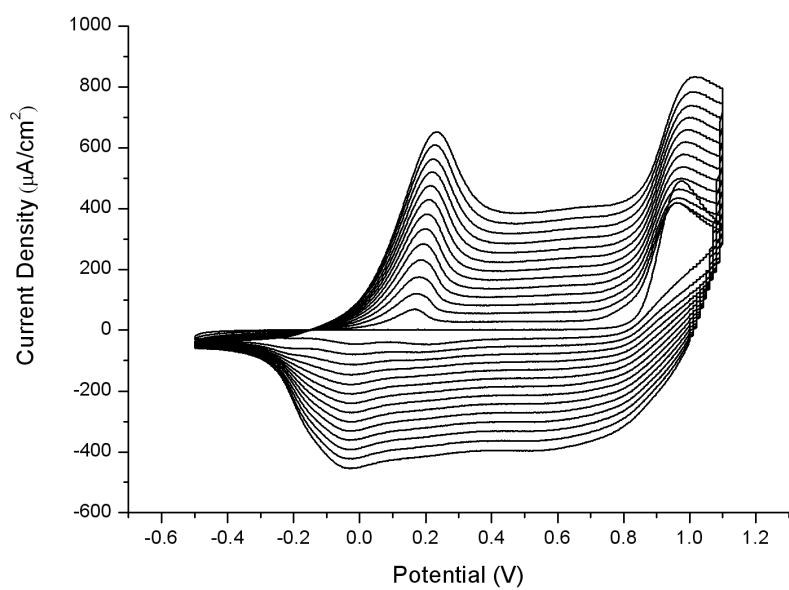
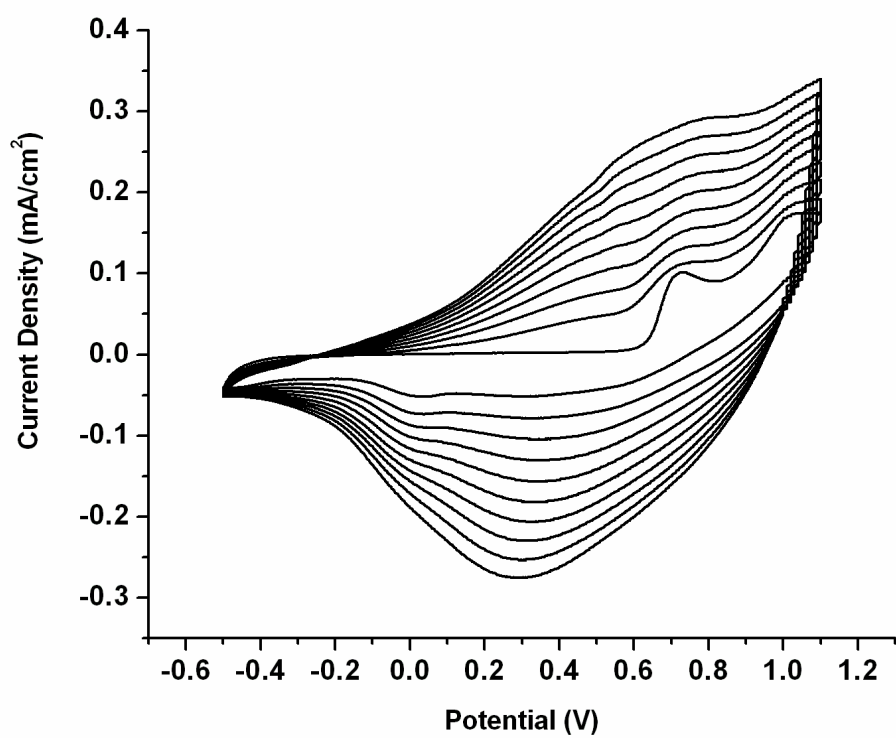


Figure.3.7 Cyclic voltammograms of (a) P(PTP-co-BEBT),
(b) pure P(BEBT)

The scan rate dependence of the P(PTQ-co-BiEDOT) and P(PTQ-co-BEBT) copolymer films were explored. A linear relationship was found between the peak current and the scan rate, indicating that the copolymer films were well adhered and the oxidation reduction processes were non-diffusion controlled (Figures.3.8(a) and (b) and Figures.3.9(a) and (b)).

