

SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING  
POLYMERS OF 4-(2,5-DI(THIOPHEN-2-YL)-1H-PYRROL-1-YL)  
BENZENAMINE AND THEIR USE IN ELECTROCHROMIC DEVICES

A THESIS SUBMITTED TO  
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES  
OF  
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ERSİN YILDIZ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR  
THE DEGREE OF MASTER OF SCIENCE  
IN  
CHEMISTRY

JANUARY 2009

Approval of the thesis:

**SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING  
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## ABSTRACT

### **SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF CONDUCTING POLYMERS OF 4-(2,5-DI(THIOPHEN-2-YL)-1H-PYRROL-1-YL) BENZENAMINE AND THEIR USE IN ELECTROCHROMIC DEVICES**

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January 2009, 123 Pages

A monomer, 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl) benzenamine (SNS-NH<sub>2</sub>), was synthesized via the reaction of 1,4-di(2-thienyl)-1,4-butanedione with benzene-1,4-diamine. Chemical polymerization of the monomer yielded a polymer which was completely soluble in organic solvents. The chemical structures of both the monomer and the polymer were characterized by Nuclear Magnetic Resonance Spectroscopy (<sup>1</sup>H-NMR and <sup>13</sup>C-NMR) and Fourier Transform Infrared (FTIR) Spectroscopy. The average molecular weight of the chemically synthesized polymer was determined by Gel Permeation Chromatography (GPC) as  $M_n = 2.2 \times 10^3$  g/mol. The electrochemical oxidative polymerization of SNS-NH<sub>2</sub> was carried out via potentiodynamic electrolysis in the presence of LiClO<sub>4</sub>, NaClO<sub>4</sub> (1:1) supporting electrolyte in acetonitrile. Electrochemical copolymerization of SNS-NH<sub>2</sub> in the presence of 3,4-ethylenedioxythiophene (EDOT) was achieved in acetonitrile (ACN) / NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1M) solvent-electrolyte couple via potentiodynamic electrolysis. Conductivities of samples were measured by four probe technique.

Cyclic Voltammetry (CV) and Ultraviolet–Visible Spectroscopy were used to investigate electrochemical behavior of the monomer and redox reactions of conducting polymers. Surface morphologies of the polymer films were investigated by Scanning Electron Microscope (SEM). Second part of the study was devoted to investigate the one of most interesting property of conducting polymers, the ability to switch reversibly between the two states of different optical properties, ‘electrochromism’. The electrochromic properties of the conducting polymers were investigated via spectroelectrochemistry, kinetic and colorimetry studies. Spectroelectrochemistry analysis of homopolymer, P(SNS-NH<sub>2</sub>), reflected electronic transitions at 376 and 650 nm indicating  $\pi$ - $\pi^*$  transition and polaron band formation respectively. The polymer has an electronic bandgap of 2.12 eV with a yellow color in the fully reduced form and a blue color in the fully oxidized form. Switching ability of the homopolymer was evaluated by kinetic studies upon measuring the % transmittance as 20.7 % at the maximum contrast point. The spectroelectrochemical behavior of the P(SNS-NH<sub>2</sub>-co-EDOT) compare to that of the homopolymer revealed solid evidence of copolymerization based upon the differences in the spectral signatures. Copolymer revealed multichromic property with five different colors at different applied potentials. Colorimetry studies for P(SNS-NH<sub>2</sub>-co-EDOT) proved that it is possible to provide fine tuning of these colors by varying applied potential during synthesis. The results of colorimetry, spectroelectrochemistry and FTIR studies showed the possible control of the color of the electrochromic material in a predictable, controlled and reproducible manner. As the last part of the study, dual-type complementary colored electrochromic devices (ECD) using P(SNS-NH<sub>2</sub>) and P(SNS-NH<sub>2</sub>-co-EDOT)/poly(3,4-ethylenedioxythiophene) (PEDOT) in sandwich configuration were constructed and evaluated. Spectroelectrochemistry, electrochromic switching and open circuit stability of the devices were investigated by UV-Vis Spectrophotometer and Cyclic Voltammetry. They have shown to possess good switching times, reasonable contrasts and high stabilities.

**Keywords :** Electrochemical polymerization; Spectroelectrochemistry; Conducting copolymers; Electrochromism; Electrochromic devices.

## ÖZ

### **4-(2,5-Dİ(TİYOFEN-2-İL)-1H-PIROL-1-İL)BENZENAMİN' İN İLETKEN POLİMERLERİNİN SENTEZİ, ELEKTROKROMİK ÖZELLİKLERİ VE ELEKTROKROMİK CİHAZLARDA KULLANIMI**

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Ocak 2009, 123 Sayfa

4-(2,5-Di(tiyofen-2-il)-1H-pirol-1-il)benzenamin (SNS-NH<sub>2</sub>) monomeri, 1,4-di(2-tiyenil)-1,4-butanedion ile benzen-1,4-diamin'in tepkimesiyle sentezlenmiştir. Monomerin kimyasal olarak polimerleştirilmesi sonucunda organik çözücülerde tamamiyle çözünen bir polimer elde edilmiştir. Monomer ile polimerin kimyasal yapıları <sup>1</sup>H, <sup>13</sup>C Nükleer Manyetik Rezonans Spektroskopisi (NMR) ve Fourier Transform İnfrared Spektroskopisi (FTIR) ile karakterize edilmiştir. Polimerin ortalama molekül ağırlığı Jel Geçirgenlik Kromatografisi (GPC) ile Mn = 2.2 x 10<sup>3</sup> gr/mol olarak belirlenmiştir. Monomerin elektrokimyasal polimerizasyonu LiClO<sub>4</sub>, NaClO<sub>4</sub> (1:1) destek elektrolitleri varlığında asetonitrilde sabit gerilim yöntemi kullanılarak gerçekleştirilmiştir. SNS-NH<sub>2</sub>'nin 3,4-etilendioksitiyofen (EDOT) varlığındaki elektrokimyasal kopolimeri ACN/ NaClO<sub>4</sub>/ LiClO<sub>4</sub> (1:1) çözücü-elektrolit ikilisinde potensiyodinamik metodla elde edilmiştir. Filmlerin iletkenlikleri dört-nokta tekniği ile belirlenmiştir.

Dönüşümlü Voltametre (CV) ve UV-VIS Spektrofotometresi kullanılarak monomerin elektrokimyasal davranışı ve iletken polimerlerin redox tepkimeleri belirlendi. Polimer filmlerinin yüzey morfolojisi Taramalı Elektron Mikroskopu ile incelendi. Çalışmanın ikinci kısmı, tersinir olarak iki farklı optik özellik arasında değişim yapma özelliğine, yani iletken polimerlerin en ilginç özelliklerinden biri olan “elektrokromizm”e adanmıştır. İletken polimerlerin elektrokromik özellikleri spektroeletrokimyasal, kinetik ve kolorimetrik analizler ile tanımlanmıştır. Spektroeletrokimyasal analizler ile P(SNS-NH<sub>2</sub>)’nin elektronik geçişleri  $\pi$ - $\pi^*$  geçisi ve polaron bantlarının oluşumuna bağlı olarak sırasıyla 376 ve 650 nm de gözlemlenmiştir. En indirgenmiş halinde sarı ve en yükseltgenmiş halinde mavi olan polimerin elektronik bant aralığı 2.12 eV olarak hesaplanmıştır. Kinetik çalışmalar sonucunda homopolimerin değişim yapma özelliği en yüksek kontrast noktasında % 20.7 olarak ölçülmüştür. Spektroeletrokimyasal analizler sonucunda kopolimerin, P(SNS-NH<sub>2</sub>-co-EDOT), her iki homopolimerden de farklı bir elektrokromik özelliğe sahip olduğu gösterilmiştir. Kopolimer, uygulanan farklı potansiyellerde beş değişik renkle multikromik özellik göstermiştir. P(SNS-NH<sub>2</sub>-co-EDOT) için yapılan kolorimetrik çalışmalar, sentez sırasında uygulanan potansiyelin değiştirilmesiyle bu renklerin kolaylıkla değiştirilebileceğini kanıtlamıştır. Kolorimetri, spektroeletrokimya ve FTIR çalışmalarının sonuçları elektrokromik malzemenin renginin önceden belirlenebilir ve tekrarlanabilir bir biçimde kontrol edilebildiğini göstermiştir. Çalışmanın son kısmında ise, P(SNS-NH<sub>2</sub>), P(SNS-NH<sub>2</sub>-co-EDOT) ve poly(3,4-etilendioksitiyofen) (PEDOT) kullanılarak dual tip elektrokromik cihazlar kurulup incelendi. Cihazların spektroeletrokimyasal özellikleri, elektrokromik çevirmeleri ve açık devre hafızaları Dönüşümlü Voltametre (CV) ve UV-VIS Spektrofotometresi yöntemleri kullanılarak araştırılmıştır. Cihazlar, iyi çevirme zamanlarının, uygun optik kontrastlarının ve yüksek dayanıklılıklarının olduğunu kanıtlamışlardır.

**Anahtar Kelimeler :** Elektrokimyasal polimerizasyon; Spektroeletrokimya; İletken kopolimerler; Elektrokromizm; Elektrokromik cihazlar.

*To My Family*

## ACKNOWLEDGMENTS

It is a great pleasure to thank my supervisor Prof. Dr. Levent Toppare for his invaluable guidance, support, suggestions and stimulating advice for the completion of my thesis.

I also would like to thank Prof. Dr. Cihangir Tanyeli for his valuable advices and helpful NMR discussions.

I owe great thanks to Dr. Pınar Çamurlu, Dr. Senem Kiralp Kayahan, Dr. Metin Ak, for their help, technical support and answering my questions anytime in the laboratory, besides their kind friendship.

Special thanks go to my dear friends Dr. Yasemin Udum Arslan, Görkem Günbaş, Simge Tarkuç, Funda Özyurt, Asuman Durmuş, Aslı Tuğba Taşkın, Başak Yigitsoy, Serhat Varış, Özlem Türkarlan, Ayşegül Yıldırım, Yusuf Nur, Halime Mehtap Cengiz, Abidin Balan and Buğra Epik for their friendship; useful conversations and cooperation. I also would like to thank all my lab-mates in our research group for their kind friendship.

Words fail to express my eternal gratitude to my parents Elif and Hasan Yıldız, my sister Dr. Filiz Yıldız and my brother Emrah Yıldız, for giving me the intellectual and emotional guidance that made me who I am, and for their never-ending support, encouragement along with understanding for my frequent absences.

Finally, I would like thank the Scientific and Technological Research Council of Turkey (TUBITAK) for financial support which enabled me to carry out this work.

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## ABBREVIATIONS

SNS-NH <sub>2</sub>	4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine
P(SNS-NH <sub>2</sub> )	Poly(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine)
EDOT	3,4-Ethylenedioxythiophene
P(SNS-NH <sub>2</sub> -co-EDOT)	Poly(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine-co-ethylenedioxythiophene)
Th	Thiophene
Py	Pyrrole
PEDOT	Poly(3,4-ethylenedioxythiophene)
ACN	Acetonitrile
PMMA	Poly(methylmethacrylate)
PC	Propylene carbonate
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectrometer
CV	Cyclic Voltammetry
SEM	Scanning Electron Microscopy
GPC	Gel Permeation Chromatography
ECD	Electrochromic Device
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
E <sub>g</sub>	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

Strength, toughness and frictional resistance are properties which are described as typical of metals, but today are also characteristic of many polymers. Metals have therefore been replaced by plastics in many areas of applications. This, however, is not the case with one of the most important properties of metals – electrical conductivity. Although the question of producing macromolecular materials which exhibit conductivity similar to that of metals has long been posed, a major breakthrough has only occurred 30 years ago. In 1977, Shirakawa, McDiarmid, and Heeger discovered that partial oxidation of polyacetylene films improved its conductivity over nine orders of a magnitude [1].

In the year 2000, twenty-three years after the first experiment demonstrating that certain plastics conduct electricity, the Nobel Prize was awarded to these three researchers for “the discovery and development of conducting polymers.” [2]. In his Nobel Lecture, Alan Heeger offers two brief explanations for the importance of the discovery of conducting polymers: 1. “they didn’t exist before,” and 2. “they offer a unique combination of properties not available from any other known materials.” The first simplistic statement embodies the academic curiosity that has attracted so many researchers in a list of varying disciplines, including chemists, physicists, and materials scientists, to study these fascinating polymers.

The second explanation encompasses the potential use of conducting polymers in a vast number of applications by replacing old materials and by developing new technologies based on their unique and unprecedented abilities.

This remarkable discovery stimulated world-wide efforts to develop new classes of CPs with properties similar to or better than those of PA. Polyacetylene is the simplest form of conducting polymer that has the characteristic structure of a conjugated  $\pi$  system extending over a large number of the chain-linked monomer units. Owing to their unique electronic properties, combined with their processing advantages and excellent mechanical properties, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of “plastic” electrical and optical devices. Hence, a great effort has been devoted to the preparation of a wide variety of conjugated polymers in order to control the structure, properties and function of resultant materials [3-5]. The creative design and development strategies of conjugated polymers have led to enhanced performance and new function for these materials.

CPs based on aromatic systems and heteroatomic compounds such as aniline, pyrrole and thiophene have been developed [6,7]. These polymers possess higher environmental stability and structural versatility. The electronic and electrochemical properties of these polymers can be manipulated by modification of the monomer structure. Moreover, many important CPs can be prepared electrochemically as high-quality conducting films that extend their potential applications. CPs have been found particularly useful as electrode materials in rechargeable batteries [8] and electrochemical sensors [9]. Apart from these, conducting polymers have potential applications as materials in electronic and optical devices including electrochromic display devices [10], light-emitting diodes (LEDs) [11] and field-effect transistors (FETs) [12].

### 1.1.1 Historical Review of Conducting Polymers

Conventional polymers, which are saturated polymers or plastics, have been used for many applications traditionally because of their attractive chemical, mechanical, and electrically insulating properties. Although the idea of using polymers for their electrically conducting properties dates back at least to the 1960s [13], the use of organic “ $\pi$  conjugated” polymers as electronic materials [14,1] in molecular based electronics is relatively new. Although the polymers were regarded as insulators about 30 years ago, the report on discovery of conducting polymers and electroactive polymers changed this narrow perspective.

An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility is called conducting polymer, more commonly, “synthetic metal”.

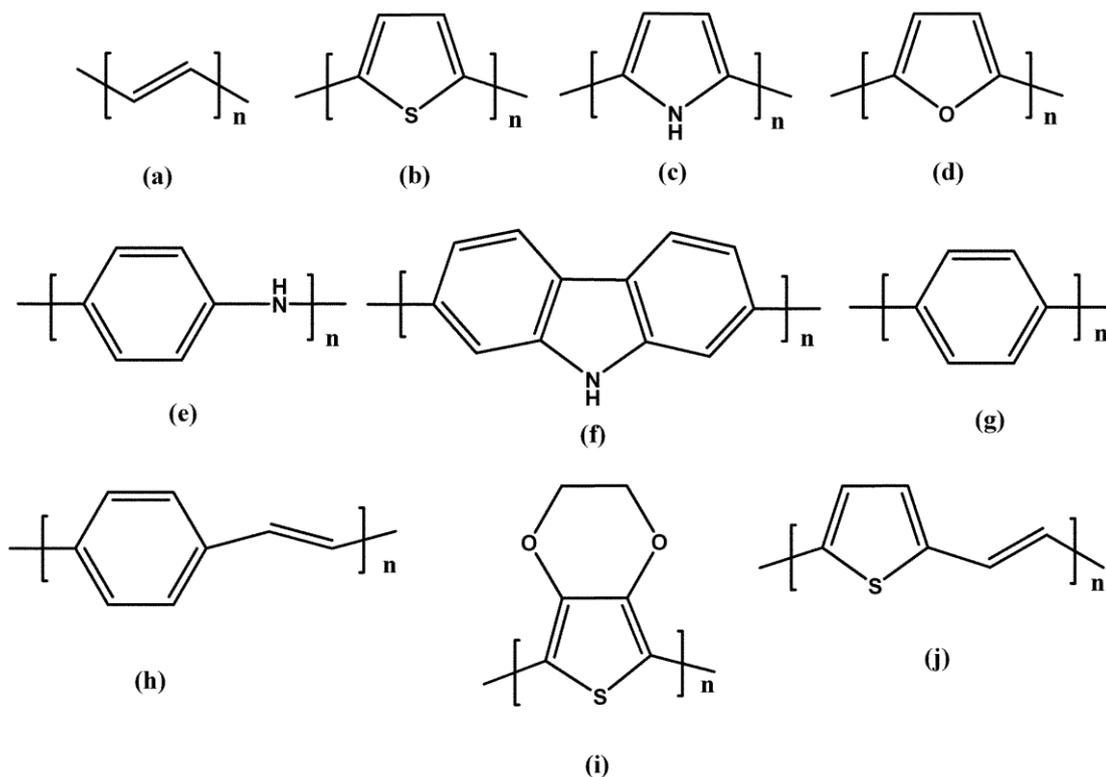
Twenty years after the discovery by Heeger, MacDiarmid and Shirakawa that an organic conjugated polymer can reach metallic-like electrical conductivity upon doping [14,1], the field of conjugated polymers has enjoyed a tremendous development culminating in 2000 when the Nobel Prize for Chemistry was awarded to the above researchers for launching a new era in polymeric materials. Conjugated polymer synthesis reaches as far back as 1862, when H. Letheby first synthesized polyaniline (PA). The anodic oxidation of aniline under mild conditions gave a black powdery deposit on the electrode that was insoluble in water and many organic solvents [15]. Known as “aniline black”, this material was used in the printing industry [16]. The first polymerization of acetylene to form polyacetylene (PAC) was reported in 1958 by Natta and coworkers [17]. Since PAC was obtained as an insoluble and infusible powder, the material received little attention at that time. The idea that conjugated polymers could be good electrical conductors has roots back to the 1960s when MacDiarmid and others discovered that poly(sulfurnitride)  $(SN)_x$ , a polymeric inorganic explosive [18], has a high conductivity [19].

The room temperature conductivity of  $(\text{SN})_x$  was of the order of  $10^3$  S/cm. [20]. As a comparison, copper has a conductivity of  $1 \times 10^6$  S/cm, and polyethylene,  $10^{-14}$  S/cm. Although it's other physical properties, such as its explosive nature, prevented it from becoming commercially important, it proved the existence of highly conducting polymers, and led to the discovery of an entirely new class of conducting polymers.

The modern era of conducting polymers began at the end of 1970s when films of PAc were found to exhibit a 12 order of magnitude increase in electrical conductivity when exposed to iodine vapors [14,1] The procedure for synthesizing PAc was based upon a route discovered in 1974 by Shirakawa through an accidental addition of 1,000 times more catalyst during the polymerization of acetylene. Although initially it was thought that PAc would replace dense metals in air and space applications, its instability to environmental conditions constituted a major obstacle for any practical use. However, PAc, being the simplest model from this class, remains the archetype of conducting polymers and is still subject to much theoretical and experimental work. Even though polyacetylene had a very high conductivity, its intractability and instability toward oxygen and water made it infeasible for commercialization [6]. For these reasons, much work has been devoted to synthesizing soluble and stable polyacetylenes [21,22]. Unfortunately, these substituted derivatives exhibit electrical conductivities that are much lower than the parent polymer. Naturally, much work has been devoted to develop stable and processable conducting polymer structures.

The opportunity to synthesize new conducting polymers with improved properties began to attract the attention of synthetic chemists in the early 1980s. During this time, the discovery that polypyrrole (PPy) can be obtained as highly conducting and homogeneous, free-standing films via oxidative electropolymerization [23] focused the research efforts towards the development of conjugated poly(heterocycles).

Electrochemical polymerization was rapidly extended to other aromatic compounds such as aniline, thiophene, furan, indole, carbazole, azulene, pyrene, and fluorene [24,25]. Although exhibiting lower conductivities than doped PAc, the most common conjugated poly(heterocycles) possess superior environmental stabilities in their p-doped form, along with other interesting properties such as electrochromism, volume change during doping, electro- and photoluminescence, etc.[26]. Among these so-called “first generation” conducting polymers, polythiophene (PTh) has rapidly become the subject of considerable interest, mainly due to its structural versatility and enhanced stability in both neutral and p-doped states. From a theoretical point of view, PTh has been often considered as a model for the study of charge transport in non-degenerate ground state polymers.



**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(3,4-ethylenedioxythiophene), (j) poly(thienylenevinylene)

New conducting polymer structures (Figure 1.1) have been developed over the past two decades with the hope of obtaining better properties than polyacetylene. New classes of conducting polymers include polythiophene [27] (PTh), polyfuran [28], polypyrrole [29] (PPy), poly(p-phenylene) [30] (PPP), poly(p-phenylene vinylene) [31] (PPV), polyfluorene [32], polyaniline [33] (PAn) and polycarbazole [34] (PCz). In Figure 1.2, conductivities and stabilities of some of these polymers were shown. Even if none has exhibited higher conductivity than polyacetylene, these polymers have been helpful in designing new monomers functionalized with Th, Py, etc. that are soluble and stable. By adding various side groups, electron donating or withdrawing, to the polymer backbone, soluble derivatives can be prepared; in addition, the electronic structure of the material can be manipulated.

<b>POLYMER</b>	<b>CONDUCTIVITY (<math>\Omega^{-1} \text{ cm}^{-1}</math>)</b>	<b>STABILITY (doped state)</b>	<b>PROCESSING POSSIBILITIES</b>
Polyacetylene	$10^3 - 10^5$	poor	limited
Polyphenylene	1000	poor	limited
PPS	100	poor	excellent
PPV	1000	poor	limited
Polypyrroles	100	good	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

**Figure 1.2** Conductivities and stabilities of some common conducting polymers

More recently, conjugated polymers are receiving attention as promising materials for electronic applications. In particular, conjugated polymers as well as  $\pi$ -conjugated oligomers [35] play a central role in organic-based transistors and integrated circuits [36, 37], photovoltaic devices [38] and especially organic-based light emitting devices [39]. Even solid state lasers are under development [40]. In fact, in the case of polymer-based light emitting devices (LEDs), the development of device structures has led to the establishment of high-tech companies and academic institutes [41,42].

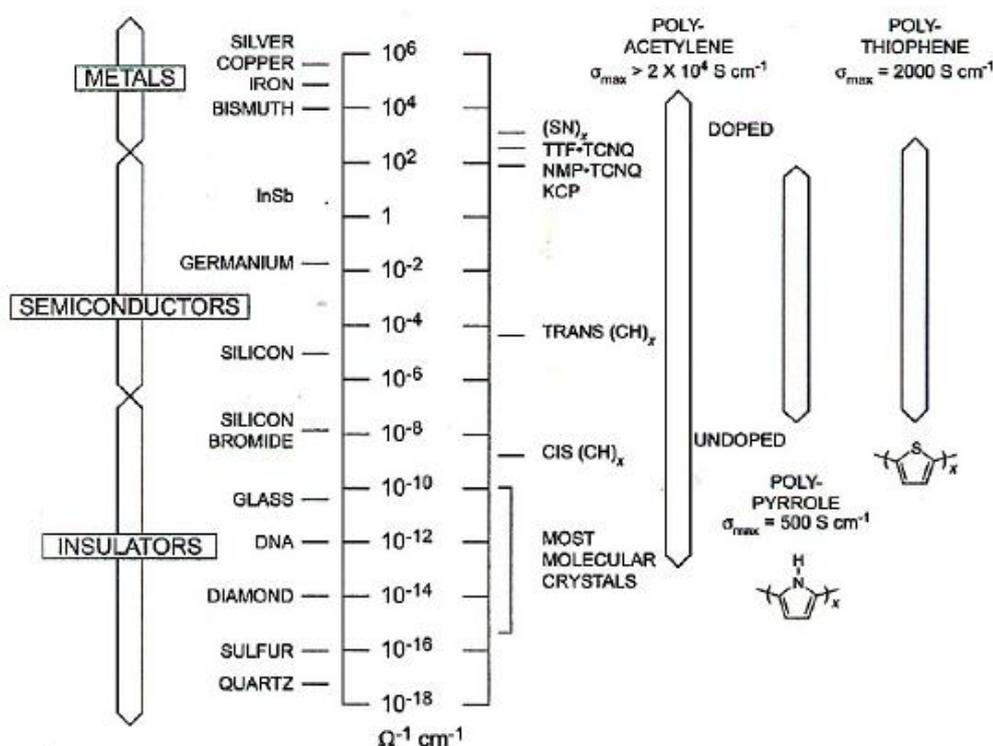
## 1.2. Band Theory and Conduction Mechanism in Conducting Polymers

Compared to conventional polymeric materials, whose useful properties are usually defined in terms of physical effects such as solubility, toughness, mechanical strength, and morphological transitions, the bulk of the interesting and useful aspects of conducting polymers originate from the electronic properties of the polymer backbone, which usually manifest themselves through the extended conjugation effects. Conducting polymers have high conductivity almost as metals due to the free movement of electrons through their structure. The movement of charge carriers such as electrons and holes through a medium (metal, polymer, etc.) under influence of an electric field is named as electronic conduction. Thus, the number of charge carriers available and their ability to move through the medium characterize the conductivity of the medium. While PA is essentially a defunct material in terms of current research interest, its structural simplicity provides a convenient entry into the band gap discussion. PA is composed of a chain of  $sp^2$  hybridized carbon atoms linked by alternating single and double bonds,  $(CH)_x$ . The theoretical work was done long before the actual synthesis and PA was assumed to have a structure where resonance causes the double bonds and single bonds to have the same bond length on average and there is extensive delocalization along a chain. The communication along the main chain of the polymer is due to the overlapping p orbitals forming  $\pi$  bonds and this material was expected to be highly conductive as a result. The electrical conductivity ( $\sigma$ ) of a conductive polymer can be given by the following equation where  $n$  is the total number of charge carriers,  $q$  is the charge on the carriers,

$$\sigma = nq\mu$$

and  $\mu$  is the mobility of the carriers. For most conducting polymers, there are very few charge carriers available in the neutral state. They usually behave as insulators or have a very low intrinsic conductivity. In order for a conducting polymer to be a semi-conductor, an external dopant has to be used like the usual practice in the semi-conductor industry. By doping a conducting polymer with external dopant, the number of charge carriers is increased, which dramatically increases the electrical conductivity of the polymer.

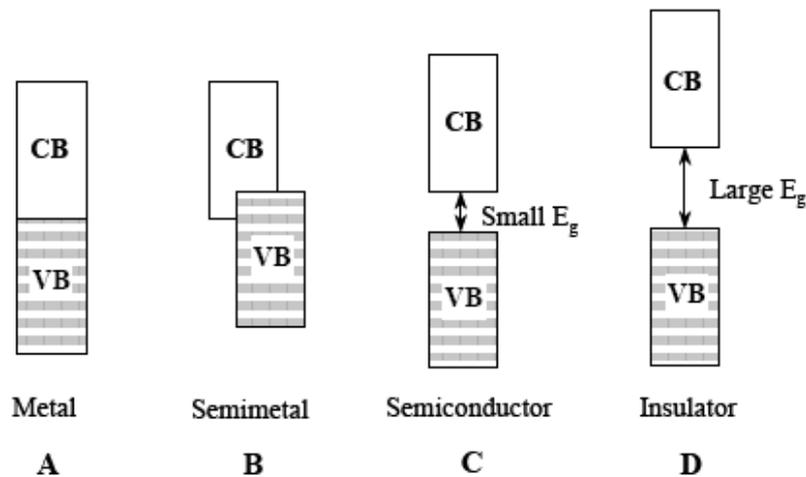
In the above equation, another factor that affects the conductivity of a conductive polymer is  $\mu$ , the mobility of the carriers along the conducting path. When a conducting polymer conducts, the electrical charge travels through the polymer. The overall mobility of electrical charges ( $\mu$ ) is dependent on how easily the charges move inside the polymer. It depends on the movement of electrical charges along the polymer chain, called intra-chain movement, and also jumping 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. Usually these factors are convoluted together. The conductivity of conducting polymers varies from  $10^{-9}$  to  $10^3$  S cm $^{-1}$ , which mainly falls into the range of semi-conductors (Figure 1.3). The basic ideas or concepts of band theory are useful frameworks for establishing the origins of electronic conduction and charge carriers.



**Figure 1.3** Conductivities of some metals, semiconductors and insulators

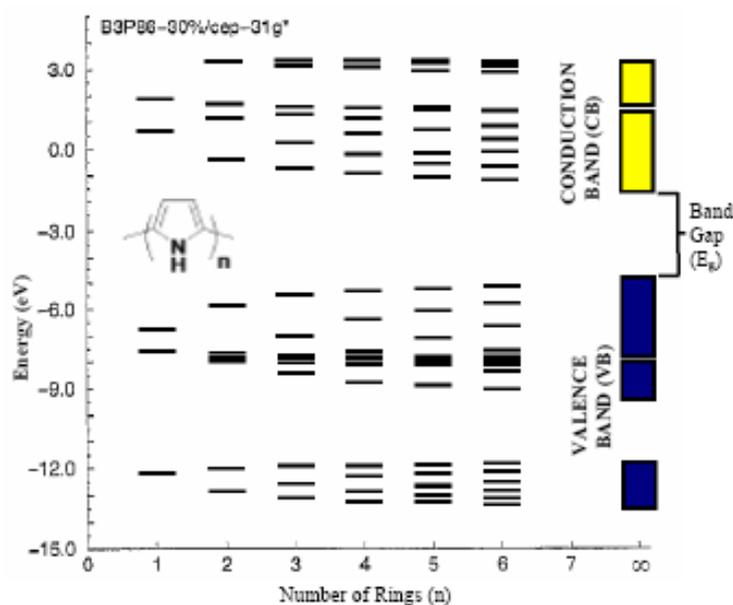
### 1.2.1. Band Theory

Band theory has been used to describe the properties of insulators, metals, and semiconductors. A semi-conductor is a material whose conductivity goes up with increasing temperature. For a metal, the conductivity goes up with decreasing temperature. Conducting polymers are semi-conductors according to their conductivity. Their electrical behavior can also be explained in terms of band theory. When two p atomic orbitals are involved in forming a  $\pi$  bond, two  $\pi$  molecular orbitals are formed. One is a filled  $\pi$  bonding orbital, and the other is an empty  $\pi$  anti-bonding orbital. There is an energy difference between these two molecular orbitals. If the number of p atomic orbitals is increased, the same number of  $\pi$  molecular orbitals must be formed. With the formation of additional energy levels, the energy difference between  $\pi$  bonding and  $\pi$  anti-bonding orbitals decreases. In addition, the energy differences between those discrete anti-bonding or bonding  $\pi$  orbitals become smaller too. In the case of highly conjugated conducting polymers, the number of  $\pi$  bonding or anti-bonding orbitals is large, the orbital energy spacing within them is very small. This provides nearly a continuum of orbitals resulting in a valence and conduction band. The valence band consists of filled  $\pi$  bonding orbitals and the conduction band consists of empty  $\pi$  anti-bonding orbitals. The energy difference between these two bands is called the bandgap;  $E_g$ , which is the energy required to promote an electron from the valence band to the conduction band.



**Figure 1.4** Band structures of (a) metal (b) semimetal (c) semiconductor (d) insulator

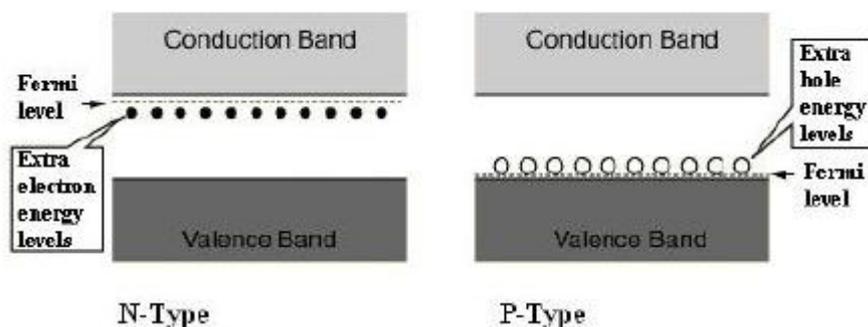
The conduction band can be populated at the expense of the valence band by exciting electrons across the band gap either thermally or photochemically. According to band theory, metallic conductors have overlapping between valence and conduction bands, which means zero band gap. Electrons, the charge carriers of metals, can move freely within the crystal lattice of the metal, leading to metallic conductivity. On the other hand, insulators have a very large bandgap. The transition of electrons from the valence band to the conduction band is not possible. All electrons are confined to the valence band, no charge carriers are available for electrical charge flow, and therefore an electrical current can not go through an insulator. The bandgap of semi-conductor lies between those of conductors and insulators (Figure 1.4), allowing some electrons to be promoted to the conduction band. In contrast to the empty conduction band of insulators, the conduction band of semi-conductors is lightly populated at ambient temperature. This gives rise to charge carriers available in semi-conductors. As the bandgap becomes smaller, the number of charge carriers increases. In addition, thermal energy stimulates more electrons to overcome the bandgap, which produces more charge carriers. At an elevated temperature, a semi-conductor has a higher conductivity.



