SYNTHESIS OF A NEW CONDUCTING POLYMER BASED ON FUNCTIONALIZED ANTHRACENE AND ITS USES AS AN ELECTROCHROMIC DEVICE COMPONENT

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ABSTRACT

SYNTHESIS OF A NEW CONDUCTING POLYMER BASED ON FUNCTIONALIZED ANTHRACENE AND ITS USES AS AN ELECTROCHROMIC DEVICE COMPONENT

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June 2008, 64 pages

2,3-Dihydro-5-(10-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno [3,4-b][1,4]dioxine (DTAT) was synthesized via linking 3,4-ethylenedioxy thiophene (EDOT) on anthracene by Stille coupling. Homopolymer P(DTAT) was achieved by electrochemical techniques. The polymer, P(DTAT) was electrosynthesized by anodic oxidation of the corresponding monomer in the presence of 0.1 M $LiClO_4$ as the supporting electrolyte in acetonitrile (ACN) solution. Copolymer of DTAT in the presence of EDOT was synthesized via potentiodynamic method in ACN/$LiClO_4$ (0.1 M) solvent-electrolyte couple. Structural characterizations of the sample was carried out via ^{1}H-Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Electrochemical behaviors of the monomer and polymers were determined by Cyclic Voltammetry (CV). Electrochromic and spectroelectrochemical behavior of the polymers were investigated on ITO glass electrode, and their ability of employment in device construction was examined. Spectroelectrochemistry analysis of P(DTAT) revealed an electronic transition at 505 nm corresponding to π-π^* transition with a band gap of 1.57 eV. In order to investigate electronic structure of the copolymers obtained by different applied potentials, spectroelectrochemistry studies were performed. Electrochromic investigations showed that P(DTAT) switches between yellow and blue while P(DTAT-co-EDOT) was found to be multichromic, switching between claret red neutral state, a gray and a red intermediate state, and a blue oxidized state. Switching time of the polymers was evaluated by a kinetic study upon measuring the percent transmittance (%T) at the maximum contrast point. Dual type polymer electrochromic devices (ECDs) based on P(DTAT-co-EDOT) with poly(3,4-ethylenedioxythiophene) (PEDOT) were constructed. Spectroelectrochemistry and electrochromic switching of the device was studied. They were found to have good switching times and reasonable contrasts.

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

ÖZ

ANTRASEN TÜREVLİ YENİ BİR İLETKEN POLİMER SENTEZİ VE ELEKTROKROMİK CİHAZ BİLEŞENİ OLARAK KULLANIMI

Yıldırım, Ayşe Gül
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2,3-Dihidro-5-(10-(2,3-dihidrotiyeno[3,4-b][1,4]dioksin-5-yl)antrasen-9-yl)tiyeno [3,4-b][1,4]dioksin (DTAT) ,4-etilendioksi tiyofenin antrasene Stille birleştirme yöntemini kullanarak bağlanması ile sentezlenmiştir. Homopolimer P(DTAT) elektrokimyasal yolla sentezlenmiştir. Monomer elektrokimyasal olarak $LiClO_4$, destek elektroliti varlığında asetonitrilde polimerleştirilmiştir. DTAT'nin EDOT varlığında kopolimeri ACN/$LiClO_4$ çözücü-elektrolit ikilisinde potensiyodinamik metotla sentezlenmiştir.Polimerlerin kimyasal yapıları ^{1}H-Nükleer Manyetik Rezonans (NMR) and Fourier Transform Infrared Spektroskopisi (FTIR) ile karakterize edildi. Monomerin ve polimerlerin elektrokimyasal davranışları Dönüşümlü Voltametri (CV) ile belirlendi. ITO üzerine kaplanmış polimerlerin elektrokromik ve spektroelektrokimyasal davranışları ve elektrokromik cihaz yapımında kullanılabilme yetisi incelendi. Spektroelektrokimyasal analizler P(DTAT)'nin spektroelektrokimyasal analizi sonucu π-π* geçişi 505 nm'de gözlenmiş ve bant aralığı 1.57 eV olarak hesaplanmıştır. Farklı potansiyellerde sentezlenen kopolimerlerin elektronik yapısı spektroelektro yöntemle incelenmiştir.

Elektrokromik çalışmalar sonucunda P(DTAT)'nin sarı ve mavi renk arasında değiştiğini, P(DTAT-co-EDOT)'nin multikromik bir malzeme olduğu; indirgen durumda bordo, ara durumda gri ve kırmızı, yükselgen durumda ise mavi renkleri arasında değiştiği gözlemlenmiştir. Renklerin değişim hızları kinetik çalışma ile yüzde geçirgenliğin en yüksek kontrast farkında ölçülmüştür (T%). P(DTAT-co-EDOT)'in poli(3,4-etilendioksitiyofen) (PEDOT) ile dual tip elektrokromik cihazı yapılmıştır. Cihazın spektroelektrokimyasal özellikleri ve elektrokromik çevirmeleri araştırılmıştır. Cihazın iyi çevirme zamanları ve uygun optik kontrastları olduğu bulundu.

Anahtar sözcükler: İletken Polimerler; Elektrokimyasal polimerleşme; Elektrokromizm; Elektrokromik malzemeler; Elektrokromik cihazlar

TO MY FAMILY

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ABBREVIATIONS

DTAT	2,3-dihydro-5-(10-(2,3-dihydrothieno [3,4b] [1,4]dioxin-5-yl)anthracen-9-yl)thieno [3,4b] [1,4]dioxine
P(DTAT)	Poly(2,3-dihydro-5-(10-(2,3-dihydrothieno [3,4b] [1,4]dioxin-5-yl)anthracen-9-yl)thieno [3,4-b] [1,4]dioxine)
EDOT	3,4-Ethylenedioxythiophene
P(DTAT-co-EDOT)	Poly(2,3-dihydro-5-(10-(2,3-dihydrothieno[3,4 b] [1,4] dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine-co-ethylenedioxythiophene)
Th	Thiophene
Py	Pyrrole
PAc	Polyacetylene
PEDOT	Poly(3,4-ethylenedioxythiophene)
ACN	Acetonitrile
PMMA	Poly(methylmethacrylate)
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectrometer
CV	Cyclic Voltammetry
ECD	Electrochromic Device
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
E_g	Band Gap Energy
CIE	La Commission Internationale de l'Eclairage
L a b	Luminance, hue, saturation

CHAPTER 1

INTRODUCTION

1.1 Conducting Polymers

Conducting polymers have emerged as a new generation of polymers in the last three decades [1]. Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. This perspective is rapidly changing as a new class of polymer known as intrinsically conductive polymer or electroactive polymers are being discovered [2]. The discovery of increase in conductivity of doped polyacetylene (PA) by many orders of magnitude [3] was a major breakthrough in the area of conducting polymers. Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa were awarded with The Nobel Prize in Chemistry for their discovery and elaboration of electronically conducting polymers in 2000.

1.1.1 Historical Survey of Conducting Polymers

The first work describing the synthesis of a conducting polymer was published in 1862 by Letheby [5]. In that time, the "aniline black" was obtained as the product of the anodic oxidation of aniline and its electronic properties were not established. Despite this initial work, in 1970s the discovery of conducting polymers as materials which present reasonable electrical conductivity is attributed to Shirakawa and co-workers, who exposed free-standing films of polyacetylene (PAc) to vapors of chlorine, bromine, iodine, arsenic pentafluoride and sodium, obtaining an increase of twelve orders of magnitude in the conductivity [6]. Polyacetylene $(CH)_x$ is the simplest form of conducting polymer that has the characteristic structure of a conjugated π-system extending over a large number of the chain-linked monomer units [7]. Although polyacetylene is the only conducting polymer that currently exhibits (copper-like conductivity) very high conductivity, its environmental instability, insolubility in solvents and lack of processability preclude its use. A number of scientific works were done to increase its stability and processability of polyacetylene. Unfortunately, the electrical conductivities of the PAc derivatives were much lower than the conductivity of PAc. Naturally, much work has been devoted to develop stable and processable conducting polymer structures. In 1980s aromatic structures and heteroatomic molecules, more stable compared to polyacetylene, were investigated (Figure 1.1).

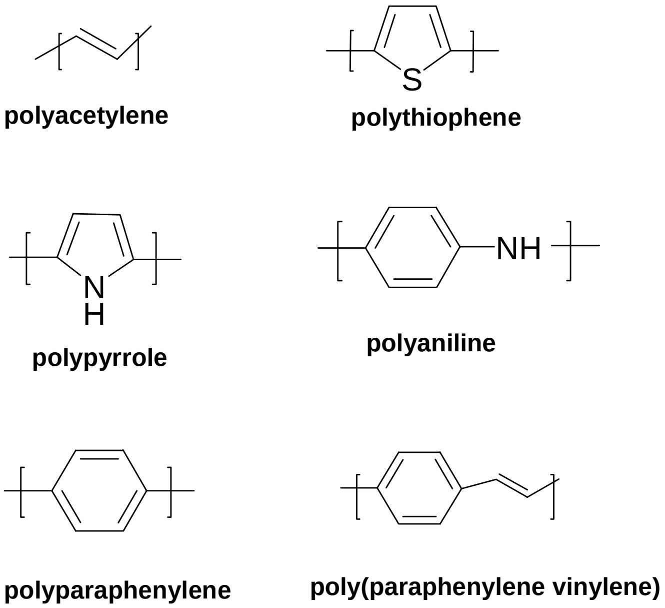


Figure 1.1 Structures of some common conducting polymers

Specifically, in 1979 syntheses of highly conducting (100 S/cm) and homogeneous free standing films of polypyrrole were reported. [8].

In addition to polypyrole, polythiophene [9], polyaniline [10], poly (*p*-phenylene) [11] and poly (p-phenylene vinylene) [12] and their derivatives e.g. poly(3,4-ethylenedioxythiophene) (PEDOT) have been studied extensively for several decades due to their lower oxidation potentials and easily processability than PAc allowing for more diversity of structures. In Table 1.1 conductivities and stabilities of some of these polymers were given. Even though, polyacetylene has the highest conductivity, the stability and processability of heterocycles make them more usefull.

Table 1.1 Conductivities and stabilities of some common conducting polymers

Derivatives of	**Conductivity (S/cm)**	**Stability (doped state)**	**Processing Possibilities**
Polyacetylene	10^3-10^5	Poor	Limited
Polypyrrole	100	Good	Good
Polythiophene	100	Good	Excellent
Polyaniline	10	Good	Good
Polyphenylene	1000	Poor	Limited

1.2 Electrical Conductivity in Conducting Polymers

1.2.1 Band Theory

Materials are typically are classified into three categories according to their room temperature conductivity properties: conductors, semiconductors and insulators. The electrical conductivity, σ, is equal to the product of the carrier mobility, μ, its charge, q, and the number of carrier or the concentration, n.

$$\sigma = \mu\, q\, n$$

Conduction mechanism can be explained using the band theory. The outermost shell of electrons in a material contains the valence electrons and these can be placed in the valence band that defines their lowest energy states. In conducting polymers for conduction to occur, an electron must obtain sufficient energy to promote it to the conduction band. The energy difference between the valence band and the conduction band is known as the band gap (E_g). The energy gap between the valence and conduction band of polymer is related to the lowest allowed energy of its monomer units and to the bandwidth resulting from the overlap between the monomer orbital as shown in Figure 1.2 [13].

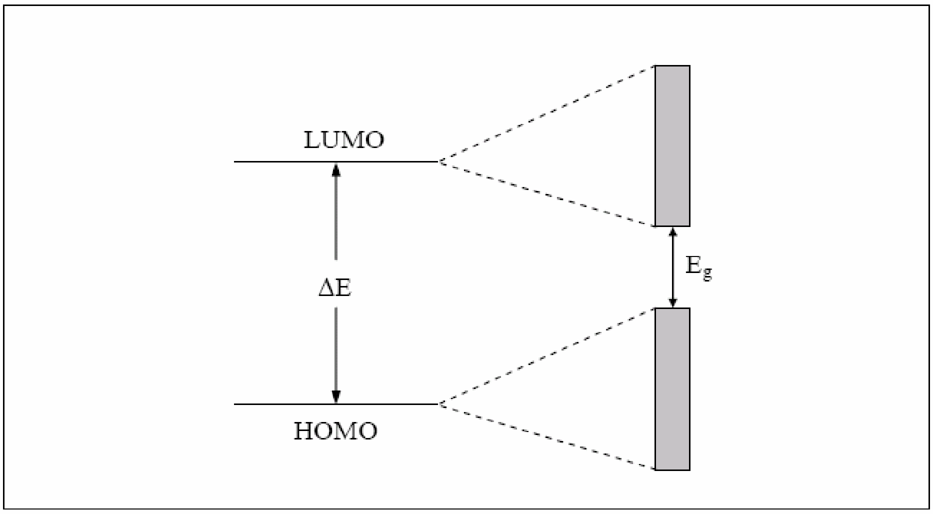


Figure 1.2 Band structure in an electronically conducting polymer

For a conductor (metal), the highest energy level of the valence band and the lowest energy level of the conduction band are similar, meaning that the band gap does not exist and electrons pass easily into the conduction band. For an insulator, the separation between the two bands is large and promotion of an electron to the conduction band is not possible. With semiconductors, the band gap is moderate and limited conduction occurs. Figure 1.3 illustrates the generic band structure for a conductor, a semiconductor and an insulator.

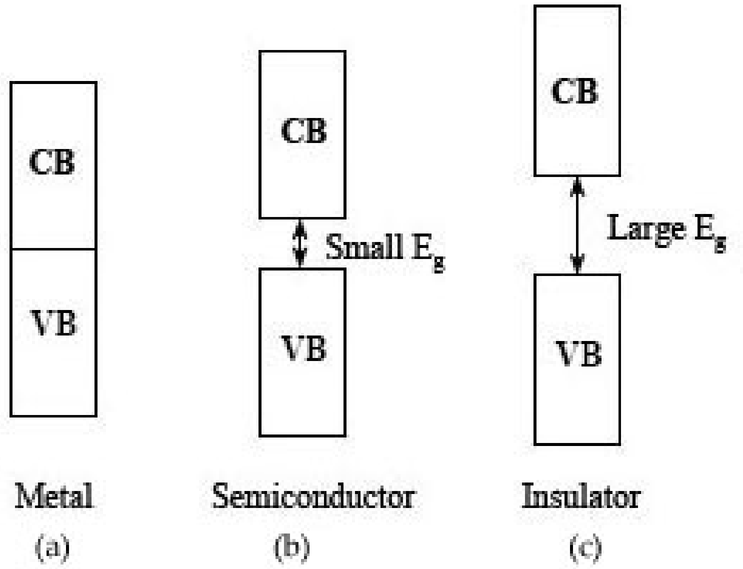


Figure 1.3 Band structure for (a) a metal (b) a semiconductor and (c) an insulator

1.2.2 Conduction Mechanism

1.2.2.1 Charge Carriers

The π-electrons in a neutral conjugated polymer chain are bound in the p-orbitals giving rise to an alternation of single and double bonds. At this state the conjugated polymer has typical semiconducting properties. To conduct electricity, charges have to be introduced into the polymer (removing or adding electrons). This results in the formation of positive or negative charges together with unpaired electrons in the polymer chain (Figure 1.4). The charge together with the distortion of the structure of the polymer is denoted to as a polaron and can be either negative or positive. When two polarons form a couple, a so called bipolaron is generated with a charge of +2 or –2.