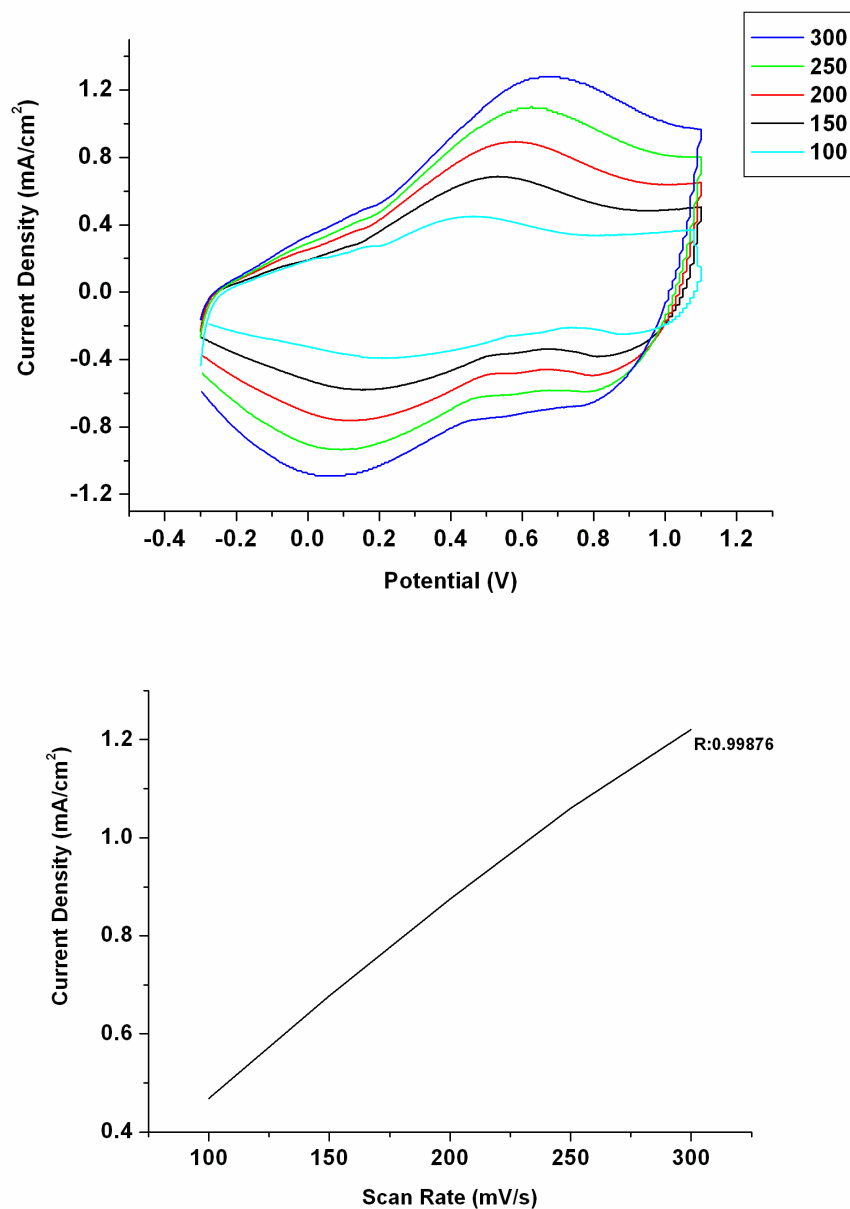


Figure.3. 8 Scan rate dependence of P(PTQ-co-BiEDOT) in TBAP/DCM (a) 100, (b)150, (c)200, (d) 250, (e) 300 mV/s. b) Linear relation between current density and scan rate