**Figure 1.5** The origin of band structure in polypyrrole

One of the most important concepts in understanding the properties of conducting polymers is the origin of band structure. As shown in Figure 1.5 for the polypyrrole [43], molecular orbital perturbation effects lead to energy states that are very close in energy to the point such that excitations can occur through thermal population. As the length of the polymer chain increases progressively from 1 to infinity, 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. The polymer HOMO is thus defined as the highest occupied state in the valence band, and the LUMO is defined as the lowest unoccupied state in the conduction band. 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.

The bandgap can be measured from the absorption band edge in the UV-vis spectrum of a conducting polymer, which is called the band edge bandgap. The absorption band edge is the minimum energy needed to excite an electron to the conduction band from the valence band, which represents the real energy gap between these two bands. However, sometimes the absorption maximum is used and referred as the bandgap. Another way to determine the bandgap is to measure the oxidation and reduction potentials of the polymer. The energy difference between these two gives the bandgap. In addition, the room temperature conductivity of semiconductors is lower than the conductivity of metals due to a reduced charge carrier density. In extrinsic semiconductors, the number of charge carriers can be increased by introduction of impurities (dopants). In these materials, the carrier density is affected more by dopant nature and concentration than by the temperature. Classical extrinsic semiconductors are silicon-based doped with small amounts of gallium (p-type semiconductor) or arsenic (n-type semiconductor) (Figure 1.6).



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

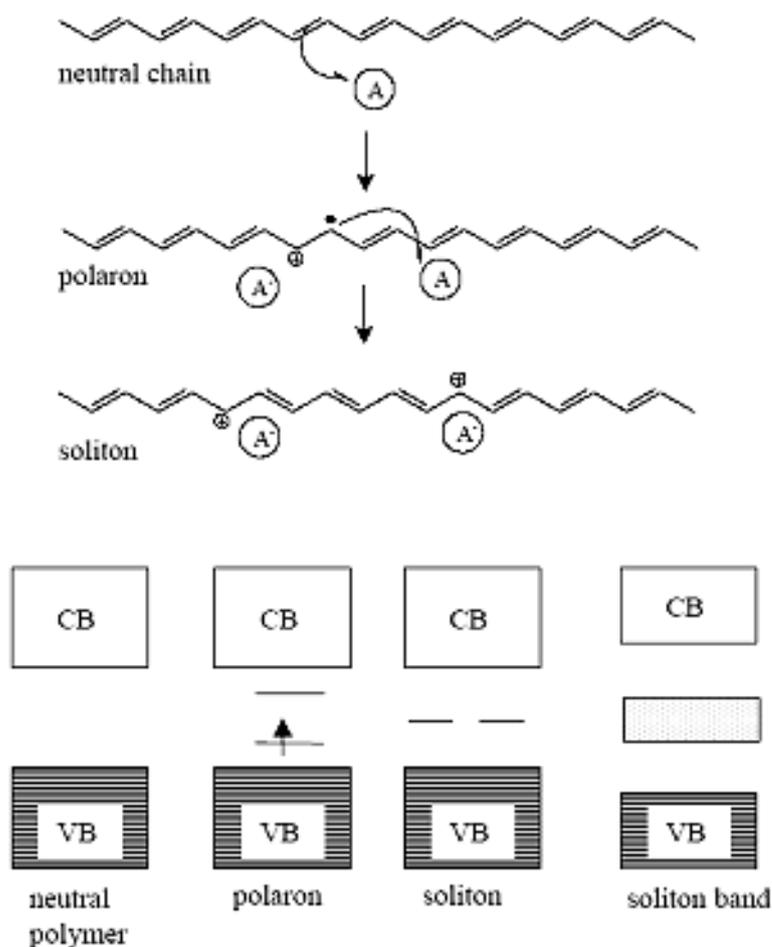
Minimizing the band gap is an important goal for maximizing the conductivity of CPs. Most CPs synthesized to date have band gaps greater than 2 eV characterizing them as mid- to high band gap polymers. Polymers with band gaps lower than 1.5 eV are considered relatively low band gap materials and few confirmed examples are available of polymers with band gaps below 0.8 eV.

## 1.2.2. Conduction Mechanism

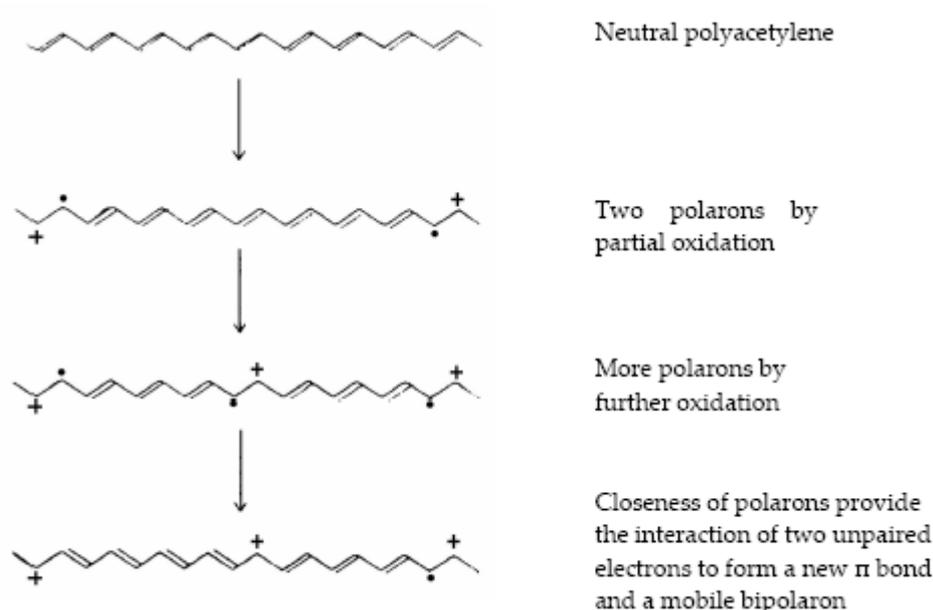
### 1.2.2.1. Charge Carriers

As a novel class of polymeric materials, conducting polymers have attracted dramatic research attention since the beginning. The envisioned optical and electronic properties together with the potential application in the fields of electronic and photonic devices have led to efforts devoted to the design and preparation of new systems with better performance. Among all approaches, bandgap control represents one of the most important ways to improve the performance of a conducting polymer in terms of conductive and optical properties. The narrowing of the bandgap would increase the number of charge carriers and thus the intrinsic conductivity of a conducting polymer. If the bandgap could be reduced to zero, an inherent organic conductor similar to a metal which has overlapping bands might be obtained. By analogy to a semi-conductor, doping of a neutral conducting polymer would change its electronic structure and dramatically increase its conductivity.

A good understanding of electronic conduction in polymers is the result of extensive research in the field. Electronic conduction in general is the transport of charge carriers (electrons, holes, polarons, solitons, etc.) through a medium (metal, polymer, etc.) under the influence of electric field. Thus, the conductivity displayed by any medium is characterized by the number of charge carriers available and their ability to move through the medium. Doping of a conducting polymer is usually accomplished by oxidation or reduction with electron acceptors or donors. Currently, most conducting polymers are known to be highly colored in the undoped state owing to optical transitions of electrons from the valence band to the conduction band.



**Figure 1.7** Polaron and soliton structures in oxidized polyacetylene



**Figure 1.8** Formation of polaron and bipolaron for polyacetylene

For example, in the case of polyacetylene (Fig. 1.8), when an electron is removed from the  $\pi$ -system of its backbone (chemical oxidation), an unpaired electron with spin  $\frac{1}{2}$  (a free radical) and a spinless positive charge (cation) are created. The radical and cation are coupled to each other via a local bond rearrangement, creating a polaron which appears in the band structure as localized electronic states symmetrically located within the gap with the lower energy states being occupied by a single unpaired electron. Further oxidation creates dicationic bipolarons in the polymer. An electron can be removed from either the polaron or the remaining neutral portion of the chain. In the former case, the free radical of the polaron is removed and a dication is created comprised of two positive charges coupled through the lattice distortion, creating a new spinless defect bipolaron. Removal of an additional electron from a neutral portion of the chain would create two polarons. Since the formation of a bipolaron produces a larger decrease in ionization energy compared to the formation of two polarons, the former process is thermodynamically favorable.

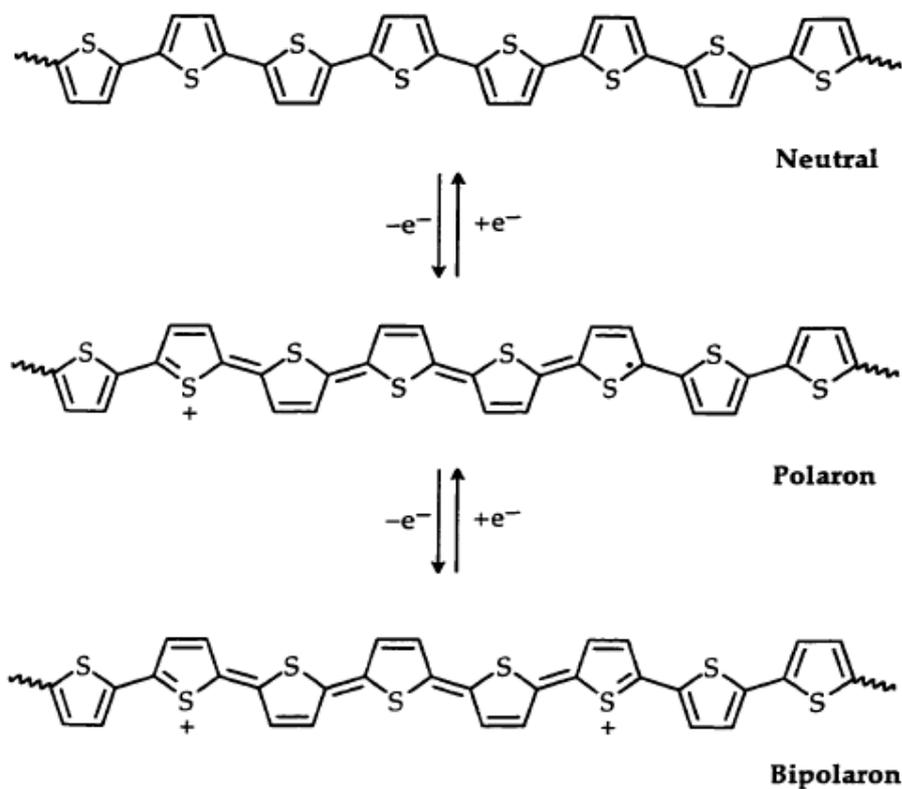
These new empty bipolaron states are also located symmetrically within the bandgap. Further doping creates additional localized bipolaron states, which eventually overlap to form continuous bipolaron bands at high enough doping levels. Similar states are formed when the polymer is reduced (n-doped), but the energy levels are below the conduction band [44]. Both polarons and bipolarons are mobile and can move along the polymer chain in an electrical field and hence conduct electrical current.

In the case of conjugated polymers with degenerate ground state structures, the situation is different. The initial oxidation of *trans*-polyacetylene also creates polarons as discussed above. When it is further oxidized, since its ground state is two-fold degenerate, the bonding configurations on either side of the charged defects only differ by a reversed orientation of the conjugated system and are energetically equivalent resonance forms. It in turn creates isolated, noninteracting charged defects that form domain walls separating two phases of opposite orientation but identical energy. Such defects are called soliton, which result in the creation of new localized electronic states that appear in the middle of the energy gap. As the doping level increases, these states can overlap to form soliton bands. It is now well accepted that in conducting polymers, transport occurs by the movement of charge carriers between localized states or between soliton, polaron, or bipolaron states.

#### **1.2.2.2. Concept of Doping**

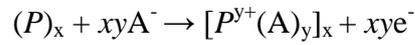
Perhaps the most significant discovery in the entire field of conducting polymers was that the conductivity of PA could be increased by twelve orders of magnitude upon chemical exposure to iodine or arsenic pentafluoride [14] or electrochemically [45]. This phenomenal effect was caused by a doping process induced by the oxidation or reduction of PA, and is analogous to the doping of semiconducting inorganic materials. 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 a small amount (10 %), (not necessarily stoichiometric quantities of chemical species), the electronic, electrical, magnetic, optical and structural properties of the polymer changes dramatically. The electrical conductivity of a “doped” material is typically 5 to 10 order of magnitudes higher than that of a “non-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. The electronic structure of many conducting polymers can be altered through oxidation or reduction. Simplistically, the oxidation of a neutral polymer by removing an electron from its valence band is referred as *p*-doping and the reduction of a polymer by adding an electron to its conduction band is referred as *n*-doping.



**Figure 1.9** p-type doping of polythiophene

Doping of a conducting polymer generates electrical charge carriers. By controllably adjusting the doping level, conductivity anywhere between that of the nondoped (insulating or semiconductor) and that of the fully doped (conducting) form of the polymer is easily obtained. In the doped state, the backbone of a conducting polymer consists of a delocalized  $\pi$  system. In the undoped state, the polymer may have a conjugated backbone which is retained in a modified form after doping, or it may have a non-conjugated backbone which becomes truly conjugated only after p-doping [46]. As an oxidation, *p*-doping takes electrons from the polymer system, producing positive charges on the polymer chain. These charges can move in the polymer when placed in an electric field, acting as charge carriers.



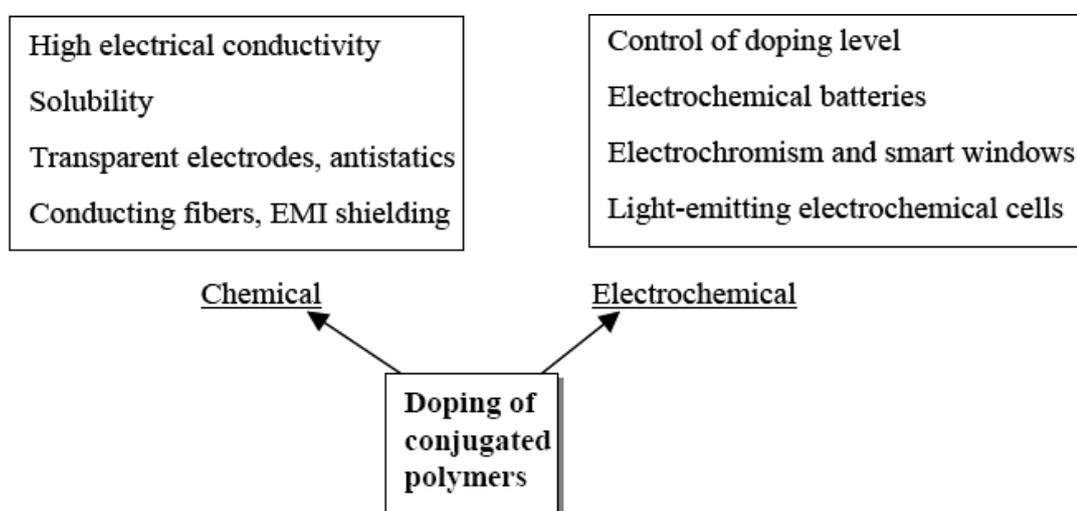
On the other hand, as a reduction, *n*-doping donates electrons to the polymer system, forming negative charges on the polymer chain. These electrons can move in the same direction in an electric field, functioning as current carriers.



Doping of conducting polymers is perhaps their most attractive property because it can not only make them highly conducting, but also can completely change their optical, magnetic, and mechanical properties. The *p*-doping process has been explored to a much greater extent than *n*-doping due to the requirement of stringently dry and oxygen-free conditions [47]. This dissertation focuses exclusively on *p*-doping effects, however there exists a body of literature on the *n*-doping process [47-50].

Conducting polymers, once studied solely for their high conductivities, are now extensively used in more dynamic applications where rapid switching from doped to neutral forms is desirable.

Charge injection (doping) in these materials leads to a wide variety of interesting and important phenomena, which now defines the conducting polymer field. This reversible intercalation of ions in the polymer matrix triggers significant changes in the materials' optical, ionic, electrical and morphological properties [51]. These properties can be tuned by varying dopant size and nature from small molecules to high molecular weight polymers as well as by using different preparation techniques [26]. As sketched in Figure 1.10, doping can be accomplished in several ways depending on the polymer nature and its intended application.



**Figure 1.10** Doping mechanisms in conjugated polymers and their applications

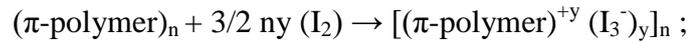
Conducting polymers can be doped either by chemical or electrochemical means. In the chemical pathway, doping is performed by reacting the polymer with suitable oxidizing or reducing agents. Electrochemical doping is performed by biasing the polymer film in a suitable solution to an appropriate potential [47].

The initial discovery of the ability to dope conjugated polymers involved chemical doping by charge transfer redox chemistry [1,14]. Oxidation (p-doping) was accomplished by exposing the polymer to iodine vapors, whereas reduction (n-doping) involved treatment with sodium naphthalenide.

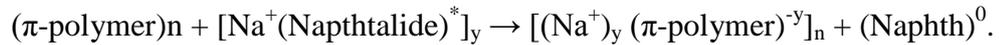
In this case, complete doping results in high quality materials with metallic-like conductivities. Another unique chemical doping procedure is PANi protonation by acid-base chemistry. This leads to an internal redox reaction converting the semiconducting form of PANi (emeraldine base) to a metal (emeraldine salt) [52].

Chemical doping involves charge-transfer redox chemistry:

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



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

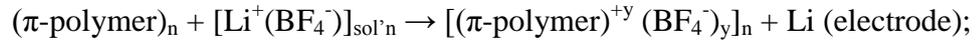


By adjusting the doping level, a conductivity anywhere between that of the non-doped (insulation or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained [53].

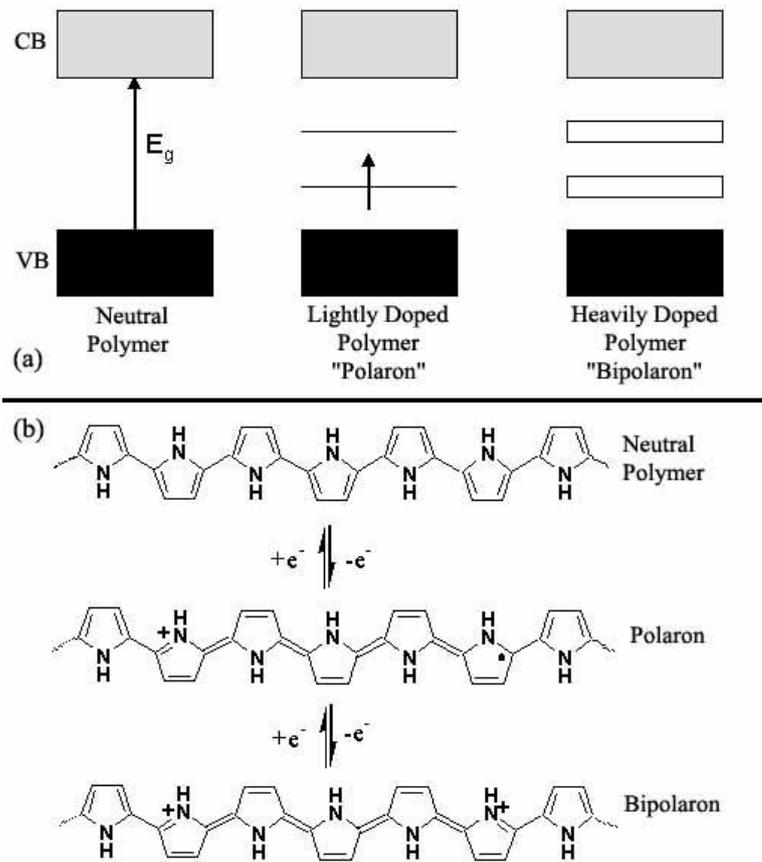
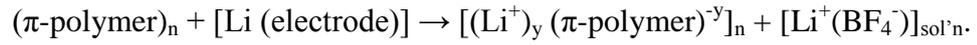
Although chemical doping is an efficient process, controlling its level is rather difficult. Attempts to reach intermediate doping levels resulted in inhomogeneous doping. As an alternative, electrochemical doping allows for fine tuning of the doping level by simply adjusting the potential between the working and counter electrodes [54]. The working electrode supplies the redox charge to the conducting polymer, while ions diffuse in or out of the electroactive film to compensate the electronic charge. Thus, any doping level can be achieved by setting the electrochemical cell to a desired potential and waiting for the system to attain an equilibrium state. This type of doping is permanent, meaning that the charge carriers remain in the film unless a neutralization potential is purposely applied.

Electrochemical doping is illustrated by the following examples:

(a) *p*-type



(b) *n*-type



**Figure 1.11** Charge carriers in PPy and its corresponding energy bands in the mid gap

The doping level is determined by the voltage between the conducting polymer and the counter electrode; at electrochemical equilibrium the doping level is precisely defined by the voltage.

Thus, doping at any level can be achieved by setting the electrochemical cell at a fixed applied voltage and simply waiting for the system to come to electrochemical equilibrium [55]. An advantage of conducting polymers is that their conductivity can be tuned over eight or more orders of magnitude for the same material. The doping level of conducting polymers affects range of conductivity from insulator to metal. Figure 1.3 shows the typical conductivity ranges of the three most common conducting polymers (PA, PPy, PTh).

### 1.2.2.3. Hopping

Although charge carriers are responsible for electrical conductivity in conjugated polymers, many structural imperfections are present in all polymers and thus when discussing mechanisms of bulk conductivity, these defects need to be considered. Conductivity is not only a result of charge transfer along the chain, but is also due to electron hopping between chains and between different conjugated segments of the same chain. The conduction process can be described with two important mechanisms, doping and hopping. Hopping is simply intra-chain, inter-chain and inter-particle motion of charges in a polymer matrix [56]. The intra-chain movement, motion of the charge carrier through a single chain, depends on the efficient conjugation. On the other hand, inter-chain movement, jumping from one chain to another, is determined by the piling of the polymer chains. The mobility also depends on the movement of electrical charges from particle to particle. Variable range hopping process in which electrons are delocalized on monomer rings is a well described conductivity mechanism. This mechanism, which is known as hopping conduction, is observed in two well-known varieties, nearest neighbor hopping and variable range hopping. The latter conduction mechanism is distinguishable from other conduction mechanisms by its different temperature dependence:

$$\sigma = \sigma_0 \exp [-(T_0/T)^\gamma]$$

$\gamma$  depends on the dimensionality of the hopping process [57].

In summary, conjugated polymers have a bulk conductivity limited not by carrier mobility in a molecule but by interchain hopping, and macroscopic conductivity measurements do not directly probe single molecule properties. The mechanism of bulk conductivity involves incoherent diffusive intra- and intermolecular electron transport where the electrons thermalize with the matrix and are dissipative. The electrical conduction in polyheterocyclics results from the mobility of the charge through the means below:

- a) Movement of the electron on the chain; called as intrachain transport of charge,
- b) Movement of the electron between the chains; the interchain transport of charge,
- c) Movement of the electron between intercrystallites; the intercrystallite transport of charge.

Cases b and c are called hopping processes.

### **1.3. Synthesis of Conducting Polymers**

The purposes of conducting polymer synthesis are, synthesizing new and novel structures, increasing the order of the polymer backbone as well as conductivity, good processability, easier synthesis, more defined three dimensional structure, stability in both conducting and nonconducting states, solubility in certain solvents such as water and many other application unique properties. Conducting polymers can be synthesized via chemical or electrochemical routes, although the former has been largely superseded by electrochemical methods. However, many polymers, most notably polyacetylene, are still only accessible via chemical synthesis. Polymers obtained by a chemical procedure are in their insulating form and can be chemically or electrochemically doped to their conducting form.

In contrast, polymers generated electrochemically are in their oxidized, conducting state. The thickness and morphology of the polymer film can be controlled during the electrolysis process [58].

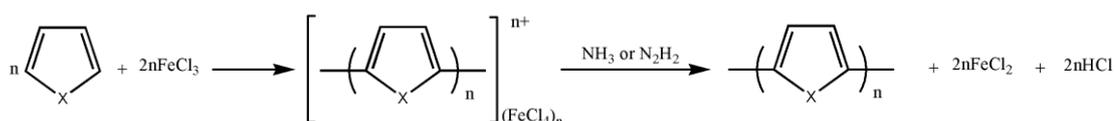
Other type of techniques used to synthesize conducting polymers includes [59].

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**

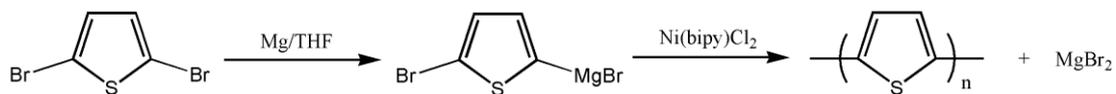
Oxidative chemical polymerization is the least expensive, most simple, and most widely used chemical synthesis of conducting polymers [60,61]. Conducting polymers can be produced by chemical polymerization following the routes of oxidative coupling and condensation of the monomeric precursors (Fig. 13). Oxidative coupling is based on the oxidation of the monomer under Friedel-Crafts conditions [62]. Oxidative chemical polymerizations are accomplished by exposing the monomer to a two-electron stoichiometric amount of oxidizing agent, resulting in the formation of the polymer in its doped and conducting state. Heterocyclic monomers, such as thiophene and its derivatives, are typically polymerized in the presence of anhydrous  $\text{FeCl}_3$  [63] (Fig. 12) although other Lewis acids can also be used [61]. Furthermore, benzene can be polymerized to form PPP by adding  $\text{AlCl}_3/\text{CuCl}_2$  [64].

These oxidants are able to oxidize the monomers in appropriate solution, leading to chemically active cation radicals of the monomers used. The cation radicals formed thus react with monomer molecules, yielding oligomers or insoluble polymers. Chemical polymerization occurs in the bulk of the solution, and the resulting polymers precipitate as insoluble solids [65]. The properly substituted heterocyclic and other aromatic monomers form highly soluble polymers. These polymers can be analyzed by traditional analytical techniques to determine their primary structure. Reduction to the neutral state is accomplished by addition of a strong base such as ammonium hydroxide or hydrazine.



**Figure 1.12** Oxidative chemical polymerization of polyheterocycles in the presence of iron (III) chloride

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. These polymers can be analyzed by traditional analytical techniques to determine their primary structure. The nature of the polymerization conditions also allows for easy scale-up and production of large quantities of polymer.

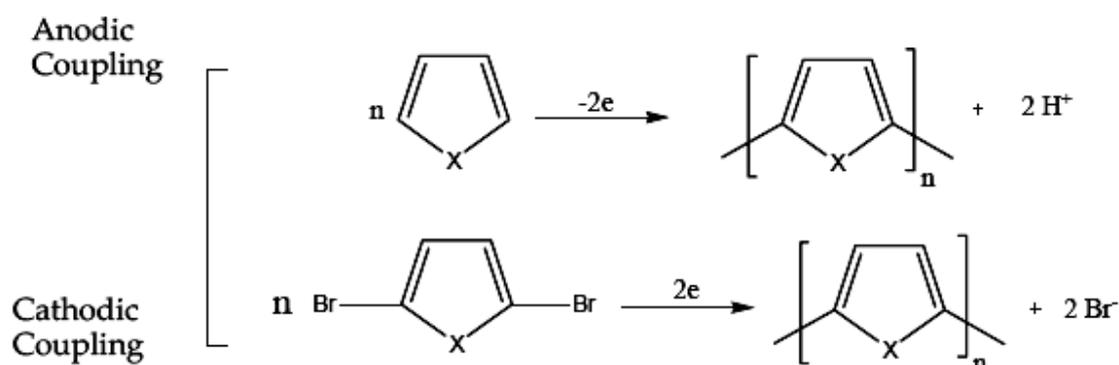


**Figure 1.13** Chemical polymerization of polythiophene in the presence of metal-catalyze

Although chemical methods for the synthesis of conducting polymers have the advantages of low cost, speed, and freedom from the restrictions of electrodes, there are many problems that are inherent to chemical polymerizations. Because the polymer is formed in its oxidized form, which is believed to be more rigid than the neutral form, the oxidized polymer chains can precipitate from the polymerization medium limiting degree of polymerization. Overoxidation and decomposition can also occur in these polymerizations as a result of the strong oxidizing agents used. Besides, there is also an abundance of side reactions occurring during chemical oxidation polymerization of heterocycles including formation of coupling defects along the backbone [66].

### 1.3.2. Electrochemical Polymerization

Electropolymerization is one of the most important tools in the synthesis of conducting polymers. It is an efficient method for synthesizing smooth polymer films on conductive substrates, and it allows for easy probing of electrical and optical properties. Electrochemical oxidation of various resonance stabilized aromatic molecules, such as pyrrole, thiophene, aniline, furan etc., produce electronically conductive polymers. The electrochemical routes for synthesis of polyheterocycles are anodic and cathodic couplings, which parallel the chemical oxidative coupling and condensation reactions (Fig. 1.14).



**Figure 1.14** Electrochemical synthetic routes to polyheterocycles.

Electrochemical synthesis is simple, selective and a reproducible method. It has the advantage of producing the material on an electrode on which to perform analysis of the growing process and the further experimental by electrochemical or spectroscopic techniques. Furthermore, the method allows easy control of the film thickness by the deposition charge. Electrochemical anodic oxidation is the most widely used technique to prepare polyheterocyclics of high conductivity. It is an efficient method to synthesize smooth polymer films on conductive substrates. Polymer films can be obtained on the electrode surface and can be easily peeled off from the surface to yield freestanding, electrically conducting films, which are homogeneous.

Anodic coupling consists of oxidation of the monomer into a polymer accompanied with proton elimination. Anodic coupling is preferred because it uses the unmodified monomer and the resultant polymer, being more easily oxidized (doped), is produced in the conductive state and therefore, allows the continuous deposition of the material up to considerable thickness.

Compared with other chemical and electrochemical methods, the advantages of oxidative electropolymerization are the followings [67,68]:

- (i) 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.
- (ii) Film thickness, morphology and conductivity can be easily controlled by the applied potential, polymerization time, and the electrochemical potential scan rate.
- (iii) They provide an in situ way to investigate the polymerization process and the properties of the resulting conducting polymer by electrochemical or spectroscopic techniques.

Although forming polymer by electropolymerization is a valuable synthetic method, this method has disadvantages. The greatest disadvantage is that the materials are obtained as insoluble films making primary structure verification difficult. The typical spectroscopic, chromatographic, and mechanical techniques used to characterize synthetic polymers cannot be used on an electrode bound material. Also, processing on substrates that are not conducting is not easily accomplished.

The type of solvent, electrolyte system, choice and concentration of monomer and electrodes strongly affect the properties of the final conducting polymer [62].

#### **1.3.2.1. Electrolytic Medium**

Various conditions such as the type of solvent used, the nature of electrolyte employed, the amount of current or potential applied to the cell, the electrode material, the concentration of monomer utilized and the temperature maintained during oxidative electrochemical polymerization can lead to different morphologies and properties of the polymer. Optimization of experimental parameters is necessary in order to obtain unparalleled results. However, an overwhelming amount of experimental parameters renders full optimization infeasible.

