

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF A MULTICHROMIC,  
CONDUCTING, SOLUBLE POLYTHIOPHENE DERIVATIVE  
AND ITS COPOLYMER

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MULTICHROMIC, CONDUCTING, SOLUBLE POLYTHIOPHENE  
DERIVATIVE AND ITS COPOLYMER**

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## ABSTRACT

### SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF A MULTICHROMIC, CONDUCTING, SOLUBLE POLYTHIOPHENE DERIVATIVE AND ITS COPOLYMER

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A new polythiophene derivative, poly-2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline PHTQ was synthesized by both chemical and electrochemical polymerization and its electrochemical properties were reported. The monomer was electrochemically polymerized in the presence of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte in dichloromethane-acetonitrile (5:95, v:v). Nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR) was utilized for the characterization of the monomer and the soluble polymer. The polymer was further characterized by Gel Permeation Chromatography (GPC). Spectroelectrochemistry and switching ability of the polymer were investigated by UV-vis spectrophotometer and cyclic voltammetry. The polymer revealed three distinctive colors upon doping which indicated that the polymer is multichromic.

Tert-butyl group on the pendant phenyl rings and hexyl groups on thiophene enhanced the solution processability of the electrochromic polymer. The electrochemical and spectral properties of the chemically synthesized polymer were investigated via spray coating on ITO glass slides. Electrochemical copolymerization of 2,3-bis(4-*tert*-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl) quinoxaline (HTQ) with 3,4-ethylenedioxythiophene(EDOT) was performed to fulfill a strategy in achieving fine-tuned electrochromic properties. The copolymer, P(HTQ-*co*-EDOT) was characterized via detailed studies of cyclic voltammetry and spectroelectrochemistry. Band gap ( $E_g$ ) of the copolymer was calculated as 1.4 eV and showed 34 % optical contrast with switching times less than 1 second.

**Keywords:** Conducting polymers, Electrochemical polymerization, Electrochromism, Electrochromic materials.

## ÖZ

### MULTİKROMİK, İLETKEN, ÇÖZÜNÜR BİR POLİTİYOFEN TÜREVİNİN SENTEZİ, ELEKTROKROMİK ÖZELLİKLERİ VE KOPOLİMERİ

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Yeni bir politiyofen türevi, 2,3-bis(4-tert-butilfenil)-5,8-bis(4-hekziltiyofen-2-yl)kinoksalin(HTQ), elektrokimyasal ve kimyasal yöntemlerle sentezlenmiş ve elektrokimyasal özellikleri çalışılmıştır. Monomer elektrokimyasal olarak TBAPF<sub>6</sub> destek elektroliti varlığında dikolorometan-asetonitril (5:95, v:v) içerisinde polimerleştirilmiştir. Monomer ve çözünür polimerin karakterizasyonunda Nükleer Manyetik Rezonans tekniği (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR) kullanılmıştır. Polimer ayrıca Jel Geçirgenlik Kromatografisi (GPC) ile de karakterize edilmiştir. Polimerin spektroeletrokimya ve çevirme zamanı çalışmaları, UV-vis spektrofotometresi ve dönüşümlü voltametri kullanılarak yapılmıştır. Bu çalışmalar sonucunda polimerin üç farklı renge sahip multikromik bir malzeme olduğu gözlemlenmiştir. Kimyasal polimerin elektrokimyasal ve spektral çalışmaları, spreyle ITO cam üzerine kaplanarak yapılmıştır.

Monomerin (HTQ), 3,4-etilendioksitiyofen (EDOT) ile elektrokimyasal kopolimerizasyonu da gerekleřtirilmiřtir. Kopolimer, donuřumlu voltametri ve spektroeletrokimya alıřmaları ile karakterize edilmiřtir. Kopolimerin bant aralıęı 1.4 eV, optik kontrastı % 34 ve evirim zamanı 1 saniyeden daha kısa olarak hesaplanmıřtır.

**Anahtar sozcukler:** İletken Polimerler; Elektrokimyasal polimerleřme; Kimyasal Polimerleřme; Elektrokromizm; Elektrokromik malzemeler.

*To Erman*

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## ABBREVIATIONS

HTQ	2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl) quinoxaline
PHTQ	Poly(2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl) quinoxaline)
cPHTQ	Chemical polymer of 2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl) quinoxaline
EDOT	3,4-Ethylenedioxythiophene
P(HTQ-co-EDOT)	Poly(2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl) quinoxaline -co-ethylenedioxythiophene)
EC	Electrochromic
CP	Conducting Polymer
Th	Thiophene
Py	Pyrrole
PAc	Polyacetylene
PEDOT	Poly(3,4-ethylenedioxythiophene)
ACN	Acetonitrile
GPC	Gel Permeation Chromatography
NMR	Nuclear Magnetic Resonance
CV	Cyclic Voltammetry
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
$E_g$	Band Gap Energy
CIE	La Commission Internationale de l'Eclairage
L, a, b	Luminance, hue, saturation

## CHAPTER I

### INTRODUCTION

#### 1.1 Conducting Polymers

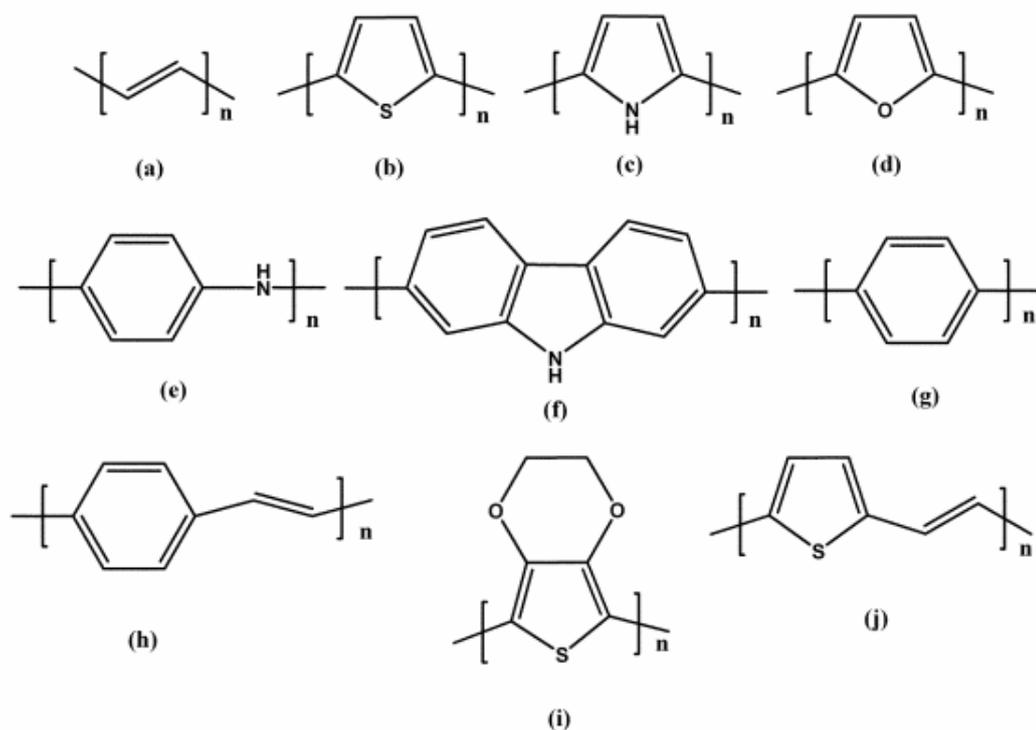
Discovery of metallic conducting polyacetylene 30 years ago introduced a new class of materials, namely conducting polymers, and its research area [1,2]. Although the history of conducting polymers is not very long, the field has been very dynamic since then. The fascinating properties of conducting polymers such as easy fabrication and processing, light weight, interesting optical behavior and metal like conductivity upon doping, attracted intensive research all over the world from different scientific disciplines and industrial research laboratories [3,4].

Conjugated polymer synthesis reaches as far back as 1862 when the first electrochemical synthesis of poly(aniline) (PANI) yielded a black powdery deposit [5]. In 1958, first polymerization of acetylene to form polyacetylene (PAC) was reported by Natta and coworkers [6]. Since PAC was obtained as an insoluble and infusible powder, the material received little attention at that time. The interest was renewed later in 1977 through the discovery of the metallic properties of polyacetylene (PAC) by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid [1,7,8] which led to a Nobel Prize in Chemistry in 2000.

The modern era of conducting polymers began when PAc was found to exhibit a 12 order of magnitude increase in electrical conductivity through an accidental addition of 1,000 times more catalyst during the polymerization of acetylene [1,8].

Even though polyacetylene had a very high conductivity, its inflexibility and instability toward oxygen and air prevented its commercialization. For these reasons, much work has been devoted to synthesizing soluble and stable polyacetylenes [9,10]. Unfortunately, these substituted derivatives exhibit electrical conductivities much lower than the parent polymer. The discovery of polyacetylene led to the search for new structures that could lead to new and improved polymer properties.

Conducting polymers represent a new generation of materials that combine the electrical properties of metals and the processability of polymers. New classes of conducting polymers (Figure 1.1) include polythiophene [11,12] (PT), polyfuran [12] (PF), polypyrrole [13] (PPy), poly(p-phenylene) [14] (PPP), poly(p-phenylene vinylene) [15] (PPV), polyfluorene [16], and polyaniline [17]. Although none have exhibited a conductivity higher than polyacetylene, these polymers were useful in designing new structures that are soluble and stable. Electron-rich heterocycle based polymers such as polythiophene and polypyrrole are very stable in the p-doped form and this has made these systems two of the most studied conducting polymers. They also have lower polymer oxidation potentials and easily modified structures than polyacetylene.



**Figure 1.1** 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(3,4ethylenedioxythiophene), (j) poly(thienylenevinylene)

More recently conjugated polymers are receiving attention as a promising material for electronic applications. In particular, conjugated polymers play a central role in organic-based transistors [18], photovoltaic devices [19] and especially organic-based light emitting diodes [20].

Recently many groups are studying electrochromism [21-26], thermochromism [27] and electrochromic devices [28,29] made from conducting polymers.

## 1.2 Band Theory and Conduction Mechanism in Conducting Polymers

Since conjugated polymers have a fully occupied valence band and an empty conduction band, they are intrinsically insulators. However, they can be highly conductive upon doping.

Semiconductors can be doped which increases the conductivity of the material, and depending on the type of dopant used, either holes (p-type) or electrons (n-type) are the charge carriers. Insulators have a band structure similar to semiconductors except they have very large band gaps which are inaccessible under normal environmental conditions.

For most conducting polymers, there are very few charge carriers available in the neutral state. In order to make a conducting polymer a semi-conductor, an external dopant has to be used. By doping a conducting polymer with an external dopant, the number of charge carriers are increased, which in return increases the electrical conductivity of the polymer. Conducting polymers have high conductivity almost as metals due to the free movement of electrons through their structure (Figure 1.2).

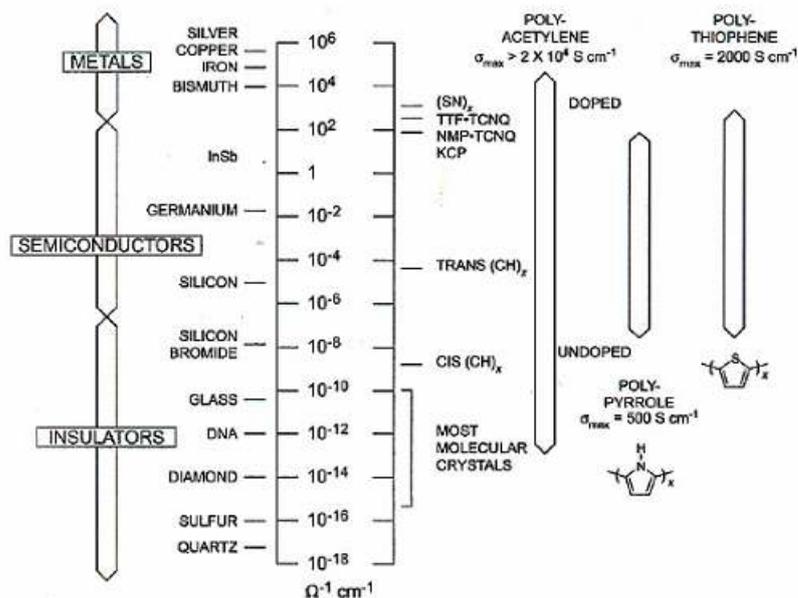


Figure 1.2 Conductivities of some metals, semiconductors and insulators

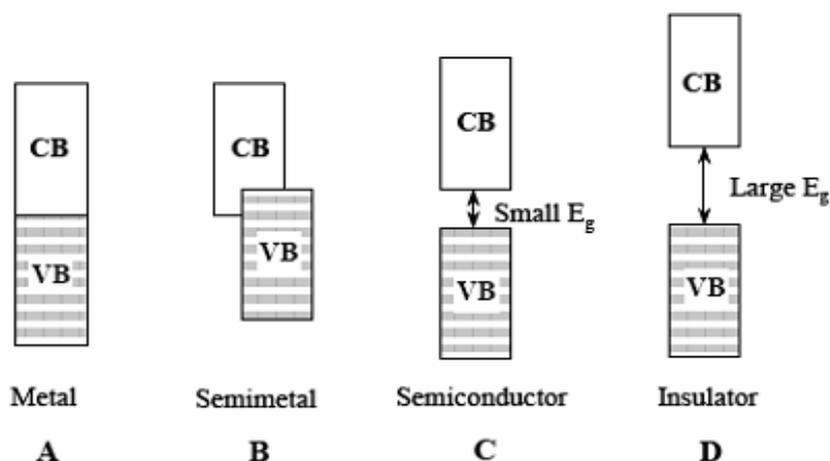
The electrical conductivity of a conductive polymer can be explained by the following equation, where  $\sigma$  is the conductivity,  $n$  is the total number of charge carriers,  $q$  is the charge on the carriers and  $\mu$  is the mobility of the carriers.

$$\sigma = nq\mu$$

For a conducting polymer, the electrical charge travels through the polymer. The overall mobility of electrical charges ( $\mu$ ) is dependent on how easily the charges move through the polymer. It depends on the movement of electrical charges along the polymer chain, called intra-chain movement, and also hopping from one chain to another, called 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. The mobility also depends on the movement of electrical charges from particle to particle. Therefore, the overall mobility of charges is related to intra-chain, inter-chain, and inter-particle mobilities.

### **1.2.1. Band Theory**

There are four classes of conductivity: metals, semimetals, semiconductors, and insulators (Figure 1.3). Metals are the most familiar and have no band gap due to their band being half-filled. Semi-metals consist of overlapping orbitals that create a partially filled band which allows the conduction processes. Neutral polyheterocycles are either semi-conducting or insulating, depending on their band gap. A semiconductor is considered to have a gap less than 3 eV but is non-conducting without doping. An insulator is any material such as poly(ethylene terephthalate) with a band gap greater than 3 eV.



**Figure 1.3** Band structures of (a) metal (b) semimetal (c) semiconductor (d) insulator

Conjugated polymers in their neutral state are generally insulators or wide band gap semiconductors, in that they have their electrons organized in bands rather than discrete energy levels, and their ground state energy bands are either completely filled or completely empty [30]. One of the most important concepts in understanding the properties of conducting polymers is the origin of band structure. The band structure of a conjugated polymer originates from the interaction of the  $\pi$ -orbitals of the repeating units through the chain. Number of energy levels within the system increases with increasing number of repeating units in a conjugated system. For the large number of repeating units, the electronic levels no longer have discrete energies but rather display a one-dimensional band of allowed energies. Interactions between adjacent and stacked  $\pi$ -electrons of conjugated polymers lead to two and three-dimensional band structures.

As conjugation increases from ethylene to polyacetylene,  $\pi$  orbitals of the repeating units can overlap throughout the chain resulting in the formation of band structure [31]. As the length of the polymer chain increases progressively, the occupied valence orbitals form continuous bands called the valence band, VB, and the empty orbitals coalesce into continuous bands called the conduction band, CB. Since conjugated polymers have completely occupied valence band and a completely empty conduction band, they can not transport charge.

According to band theory, for a polymer to be conductive an electron must be moved from the highest occupied state to the next lowest unoccupied state, i.e. from the valence band to the conduction band.

The difference in energy between HOMO(defined as the highest occupied state in the valence band) and the LUMO(defined as the lowest unoccupied state in the conduction band) is defined as the band gap,  $E_g$ . The band gap has an enormous effect on the properties of the conducting polymer, with the greatest effect on the optical absorption spectrum. The band gap represents the lowest energy transition for a photoexcitation and thus, the onset of the polymer absorbance spectrum will be equal to or greater than the band gap. Typically, a semiconductor has a band gap in the range of 0.5 to 3.0 eV, while insulators have gaps greater than 3.0 eV.