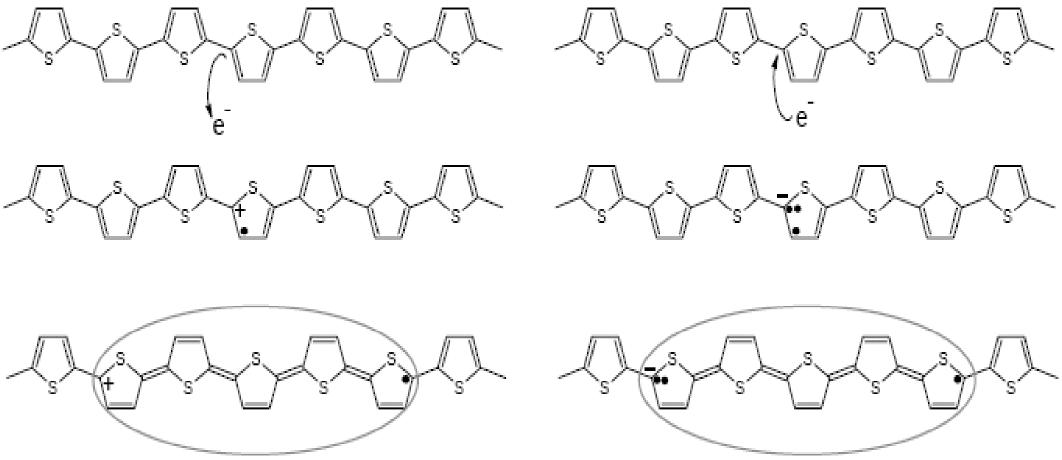


Figure 1.4 The doping of the polymer and creation of a positive (left) and a negative (right) polaron.

The number of free charge carriers can be increased through doping. Chemical doping involves charging the polymer film through chemical oxidation or reduction by dopant species. The dopant, with opposite charge, stays in the film and balances the charge of the polymer. In many electrochemical systems, the polymer film can be doped and dedoped reversibly via oxidation and reduction [14].

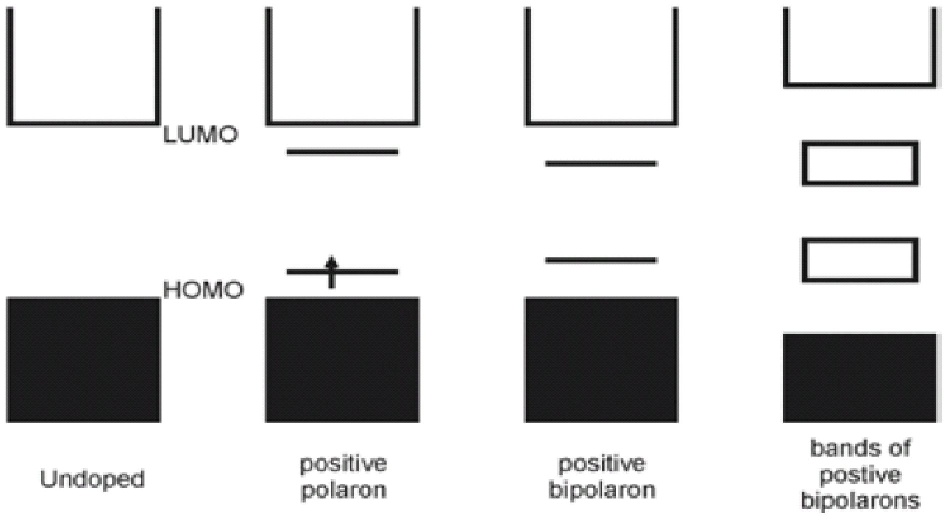


Figure 1.5 Positive polaron and bipolaron in a conjugated polymer. Overlap between charge carriers at high doping levels results in the formation of bands.

Upon doping, the charge carriers alter the structures of the polymer and increase the length of the double bonds and shortens the single bond; thus giving a more quinoid character. This results in a decreased energy splitting between the HOMO and the LUMO levels, moving those states towards each other inside the band gap (Figure 1.5). As the doping level increases, the number of states inside the band gap increases. At high doping levels, the states inside the band gap start to overlap and create bands of bipolaronic states (Figure 1.5).

1.2.2.2 Doping

The term doping originates from the physics field of inorganic semiconductors and is utilized in conducting polymers, as it changes the oxidation state without manipulating the structure. The doping process in conducting polymers as currently understood introduces deformations called solitons, polarons, and bipolarons into the polymer system causing new levels to form in the band gap, increasing the amount of possible energy transitions [15],[16].

In CPs the doping which refers to the oxidation or reduction leads to the carbon chain to become positive or negative respectively. Doping can be accomplished via several methods, chemical, electrochemical, ion implantation and photochemical. In each case, the polymer doping is always accompanied by a counter ion to maintain electro neutrality. The counter ion (dopant) incorporated into the polymer can significantly change its chemical properties and must therefore be carefully chosen based on the desired task.

Chemical doping is carried out on the polymer by either an electron acceptor, through oxidation (oxidant, A) or an electron donor, through reduction (reductor, B), following reaction:

$$\text{p-doping} \qquad (P)_n + A \longrightarrow (P)_n^{+}A^{-}$$

$$\text{n-doping} \qquad (P)_n + B \longrightarrow (P)_n^{-}B^{+}$$

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

In electrochemical doping, the monomer/polymer is exposed to an applied potential, leading to the oxidized or reduced form, which is given in below equations:

$$\text{p-doping} \qquad P + C^{-} \longrightarrow 1/n(P)_n^{+}C^{-} + e^{-}$$

$$\text{n-doping} \qquad P + D^{+} + e^{-} \longrightarrow 1/n(P)_n^{-}D^{+}$$

Both C^- and D^+ are the relevant counterions that are incorporated into the polymer upon its oxidation/reduction to maintain electroneutrality.

Electrochemical doping is preferred to chemical doping as it allows for better control of the doping level. Any doping level can be achieved by the application of a constant potential over a length of time, and the level at which the polymer is doped is directly related to the voltage at electrochemical equilibrium, as determined by a reduction in current to zero. The conductivity of the polymer can be significantly increased from $10^{-10} – 10^{-5}$ S cm^{-1} (non-doped) to ~ $1\text{-}10^{4}$ S cm^{-1} (fully doped). As a result electrochemical doping has more advantages than chemical doping. Conductivity of CPs can be tuned over eight or more orders of magnitude in the same material. The doping level of conducting polymers affects range of conductivity from insulator to metal. Figure 1.6 shows the typical conductivity ranges of the three most common conducting polymers (PA, PPy, PTh).

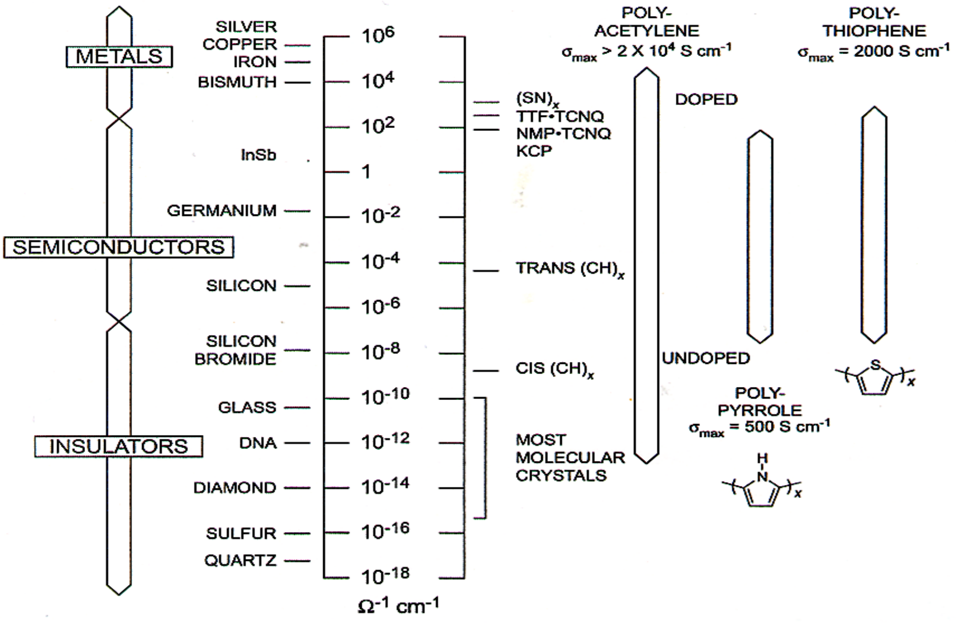


Figure 1.6 Conductivities of some metals, semiconductors and insulators

1.2.2.3 Hopping

The charge transport characteristics of conjugated polymers are, of course, primarily governed by the nature of the polymer backbone itself, but intermolecular interactions also exert an important influence on the macroscopic materials properties. The charge carrier mobility of conjugated polymers is a function of intrachain charge diffusion and interchain interactions, i.e., hopping (Figure 1.7) [17],[18]. Both factors depend on a number of variables; the former is mostly based on the polymer's chemical structure, the number and nature of defect sites, conformation of the polymer backbone, and the molecular weight, while the latter strongly depends on the supramolecular architecture, i.e., the degree of contact, order and orientation [19].

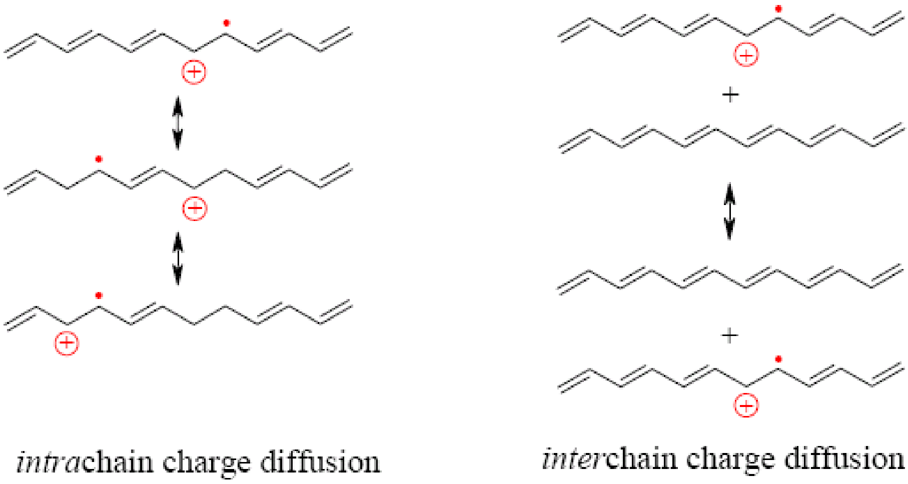


Figure 1.7 Schematic representation of intrachain charge diffusion (left) and interchain charge diffusion (“hopping”, right) in polyacetylene.

The fact that conducting polymers usually show a different dependence of conductivity with temperature than metals has been related to disorder effects, which may dramatically limit interchain interaction charge transport in these systems.

1.3 Synthesis of Conducting Polymers

Electrically conducting polymers (CPs) with conjugated double bonds can be synthesized by electrochemical or chemical polymerization of the corresponding monomers [20],[21]. Other type of techniques used to synthesize conducting polymers includes photochemical polymerization, metathesis polymerization, plasma, pyrolysis and solid state polymerizations [22].

1.3.1 Chemical Polymerization

For preparing conductive polymers in large amounts chemical polymerization is the most useful technique [23],[24]. In chemical polymerization oxidative coupling of heterocyclic ring systems such as pyrrole, thiophene, indole, aniline, etc., utilizing strong chemical oxidants such as ferric chloride, iodine, ammonium persulfate, etc. [25]. 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 upon attack of the oxidants react with monomer molecules, yielding oligomers and then polymers. Chemical polymerization occurs in the bulk of the solution, and the resulting polymers precipitate as insoluble solids. However, a part of conducting polymer can deposit spontaneously on the surface of various materials, immersed into the polymerization solution [26]. In Figure 1.8, oxidative polymerization of a five membered heterocyclic compound with $FeCl_3$ is shown [27].

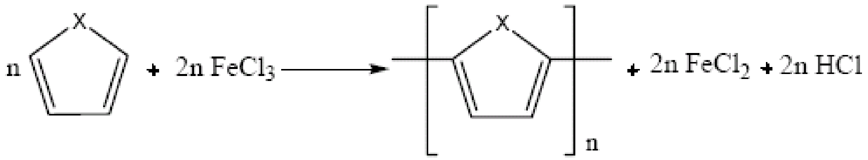


Figure 1.8 Oxidative chemical polymerization of polyheterocycle in the presence of iron (III) chloride

1.3.2 Electrochemical Polymerization

Electrochemical synthesis of conducting polymers offers many advantages over chemical synthesis, including the in situ deposition of the polymer at the electrode surface, and, hence, eliminating processibility problems and the control of the thickness, morphology and degree of polymer doping by quantity of passed charge. In addition, the polymers are simultaneously oxidized to their doped conducting forms during polymer growth.

Electrochemical oxidative polymerization is an easy technique that has been utilized to precisely control the oxidation potential for polymerization and to study the resulting electronic properties of the polymer. Typically, electrochemical polymerization entails oxidative coupling of monomers in a stepwise manner to produce insoluble oligomers that precipitate onto the working electrode surface. Electrochemical syntheses of poly (heterocycles) have been carried out by an anodic or a cathodic route (Figure 1.9). Electrochemical polymerizations carried out in this fashion are low yielding with a predominance of the starting monomer residing in the electrolyte solution after polymerization. Often, due to the rigid character of the polymers, ICPs are infusible and are not soluble in many common organic solvents, thereby leading to major difficulty in their processing [25].