One of the most important of these parameters is the electrolytic medium. The type of solvent used during the electrochemical synthesis has a strong effect on both the physical and electrical properties of the resultant polymer. For a solvent to be utilized in electrochemical polymerization, it should possess high dielectric constant to ensure ionic conductivity of the electrolytic medium and it should have high resistance against decomposition upon applied potential. Since oxidative electrochemical polymerization involves the formation of radical cations, the nucleophilicity of the solvent should be kept low.

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 a good ionic conductivity [69,70]. These solvents are known to result in an optimal current response during electrochemical synthesis.

The electrolyte chosen during the course of polymerization has been shown to significantly affect the morphology of the resulting film [24]. A good electrolyte possesses qualities similar to that of a good solvent in that it must be non-nucleophilic and electrochemically inert. Studies showed that anion affects primarily the electrodeposition process and polymer structure, whereas the nature of cation affects essentially the charge-discharge process for the polymer [71].

Supporting electrolyte used in electrochemical polymerization serves for two purposes [72]:

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

Tetraalkylammonium or lithium salts of either perchlorate,  $\text{ClO}_4^-$ , hexafluorophosphate,  $\text{PF}_6^-$ , tetrafluoroborate,  $\text{BF}_4^-$ , or hexafluoroarsenate,  $\text{AsF}_6^-$ , are known to be excellent choices, whereas the use of anions such as persulfate and sulfate are known to lead to materials with low conductivities.

Selection of electrode is important for electrochemical polymerization. Since the polymerization proceeds via oxidation and reduction reactions, the electrode should not be oxidized or reduced. The polymers are generally deposited on inert substrate such as platinum and gold or optically transparent electrodes such as indium-tin-oxide (ITO) coated glass. As reference electrode saturated calomel electrode (SCE), Ag wire and Ag/AgCl electrodes can be used.

The most conductive polymers have been obtained on bulk platinum, presumably because thiophene adsorbs more efficiently on platinum and also presents a larger number of potentially active sites leading to a high density of nucleation sites and to more compact materials. The electrolysis potential should be also carefully controlled since high potentials may lead to the breakdown of electrolytes.

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. The probability of the occurrence of these reactions depends on the oxidation potential of monomer. While the oxidation potential of the monomer decreases, the occurrence of the competition reaction also decreases. Therefore, millimolar concentrations may be used to perform efficient polymerization [62].

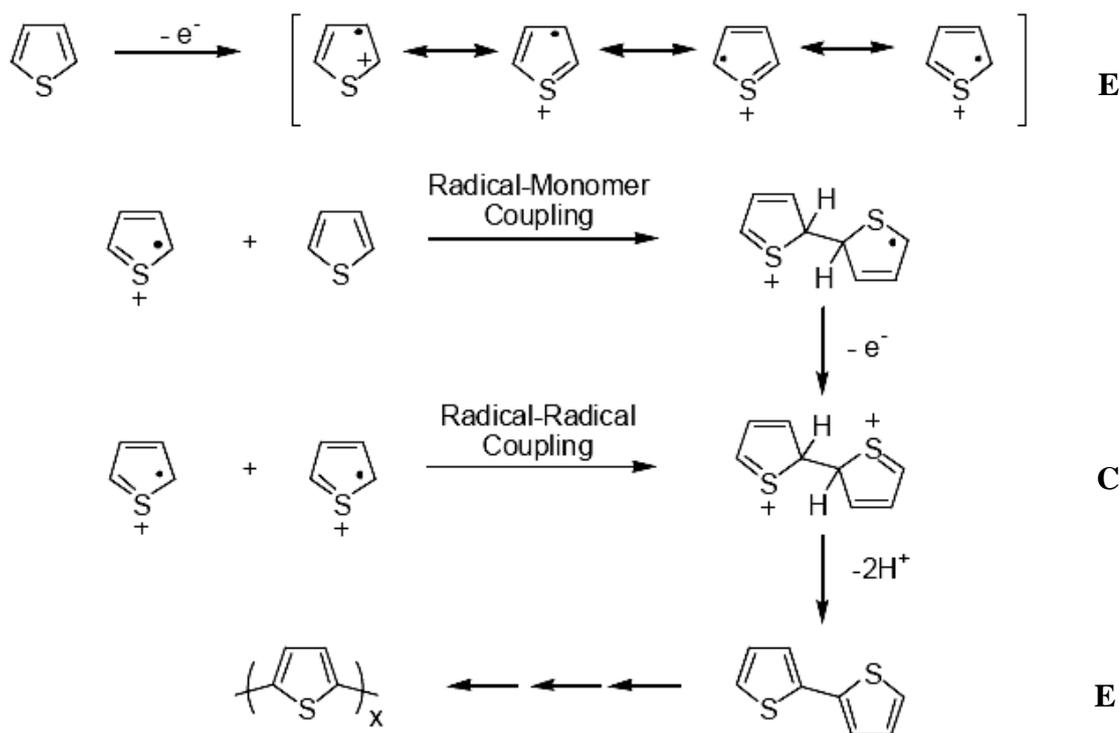
One should also pay attention to the temperature during electrochemical polymerization. With increasing temperature, it is possible that the conductivity and yield decreases. Temperature promotes termination step and therefore, oligomers with small conjugation length are formed instead of being deposited as an insoluble polymer at the electrode surface [73].

### **1.3.2.2. Mechanism of Electrochemical Polymerization**

Electropolymerization is achieved by the electro-oxidation of the heterocycle in an inert organic solvent containing supporting electrolyte. A schematic of the generally accepted mechanism for electropolymerization of five membered heterocycles is shown in Fig. 1.15.

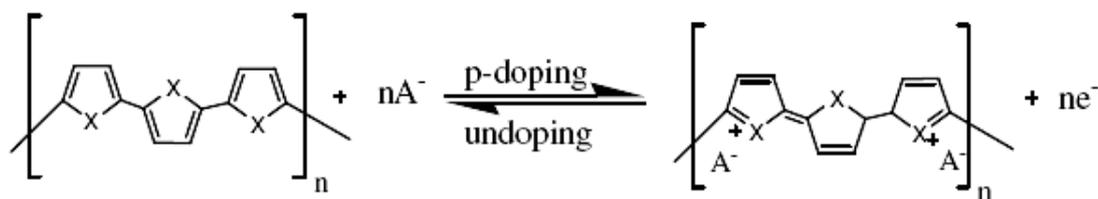
The first electrochemical step (E) consists of the oxidation of the monomer to its radical cation. Since the electron-transfer reaction is much faster than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step is controversy step because coupling may proceed via two different routes. The coupling proceeds either by the combination of two radical cations or addition of radical cation to heterocyclic monomer. In the radical-radical coupling, the second step, a chemical reaction (C), involves the spin-pairing of two radical cations to form a dihydro dimer dication, which subsequently undergoes the loss of two protons and rearomatization to form the dimer. Aromatization is the driving force of the chemical step (C). Coupling occurs primarily through the  $\alpha$ -carbon atoms of the heterocyclic ring since these are the positions of highest unpaired electron  $\pi$ -spin density and hence reactivity. Due to extended conjugation over two rings, the dimer has a lower oxidation potential than the monomer itself, and therefore it oxidizes easily to form the radical cation and undergoes further coupling reactions with other radical cations.

In a radical–monomer coupling mechanism, the radical cation reacts with the monomer to yield a neutral dimer by the loss of another electron and two protons. The oxidized dimer radical cation again attacks a monomer to form a trimer and the propagation proceeds to form polymer. Electropolymerization proceeds then through successive electrochemical and chemical steps according to a general E(CE) $_n$  scheme, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface [67].



**Figure 1.15** Proposed mechanism of the electropolymerization of thiophene.

Polymer oxidation occurs concurrently with electro-deposition; because conjugated oligomers are oxidized at less positive potentials than their corresponding monomer. In the oxidized state, conducting polymers are p-doped and have delocalized  $\pi$ -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 1.16).



**Figure 1.16** Undoping, p-doping in a conducting polymer

### 1.3.2.3. Monomer Structure and Substituent Effects in Electropolymerization

The goals in the synthesis of conducting polymers are to design new and novel structures, to increase the order of the polymer backbone and also the conductivity, processability, solubility in certain solvents [74]. Convenient and reproducible syntheses are required before materials can be developed for a particular application. In recent times an extensive worldwide research effort has been specifically directed towards synthetic aspects, since the structure and reactivity of the monomer will greatly affect the properties of the resulting polymer.

Although considerable success has been obtained using conducting polymers containing  $\pi$ -conjugated systems, many of these polymers have problems with processability and mechanical properties. Due to electron transfer and coupling, interchain interactions in  $\pi$ -conjugated polymers are relatively strong. These polymers are often insoluble in common organic solvents and infusible. It is usually difficult to characterize their structure, understand electronic interactions and process them. This greatly limits their practical applications [75].

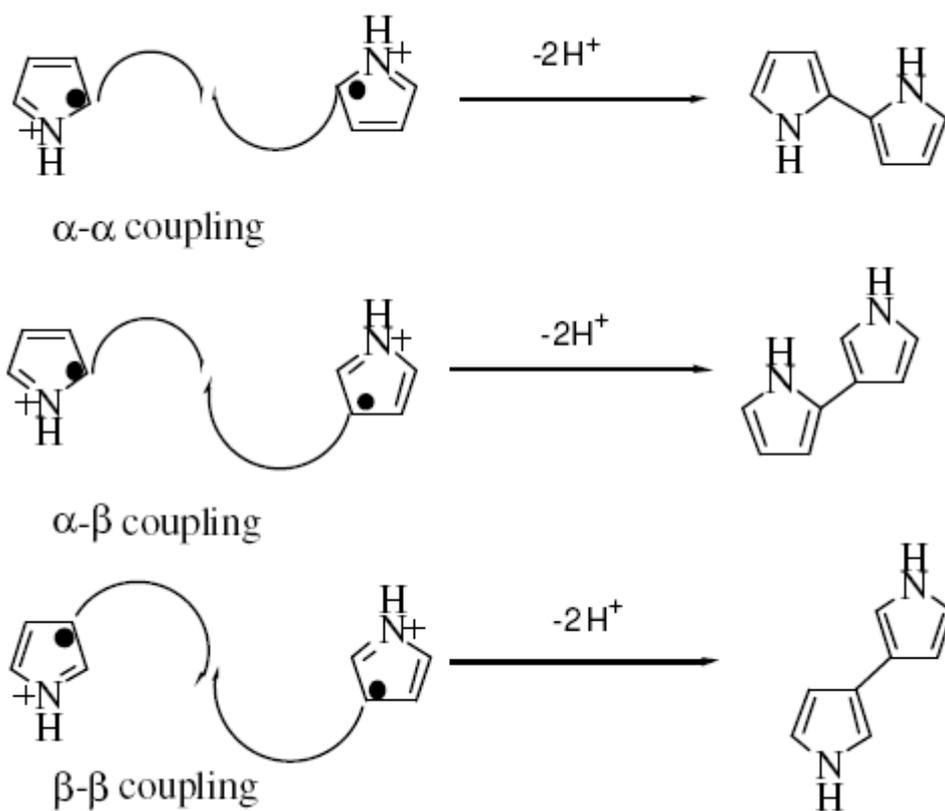
Electron-rich heterocycles such as Th and Py are the most common monomers for electropolymerization due to their availability and relative ease of polymerization. Since PTh has shown higher chemical and electrochemical stability in air and moisture in both their doped and undoped states than others such as polypyrrole, thiophene-based polymers have received significant attention.

Substitution is a very powerful tool for the design of thiophene-based polymers for different applications. The character and position of the side chain will influence properties like solubility, band gap, ionic conductivity, morphology and miscibility with other substances [76]. Electronic effects arising from electron-withdrawing and electron donating substituents drastically affect the electron density of the thiophene ring.

Thiophenes substituted with electron-withdrawing groups such as cyano, aldehydes and nitro groups have oxidation potentials that are higher than thiophene, and they do not electropolymerize. In the case of electron-donating groups, the oxidation potential decreases due to the stabilization of the radical cation formed upon oxidation.

Substituents not only affect the oxidation potential of the monomers and polymers, but also the band gap and optical absorption of these systems. Electron-donating groups lower the band gap by raising the valence band or HOMO level. This is illustrated by comparing the band gaps of polythiophene (2.0 eV) and poly(3,4-ethylenedioxythiophene) (PEDOT) (1.6 eV) [77]. The addition of relatively long, flexible, hydrocarbon chains to the thiophene ring has increased solubility and processibility of this conjugated polyheterocycles without significantly changing the  $\pi$ -electronic structure.

Basically, substituent groups on the 3- and/or 4-positions of the thiophene ring minimize the occurrence of mislinkages such as  $\alpha$ - $\beta$  coupling or  $\beta$ - $\beta$  coupling during polymer synthesis (Figure 1.17). The occurrence of a  $\alpha$ - $\alpha$  linkage in a given chain modifies its electronic distribution and could promote the formation of branching in energetically favorable sites. Furthermore, the presence of these linkage defects twists in adjacent chains, and thus modifies their electronic distribution promoting the propagation of more defects in the resulting materials. This is consistent with the considerable increase in the content of disorder as well as the decrease in conductivity as the polymerization proceeds. Fewer  $\alpha$ - $\beta$  linkage defects in the final structures lead to more effective conjugation, which is an essential feature to produce more conductive polymer [78].



**Figure 1.17** Coupling reactions of pyrrole during oxidative polymerization.

In general, disubstitution at the 3 and 4 positions, which eliminates the possibility of  $\beta$  coupling and reduces the likelihood of cross-linking, leads to severe steric interactions and reduces the extent of conjugation. 3,4-dialkyl substitution results in severe steric hindrance, decreasing conjugation. Alkoxy substituents were found to lower conductivity as a consequence of repulsive interaction between adjacent side chains.

Monomers containing 3,4-dialkoxy substituents are also poorly reactive to oxidative polymerization because of stabilization caused by conjugation with the thiophene [79]. These are overcome by fusing the ring onto the heterocycle, effectively pinning the substituents back from the main chain.

The electrochemical synthesis of conducting polymers from multi-ring aromatic monomers with electron-rich terminal heterocycles has attracted considerable attention as they have significantly lower oxidation potentials than the corresponding parent heterocycle due to the extended conjugation of the multi-ring system. The presence of electron-rich heterocycles (e.g., pyrrole, thiophene, 3,4-ethylenedioxythiophene) as terminal electropolymerizable moieties on multi-ring conjugated monomers leads to stabilization of the cation radical intermediates allowing to proceed at low potentials and with minimum side reactions. These include  $\beta$ -coupling, crosslinking, and overoxidation of the resultant polymer leading to polymer degradation and defect-containing materials [80,81].

The processability of a conducting polymer can be improved by copolymerization through increase of chain flexibility via incorporation of flexible centers in the main chain side chain substitution [82].

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

Conducting polymers have become very promising materials for numerous applications because they can be formed into thin, mechanically strong films, and it is desirable to confer the additional property of electrical conductivity on polymers that already benefit from being flexible and compact. These materials also stand out as an excellent class of materials due to their high conductivity, stability against environmental conditions and the ease of preparation. However, their poor mechanical properties and processability constitute major obstacle to their applications. 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. 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 [83].

Copolymerization, a process in which two or more monomers are incorporated as integral segments of a polymer, is used to produce copolymers with properties that are different from those of homopolymers. In general copolymers possess physical and mechanical properties intermediate between both homopolymers. The magnitude of the numerical values of these properties generally depends on the concentration of the monomer units incorporated into the copolymer. The primary advantage of copolymerization is that it leads to a homogeneous material, the properties of which can be regulated by adjusting the ratio of the concentration of monomer in the feed [84].

In comparison with the chemical copolymerization, one of the advantages for the electrochemical copolymerization is that the effect of the applied potential and the monomer concentration ratio on the copolymerization rate and on the copolymerization behavior is readily observable. This is much more favorable for determining the optimum copolymerization conditions. In addition, the copolymerization potential of two different monomers plays an important role in the properties of a copolymer [85]. Synthesis and characterization of conducting copolymers of pyrrole and thiophene with various other polymers were reported in the literature [86,87]. The strong electron donor properties of EDOT represent an interesting tool for the molecular engineering of the band gap of  $\pi$ -conjugated systems. One of the simplest ways to take advantage of these properties is to associate EDOT with electron withdrawing groups by synthesizing copolymers [88].

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 [89]. Structural and electrical properties can be improved by the preparation of composite materials containing a conducting polymer composed with a nonconducting polymer such as poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA) and natural rubber [90-92].

## **1.5. Characterization of Conducting Polymers**

Conventional techniques for polymer characterization can not be applied to conductive polymers, because the highly conjugated backbone causes insolubility of the polymer in common solvents. Therefore, the following are mostly used to characterize conductive polymers.; cyclic voltammetry (CV) for understanding redox processes in conducting polymers, optical characterization of conducting polymers for non-linear optical materials, nuclear magnetic resonance and FTIR for structure confirmation, chain orientation and molecular motion, gel permeation chromatography for molecular weight, Raman analysis for vibrational assignments, differential scanning calorimetry and thermogravimetric analysis for evidence of glass and melting transitions and decomposition temperatures, dependence of conductivity on temperature and electrical field and magnetic susceptibility to understand the conductivity mechanism; electroluminescence to screen for potential use light emitting diodes (LEDs) various types of X-ray analysis to understand the crystal structure [74]. Morphology of CPs film has been described by scanning electron microscopy.

## **1.6. Applications of Conducting polymers**

While the polymers discussed herein are typically referred to as “conducting polymers”, it is perhaps better to characterize them as “electroactive” because the majority of applications take advantage of properties of these materials resulting from electroactivity. Conductivity in these polymers is typically poor relative to metal conductivities (though if densities are compared, copper and polyacetylene exhibit comparable conductivities), so it is unlikely that they will be used as replacement for metal wires. However, changes in redox state are accompanied by changes in other physical properties in the polymers, and many applications have emerged to capitalize on these changes. Among the properties that vary with oxidation state are conductivity, solubility, reactivity, color and volume.

The recent developments towards the syntheses of new and processable as well as discovering the broad range of chemical flexibility opens up opportunities for new technological applications. The higher environmental stability and modification of properties to suit a given end use and processability achieved with the polymers derived from acetylene, pyrrole, thiophene, aniline and their derivatives, polyphenylene, poly(phenylene vinylenes) have emerged as materials to replace metals and semiconductors in electrical and electronics industry. Some of the present and potential commercial applications of these systems are storage batteries, supercapacitors, electrolytic capacitors, fuel cells [93], sensors; biosensors and chemical sensors, ion-specific membranes, electrochromic displays, electromagnetic shutters, corrosion protection, transparent conductors, gas separation membranes, EMI shielding, conductive textiles, anti-static films and fibers, conductor/insulator shields, photoconductive switching, conductive adhesives and inks, non-linear optics [94], electroluminescence, electronic devices [95-97].

In thin film technologies, conducting polymers can be used as conducting layers. A field with a wide technical importance is the antistatic protection and the electromagnetic interference shielding by conducting polymers. The possibility of a reversible switching of conducting polymers between two redox states rose speculations for rechargeable batteries. Conducting polymers can be regarded as membranes due to their porosity. They could be used for separation of a gas or liquids. The use of conducting polymers in sensor technologies consists as an electrode modification to improve selectivity, to impart selectivity, to suppress interference and to support as a matrix for sensor molecules [51].

For such applications as switchable windows and mirrors, active advertising displays, and dynamic camouflage, electrochromic devices based on conducting polymers have become a recent focus of research. This is due in part to the fact that all electroactive and conducting polymers are potentially electrochromic materials, are more processable than inorganic electrochromic materials, and offer the advantage of a high degree of color tailorability [98].

The use of conducting polymers as potentially electrochromic materials is the most pertinent to the work in this thesis.

## **1.7. Chromism**

Chromic behavior is another characteristic of CPs. Chromism is a reversible change in a substance's color resulting from a process caused by some form of stimulus. There are several types of chromism like thermochromism, photochromism, halochromism, solvatochromism, piezochromism and electrochromism. These different chromic behaviors originate from conformational modification and the energy change in  $\pi$ - $\pi^*$  transition band gap induced by the corresponding environmental changes such as temperature, solvent power, pressure, ion strength, and applied potential, respectively [99].

### **1.7.1. Electrochromism**

Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation–reduction reaction. An electrochromic material is one that changes color in a persistent but reversible manner by an electrochemical reaction. As an electrochromic material undergoes electron transfer, new optical absorption bands appear and the material exhibits coloration. Electron transfer in the opposite direction reverses the electrochemical process and the materials revert to the colorless state. The color change is commonly between a transparent (“bleached”) state and a colored state, or between two colored states. The electrochromic materials may exhibit several colors and termed as polyelectrochromic and the process is called to be multicolor electrochromism. [100].

Electrochromic materials can be useful in various applications such as optical displays, automotive applications (e.g. dimming rear-view mirrors) and smart windows for buildings.

Self-dimming rear-view mirrors are designed to avoid dazzle from the headlights of a following car. This technology uses an electrochromic film to produce a mirror with variable specular reflectance. Most new luxury cars have adapted self-dimming mirrors.

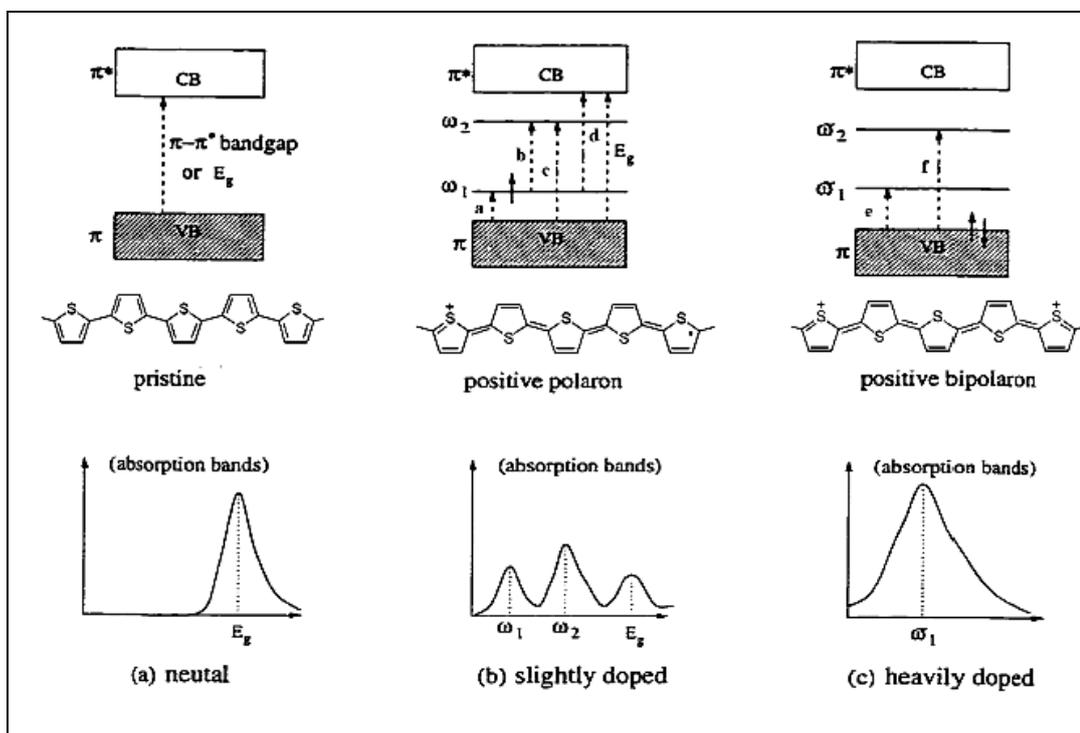
Smart windows are designed to automatically control the amount of visible or infrared light entering a room when they are used in conjunction with thermal and optical sensing devices [101]. When electrochromic materials can control infrared emissivity, these also can be used for the thermal emittance control (e.g. infrared camouflage and aerospace) and optoelectronic devices.

There is a vast number of chemical species possessing electrochromic properties. Viologens [102], transition metal oxides, most famously tungsten trioxide ( $\text{WO}_3$ ) [103-105], prussian blue [106], phthalocyanines [107,108], and conducting polymers are widely utilized electrochromic materials.

Conducting polymers have received more attention than inorganic materials owing to their advantages over inorganic compounds and they have attracted significant interest in the field of electrochromism, since they offer additional advantages, such as, low processing cost, enhanced mechanical properties, no dependence with angle of vision, good UV stability, high coloration efficiency, fast switching ability and fine-tuning of the band gap through the modification of polymer's chemical structure. By adjusting the electronic character of the  $\pi$  system along the neutral polymer backbone, the  $\pi$ - $\pi^*$  transition can be adjusted across the electromagnetic spectrum from the UV, through the visible and into the near-infrared [109].

Electrochromic changes are induced by redox processes which are accompanied by ion insertion/expulsion and result in a modification of the polymer's electronic properties giving rise to changes in the color of the material.

The color exhibited by the polymer is closely related to the band gap. Tuning of color states is possible by suitable choice of monomer. This represents a major advantage of using conducting polymers for electrochromic applications. Subtle modifications to the monomer can significantly alter spectral properties [110].



**Figure 1.18** a. Polaron and bipolarons in non-degenerate ground state polymers: band diagrams for neutral (left), positive polaron (center) and positive bipolaron (right); b. neutral (left), lightly doped (center) and heavily doped (right)

The redox switching of conjugated polymers is accompanied by changes in electronic transitions. Figure 1.18 shows the expected transitions in a conjugated polymer according to literature [111]. In the neutral state, the polymer exhibits single broad transition from the valence band to the conduction band ( $\pi$  to  $\pi^*$ ). The energy difference between these two levels is the band gap ( $E_g$ ), and it is measured as the onset of the  $\pi$  to  $\pi^*$  absorption in the neutral state of the polymer.

Upon oxidation, removal of an electron from the valence band, leads to the formation of polaron. This results in state with an unpaired electron whose energy state is higher than the valence band. Accordingly, there occurs the lowering of the corresponding antibonding level in the conduction band; leading to formation of new two intragap states. This should lead to possible four new transitions. However, since the oscillator strength of transitions a and b are much greater than transitions c or d, two low energy transitions are expected as the signature for a polaron. Upon oxidation, the absorbance of the main inter-band peak ( $\pi$  to  $\pi^*$ ) decreases along with a formation of a new peak at lower energy region of the spectrum. Further oxidation of the polymer will create more polarons by the removal of electrons from the valence band. The unpaired electron of the polaron will be removed to form a dication. Thus, bipolaron will be formed. Since the bipolaron levels are unoccupied, only transitions from valence band are possible. The signature of a bipolaron is one broad low energy transition. This is because of the stronger nature of the transition e with respect to transition f. Yet, basically conducting polymers change color by the creation and destruction of polarons and bipolarons.

Color changes involve the movement of counter ions in and out of the electrochromic matrix. The charged species enters the polymer matrix and migrates slowly through the film. The speed of the color change depends on the speed at which the dopant ions can migrate in and out of the polymer matrix. As the response time is dependent on the movement of charge compensating counter ions, open polymer morphology often results in a reduced response time [112]. The ideal electrochromic polymer should have a high contrast between its extreme states, having short switching time. Stability and maintenance of color after the current has been switched off are also among the expected features to be fulfilled.

The introduction of electron donating substituents into a conjugated chain is a widely utilized approach to decrease the polymers oxidation potential by raising the energy of the valence band electrons (HOMO of the conjugated chain). At the same time, there is a small perturbation on the energy of the conduction band (LUMO of the conjugated chain), which leads to a decrease in the polymer's electronic band gap [113].

Conjugated polymers with aromatic like structure are more promising as electrochromic materials when the p-doping process is involved, since n-doping is greatly affected by the nature of the cation in the charge balancing process; n-doped forms are also less stable than p-doped ones. Short electrochromic response time, long switching life and optical memory are the most important requisites for electrochromic materials in device technology. Electrochromic response time is the time the polymer takes in response to the potential pulse to go one color state to the other. Switching life is related to the ratio of the reduction to the oxidation charges involved in the electrochromic process. The optical memory is the persistence of the colored state even when the driving voltage is removed [114]. Tin doped indium oxide (ITO) is routinely used as an electrode in electrochromic applications due to its unique combination of properties including optical transparency, low electrical resistance and excellent surface adhesion.

### **1.7.2. Types of Electrochromic Materials**

A large variety of materials are known to display electrochromism. Four main types of electrochromic materials are reported in the literature: a) transition-metal oxides (e.g.  $\text{WO}_3$ ,  $\text{IrO}_2$  etc.), b) conductive polymers, c) organic and d) intercalated materials. They are also classified as cathodic and anodic electrochromic materials, depending on the coloration mechanism [115].

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. Crystalline  $\text{WO}_3$  is one of the most studied electrochromic materials not only as a result of its transparent/ intense blue electrochromism, but it also has some specific switching properties in the infrared region, of relevance to 'smart windows' technology. 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). Although complementary electrochromic windows based on cathodically coloring  $\text{WO}_3$  and anodically coloring  $\text{IrO}_2$ , have been fabricated, their development is still limited. Due to their high cost for fabrication and short term stability, extended works have been carried out on conductive polymers [116].

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 PAN are widely studied [117]. Conductive polymers are classified into three groups 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 poly(3,4-ethylenedioxythiophene) (PEDOT). A second class of materials consists of electrochromes with two distinctive colored states. These electrochromic materials lack a transmissive state but are useful for display-type applications where different colors are desired in different redox states. Polythiophene is a good example of this type, where the thin films of this polymer switch from red to blue upon oxidation. A third class includes the growing interest in the electrochromic field, where more than two color states are accessible depending on the redox state of the material.

This is the area where conjugated polymers have found the most interest due to their versatility for making blends, laminates, and copolymers [118].

One of the more prominent uses for electrochromic polymers is for window applications, where a device can be cycled between transparent and tinted states through the use of a polymer with transmissive and absorptive color states. Also, as the palette of available colors in electrochromic polymers grows, these materials should become more useful for display technology [119]. In addition to applications as smart windows, displays, and storage devices, electrochromic materials have attracted a great deal of interest for use in devices that operate in the infrared and microwave regions, as well in key components (i.e., variable optical attenuators) in telecommunications that operate in the NIR region (e.g., around 1310 and 1550 nm) [120].

### **1.7.3. Spectroelectrochemistry**

Spectroelectrochemistry plays a key role in probing the electronic structure of conducting polymers as well as in examining the optical changes that occur upon doping. It provides information about the material's band gap and intraband states created upon doping as well as gives some insight into a polymer color through the location of the absorption maxima and the ratio of peak intensities if the material shows fine structure on the main  $\pi-\pi^*$  transition peak.

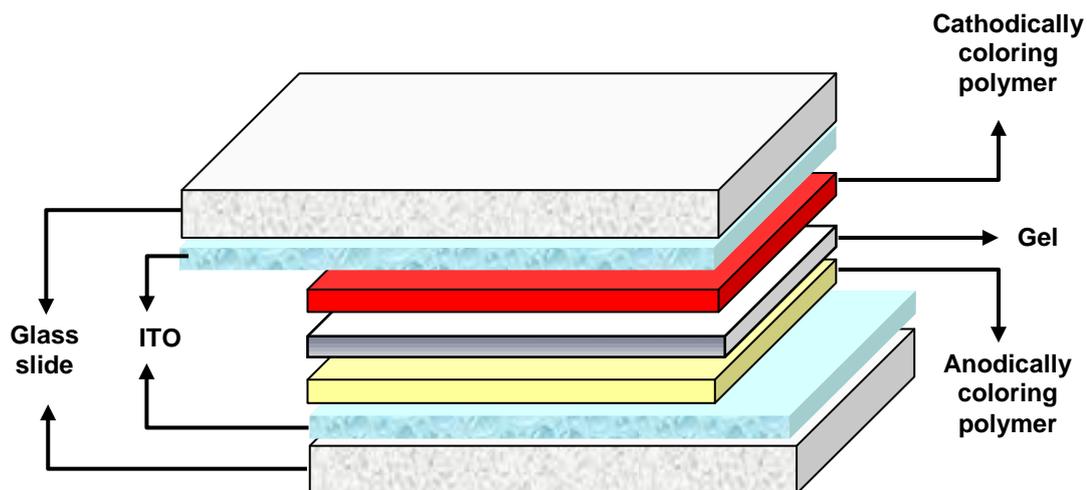
### **1.8. Electrochromic Devices**

In the recent years, a lot of attention has been paid in understanding the physical and chemical properties of various electrochromic materials and particularly on CPs, not only from basic research point of view but also from the commercial view [100]. It has brought various electrochromic materials and devices actually in the market also, such as, in automobile sector rear view mirrors and several others like sunroofs and visors are under prototype production.