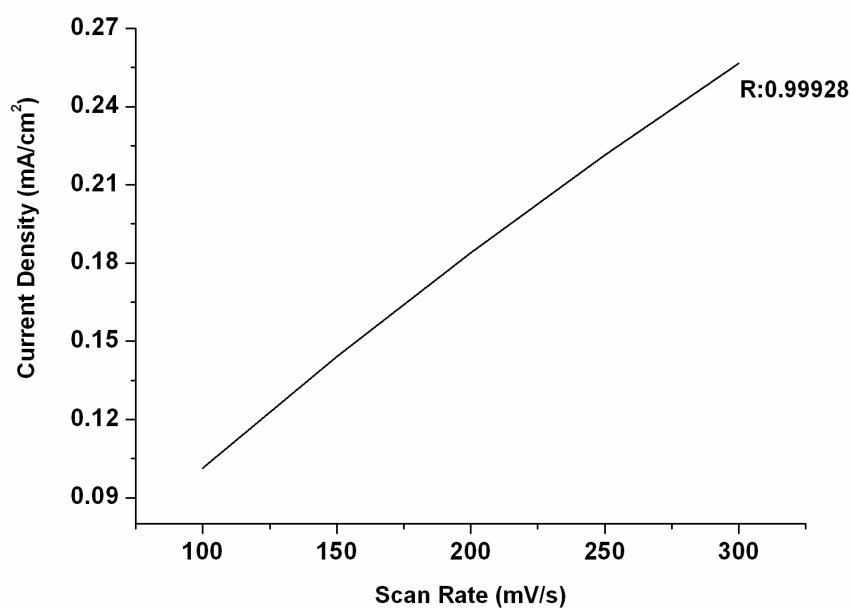
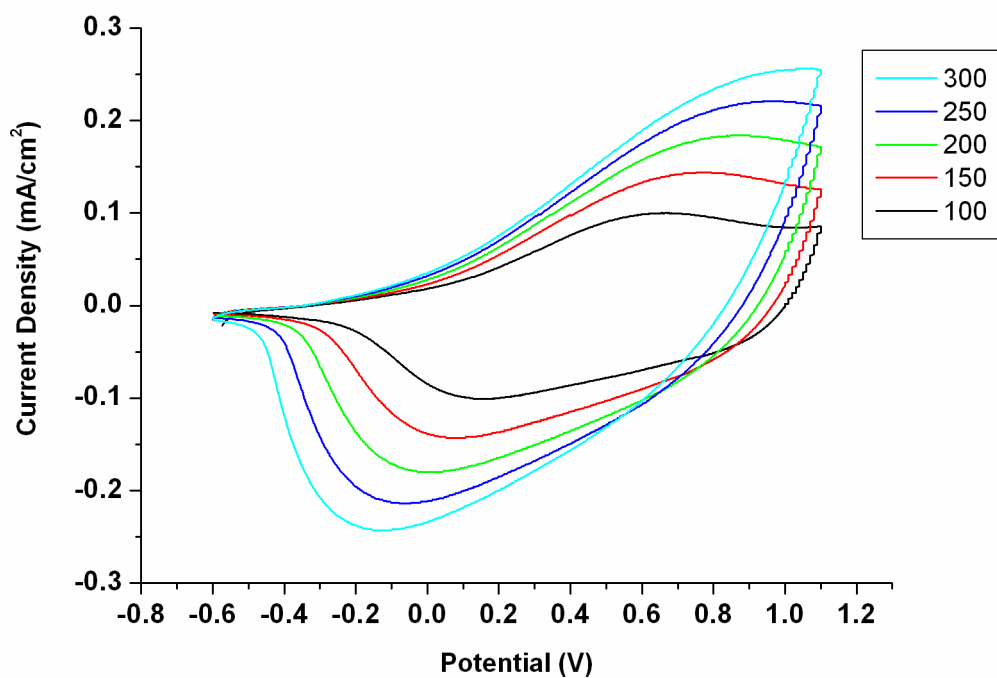


Figure.3. 9 (a) Scan rate dependence of P(PTQ-co-BEBT) in TBAP/DCM (a) 100, (b)150, (c)200, (d) 250, (e) 300 mV/s. b) Linear relation between current density and scan rate

3.4 Conductivities of the Films

The conductivities of the solution and the electrode sides were measured by the standard four-probe technique. When the electrode side and the solution side conductivities were compared, equal conductivities were observed almost in each case. This reveals the homogeneity of the films. The conductivity of the P(PTQ) was found to be $10.10^{-1} \text{ S.cm}^{-1}$. The conductivities of P(PTQ-co-BiEDOT) and P(PTQ-co-BEBT) were $14.10^{-1} \text{ S.cm}^{-1}$ and $20.10^{-1} \text{ S.cm}^{-1}$ respectively. It was observed that the conductivity increased via copolymerization. This is expected as the conjugation length of the P(PTQ) increases with the presence of BiEDOT and BEBT.

Table.3. 1 Conductivities of Films of Polymers (S.cm^{-1})

Polymer	Conductivity (S.cm^{-1})
P(PTQ)	10.10^{-1}
P(PTQ-co-BiEDOT)	14.10^{-1}
P(PTQ-co-BEBT)	20.10^{-1}

3.5 Investigation of Electrochromic Properties of Polymers

3.5.1 Spectroelectrochemistry of P(PTQ)

In its neutral state, the color of the polymer depends on the energy gap between the valence and conduction bands. The energy gap between bipolaron band and conduction band determines the color in oxidized state. These are all dependent on the conjugation of the polymer, the electrochemical nature of side groups and their effects on the polymer backbone. There are basically five documented contributors that influence the band gap of the conjugated polymer, namely the energy related to the bond alternation ($E^{\Delta r}$), the mean deviation from planarity (E^{θ}), the aromatic

resonance energy (E^{Res}), the inductive and mesomeric electronic effects of substituents (E^{Sub}) and interchain interactions (E^{Int}).