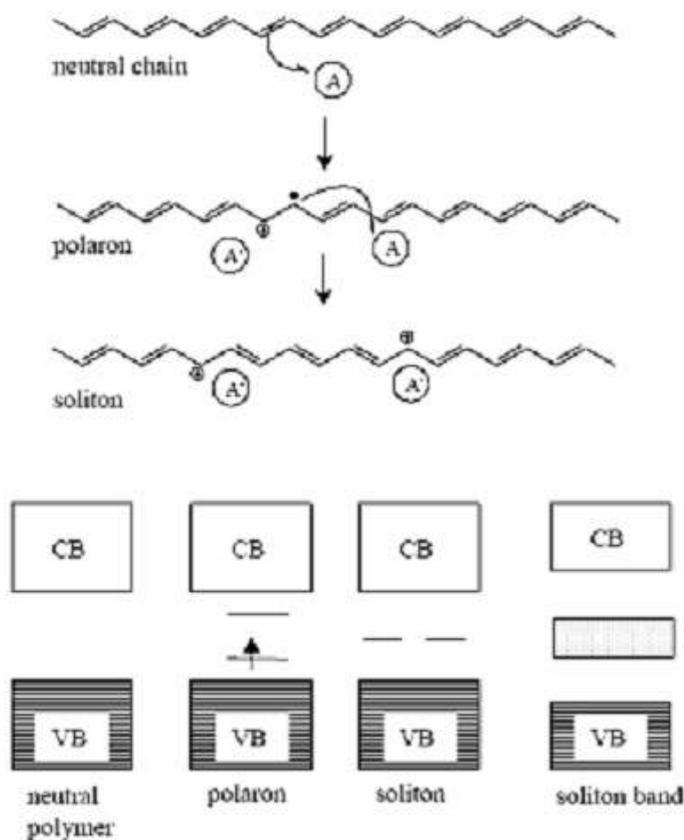
## **1.2.2. Conduction Mechanism**

### **1.2.2.1. Charge Carriers**

To understand the conduction mechanism in polymers, in addition to band theory, solitons, polarons and bipolarons are defined (Fig.1.4). It is generally agreed that the mechanism of conductivity in the conjugated polymers based on the motion of charge defects within the conjugated framework.

At the defect site, a single unpaired electron exists, although the overall charge remains zero, creating a new energy level at mid-gap (a non-bonding orbital). This neutral defect state, known as a 'soliton', is singly occupied, possessing a spin of  $\frac{1}{2}$  [32]. The soliton energy level can accommodate zero, one or two electrons and thus the soliton can also be positively or negatively charged, giving the unusual property of separating spin and charge, with neutral solitons possessing spin, but no charge, and charged solitons having no spin. In a doped polymer, charge is located in the mid-gap states, since these provide the HOMO for charge removal and the LUMO for charge injection.

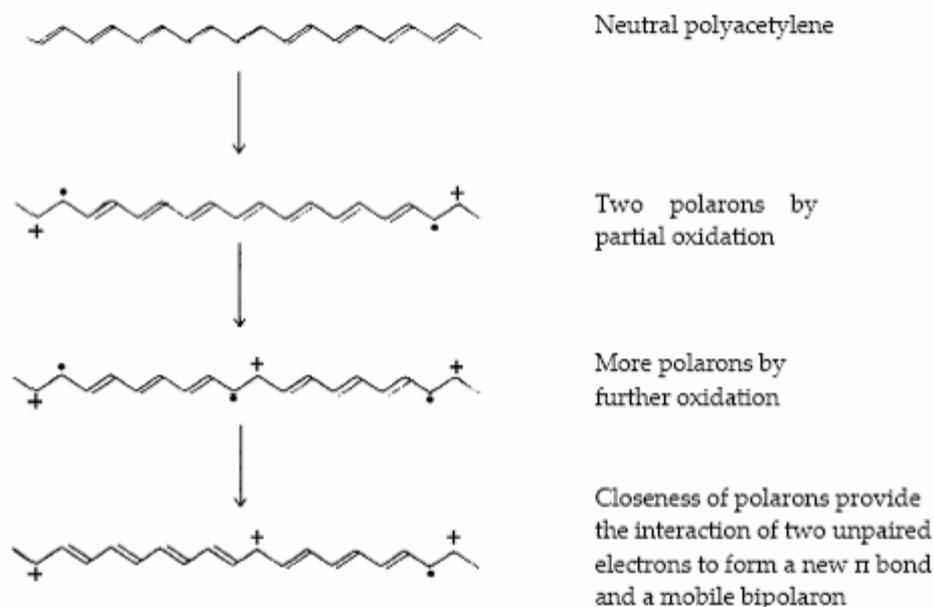
Since a defect can occur anywhere along the chain, there is translational symmetry in the system, providing mobility of the soliton along the chain, offering a mechanism for electronic conductivity. Two neutral solitons usually recombine eliminating structural defects, although single solitons can arise on chains with imperfections [33,34]. In contrast, charged solitons repel each other and lead to isolated charged defects [32].



**Figure 1.4** Polaron and soliton structures in oxidized polyacetylene

A radical ion that is partially delocalized over some polymer segment and can travel along the chain is called “polaron” which has a spin of  $\frac{1}{2}$ . If another electron is removed from or added to the polaron, the resulting spinless ion is called a “bipolaron” [35-38]. According to polaron-bipolaron theory an oxidant (or reductant) ionizes polymer chain to produce a polaron but it does not contribute significantly to conductivity at low oxidation levels.

As more oxidant is added, the polarons can be further ionized to produce bipolarons, and as the polaron concentration increases, polarons can interact to produce bipolarons. Bipolarons can move along the polymer chain by rearrangement of single and double bonds in the conjugated systems.



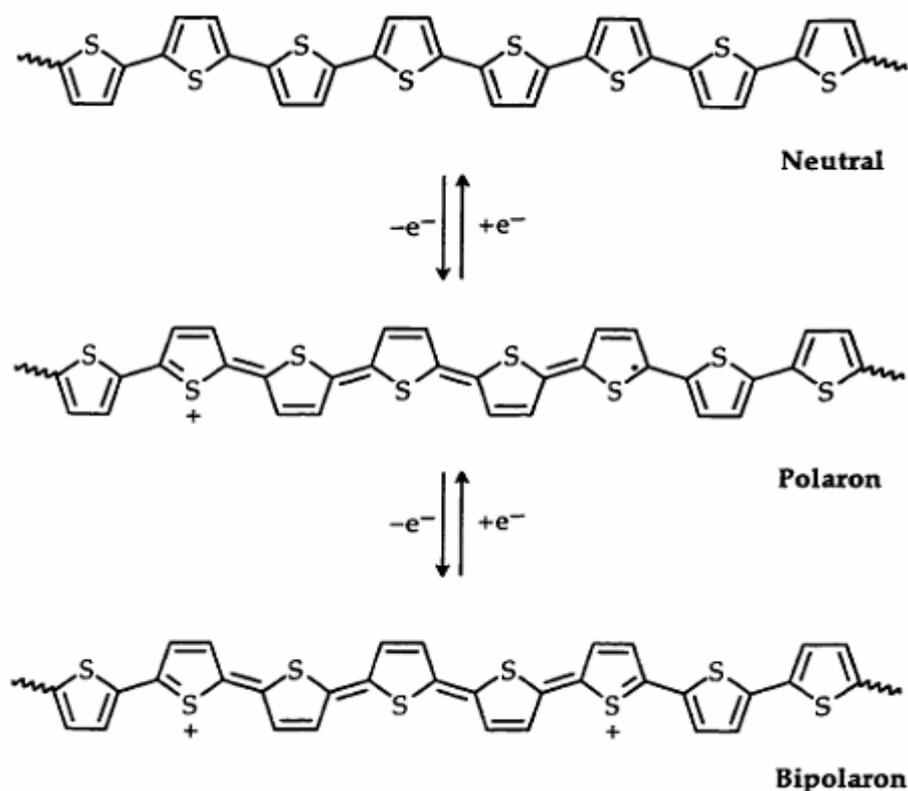
**Figure 1.5** Formation of polaron and bipolaron for polyacetylene

#### 1.2.2.2. Concept of Doping:

The concept of doping is the most important concept in conducting polymers. Conducting polymers can exist in two different forms: non-conductive form (“un-doped” polymer) and conductive form (“doped” polymer). Most conducting polymers are insulators or semiconductors in their neutral (“un-doped”) form [39]. The process which converts the neutral polymer backbone to a charged  $\pi$ -conjugated system is known as “doping”.

By treatment of the neutral form of polymer with small amount (~10%) of chemical species, the electronic, electrical, magnetic, optical and structural properties of the polymer change dramatically.

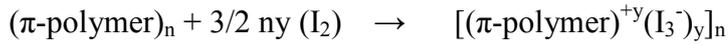
The electrical conductivity of a “doped” material is typically ~ 5 to 10 order of magnitudes higher than that of a “un-doped” material. It should be noted that doping and dedoping are generally reversible processes which do not change the chemical nature of the original polymer backbone. Both doping and undoping(or de-doping) processes can be carried out chemically or electrochemically.



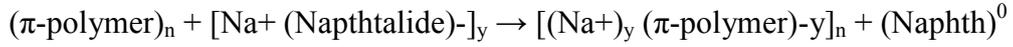
**Figure 1.6** p-type doping of polythiophene

Chemical doping with charge transfer allows high electrical conductivities in the conjugated polymers. The initial discovery of the way of doping conjugated polymers involved charge transfer redox chemistry: oxidation (p-type doping: the system loses electrons) or reduction (n-type doping: the system gets electrons) [40-42] (Fig.1.6). Chemical doping can be performed either by reaction with gaseous species, such as  $\text{AsF}_3$ ,  $\text{PF}_3$ , or  $\text{I}_2$ , or in solution by reaction with  $\text{FeCl}_3$  in aqueous solution.

For p-type:



For n-type:

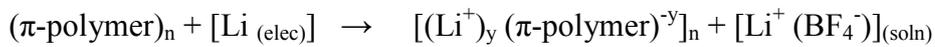


A complete chemical doping to the highest concentration gives high quality doped materials. However, getting intermediate homogenous doping levels by chemical doping process is very difficult. Electrochemical doping gives way to control the doping process [43]. In electrochemical doping, the electrode gives electrons to the conjugated polymer in reduction process, at the same time counterions in the electrolyte diffuse in or out between the polymer chains for charge compensation. Electrochemical doping is illustrated by the following examples.

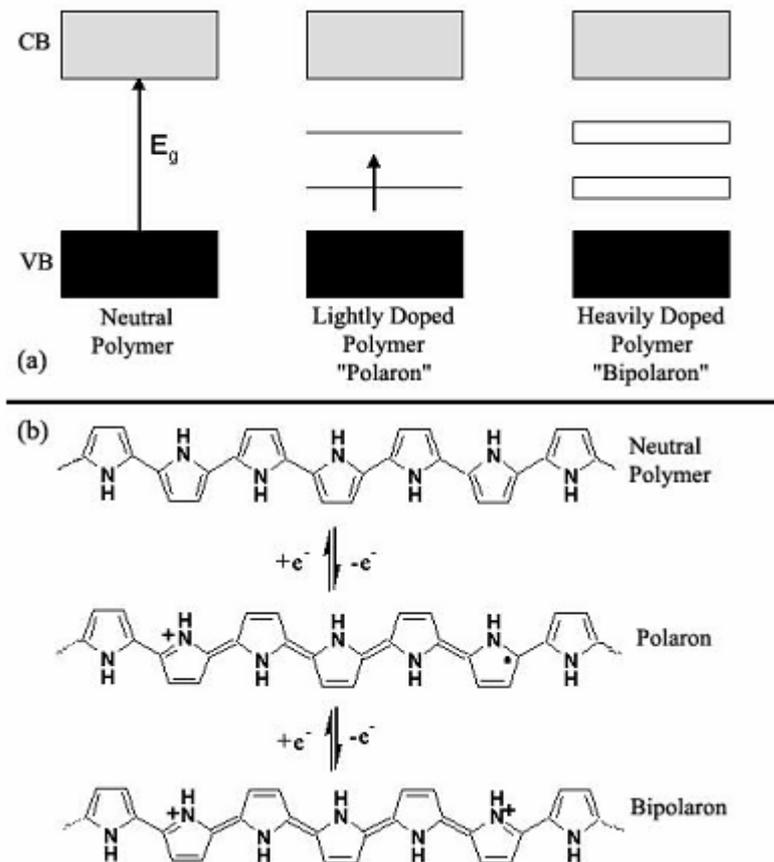
For p-type:



For n-type:



where soln is solution and elec is electrode.



**Figure 1.7** Charge carries in PPy and its corresponding energy bands in the mid gap

### 1.2.2.3. Hopping Process

Carrier mobility is the main reason of electrical transport in conducting polymers. Mobility of the charge carriers can be restricted as the degree of overlapping decreases in molecular or atomic levels. As the electronic states become increasingly localized, transport of the particle occurs through hopping process. In order to obtain hopping conduction, it is necessary to have an insulating or semiconducting material exhibiting a few intrinsic thermal free carriers at least over a limited energy region, a large density of sites through which charge transfer can take place.

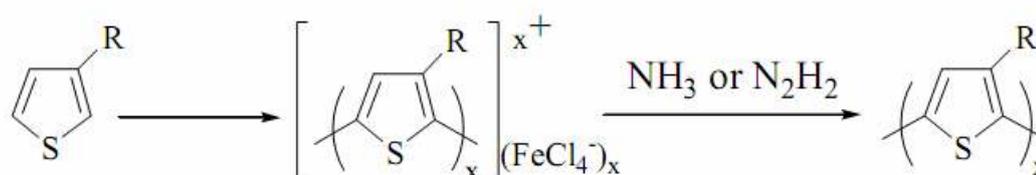
Hopping is simply inter-chain and inter-particle motion of charges in a polymer matrix [44]. The intra-chain movement, motion of the charge carrier through a single chain, depends on the efficient conjugation. On the other hand, the inter-chain movement, jumping from one chain to another, is determined by the stacking of the polymer chains. The mobility also depends on the movement of electrical charges from particle to particle.

### 1.3 Synthesis of Conducting Polymers

Chemical and electrochemical polymerizations are widely used techniques in the synthesis of conductive polymers. Other techniques used to synthesize conducting polymers include photochemical polymerization, metathesis polymerization, plasma, inclusion, pyrolysis and solid state polymerizations [45].

#### 1.3.1 Chemical Polymerization

Within the chemical polymerization techniques, oxidative methods represent the least expensive and most simple way for synthesis of conducting polymers [46]. Oxidative coupling and condensation of the monomeric precursors are the other routes for chemical polymerization. The mechanism of oxidative chemical polymerizations is thought to be very similar to that of electrochemical polymerizations. Heterocyclic monomers, such as thiophene and its derivatives, are typically polymerized in the presence of anhydrous  $\text{FeCl}_3$  [47] although other Lewis acids can also be used [48]. Reduction to the neutral state is accomplished by the addition of a strong base such as ammonium hydroxide or hydrazine.



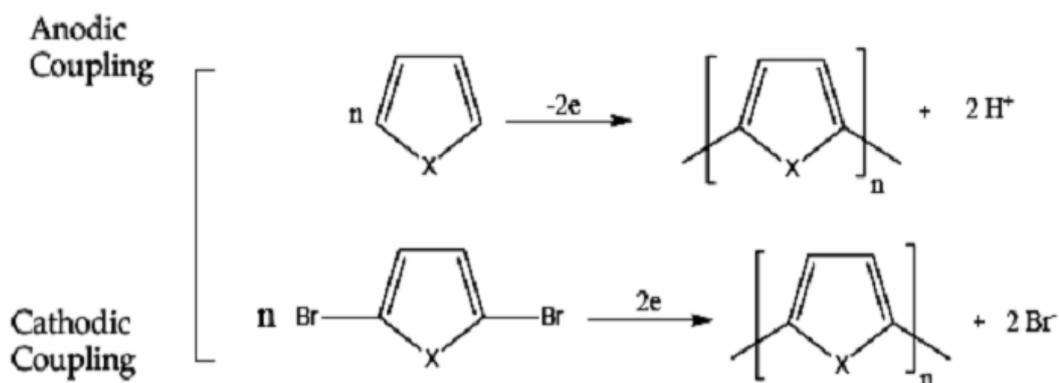
**Figure 1.8** Lewis acid oxidative polymerization of an alkyl substituted thiophene.

A tremendous advantage of chemical oxidative polymerizations is that, unlike unsubstituted heterocycles that form insoluble powders, properly substituted heterocyclic and other aromatic monomers form highly soluble polymers. Easy scale-up and production of large quantities of polymer is also an advantage of chemical polymerization. Unfortunately, chemical oxidative polymerizations suffer from several disadvantages that often result in poor quality polymers. Lewis acid catalyzed polymerizations yield the oxidized polymer, which is thought to be more rigid, resulting in its precipitation from the polymerization medium, limiting the degree of polymerization. Use of strong oxidizing agents leads overoxidation and eventual decomposition of the polymer which is yet another disadvantage of chemical polymerization. Also, there is an abundance of side reactions occurring during chemical oxidation polymerization of heterocycles including formation of coupling defects along the backbone [49].

### **1.3.2. Electrochemical Polymerization**

Electrochemical polymerization is a standard oxidative method for preparing electrically conducting conjugated polymers. Smooth, polymeric films can be efficiently synthesized and their resultant electrical and optical properties can be probed easily by several electrochemical techniques. Perhaps one of the most useful methods for the synthesis and characterization of electroactive polymers is electrochemical polymerization [50,51]. This method consists of dissolving monomer into a solvent/electrolyte medium followed by the electrodeposition of a polymer film onto an electrode surface.