Widespread applications of ECDs, particularly, for architectural applications depend on reducing costs, increasing device lifetime and overcoming the problem of ECD degradation. Commercial production of all plastic electrochromic devices, smart windows, for monitoring time–temperature application has been already achieved.

An electrochromic device is essentially a rechargeable battery in which the electrochromic electrodes are separated by a suitable solid or liquid electrolyte from a charge balancing counter electrode, and the color changes occur by charging and discharging the electrochemical cell with applied potential of a few volts [121]. The second electrode in some systems may also be electrochromic and in any case must undergo electron transfer in the reverse sense to that of the first electrode [122]. The arrangements of these layers depend on the operation mode. Electrochromic devices take part in various applications, such as display panels [123], camouflage materials [124], variable reflectance mirrors [125] and variable transmissive windows [74].

A dual-type ECD consists of two electrochromic materials (one revealing anodic coloration, the other revealing cathodic coloration) deposited on transparent ITO, placed in a position to face each other and a gel electrolyte in between. The ion-conducting electrolyte must not only provide physical separation between cathode and anode, a source of cations and anions to balance redox reactions, but must also be transparent in the given region of the spectrum. The ion conducting electrolyte (gel electrolyte) is usually an inorganic salt dissolved in a solvent such as propylene carbonate with a stiffener polymer poly(methylmethacrylate) [126]. In order to maintain a balanced number of redox sites for switching, the redox charges of the two complementary polymer films were matched by chronocoulometry. Before constructing the ECD, the anodically coloring polymer film was fully reduced and the cathodically coloring polymer film was fully oxidized. Upon application of voltage, the doped polymer will be neutralized, whereas the other will be reduced, thus will result in the color change. Schematic representation of devices is given in Figure 1.19.



**Figure 1.19** Schematic representation of ECDs

Change in the color of the device is achieved by the change in the electronic properties of the polymers due to applied potential across the device. Since this is a two-electrode electrochemical cell, during functioning of the device, one of the polymers should be oxidized while the other is reduced. A change in applied voltage results in the neutralization of the doped polymer with simultaneous oxidation of the complementary polymer, generating color change in the device.

Tin doped indium oxide (ITO) is routinely used as an electrode in electrochromic applications due to its unique combination of properties including optical transparency, low electrical resistance and excellent surface adhesion. Cathodically coloring polymer is the one that passes from an almost transparent state to a highly colored state upon reduction of the p-doped form. Poly(isothianaphthene) (PITN) was reported as the first example of a low band gap, cathodically coloring CP [127]. For a number of synthetic and electrochemical reasons, PITN has not found a high level of applicability in ECDs. Recently, poly(3,4-ethylenedioxythiophene) (PEDOT) has emerged as a low band gap ( $E_g = 1.6$  eV, 775 nm), cathodically coloring CP [128]. In addition to its low band gap, PEDOT has a low redox potential, is very stable to multiple redox switching, and has a high conductivity.

Ideally, an anodically coloring CP is chosen to have a high band gap ( $E_g$ )  $\geq 3.0$  eV ( $< 410$  nm) with  $\pi$  to  $\pi^*$  electronic transitions extending from the high-energy end of the visible spectrum into the ultraviolet region. In its reduced form, the polymer is transmissive to a major portion of the visible spectrum. Upon oxidation, charge carrier absorptions are induced in the visible region, resulting in an opaque and/or colored state. This anodically coloring behavior is observed for many of the common conjugated polymers, including poly(p-phenylene), polypyrrole, and poly(p-phenylene vinylene) [129].

The requirements for high performance electrochromic devices are:

- a) High electrochromic efficiency, expressed in  $\text{cm}^2\text{C}^{-1}$  and related to the injected charge in the material to change its color;
- b) Short electronic response time;
- c) Good stability;
- d) Optical memory, defined as the color stability under open circuit potential conditions;
- e) Optical contrast, also called write-erase efficiency;
- f) Color uniformity.

### **1.9. Characteristics of Electrochromic Device**

Several characterization methods have been developed in order to have a better understanding of the electrochromic processes in ECDs. As discussed in the previous section, the most commonly used technique to study the electrochromic processes in conjugated polymers is spectroelectrochemistry. However, spectroelectrochemistry does not allow one to precisely define contrast ratios or switching speeds. Thus, other characterization methods such as switching, stability, and open circuit memory experiments have been developed in addition to spectroelectrochemistry.

### **1.9.1. Electrochromic Contrast and Switching Speed**

One of the most important characteristics of evaluating ECDs is electrochromic contrast. Electrochromic switching studies are carried out to monitor absorbance changes with time during repeated potential stepping between reduced and oxidized states to obtain an insight into changes in the optical contrast. It is often reported as a percent transmittance change ( $\% \Delta T$ ) at a specified wavelength where the electrochromic material has the highest optical contrast. The response time required to switch between bleached and colored state is reported as the switching time. The switching speed of electrochromic materials is dependent on several factors such as the ionic conductivity of the electrolyte, accessibility of the ions to the electroactive sites (ion diffusion in thin films), magnitude of the applied potential, film thickness, and morphology of the thin film [118].

### **1.9.2. Open Circuit Memory and Stability**

The color persistence in the ECDs is a significant character since it is directly related to aspects involved in its utilization and energy consumption during application. This feature is known as the optical memory of an electrochromic device. Open circuit memory is defined as the time the material retains its absorption state after the electrical field is removed.

The stability of the polymer for long term switching between oxidized and neutral states is another important feature for practical applications. The stability of the devices towards multiple redox switching usually limits the utility of electrochromic materials in ECD applications. Electrochromic stability is associated with electrochemical stability since the degradation of the active redox couple results in the loss of electrochromic contrast and hence the performance of the ECDs. Different applied voltages and environmental conditions of the materials are responsible for the device failure. Therefore, ECDs with good environmental and redox stability are required for future applications [118].

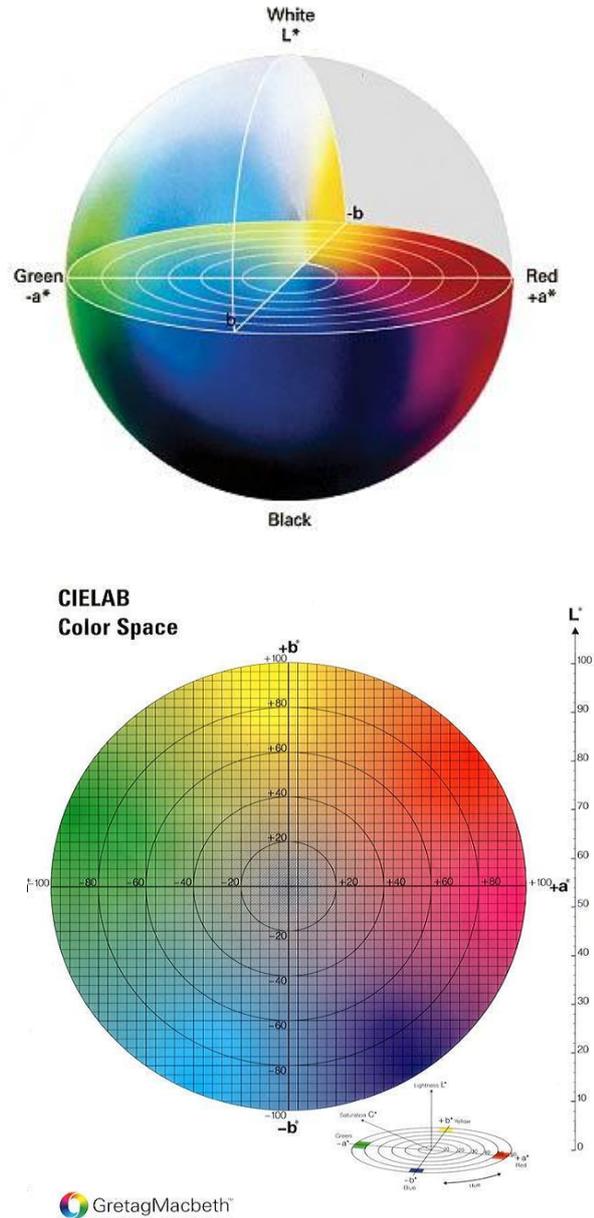
## 1.10. Colorimetry

The color is a subjective phenomenon causing the description of color, or the comparison of two colors to be difficult. Much effort has been given to transforming the description of color from a subjective matter to an objective, quantitative nature, which is the focus of colorimetry. The colors of the electrochromic materials were defined scientifically by achieving colorimetry measurements. Colorimetry is defined as the measurement of color. The measurement of color allows colored objects to be described, ordered and compared. Colorimetry provides a more precise way to define color than spectrophotometry.

In-situ colorimetric analysis is rapidly becoming a popular technique in the study of electrochromic polymers. This method allows for accurately reporting a quantitative measure of the color and graphically representing the track of doping-induced color changes of an electrochromic material or device. A commonly used scale that numerically defines colors has been established in 1931 by The Commission Internationale de l'Eclairage (CIE system). This method takes into consideration the response of a standard observer to various color stimuli, the nature of the light source, and the light reflected by the object under study.

The colorimetry analysis is based on a mathematical representation of a color on CIE Yxy or L a b color space. There are three attributes that are used to describe the color: hue, saturation or luminance and brightness. Y coordinate represents brightness of a color whereas xy coordinate defines hue and saturation. After the color of the material is measured with a colorimeter on Yxy coordinates, throughout a computer program Yxy values can be transformed to its L a b reciprocals. In L a b system, L, a and b stand for luminance, hue and saturation, respectively. Hue represents the wavelength of maximum contrast (dominant wavelength) and is commonly referred to as color.

Saturation takes into consideration the purity (intensity) of a certain color, whereas the third attribute, brightness, deals with the luminance of the material, which is the transmittance of light through a sample as seen by the human eye. Figure 1.20 shows the color space used to determine the color of the copolymers. On this chart, x-axis corresponds to  $a$ , which is hue, y-axis corresponds to  $b$  which is intensity and z-axis corresponds to  $L$ , luminance.



**Figure 1.20** CIELAB color space

### 1.11. Aims of the Work

This dissertation focuses on the synthesis of new electrochromic polymers as high contrast 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 placed on the synthesis and fundamental structural and electrochemical properties of each polymer. In addition, polymers were incorporated into an electrochromic absorptive / transmissive type devices. Aims of this work can be listed as ;

- ✓ To synthesize thiophene functionalized monomer namely; 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine (SNS-NH<sub>2</sub>)
- ✓ To perform the chemical polymerization of SNS-NH<sub>2</sub>
- ✓ To characterize monomer and chemically synthesized polymer.
- ✓ Electrochemically polymerize and copolymerize it with a well known comonomer (EDOT) in thin film forms.
- ✓ To investigate electrochromic and spectroelectrochemical properties of homopolymer and copolymer
- ✓ To construct electrochromic devices with PEDOT and finally evaluate the electrochromic performance of these devices.

## CHAPTER II

### EXPERIMENTAL

#### 2.1. Materials

$\text{AlCl}_3$  (Aldrich), succinyl chloride (Aldrich), dichloromethane (DCM) (Sigma–Aldrich), toluene (Sigma), propionic acid (Aldrich), benzene-1,4-diamine (Aldrich), nitromethane (Aldrich), methanol (Merck), iron (III) chloride (Aldrich), acetonitrile (AN) (Merck),  $\text{LiClO}_4$  (Aldrich),  $\text{NaClO}_4$  (Aldrich), propylene carbonate (PC) (Aldrich) and poly(methylmethacrylate) (PMMA) (Aldrich) were used as received. Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich) and EDOT (Aldrich) were used without further purification.

#### 2.2. Equipment

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

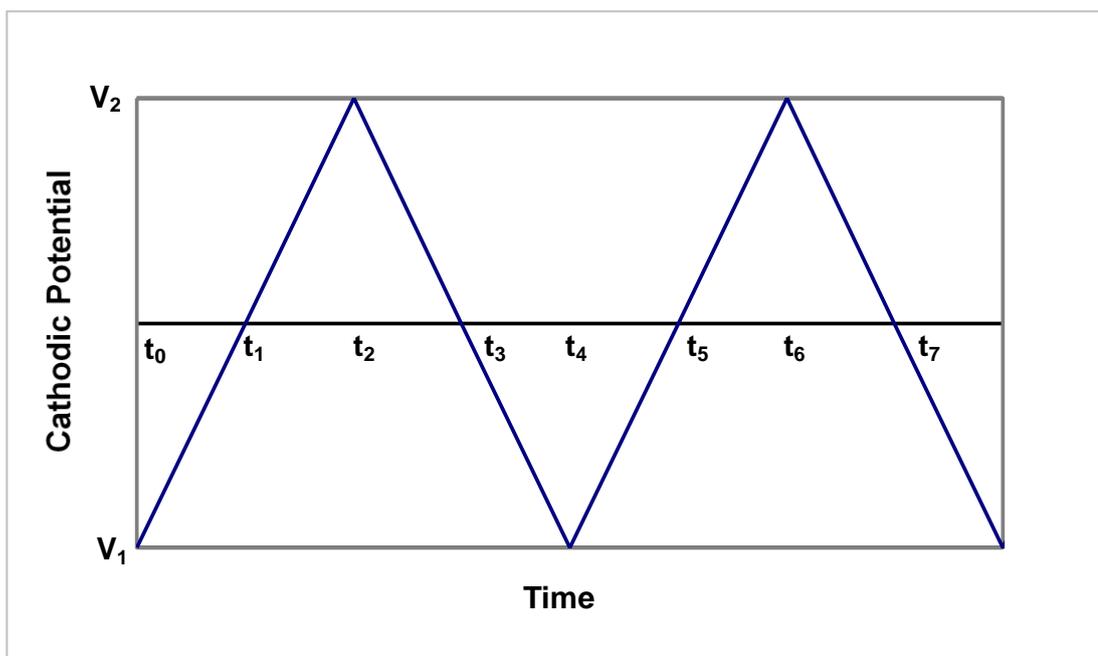
$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the monomers and the catalytically produced polymer of SNS-NH<sub>2</sub> were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) with  $\text{CDCl}_3$  as the solvent and chemical shifts ( $\delta$ ) were given in ppm relative to tetramethylsilane as the internal standard.

### 2.2.2. Fourier Transform Infrared (FTIR) Spectrometer

FTIR is a useful method for the characterization of monomers and conducting polymers because it does not require polymers to be soluble. FTIR spectra of the samples were recorded on a Varian 5000 FT-IR spectrometer for the detection of functional groups. Samples were prepared as KBr pellets.

### 2.2.3. Cyclic Voltammetry (CV) System

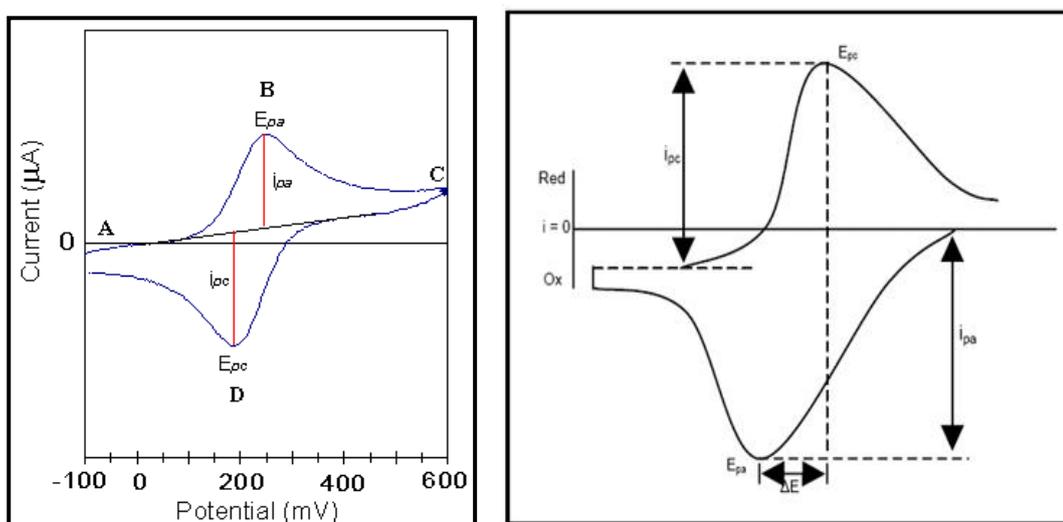
Among the electrochemical methods that can be applied to the study of conducting polymer films deposited on a conducting surface, cyclic voltammetry (CV) is the most widely used technique to assay the electroactivity of the polymers and to determine the oxidation–reduction peak potentials of the monomer and the polymers. Cyclic voltammetry measurements were carried out by cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current at the working electrode.



**Figure 2.1** Triangular wave function

In cyclic voltammetry (CV), the current response is monitored as a function of the applied potential while the potential is linearly increases from an initial potential to a peak potential and back to initial potential again. During these measurements, potential-time response and current (I) versus potential (V) curves are recorded (Fig. 2.1).

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in Figure 2.2. A is the low potential point where no redox reactions occur. The polymerization of electron rich monomers starts at this point and followed by scanning in the anodic direction. The electrode has strong oxidizing character to oxidize the monomer to its radical cation at potential B. From potential B to C, the anodic current increases swiftly until the concentration of the monomer at the electrode surface approaches zero, causing the current peak C, and then decay as the solution surrounding the electrode is depleted of monomer. After monomer oxidation, chemical coupling that affords oligomers in the vicinity of the electrode occurs immediately. Once these oligomers reach a certain length, they precipitate onto the electrode surface. The electroactivity of the polymer deposited onto the working electrode (WE) can be monitored by the appearance of a peak corresponding to the reduction of the oxidized polymer while scanning in the cathodic direction, D. The increase of the redox wave current of the polymer indicates the increase of polymer deposition on the working electrode.



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

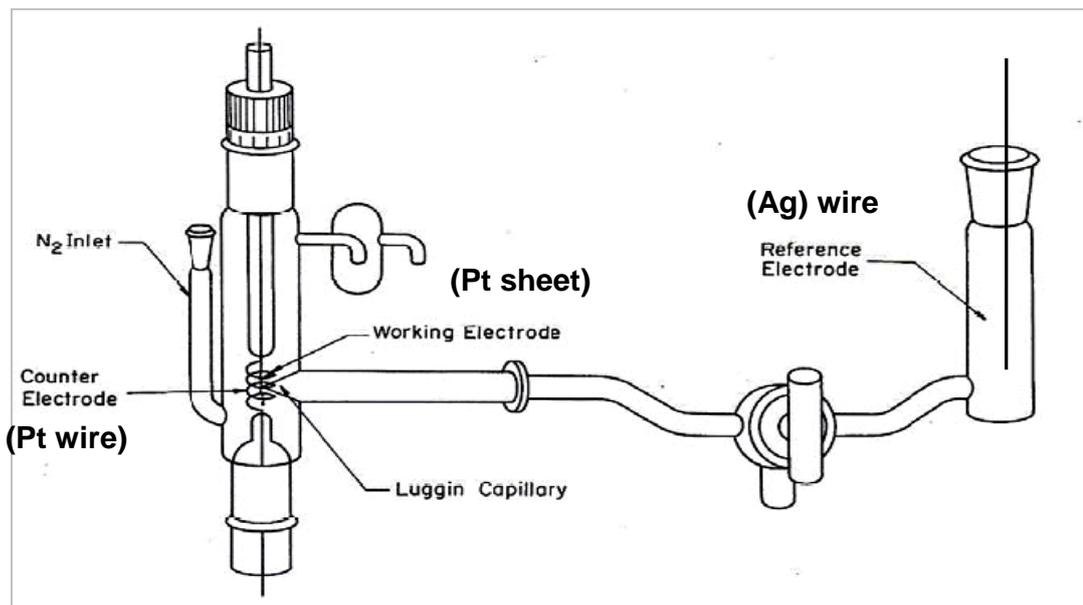
The Randles-Sevcik equation states that the current at the peak potential is given by:

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

where  $n$  is the number of moles of electrons transferred in the reaction,  $A$  is the electrode surface area (in  $\text{cm}^2$ ),  $D$  is the diffusion constant (in  $\text{cm}^2\text{s}^{-1}$ ),  $C$  is the bulk concentration of electroactive species (in  $\text{mol}\cdot\text{cm}^{-3}$ ) and  $V$  is the scan rate (in  $\text{Vs}^{-1}$ ). Therefore, 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 containing indium tin oxide (ITO) coated glass plate as the working electrode, platinum wire counter and Ag wire pseudo reference electrodes. The desired potential is applied between a working electrode (WE) and a reference electrode (RE). WE is the electrode at which the electrolysis of interest takes place.

An auxiliary (counter) electrode (CE) provides the current required to sustain the redox process developing at the working electrode. This arrangement prevents large currents from passing through the reference electrode, which could change its potential. The measurements were carried out in  $\text{NaClO}_4$  (0.1 M) and  $\text{LiClO}_4$  (0.1 M)/acetonitrile (ACN) solvent–electrolyte couple at room temperature under nitrogen atmosphere. Bank Wenking POS 2 and Solartron 1285 potentiostat/galvanostat were utilized for electrochemical studies.



**Figure 2.3** Cyclic voltammetry cell

#### 2.2.4. Electrolysis Cell

In the electrochemical synthesis of conducting polymers, constant potential (potentiostatic) electrolysis was used. Electrolysis were performed in a single compartment cell equipped with two Pt foil electrodes, which are working and counter electrodes and a silver (Ag) wire as the reference electrode.

#### 2.2.5. Potentiostat

Potentiostat controls the voltage difference between a working electrode (WE) and a reference electrode (RE) by passing current into the cell through the counter electrode (CE) minimizing the effect of IR drop by positioning reference electrode close to the working electrode. To compensate the changes in potential of working electrode, potentiostat continuously checks the potential of working electrode measured with respect to reference electrode, and changes the potential difference in between to maintain the desired potential value that was set.

During the electrolysis, Wenking Pos 73 potentiostat was utilized to supply the polymerization potential. For the electrochromic properties of the polymers, Solatron 1285 and Volta Lab® PST050 potentiostats were used.

#### **2.2.6. Scanning Electron Microscopy (SEM)**

SEM is a surface analytical technique which is employed to study the morphology of conducting polymer film surfaces and provides valuable information on the structure of the monomer, the nature of dopant and the thickness of the film. SEM of polymer films was performed using a JEOL model JSM-6400 scanning electron microscope at 20 kV with varying levels of magnification.

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

$M_n$  and  $M_w$  of the polymer obtained by chemical polymerization were determined with PL-220 gel permeation chromatography.

#### **2.2.8. Four-Probe Conductivity Measurements**

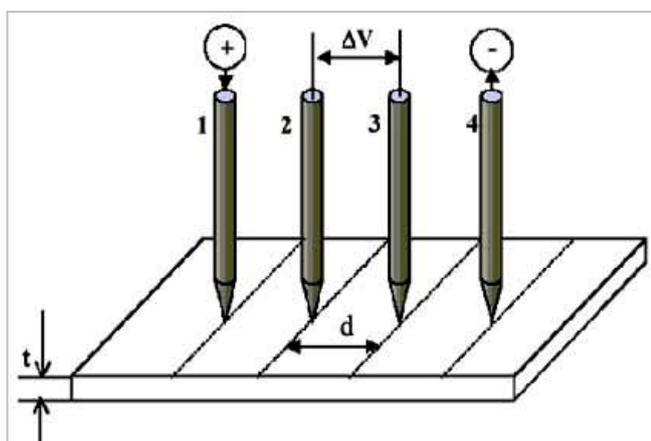
The Four Probe Method is one of the standard and most widely used methods for the measurement of conductivity. This method has several advantages for measuring electrical properties of conducting polymers. First, four probe techniques eliminate errors caused by contact resistance, since the two contacts measuring the voltage drop are different from the contacts applying the current across the sample. Second, this technique allows for conductivity measurements over a broad range of applied currents, usually varying between 1  $\mu$ A and 1mA for conducting polymers. Figure 2.4 demonstrates a simple four-probe measurement setup. The four osmium probes are aligned in a collinear geometry. A row of pointed electrodes touches the surface of a polymer film taped on an insulating substrate. A known current  $I$  is injected at electrode 1 and collected at electrode 4, while the potential difference,  $\Delta V$  between contacts 2 and 3 is measured.

The four probe method allows for the contact points to be easily repositioned in various area of the film, thus 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.



**Figure 2.4** Four-probe conductivity measurement

### 2.2.9. Spectroelectrochemistry Experiments

Spectroelectrochemical and kinetic studies of the polymers and the characterization of the devices were performed on Solatron 1285 potentiostat/galvanostat attenuated with Agilent HP8453A UV-Vis spectrophotometer in addition to VoltaLab® PST050 potentiostat coupled with Varian Cary 5000 UV-Vis-NIR spectrophotometer in a cell furnished with ITO coated glass working, Pt wire counter electrodes and a Ag wire reference electrode at room temperature.

## 2.2.10. Colorimetry Measurements

Colorimetry measurements were done via Conica Minolta CS-100 spectrophotometer. During measurement, samples were placed in a light booth system where it was illuminated from behind by a D65 light source.

## 2.3. Procedure

### 2.3.1. Synthesis of monomer

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

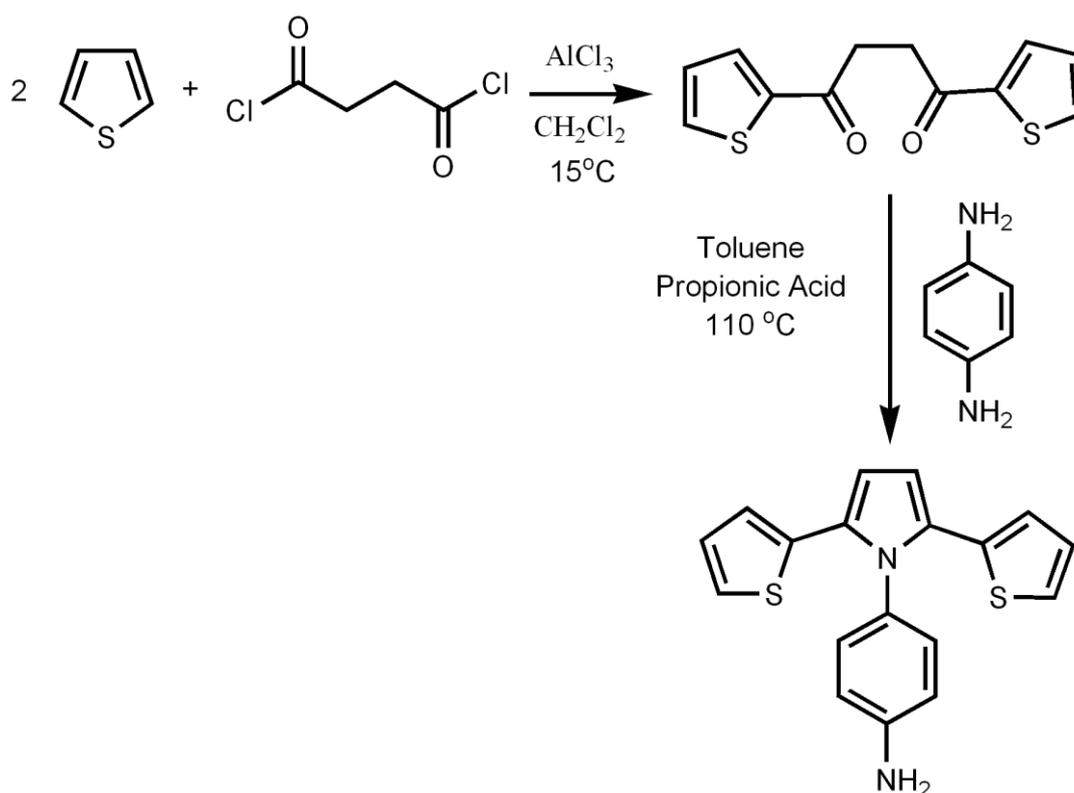
Within the different methods leading to 1,4-di(2-thienyl)-1,4-butanedione [13–21], the double Friedel–Crafts reaction, first suggested by Merz and Ellinger [22] was chosen. Utilizing the thiophene and succinyl chloride as the reactants, aluminium chloride was used as the Lewis acid catalyst, since it is the most direct one-step procedure with good yields. Yet, we noticed that the reaction time can be considerably reduced, the reaction mixture being mixed for 4 h (instead of 24 h stirring at ambient temperature) without loss of yield (78%).

A solution of thiophene (0.12 mol, 9.61 ml) and succinyl chloride (0.05 mol, 5.51 ml) in  $\text{CH}_2\text{Cl}_2$  (30 ml) was added dropwise into a suspension of  $\text{AlCl}_3$  (16 g, 0.12 mol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) at  $15^\circ\text{C}$ . The red mixture was stirred at  $15^\circ\text{C}$  for 4 h. This was then poured into a concentrated HCl (5 ml) and ice mixture.

After stirring, a dark green organic phase separated out. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 30 mL). The combined organic layers were washed with saturated  $\text{NaHCO}_3$  and brine solutions and then dried over  $\text{MgSO}_4$ . After removal of the solvent under reduced pressure, the blue-green solid was washed with ethanol and then dried. The synthetic route of 1,4-di(2-thienyl)-1,4-butanedione is shown in Scheme 2.1.

### 2.3.1.2. Synthesis of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine (II)

The monomer (SNS-NH<sub>2</sub>) was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and benzene-1,4-diamine in the presence of catalytical amount of propionic acid. A round-bottomed flask equipped with an argon inlet and magnetic stirrer was charged with 1,4-di(2-thienyl)-1,4-butanedione (0.35 M), benzene-1,4-diamine (0.45 M), propionic acid (0.36 M) and toluene. The resultant mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by flash column chromatography (SiO<sub>2</sub> column, elution with dichloromethane), afforded the desired compound as pale yellow powder. The synthetic route of the monomer is shown in Scheme 2.1.



**Scheme 2.1** Synthetic route of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine (SNS-NH<sub>2</sub>)

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

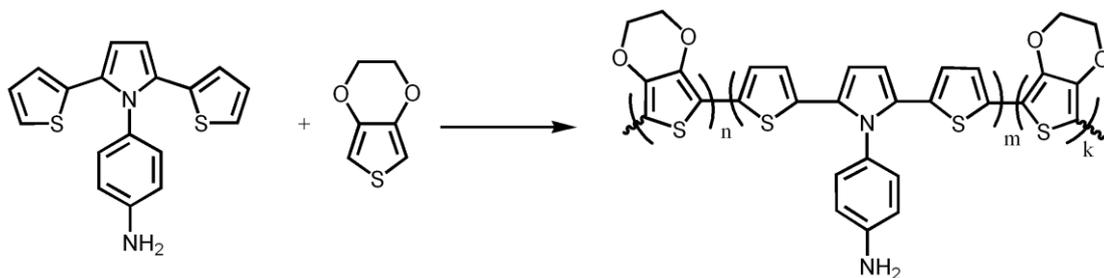
### **2.4.1. Electrochemical Polymerization**

#### **2.4.1.1. Synthesis of Homopolymer of SNS-NH<sub>2</sub>**

Electrochemical polymerization of SNS-NH<sub>2</sub> was performed in the presence of 50 mg SNS-NH<sub>2</sub>, 0.1 M NaClO<sub>4</sub> / LiClO<sub>4</sub> in ACN in a single-compartment cell equipped with Pt working and counter electrodes and a Ag wire reference electrode. Potentiodynamic electrolysis was run by sweeping the potential between -0.5 V and +1.2 V with 500 mV.s<sup>-1</sup> scan rate. The free standing film that formed was washed with ACN to remove unreacted monomer and excess NaClO<sub>4</sub>/LiClO<sub>4</sub> after electrolysis.