In order to explore the optical changes upon doping and the electrochromic properties of conjugated polymers spectroelectrochemistry studies were performed. P(PTQ) was coated on ITO and spectral changes were explored by UV-Vis-NIR spectrometer in a monomer free 0.1 M TBAP/DCM via incrementally increasing applied potential between -0.3 V and +1.1 V. It also provides information on the properties of conjugated polymers, such as band gap (E_g) and the intergap states that appear upon doping.

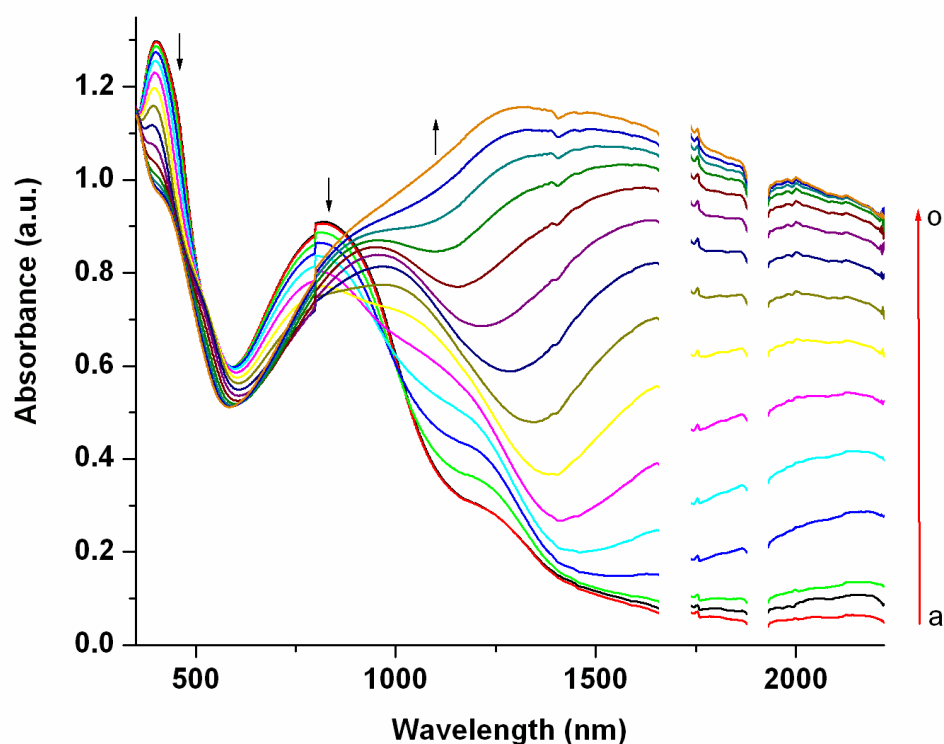


Figure.3. 10 Spectroelectrochemistry of P(PTQ) film on an ITO coated glass slide in monomer-free 0.1 M TBAP/DCM electrolyte-solvent couple at applied potentials (V), (a) -0.3, (b) -0.2, (c) -0.1, (d) 0.0, (e) 0.1, (f) 0.2, (g) 0.3, (h) 0.4, (i) 0.5, (j) 0.6, (k) 0.7, (l) 0.8, (m) 0.9, (n) 1.0, (o) 1.1

A spectroelectrochemical series for P(PTQ) is shown in Figure. 3.10. In the neutral state the polymer exhibits two transitions from the valence band to conduction band (π - π^*). The band gap energy which is measured as the onset of the π - π^* absorption was calculated for P(PTQ). The wavelength at which homopolymer shows π - π^* transition is defined as the maximum wavelength (λ_{max}). Using de Broglie equation, the band gap (E_g) is found as 1.0 eV at 815 nm for P(PTQ).

Polymers with donor acceptor units generally show band-gaps between 0.9 eV to 1.3 eV [107,108]. Upon applying voltage, reduction in the intensity of the π - π^* transitions along with evolution of new absorption bands in the NIR region was observed. Polaron and bipolaron charge carrier bands are the reason for these transitions. This resulted in an extremely transmissive colorless oxidized state. The band gap of the polymer is 1.0 eV as calculated from the onset of the π - π^* transition. This value is way below than that of PPy (2.7 eV) [88,109].