In this process, when a potential is applied, the monomer approaches the working electrode surface, where it is oxidized. Oxidized monomers then couple to form oligomers, which deposit onto the electrode surface when they become insoluble in the polymerization medium. Electropolymerization can be accomplished using cyclic voltammetry with a standard three-electrode setup. Since it usually takes more than one scan to synthesize a conducting polymer film on the electrode surface, this technique is called repeated scan electropolymerization.



**Figure 1.9** Electrochemical synthetic routes to polyheterocycles.

Electrochemical polymerization is not practical for the large scale synthesis of conducting polymers, but presents a valuable method for the exploration of materials' properties. Compared to chemical polymerization, electrochemical polymerization has following advantages,

1. Many cations and anions can be chosen as the dopant ions.
2. The amount of electroactive polymer materials or the thickness of electroactive polymer films can be easily controlled.
3. Polymerization, doping and processing take place simultaneously.
4. Since polymer films are formed at the surface of the electrodes directly during polymerization, it is not necessary for polymers to be soluble in solvents. It provides the possibility to form films at different surfaces of conductive substrates.

Due to its interesting advantages, electrochemical polymerization has been widely applied in preparing redox and conducting polymer, films on the surface of conductive substrates [3,52].

The type of solvent, electrolyte system, choice and concentration of monomer and electrodes strongly affect the properties of the final conducting polymer [53].

### 1.3.2.1 Electrolytic Medium

The choice of appropriate solvent and electrolyte is essential in electrochemical polymerization since they have a strong effect on both the physical and electrical properties of the resultant polymer. Electrochemical solvents must be inert and non-nucleophilic in order to avoid reaction of the solvent at the potentials applied (usually defined as background current densities less than  $1 \mu\text{A cm}^{-2}$ ). Typically, solvents with high dielectric constants, such as acetonitrile, are ideal for electrochemistry.

Polar aprotic solvents like acetonitrile or propylene carbonate have very large potential windows, and high relative permittivities, which allow a good dissociation of the electrolyte and hence good ionic conductivity [54,55]. Nitriles are favored due to their widest range in both oxidation and reduction with a high dielectric constant ( $\epsilon=37$  for ACN) [53].

The electrolyte serves to help current pass through the solution, and also to compensate charges that form on the polymer during oxidation and reduction. Salts of perchlorates, tetrafluoroborates and hexafluorophosphates are broadly used as supporting electrolytes for the synthesis of conducting polymers.

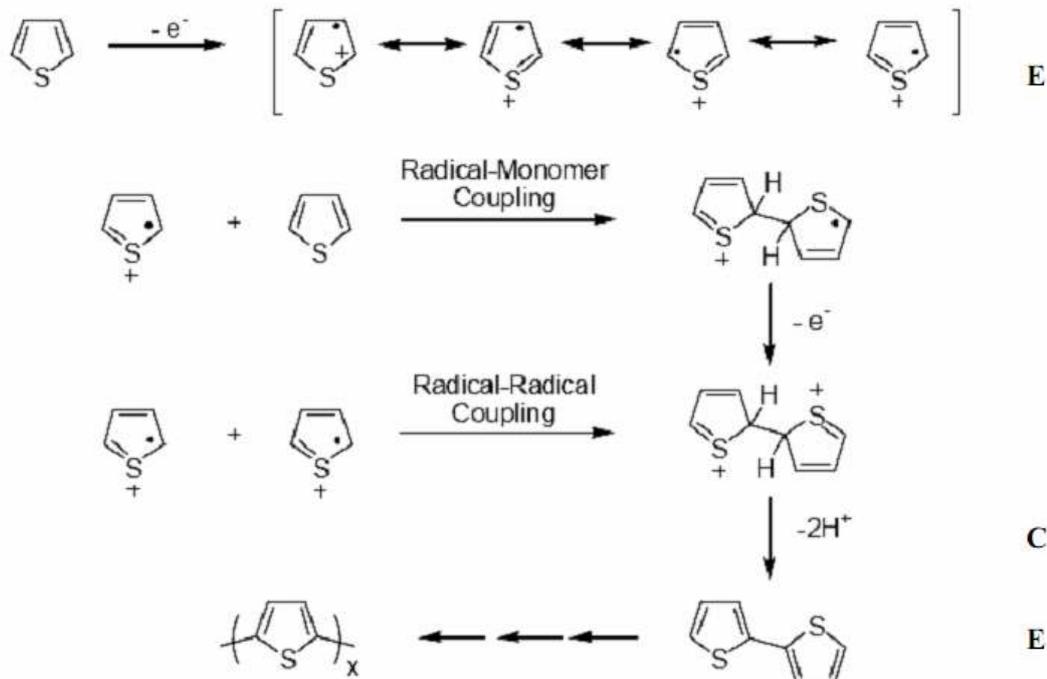
Selection of electrode is important for electrochemical polymerization. Inert materials are used in electrochemical polymerization as electrodes such as platinum, gold, carbon electrodes and indium-tin-oxide (ITO). Saturated calomel electrode (SCE),  $\text{Ag}/\text{Ag}^+$  and  $\text{Ag}/\text{AgCl}$  electrodes can be used as the reference electrodes.

The monomer concentration is generally high (0.1 M or more) to avoid competitive reactions of the radical cations or of the oxidized polymer with nucleophiles in the medium.

### 1.3.2.2 Mechanism of Electrochemical Polymerization

Electropolymerization involves the oxidation of a monomer dissolved in a supporting electrolyte solution by applying an external potential to form reactive radical cations (also known as the monomer oxidation potential). After the initial oxidation, two routes for polymer formation are possible. In the first pathway, a monomer radical cation can couple with neutral monomer, and after a second oxidation and loss of two protons, forms a neutral dimer [56]. The second route involves the coupling of two radical cations followed by the loss of two protons to yield neutral dimer [57-59]. Then the neutral dimer is oxidized and the process is repeated until an electroactive polymer film is deposited onto the conducting substrate. Electropolymerization proceeds then through successive electrochemical and chemical steps according to a general ECE scheme (Fig 1.10), until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface [3].

Due to the oxidative nature of electropolymerizations, the deposited polymer is typically in its oxidized state, thus necessitating the presence of a supporting electrolyte anion to compensate the positive charges along the polymer backbone.



**Figure 1.10** Proposed mechanism of the electropolymerization of thiophene.

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



**Figure 1.11** Undoping, p-doping in a conducting polymer

### 1.3.2.3 Monomer Structure

In the field of EC materials, one of the great strengths of conjugated polymers is the ability to tailor the EC properties via modification of the polymer structure. In order to functionalize a polymer to have desired electrochemical and optical properties, both valence and conduction energies can be controlled by the energy gap (the relation of the energy levels to one another) or the position of the energies (oxidation or reduction potentials) [60].

In designing low band gap systems, there are a variety of methodologies that can be used to achieve polymers with a band gap less than 2 eV. Five basic approaches have been used to reduce band gap that include controlling bond-length alternation (Peierls distortion), creating highly planar systems, inducing order by interchain effects, resonance effects along the polymer backbone, and donor-acceptor concept. Work in this dissertation involves manipulation of donor-acceptor effects where control of the band gap and relative position of the valence and conduction bands yield desired results. In this technique, a donor molecule is chosen such that its valence band complies with the properties desired. An acceptor molecule is then chosen such that its reduction potential is suitable. By coupling these systems alternately across the polymer backbone, the polymer has the valence band of the donor and the conduction band of the acceptor. This results in “band gap compression.” The hybridized system has the properties of the parents. This approach has been the most effective for low band gap materials and has been extensively reviewed [61].

Homopolymerization of comonomers or copolymerization of distinct monomers also give rise to a modification of main chain polymer structure and allows for an interesting combination of the properties supplied by each monomer unit.

Additionally, conjugated polymers can be utilized in blends [62], laminates [63], or composites [64] to affect the ultimate color exhibited by the material, however, here we shall only consider color control which derives directly from modification of the chemical structure of a conjugated polymer. Using PEDOT as a platform, several approaches have been used to produce a wide variety of multi-color, variable gap electrochromic polymers. Two such methods, chemical modification of the monomer and copolymerization, have proven to be effective routes.

Solubility and processability of conjugated polymers have been challenging endeavors since this class of material was developed. Polythiophenes containing alkyl [65-67] and alkoxy [68] substituents are soluble in common organic solvents in the conducting state, considerably aiding processability and characterization of these electroactive materials. Poly(3-alkylthiophenes) with alkyl groups with chain lengths equal or greater than four (i.e. butyl) are readily soluble in THF, dichloromethane, chloroform, benzene, toluene, xylene, benzonitrile and nitrobenzene at room temperature. Solubilized polymers can subsequently be processed into films, which show similar electrochemical properties to those produced directly. Rendering a material more soluble and processable is easily accomplished by substitution of flexible side groups, but interrupting the interchain interactions likely decreases conductivity and charge mobility. Therefore, structural design of processable conjugated polymers that retain the desirable electronic properties has focused on solubilizing groups that aid in the ordering of the solid state after casting from solution.

#### **1.4 Conducting Copolymers, Composites and Blends**

Conducting polymers are promising materials due to their ease of synthesis, good environmental stability, and long term stability of electrical conductivity; however, there are several drawbacks restricting their processing and applications for practical use.

The  $\pi$ -electron system along the polymer backbone leads to rigidity and crosslinking. The crosslinking in the polymer chain makes it insoluble, hard, brittle and therefore, poorly processable. In order to obtain a material suitable for applications in various technological fields certain limitations need to be overcome [65]. Various methods such as the introduction of alkyl groups into the main chain, the synthesis of soluble precursors and preparation of conducting polymer composites, blends and copolymers can be used to improve mechanical properties [66].

A method to impart processability into a conducting polymer is to copolymerize it with other monomers. Copolymerization is a major focus in the study of electrochromic materials, since it is an easy method to combine and improve the properties of comonomers. In general copolymers possess physical and mechanical properties intermediate between both homopolymers [67]. Today, the synthesis of copolymer is mainly performed with 3,4-ethylenedioxythiophene (EDOT) that is superior to its parent polythiophene in many categories crucial to organic electrochromic materials such as rapid switching and lower oxidation potential [68]. In this way, the resultant copolymer could reveal better electrochemical and optical properties than its homopolymers.

A blend of a conducting polymer with an insulating polymer also has considerable utility for improving the processing of the conducting polymer. Several attempts have been described to produce conducting polymer composites with better physical properties by either chemically or electrochemically [69].

When an electrically conducting phase is dispersed with a sufficient quantity in a polymeric resin, a conductive composite is formed. The unique properties of such composites make them technologically superior to or more cost effective than alternative materials [70].

## **1.5 Characterization of Conducting Polymers**

Since the highly conjugated backbone causes insolubility in most of the conducting polymers, conventional techniques for polymer characterization cannot be applied for such systems. Therefore, the following are mostly used to characterize conductive polymers. Primary characterization of CPs is done by cyclic voltammetry that shows the potentials at which oxidation or reduction processes occur, and the degree of reversibility of the electrode reaction [71]. FTIR spectroscopy is used to differentiate and identify functional groups rapidly due to its speed and low cost [72]. Structural information can be provided by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Morphology of CPs film has been described by scanning electron microscopy [73]. Also gel permeation chromatography for molecular weight determination, differential scanning calorimetry and thermogravimetry analysis for evidence of glass and melting transitions and decomposition temperatures are other methods used for the characterization of polymers.

## **1.6 Applications of Conducting polymers**

Since conducting polymers exhibit novel properties, which are not typically available in other materials, they have numerous applications. These can be categorized into three main classes. The first use of conjugated polymers is in their neutral form, which takes advantage of their semi-conducting and luminescent properties. Examples are field effect transistors [74] and as the active material in electroluminescent devices [75]. The second category of applications involves using the polymer in its doped or conducting form. Some representative applications in this category are electrostatic charge dissipation and EMI shielding [76,77], and as electrode materials for capacitors [78]. The third category uses the ability of the polymer to reversibly switch between its conducting and reduced forms.

Upon switching between these two states, the polymer undergoes color, conductivity, and volume changes. Applications that use these properties include battery electrodes [79], mechanical actuators [80], sensors [81], drug delivery [82], and electrochromics [83].

Electrochromic devices based on conducting polymers have become a recent focus of research. This is due in part to the fact that all electroactive and conducting polymers are potentially electrochromic materials, are more processable than inorganic electrochromic materials, and offer the advantage of a high degree of color tailorability [84]. The use of conducting polymers as potentially electrochromic materials is the most pertinent to the work in this thesis.

## **1.7 Electrochromism**

Electrochromism is a phenomenon in which there is a persistent optical absorbance change in the visible region of the spectrum with the application of an external potential and the materials that can display distinct color changes under different redox states are considered as electrochromic materials. Suggested theoretically by J.R. Platt [85] in 1961, the first examples of electrochromic materials and devices were demonstrated by Deb [86] when he started to work on amorphous and crystalline metal oxides at Cyanamid Corp. Among electrochromic (EC) materials, transition metal oxides, especially the high band gap semiconductor tungsten oxide,  $\text{WO}_3$ , have received extensive attention over the past 30 years [87].

Thin films of amorphous or polycrystalline  $\text{WO}_3$  can be prepared by vacuum evaporation, reactive sputtering, and sol-gel methods. Initially transparent in the visible region, cation intercalation (reduction) of  $\text{WO}_3$  to  $\text{M}_x\text{WO}_3$  (M can be hydrogen or an alkali metal) leads to strong absorption bands in the visible region, making it a cathodically coloring material.

Many other inorganic materials have been studied for their electrochromic properties such as Prussian blue, oxides of V, Mo, Nb, and Ti (cathodically coloring), and oxides of Ni, Co, and Ir (anodically coloring) [88]. Other EC materials include organic molecules, such as the bipyridiliums (viologens), which are a class of materials that are transparent in the stable dicationic state. Upon one-electron reduction, a highly colored and exceptionally stable radical cation is formed. Thin film electrochromism is observed for polyviologens and N-substituted viologens such as heptyl viologen [89]. More recently, composite systems, where organic molecules are adsorbed on mesoporous nanoparticles of doped metal oxides, have shown improved electrochromic properties [90].

Conjugated polymers are a third class of EC materials that have gained popularity due to their ease of processability, rapid response times, high optical contrasts, and the ability to modify their structure to create multi-color electrochromes. Of the conjugated EC polymers, derivatives of PTh, PPy, and PANI are widely studied [91]. Conducting polymers are electrochromic due to the transition between neutral and conducting forms. Upon oxidation, the change from a benzenoid to a quinoid structure results in a drastic modification of the electronic properties, which is commonly associated with a change in color. Due to the ability of conducting polymers to reversibly switch between the neutral and conducting form, the electromagnetic spectrum, (and thus the color in most cases) can be controlled by applying a potential. Conjugated polymers, while not as developed as the other systems, promise high contrast ratios, rapid response times, and long lifetimes for use in EC display technology. The ability to physically structure polymer-based electrochromic devices (ECDs) and exert control over their EC responses are addressed in the following sections.

### **1.7.1 Types of Electrochromic Materials**

There are three main types of electrochromic materials in terms of their electronically accessible optical states.

The first type includes materials with at least one colored and one bleached state. These materials are especially useful for absorption/transmission type device applications such as smart windows and optical shutters. Typical examples of this area are metal oxides, viologens, and polymers such as PEDOT. A second class of material consists of electrochromes with two distinctive colored states. These EC materials lack a transmissive state but are useful for display type applications where different colors are desired in different redox states. Polythiophene is a good example for this type where the thin films of this polymer switch from red to blue upon oxidation. A third class includes the growing interest in the electrochromic field where more than two color states are accessible depending on the redox state of the material. This is the area where conjugated polymers have found the most interest due to their versatility for making blends, laminates, and copolymers. Additionally, there are inherently multi-color EC polymers such as PANI or poly(3,4-propylenedioxyppyrole) (PProDOP).

### **1.7.2 Spectroelectrochemistry**

Spectroelectrochemistry combines electrochemical and spectroscopic techniques that can be operated at the same time. Compared to common electrochemical methods, it can provide information on both electrochemical response and accompanying optical characteristics of all states of the electrochemical reaction. Spectroelectrochemistry is a powerful tool to probe unique species that are generated in-situ during redox reactions at electrode surfaces. The redox switching of conjugated polymers is accompanied by changes in electronic transitions. This absorption change is the property that makes conjugated polymers useful in electrochromic applications such as smart windows, mirrors, etc. These electronic transitions can be probed by UV-Vis spectroscopy. Spectra are recorded while the polymer is oxidized by stepwise increasing the potential. This experiment is commonly referred as spectroelectrochemistry, and can be easily accomplished by constructing a three electrode cell inside a UV cuvette.

Spectroelectrochemistry experiments reveal key properties of conjugated polymers such as band gap ( $E_g$ ),  $\lambda_{max}$ , the intergap states that appear upon doping and evolution of polaron and bipolaron bands.