#### **2.4.1.2. Synthesis of Copolymer of SNS-NH<sub>2</sub> with 3,4-Ethylenedioxythiophene (EDOT)**

For the synthesis of conducting copolymer P(SNS-NH<sub>2</sub>-co-EDOT), EDOT was used as the comonomer. 2.5x10<sup>-4</sup> M of SNS-NH<sub>2</sub> were dissolved in acetonitrile, and 2 μL of EDOT were introduced into a single compartment electrolysis cell. NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M) were used as the supporting electrolyte. The working and counter electrodes were Pt wires and the reference electrode was Ag wire electrode. The potentiodynamic polymerization was carried out by sweeping the potential between -0.5 V and +1.3 V with 500 mV/sec scan rate for 1 minute at room temperature under inert atmosphere. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomers. Scheme 2.2 shows copolymerization reaction.

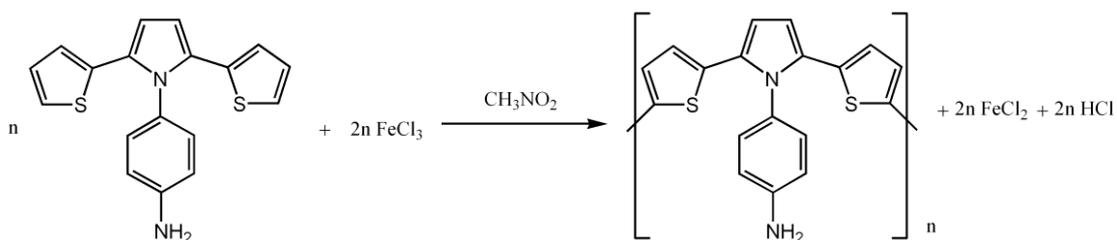


**Scheme 2.2** Copolymerization reaction of SNS-NH<sub>2</sub> with EDOT

#### 2.4.2. Chemical Polymerization of SNS-NH<sub>2</sub> with Ferric Chloride

Chemical polymerization of SNS-NH<sub>2</sub> was fulfilled using ferric chloride as the oxidizing agent. SNS-NH<sub>2</sub> ( $1 \times 10^{-3}$  M) was dissolved in nitromethane. A solution of iron(III) chloride ( $4 \times 10^{-3}$  M) dissolved in nitromethane was dropwise added to the monomer solution.

The reaction was carried out for 15 min. The dark colored polymer was first washed with methanol to stop polymerization, then extracted with sodium hydroxide and water for several times for compensation of FeCl<sub>3</sub> and dried under vacuum for <sup>1</sup>H NMR analysis.



**Scheme 2.3** Oxidative chemical polymerization of SNS-NH<sub>2</sub>

## 2.5. Gel Permeation Chromatography (GPC)

GPC is a widely used method for determining the molecular weight of a polymer. Most GPC results are reported as values relative to nearly monodisperse polystyrene standards. This technique 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, chemically synthesized P(SNS-NH<sub>2</sub>) was dissolved in tetrahydrofuran and GPC studies were conducted.

## 2.6. Potentiodynamic Studies of Conducting Polymers

CV was employed in order to assay the electroactivity of the polymers and to accomplish the oxidation-reduction peak potentials of the polymer. The measurements were achieved at room temperature under nitrogen atmosphere by using NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M) / ACN solvent-electrolyte couple.

A background voltammogram was run to ensure that no impurity was present before the addition of substrate. Experiments were carried out sweeping the potential between -0.5 V and +1.2 V with 500 mV/sec scan rate. Solution contained 50 mg SNS-NH<sub>2</sub>. For the investigation of oxidation and reduction potentials of P(SNS-NH<sub>2</sub>-co-EDOT) copolymer, same conditions were employed and the solutions contained 2 μL EDOT in addition to 50 mg SNS-NH<sub>2</sub>. The potential was swept between -0.5 V and +1.3 V with 500 mV/sec scan rate.

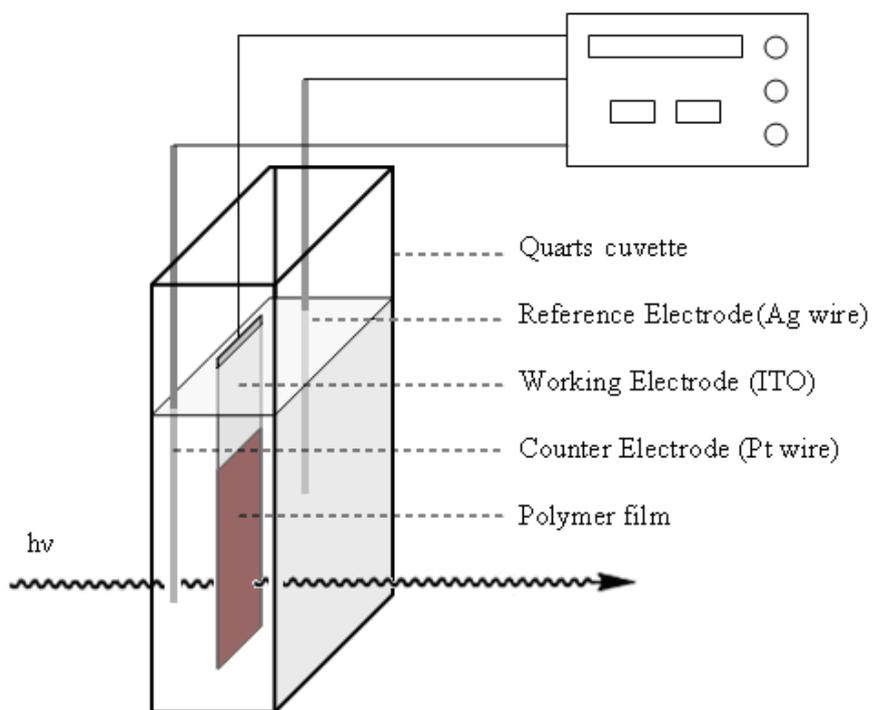
## 2.7. Electrochromic Properties of Conducting Polymers

### 2.7.1. Spectroelectrochemical Studies

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

Compared to common electrochemical methods, it can provide information on both electrochemical response and accompanying optical characteristics of all states of the electrochemical reaction. It is essential to gather information in-situ, during electrochemical process. Homopolymer film was potentiodynamically deposited on indium tin oxide (ITO) coated glass slides, sweeping the potential between -0.5 V and 1.2 V in the presence of 50 mg SNS-NH<sub>2</sub> and ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M) solvent-electrolyte couple. For the investigation of copolymer, the potentiodynamic polymerization was carried out by sweeping the potential between -0.5 V and +1.3 V in the presence of 50 mg SNS-NH<sub>2</sub> and 2  $\mu$ L EDOT in same solvent-electrolyte couple system. Then 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 that is equipped with a reference electrode (Ag wire) and a Pt wire counter electrode (Figure 2.4). Different potentials from fully reduced states of polymers to fully oxidized states were applied to the coated ITO glass slides in a monomer and also comonomer free solvent electrolyte couple, while spectroelectrochemical series were taken at the same time. The types and concentrations of electrolytes were same as those in electrolysis solutions. The results were then recorded as a graph of the extent of absorption as a function of wavelength.



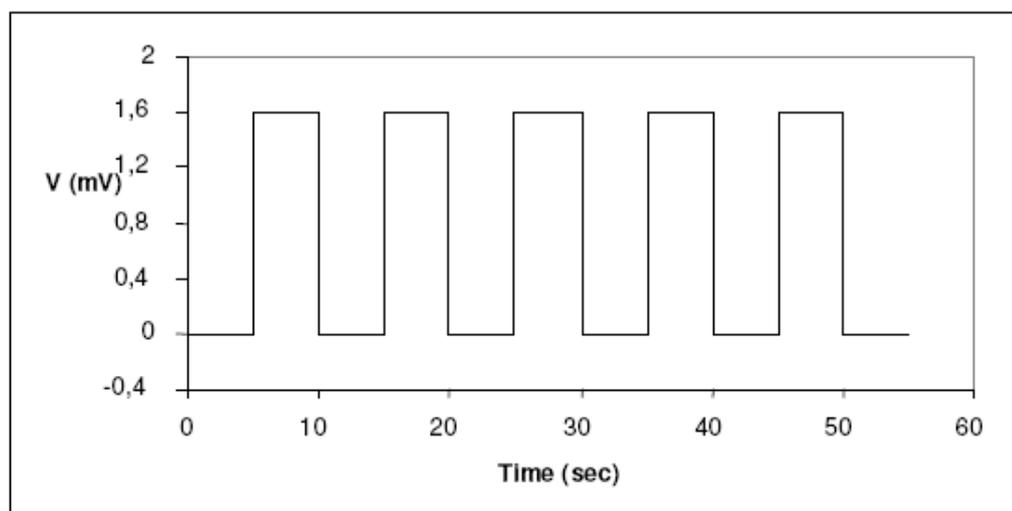
**Figure 2.5** In-situ optoelectrochemical analysis

### 2.7.2. 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 into changes in the optical contrast (Figure 2.6).

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.

In order to study switching properties of polymers, homopolymer and copolymer were deposited on ITO-coated glass slides as in the form of thin films. After coating the polymers on ITO electrode, a potential square wave was applied in the monomer free ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M) solution while recording the percent transmittance between its neutral and doped states at a fixed maximum absorption wavelength. Switching properties of polymer films were investigated by application of potential square wave technique with a residence time of 5 seconds between -0.5 V and 1.2 V for the homopolymer, between -0.5 V and 1.3 V for the copolymer.



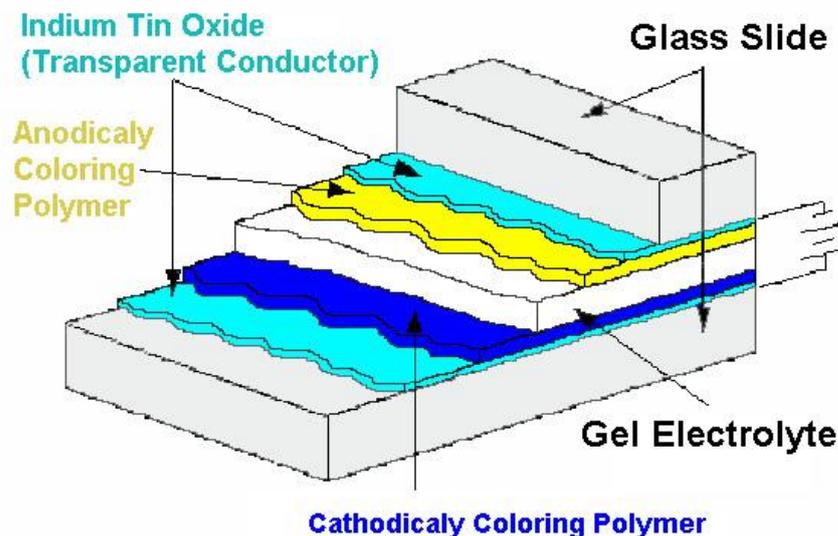
**Figure 2.6** Square wave voltammetry

### 2.7.3. 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.

## 2.8. Electrochromic Device (ECD) Construction

Electrochromic devices (ECDs) were constructed by sandwiching the gel electrolyte between anodically and cathodically coloring polymers, which were electrochemically deposited onto ITO coated glass electrodes, as shown in Figure 2.7. Polymer films used to assemble a device will be obtained by constant potential oxidative polymerization. Duration of polymerization was determined according to chronocoulometry studies. Before assembling the devices, it was important to balance the charge capacities of the electrochromic layers. Otherwise, it would result in incomplete electrochromic reaction and residual charges will remain during the coloring/bleaching processes, which would lead to residual coloration of the ECD in the bleached state. To minimize the effect of charge imbalances in ECD, the redox charges of the two complementary polymer films were matched by chronocoulometry and we provided a balanced number of redox sides for switching.



**Figure 2.7** Schematic illustration of dual type absorptive/transmissive type P(SNS-NH<sub>2</sub>)/PEDOT ECD configuration

### **2.8.1. P(SNS-NH<sub>2</sub>)/PEDOT Electrochromic Device**

Electrochromic device of the homopolymer was constructed by two complementary polymers, P(SNS-NH<sub>2</sub>) as the anodically and PEDOT as the cathodically coloring materials as deposited onto transparent electrodes.

Cathodically coloring polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was electrochemically deposited onto the ITO-coated glass from a 0.01 M solution of EDOT in NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M)/ACN solvent-electrolyte couple at +1.4 V versus Ag wire. The anodically coloring homopolymer, P(SNS-NH<sub>2</sub>) was potentiodynamically deposited onto the ITO-coated glass sweeping between -0.5 V and 1.2 V in the presence of 50 mg SNS-NH<sub>2</sub> in ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M) solvent-electrolyte couple. Prior to assembly, cathodically coloring films were fully oxidized and anodically coloring polymers were fully neutralized, to provide the ion exchange within the device. The films were then coated with gel electrolyte by the casting solution until the entire polymer surface is uniformly covered. The gel electrolyte forms a seal around the edges, the devices become self-encapsulated.

### **2.8.2. P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT Electrochromic Device**

For the investigation of copolymer, P(SNS-NH<sub>2</sub>-co-EDOT) was utilized as the anodically, and PEDOT as the cathodically coloring materials to construct electrochromic devices. The anodically coloring polymer P(SNS-NH<sub>2</sub>-co-EDOT) was potentiodynamically deposited onto the ITO-coated glass sweeping between -0.5 V and +1.3V 50 mg SNS-NH<sub>2</sub> and 20 $\mu$ L EDOT in NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M)/ACN solvent-electrolyte couple. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomers.

Cathodically coloring polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was electrochemically deposited onto the ITO-coated glass from a 0.01 M solution of EDOT in NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M)/ACN solvent-electrolyte couple at +1.3 V versus Ag wire.

The film was fully reduced by polarizing to -1.3 V vs Ag wire in the monomer free solution. The gel electrolyte was spread on the polymer-coated sides of the electrodes (one doped, the other neutral) and the electrodes were sandwiched under atmospheric conditions.

### **2.8.3. Preparation of Gel Electrolyte**

The fully transparent and highly conducting gel electrolyte was prepared using NaClO<sub>4</sub>:LiClO<sub>4</sub>:AN:PMMA:PC in the ratio of 1.5:1.5:70:7:20 by weight. PMMA was added into the solution after NaClO<sub>4</sub>/LiClO<sub>4</sub> was dissolved in ACN. Vigorous stirring and heating at 70°C was applied to dissolve PMMA. Propylene carbonate (PC), as the plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced.

## **2.9. Characterization of Electrochromic Devices**

### **2.9.1. Spectroelectrochemistry Studies of Electrochromic Devices**

Varian Cary 5000 UV-Vis-NIR and Agilent 8453 UV-Vis spectrophotometers were used to characterize the optical properties of electrochromic devices (ECDs). A device without the active polymer layer was used as the reference during spectroscopic studies. Applied potentials were delivered via a potentiostat where the counter and the reference electrodes were short cut and working electrode was connected to anodically coloring polymer layer.

Optoelectrochemical analyses of the devices were obtained by sequentially stepping the applied potential of the polymer. Spectroelectrochemical UV-Vis transmittance of electrochromic device of P(SNS-NH<sub>2</sub>)/PEDOT measured under miscellaneous applied potentials between -1.2 V and +1.2 V while measuring the absorbance as a function of wavelength. Spectroelectrochemical study of P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device was carried out varying the voltage between -1.5 V and +1.5 V and absorbance was measured as a function of wavelength.

### **2.9.2. Switching Properties of Electrochromic Devices**

Potential square wave technique, similar to described procedure in section 2.7.2 was applied to determine switching properties of ECDs, where the applied potentials and wavelength of inspection were determined according to spectroelectrochemistry studies. The potential was stepped between -1.2 V and +1.2 V with a residence time of 5 s for P(SNS-NH<sub>2</sub>)/PEDOT. The P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT was switched between -1.5 V and +1.5 V with a residence time of 5 s to probe switching time and optical contrast of the device.

### **2.9.3. Stability of Electrochromic Devices**

Construction of ECDs with long life time is targeted in electrochromic applications. The stability of the devices for long term switching between oxidized and neutral states was evaluated by CV studies. P(SNS-NH<sub>2</sub>)/PEDOT device repeatedly switched up to 500 cycles with CV sweeping voltage of -0.5 V and +1.3 V range with 500 mV/s scan rate under atmospheric conditions. P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device were repeatedly switched up to 250 cycles with a voltage range of -0.5 V and +1.5 V.

#### **2.9.4. Open Circuit Memory**

For the application of electrochromic device, the color persistence is an important character since it is directly related to its utilization and energy consumption during use. Optical memory is the time during which the material retains its color under open circuit conditions. This property was studied by polarizing the device between two states and measuring its spectra under open circuit conditions at regular time intervals.

Open circuit memory of P(SNS-NH<sub>2</sub>)/PEDOT ECD was monitored simultaneously at 373 nm by an applied pulse ( $0.0 \pm 1.2V$ ) for 1 s and kept under open-circuit conditions for 200 s. Open circuit memory of P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT ECD was monitored simultaneously at 491 nm by an applied pulse (0.3 V and  $\pm 1.5V$ ) for 1 s and kept under open-circuit conditions for 200 s. Simultaneously the optical spectrum at maximum optical contrast point as a function of time at open circuit conditions was monitored.

#### **2.9.5. Colorimetry Studies of Electrochromic Devices**

Colorimetry analysis, which enables numeric determination of color, is considered as a valuable method for electrochromic device applications. The colors of polymer films and devices were determined by spectrophotometer at the reduced and oxidized states of P(SNS-NH<sub>2</sub>)/PEDOT and P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT devices.

## CHAPTER III

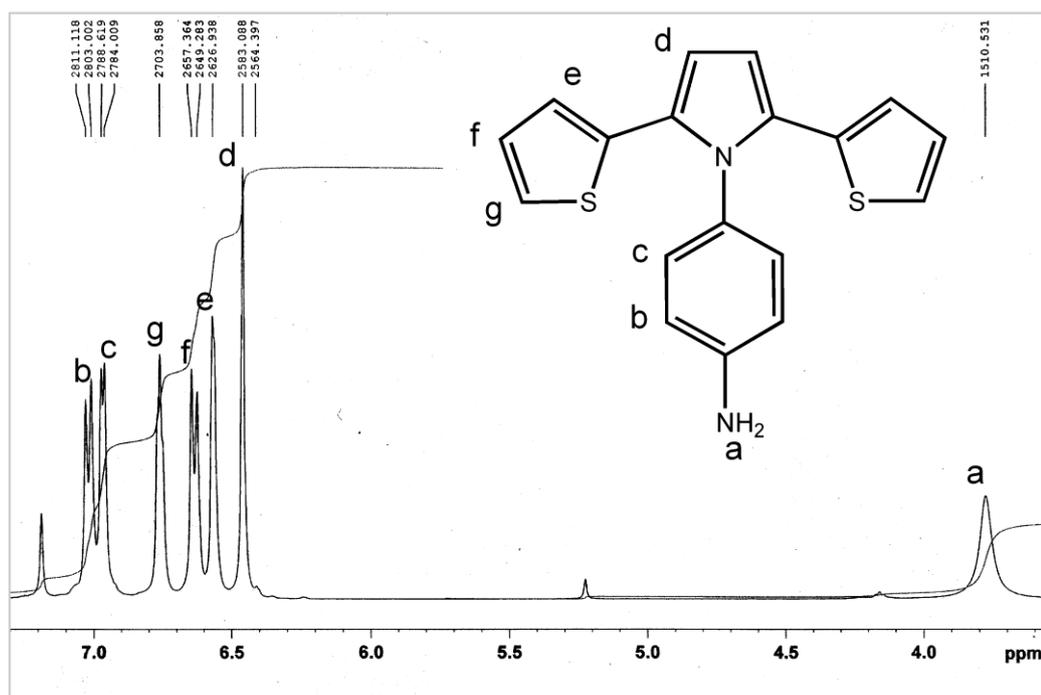
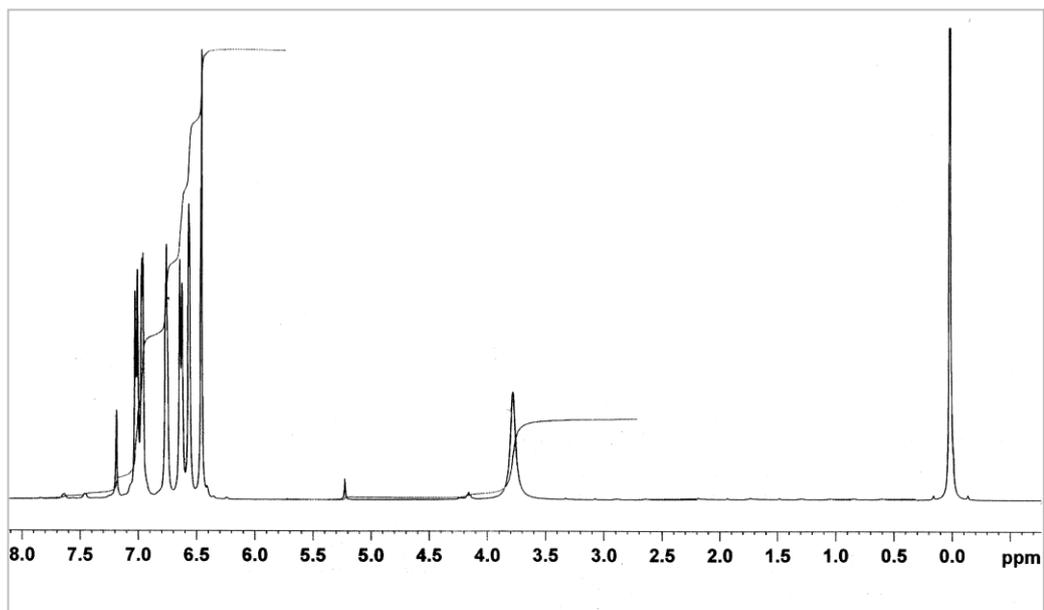
### RESULTS AND DISCUSSION

#### 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.

Pale yellow powder ; mp 184 °C;  $^1\text{H}$  NMR spectrum of monomer (Figure 3.1):  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{S}_2$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 3.75 (s, 2H, Ha), 6.46 (dd, 2H, pyrrolyl-Hd), 6.58 (s, 2H, thienyl-He) , 6.73 (dd, 2H, thienyl-Hf), 6.80 (d, 2H, thienyl-Hg), 6.97 (dd, 2H, phenyl-Hc), 7.12 (d, 2H, phenyl-Hb).  $^{13}\text{C}$  NMR spectrum of the monomer  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{S}_2$  (Figure 3.2):  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 109.5, 115.1, 124.2, 124.4, 124.5, 127.0, 129.1, 130.3, 135.7, 146.5.

$^1\text{H}$  NMR spectrum of chemically synthesized polymer (Figure 3.3):  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 3.75 (s, Ha), 6.40–6.60 (broad s, pyrrolyl-Hd), 6.60–6.75 (broad s, thienyl-He), 7.15–7.20 (broad s, thienyl-Hf), 7.20–7.35 (broad d, phenyl-Hc), 7.45–7.50 (broad s, phenyl-Hb). The decrease in the intensity of  $\alpha$ -hydrogen peak confirms the polymerization from 2 position of thiophene moiety of the monomer.



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

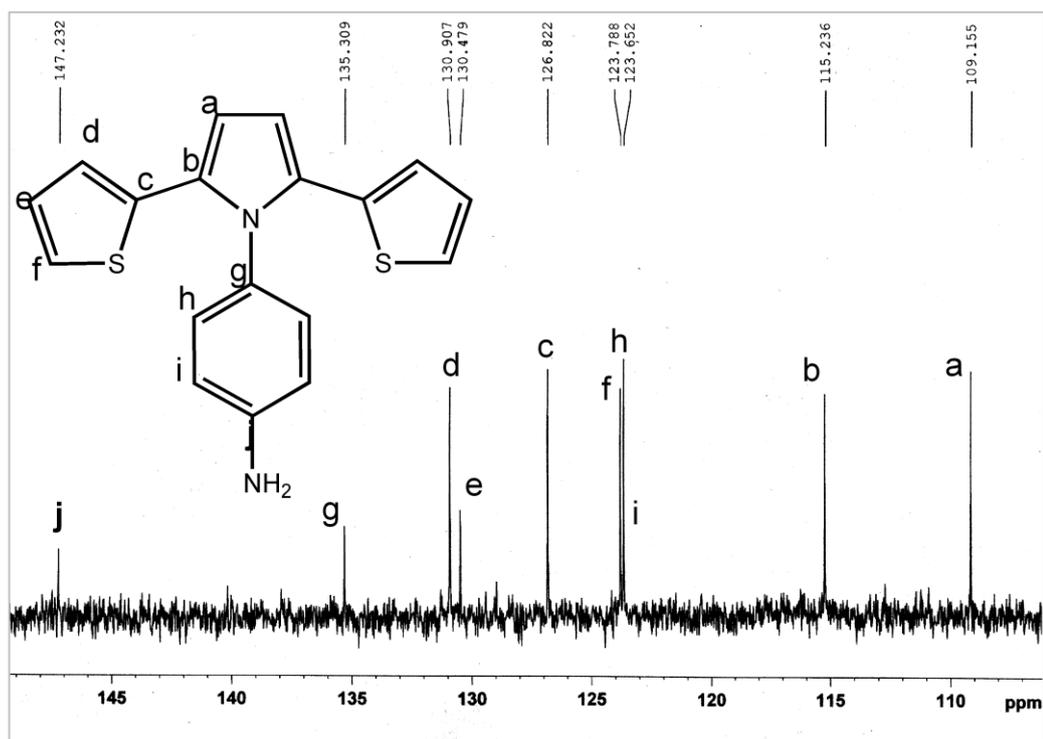
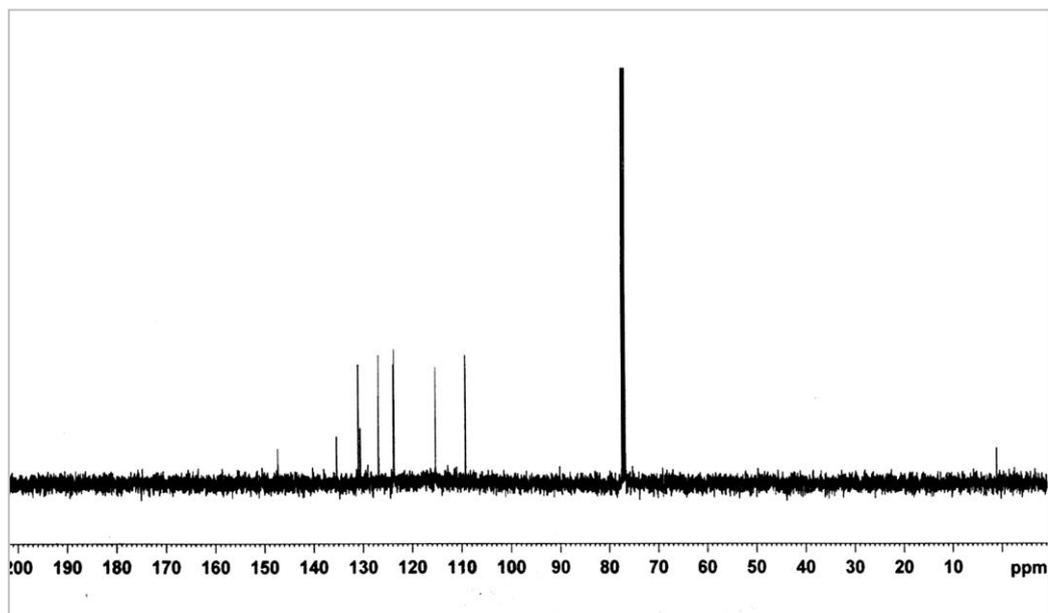
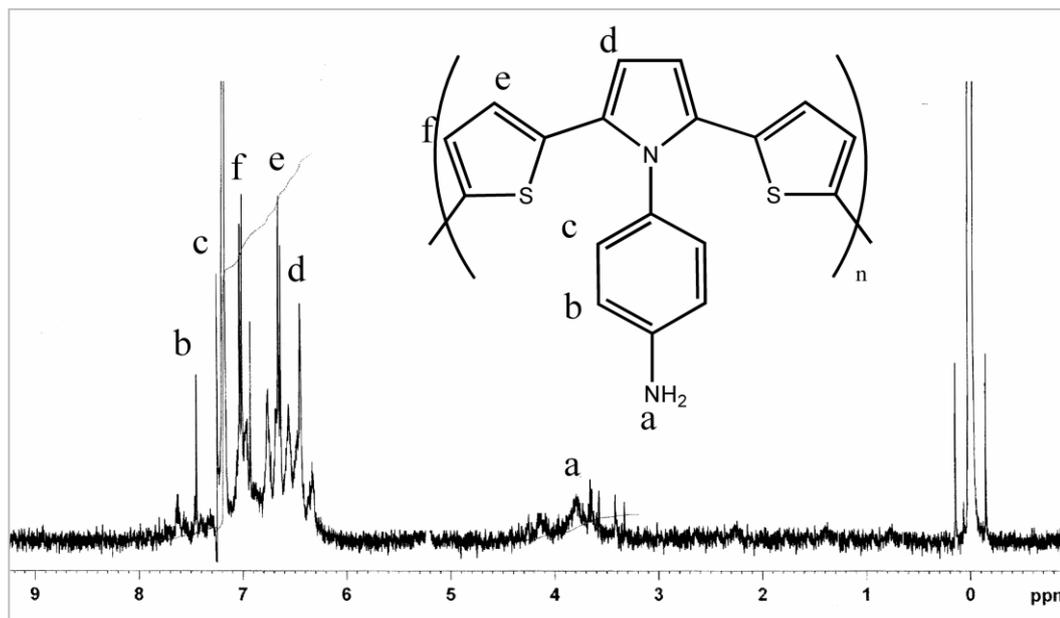


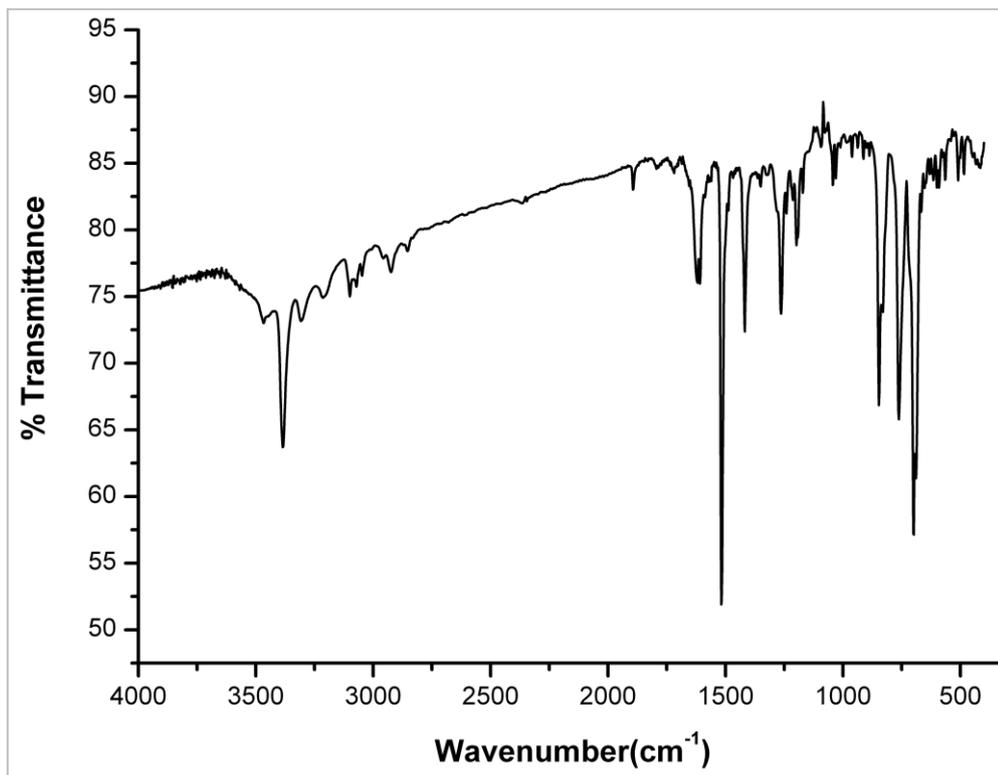
Figure 3.2  $^{13}\text{C}$ -NMR spectrum of the monomer



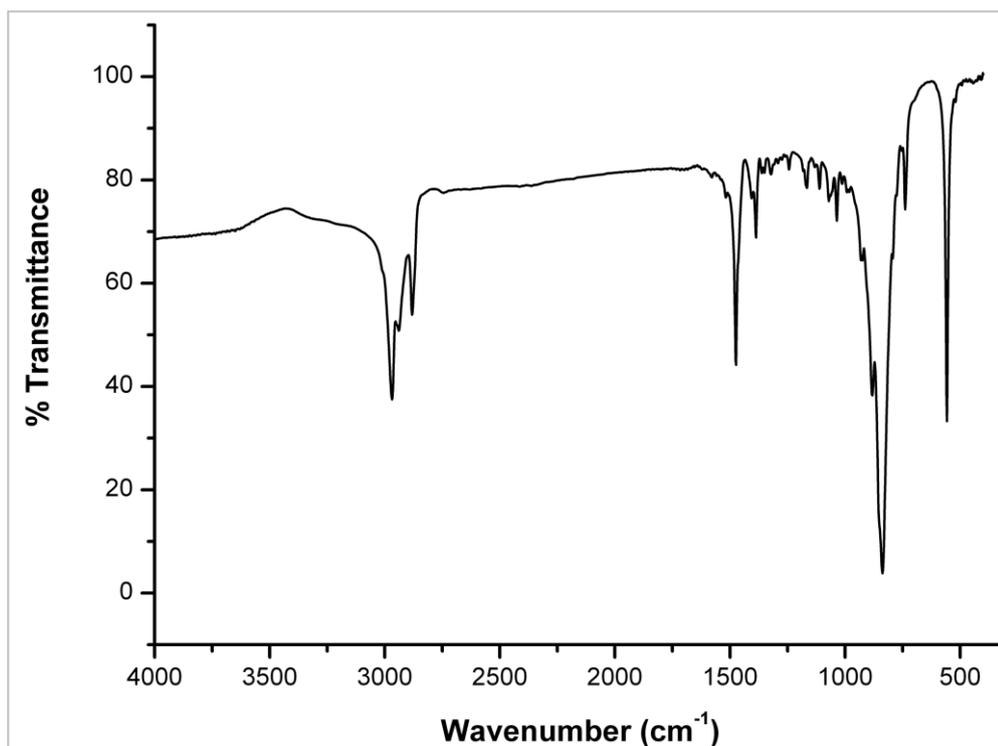
**Figure 3.3**  $^1\text{H}$ -NMR spectrum of the chemically synthesized P(SNS-NH<sub>2</sub>)

### 3.2. FTIR Spectra

FTIR spectrum (Figure 3.4) of the SNS-NH<sub>2</sub> shows the following absorption peaks: 3400 cm<sup>-1</sup> (N-H stretching), 3100 cm<sup>-1</sup> (aromatic C-H stretching of thiophene), 3020 cm<sup>-1</sup> (C-H stretching of thiophene), 1550-1380 cm<sup>-1</sup> (aromatic C=C, C-N stretchings due to pyrrole and benzene), 1110 cm<sup>-1</sup> (C-H in plane bending of benzene), 850 cm<sup>-1</sup> (C-H out of plane bending of thiophene), 685 cm<sup>-1</sup> (monosubstituted benzene). FTIR spectrum of electrochemically synthesized P(SNS-NH<sub>2</sub>) showed the characteristic peaks of the monomer (Figure 3.5). The peaks related to C-H stretching of thiophene disappeared completely. The new broad band at around 1620 cm<sup>-1</sup> was due to polyconjugation. The strong absorption peak at 1120, 1050 cm<sup>-1</sup> were attributed to the incorporation ClO<sub>4</sub><sup>-</sup> ions into the polymer film during doping process. The baseline shift in FTIR spectrum also implies the conducting polymer formation. Results of the FTIR studies clearly indicated the polymerization of the monomer.