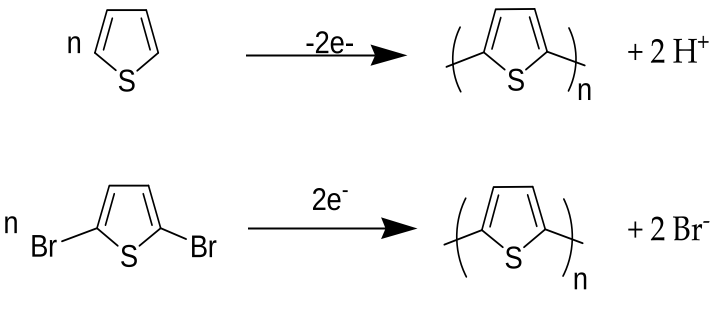


Figure 1.9 Electrochemical synthetic routes to polythiophene

The type of solvent, electrolyte system, choice and concentration of monomer and electrodes strongly affect the properties of the final conducting polymer [28].

1.3.2.1 Mechanism of Electrochemical Polymerization

Electropolymerization is achieved by the electrooxidation of the heterocycle in an inert organic solvent containing supporting electrolyte [29]. A schematic of the generally accepted mechanism for electropolymerization of five membered heterocycles [30] is shown in Figure 1.10. The initial electrochemical step (E) is a one-electron oxidation of the monomer to form its radical cation. A high concentration of these species is maintained at the anode surface because the rate of electron transfer greatly exceeds the monomer diffusion rate to the electrode surface. 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 α – carbon atoms of the heterocyclic ring since these positions have the highest unpaired electron π-spin density and hence reactivity. At the applied potential, the dimer, which is more easily oxidized than the monomer, exists in a radical cation form and undergoes further coupling reactions with other radical cations. This electropolymerization mechanism, according to the general scheme ECE, continues until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the anode surface [31]. However, this mechanism of electropolymerization is greatly simplified with regard to the nature of the rate limiting step and the exact role of oligomers in the initial deposition step, which are remaining unresolved [32].

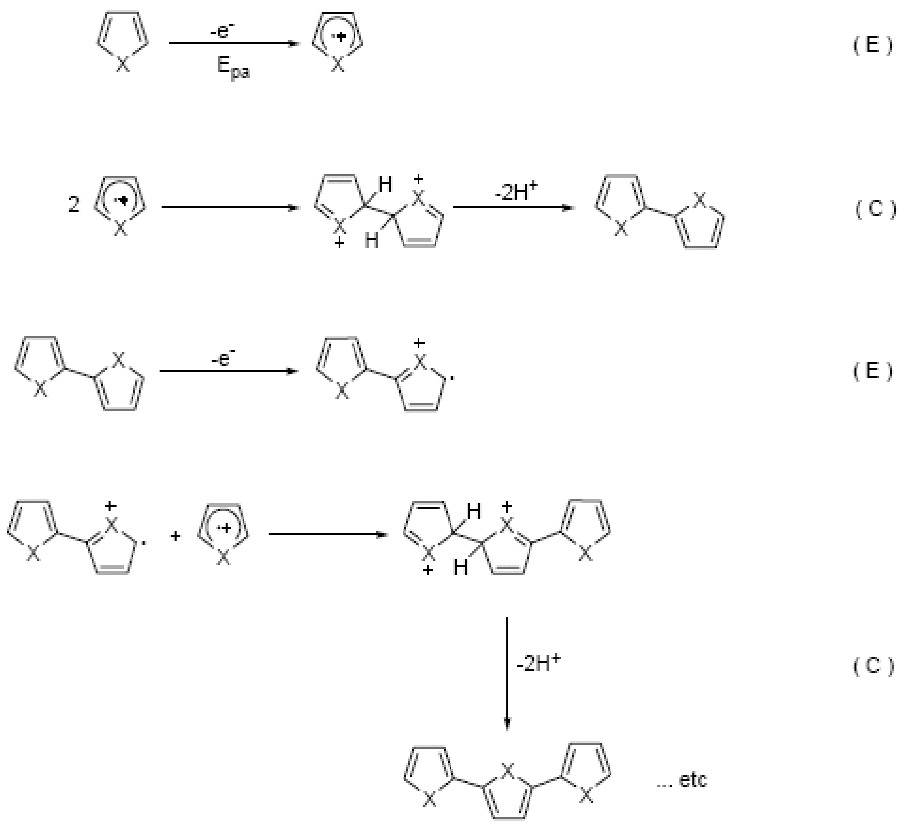


Figure 1.10 Proposed mechanism (ECE) of the electrochemical polymerization of five membered aromatic heterocycles; where X = NH, S or O.

1.3.2.2 Electrolytic Medium

In order for the electropolymerization to proceed as intended, certain conditions in the electrochemistry, solvent, supporting electrolyte, monomer and electrode material must be met.

The solvent used in the electrochemical polymerization needs to have a high enough dielectric constant to ensure sufficient ionic conductivity. The solvent dissolves and dissociates the supporting electrolyte and posses a potential window open at the potentials required to oxidize or reduce polymer. Nitriles are preferred due to their wide range in both oxidation and reduction with a high dielectric constant (ε= 37 for ACN) [28].

The ionic conduction medium between the electrodes is generally called an electrolyte and can be either liquid or solid. The supporting electrolyte depends on the solubility, degree of dissociation and its nucleophilicity. Morphology of the resulting film is significantly affected by the nature of electrolyte used. Supporting electrolyte used in electrochemical polymerization makes electrolytic bath solution conducting and dopes the polymer by allowing one of its ions to couple with monomer unit. Lithium or tetraalkylammonim salts of either ClO_4^- or BF_4^- are generally used as supporting electrolytes in conducting polymer synthesis [34].

The monomer should be in a relatively high concentration in order to avoid competitive reactions of the free radicals. At low monomer concentrations the polymer can undergo degradation instead of deposition. As the oxidation potential of the monomer decreases, the number of competitive reactions decreases, hence, even milimolar concentrations can be used for efficient polymerization [33].

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

1.3.2.3 Monomer Structure

Conducting polymers are synthesized to design new and novel structures, to increase the conjugation length and also the conductivity, processability, solubility in certain solvents [35].

Electron-rich heterocycles such as Th and Py are the most common monomers for electropolymerization because of their availability and relative ease of polymerization. Since PTh have 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.

Non-α,α′-linkages (e.g. α,β′ and β,β′ couplings (Figure 1.11)) can occur to variable extents, causing breaks in the conjugation and hence, reduction in film conductivity. Substitution of monomers at the 3 or 4 positions by the attachment of various alkyl and alkoxy groups protect the monomer against β coupling [36].

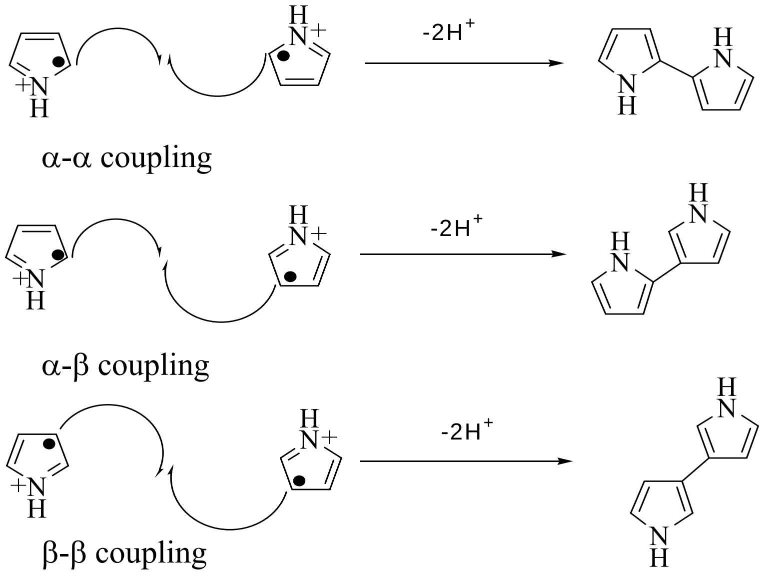


Figure 1.11 Potential coupling reactions for pyrrole during oxidative polymerization

Pyrroles and thiophenes substituted at the 3-(β-) position (and also the *N*-position for pyrrole) can often undergo electropolymerization to produce conducting polymers, since the 2- and 5-(α-) positions remain available for monomer coupling [37].

Thiophenes substituted by electron withdrawing groups have higher oxidation potentials than Th and introduction of electron donating groups to Th decreases the oxidation potential with respect to Th [38]. The solubility of polymers is possible by substitution with long alkyl chains [39]. Polythiophenes containing alkyl [40] and alkoxy [41] β–substituents are soluble in common organic solvents in the conducting state, considerably aiding processibility and characterization of these electroactive materials. Poly-(3 alkythiophenes) with alkyl groups with chain lengths equal or greater than four carbons (i.e. butyl) are readily soluble in THF, dichloromethane, chloroform, benzene, toluene, xylene, benzonitrile and nitrobenzene at room temperature.

1.4 Conducting Copolymers and Composites

Copolymerization is a general process to expand the range of properties of polymers and to create self-assembling supramolecular structures. In this process 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 addition to the variation of comonomers, the copolymer microstructure (random, alternating, block, graft) also plays a large role on the properties.

Electrochemical polymerization of the conducting component on an electrode previously coated with the insulating polymer is one of the most widely used methods for copolymerization. A second type of copolymer involves two electroactive monomers. Today, the synthesis of copolymer is mainly performed with 3,4-ethylenedioxythiophene (EDOT) that is superior to its parent polythiophene in many categories crucial to organic electrochromic materials such as rapid switching and lower oxidation potentials [42]. In this way, the resultant copolymer could indicate better electrochemical and optical properties than its homopolymers.

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 [43]. 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.

1.5 Characterization of Conducting Polymers

To gain a deeper understanding of the electrochromic processes in conjugated polymers, multiple characterization methods have been developed. For the characterization of conducting polymer, cyclic voltammetry has been commonly used to study potentials at which oxidation or reduction process occurs and the degree of reversibility of the electrode reaction [44].

FTIR spectroscopy has always found wide applications in the characterization of polymeric materials due its ability to differentiate between functional groups, to identify specific polymer systems in addition to its speed and low cost [45].

Furthermore, nuclear magnetic resonance for structure confirmation, chain orientation and molecular motion, gel permeation chromatography for molecular weight, differential scanning calorimety and thermogravimetric analysis for evidence of glass and melting transitions and decomposition temperatures are the other techniques used for conducting polymer characterization.

1.6 Applications of Conducting Polymers

Conjugated polymers have been applied to many areas. In the neutral state, conjugated polymers are utilized as semiconductors in electronic devices such as light emitting diodes (LED) [46], field effect transistors (FET) [47],[48], nonlinear optical (NLO) devices, photovoltaic cells, solar cells, chemical, biochemical and thermal sensors. In the doped state, conjugated polymers are used as electrostatic dissipation materials, electromagnetic shielding materials and electronic conductors. In addition, the reversible switching between neutral and doped states leads to the construction of electrochromic devices, battery electrodes and biosensors.

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.

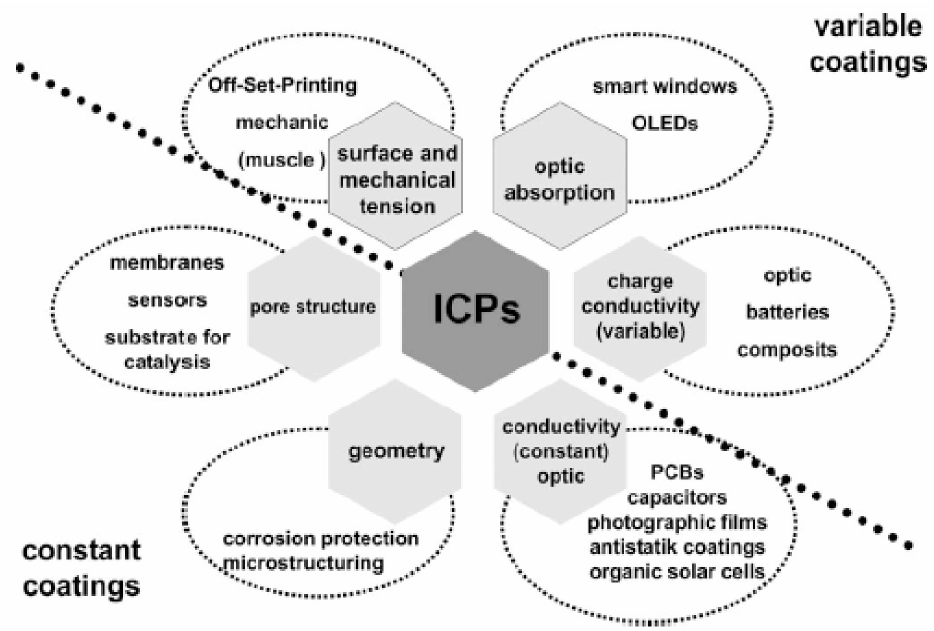


Figure 1.12 Applications of conducting polymers.

1.7 Electrochromism

Electrochromism is defined as the electrochemically induced color change. In particular, it is the change in optical absorption bands brought on by an electrochemical redox reaction in a material. A discussion of electrochromism first appeared in the literature in the early 1960's [49].

Metal oxides such as WO_3 [50], metal complexes [51] and conjugated polymers [52] are presently known electrochromic materials. Conjugated polymers are a third class of electrochromic (EC) materials that have gained popularity due to their ease of processability, rapid response times, high optical contrasts, and the ability to modify their structure to create multi-color electrochromes. Of the conjugated EC polymers, derivatives of PTh, PPy, and PANI are widely studied [53]. Conjugated polymers, while not as developed as the other systems, promise high contrast ratios, rapid response times, and long lifetimes for use in EC display technology.

Electrochromism in conjugated polymers occurs through changes in the conjugated polymer's π-electronic character accompanied by reversible insertion and extraction of ions through the polymer film upon electrochemical oxidation and reduction. In their neutral (insulating) states, these polymers show semiconducting behavior with an energy gap (Eg) between the valence band (HOMO) and the conduction band (LUMO). Upon electrochemical or chemical doping ("p-doping" for oxidation and "n-doping" for reduction), the band structure of the neutral polymer is modified generating lower energy intra-band transitions and creation of charged carriers (polarons and bipolarons), which are responsible for increased conductivity and optical modulation.

1.7.1 Types of Electrochromic Materials

There are three main types of electrochromic materials in terms of their electronically accessible optical states. The first type includes materials with at least one colored and one bleached state. These materials are especially useful for absorption/transmission-type device applications such as smart windows and optical shutters. Typical examples of this area are metal oxides, viologens, and polymers such as 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 [54].

1.7.2 Spectroelectrochemistry

Spectroelectrochemistry plays a key role in examining the optical changes that occur upon doping or dedoping of conducting polymers. It provides information about the electrochromic polymer's band gap and intraband states created upon doping. Spectroelectrochemistry is crucially important in determination of π to π^*, polaronic and bipolaronic transitions in addition to calculation of band gap energy.