Polymer in the neutral state shows two absorption bands at 400 nm and 815 nm. At the reduced state, polymer has green color. Following successive oxidation, intensities of both absorption bands steadily decrease, with the formation of a radical cation and polymer color changes to gray at the oxidized state. As a result of charge carrier formation upon oxidation, the absorption in the visible region reduces and new absorption bands evolve at 943 nm and 1460 nm representing the formation of polaronic and bipolaronic bands respectively [110].

3.5.2 Spectroelectrochemistry of P(PTQ-co-BiEDOT)& P(PTQ-co-BEBT)

In order to investigate electronic structure of the copolymers obtained by different applied potentials, spectroelectrochemistry studies were carried out. The composition of the copolymer depends on monomer feed concentration, the reactivity of monomer radical cations and applied potential.

Most persuasive proof of copolymerization is the determination of the differences between the spectroelectrochemical behavior of the copolymers and the homopolymer [111].

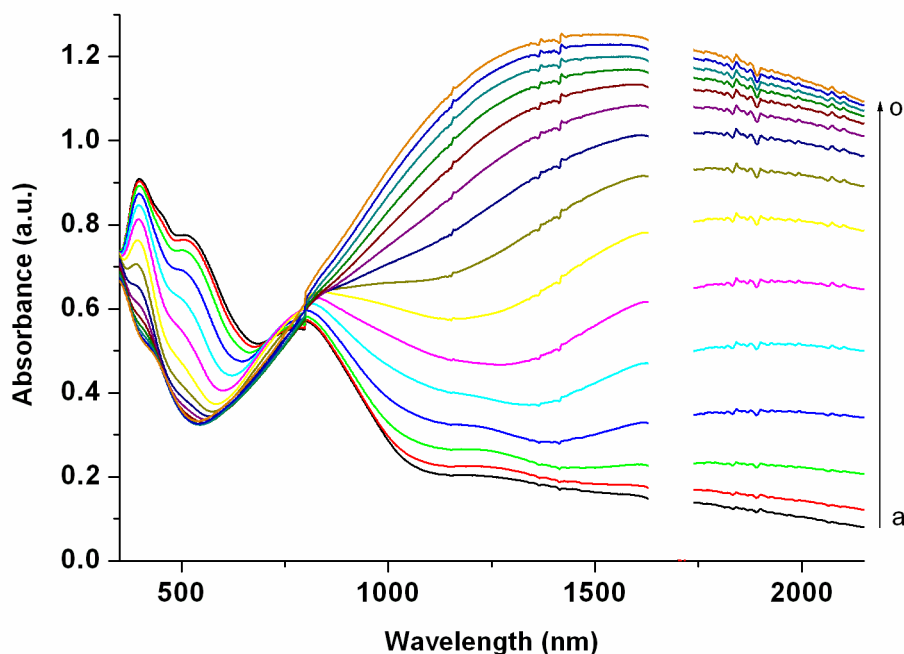


Figure.3. 11 Spectroelectrochemistry of P(PTQ-co-BiEDOT) film on an ITO coated glass slide in monomer-free 0.1 M TBAP/DCM electrolyte-solvent couple at applied potentials (V), (a) -0.3, (b) -0.2, (c) -0.1, (d) 0.0, (e) 0.1, (f) 0.2, (g) 0.3, (h) 0.4, (i) 0.5, (j) 0.6, (k) 0.7, (l) 0.8, (m) 0.9, (n) 1.0, (o) 1.1

P(PTQ-co-BiEDOT) has a λ_{max} at 525 nm with a purple color at -0.3 V, calculated band gap of 1.4 eV (Figure.3.11). Upon oxidation, the $\pi-\pi^*$ transition was depleted at the expense of a peak at about 800 nm producing a bluish-green color at +1.1 V.