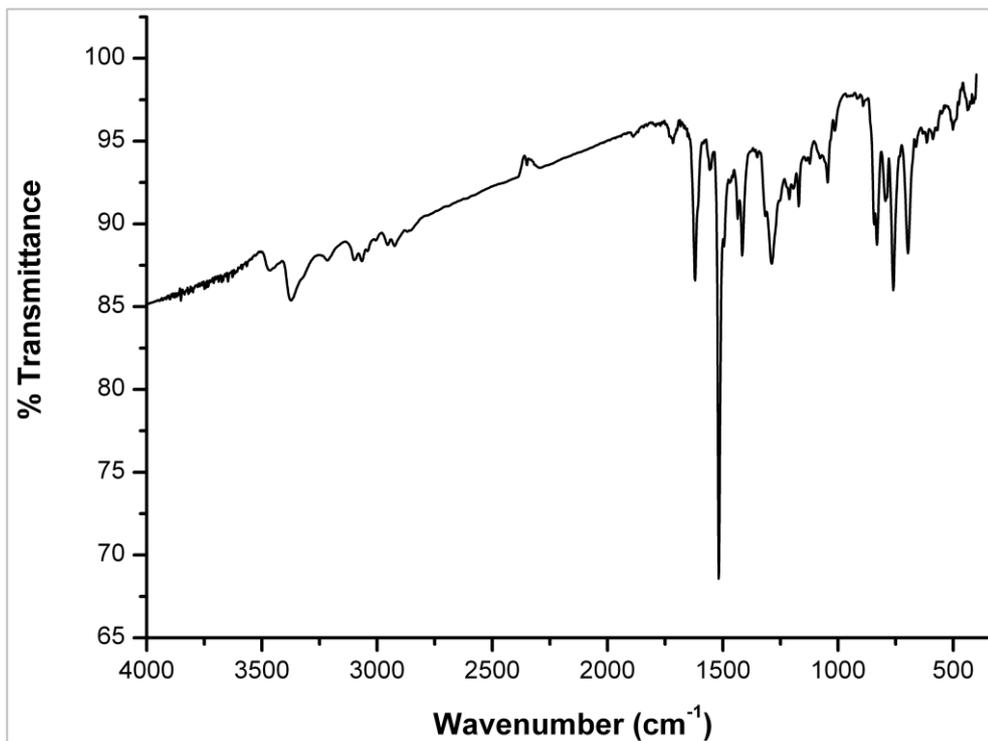


**Figure 3.4** FTIR spectrum of SNS-NH<sub>2</sub>



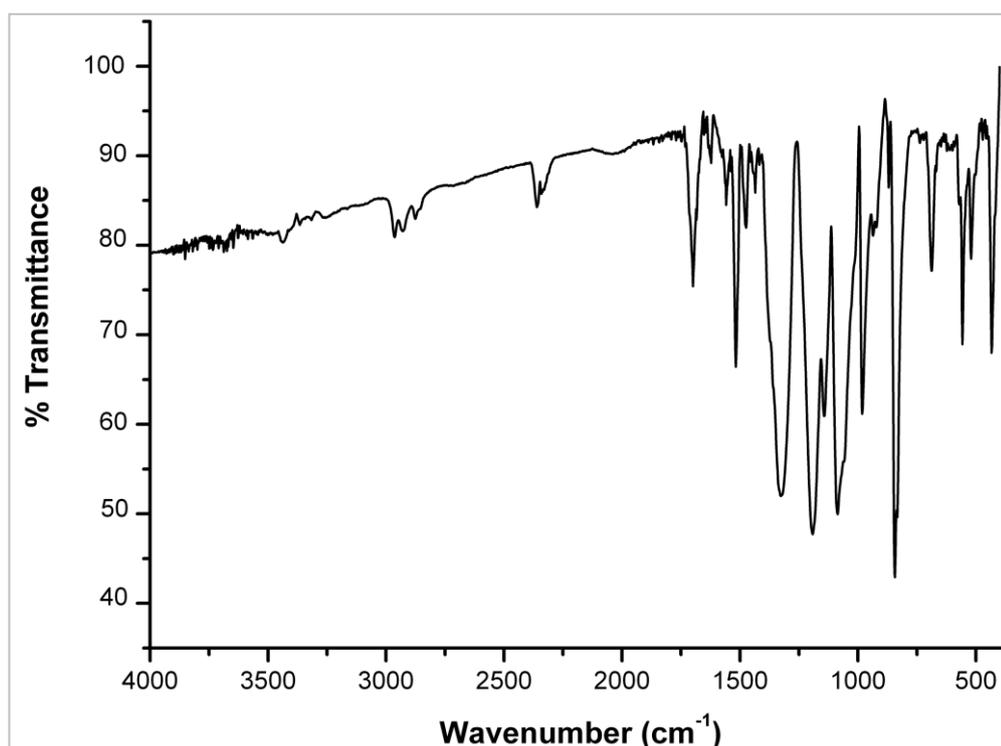
**Figure 3.5** FTIR spectrum of electrochemically synthesized P(SNS-NH<sub>2</sub>)

Most of the characteristic peaks of SNS-NH<sub>2</sub> remained unperturbed upon chemical polymerization (Figure 3.6). The absorption bands of the monomer at 3020 cm<sup>-1</sup> arising from C–H stretching of thiophene moiety disappeared completely. This is an evidence of the polymerization from 2 and 5 positions of thiophene moiety of the monomer. Whereas, two new bands related to C–H out-of plane bending of 2,5 disubstituted thiophene and C–S stretching appeared at 840 and 770 cm<sup>-1</sup>, respectively. The intensity of the peak around 700 cm<sup>-1</sup> also decreased. The broad band observed at around 1645 cm<sup>-1</sup> proves the presence of polyconjugation and the new peak at 640 cm<sup>-1</sup> indicates the presence of the dopant ion (Cl<sup>-</sup>).



**Figure 3.6** FTIR spectrum of chemically synthesized P(SNS-NH<sub>2</sub>)

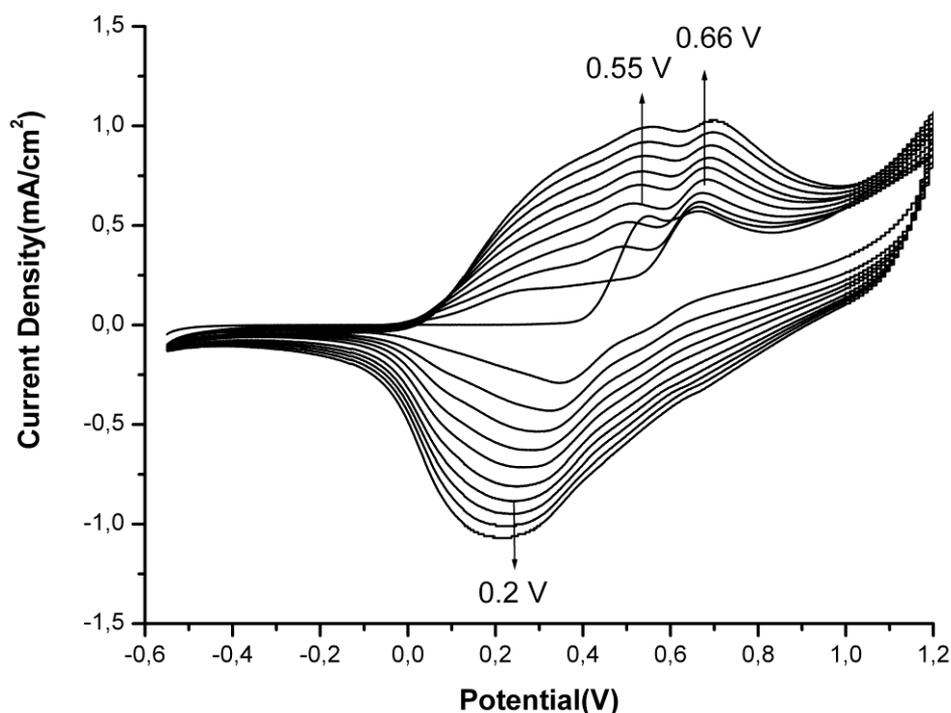
FTIR spectrum (Figure 3.7) of electrochemically synthesized copolymer P(SNS-NH<sub>2</sub>-co-EDOT) shows the following absorption peaks: 2965 cm<sup>-1</sup> (aromatic C–H stretching) and 2924 cm<sup>-1</sup> (C–H stretching of thiophene). The broad band observed at around 1698 cm<sup>-1</sup> proves the presence of polyconjugation. On the other hand, evolution of new peaks was observed at 2876 and 2858 cm<sup>-1</sup>, which are attributed to the aromatic ethylene group belonging to EDOT. Stretching arising from ethylene-dioxy group appeared at 1085 and 1192 cm<sup>-1</sup>. Decreasing the intensity of the absorption band of the monomer at 3020 cm<sup>-1</sup> arising from C–H stretching of thiophene is an evidence of the polymerization from 2 and 5 positions of thiophene moiety of the monomers. The strong absorption peak at 838 cm<sup>-1</sup> was attributed to the incorporation of PF<sub>6</sub><sup>-</sup> ions into the polymer film during doping process. Results of the FTIR studies clearly indicated the copolymerization was successfully achieved.



**Figure 3.7** FTIR spectrum of P(SNS-NH<sub>2</sub>-co-EDOT)

### 3.3. Cyclic Voltammograms

Conducting polymers are an interesting class of materials that are able to exhibit very different properties depending on their redox state. Therefore, it is necessary to probe these states via cyclic voltammetry. With cyclic voltammetry, electrochemical polymerization of a monomer, along with the accessibility of the redox sites of the polymer, can be investigated.

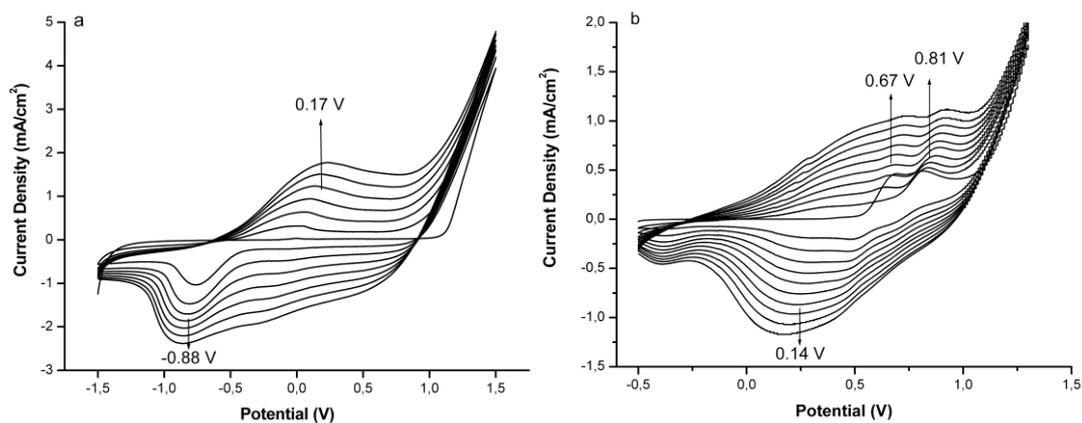


**Figure 3.8** Cyclic voltammogram of P(SNS-NH<sub>2</sub>)

Cyclic voltammetry experiments were carried out in ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> solvent electrolyte couple on bare Pt electrode with a 500 mV/s scan rate. Cyclic voltammogram of (SNS-NH<sub>2</sub>) indicated two consecutive oxidation peaks at 0.55 V and 0.66 V when the range between -0.5 V and +1.2 V was scanned. In the cathodic run, reduction of the deposited polymer was observed at 0.2 V. Upon consecutive cycle formation, a new oxidation peak appeared at 0.47 V due to the oxidation of the polymer (Figure 3.8).

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 electroactive polymer coating on the metal electrode. A greenish cloud was also formed around the electrode due to the partial dissolution of neutral linear oligomers of low molecular weight. For studying the electrochemistry of the polymer, a monomer free system was used.

The oxidation/reduction behavior of the SNS-NH<sub>2</sub> through copolymerization in the presence of EDOT was investigated via cyclic voltammetry. Oxidative electropolymerization of SNS-NH<sub>2</sub> with EDOT was carried out in acetonitrile with 0.1 M NaClO<sub>4</sub> / LiClO<sub>4</sub> as supporting electrolyte. There was a drastic change in the voltammogram, both the increase in the increments between consecutive cycles and the oxidation potential of the material were different than those of from both monomer and pure EDOT. The oxidation peaks of SNS-NH<sub>2</sub> drastically shifted to + 0.67 V and + 0.81 V when EDOT was added into the system.



**Figure 3.9** Cyclic Voltammograms of (a) pure EDOT, (b) SNS-NH<sub>2</sub> in the presence of EDOT, P(SNS-NH<sub>2</sub>-co-EDOT)

Figure 3.9b shows the redox behavior of SNS-NH<sub>2</sub> in the presence of EDOT. When CV of P(SNS-NH<sub>2</sub>-co-EDOT) is compared with the voltammogram of pristine EDOT (Figure 3.9a), the redox peaks are not at the same positions. Pure EDOT in ACN/LiClO<sub>4</sub>(0.1 M)/NaClO<sub>4</sub>(0.1 M) reveals an oxidation peak at +0.17 V and a reduction peak at -0.88 V with a scan rate 500 mV/s. The quality of film coated on Pt electrode during copolymerization was better than P(SNS-NH<sub>2</sub>), since the polymer chain was growing steadily without getting dissolved partially in the medium. Both the current increase in the increments between consecutive cycles and the redox potentials of the copolymer compare to those of pure PEDOT and P(SNS-NH<sub>2</sub>) are different. These differences are known to be an indication for the reaction between EDOT and the thiophene moiety of SNS-NH<sub>2</sub>, resulting copolymer formation.

### 3.4. Conductivities

Four probe technique was employed to measure the conductivities of electrochemically and chemically prepared SNS-NH<sub>2</sub>. Room temperature (20 °C) conductivities of the polymer films were summarized in Table 3.1. 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(SNS-NH<sub>2</sub>-co-EDOT) is found to be  $2.4 \times 10^{-3} \text{ S.cm}^{-1}$ . The conductivities of pristine PEDOT and P(SNS-NH<sub>2</sub>) are  $1 \times 10^{-2} \text{ S.cm}^{-1}$  and  $1.6 \times 10^{-4} \text{ S.cm}^{-1}$ , respectively. It is observed that the conductivity increased by about 10 orders of magnitude upon copolymerization. This is expected since the presence of EDOT increases the conjugation in pristine P(SNS-NH<sub>2</sub>) chains. The difference between the conductivities of chemical and electrochemical polymers is due to the different dopant anions on the polymer chains. The chemical polymer has both Cl<sup>-</sup> and FeCl<sub>4</sub><sup>-</sup>; thus shows lower conductivity; whereas the electrochemical polymer has only ClO<sub>4</sub><sup>-</sup> dopant.

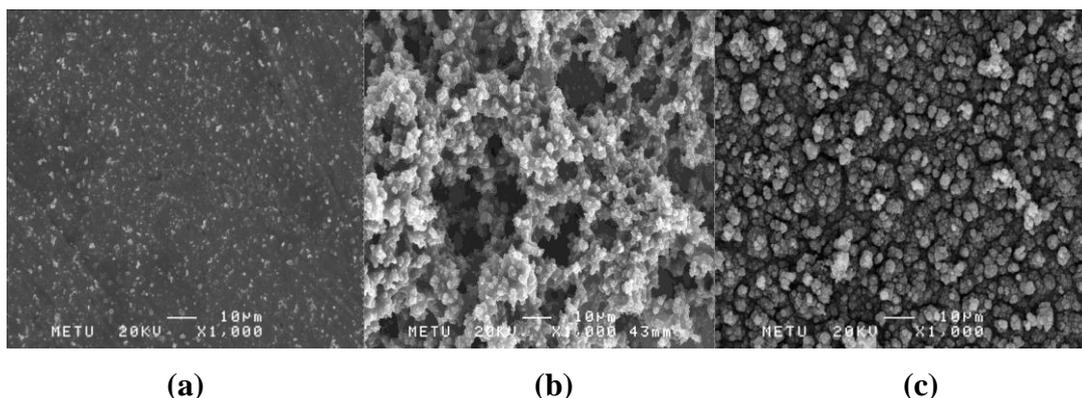
**Table 3-1.** Conductivities of P(SNS-NH<sub>2</sub>), P(SNS-NH<sub>2</sub>-co-EDOT) and PEDOT

Sample	Conductivity (S.cm <sup>-1</sup> )	
	<i>Chemically Prepared</i>	<i>Electrochemically Prepared</i>
<b>P(SNS-NH<sub>2</sub>)</b>	1.3x10 <sup>-5</sup>	1.6x10 <sup>-4</sup>
<b>P(SNS-NH<sub>2</sub>-co-EDOT)</b>	2.4x10 <sup>-3</sup>	
<b>PEDOT</b>	1.0x10 <sup>-2</sup>	

### 3.5. Morphologies of Films

Surface morphologies of P(SNS-NH<sub>2</sub>), P(SNS-NH<sub>2</sub>-co-EDOT) and PEDOT were examined by employing Scanning Electron Microscope. SEM micrographs of polymers show the excellence of film forming ability of the polymers. All polymers exhibited homogeneous and compact structure. Spheroids like droplets were observed on the solution side of P(SNS-NH<sub>2</sub>) film (Fig. 3.10a).

As far as the SEM micrograph of copolymer of SNS-NH<sub>2</sub> with EDOT is concerned (Fig. 3.10b), the solution side of copolymer film differs from SEM micrograph of PEDOT (Fig. 3.10c) and P(SNS-NH<sub>2</sub>), considerably. At the solution side of P(SNS-NH<sub>2</sub>-co-EDOT), popcorn-like structures were observed. The topology of PEDOT reveals globules.



**Figure 3.10** SEM micrographs of (a) solution side of P(SNS-NH<sub>2</sub>) (b) solution side of P(SNS-NH<sub>2</sub>-co-EDOT) (c) solution side of PEDOT

### 3.6. Gel Permeation Chromatography (GPC)

GPC is the best and exact way of measuring molecular weights of polymers. The weight average and number average molecular weight of chemically synthesized P(SNS-NH<sub>2</sub>) were determined by GPC in THF solution. The results of GPC studies are given in Table 3.2. The polydispersity (PD=M<sub>w</sub>/M<sub>n</sub>) of P(SNS-NH<sub>2</sub>) was found as 1.35 which means all polymer chain have almost the same number of repeating units. The number of repeating unit is determined as 12.

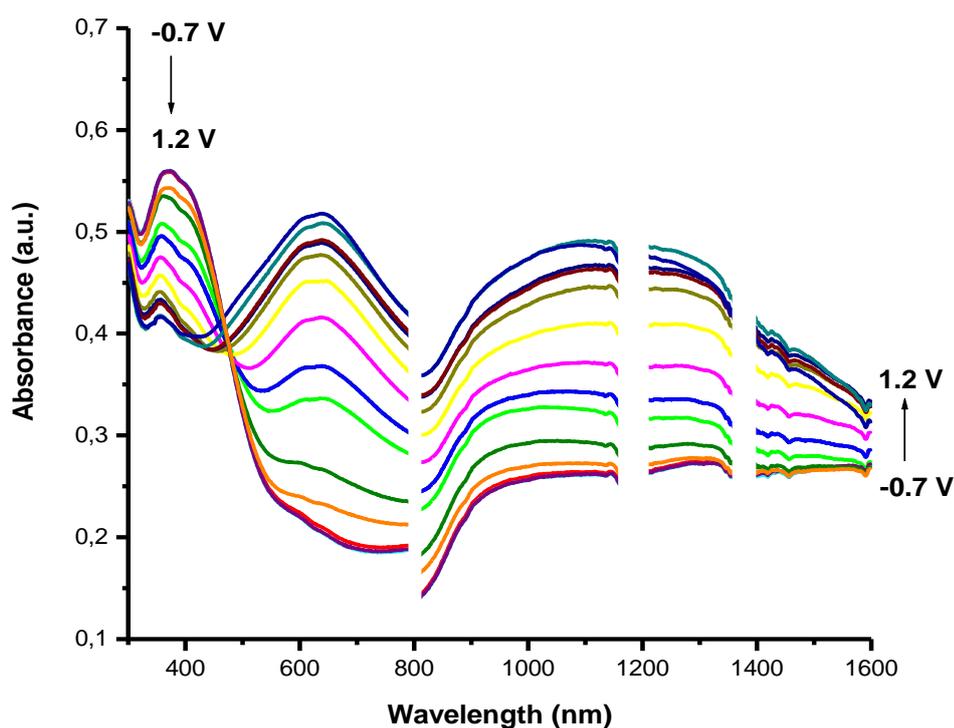
**Table 3.2** GPC Results

<b>M<sub>o</sub></b>	<b>322 g/mol</b>
<b>M<sub>n</sub></b>	<b>2.8x10<sup>3</sup> g/mol</b>
<b>M<sub>w</sub></b>	<b>3.7x10<sup>3</sup> g/mol</b>
<b>PD</b>	<b>1.35</b>

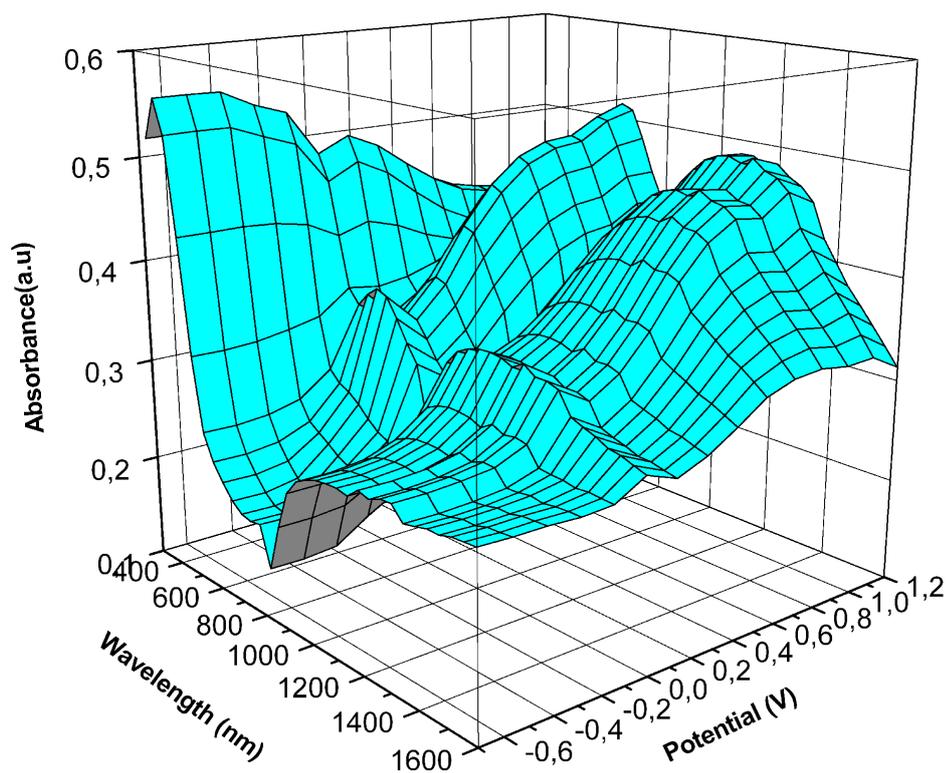
### 3.7. Investigation of Electrochromic Properties of Polymers

#### 3.7.1. Spectroelectrochemistry

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques that can be operated simultaneously. It provides information on both electrochemical response and accompanying optical characteristics of all states of the electrochemical reaction. Spectroelectrochemistry experiments reveal key properties of conjugated polymers, such as band gap ( $E_g$ ) and the intergap states that appear upon doping. For the spectroelectrochemistry of the homopolymer, the film was deposited on ITO via potentiostatic electrochemical polymerization of SNS-NH<sub>2</sub> in the presence of NaClO<sub>4</sub> / LiClO<sub>4</sub>/ ACN at -0.5 V and +1.2V.



**Figure 3.11** 2D Spectroelectrochemical spectrum of P(SNS-NH<sub>2</sub>) with applied potentials between -0.7 V and 1.2 V in ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M)

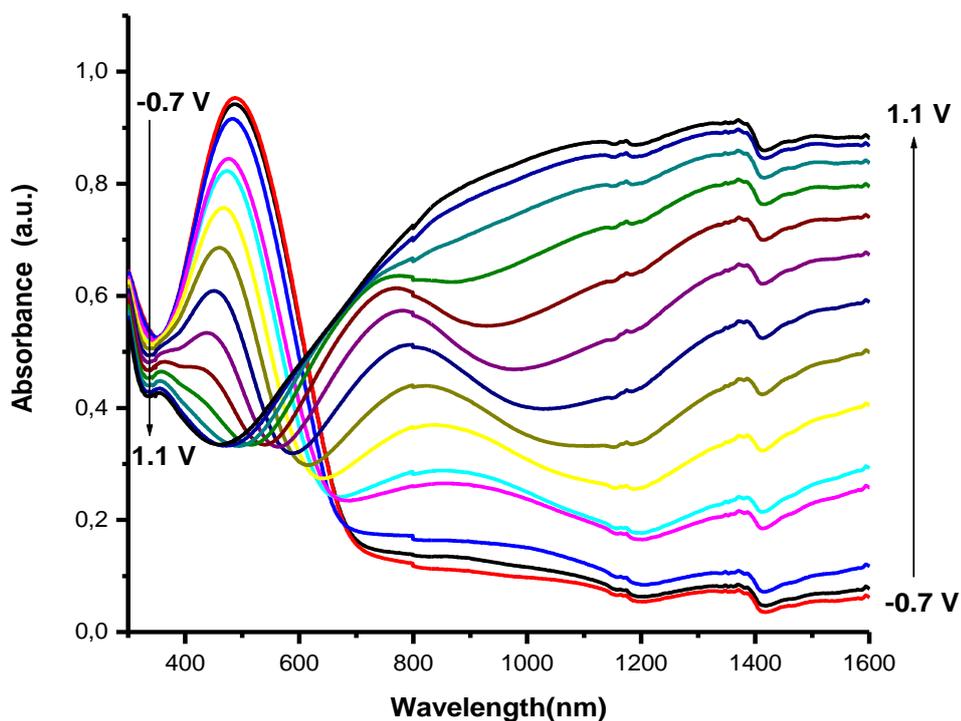


**Figure 3.12** 3D Spectroelectrochemical spectrum of P(SNS-NH<sub>2</sub>) with applied potentials between -0.7 V and 1.2 V in ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M)

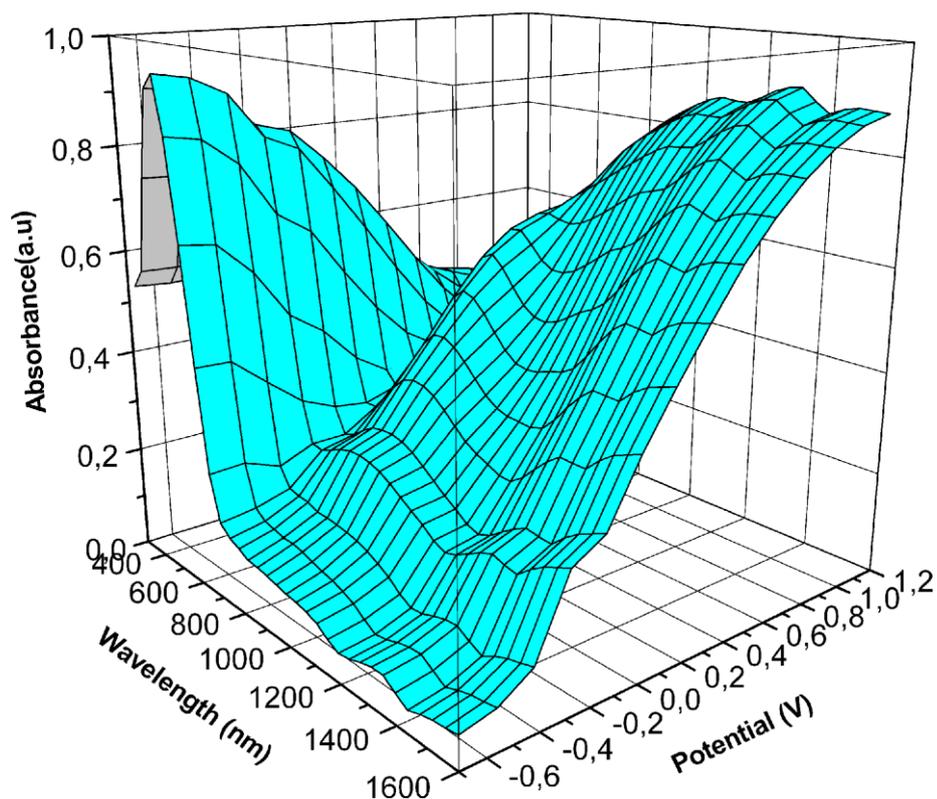
P(SNS-NH<sub>2</sub>) coated ITO was then investigated by UV-vis spectroscopy in the same but monomer free electrolytic system by switching the potential between -0.7 V and +1.2V with incremental increase in applied potential. At the neutral state  $\lambda_{\max}$  due to the  $\pi$ - $\pi^*$  transition of the polymer was found to be 376 nm and  $E_g$  was calculated as 2.12 eV. Upon applied voltage, reduction in the intensity of the  $\pi$ - $\pi^*$  transitions and formation of charge carrier bands were observed. Thus, peak around 650 nm is attributed to the evolution of polaron bands (Figure 3.11).