1.8 Electrochromic Devices (ECD)

A solid-state device that changes color upon application of an external bias is called an electrochromic device (ECD). Such devices can be assembled into a display. Electrochromic displays are passive; that is, they require external lighting to view. Therefore, the primary competing technology is liquid crystal displays (LCD's). The advantages of ECD's for display application are the persistent image with little or no additional power input, the ability to make large area displays, and the ability to use polyelectrochromic materials for multiple colors per pixel. Currently commercial applications for ECD's include darkening rear-view mirrors (Baucke 1987) and limited display applications.

The electrochromic devices presented in this work are constructed using the sandwich structure illustrated in Figure 1.13. An anodically coloring and cathodically coloring polymers are coated electrochemically on two pieces of ITO glasses and a gel electrolyte layer is applied on coated surfaces. The two are then pressed together and dried overnight. In this device structure the ITO layer at which the redox reaction takes place is working electrode and the other ITO layer is referred to as the counter electrode since it is the electrode that completes the circuit. The device is operated with the working electrode biased as the anode and the counter electrode as the cathode. Upon application of the external voltage, the anions in the electrolyte diffuse into the polymer layer and oxidize it near the working electrode [49].

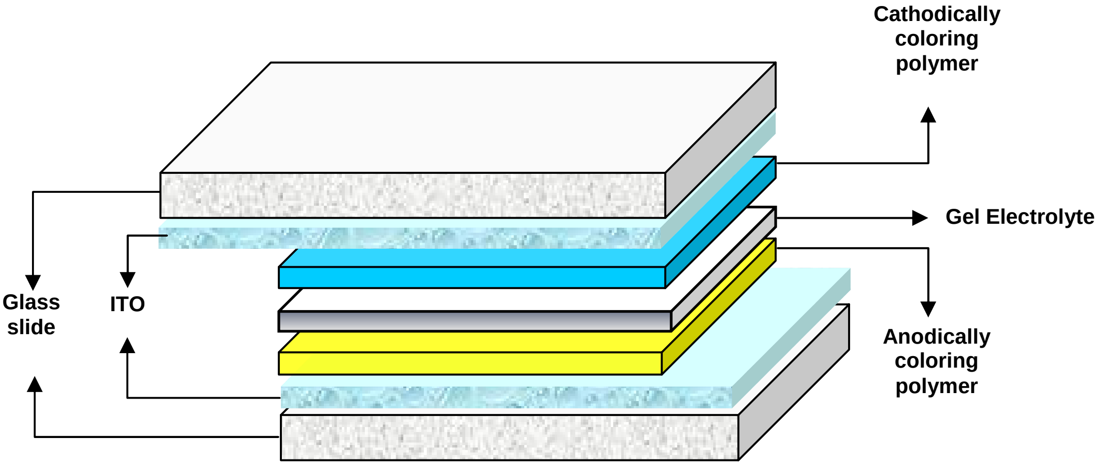


Figure 1.13 Schematic representation of ECDs

The requirements for high performance electrochromic devices are: a) high electrochromic efficiency, expressed in $cm^2\ C^{-1}$ and related to the injected charge in the material to change its color; b) short 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, and f) color uniformity [55].

1.9 Characteristics of Electrochromic Device

The analysis of an ECD typically consists of measuring the change in the absorption of the polymer layer in the non-doped and the doped state. Properties of interest of an ECD determined in this way include $\%\Delta T$, or the change in percent transmission, measuring the current and time of voltage application also allows the characterization of the response time and the coloration efficiency [49].

1.9.1 Electrochromic Contrast and Switching Speed

Electrochromic contrast is probably the most important factor in evaluating an electrochromic material. It is often reported as a percent transmittance change ($\%\Delta T$) at a specified wavelength where the electrochromic material has the highest optical contrast. Switching speed is often reported as the time required for the coloring/bleaching process of an electrochromic material. 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 [54].

1.10 Colorimetry

When light hits our eyes, it is absorbed by the rods and cones on the retina and transformed into nerve signals translated into a perception of color by the brain. Since humans have a three-dimensional color space, many of the existing color systems have three coordinates. In electrochromic materials, three pixels with red, green and blue (RGB) color are used to span color space. The RGB color system is practical for creating a display but is actually not a good description of the full color space accessible with human eyes. In 1931, the International Commission on

Illumination (Commission Internationale de l'Eclairage, CIE) developed a model defining colors by three coordinates by *X*, *Y* and *Z*, corresponding to different biological receptors in the human eye (Figure 1.14).

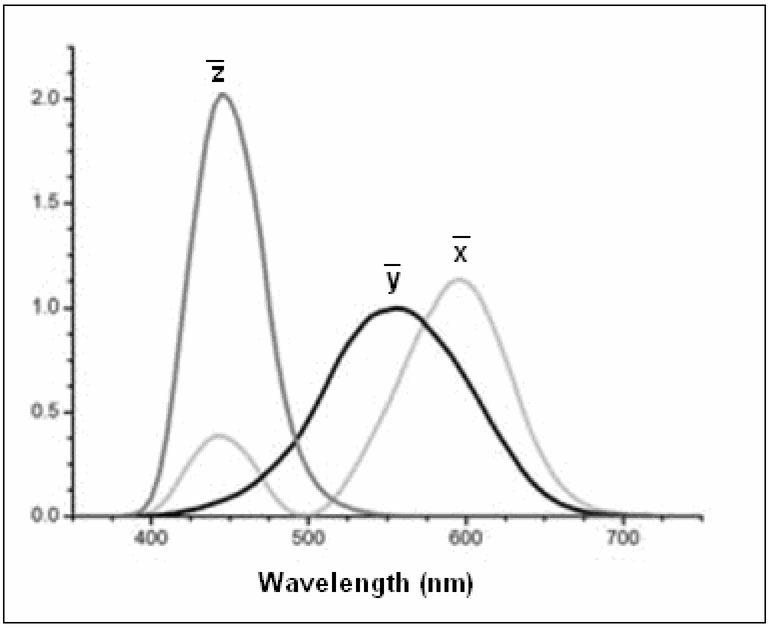


Figure 1.14 The experimentally measured x, y and z, which correspond to the sensitivity of the various receptors in the human eye.

The model was improved in 1976 to be able to further adapt to the way the human eye perceives colors by introducing the CIE L, a, b color system, where the non-linear behavior of the eye is considered. In the CIE L, a, b system the color is represented by L, a and b coordinates. L gives the luminance (lightness), while *a* refers to hue, dominant wavelength, or chromatic color, and *b* known as the saturation, chroma, tone, or purity (Figure 1.15). L has values from 0 (dark) to 100 (light), a ranges from –128 (green) to 127 (red) and b from –128 (blue) to 127 (yellow) [14].

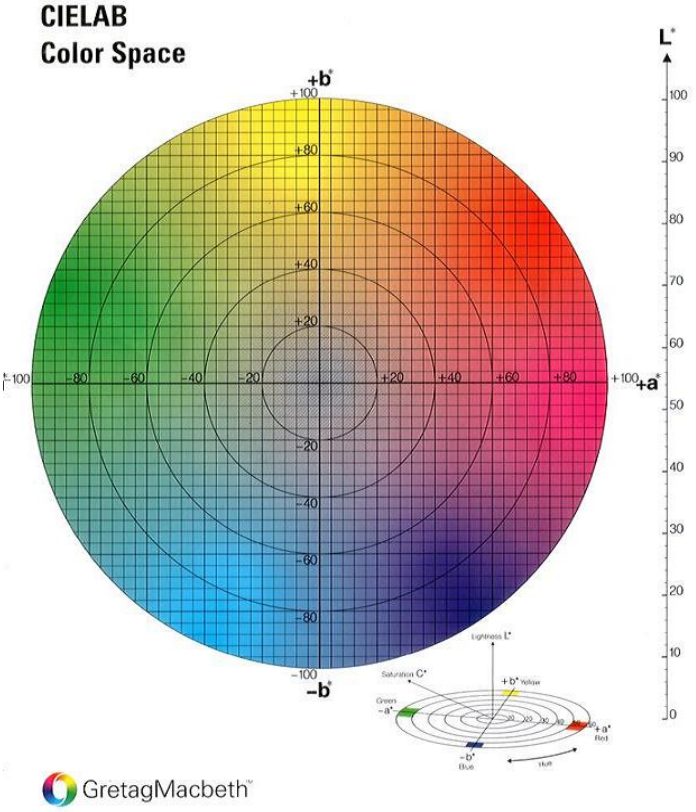


Figure 1.15 The CIE L, a, b color system.

1.11 Aims of the Work

Aims of this work are;

i) To synthesize target monomer named as 2,3-dihydro-5-(10-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine (DTAT) and characterize it together with its polymer

ii) To electrochemically polymerize or copolymerize DTAT with a comonomer (EDOT)

iii) To examine the electrochromic properties of the homopolymers and copolymers and construct electrochromic devices with PEDOT

iv) To evaluate the electrochromic performances of the device

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Bromine, acetone, EDOT, *n*-butyl lithium and tributyltin chloride were obtained from Aldrich Chemicals and used as received. Acetic acid (Aldrich) and dry tetrahydrofuran (THF) (Aldrich) were used without further purification. The electrolysis solvents, acetonitrile (ACN) and dichloromethane (DCM) (Merck) were used without further purification. The supporting electrolyte, lithium perchlorate (LiClO4) (Aldrich) was used as received.

2.2 Instrumentation

2.2.1 Potentiostat

A VoltaLab PST050 and a Solartron 1285 Potentiostats were used to provide constant potential in the electrochemical polymerization. This device can attain to keep the voltage difference between the working and reference electrodes at a constant desired value during the electrolysis and compensates for the voltage drop in the electrolysis solution.

2.2.2 Cyclic Voltammetry System

Cyclic voltammetry measurements were carried out by cycling the potential of the working electrode with respect to a reference electrode and measuring the resulting current.

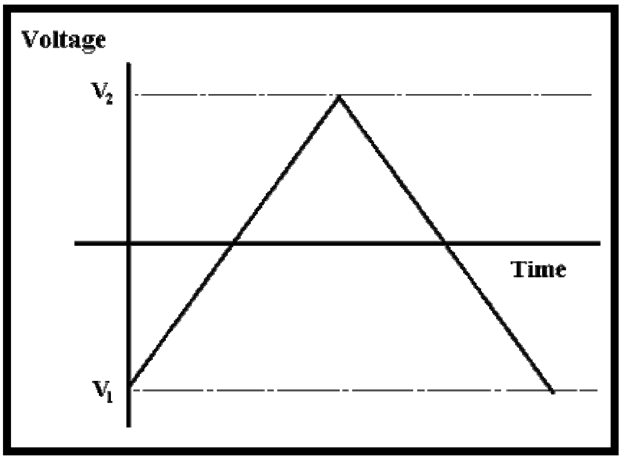


Figure 2.1 Triangular wave function

In cyclic voltammetry (CV) the current response is measured while the potential is linearly increases from an initial potential to a peak potential and back to the initial potential again.

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

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

$$i_p = (2.69 \text{ x } 10^5)n^{3/2}AD^{1/2}C^bV^{1/2}$$

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

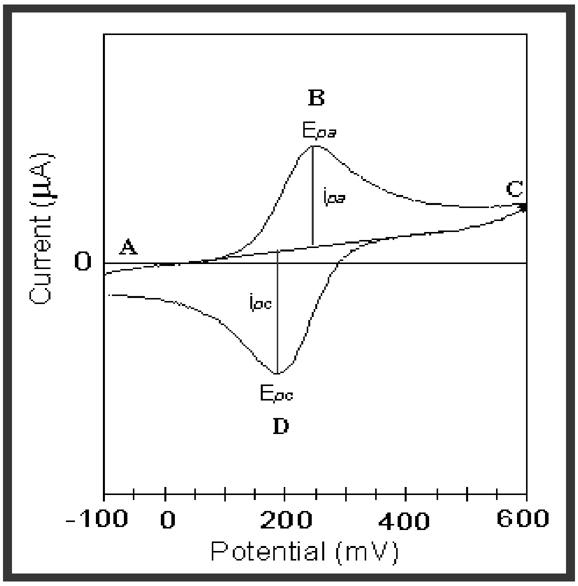


Figure 2.2 A cyclic voltammogram for a reversible redox reaction

The cyclic voltammetry system consists of a potentiostat, an XY recorder and a CV cell. The cyclic voltammetry cell (Figure 2.3) consists of a platinum bead working electrode 1 cm in length, a platinum spiral counter electrode made from 3 cm wire, and a Ag/Ag$^+$ reference electrode. The total volume of cell was about 15 mL. The VoltaLab PST050 potentiostat was used to provide voltage. An X-Y recorder was used to obtain the voltammograms.

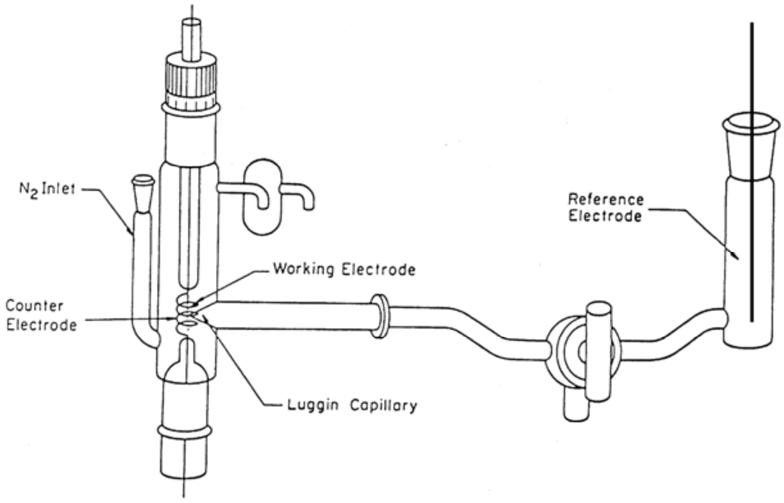


Figure 2.3 Cyclic voltammetry cell

2.2.3 Electrolysis Cell

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

2.2.4 Nuclear Magnetic Resonance (NMR)

^{1}H-NMR spectrum of the sample was recorded on a Bruker Spectrospin Avance (DPX-400) Spectrometer using $CDCl_3$ as the solvent.

2.2.5 Fourier Transform Infrared Spectrometer (FTIR)

The FTIR spectra of monomer (DTAT), homopolymer P(DTAT) and copolymer P(DTAT-co-EDOT) was recorded on Varian 1000 FTIR spectrometry, where samples were dispersed in KBr.

2.2.6 UV-VIS Spectrophotometer

Varian Cary 5000 UV-Vis-NIR spectrophotometer and Agilent 8453 UV-Vis spectrophotometer were used in order to perform the spectroelectrochemical studies of the polymer and copolymer and the characterization of their devices.

2.2.7 Colorimetry Measurements

Colorimetry measurements were done via Minolta CS-100 spectrophotometer.