### 1.8 Aims of the Work

This dissertation focuses on the synthesis of new electrochromic polymers as soluble and multi-color electrochromic materials. The structural, optical, and electrochemical properties were determined and the development of new thin film processing techniques was explored. Throughout this work, emphasis is given on the synthesis and fundamental structural and electrochemical properties of each polymer. Aims of this work can be listed as;

- ✓ To synthesize the target monomer; 2,3-bis(4-*tert*-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline (HTQ)
- ✓ To perform chemical polymerization of HTQ
- ✓ To perform potentiostatic polymerization of HTQ
- ✓ To achieve the potentiostatic polymerization of HTQ in the presence of EDOT to obtain the conducting copolymers with better mechanical and physical properties
- ✓ To characterize conducting poly(HTQ), poly(cHTQ) and poly(HTQ-co-EDOT) with common characterization techniques
- ✓ To investigate electrochromic and spectroelectrochemical properties of homopolymers and copolymer

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Materials

All chemicals were purchased from Aldrich except for THF which was purchased from Acros. 4,7-Dibromobenzo[1,2,5]thiadiazole [92], 3,6-dibromo-1,2-phenylenediamine [93], 1,2-bis(4-tert-butylphenyl)-2-hydroxyethanone [94], 1,2-bis(tert-butylphenyl) ethane-1,2-dione [94], tributyl(4-hexylthiophen-2-yl)stannane [95] were synthesized according to literature procedure.

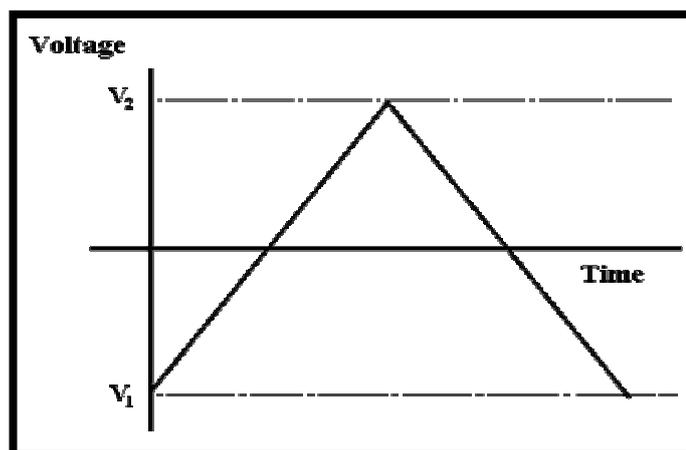
#### 2.2. Equipment

##### 2.2.1 Nuclear Magnetic Resonance (NMR) Spectrometer

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of polymers were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) using  $\text{CDCl}_3$  as the solvent.

##### 2.2.2 Cyclic Voltammetry (CV) System

Cyclic voltammetry is one of the most useful methods, which provides a great deal of useful information about the electrochemical behavior of electroactive species. The CV system was composed of a potentiostat, a function generator, an XY recorder, and a cyclic voltammetry cell. Function generator or wave generator applies a triangular wave potential to the cell so that the working electrode potential is swept linearly through the voltammetry wave (Figure 2.1). During these scans, potential-time response and current (I) versus potential (V) curves are obtained.



**Figure 2.1** Triangular wave function

In cyclic voltammetry (CV) the current response is measured while the potential is linearly increases from an initial potential to a peak potential and back to the initial potential again. Cyclic voltammetry measurements were carried out by cycling the potential of the working electrode with respect to a reference electrode and measuring the resulting current. CV shows the potentials at which oxidation and reduction processes occur, the potential range over which the solvent is stable, and the degree of reversibility of the electrode reaction. Furthermore, repeated cycling reveals the electrochemical stability of electroactive species.

CV may also be used to show the ability of the film to store charge and to respond to the applied potential. The areas underneath the oxidation and reduction peaks show that approximately equal amounts of charge accompany each process demonstrating the electrochemical reversibility and efficiency of the redox process.

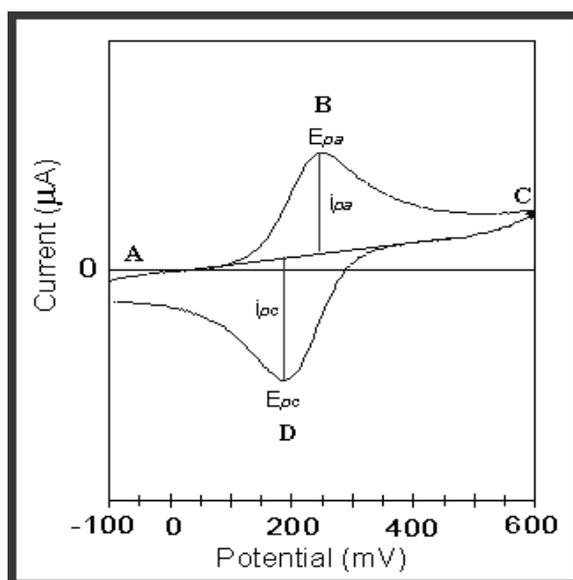
Important parameters of a polymer cyclic voltammogram are the scan rate, switching potentials, as well as the magnitudes of the anodic peak current ( $i_{pa}$ ), cathodic peak current ( $i_{pc}$ ), anodic peak potential ( $E_{pa}$ ) and cathodic peak potential ( $E_{pc}$ ).

Continuous deposition of the polymer onto the working electrode can be monitored by the increase in the polymer's anodic and cathodic peak currents, while the polymer redox properties are characterized by the magnitudes of its peak potential.

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

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

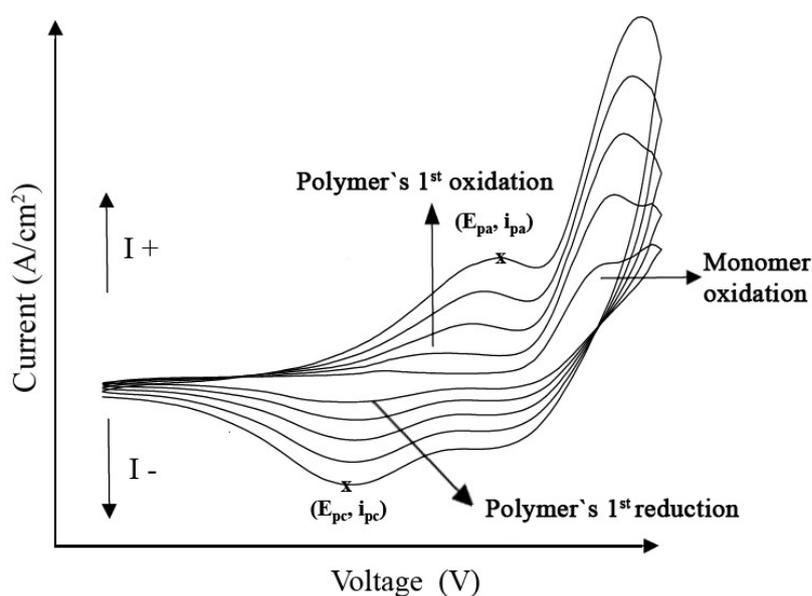
where  $n$  is the number of electrons,  $A$  is the surface area of the electrode ( $\text{cm}^2$ ),  $D$  is the diffusion constant ( $\text{cm}^2/\text{s}$ ),  $C^b$  is the bulk concentration of electroactive species ( $\text{mol}/\text{cm}^3$ ), and  $V$  is the scan rate ( $\text{V}/\text{s}$ ). Therefore, for a diffusion-controlled system, the peak current is proportional to the square root of the scan rate.



**Figure 2.2** A cyclic voltammogram for a reversible redox reaction

A typical CV investigation generally starts at low potentials where no redox reactions occur in anodic direction. Anodic current starts to increase in the vicinity of the potential where the electrode has reached sufficient potentials at which the monomer starts to oxidize to its radical cation.

The anodic current increases rapidly until the concentration of the monomer at the electrode surface approaches zero, which is signified by the formation of a peak. The intensity of the current starts to decay since the solution in the vicinity of the electrode has almost zero monomer concentration. Monomer oxidation is immediately followed by chemical coupling which results in the formation of the dimer and the oligomers. Once these oligomers reach a certain length, they precipitate onto the electrode surface where the chains can continue to grow in length. In the cathodic run the reduction of the deposited polymer is observed. Upon consecutive cycle formation of a new oxidation peak is appear due to the re-oxidation of the polymer which is followed by the monomer oxidation peak again. It should be noted that as the number of cycle increases there is an increase in the intensity of the current. This is due to increase in the active area of the working electrode owing to coating of already electroactive polymer on the metal electrode (Figure 2.3) [96].



**Figure 2.3** Cyclic Voltammogram of a representative type of electroactive monomer [96]

To study the electrochemistry of a polymer, a monomer free system should be used. The polymer redox process is quasi-reversible and since the polymer is immobilized at the electrode surface, the redox process is not diffusion controlled. Thus under these circumstances Randles & Sevcik equation is no longer valid. Instead, according to the theory of immobilized redox centers, the peak current is given by ;

$$i_p = n^2 F^2 \Gamma v / 4RT$$

where  $\Gamma$  is the total amount of active species present at the electrode surface. According to this equation the polymer redox peak currents should increase linearly with increasing scan rate, assuming that fast, non-diffusion limited migration of the dopant counter ions and efficient charge percolation are occurring. Thus investigation of peak current intensity with respect to scan rate will indicate the nature of electrochemical process being diffusion controlled or the polymer is well adhered to the electrode surface [97,98].

### **2.2.3 Electrolysis Cell**

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

### **2.2.4 Potentiostat**

Wenking POS 73 and Solartron 1285 potentiostats were employed to supply a constant potential in electrochemical synthesis. The function of potentiostat is to maintain the potential of the working electrode (WE) at an adjusted level with respect to a fixed reference electrode (RE). The potential difference between the WE and reference electrode is equal to input potential that can be controlled externally. The current driven by the potentiostat (between WE and RE) can be determined by measuring the voltage drop across a small resistance R connected to the counter electrode in series.

In a three electrode potentiostatic system, the major current passes through the counter electrode (CE) and WE. The current amplifier supplies current to the cell (between the WE and CE), regardless of the solution resistance. By this way the purpose of maintaining potential control between the two electrodes has been accomplished.

### **2.2.5 Gel Permeation Chromatography (GPC)**

Mn and Mw of both chemical and electrochemical polymers were determined with PL-220 gel permeation chromatography.

### **2.2.6 Spectroelectrochemistry Experiments**

Varian Cary 5000 UV-Vis-NIR and Agilent 8453 UV-Vis spectrophotometers were used in order to perform the spectroelectrochemical studies of the polymers.

### **2.2.7 Colorimetry Measurements**

Colorimetry measurements were done via Minolta CS-100 spectrophotometer

## **2.3 Procedure**

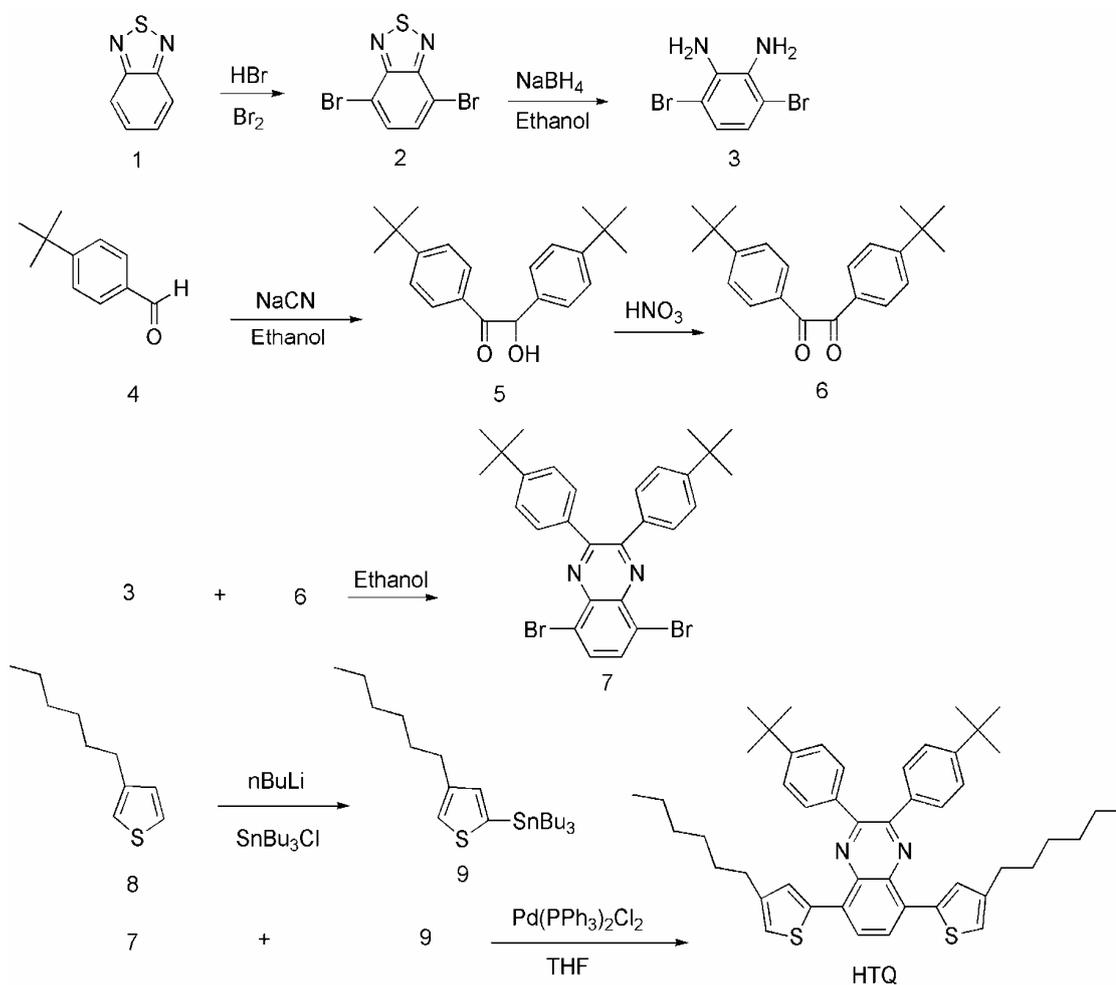
### **2.3.1 Synthesis of Monomer**

#### **2.3.1.1 Synthesis of 2,3-Bis(4-tert-butylphenyl)-5,8-dibromoquinoxaline:**

A solution of 3,6-dibromo-1,2-phenylenediamine (1.0 g, 3.8 mmol) and 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione (1.223 g, 3.8 mmol) in EtOH (40 ml) was refluxed overnight by with a catalytic amount of paratoluenesulfonic acid (PTSA). The mixture was cooled to 0 °C. The precipitate was isolated by filtration and washed several times with EtOH to afford the desired compound. (1.5 g, 72 %).

### 2.3.1.2 Synthesis of 2,3-Bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline:

2,3-Bis(4-tert-butylphenyl)-5,8-dibromoquinoxaline (400 mg, 0.8 mmol) and tributyl(4-hexylthiophen-2-yl)stannane (1832 mg, 4 mmol) were dissolved in dry THF (100 ml), the solution was purged with argon for 30 min and  $\text{PdCl}_2(\text{PPh}_3)_2$  (120 mg, 0.171 mmol) was added at room temperature under argon atmosphere. The mixture was stirred at  $100^\circ\text{C}$  under argon atmosphere for 15 h, cooled and concentrated on the rotary evaporator. The residue was subjected to column chromatography to afford an orange solid (320 mg, 55%).



**Scheme 2.1** Synthetic route for monomer HTQ

## **2.4. Synthesis of Conducting Polymers**

### **2.4.1. Electrochemical Polymerization**

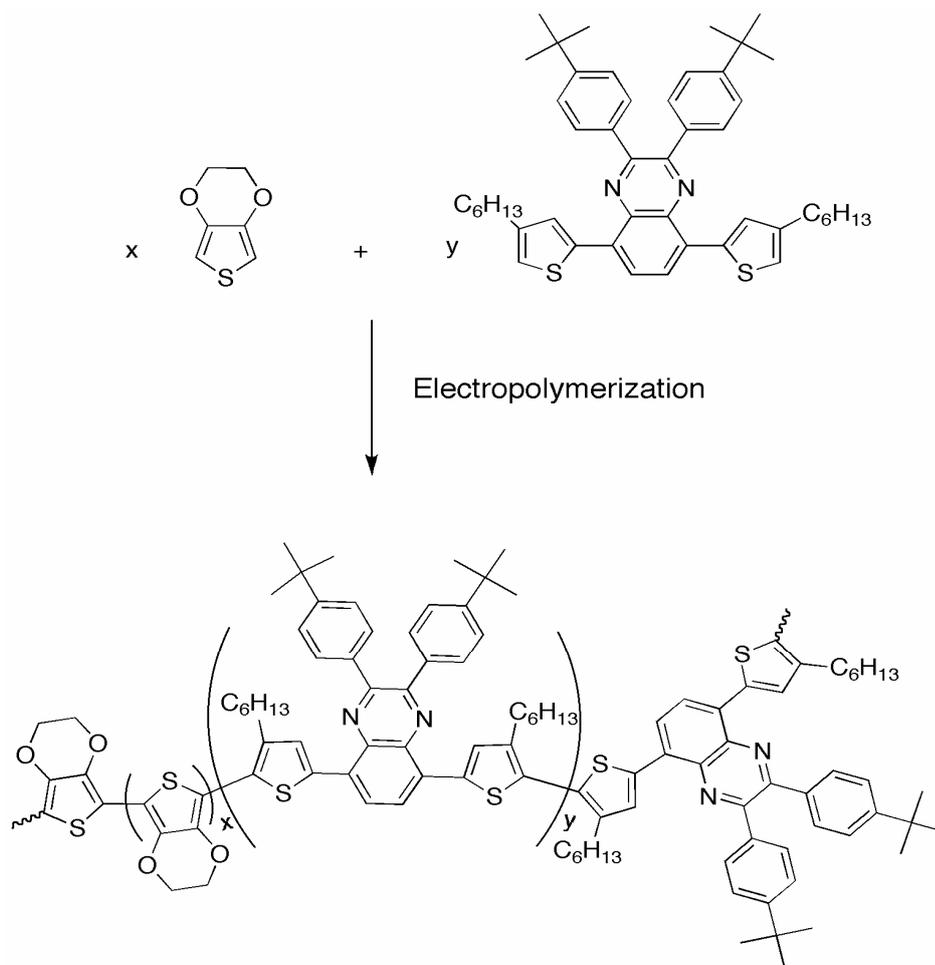
#### **2.4.1.1 Synthesis of Homopolymer of HTQ**

To directly synthesize and investigate potential electrochromic characteristics of the polymer film, electrochemical polymerization was carried out. For electrochemical synthesis of PHTQ, 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was used as the supporting electrolyte in dichloromethane (DCM): acetonitrile (ACN) (5/95, v/v) solvent mixture.