For the spectroelectrochemistry of the copolymers, the film was deposited on ITO via potentiostatic electrochemical polymerization of SNS-NH<sub>2</sub> (0.01 M) in the presence of EDOT and NaClO<sub>4</sub>/LiClO<sub>4</sub>/ACN while the potential was swept between -0.5 V and +1.3V. P(SNS-NH<sub>2</sub>-co-EDOT) coated ITO was investigated by UV-vis spectroscopy in monomer free electrolytic system by switching the potential between -0.7 V and +1.1V.

At the neutral state  $\lambda_{\max}$  value due to the  $\pi\text{-}\pi^*$  transition of the copolymer was found to be 486 nm and  $E_g$  was calculated as 1.7 eV. Peak around 1380 nm is attributed to the evolution of bipolaron bands. Figure 3.13 represents the spectrum of copolymer in neutral state where a gradual shift and a broadening of the  $\lambda_{\max}$  were observed with increasing potential. When the applied potential increased, intensity of  $\lambda_{\max}$  peak decreased.



**Figure 3.13** 2D Spectroelectrochemical spectrum of P(SNS-NH<sub>2</sub>-co-EDOT) with applied potentials between -0.7 V and 1.1 V in in ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1 M)



**Figure 3.14** 3D Spectroelectrochemical spectrum of P(SNS-NH<sub>2</sub>-co-EDOT) with applied potentials between -0.7 V and 1.1 V in ACN/NaClO<sub>4</sub>/LiClO<sub>4</sub> (0.1M)

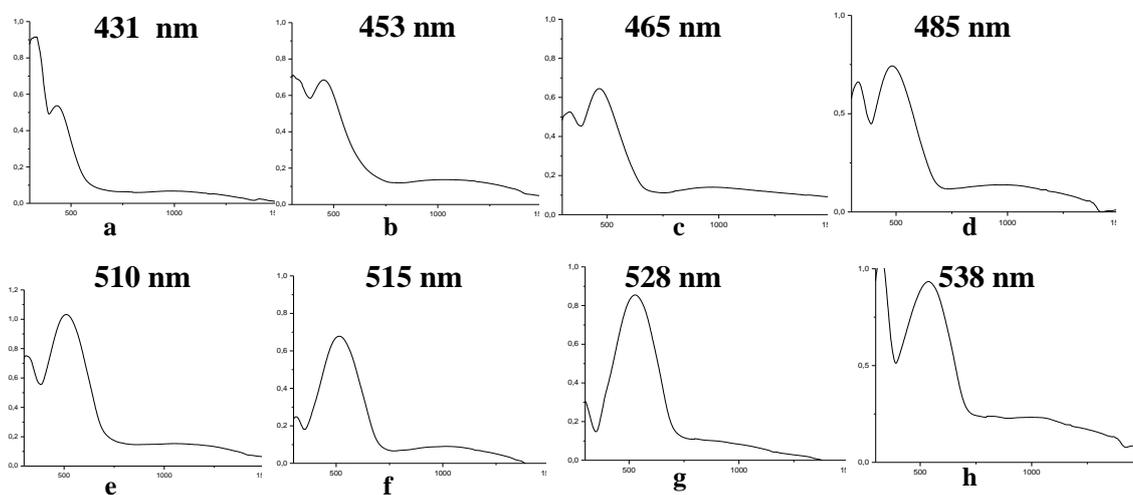
Low band gap for the copolymer results from the presence of PEDOT where pristine PEDOT has a band gap of 1.6 eV. Table 3.3 is a good summary of comparison of the homopolymer, copolymer and PEDOT.  $\lambda_{\max}$  value of the copolymer is between those of the PEDOT and the homopolymer. These numerical values also support the copolymerization phenomenon.

**Table 3.3** Comparison of homopolymer, copolymer and PEDOT in terms of  $E_g$  and  $\lambda_{\max}$  values

	Homopolymer	Copolymer	PEDOT
$\lambda_{\max}$	376 nm	486 nm	600 nm
$E_g$	2.12 eV	1.7 eV	1.6 eV

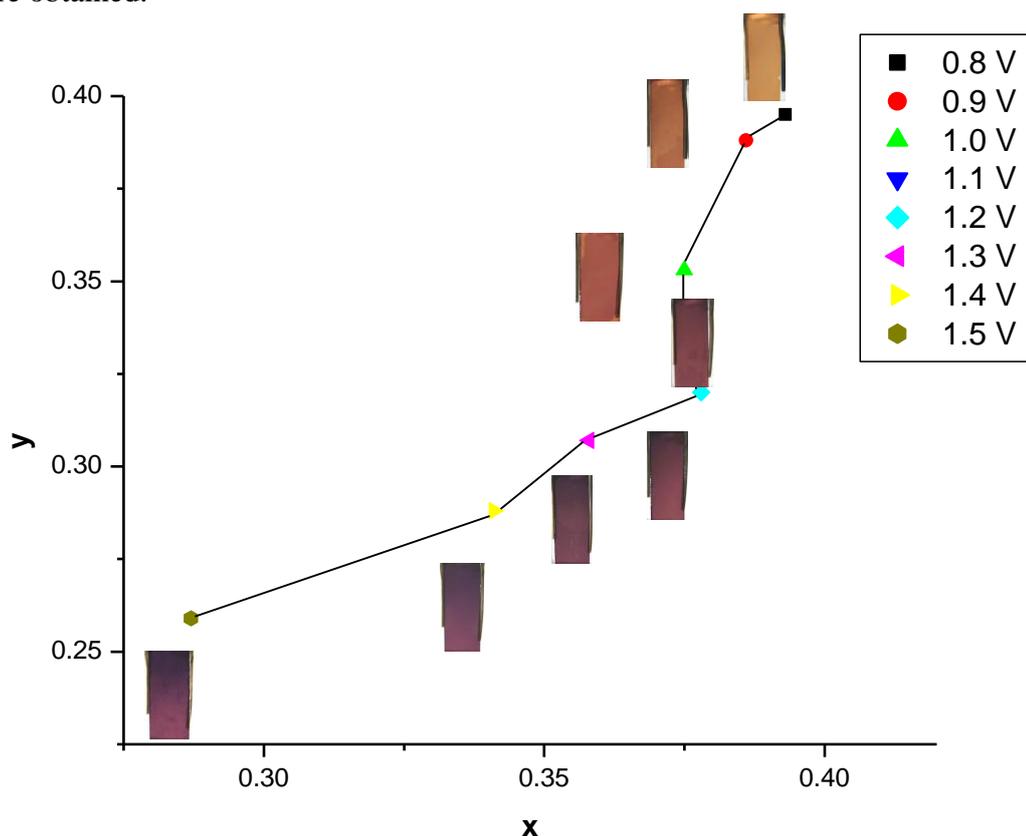
### 3.7.2. Property differences based on change in the amount of PEDOT in copolymer composition

The effects of synthesis conditions on the spectroelectrochemical properties of polymers were investigated. Copolymers were synthesized with the same comonomer feed ratio using different applied potentials. It is notable that this approach is one of the unique properties (selectivity) of electrochemical polymerization. Polymers were obtained by constant potential polymerization in the presence of ACN/LiClO<sub>4</sub>/NaClO<sub>4</sub> solvent-electrolyte couple by varying the potential between 0.8 V and 1.5 V. Spectroelectrochemistry studies were performed in order to see the differences in  $\lambda_{\text{max}}$  for the samples. Figure 3.15 represents the spectra of copolymers in neutral state where a gradual shift and a broadening of peak were observed with increasing polymerization potential. As a consequence the amount of PEDOT in the copolymer composition increased and  $\lambda_{\text{max}}$  value for the copolymer came closer to 610 nm.

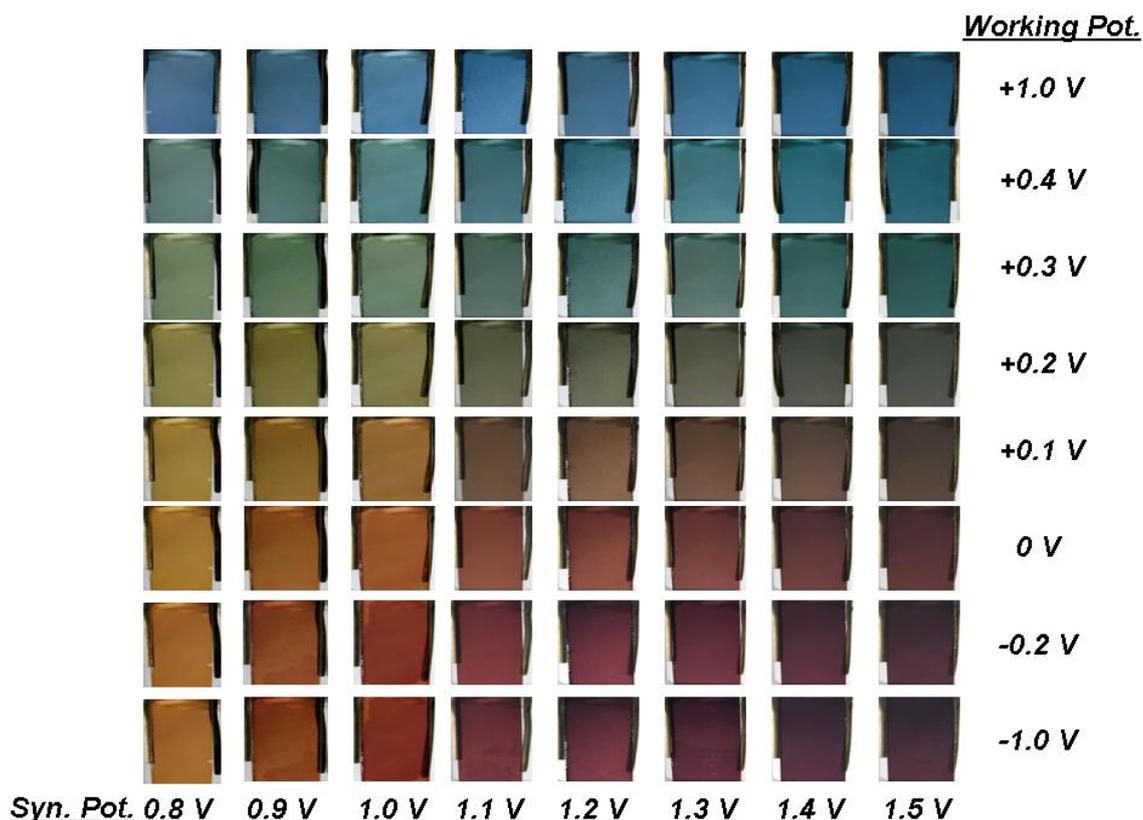


**Figure 3.15** Optoelectrochemical spectra of P(SNS-NH<sub>2</sub>-co-EDOT) at applied potentials a. 0.8 V, b. 0.9 V, c. 1.0 V, d. 1.1 V, e. 1.2 V, f. 1.3 V, g. 1.4 V, h. 1.5 V

In addition to the spectroelectrochemistry studies, results showed that there is a direct relation between the color of the polymer in the neutral state and the amount of the PEDOT in the copolymer. It was possible to obtain color grading from blue to tale, green, brown and purple with the applied potential. Therefore, this type of copolymerization not only provides multichromism for the end product but also satisfies fine tuning of several colors (Figure 3.16). In addition to these observations, FTIR studies were also performed in order to investigate the difference caused by changing the amount of PEDOT in the copolymer composition. It was observed that the peak intensity of  $-C-O-C-$  in EDOT structure around  $1100\text{ cm}^{-1}$  increases with respect to the change in the potential of the polymerization. Results of the spectroelectrochemistry, FTIR and colorimetry studies proved that as the potential of the polymerization increases, the amount of PEDOT in the copolymer composition increases and as a result significant changes in the optical properties of copolymers are obtained.



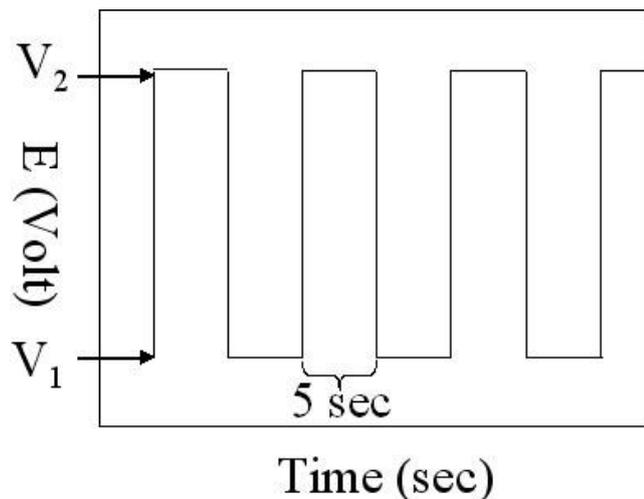
**Figure 3.16** Color coordinates of P(SNS-NH<sub>2</sub>-co-EDOT). xy values of reduced state (-1.0 V) of copolymer synthesized at different potentials



**Figure 3.17** Colors of P(SNS-NH<sub>2</sub>-co-EDOT) synthesized at different potentials

### 3.7.3. Electrochromic Switching

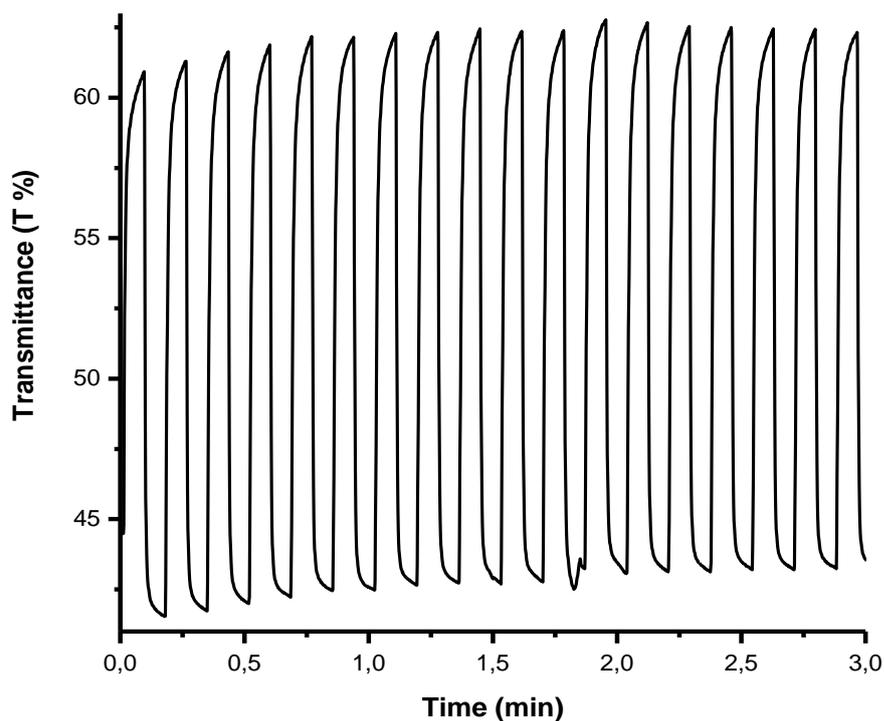
For electrochromic applications, the ability of a polymer to switch rapidly and exhibit a striking color change is important. Electrochromic switching studies can supervise these types of properties. A square-wave potential step method (Figure 3.18) coupled with optical spectroscopy known as chronoabsorptometry is used to investigate switching time and optical contrast in the polymer. In this double potential step experiment, the potential is set at an initial potential for a set period of time (5 s) and stepped to a second potential for the same period of time before being switched back to the initial potential again.



**Figure 3.18** Square wave potential step method

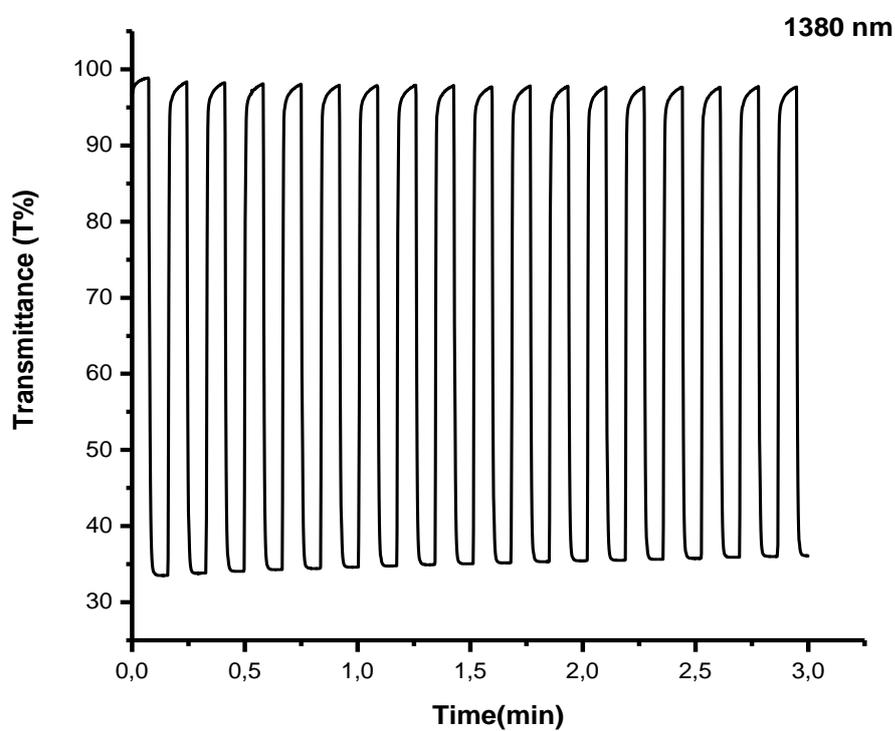
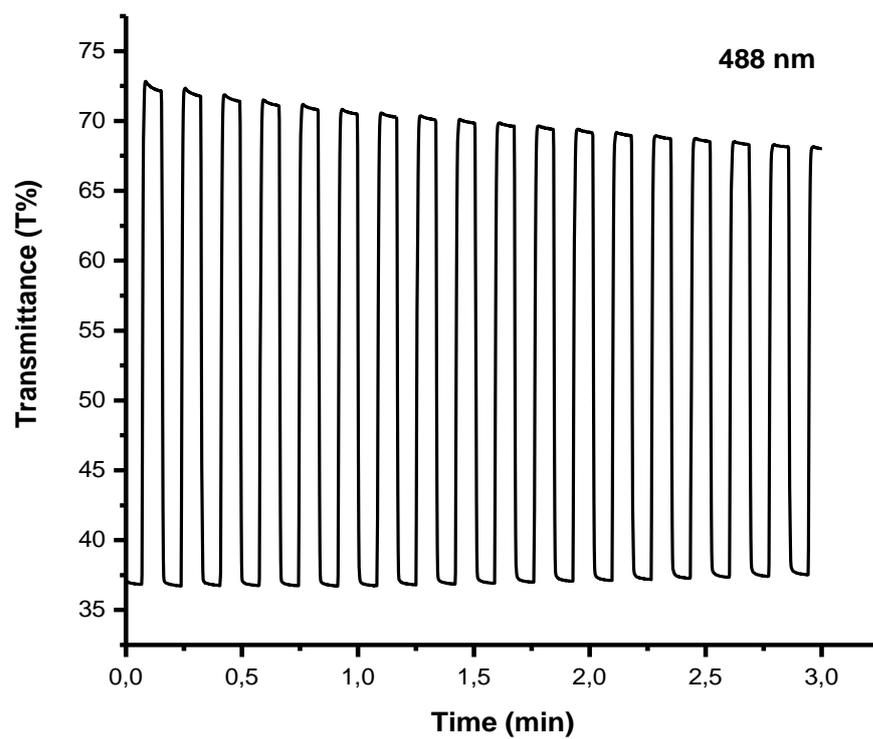
The experiments carried out by spectroelectrochemistry showed the ability of P(SNS-NH<sub>2</sub>) to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. During the experiment, the percent transmittance (T %) at 376 nm was monitored using a UV-Vis spectrophotometer. The polymer film was synthesized on ITO-coated glass slides.

Upon switching P(SNS-NH<sub>2</sub>) between -0.7 V and +1.2 V with a residence time of 5 s, optical contrast and the time needed to reach 95% of the total transmittance change for the homopolymer was measured. P(SNS-NH<sub>2</sub>) was found to have 20.7% optical contrast with a switching time of 3.0 s. As seen in Fig. 3.19, homopolymer has reasonable stability and switching time.



**Figure 3.19** Electrochromic switching, optical absorbance change monitored at 376 nm for P(SNS-NH<sub>2</sub>) between -0.7 V and 1.2 V

Same procedure was also applied for the copolymer. P(SNS-NH<sub>2</sub>-co-EDOT) was found to have 34% optical contrast with a switching time of 0.6 s at 488 nm and 62% optical contrast with a switching time of 0.6 s at 1380 nm. As seen in Figure 3.20, copolymer has a reasonable stability and switching time. The optical contrast of the homopolymer at its  $\lambda_{\text{max}}$  was 20.7 %. The copolymerization with EDOT increased the optical contrast from 20.7 % to 34 %. Table 3.4 is a comparison of homopolymer and copolymer in terms of switching time and optical contrast. Introduction of EDOT to the polymer chain led to a tremendous decrease in the switching time and an increase in the optical contrast.



**Figure 3.20** Electrochromic switching, optical absorbance change monitored at 488 and 1380 nm for P(SNS-NH<sub>2</sub>-co-EDOT) between -0.7 V and 1.1 V

**Table 3.4** Comparison of homopolymer and copolymer in terms of switching time and optical contrast values

	Switching Time		Optical Contrast	
<b>Homopolymer</b>	376 nm		376 nm	
	3 s		20.7 %	
<b>Copolymer</b>	<b>488 nm</b>	<b>1380 nm</b>	<b>488 nm</b>	<b>1380 nm</b>
	0.6 s	0.6 s	34 %	62 %

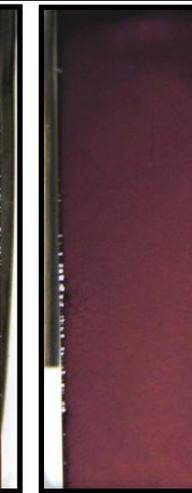
#### 3.7.4. Colorimetry Studies

The colors 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 and recorded in Table 3.5. The P(SNS-NH<sub>2</sub>) film shows different colors in the neutral (-0.5 V) and fully oxidized states (+1.0 V). The color of the film switches from blue in the oxidized form to yellow in the reduced state.

The copolymer revealed completely different spectroelectrochemical behavior in comparison to both of the homopolymers, where synergy was achieved due to copolymerization. It was important to note that only the copolymer displayed distinct multichromism. The copolymer shows five different colors upon applied potentials between -0.5 V and +0.8 V, purple, brown, green, teal, blue. 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** Colors and corresponding Y, x, y values of the P(SNS-NH<sub>2</sub>) and P(SNS-NH<sub>2</sub>-co-EDOT) films at different applied potentials

		
<p><b>+ 1.0 V</b>            Y:98            x:0.248            y:0.269</p>	<p><b>+ 0.3 V</b>            Y:203            x:0.307            y:0.370</p>	<p><b>- 0.5 V</b>            Y:487            x:0.418            y: 0.458</p>

				
<p><b>+ 0.8 V</b>            Y:476            x:0.271            y:0.306</p>	<p><b>+ 0.4 V</b>            Y:519            x:0.282            y:0.331</p>	<p><b>+ 0.2 V</b>            Y:467            x:0.331            y: 0.355</p>	<p><b>0 V</b>            Y:335            x:0.372            y:0.337</p>	<p><b>- 0.5 V</b>            Y:237            x:0.358            y:0.307</p>

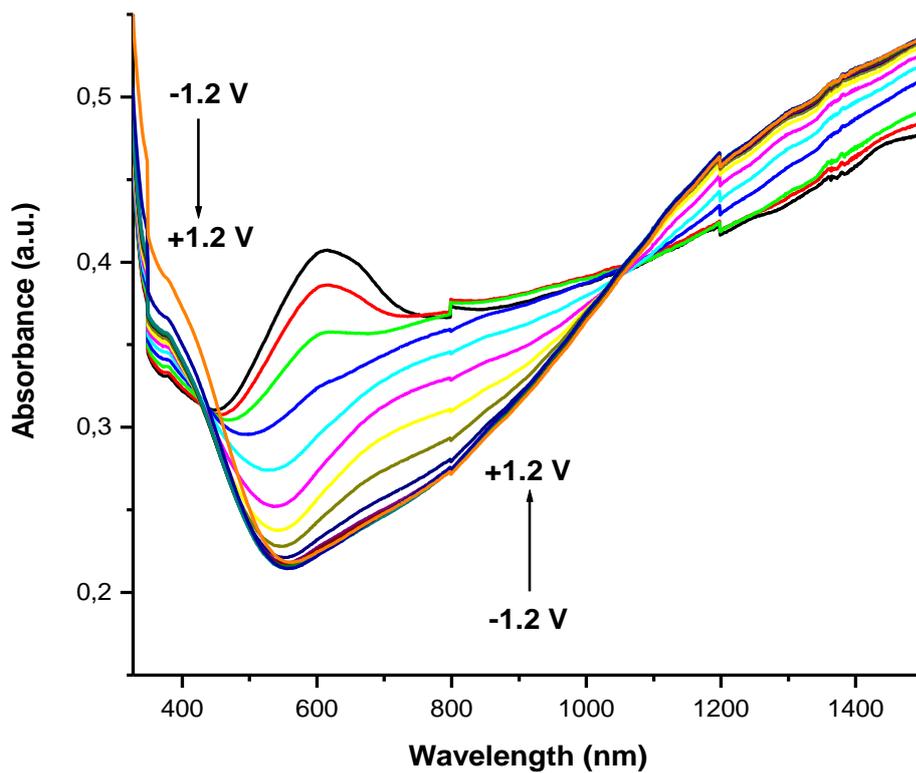
### 3.8. Characterization of Electrochromic Devices (ECDs)

#### 3.8.1. Spectroelectrochemistry of ECDs

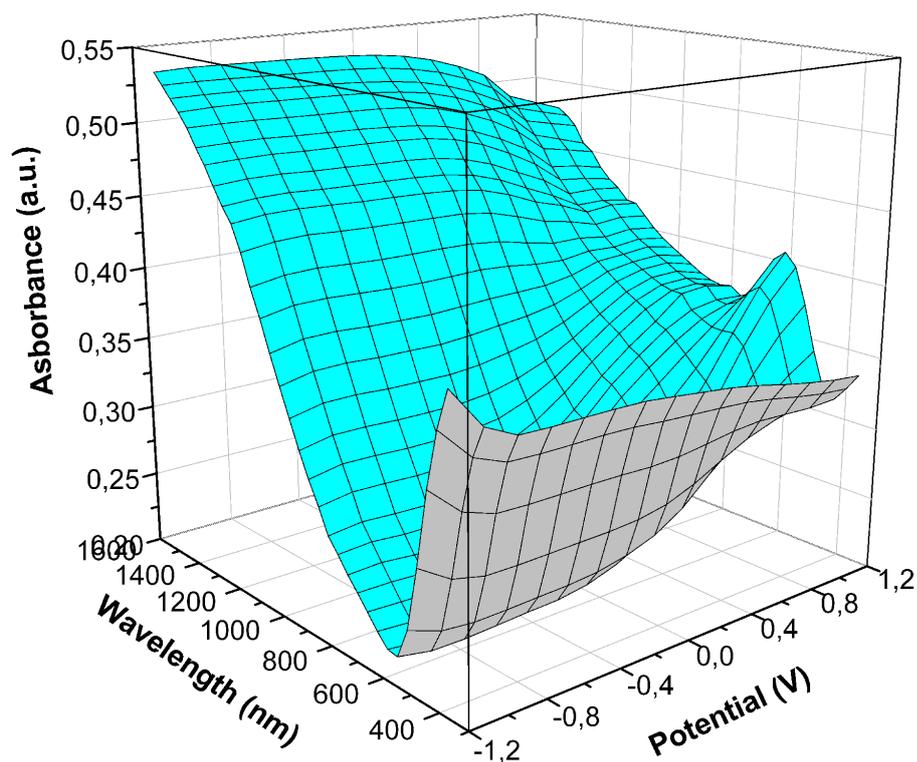
Spectroelectrochemical studies were carried out to examine the optical properties of the ECDs that occur upon doping or dedoping, and to obtain information on the electronic structure. A dual-type ECD consists of two electrochromic materials (one revealing anodic coloration, the other revealing cathodic coloration) deposited on transparent ITO, placed in a position to face each other and with a gel electrolyte in between. The spectral behavior of the absorption/transmission type electrochromic device could be considered as the rough summation of spectral signatures of the two active layers. In order to maintain a balanced number of redox sites for switching, the redox charges of the two complementary polymer films were matched by chronocoulometry.

ECDs were constructed with the following configuration; ITO/ P(SNS-NH<sub>2</sub>) or P(SNS-NH<sub>2</sub>-co-EDOT) || gel electrolyte || PEDOT/ ITO. Their characteristics were investigated. While constructing the electrochromic device, the anodically coloring polymer film P(SNS-NH<sub>2</sub>) was fully reduced and the cathodically coloring polymer, PEDOT, was fully oxidized. Upon application of voltage, the doped polymer will be neutralized, whereas the other component will be oxidized, resulting in the color change. Fig. 3.21 exhibits spectroelectrochemical UV–Vis absorbance of P(SNS-NH<sub>2</sub>)/PEDOT device under miscellaneous applied potentials between -1.2 V and +1.2 V bias to anodically coloring layer. The alternation of the color from yellow to blue was observed upon stepwise increase of the potential between -1.2 V and 1.2 V. The homopolymer was in its neutral state at -1.2 V, where the absorption at 373 nm was due to  $\pi$ - $\pi^*$  transition of the homopolymer. At this potential, PEDOT was in oxidized state showing no pronounced absorption at the UV–Vis region of the spectrum, thus the color of the device was yellow.

As the applied potential increased, the homopolymer layer started to get oxidized, and a decrease in the intensity of the absorption was observed. Meanwhile, PEDOT layer was in its reduced state, which was followed by the appearance of the new absorption at 615 nm, dominating the color of the device as blue.