2.3 Procedure

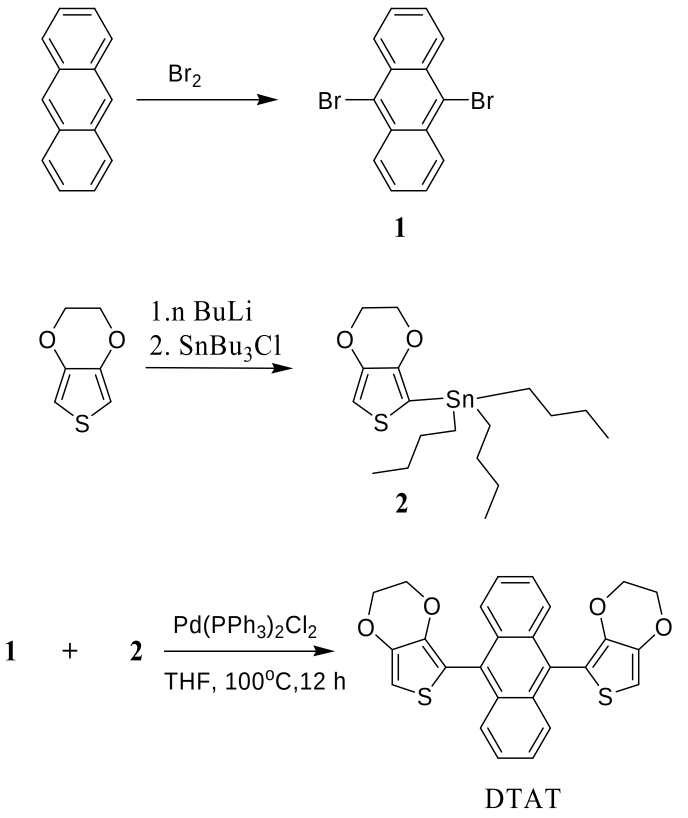
2.3.1 Synthesis of Monomer

2.3.1.1 Synthesis of 9,10-Dibromoanthracene

Bromine (17.9 g, 5.8 mL, 0.112 mol) in acetic acid (50 mL) was added dropwise over a period of 5 minutes to a vigorously stirred suspension of anthracene (10.0 g, 0.056 mol) in acetic acid (300 mL) at room temperature. Since during the reaction HBr evolves, the reaction is connected to gas trap (bubbler containing 1 M NaOH solution). The reaction was stirred for 30 minutes during which a canary yellow precipitate formed. Water (300 mL) was added, the suspension was stirred for 10 minutes, then filtered and washed with water. The yellow solid was dried in vacuum for 24 hours to give the 9,10-dibromoanthracene.

2.3.1.2 Synthesis of 2,3-dihydro-5-(10-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine monomer

A palladium-catalyzed Stille coupling was used as the key reaction to build the target molecule (DTAT). Synthetic approaches of necessary intermediates are outlined in Scheme 2.1. 9,10-Dibromoanthracene (**1**) was prepared with bromine in acidic medium in accordance with above procedure [56]. Tributyltin substituted EDOT (**2**) was prepared in 70% yield by lithiation with *n*-butyl lithium and subsequent quenching with tributyltin chloride [57]. Through coupling of tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (4mmol) (**2**) with **1** (1mmol) in THF (100mL) , 2,3-dihydro-5-(10-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine (DTAT) was obtained in 41% yield. Column chromatography (silica, hexane/DCM, 3:2) gave DTAT as a yellow solid.



Scheme 2.1 Stille coupling route to EDOT-anthracene (DTAT)

2.4 Potentiodynamic Study of Polymers

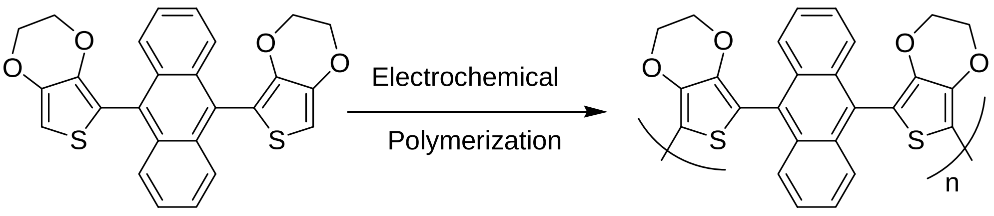
CV was employed in order to assay the electroactivity of the polymers and to accomplish the oxidation-reduction peak potentials of the polymer. The measurements were achieved at room temperature under nitrogen atmosphere using $LiClO_4$ (0.1 M) / ACN solvent-electrolyte couple. A background voltammogram was run to ensure that no impurity was present before the addition of substrate. Experiments were carried out sweeping the potential between - 0.8 V and +1.3 V with 200 mV/sec scan rate. Solution contained $1.3x10^{-3}$ M DTAT.

For the investigation of oxidation and reduction potentials of P(DTAT-co-EDOT) copolymer, same conditions were employed and the solutions contained $1.3x10^{-3}$ M EDOT in addition to $1.3x10^{-3}$ M DTAT. The potential was swept between -0.8 V and +1.3 V with 200 mV/sec scan rate.

2.5 Electrochemical Synthesis of P(DTAT) and P(DTAT-co-EDOT

2.5.1 Synthesis of Homopolymer of DTAT

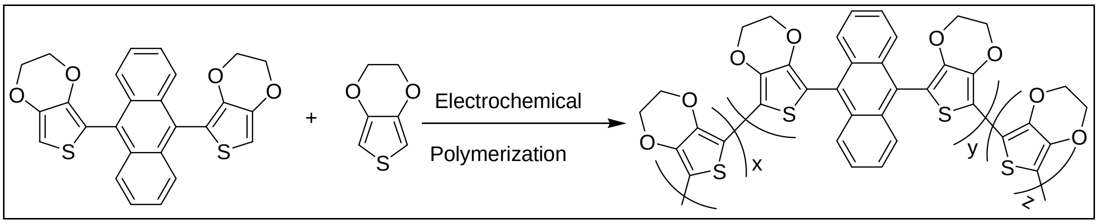
Electrochemical polymerization of DTAT was carried out by sweeping the potential between -0.8 V and +1.3 V with 200 mV/sec scan rate, in the presence of $1.3x10^{-3}$ M DTAT in $LiClO_4$ (0.1 M)/ACN solvent-electrolyte couple. The working and counter electrodes were Pt wires and the reference electrode was Ag wire electrode. P(DTAT) was washed with ACN in order to eliminate excess $LiClO_4$ and unreacted monomer after the potentiodynamic electrochemical polymerization.



Scheme 2.2 Electrochemical polymerization of DTAT in $LiClO_4$ (0.1 M)/ ACN

2.5.2 Synthesis of Copolymer of DTAT with 3,4-Ethylenedioxythiophene (EDOT) P(DTAT-co-EDOT)

The potentiodynamic polymerization of DTAT with EDOT was carried out in a solution containing 1.3×10^{-3} M DTAT and 1.3×10^{-3} M EDOT in $LiClO_4$ (0.1 M)/ACN solvent-electrolyte couple by sweeping the potential between -0.8 V and +1.3 V with 200 mV/sec scan rate in a one compartment cell with ITO electrode as the working electrode, platinum wire as the counter electrode and Ag wire as a pseudo reference electrode (Scheme 2.3). P(DTAT-co-EDOT) was washed with ACN in order to remove excess $LiClO_4$ and unreacted monomer after the potentiodynamic electrochemical polymerization.



Scheme 2.3 Electrochemical copolymerization of DTAT with EDOT

2.6 Investigation of Electrochromic Properties of Polymers

2.6.1 Spectroelectrochemical Studies

Homopolymer film was potentiodynamically deposited on indium tin oxide (ITO) coated glass slides by sweeping the potential between -0.8 V and +1.3 V in the presence of 1.3×10^{-3} M DTAT and ACN/$LiClO_4$ (0.1 M) solvent-electrolyte couple. For the investigation of copolymer, same conditions were used while the solution contained 1.3×10^{-3} M EDOT.

Spectroelectrochemical studies of the homopolymer film were carried out sweeping the potentials between -0.6 V and +1.0 V in a monomer free DCM/$LiClO_4$ (0.1 M) solution while spectroelectrochemical series were taken at the same time.

Spectroelectrochemical studies of the copolymer film were carried out sweeping the potentials from -0.6 V to +1.0 V in the monomer free DCM/$LiClO_4$ (0.1 M) solution while spectroelectrochemical series were in situ taken.

2.6.2 Switching Properties of Polymers

After coating the polymers on ITO electrode, a potential square wave was applied in the monomer free DCM/$LiClO_4$ (0.1 M) solution while recording the percent transmittance between its neutral and doped states at a fixed maximum absorption wavelength.

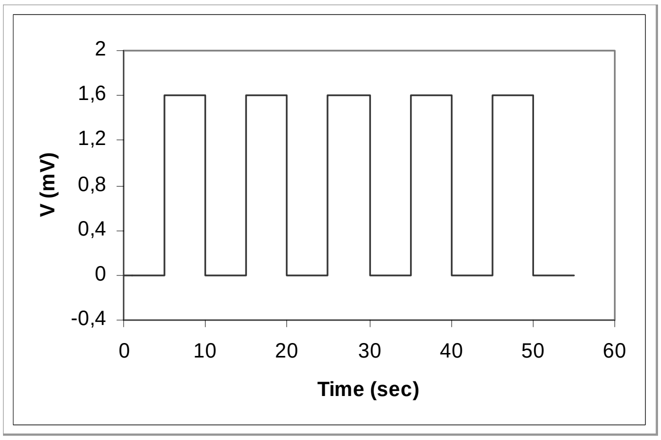


Figure 2.4 Square wave voltammetry

Switching properties of polymer films were investigated via applying potential square wave technique with a residence time of 5 seconds between -0.6 V and +1.0 V for homopolymer, between -0.6 V and +1.0 V for copolymer.

2.6.3 Colorimetry Studies of Polymers

The colors of polymer films and devices were determined by spectrophotometer at the reduced and oxidized states of polymers.

2.7 Electrochromic Device (ECD) Construction

2.7.1 P(DTAT-co-EDOT)/PEDOT Device

The anodically coloring polymer P(DTAT-co-EDOT) was potentiodynamically deposited onto the ITO-coated glass sweeping between -0.8 V and +1.3 V 1.3×10^{-3} M DTAT and 1.3×10^{-3} M EDOT in $LiClO_4$ (0.1 M)/ACN solvent-electrolyte couple. Cathodically coloring film which is PEDOT was fully reduced by polarizing to -1.5 V vs Ag/Ag^+ (Ag wire), anodically coloring films were fully oxidized by polarizing to +1.0 V vs Ag/Ag^+, 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.

2.7.3 Preparation of the Gel Electrolyte

Gel electrolyte was prepared using $LiClO_4$: AN: PMMA: PC in the ratio of 3:70:7:20 by weight. After $NaClO_4$/$LiClO_4$ was dissolved in AN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating was required. Propylene carbonate (PC), as a 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.

2.8 Characterization of Electrochromic Devices

2.8.1 Spectroelectrochemistry Study of Devices

Varian Cary 5000 UV-Vis-NIR spectrophotometer and Agilent 8453 UV-Vis spectrophotometer were used in order to characterize optical properties of electrochromic devices (ECDs). A device without the active polymer layer, but otherwise with the same construction, was used as the reference. In order to apply voltage across the device, the counter and the reference leads are connected to one another.

Spectroelectrochemical study of P(DTAT-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.

2.8.2 Switching Properties of Devices

Potential square wave technique was used to determine switching properties of ECDs between –1.5 V and +1.5 V with a residence time of 5 s for for P(DTAT-co-EDOT)/PEDOT device.

2.8.5 Colorimetry Studies of ECDs

The colors of polymer films and devices were determined by Coloreye XHT spectrophotometer (GretagMacbeth) at the reduced and oxidized states of P(DTAT-co-EDOT)/PEDOT device.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of monomer by ^{1}H-NMR Spectroscopy

^{1}H-NMR spectrum of DTAT was obtained on a Bruker-Instrument-NMR Spectrometer (DPX-400) in $CDCl_3$, and chemical shifts (δ) were given relative to tetramethylsilane.

Pale white powder; mp 161 °C; ^{1}H-NMR spectrum of monomer (Figure 3.1): $C_{26}H_{18}O_4S_2$, δ_H (CDC_{l3}) 4.1 (t, 4H), 4.36 (t, 4H), 6.6 (s, 2H), 7.3 (t, 4H), 7.9 (d, 4H). The protons at ethylene bridge of EDOT are observed at 4.1 ppm. The α-proton of EDOT is at 6.6 ppm. The protons of anthracene unit are observed at 7.3 and 7.9 ppm.