Potentiodynamic electrolysis was run by sweeping the potential between 0.5V and +1.3 V with 100 mV.s<sup>-1</sup> scan rate. The free standing film was washed with ACN to remove unreacted monomer and excess TBAPF<sub>6</sub> after electrolysis.

#### **2.4.1.2 Synthesis of Copolymer of HTQ with 3,4-Ethylenedioxythiophene (EDOT)**

The potentiodynamic copolymerization of HTQ with EDOT was carried out in a solution containing 4.6x10<sup>-2</sup> M HTQ and 6.1x10<sup>-3</sup> M EDOT in TBAPF<sub>6</sub> and ACN/DCM (5 / 95, v/v) solvent electrolyte couple by applying a constant potential of 1.0 V under nitrogen atmosphere. The working and counter electrodes were Pt wires and the reference electrode was Ag wire electrode. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomer.



**Scheme 2.2** Copolymerization reaction of HTQ with EDOT

#### 2.4.2 Chemical Polymerization of HTQ

Oxidative polymerization of HTQ was achieved using  $4 \times 10^{-2}$  M  $\text{FeCl}_3$  in a 50 ml mixture of nitromethane and chloroform (90/10, v/v) containing  $10^{-2}$  M monomer. After the addition of  $\text{FeCl}_3$  the solution turned into a dark green solution immediately. The solution was stirred for 4 h at room temperature and washed with methanol and dedoped with a hydrazine solution to yield a saturated red color polymer with high solubility in common organic solvents.

## **2.5. Gel Permeation Chromatography (GPC)**

GPC provides number average ( $M_n$ ) and weight average ( $M_w$ ) molecular weight as well as molecular distribution (polydispersity,  $M_w/M_n$ ). For determination of molecular weight, both chemical and electrochemical polymers were dissolved in tetrahydrofuran and GPC studies were conducted.

## **2.6. Electrochromic Properties of Polymers**

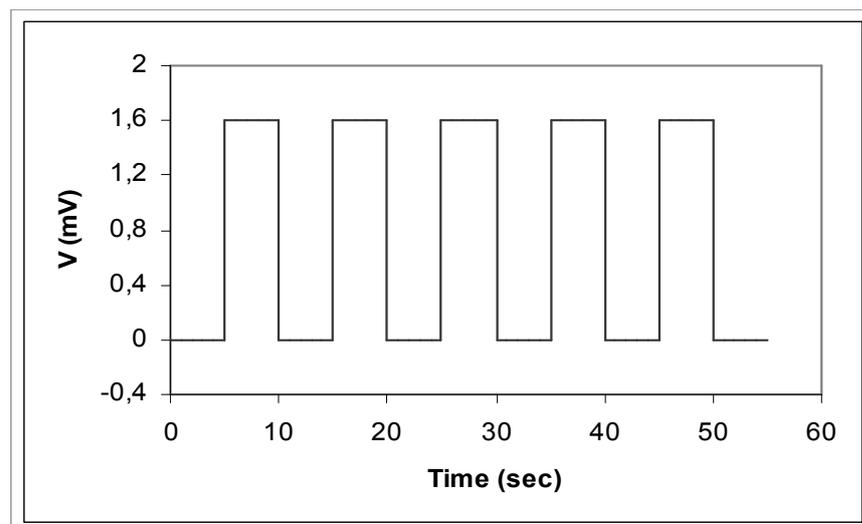
### **2.6.1 Spectroelectrochemical Studies**

To investigate the optical changes upon doping, spectroelectrochemistry studies were performed. PHTQ was coated on ITO glass slides and spectral changes were investigated by UV–vis-NIR spectrometer in a monomer-free 0.1 M TBAPF<sub>6</sub> solution via incrementally increasing applied potential between 0.4 V and 1.2 V.

For the investigation of copolymer and chemically synthesized polymers, same conditions were used. Spectroelectrochemical studies of the copolymer and chemically synthesized polymer films were carried out sweeping the potentials between -0.2 V and +1.05 V and -0.5 V to +1.2 V respectively.

### **2.6.2. Switching Studies**

The capability of a polymer to switch rapidly and demonstrating a remarkable color change are essential properties for an electrochromic polymer. Electrochromic switching is proven to be one of the most efficient and easiest ways to observe these properties. The % transmittance values (T%) at different wavelengths including the  $\lambda_{max}$  of the polymers were measured using a UV–vis-NIR spectrophotometer when the applied potential was switched with a period of 5 s between 0.4 V and 1.2 V for the homopolymer, between -0.5 V and 1.05 V for the copolymer.



**Figure 2.4** Square wave voltammetry

### 2.6.3. 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; Yxy values, were measured at the fully oxidized and reduced states of the homopolymer and copolymer.

## CHAPTER III

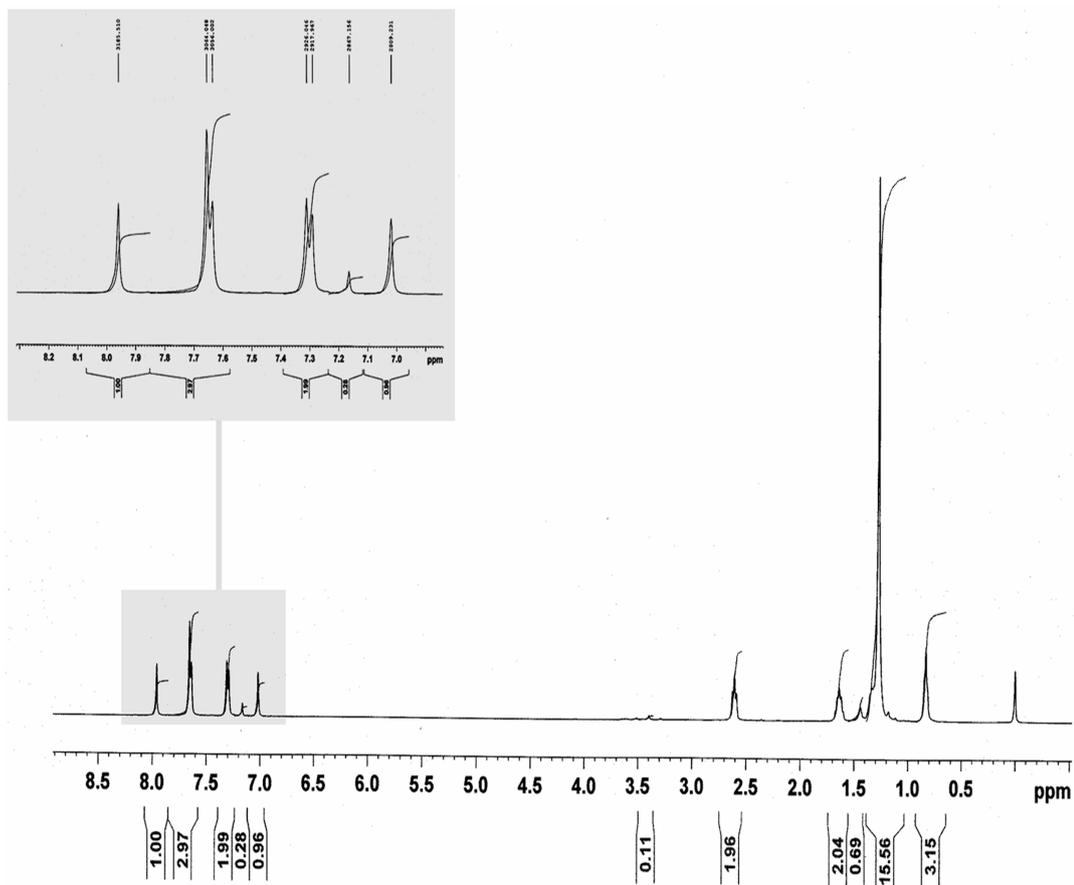
### RESULTS AND DISCUSSION

#### 3.1. Characterization by $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectroscopy

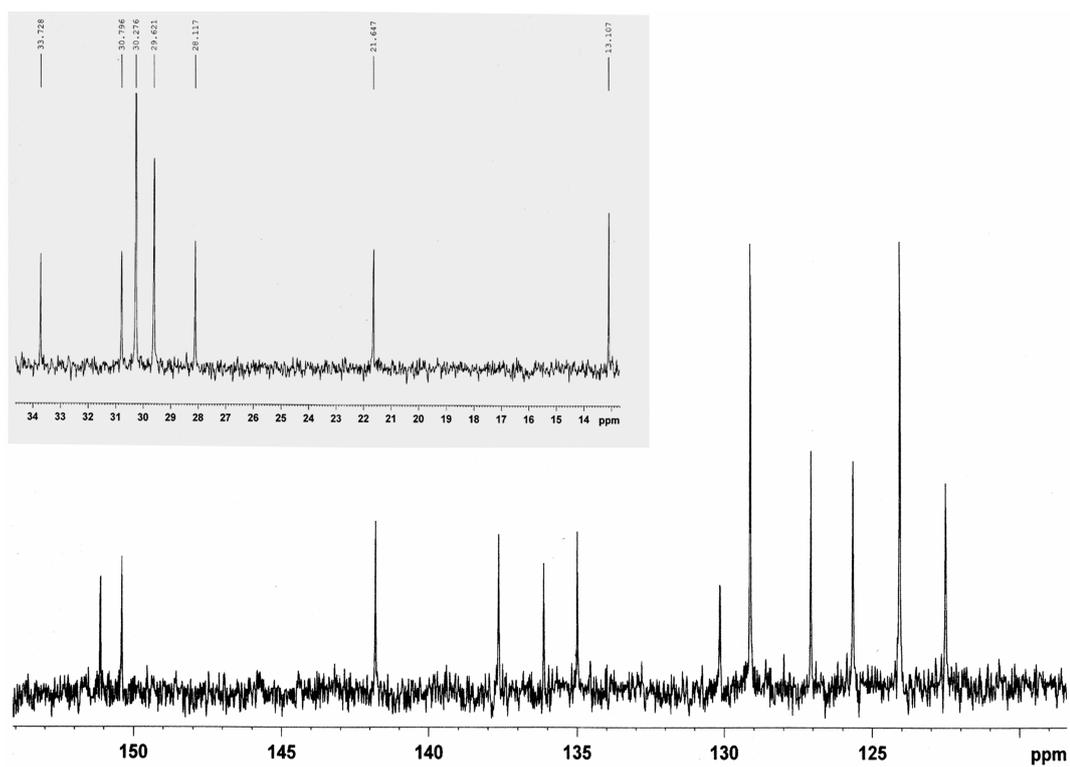
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the monomer and  $^1\text{H}$ -NMR spectrum of chemically synthesized polymer were taken on a Bruker-Instrument-NMR Spectrometer (DPX-400) monomer with  $\text{CDCl}_3$  as the solvent and chemical shifts ( $\delta$ ) are given relative to tetramethylsilane as the internal standard.

$^1\text{H}$  NMR spectrum of monomer (Figure 3.1):  $\text{C}_{48}\text{H}_{58}\text{N}_2\text{S}_2$   $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 0.83 (t, 6H), 1.27 (m, 30H), 1.64 (m, 4H), 2.60 (t, 4H,  $J = 7.3$  Hz), 7.02 (s, 2 H), 7.30(d, 4H,  $J = 8$  Hz), 7.65(d, 4H,  $J = 8$  Hz), 7.66 (s, 2H), 7.96(s, 2H),  $^{13}\text{C}$  NMR spectrum of the monomer  $\text{C}_{48}\text{H}_{58}\text{N}_2\text{S}_2$  (Figure 3.2):  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 13.11, 21.65, 28.12, 29.62, 30.28, 30.80, 33.73, 122.51, 124.07, 125.65, 127.07, 129.13, 130.14, 134.97, 136.12, 137.65, 141.81, 150.40, 151.11.

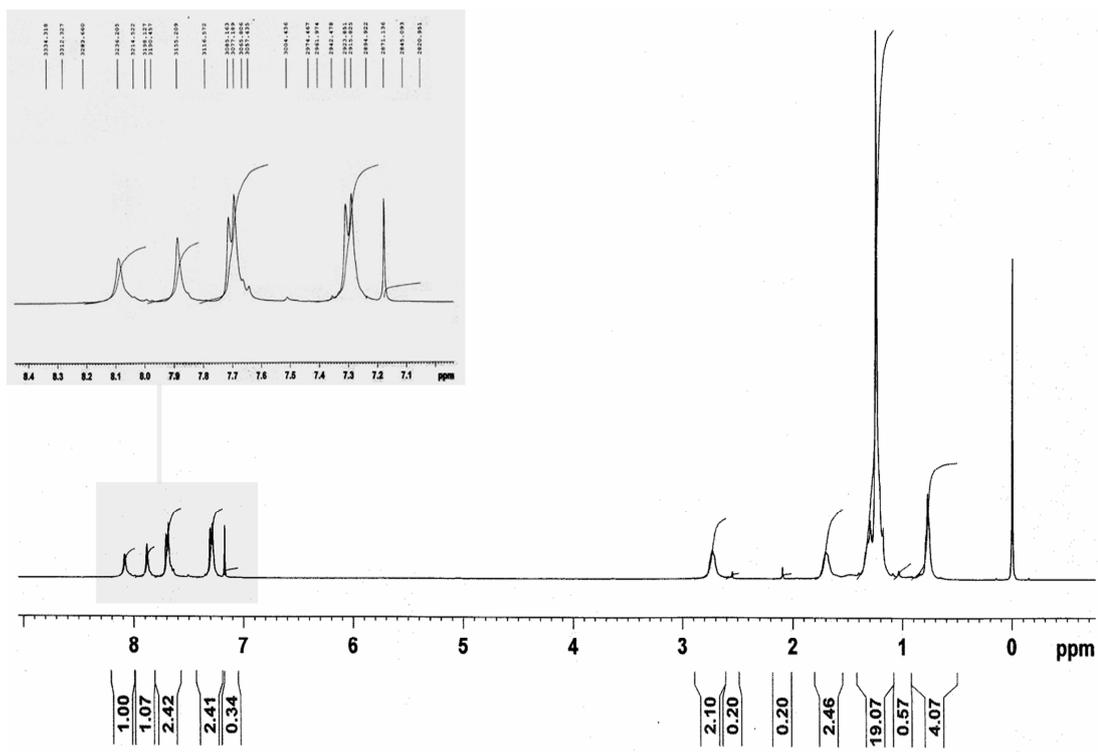
$^1\text{H}$  NMR spectrum of chemically synthesized polymer (Figure 3.3):  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 0.77, 1.25, 1.66, 2.73, 7.18, 7.30, 7.68, 7.89, 8.09.