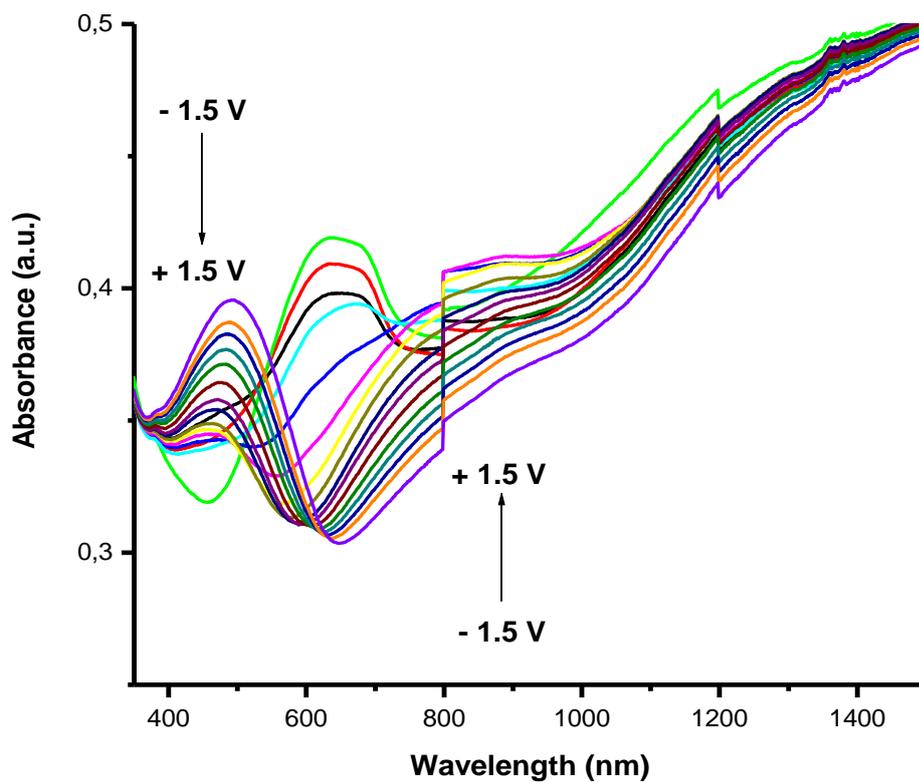


**Figure 3.21** 2D Spectroelectrochemical spectrum of the P(SNS-NH<sub>2</sub>)/PEDOT ECD with applied potentials between -1.2 V and 1.2 V.

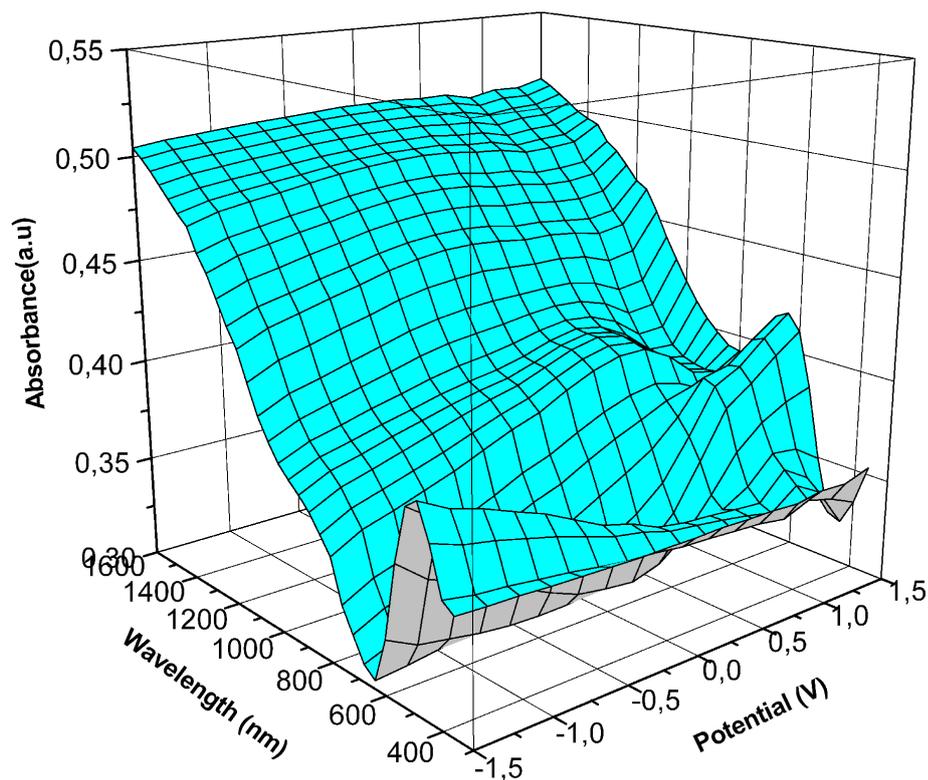


**Figure 3.22** 3D Spectroelectrochemical spectrum of the P(SNS-NH<sub>2</sub>)/PEDOT ECD with applied potentials between -1.2 V and 1.2 V.

The same configuration was used to assemble ECD of the copolymer. The anodically coloring polymer film P(SNS-NH<sub>2</sub>-co-EDOT) was fully reduced and the cathodically coloring polymer (PEDOT) was fully oxidized prior to construction of electrochromic devices (ECD). Optoelectrochemical spectrum of the dual type ECD as a function of applied potential (from -1.5 V to 1.5 V) are given in Figure 3.23. Maximum absorption at 491 nm revealing purple color was observed due to  $\pi$ - $\pi^*$  transition upon application of positive voltages. At that state, PEDOT did not reveal an obvious absorption at the UV-Vis region of the spectrum and device revealed purple color. When the applied potential increased, due to reduction of PEDOT layer, blue color became dominant and a new absorption observed at 633 nm.



**Figure 3.23** 2D Spectroelectrochemical spectrum of the P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT ECD with applied potentials between -1.5 V and 1.5 V.

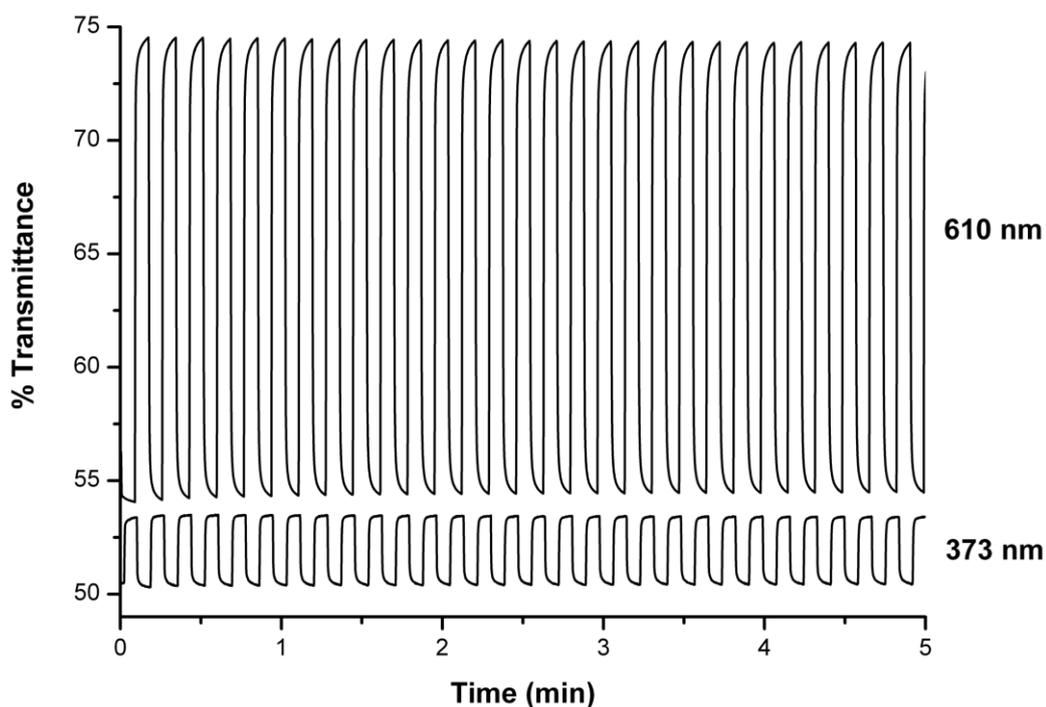


**Figure 3.24** 3D Spectroelectrochemical spectrum of the P(SNS-NH<sub>2</sub>-co-EDOT) /PEDOT ECD with applied potentials between -1.5 V and 1.5 V.

### 3.8.2. Switching of ECDs

Response time, one of the most important characteristics of electrochromic devices, is the time needed to perform switching between two states. Another important parameter is the optical contrast, which can be defined as the transmittance difference between the redox states. Chronoabsorptometry, a square wave potential step method coupled with optical spectroscopy, was performed to estimate the response time of the device and its stability during consecutive scans. In this double potential step experiment, the potential was set at an initial potential for 5 s, and was stepped to a second potential for a set period of time (5 s), before being switched back to the initial potential again. Applied potentials were determined from the spectroelectrochemical studies, where the ultimate states of the devices were achieved.

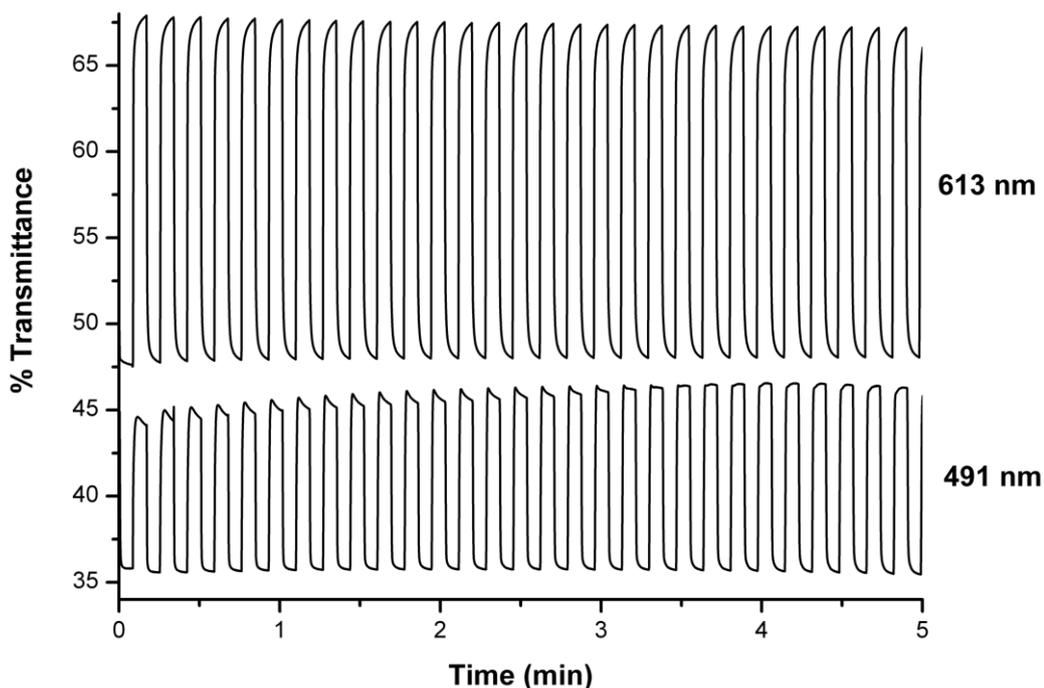
To investigate switching characteristics of the P(SNS-NH<sub>2</sub>)/PEDOT ECD, the transmission and the response time at the maximum contrast wavelength was monitored during repeated redox stepping experiments. For the homopolymer device, a little optical contrast (%T) at 373 nm was measured as 3 % by stepping potential between -1.2 V and + 1.2 V with a switching time of 0.8 s. However, a significant contrast was obtained as 20 % at 610 nm by stepping potential between -1.2 V and + 1.2 V with a switching time of 0.9 s (Fig 3.25).



**Figure 3.25** Electrochromic switching, optical absorbance change monitored at 373 nm and 610 nm for P(SNS-NH<sub>2</sub>)/PEDOT device between -1.2 V and 1.2 V

In order to investigate the electrochromic switching properties of P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device, potential was stepped between -1.5 and 1.5 V with a residence time of 5 s and % T was monitored at 491 nm and 613 nm (wavelength of maximum contrast). For P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device, an optical contrast (%T) at 491 nm was measured as 11 % with a switching time of 0.8 s (Fig. 3.26). Moreover, maximum contrast was observed as 19 % at 613 nm with a switching time of 1.2 s.

The polymer switching time was calculated at 95 % of the full switch because it is difficult to perceive any further color change with the naked eye beyond this point. The P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT showed a more steady graph compared to that of P(SNS-NH<sub>2</sub>)/PEDOT.



**Figure 3.26** Electrochromic switching, optical absorbance change monitored at 491 nm and 613 nm for P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device between -1.5 V and 1.5 V.

**Table 3.6** Electrochromic properties of P(SNS-NH<sub>2</sub>)/PEDOT and P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT ECDs

	Switching Time		Optical Contrast	
	<b>Homopolymer Device</b>	373 nm	610 nm	373 nm
	0.8 s	0.9 s	3 %	20 %
<b>Copolymer Device</b>	491 nm	613 nm	491 nm	613 nm
	0.8 s	1.2 s	11 %	19 %

### 3.8.3. Colorimetry of ECDs

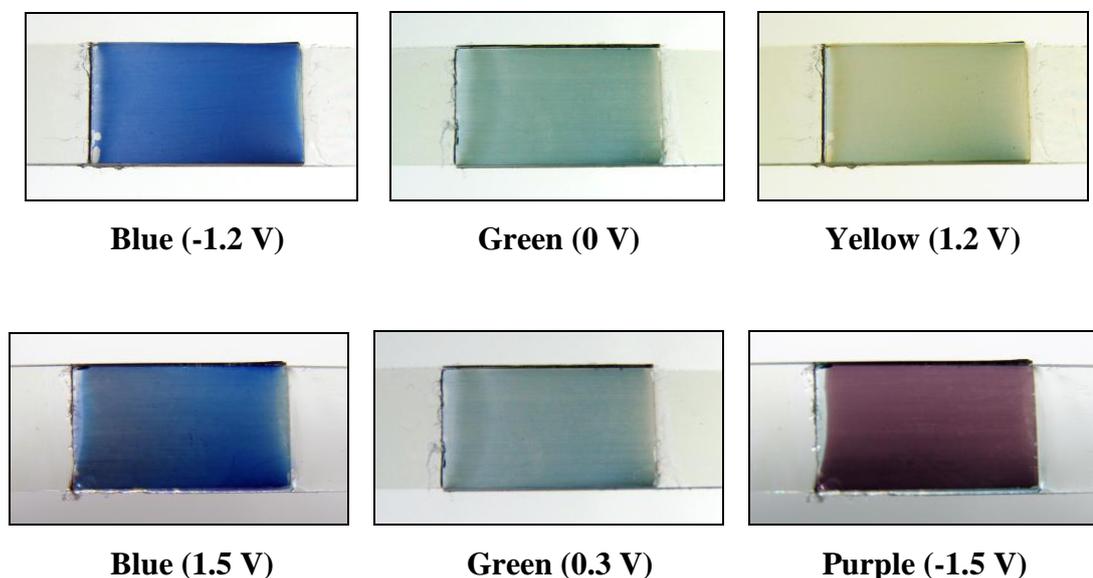
Colorimetry analyses of the ECDs were performed using the same procedure as described earlier. The P(SNS-NH<sub>2</sub>)/PEDOT ECD was yellow at -1.2 V when the P(SNS-NH<sub>2</sub>) layer was in its reduced and PEDOT was in its oxidized state. Blue color was observed at 1.2 V when PEDOT was in its reduced state and P(SNS-NH<sub>2</sub>) layer in its oxidized state. The identifications of the colors (Yxy values) of the device were given in Table 3.7.

When -1.5 V was applied to the P(SNS-NH<sub>2</sub>-co-EDOT), anodically coloring polymer layer, the copolymer was completely reduced and the P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT ECD has purple color. With the application of 1.5 V, the copolymer was entirely oxidized whereas the PEDOT layer was in its neutral state, at this voltage the color of the ECD was blue. At 0.3 V, an intermediate state was observed.

**Table 3.7** Colorimetry data for P(SNS-NH<sub>2</sub>)/PEDOT and P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT ECDs

Electrochromic Device	Color	Y	x	y
P(SNS-NH <sub>2</sub> )/PEDOT	Blue (-1.2 V)	554	0.294	0.337
	Green (0 V)	262	0.246	0.270
	Yellow (1.2 V)	600	0.300	0.342
P(SNS-NH <sub>2</sub> -co-EDOT)/PEDOT	Blue (1.5 V)	185	0.243	0.280
	Green (0.3 V)	291	0.310	0.358
	Purple (-1.5 V)	201	0.341	0.302

**Table 3.8** Colors of the P(SNS-NH<sub>2</sub>)/PEDOT and P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT ECDs at different applied potentials



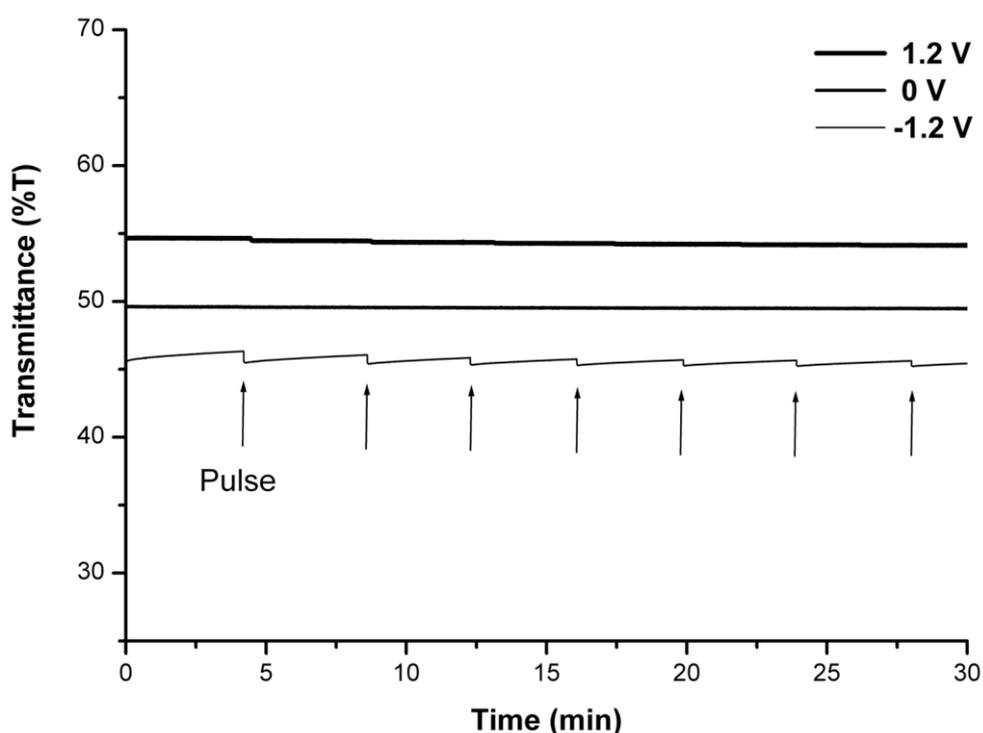
#### 3.8.4. Open Circuit Stability

For an electrochromic device, the color persistence is an important character since it is directly related to its utilization and energy consumption during use. Optical memory is the time during which the material retains its color under open circuit conditions. This property was studied by polarizing the device between two states and measuring its spectra under open circuit conditions at regular time intervals.

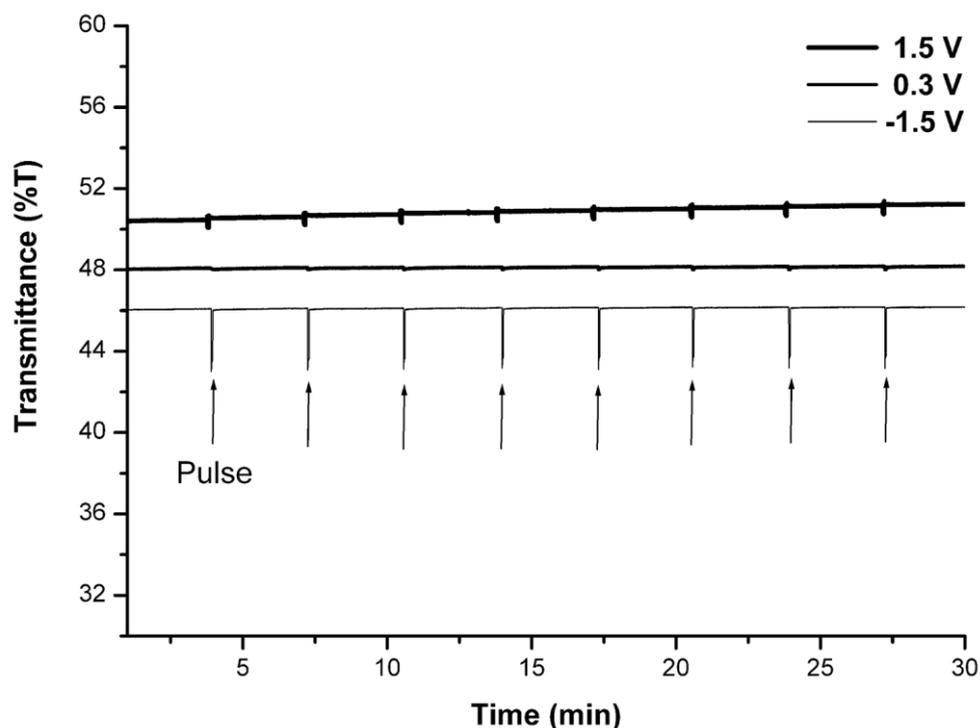
In order to investigate open circuit memory of P(SNS-NH<sub>2</sub>)/PEDOT device, experiments were carried out by polarizing the device in the yellow, green and blue states by an applied pulse for 1s and then holding at open circuit conditions for 200 s. Simultaneously the optical spectrum as a function of time was recorded (Figure 3.27). When polarized in the blue colored state, initially the device presents 46 % transmittance after 200 s, it decreases to 45 % only.

A reasonable optical memory in blue colored state was observed under open circuit conditions. Moreover, P(SNS-NH<sub>2</sub>)/PEDOT device is stable in yellow and green colored states declared by the insignificant variations in %T.

The color persistence in P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT was examined by polarizing the device at purple, green and blue states by an applied pulse (-1.5 V/ 0.3 V/ 1.5 V, respectively) for 1 s and then holding at open circuit conditions for 200 s. At the green colored state, device shows a true permanent memory (Figure 3.28). However, system does not truly reach equilibrium under open circuit conditions in other colored states. However, this matter can be overcome by the application of current pulses to freshen the fully colored states. These results imply the presence of a reasonable optical memory for the device in green colored state.



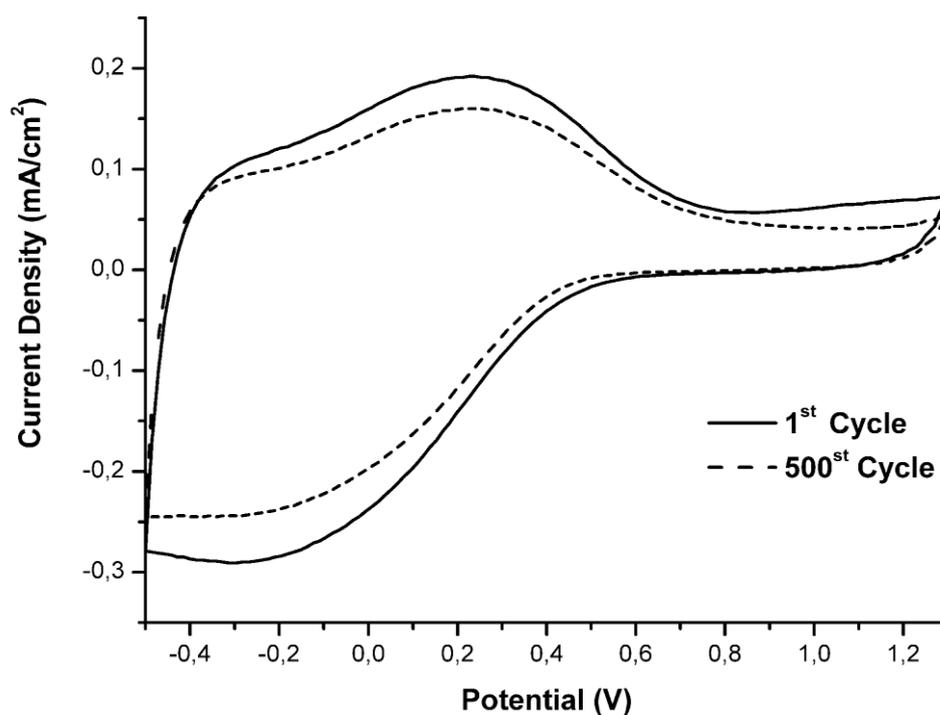
**Figure 3.27** Open circuit memory of P(SNS-NH<sub>2</sub>)/PEDOT device monitored at -1.2 V, 0 V and 1.2 V potentials applied for one second for each 200 seconds time interval at 373 nm.



**Figure 3.28** Open circuit memory of P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device monitored at -1.5 V, 0.3 V and 1.5 V potentials applied for one second for each 200 seconds time interval at 491 nm.

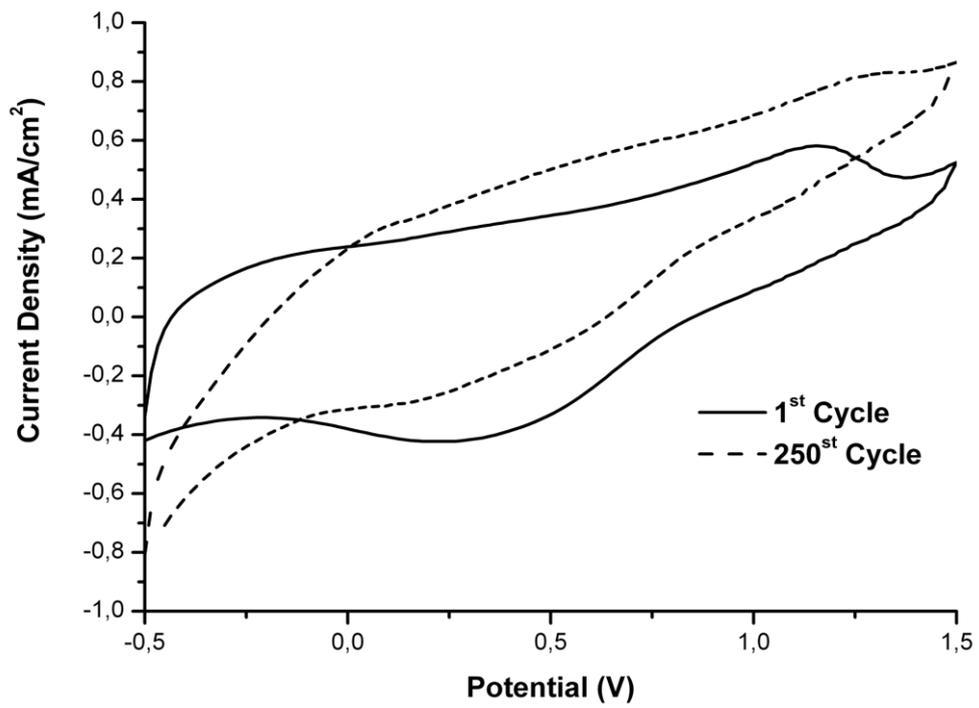
### 3.8.5. Stability of Electrochromic ECDs

The stability of the devices toward multiple redox switching usually limits the use of electrochromic materials in ECD applications. Hence, redox stability is an important requirement for production of reliable electrochromic devices with long lifetimes. Cyclic voltammetry was employed to figure out the long-term stability of devices. Continuous cycling of the applied potential between -0.5 V and +1.3 V for P(SNS-NH<sub>2</sub>)/PEDOT device with 500 mV.s<sup>-1</sup> was performed to analyze the stability of device. Figure 3.29 presents the change in the anodic and cathodic peak currents, as a function of the potential. Device showed only a slight decrease in electroactivity accompanied by unperturbed color change from yellow to blue. The device retained 85 % of its initial color after 500 redox cycles.



**Figure 3.29** Stability test of P(SNS-NH<sub>2</sub>)/PEDOT device via cyclic voltammetry with a scan rate of 500 mV.s<sup>-1</sup>.

The stability measurements for P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device were also carried out by cyclic voltammetry. Non-stop cycling between -0.5 V and +1.5 V for P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT with 500 mVs<sup>-1</sup> was performed to analyze the stability of device. Only a slight decrease in electroactivity accompanied by unperturbed color change from purple to blue was observed after 250 cycles (Figure 3.30). This result revealed that ECD has reasonable environmental and redox stability. Therefore, the device can be operated with applied potentials between -0.5 V and +1.5 V for future applications.



**Figure 3.30** Stability test of P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT device via cyclic voltammetry with a scan rate of 500 mV.s<sup>-1</sup>.

## CHAPTER IV

### CONCLUSION

In this study, a thiophene-functionalized monomer; 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine, and its copolymer with EDOT were successfully synthesized. The polymerization of the monomer was accomplished via both chemical and electrochemical methods. Insolubility is the major limitation of conducting polymers. Synthesis of soluble conducting polymers enables direct application of these polymers to any substrate using conventional printing techniques. In this study, a soluble polymer (CSNS-NH<sub>2</sub>) was obtained as a result of chemical polymerization. The structures of both the monomer and the soluble polymer were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and Fourier Transform Infrared (FTIR) spectroscopy.

Electrochemical synthesis of the conducting homopolymer and copolymer of SNS-NH<sub>2</sub> were achieved in the presence of NaClO<sub>4</sub> (0.1 M) and LiClO<sub>4</sub> (0.1 M) in ACN solvent-electrolyte couple. As a result, free-standing and electrically conducting polymers were obtained. Characterization of the electrochemically synthesized polymers was carried out by FTIR, SEM, spectroelectrochemical analysis, electrochromic switching and colorimetry studies.

Spectroelectrochemistry experiments for the homopolymer revealed  $\pi$ - $\pi^*$  transition and polaron bands at 376 nm and 650 nm respectively. The band gap of the homopolymer was found to be 2.12 eV. Moreover, it was found that 3 s is required to attain 95% of the total transmittance difference. The % $\Delta$ T was found to be 20.7% at 376 nm. For the copolymer,  $\pi$ - $\pi^*$  transition and polaron bands were observed at 488 nm and 1380 nm respectively.

The band gap of the copolymer was calculated as 1.7 eV and 0.6 s was found as the time required to attain 95% of the total transmittance difference. The % $\Delta T$  was measured to be 34 % at 488 nm. Fine tuning of the colors of the polymers was accomplished by copolymerization. Via copolymerization, it was able to tune the color of the polymers between different tones of purple, brown, green, teal and blue. This color variation was followed by UV-Vis spectroscopy where gradual shift of the  $\lambda_{\max}$  was observed. Similarly, compositional changes upon copolymerization were evaluated via FTIR spectroscopy.

Second part of this thesis was devoted mainly to the investigation of spectroelectrochromic properties and electrochromic window applications of these polymers. In recent years, there has been a growing interest on the application of conducting polymers in electrochromic devices. Thus, electrochromic properties of the synthesized conducting polymers were investigated by several techniques like spectroelectrochemistry, kinetic and colorimetry studies. Spectroelectrochemistry experiments were performed in order to investigate key properties of conjugated polymers such as band gap, maximum absorption wavelength, the intergap states that appear upon doping and evolution of polaron and bipolaron bands. Dual-type P(SNS-NH<sub>2</sub>)/PEDOT and P(SNS-NH<sub>2</sub>-co-EDOT)/PEDOT electrochromic devices were assembled with a configuration ITO coated glass/anodically coloring polymer||gel electrolyte||cathodically coloring polymer (PEDOT)/ITO coated glass. The P(SNS-NH<sub>2</sub>)/PEDOT device was operated between -1.2 V and 1.2 V, exhibiting an optical contrast of 3 % at  $\lambda_{\max}$  with a switching time of 0.8 s.

Suitable potential range for operating the copolymer device between purple to blue was found to be between -1.5 V and +1.5 V. Electrochromic switching study results revealed that optical contrast (% $\Delta T$ ) and switching time were 11 % and 0.8 s at 491 nm respectively. Colorimetry is a quantitative analytical tool that has proven an effective objective method to compare and evaluate the optical responses of electrochromic polymers and devices.

Color can be described in terms of three attributes; hue, saturation, and luminance, since the subjective nature of the art, color matching can be difficult. Using CIE methodology of colorimetry, neutral and oxidized colors of all the polymers and devices were determined. Cyclic voltammetry technique was used for the stability experiments of the devices. Results indicated reasonable stability of the devices under atmospheric conditions, where there exists only limited decrease in the current response.

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