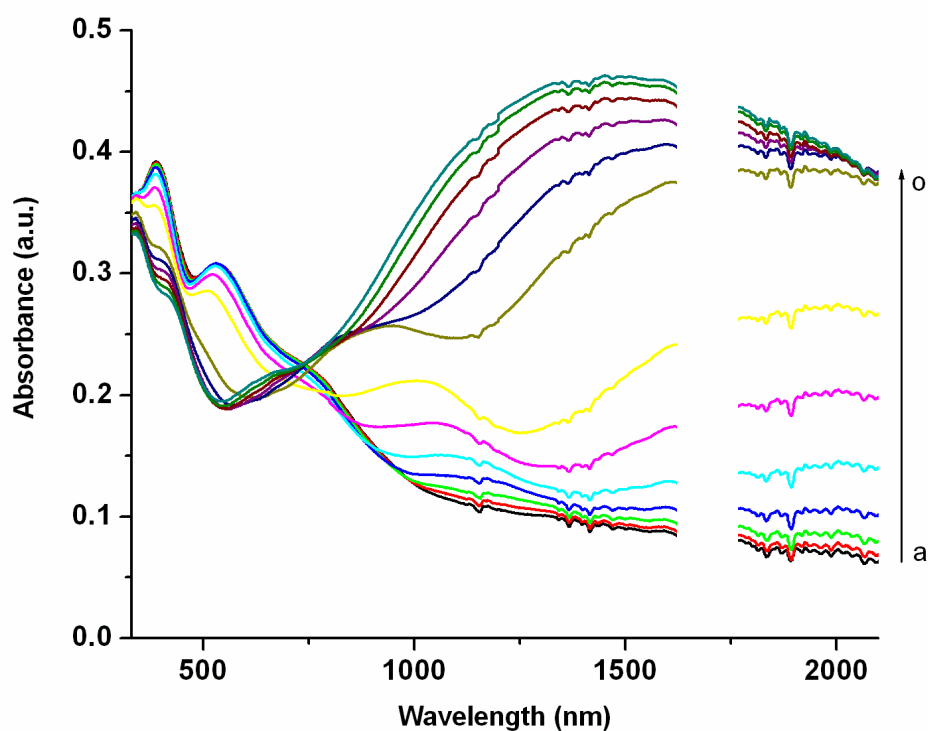


Figure.3. 12 Spectroelectrochemistry of P(PTQ-co-BEBT) film on an ITO coated glass slide in monomer-free 0.1 M TBAP/DCM electrolyte-solvent couple at applied potentials (V), (a) -0.3, (b) -0.2, (c) -0.1, (d) 0.0, (e) 0.1, (f) 0.2, (g) 0.3, (h) 0.4, (i) 0.5, (j) 0.6, (k) 0.7, (l) 0.8, (m) 0.9, (n) 1.0, (o) 1.1

P(PTQ-co-BEBT) has a λ_{\max} at 530 nm (light brown), with a band gap of 1.1 eV the $\pi-\pi^*$ transition was depleted at the expense of a peak at about 750 nm, corresponding to the charge carrier (radical cations) at +1.1 V (green) (Figure.3.12). Copolymers show different λ_{\max} values compared to the corresponding comonomers which indicates copolymer formation also. Copolymerization enhances the optical properties of the homopolymer PTQ.

3.5.3 Electrochromic Switching of Polymers

The capacity of a polymer towards changing its color rapidly accompanied with a significant change is vital properties for an electrochromic polymer. Response time of the polymer films to the applied potential was measured with chronoabsorptometry. In this technique, the polymer film was kept at its fully oxidized state for 5 sec, and then it was stepped to its reduced form and kept at this state for another 5 sec before being switched back to the initial potential again. Time required switching between the redox states were recorded as the switching time. The optical contrast in the reduced and oxidized forms were measured and noted as ΔT %.

The stabilities, optical contrasts, and response times upon electrochromic switching of the polymer films between their neutral and oxidized states were monitored both in the visible and NIR regions. A square-wave potential step method coupled with optical spectroscopy was used to explore switching time and contrast for the polymer.

Electrochromic switching studies were carried out to determine the percent transmittance changes as a function of time. The % transmittance (T %) at different wavelengths including the λ_{max} of the doped polymer were measured using a UV-Vis-NIR spectrophotometer. The optical contrast for P(PTQ) was measured as the difference between T % in the neutral and oxidized states and calculated as 10 % at 400 nm. The optical contrast however, is 66 % at 1460 nm with a switching time of 1.2 s in the NIR (Figure.3.13).