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



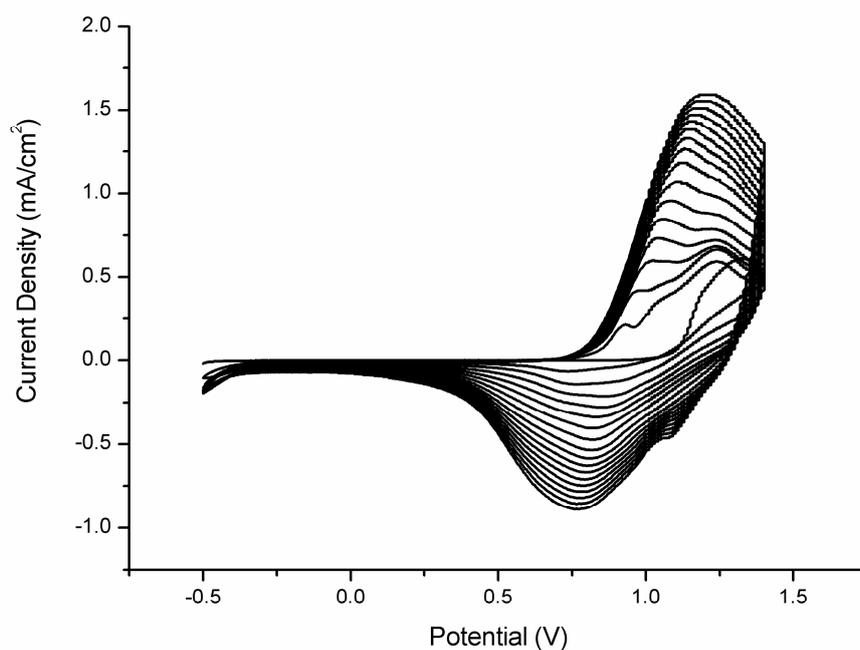
**Figure 3.2**  $^{13}\text{C}$ -NMR spectrum of the monomer



**Figure 3.3**  $^1\text{H-NMR}$  spectrum of the chemically synthesized PHTQ

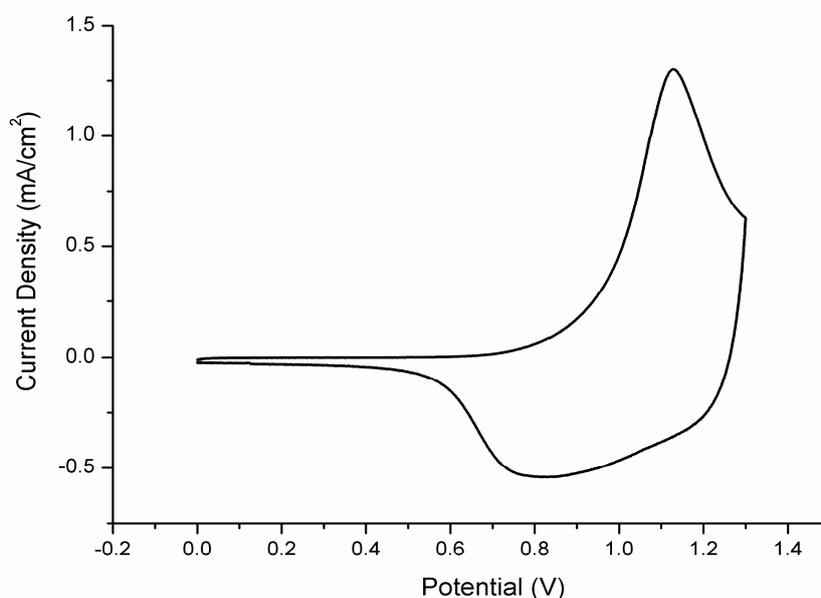
### 3.2. Cyclic Voltammograms

To directly synthesize and investigate potential electrochromic characteristics of the polymer film, electrochemical polymerization was carried out. For electrochemical synthesis of PHTQ, 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was used as the supporting electrolyte in dichloromethane (DCM): acetonitrile (ACN) (5/95, v/v) solvent mixture. The irreversible oxidation of HTQ was observed clearly on the first cycle at 1.3 V versus Ag wire pseudo reference electrolyte. Fig. 3.4 shows the repeated cyclic voltammogram of HTQ on ITO at 100 mV/s. Polymer redox couple reveal the formation of an electroactive polymer film (PHTQ) with an oxidation potential of 1.1 V and a reduction potential of 0.76 V.



**Figure 3.4** Repeated potential scan electropolymerization of HTQ at 100 mV/s in 0.1 M TBAPF<sub>6</sub>/DCM/ACN on ITO electrode.

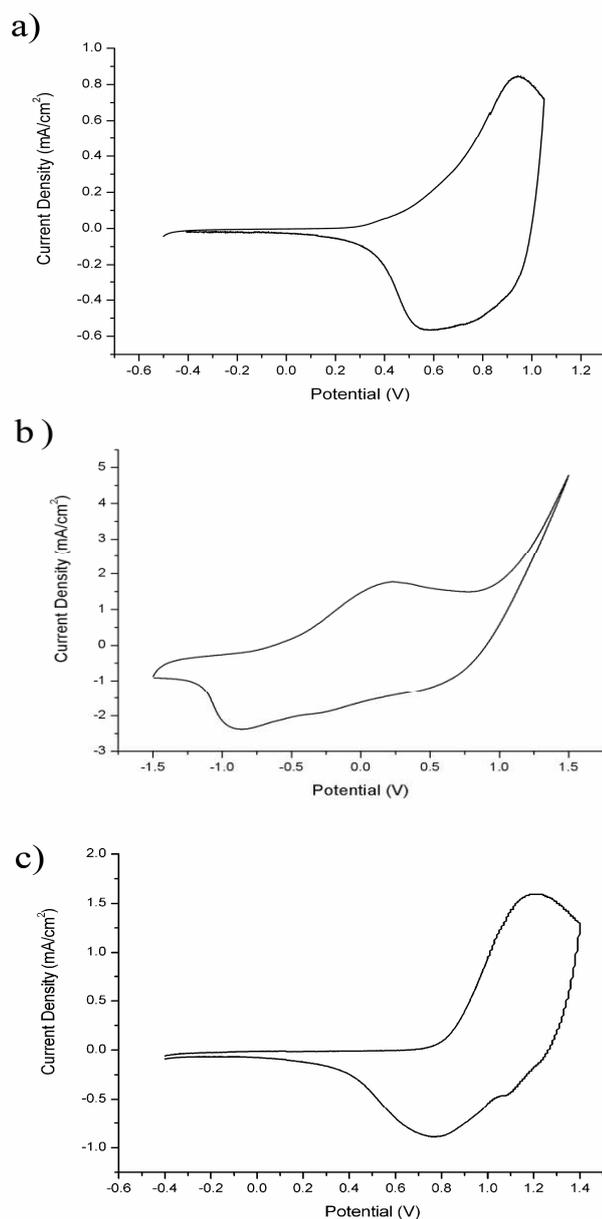
After chemical polymerization, a saturated red color polymer with high solubility in common organic solvents was obtained. A saturated chloroform solution was prepared and the polymer was spray-coated on ITO glass for electrochemical characterization. The polymer revealed similar cyclic voltammogram as seen in Fig. 3.5. The oxidation and reduction potentials were found to be almost the same with those given for the film synthesized electrochemically.



**Figure 3.5** Cyclic voltammogram of chemically produced PHTQ that spray-coated on ITO glass at 100 mV/s in 0.1 M TBAPF<sub>6</sub>/DCM/ACN.

The oxidation/reduction behavior of the HTQ through copolymerization in the presence of EDOT was investigated via cyclic voltammetry. Both EDOT and HTQ were oxidized within the same potential range hence the radical cations of both monomers were simultaneously formed at the working electrode surface. The potentiodynamic polymerization of HTQ with EDOT was carried out in a solution containing  $4.6 \times 10^{-2}$  M HTQ and  $6.1 \times 10^{-3}$  M EDOT in TBAPF<sub>6</sub> and ACN/DCM (5 / 95, v/v) solvent couple by applying a constant potential of 1.0 V under nitrogen atmosphere.

After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomer. When the applied potential was higher than 1.0 V, the product mainly consisted of PEDOT as revealed from CV and spectroelectrochemistry studies. At 1.0 V when the monomer feed ratios are the same, the copolymer has characteristics of rather PHTQ as given by its high electroactivity. Hence, 1.0 V was chosen as the electrolysis potential with a monomer feed ratio of 1:8 (HTQ:EDOT) to form the copolymer.

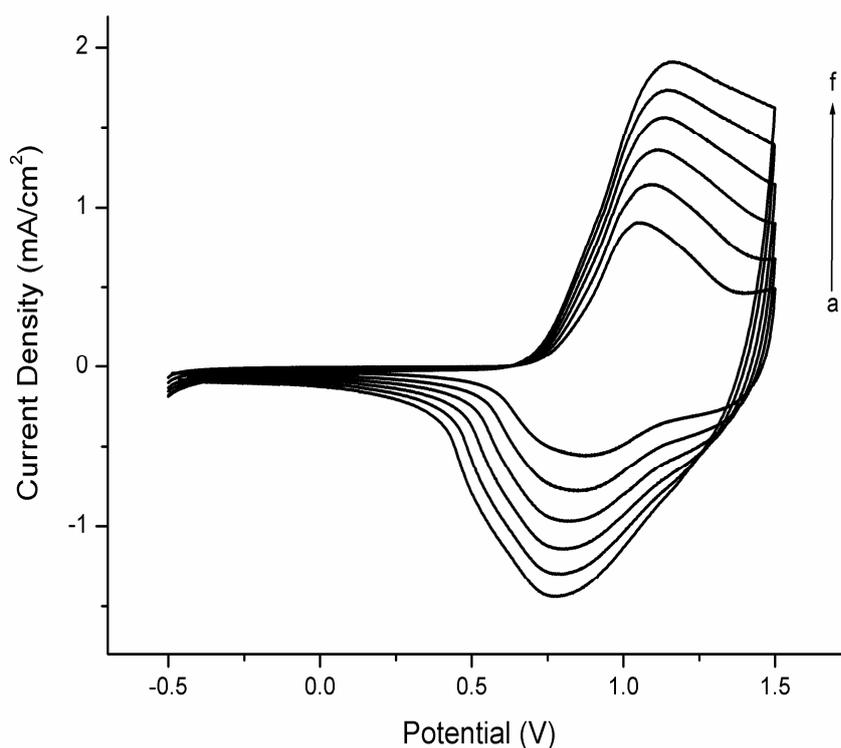


**Figure 3.6** Cyclic Voltammograms of ; a) Copolymer , b) PEDOT, c) PHTQ in 0.1 M TBAPF<sub>6</sub> /DCM/ ACN.

The cyclic voltammograms of the homopolymer, PEDOT and the copolymer were shown in Figure 3.6. As seen, the oxidation potential of the copolymer is quite lower than the parent homopolymer and shifted towards the oxidation potential of PEDOT which is a clear indication of copolymer formation.

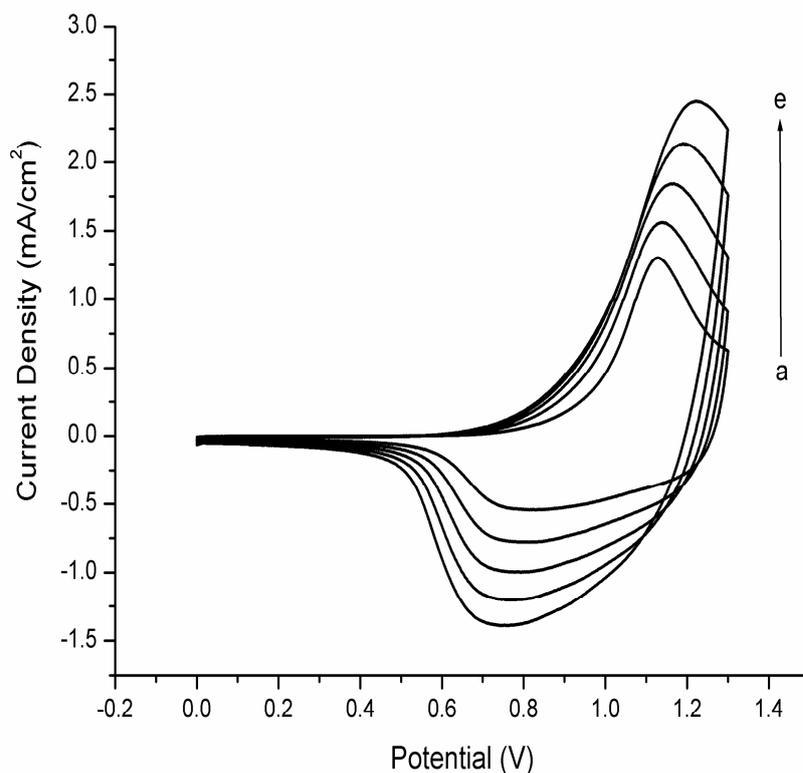
### 3.3 Scan Rate Dependency of Polymers

The anodic and cathodic peak current intensities increased regularly with the number of cycles due to the progressive growth of the P(HTQ) film on the electrode surface. The intensity of these peaks increased linearly with the scan rate ( $\nu$ ) in between 100 and 1000  $\text{mV}\cdot\text{s}^{-1}$ , which is characteristic of a reaction of surface-localized electroactive species (Figure 3.7).



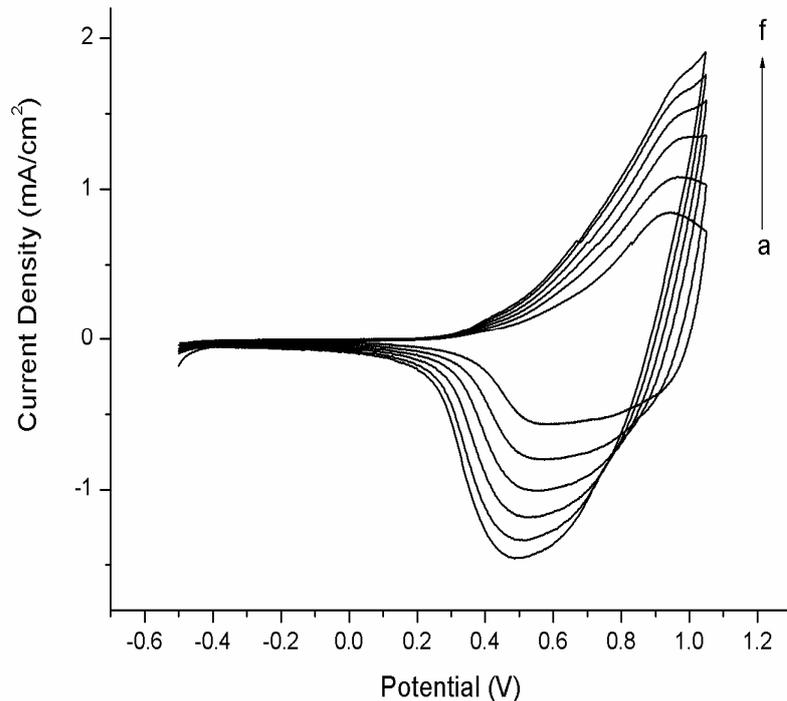
**Figure 3.7** Scan rate dependence of PHTQ film in  $\text{TBAPF}_6/\text{ACN}$  (a) 100, (b) 150, (c) 200, (d) 250, (e) 300, (f) 350  $\text{mV}/\text{s}$ .

Current response versus scan rate graph (Fig. 3.7) showed a linear relation which proves that the PHTQ film was electroactive and well adhered to the ITO electrode. Additionally, linear relation between anodic peak potentials and scan rate indicates that electrochemical processes are not diffusion limited and are reversible.



**Figure 3.8** Scan rate dependence of cPHTQ film in TBAPF<sub>6</sub>/ACN (a) 100, (b) 150, (c) 200, (d) 250, (e) 300 mV/s.

P(HTQ-co-EDOT) film also exhibited an electroactivity. The film was reversibly driven between the oxidized and neutral states, at various scanning rates, and the  $I_{p,a}$  values varied linearly with the sweep rate (Figure 3.9).



**Figure 3.9** Scan rate dependence of copolymer; (a) 100, (b) 150, (c) 200, (d) 250, (e) 300, (f) 350 mV/s in 0.1 M TBAPF<sub>6</sub>/DCM/ACN.

### 3.4 Gel Permeation Chromatography (GPC)

GPC is the best and exact way of measuring molecular weights of polymers. The weight average and number average molecular weight of both chemically and electrochemically synthesized polymers were determined by GPC in THF solution.

GPC measurements reveal that the heterogeneity index of the chemically polymerized polymer was higher compared to that of the electrochemically synthesized one. This is due to the rather more controlled polymerization on the surface of metal electrode in electrochemical polymerization.