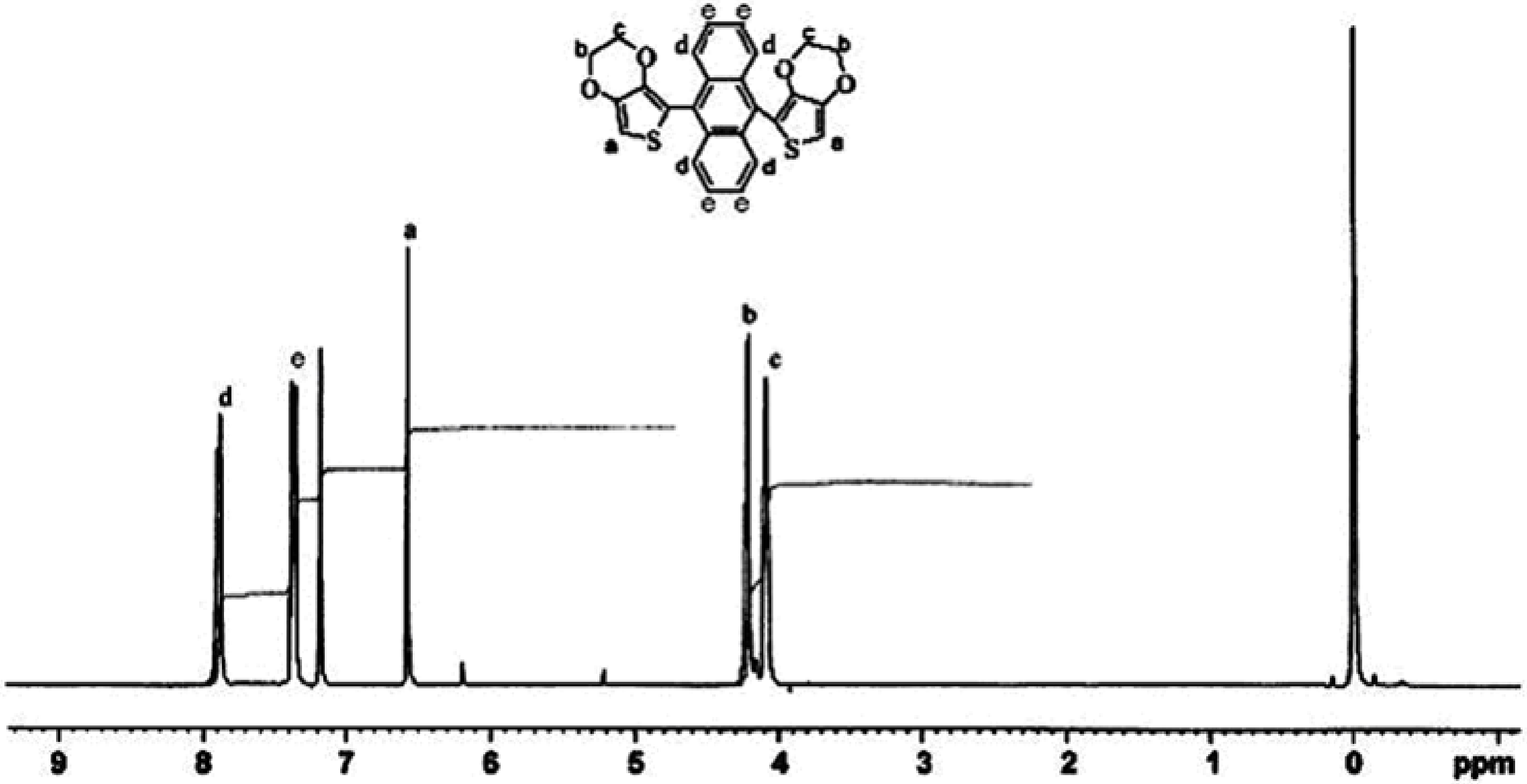


Figure 3.1 ^{1}H-NMR spectrum of the monomer

3.2 FTIR Spectra

FTIR spectrum of DTAT shows the following absorption peaks (Figure 3.2): 3060 cm^{-1} (aromatic C–H stretching of anthracene), 1633 cm^{-1} (C–O stretching of EDOT), 1355–1446 cm^{-1} (ring stretching of thiophene moiety of EDOT), 1554 cm^{-1} (ring stretching of benzene), 1059 cm^{-1} (ring vibration of substituted benzene), 771 cm^{-1} (C–H stretching of EDOT) and 709 cm^{-1} (C–S stretching of thiophene moiety of EDOT) [58].

FTIR spectrum of electrochemically synthesized P(DTAT) showed the characteristic peaks of the monomer. The peaks related to C–Hα stretching of EDOT disappeared completely. The new broad band at around 1641 cm^{-1} was due to polyconjugation. The strong absorption peak at 1121 and 668 cm^{-1} were attributed to the incorporation of ClO_4^- ions.

FTIR spectrum of electrochemically synthesized P(DTAT-co-EDOT) showed the characteristic peaks of both monomers. Intensity of peak 1633 cm^{-1} arising from aliphatic C–O stretching (EDOT) increased. This is an evidence of the copolymerization of DTAT with EDOT. The new broad band at around 1640 cm^{-1} was due to polyconjugation. The strong absorption peak at 1122 and 668 cm^{-1} were attributed to the incorporation ClO_4^- ions into the polymer film during doping process.

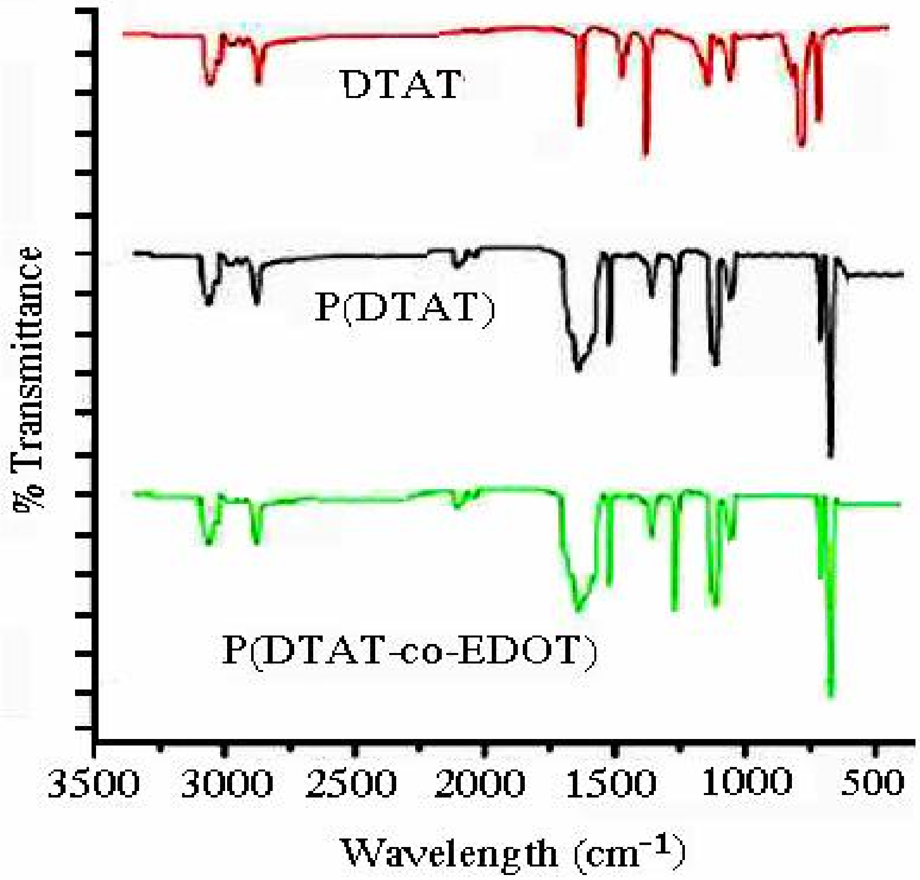


Figure 3.2 FTIR spectra of DTAT, P(DTAT) and P(DTAT-co-EDOT)

3.3 Cyclic Voltammograms

Cyclic voltammetry experiments for DTAT (1.3×10^{-3} M) was carried out in ACN containing 0.1 M $LiClO_4$ solvent electrolyte system on bare Pt electrode. Potential scanning was performed between -0.8 V and 1.3 V with a scan rate of 200 $mV.s^{-1}$. The voltammogram exhibited reversible redox waves at Ep,a = 0.87 V and $E_{p,c}$ = 0.65 V, and an irreversible oxidation at 1.2 V which refers to the further oxidation of the monomer (Figure 3.3). The redox activity of the polymer occurs around 0.6 V after the first cycle, the quasi reversible process with an average potential (0.87−(0.87−0.65)/2) = 0.76 V is related to a monomer site that does not allow polymerization that occurs on another site that irreversible oxidized at 1.2 V. The reduction wave at 0.65 V is the reduction of the radical cation during each cycle. The enhancement of the current after the first cycle should be due to the overlapping of the oxidation current of the polymer or to the incremental increase in the surface area of the electrode due to the polymer precipitation.

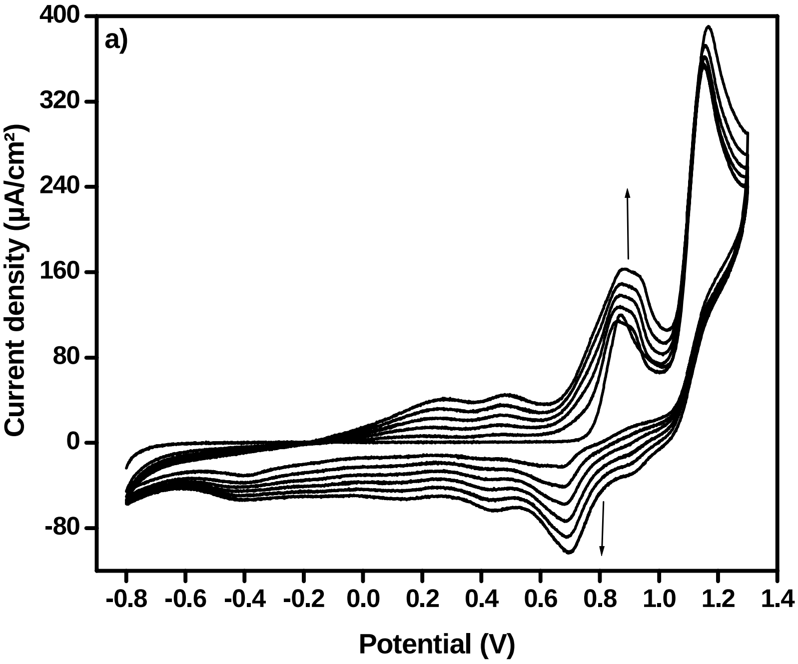


Figure 3.3 Cyclic voltammogram of P(DTAT)

Electrochemical copolymerization of DTAT with EDOT was carried out in 0.1 M $LiClO_4$ /ACN solution via potentiodynamic electrolysis. Upon repeated scanning of the potential between -0.8 and 1.3 V at 200 $mV.s^{-1}$, formation of electroactive P(DTAT-co-EDOT) film on the ITO electrode was observed. The redox behavior and the increments between consecutive cycles of DTAT in the presence of EDOT were completely different than that of P(DTAT) and PEDOT. A broad oxidation wave and a narrower peak were observed at about 0.3 and 0.9 V, respectively, whereas a broad reduction peak appeared at -0.3 V (Figure 3.4). The broad, oxidation peak, at 0.3 V during the second voltammetric cycle can be attributed to the appearance of oligomeric species (dimers, trimers etc.) with variable chain lengths.

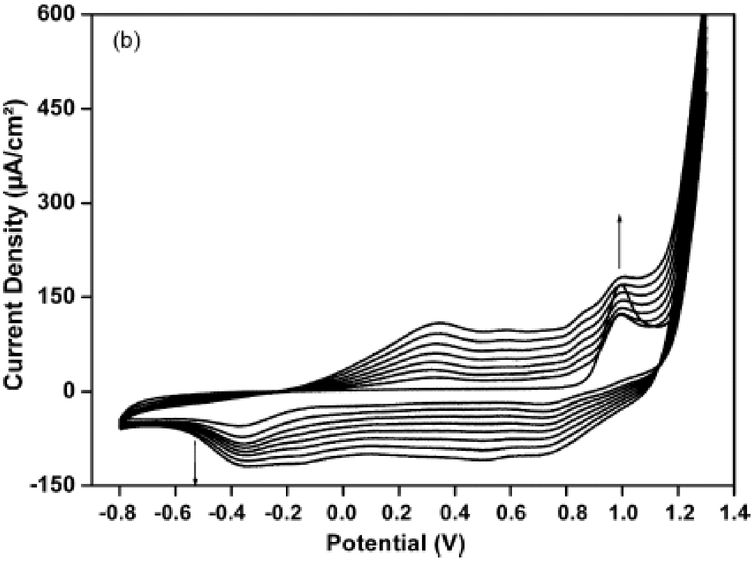


Figure 3.4 Cyclic voltammograms of DTAT in the presence of EDOT, P(DTAT-co-EDOT)

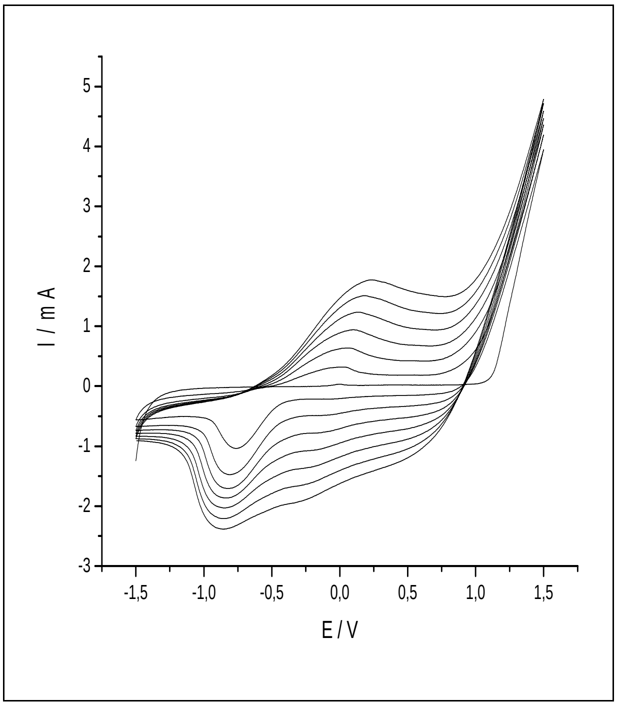


Figure 3.5 Cyclic voltammograms of pure PEDOT

3.4 Scan Rate Dependence of P(DTAT) and P(DTAT-co-EDOT)

Well-defined oxidation and reduction peaks, at 0.87 and 0.65 V confirmed the electroactivity of film. The anodic and cathodic peak current intensities increased regularly with the number of cycles due to the progressive growth of the P(DTAT) film on the electrode surface. The intensity of these peaks increased linearly with the scan rate (*v*) in between 100 and 1000 mV.s^{-1}, which is characteristic of a reaction of surface-localized electroactive species (Figure 3.6).

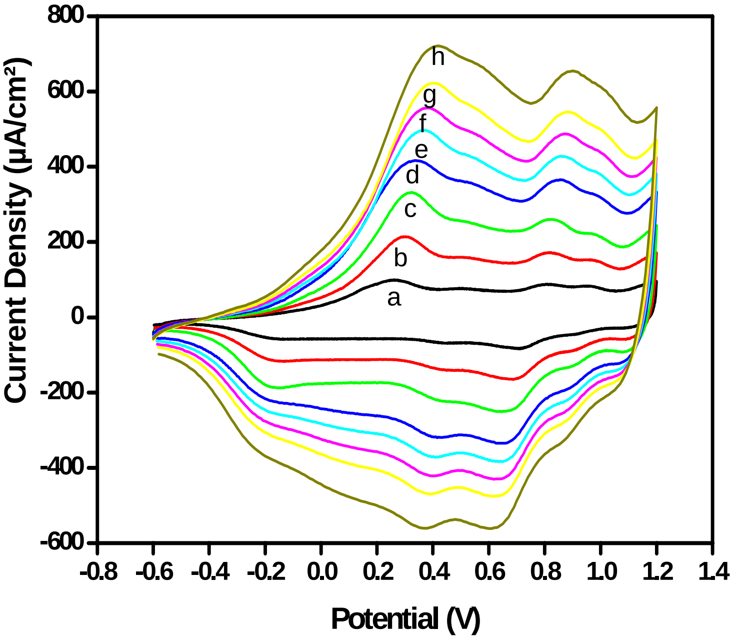


Figure 3.6 Cyclic voltammograms of P(DTAT) performed at various scan rates a)100, b)200, c)300, d)500, e)600, f)700 g)800 h)1000.

