SYNTHESIS OF BENZOTRIAZOLE BEARING DONOR ACCEPTOR TYPE ELECTROACTIVE MONOMERS TOWARDS HIGH OPTICAL CONTRAST AND FAST SWITCHING ELECTROCHROMIC MATERIALS

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SYNTHESIS OF BENZOTRIAZOLE BEARING DONOR ACCEPTOR TYPE ELECTROACTIVE MONOMERS TOWARDS HIGH OPTICAL CONTRAST AND FAST SWITCHING ELECTROCHROMIC MATERIALS

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ABSTRACT

SYNTHESIS OF BENZOTRIAZOLE BEARING DONOR ACCEPTOR TYPE ELECTROACTIVE MONOMERS TOWARDS HIGH OPTICAL CONTRAST AND FAST SWITCHING ELECTROCHROMIC MATERIALS

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Synthesis of new electroactive monomers are highly desired since these compounds can be utilized as active layers in many device applications such as ECDs, LEDs and solar cells. EDOT (3,4 ethylenedioxythiophene) and thiophene bearing polymers were also proven to be excellent candidates as electrochromic materials. Benzotriazole can be coupled to EDOT and thiophene to yield materials that can be polymerized to give donor acceptor type polymers. These materials are promising candidates as components in fast switching polymeric electrochromic devices. Donor acceptor type materials; 2-dodecyl-4-(2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl)-7- (2,3-dihydrothieno[3,4-b] [1,4] dioxin-7-yl)-2H-benzo [d][1,2,3]triazole and 2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole were synthesized via N-alkylation, bromination, stannylation and Stille coupling reactions. Electrochemical and electrochromic properties of the polymers were examined in detail.

Keywords: Electrochromism, Donor-Acceptor Polymers, High Optical Contrast, Fast Switching

ÖZ

YÜKSEK OPTİK KONTRASTA SAHİP ELEKTROKROMİK MALZEMELERİN BENZOTRİAZOL İÇEREN DONÖR AKSEPTÖR TİPİ ELEKTROAKTİF MONOMERLERLE SENTEZİ

Abidin Balan
Yüksek Lisans, Kimya Bölümü
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Elektroaktif monomerler elektrokromik cihazlar, LED ve güneş pilleri gibi birçok cihaz uygulamalarında aktif yüzey olarak kullanılırlar. EDOT(3,4 etilendioksitiyofen) ve tiyofen içeren polimerler elektrokromik komponentlerden biri olarak işlev görürler. Benzotriazolün, EDOT ve tiyofen birimleri ile eşleştirilmesi ile sentezlenen monomerler donör akseptör tipi polimerlerin eldesinde kullanılabilir. Bu monomerler yüksek iletkenlik, yüksek optik kontrast ve hızlı değişen polimerik elektrokromiklerin sentezi için ideal adaylardır. Donör akseptör tipi monomerler 2-dodesil-4-(2,3-dihidrotiyeno[3,4-b][1,4]dioksin-7-il)-2H-benzo [d] [1,2,3]triazol ve 2-dodesil-4,7-di(tiyofen-2-il)-2H-benzo[d] [1,2,3]triazol sırası ile N-alkilasyon, brominasyon, stanilasyon ve Stille-coupling reaksiyonları ile sentezlenmiştir. Polimerlerin elektrokimyasal ve elektrokromik özellikleri ayrıntılı olarak incelenmiştir.

Anahtar Sözcükler: Elektrokromizm, donör-akseptör polimerler, yüksek optik kontrast, hızlı renk geçişi

To My Parents and The One That I Love

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INTRODUCTION

1.1 Conducting Polymers

All carbon based polymers were rigidly regarded as insulators until when plastics could be made to conduct electricity. A postgraduate student of Hideki Shirakawa at the Tokyo Institute of Technology synthesized polyacetylene (PA) as silvery thin film by mistake. It was later found that 1000 times of Ziegler-Natta catalyst, $Ti(O\text{-}n\text{-}But)_4$ - Et_3Al, had been used. It was found to be semiconducting and further investigations showed that exposure of PA to halogens increased its conductivity a billion fold [1,2]. The discovery of this huge increase in the conductivity of PA upon doping via iodine was a major breakthrough in the area of conducting polymers. Honoring Hideki Shirakawa, Alan MacDiarmind and Alan Heeger with Chemistry Nobel Prize in 2000 by their research in this field was the forerunner of very significant progress and tremendous advancements in a variety of application of conducting polymers towards technology. Conducting polymers triggered a scientific challenge in chemistry, physics material science and technology in general ever since.

Due to this remarkable discovery, that conjugated polymers can be converted into metals upon doping and hence generate a new class of materials referred as synthetic metals. This stimulated world-wide efforts to develop new classes of conducting polymers such as polythiophenes, polypyrroles and many others with properties similar to or better than those of PA [3-11] (Figure 1.1).