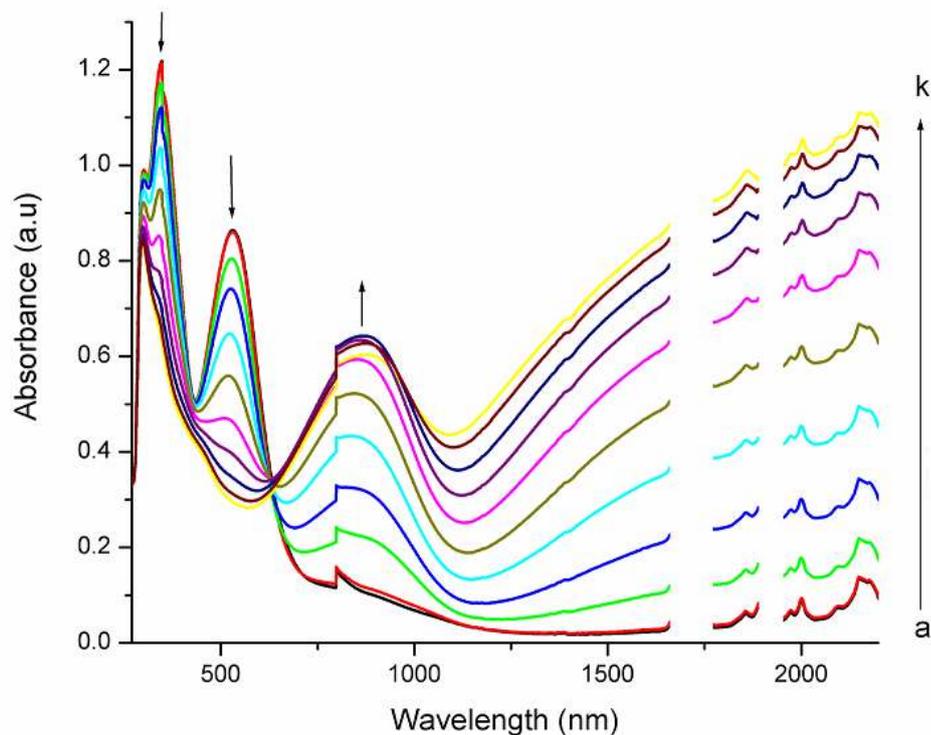
**Table 3.1** GPC Results

	<b>PHTQ</b>	<b>cPHTQ</b>
<b>M<sub>n</sub></b>	22,450	26,950
<b>M<sub>w</sub></b>	38,400	56,890
<b>HI</b>	1.71	2.11

### 3.5. Investigation of Electrochromic Properties of Polymers

#### 3.5.1 Spectroelectrochemistry

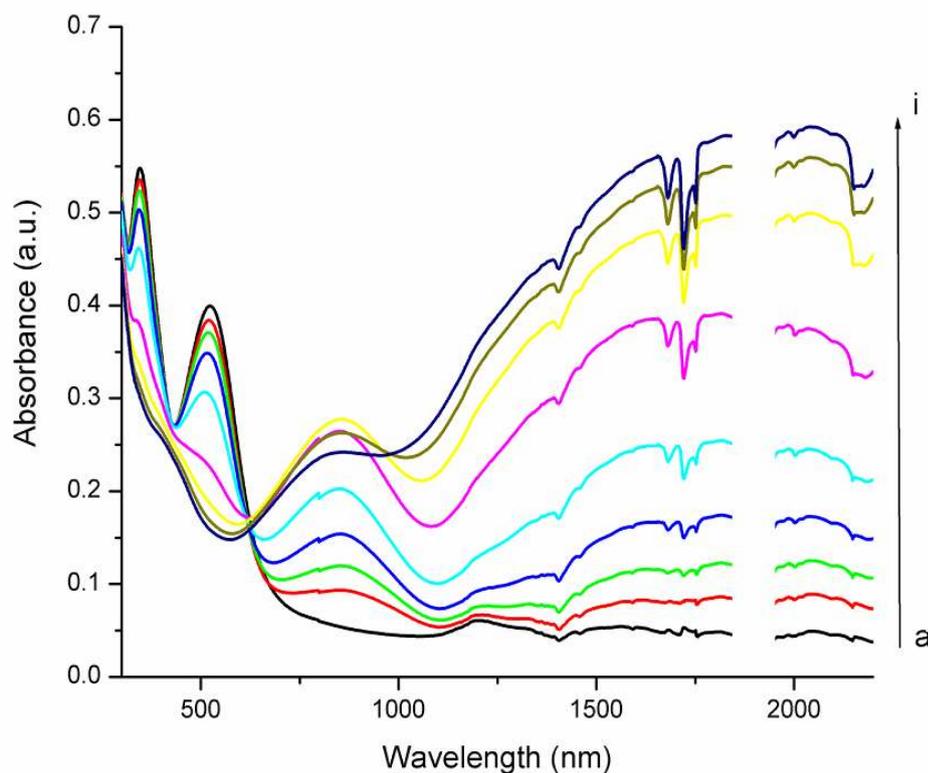
To investigate the optical changes upon doping, spectroelectrochemistry studies were performed. PHTQ was coated on ITO glass slides and spectral changes were investigated by UV–vis-NIR spectrometer in a monomer-free 0.1 M TBAPF<sub>6</sub> solution via incrementally increasing applied potential between 0.4 V and 1.2 V. As illustrated in Fig. 3.10, the donor–acceptor type polymer, PHTQ reveals two distinct absorption bands centered at 345 nm and 538 nm. Upon successive oxidation, intensities of both absorption bands gradually decrease leaving a residual tail centered at 350 nm. Additionally low intensity absorption centered between 430 nm and 600 nm and absorption at around 800 nm (due to the formation of polaronic band) are formed. Upon further oxidation the absorptions at 345 and 538 nm deplete totally and the absorption at 800 nm increases to greater.



**Figure 3.10** Spectroelectrochemistry of PHTQ film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF<sub>6</sub>/ACN electrolyte solvent couple at applied potentials (V): (a) 0.4, (b) 0.6, (c) 0.8, (d) 0.9, (e) 1.0, (f) 1.05 (g) 1.1, (h) 1.125, (i) 1.15 (j) 1.175 (k) 1.2.

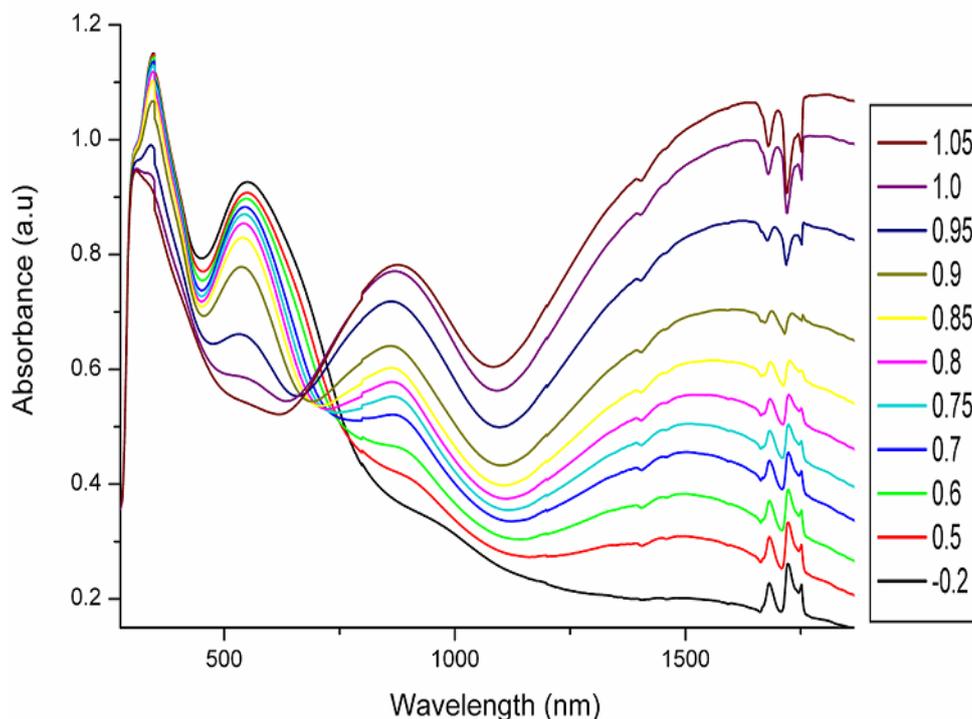
The electronic band gaps of the polymer were calculated as 1.75 eV and 2.46 eV for the two transitions observed at 345 nm and 538 nm. The increase in absorption centered at 800 nm corresponds to the formation of polaronic bands.

Spectroelectrochemistry of the chemically synthesized polymer was also investigated. A very similar spectrum was obtained for the chemically synthesized polymer at different applied potentials. The maximum absorption wavelength for both bands was found to be almost the same with the ones synthesized electrochemically.



**Figure 3.11** Spectroelectrochemistry of cPHTQ film on an ITO coated glass slide in monomer-free, 0.1M TBAPF<sub>6</sub>/ACN electrolytesolvent couple at applied potentials (V): (a) -0.5, (b) 0.85, (c) 0.9, (d) 0.95, (e) 1.0, (f) 1.05 (g) 1.1, (h) 1.15, (i) 1.2.

Spectroelectrochemistry studies of the copolymer were carried out in order to evaluate electronic transitions upon doping and dedoping. Copolymer films were deposited on ITO-coated glass in ACN/TBAPF<sub>6</sub>. The most convincing evidence of copolymerization was revealed by studying the spectroelectrochemical behavior of the copolymer which enables the evaluation of the differences of the spectral signatures of the material compare to those of the pristine homopolymer.



**Figure 3.12** Spectroelectrochemistry of copolymer film on an ITO coated glass slide in a monomer-free, 0.1 M TBAPF<sub>6</sub>/ACN electrolyte-solvent couple at applied potentials(V); (a) -0.2, (b) 0.5, (c) 0.6, (d) 0.7, (e) 0.75, (f) 0.8 (g) 0.85, (h) 0.9, (i) 0.95 (j) 1.0 (k) 1.05

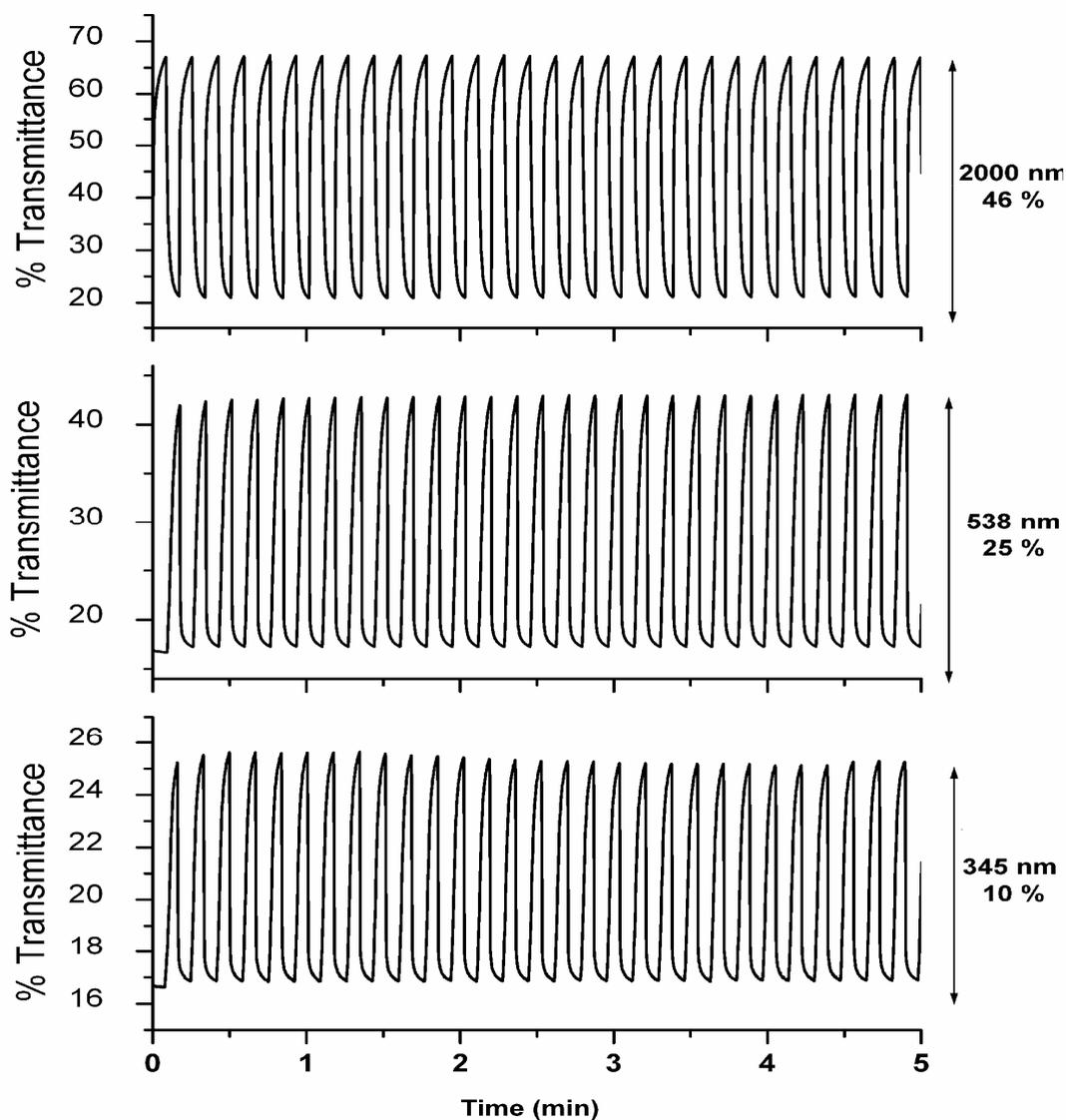
PEDOT reveals a  $\pi-\pi^*$  transition centered at 610 nm with a band gap of 1.6 eV whereas P(HTQ-co-EDOT) has a  $\lambda_{\max}$  at 550 nm with a band gap of 1.4 eV. The parent homopolymer has a  $\lambda_{\max}$  value at around 538 nm. The  $\lambda_{\max}$  value of the copolymer is between the  $\lambda_{\max}$  values of the corresponding homopolymers which is a clear indication of copolymer formation. Due to the unique donor-acceptor nature of the copolymer, a broader absorption band was resulted in a lower band gap value compared to the corresponding homopolymers.

**Table 3.2** Comparison of homopolymer, copolymer and PEDOT in terms of  $E_g$  and  $\lambda_{max}$  values

	<b>Homopolymer</b>	<b>Copolymer</b>	<b>PEDOT</b>
$\lambda_{max}$	538 nm	550 nm	610 nm
$E_g$	1.75 eV	1.4 eV	1.6 eV

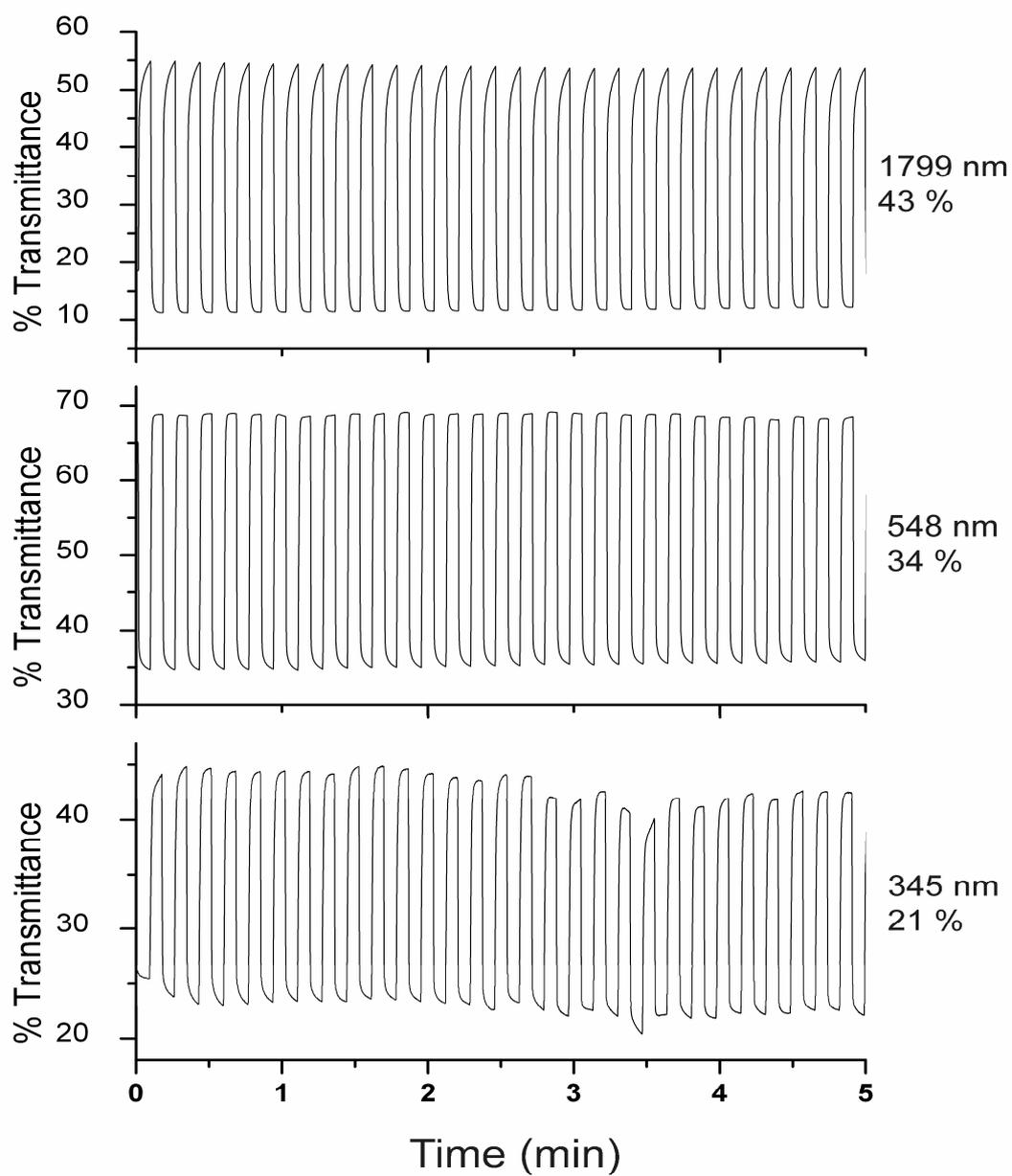
### 3.5.2 Electrochromic Switching

The capability of a polymer to switch rapidly and demonstrating a remarkable color change are essential properties for an electrochromic polymer. Electrochromic switching is proven to be one of the most efficient and easiest ways to observe these properties. The % transmittance (T %) at different wavelengths including the  $\lambda_{max}$  of the polymer was measured using a UV-vis-NIR spectrophotometer when the applied potential was switched between 0.4 V and 1.2 V with a period of 5 s. The optical contrast for PHTQ was measured as the difference between T% in the neutral and oxidized states and calculated as 10 % and 25 % at 345 and 538 nm, respectively Fig. 3.12). Polymer switches between its reduced and oxidized states in less than 2 s at both absorption maxima (345 and 538 nm). PHTQ has an excellent optical contrast of 46 % in the NIR region which makes this polymer a good candidate for NIR electrochromic device applications.