P(DTAT-co-EDOT) film also exhibited an electroactivity. The film was reversibly driven between the oxidized and neutral states, at various scanning rates, and the $I_{p,a}$ values varied linearly with the sweep rate (Figure 3.7).

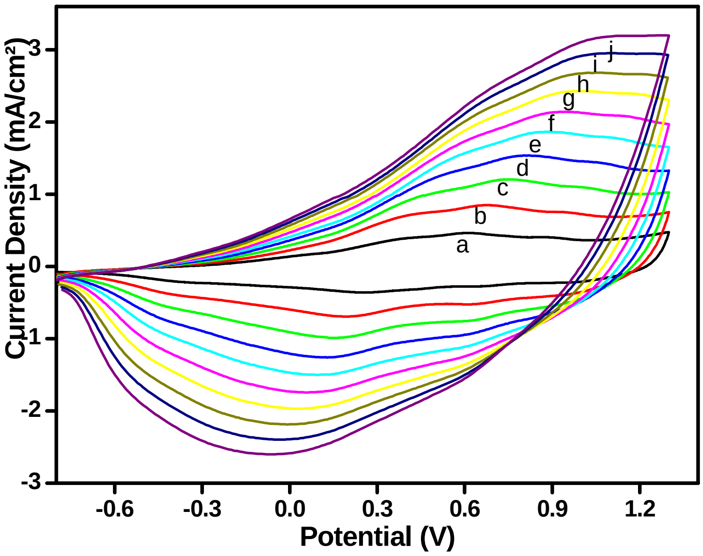


Figure 3.7 Cyclic voltammograms of P(DTAT-co-EDOT) performed at various scan rates a) 100, b) 200, c) 300, d) 400, e) 500, f) 600, g) 700, h) 800, i) 900, j) 1000 mV.s-1.

Anodic and cathodic peak currents revealed a linear relationship as a function of scan rate for both polymers, indicating that electrochemical processes are not diffusion controlled (Figures 3.8 and 3.9).

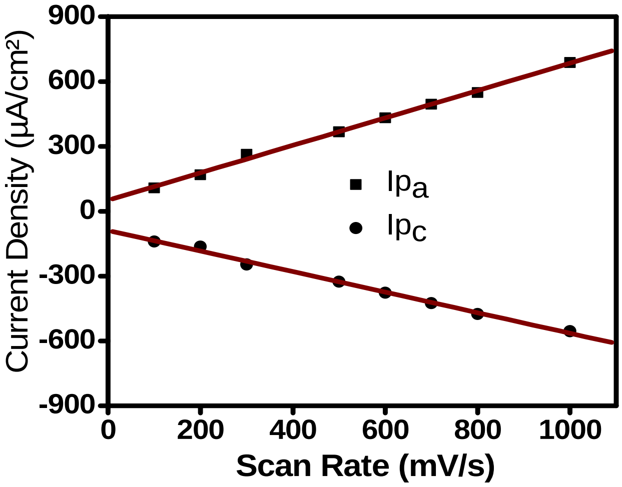


Figure 3.8 Scan rate dependence of P(DTAT)

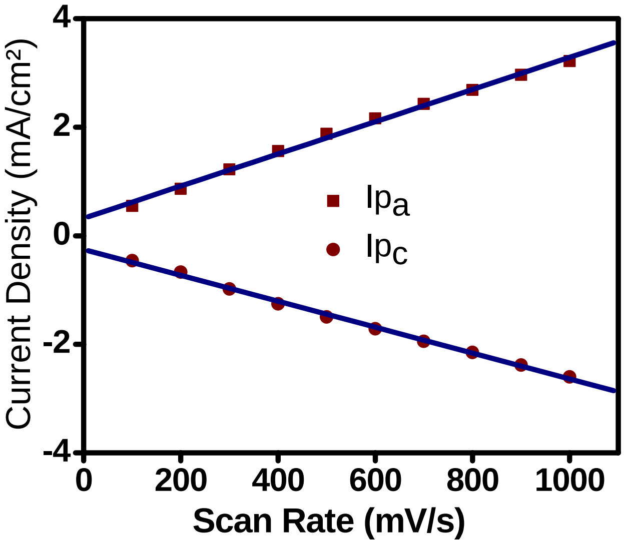


Figure 3.9 Scan rate dependence of P(DTAT-co-EDOT)

3.5 Investigation of Electrochromic Properties of Polymers

3.5.1 Spectroelectrochemistry of Homopolymer

Spectroelectrochemistry is the best way of examining the changes in optical properties of a polymer on ITO upon applied potentials. It also provides information on the properties of conjugated polymers, such as band gap (E_g) and the intergap states that appear upon doping. P(DTAT) film was potentiodynamically synthesized on ITO electrode in the presence of $1.3x10^{-3}$ M DTAT, sweeping the potential between - 0.8 V and 1.3 V in the presence of ACN/$LiClO_4$ (0.1 M) solvent-electrolyte couple.

In this study, the UV–vis absorption properties of P(DTAT) film, prepared via cyclic voltammetry, were investigated. Spectroelectrochemical studies of the resulting homopolymer were carried out sweeping the potentials from -0.6 V to 1.0 V in the monomer free DCM/$LiClO_4$ (0.1 M) solution. In the neutral state the polymer exhibits one transition from the valence band to conduction band (π-π*).

The band gap energy which is measured as the onset of the π-π*absorption was calculated from Figure 3.10 for P(DTAT). Using de Broglie equation, the band gap (Eg) is found as 1.57 eV (776 nm) for P(DTAT).

A spectroelectrochemical series for P(DTAT) in 0.1 M $LiClO_4$/DCM is shown in Figure 3.8. The neutral form of the polymer shows a distinct π-π* transition at 505 nm. The wavelength at which homopolymer shows π-π^* transition is defined as the maximum wavelength (λ_{max}) which was 505 nm for the homopolymer at -0.6 V. Stepwise oxidation of the polymer results in the formation of a radical cation as the color changes from yellow to blue oxidized state. Further oxidation of the polymer forms a new absorption band around 1008 nm due to the formation of bipolarons.

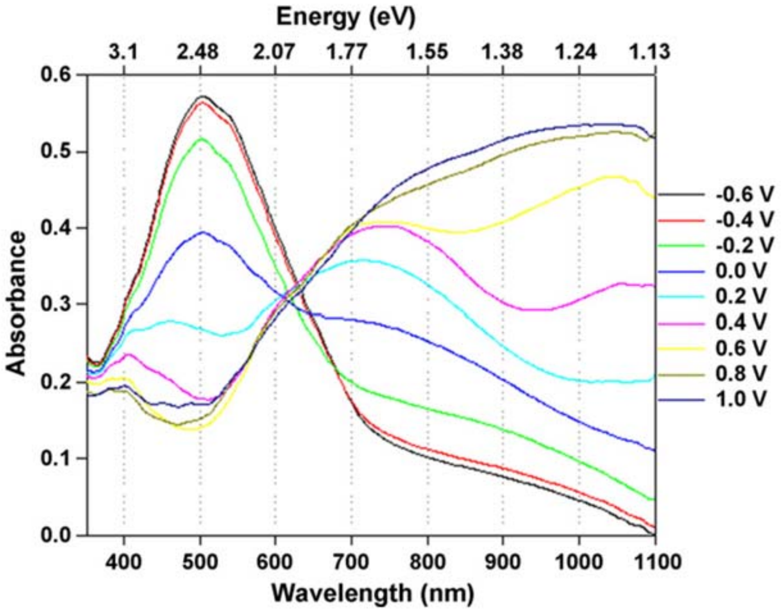


Figure 3.7 Spectroelectrochemical spectrum of P(DTAT) with applied potentials between -0.6 and +1.0 V in 0.1 M LiClO4/DCM.

3.5.2 Spectroelectrochemistry of Copolymer

The composition of the copolymer depends on monomer feed concentration, the reactivity of monomer radical cations and applied potential. In order to investigate electronic structure of the copolymers obtained by different applied potentials, spectroelectrochemistry studies were performed. Polymers were obtained via constant potential polymerizations at 0.9 V, 1.1 V and 1.3 V.

As the applied potential was close to the oxidation potential of EDOT, a copolymer with a higher content of EDOT separated by anthracene units was synthesized. Band gap (E_g) of the copolymer increases and λ_{max} of the copolymer shifts and becomes closer to 600 nm (Figure 3.9, 3.10, 3.11). Conversely, a higher DTAT concentration results in a copolymer with a decreased applied potential (at 0.9V).

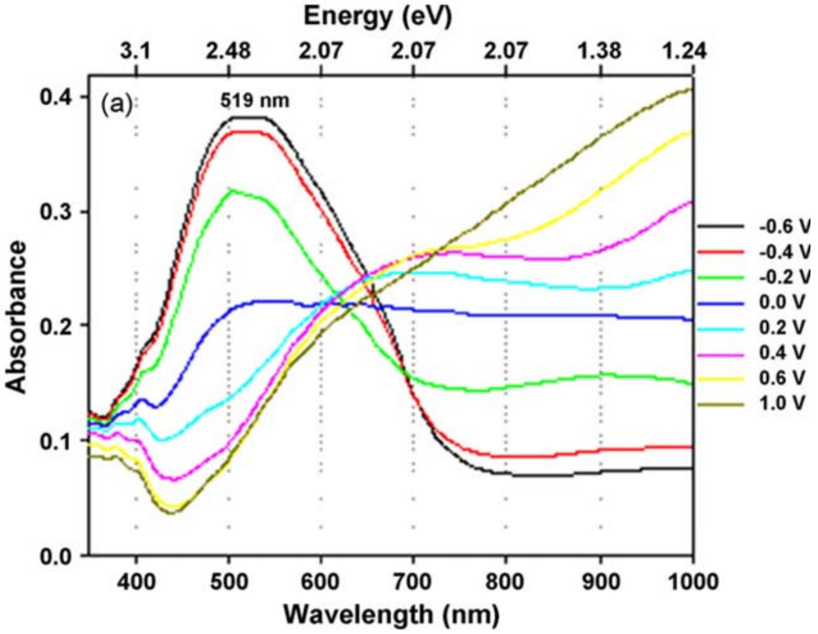


Figure 3.8 Spectroelectrochemistry of copolymers synthesized at 0.9 V

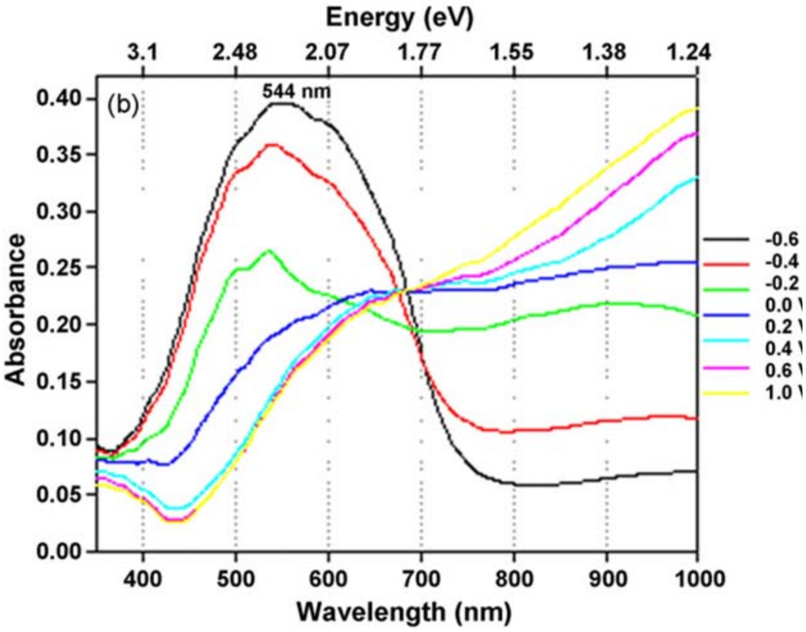


Figure 3.9 Spectroelectrochemistry of copolymers synthesized at 1.1 V

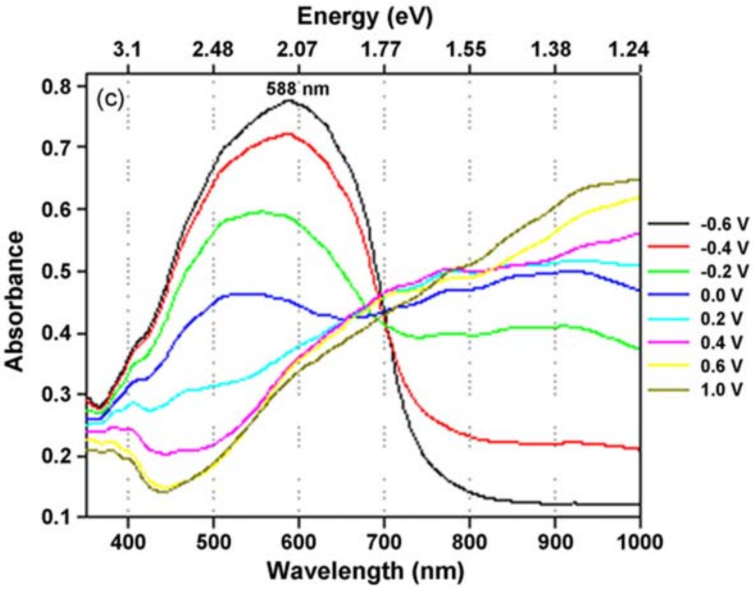


Figure 3.10 Spectroelectrochemistry of copolymers synthesized at 1.3 V

Table 1 summurize the electrochromic properties of the homopolymer, PEDOT and copolymers prepared by applying different potentials. Maximum absorption wavelengths are between those of the PEDOT and the homopolymer. Introduction of EDOT to the polymer chain leads to a slightly increase in the band gap.

Table 3.1 Electrochromic properties of Copolymers, P(DTAT) and PEDOT

Material	Applied Potential (V)	$\lambda_{max\ (nm)}$	$E_{g\ (eV)}$
P(DTAT)	1.2	505	1.573
P(DTAT-co-EDOT(1)	0.9	519	1.579
P(DTAT-co-EDOT(2)	1.1	544	1.584
P(DTAT-co-EDOT(3)	1.3	588	1.591
PEDOT	1.2	600	1.600

Copolymerization of DTAT with EDOT enhanced the optical properties of P(DTAT). Although P(DTAT) film showed two distinct colors, P(DTAT-co-EDOT) film exhibited multichromic properties with a claret red neutral state, a gray and a red intermediate states, and a blue oxidized state.