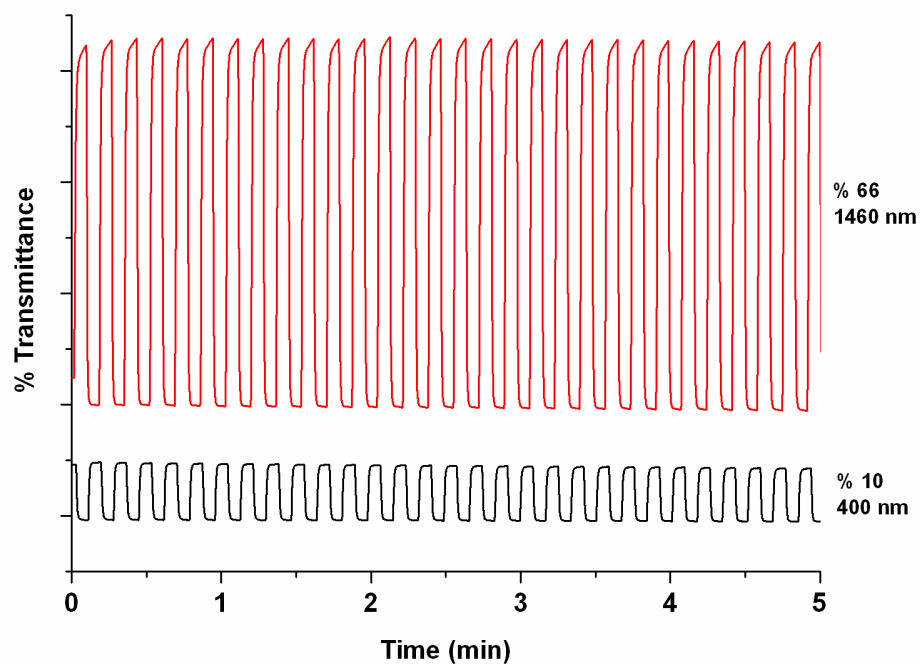


Figure.3. 13 Optical absorbance change monitored at 400 nm and 1460 nm for P(PTQ)

The electrochromic switching properties of P(PTQ-co-BiEDOT) and P(PTQ-co-BEBT) were investigated by switching a film between -0.5 V and + 1.1 V versus Ag wire in 0.1 M TBAP in DCM. An enhancement was observed by the copolymerization on kinetic properties compared to homopolymer. P(PTQ-co-BiEDOT) copolymer achieves 10 % optical contrast in 2.1 second at 400 nm, 56 % in 1.8 seconds at 525 nm and 68 % in 1.8 seconds at 1450 nm (Figure.3.14) where as P(PTQ-co-BEBT) reveals 24 % optical contrast at 530 nm in 0.5 seconds, 80 % in 0.5 seconds at 1450 nm (Figure.3.15). Homopolymer achieves 66 % at 1460 nm in 1.2 seconds.

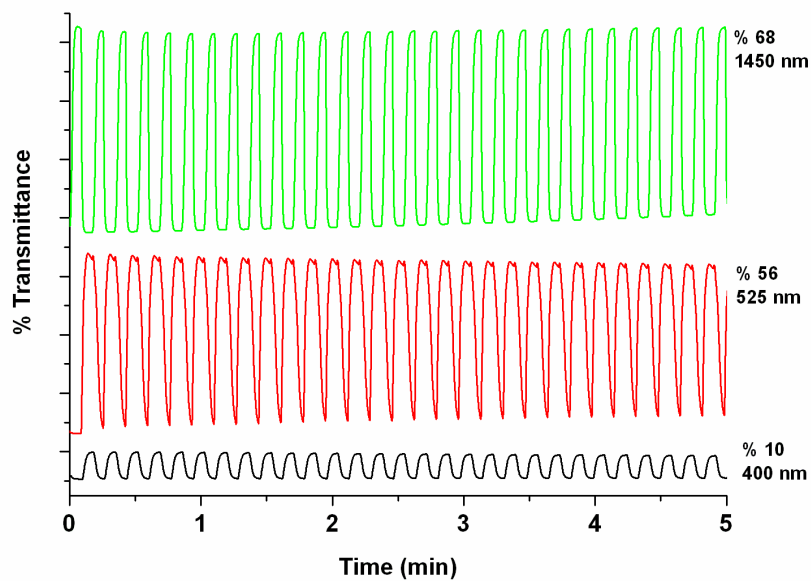


Figure.3. 14 Optical absorbance change monitored at 400 nm, 525 nm and 1450 nm for P(PTQ-co-BiEDOT)