**Figure 3.13** Electrochromic switching, optical absorbance change monitored at 345, 538 and 2000 nm for PHTQ in 0.1M TBAPF<sub>6</sub>/ACN.

A striking enhancement was observed on kinetic properties via copolymerization. The copolymer achieves 34 % optical contrast in less than 1 second where for the parent homopolymer it took nearly 2 seconds for a 25 % optical contrast. As expected, copolymerization with EDOT improved both the optical contrast and the switching time of the material.



**Figure 3.14** Electrochromic switching, optical absorbance change of the copolymer monitored at 345, 548 and 1799 nm in 0.1 M TBAPF<sub>6</sub>/ACN.

**Table 3.3** Comparison of homopolymer and copolymer in terms of switching time and optical contrast

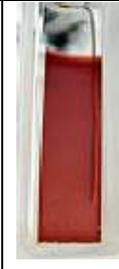
	Switching Time		Optical Contrast	
	<b>Homopolymer</b>	<b>348 nm</b>	<b>538 nm</b>	<b>538 nm</b>
<b>2.4 s</b>		<b>2.5 s</b>	<b>25%</b>	<b>46%</b>
<b>Copolymer</b>	<b>345 nm</b>	<b>550 nm</b>	<b>550 nm</b>	<b>1800 nm</b>
	<b>0.75 s</b>	<b>0.8 s</b>	<b>34%</b>	<b>43%</b>

### 3.5.3 Colorimetry Studies

The colors of the electrochromic materials were defined accurately by performing colorimetry measurements. CIE system was used as a quantitative scale to define and compare colors. Three attributes of color; hue (a), saturation (b) and luminance (L) were measured and recorded. The P(HTQ) film shows different colors in the reduced state (0.4V), half oxidized state (1.05 V) and fully oxidized state (1.2 V). At the reduced state, polymer has a red-purple color (Y: 144, x: 0.407, y: 0.319), a green color in the oxidized state (Y: 255 x: 0.314 y: 0.373) and upon further oxidation polymer have a dark gray color (Y: 243, x: 0.304 y: 0.349).

Colorimetry studies were performed to determine the Y,y,x coordinates of the colors of chemically synthesized polymer. As seen in Table 3.4 chemically synthesized polymer revealed very similar colors with electrochemically synthesized one.

**Table 3.4** Electrochromic properties of PHTQ and cPHTQ

					
<b>1.2 V</b> Y= 243 x= 0.304 y= 0.349	<b>1.05 V</b> Y= 255 x= 0.314 y= 0.373	<b>0.4 V</b> Y= 144 x= 0.407 y= 0.319	<b>1.2 V</b> Y= 255 x= 0.314 y= 0.373	<b>1.0 V</b> Y= 235 x= 0.316 y= 0.323	<b>-0.5 V</b> Y= 144 x= 0.407 y= 0.319

The copolymer revealed completely different spectroelectrochemical behavior in comparison to both of the homopolymers. The copolymer was purple in its neutral state and green in its oxidized state. The color coordinates of the copolymer were also determined by colorimetry in order to have an accurate objective measurement (Table 3.5).

**Table 3.5** Electrochromic properties of P(HTQ-*co*-EDOT)

	
<b>-0.5 V</b> Y= 434 x= 0.305 y= 0.305	<b>1.05 V</b> Y= 672 x= 0.302 y= 0.342

## CHAPTER IV

### CONCLUSION

In this study, 2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2yl) quinoxaline (HTQ) was synthesized via Stille coupling reaction. PHTQ was synthesized by means of both electrochemical and chemical polymerization methods and electrochromic properties of both polymers were investigated in detail. PHTQ showed satisfactory optical contrasts in the visible region with three distinctive colors upon doping. The polymer showed an excellent optical contrast of nearly 50 % in the NIR region which makes this solution processable polymer a remarkable choice for NIR device applications. The switching times of the polymer both in the visible and NIR regions were shown to be less than 2 seconds. Multichromic soluble polymer, PHTQ, also stands for an excellent choice for many electrochromic device applications. In addition, deep red fluorescence in the dedoped state makes this polymer a promising candidate as an active layer in organic solar cells.

Copolymerization of monomer with EDOT was also achieved successfully. A novel copolymer, P(HTQ-co-EDOT), was electrochemically synthesized and several improvements were achieved compared to the parent homopolymer. Especially the increase in the optical contrast and a satisfactory decrease in switching time are noteworthy. It is a fact that this class of donor-acceptor type copolymers will have great contribution to the field of organic electronic and soluble copolymers also synthesized by chemical modification of structures which enable their use as active layers in solar cells and light emitting diodes.

## REFERENCES

- [1] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* 39 (1977) 1098.
- [2] T. Ito, H. Shirakawa, S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* 12 (1974) 11.
- [3] Roncali, *J. Chem. Rev.* (1992), 92, 711.
- [4] J. R. Reynolds, M. Pomerantz, *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker; New York (1991) 187.
- [5] H. Letheby *J. Chem. Soc.* 15 (1862) 61.
- [6] G. Natta, G. Mazzanti, P. Corradini, *Atti Accad. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* 25 (1958) 3.
- [7] A. G. Macdiarmid, M. Akhtar, C. K. Chiang, M. J. Cohen, J. Kleppinger, A. J. Heeger, E. J. Louis, J. Milliken, M. J. Moran, D. L. Peebles, H. Shirakawa, *Journal Electrochem. Soc.* 124 (1977) 304.
- [8] H. Shirakawa, E. J. Louis, A. G. Macdiarmid, C. K. Chiang, A. J. Heeger, *Chem. Commun.* (1977) 578.
- [9] H. Shirakawa, *Handbook of Conducting Polymers*, 2<sup>nd</sup> ed.; Skotheim, T. A.; R. L. Elsenbaumer, J. R. Reynolds New York 197 (1998) 208.
- [10] J. C. W. Chien, *Polyacetylene: Chemistry, Physics, and Materials Science*, Academic: Orlando (1984).

- [11] A. F. Diaz, Chem. Scr. 17 (1981) 142.
- [12] G. Tourillon, F. J. J. Garnier, Electroanal. Chem. 135 (1982) 173.
- [13] A. F. Diaz, K. K. Kanazawa, G. P. Gardini, J. Chem. Soc., Chem. Commun. (1979) 635.
- [14] G. Grem, G. Leditzky, B. Ullrich, G. Leising, Adv. Mater. 4 (1992) 36.
- [15] Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. Nature 347 (1990) 539.
- [16] Rault-Berthelot, J.; Simonet, J. J. Electrochem. Soc. 182 (1985) 187.
- [17] MacDiarmid, A. G.; Epstein, A. J. Faraday Discuss. Chem. Soc. 88 (1989) 317.
- [18] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava. Science 265 (1992) 684.
- [19] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes. Nature 376 (1985) 498.
- [20] R. H. Friend, R. W. Gymer, A. B. Holmes, E. G. J. Staring, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Lögdlund, W. R. Salaneck. Nature 397 (1998) 121.
- [21] J. C. Gustafsson, B. Liedberg, O. Inganäs. Solid State Ionics 69 (1994) 145.
- [22] T. C. Chung, J. H. Kaufman, A. J. Heeger, F. Wudl. Phys. Rev. B, 30 (1983) 702.
- [23] G. A. Sotzing, J. R. Reynolds. Chem. Mater. 8(1996) 882.

- [24] B. Sankaran, J. R: Reynolds. *Macromolecules* 30(1997) 2582.
- [25] A. Kumar, D. Welsh, M. C. Morvant, F: Piroux, K. A: Abboud, J. R: Reynolds. *Chem. Mater.* 10 (1997) 896.
- [26] D. Welsh, A. Kumar, E. W. Meijer, J. R. Reynolds, *Adv. Mater.* 11, (1999) 1379.
- [27] S. D. D. V. Rughooputh, S. Hotta, A. J. Heeger, F: Wudl. *J. Poly. Sci.:Part B: Poly. Phys.* 25 (1987)1071.
- [28] I. Schwendeman, J. Hwang, D. M. Welsh, D. B: Tanner, J. R: Reynolds. *Adv. Mater.*(2001).
- [29] P. Topart, P. Hourquebie. *Thin Solid Films*, (1999), 352, 243.
- [30] J. Nakayama, T. Fukimori. *Heterocycles*, (1991), 32, 991.
- [31] K. Shimamura, F.E. Karasz, J.A.Hirsch, J.C. Chien, *Makromol. Chem. Rapid. Commun.* 2 (1981) 443.
- [32] J. L. Bredas, R. R. Chance and R. Silbey, *Phys. Rev., Part B.* 10 (1982) 5843.
- [33] B. R. Weinberger, E. Ehrenfreund, A. J. Heeger and A. G. MacDiarmid, *J. Chem. Phys.* 72 (1980) 4749.
- [34] J. B. Goldberg, H. R. Crowe, P. R. Neuman, A. J. Heeger and A. G. McDiarmid, *Mol. Cryst. Liq. Cryst.* 72 (1981) 253.
- [35] J. L. Bredas, B. Themans, J. G. Fripiat, J. M. Andre, R. R: Chance, *Phys. Rev. B*, 29 (1984) 6761.

- [36] R.R. Chance, D.S. Boudreaux, Handbook of Conducting Polymers, Vol.2, pp. 825, New York (1986).
- [37] M. Nechtschein, F. Devreux, F. Genoud, Synth. Met. 15 (1986) 59.
- [38] C.J. Zhong, J. Phys. Chem. 94 (1990) 2171.
- [39] T. A. Skotheim, Handbook of Conducting Polymers, Marcel Dekker, New York (1986).
- [40] C. K. Chiang, C. R. Fincher, Y. W. Park, A.J. Heeger, H. Shirakawa, E. J. Louis, S.C. Gua, A. G. MacDiarmid, Phy. Rev. Lett. 39 (1977) 1098.
- [41] H. Naarmann, German Patents 1179715, 1197228, 1179716.Germany (1963).
- [42] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, A. J. Heeger, J. Chem. Soc., Chem. Comm. (1977) 578.
- [43] A. G. MacDiarmid, R. B. Kaner, Handbook of Conducting Polymers, Marcel Dekker, NY (1986).
- [44] N. F. Mort, E. A. Davis, Electronic Processes in Non-Crystalline Materials, Iarendon Press, Oxford (1979).
- [45] D. Kumar, R.C. Sharma, Eur. Polym. J. 34 (1998) 1053.
- [46] T. Okada, T. Ogata, M. Ueda, Macromolecules 40 (1996) 3963.
- [47] R. Sugimoto, S. Takeda, H.B. Gu, K. Yoshino, Chem. Express (1986) 635.
- [48] N. Toshima, S. Hara, Prog. Polym. Sci. 20 (1995) 155.

- [49] R.H. Baughman, J.L. Bredas, R.R.Chance, R.L. Elsenbaumer, L.W. Shacklette, *Chem. Rev.* 82 (1982) 209.
- [50] Groenendaal, L.; Zotti, G.; Aubert, P.-H.; Waybright, S.; Reynolds, J. R. *Adv. Mater.* 15 (2003) 855.
- [51] Doblhofer, K.; Rajeshwar, K., *Electrochemistry of Conducting Polymers*. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds. Marcel Dekker: New York (1998) pp 531-588.
- [52] H.S.O. Chan, S.C. Ng, *Prog. Polym. Sci.* 23 (1998) 1167.
- [53] G. Zotti, *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, Wiley, Chichester (1997) Vol. 2, Ch. 4.
- [54] Delabougles, D., Garreau, R., Lemaire, M., J. Roncali, *New J. Chem.* 12 (1988) 155.
- [55] Hillman, A.R., Mallen, E., *J Electroanal. Chem.*, (1998), 243, 403.
- [56] S. Asavapiriyonont, G.K. Chandler, G.A. Gunawardena, D. Pletcher, *J. Electroanal. Chem.*, 177 (1984) 229.
- [57] E. Genies, G. Bidan, A.F. Diaz, *J. Electroanal. Chem.*, 149 (1983) 113.
- [58] A.F. Diaz, J. Bargon, In *Handbook of Conducting Polymers*; Vol. 1; T.A. Skotheim, Ed.; Marcel Dekker: New York (1986) p 82.
- [59] C. Pinzino, R. Angelone, F. Benvenuti, C. Carlini, A.M.R.Galletti, G. Sbrana, *J. Polym. Chem.* 36 (1986) 1901.
- [60] C. Amatore, A. Jutand, *Acc. Chem. Res.* 33 (2000) 314.

- [61] C. C. Anderson, M. D. DeLaura, D. Majumdar, Photographic Element Containing an Electrically-conductive Layer. US Patent 6,440,654 (2002).
- [62] D. L. Meeker, D. S. K. Mudigonda, J. M. Osborn, D. C. Loveday, , J. P. Ferraris, *Macromolecules* 13 (1998) 2943.
- [63] J. L. Boehme, D. S. K. Mudigonda, J. P. Ferraris, *Chem. Mater.* 13 (2001), 4469.
- [64] D. M. DeLongchamp, M. Kastantin, Hammond, P. T. *Chem. Mater.* 15 (2003) 1575.
- [65] A. Battacharya, A. De, *Prog. Solid. St. Chem.* 24 (1996) 141.
- [66] F. Selampinar, U. Akbulut, T. Yilmaz, A. Gungor, L. Toppare, *J. Of Polym. Sci: Part A Polym.Chem.* 35 (1997) 3009.
- [67] J.P. Ferraris, D.G. Guerrero, in: T.A. Skotheim, R.A. Elsenbaumer, J.R.Reynolds (Eds.), *Handbook of Conducting Polymers*, New York, (1998).
- [68] H. S. Nalwa, *Sythetic Metals*, 35 (1990) 387.
- [69] M. De Paoli, R.J. Waltman, A.F. Diaz, J. Bargon. *J. Polym. Sci., Polym. Chem. Ed.*, 23 (1985) 1687.
- [70] Struè Mpler, R., Glatz-Reichenbac, J., *J. Electroceramics*, (1999), 4, 329.
- [71] K. Kaneto, Y. Kohno, K. Yoshino, Y. Inushi, *Chem. Commun.*, 382 (1983).
- [72] Q. T. Zhang, J. M. Tour, *J. Am Chem. Soc.*, 119 (1997) 5065.

- [73] G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, P. R. Teasdale, *Conductive Electroactive Polymers*, CRC Press, New York, (2003), Ch.2, 51.
- [74] A. Dodabalapur, L. Torsi, H. E. Katz, *Science* (1995) 268.
- [75] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* 37 (1998) 402.
- [76] F. Jonas, G. Heywang, W. Schmidtberg, J. Heinze, M. Dietrich, *Europ. Pat. Appl.* (1988) 339.
- [77] J. C. DuBois, O. Sagnes, F. Henry, *Synth. Met.* 28 (1989) 871.
- [78] G. Heywang, F. Jonas, *Adv. Mater.* 4 (1992) 116.
- [79] P. Novak, K. Muller, K. S. V. Santhanam, O. Haas, *Chem. Rev.* 97 (1997) 207.
- [80] T. F. Otero, H. J. Grande, *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998, Chapter 36.
- [81] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* 100 (2000) 2537.
- [82] J. M. Pernaut, J. R. Reynolds *J. Phys. Chem. B.* 104 (2000) 4080.
- [83] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, 1995.
- [84] I.D. Brotherson, D.S.K. Mudigonda, J.M. Osborn, J. Chen, D.C. Loveday, J.L. Boehme, J. P. Ferraris, D.L. Meeker, *Electrochim. Acta* 44 (1999) 2993.
- [85] J. R. Platt, *Journal of Chem. Phys.* 34 (1961) 862.

- [86] S. K. Deb, *Applied Optics*, Supplement 3 (1969) 192.
- [87] B. W. Faughnan, R. S. Crandall, P. M. Heyman, *RCA Review* 36 (1975) 177.
- [88] M. A. Habib, *Electrochem. Transition* (1992) 51.
- [89] P. R. Somani, S. Radhakrishnan, *Mater Chem and Phys* 77 (2003) 117.
- [90] U. Bach, D. Corr, D. Lupo, F. Pichot, M. Ryan, *Adv. Mater.* 14 (2002) 845.
- [91] Mortimer, R. J. *Electrochim. Acta* 44 (1999) 2971.
- [92] A.B. Da Silveria Neto, A. Lopes Sant'Ana, G. Ebeling, S.R. Goncalves, E.V.U. Costa, H.F. Quina, J. Dupont, *Tetrahedron* 61 (2005) 1975.
- [93] Y. Tsubata, T. Suzuki, T. Miyashi, Y. Yamashita, *J. Org. Chem.* 57 (1992) 6749.
- [94] G.Y. Han, P.F. Han, J. Perkins, H.C. McBay, *J. Org. Chem.* 46 (1981) 4695.
- [95] Q. Hou, Q. Zhou, Y. Zhang, W. Yang, R. Yang, Y. Cao, *Macromolecules* 37 (2004) 6299.
- [96] I. Schwendeman, PhD. Thesis, University of Florida, 2002.
- [97] R. F. Lane, A. T. Hubbard, *J. Phys. Chem.* 77 (1973) 1401.
- [98] E. Lavion, *J. Electroanal. Chem.*, (1972) 39