3.5.3 Electrochromic Switching

The ability of a polymer film to switch rapidly between its redox states is important for electrochromic applications. Response time of the polymer films to the applied potential was measured with chronoabsorptometry. In this technique, the polymer film was kept at its fully oxidized state for 5 sec, and then it was stepped to its reduced form and kept at this state for another 5 sec before being switched back to the initial potential again. Time is needed to switch between the redox states were recorded as the switching time. The optical contrast in the reduced and oxidized forms were measured and noted as % ΔT.

For electrochromic switching studies, P(DTAT) film was synthesized as described in Section 2.3. The film was stepped between its reduced (-0.6 V) and oxidized states (1.0 V). During switching, the % ΔT at 500 nm was monitored as a function of time (Figure 3.12). The response time to reach 33 % optical contrast was found to be 1.0 s.

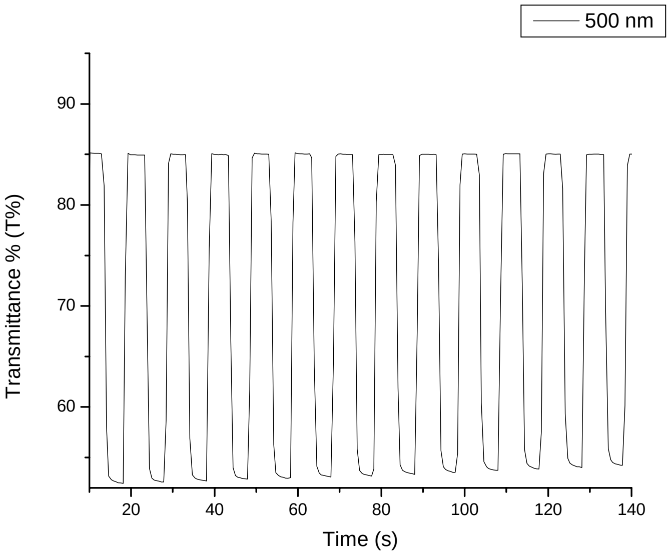


Figure 3-11. Electrochromic switching for P(DTAT) at 500 nm

Copolymerization of DTAT with EDOT caused several changes in the electrochromic properties of P(DTAT). Percent transmittance of the copolymer film was found to be 11 %. The response time to full contrast was 2.1 s (Figure 3.13).

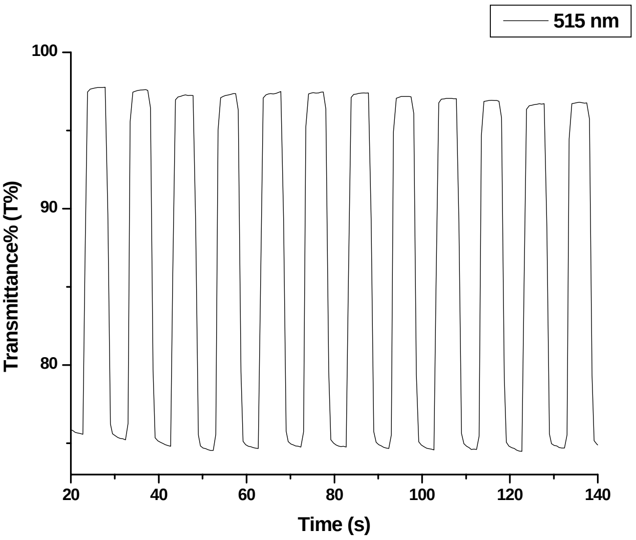


Figure 3-12 Electrochromic switching for P(DTAT-co-EDOT) at 515 nm.

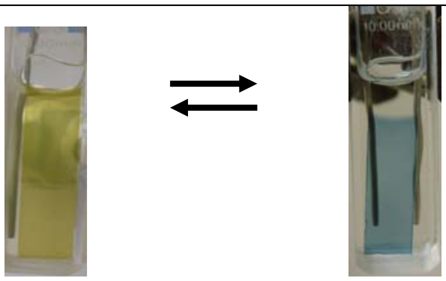
3.5.4 Colorimetry of Polymers

The luminance of a polymer film is a quantity that is highly dependent on the light source and is usually reported relative to the background luminance of a standard light source. Relative luminance studies are unique and valuable since, unlike chronoabsorptometry experiments that monitor a single wavelength, they allow the examination of the spectral changes across the entire visible region for a polymer. In a typical experiment, the polymer, immersed in a monomer-free electrolyte solution inside a quartz cuvette, is placed in front of a standard light source (D65) in a specially designed light booth that excludes all external light. Color and luminance (L) changes were then monitored as the potential was increased. According to the CIE (Commission Internationale de I'Eclairage) system of colorimetry, the color is made up of three attributes; luminance (L), hue (a), and saturation (b).

L, a, b values of the films were measured at the fully oxidized and reduced states and the results were recorded in Table 3.2. The P(DTAT) film was yellow (-0.8 V) in the reduced state and blue (+1.3 V) in the oxidized state.

Copolymerization of DTAT with EDOT enhanced the optical properties of P(DTAT). Although P(DTAT) film showed two distinct colors, P(DTAT-co-EDOT) exhibited multichromic properties with a claret red neutral state, a gray and a red intermediate states, and a blue oxidized state. L, a, b values of the films were measured at the fully oxidized and the fully reduced states in addition to a state in between and the results were recorded in Figure 3.14.

Table 3.2 Electrochromic properties of P(DTAT)



(-0.8 V)	(+1.3 V)
L= 54	L= 49
a= -4	a= -9
b= 35	b= -1

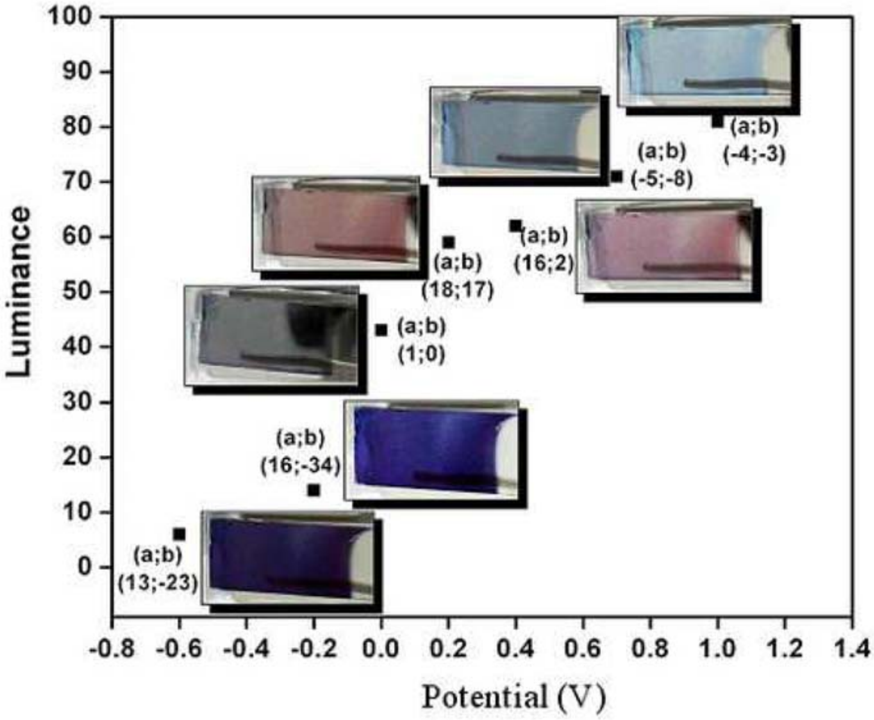


Figure 3.13 Relative luminance changes of P(DTAT-co-EDOT)film with applied potential.

A background measurement was also made using a blank ITO slide in the same electrolyte solution. When the polymer was held in its neutral state, it is very absorptive and does not permit much of the light to the colorimeter. However, upon oxidation, firstly the polymer becomes more transmissive (1.2 V) and a large amount of light reaches the colorimeter and then becomes less transmissive at the reduced state (-0.3 V).

3.6 Characterization of Electrochromic Devices

3.6.1 Spectroelectrochemistry of Device

Electrochromic devices prepared using conducting polymers (CPs) was constructed by sandwiching a gel electrolyte between the polymers previously deposited on ITO. In this study, P(DTAT-co-EDOT) was used as the anodically coloring material while PEDOT as the cathodically coloring material. Films were deposited onto ITO glass electrode via potentiodynamic electrolysis. Chronocoulometry was employed to match the redox charges of the two complimentary polymer films to maintain a balanced number of redox sites for switching.

The concept of complementary conducting polymers in dual polymer ECDs yields highly transmissive and absorptive states with a high optical contrast. A problem with the designed ECDs was the poor anodically coloring behavior of P(DTAT-co-EDOT) layer which switches between claret red (-1.5 V) and blue (1.5 V). Colored reduced state caused to lose the transmissive property of the PEDOT layer in the ECDs (Figure 3.15). There was a maximum absorption at 541 nm due to the π-π* transition of the electrochromic layer, P(DTAT-co-EDOT). Upon application of positive potentials, P(DTAT-co-EDOT) layer started to get oxidized and the intensity of the peak due to the π-π* transition decreased and there appears to be a second intense absorption at around 615 nm due to the reduction of PEDOT layer.

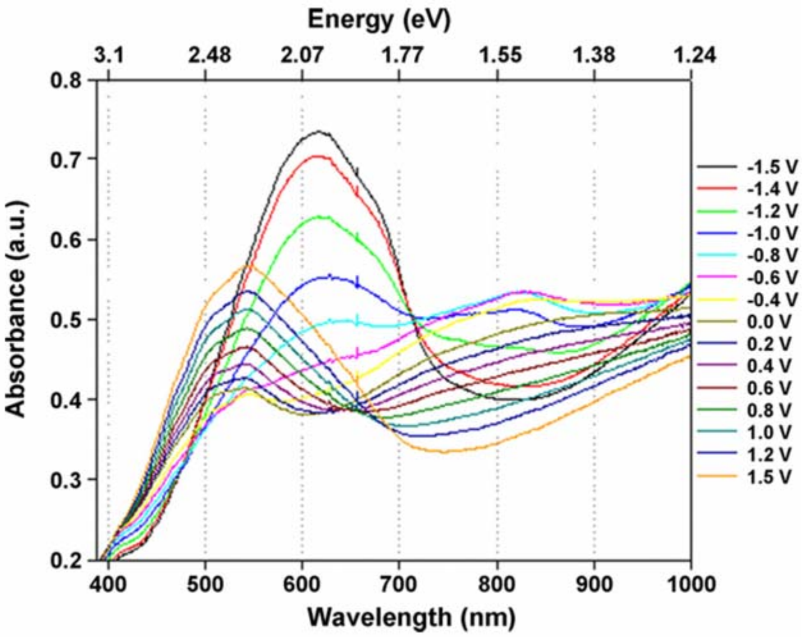


Figure 3.14 Optoelectrochemical spectrum of P(DTAT-co-EDOT)/ PEDOT device.

3.6.2 Switching of ECDs

Response time, one of the most important characteristics of electrochromic devices, is the time needed to perform switching between the two states. Chronoabsorptometry was performed to estimate the response times of the devices and their stability during consecutive scans.

The response time that needed to switch between the two colored states and the device's stability during repeated cycles were evaluated by stepping the potential between –1.5 V and + 1.5 V with a residence time of 5 s. The percent transmittance change at 620 nm was found to be 23% for P(DTAT-co-EDOT)/PEDOT with 1.2 s switching time (Figure 3.16).

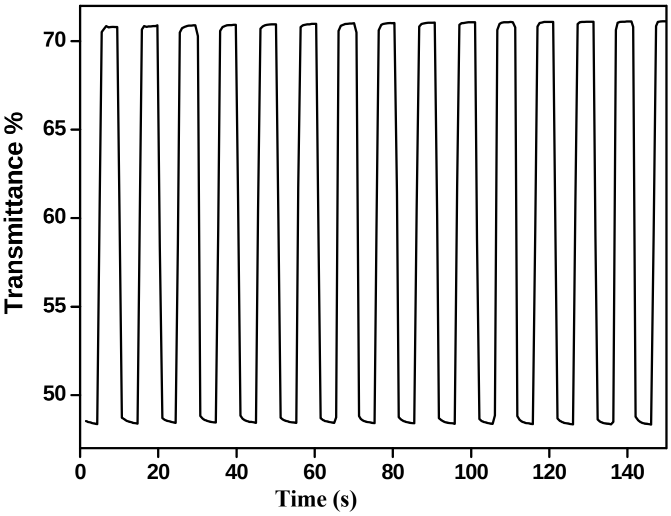


Figure 3.15 Kinetic study of P(DTAT-co-EDOT)/ PEDOT device at 617 nm, between -1.5 V and +1.5 V

3.6.3 Colorimetry of ECDs

L, a, b values of the ECDs were measured at the fully oxidized and the fully reduced states of devices and the results were recorded. The P(DTAT-co-EDOT)/PEDOT ECD was claret red at -1.5 V when the P(DTAT) layer was in its reduced and PEDOT was in its oxidized state. Blue color was observed at +1.5 V when PEDOT was in its reduced state and P(DTAT) layer in its oxidized state. L, a, b values of P(DTAT)/PEDOT ECD are given in Table 3.3.

Table 3.3 Electrochromic Properties of P(DTAT)/PEDOT ECD

	
-1.5 V L= 46 a= -20 b= 37	**+1.5 V** L= 33 a= 5 b= -15

CHAPTER 4

CONCLUSION

Synthesis of a novel conjugated monomer, 2,3-dihydro-5-(10-(2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine (DTAT) was successfully accomplished. Oxidative polymerization was achieved via electrochemical method. Conducting copolymer of DTAT with EDOT was synthesized electrochemically. Cyclic voltammetry studies revealed the electroactivity of DTAT. Copolymers of P(DTAT-co-EDOT) have different redox behaviors than that of both monomers and pure EDOT. Copolymerization was also proved by FTIR. Spectroelectrochemical analyses revealed that P(DTAT) and P(DTAT-co-EDOT) can be switched between their fully oxidized and fully reduced states with distinct color changes. Spectroelectrochemistry experiments showed that π to π^* transition occurs at 505 nm with a band gap 1.57 eV for P(DTAT). On the other hand, spectroelectrochemistry of P(DTAT-co-EDOT) was studied at three different applied potentials. Electrochromic investigations showed that P(DTAT) switches between yellow and blue while P(DTAT-co-EDOT) was found to be multichromic material switching between claret red, gray, red and blue.

Dual-type P(DTAT-co-EDOT)/PEDOT electrochromic device was assembled with a configuration ITO coated glass/anodically coloring polymer ||gel electrolyte||cathodically coloring polymer (PEDOT)/ITO coated glass. The color of P(DTAT-co-EDOT) device changed between claret red and blue upon applied potential. ECD was found to have reasonable switching times and contrasts.

Considering these results, P(DTAT-co-EDOT) is a promising candidate as one of the electrochromic layers in ECDs.

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