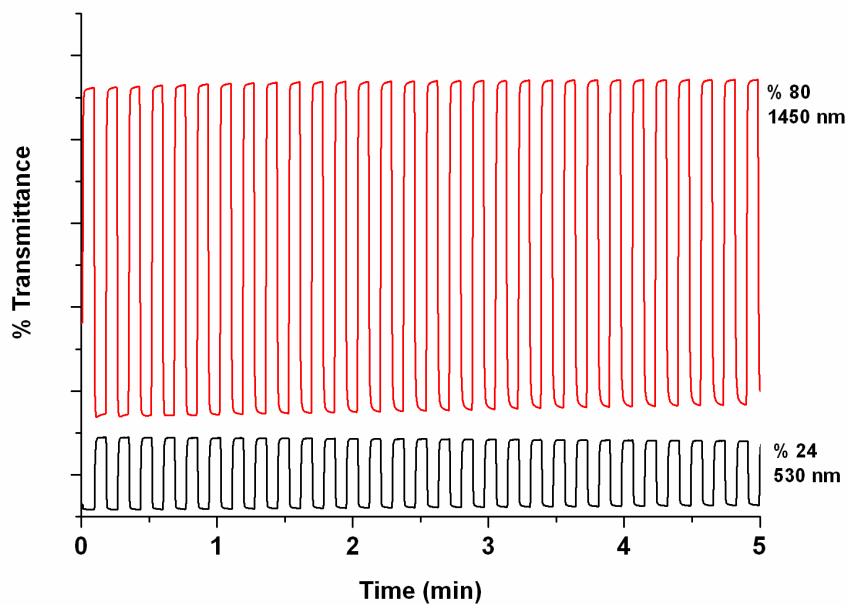


Figure.3. 15 Optical absorbance change monitored at 530 nm and 1450 nm for P(PTQ-co-BEBT)

3.5.4 Colorimetry of Polymers

The color of the film switches from green in the reduced state (-0.3 V) to gray in the oxidized state (+1.1 V). The relative luminance (Y) and the x (hue) and y (saturation) values (Table 3.1) were measured at the fully oxidized and reduced states of P (PTQ) (Table 3.1).

In comparison to homopolymer both copolymers revealed entirely different spectroelectrochemical behaviors where a synergy was accomplished as a result of copolymerization. The color coordinates of the copolymer were also determined by colorimetry in order to have an accurate objective measurement (Table 3.2).

Table 3. 1 Colors of P(PTQ)







	
(-0.3 V)	(+1.1 V)
Y: 691	Y: 392
x:0.341	x: 0.371
y:0.379	y: 0.442

Table 3. 2 Colors of (a) P(PTQ-co-BiEDOT), (b)P(PTQ-co-BEBT)

	
(-0.3 V) Y: 165 x:0.335 y:0.315	(+1.1 V) Y: 426 x: 0.294 y: 0.346

	
(-0.3 V) Y: 367 x:0.396 y:0.414	(+1.1 V) Y: 497 x: 0.386 y: 0.429

Coloration efficiency is the ratio between the injected/ ejected change per unit area of the electrode and the change in the optical density at a dominant wavelength. Coloration efficiencies of the P (PTQ), P (PTQ-co-BiEDOT) and P (PTQ-co-BEBT) were found to be $116 \text{ cm}^2 \text{ C}^{-1}$, $97 \text{ cm}^2 \text{ C}^{-1}$ and $132 \text{ cm}^2 \text{ C}^{-1}$ respectively at 100 % full switch at 400 nm.

CHAPTER IV

CONCLUSION

Synthesis of 5,8-di(1H-pyrrol-2-yl)-2,3-di(thiophen-2-yl) quinoxaline (PTQ) was successfully achieved by Stille coupling of 5,8-dibromo-2,3-di(thiophen-2-yl) quinoxaline and *N*-(*tert*butoxycarbonyl)-2-(tributylstannyl)pyrrole. The structures of both the monomer and the soluble polymer were investigated by ^1H and ^{13}C -NMR spectroscopies.

Electrochemical polymerization of PTQ was accomplished potentiodynamically in the presence of the TBAP/ CH_2Cl_2 , solvent–electrolyte couple. As a result, a free standing, electrochromic and electrically conducting polymer was obtained. Spectroelectrochemical studies revealed that the polymer has an electronic band gap of 1.0 eV. This novel polymer proved that polymers having pyrrole as the donor moiety are good candidates to for display technologies and NIR applications.

Successful syntheses of conducting copolymers of PTQ with BiEDOT and BEBT were achieved with improved electrochromic properties. Electrochromic investigations showed that P(PTQ) switches between green and gray. P(PTQ-co-BiEDOT) switches between purple and greenish-blue and P(PTQ-co-BEBT) switches between light brown and green. By the help of copolymerization color tuning was realized. A profound understanding of these materials' optical properties allows the construction of electrochromic devices with high contrast, long term switching stability and fast optical response.

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