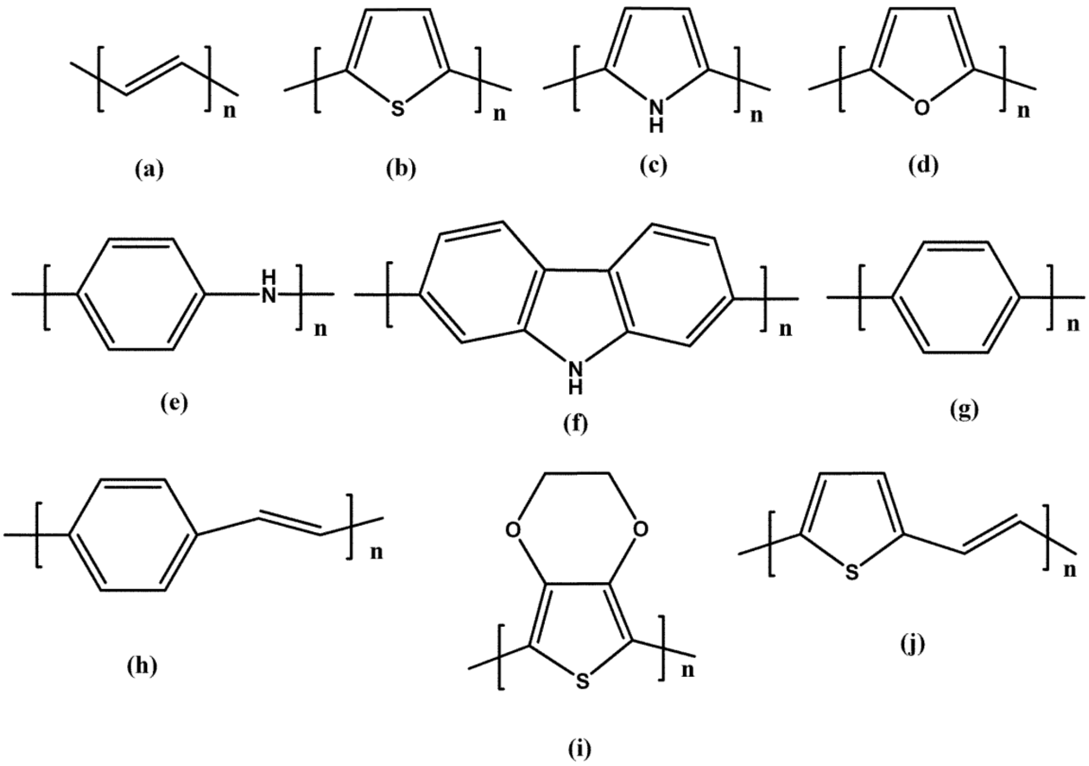


Figure 1.1. Chemical structure of some common conjugated polymers. (a) polyacetylene, (b) polythiophene, (c) polypyrrole, (d) polyfuran, (e) polyaniline, (f) polycarbazole (g) poly(p-phenylene), (h) poly(p-phenylenevinylene), (i) poly(3,4-ethylenedioxy-thiophene), (j) poly(thienylenevinylene)

1.2 Band Theory

The excitation and/or removal/insertion of electrons in conjugated polymers as a result of electrochemical or photochemical doping processes necessitate the discussion of band theory. In its most simple form for conjugated polymers, there are two discrete energy bands; the highest occupied molecular orbital (HOMO), also known as the valence band (VB); and the lowest unoccupied molecular orbital (LUMO), known as the conduction band (CB). The energy between these two bands is defined as the band gap (Eg), and in neutral conjugated polymers it can be approximated from the onset of the π-π* transition in the UV-Vis spectrum

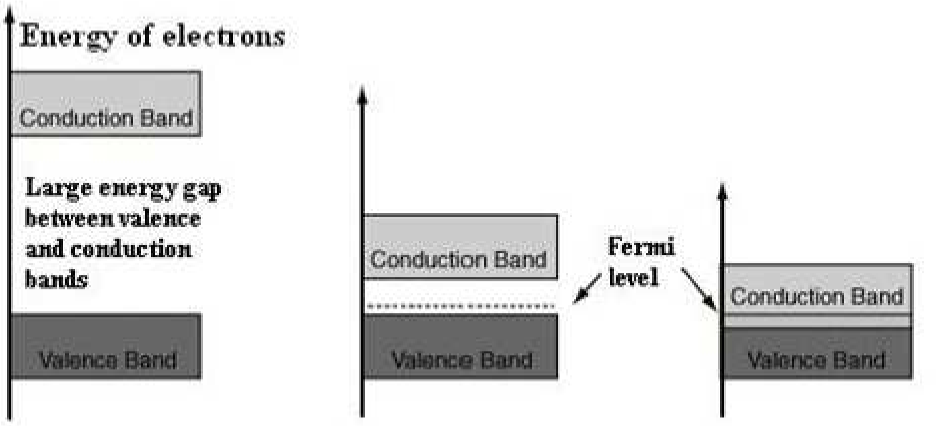


Figure 1.2 Band gap illustrations for an insulator, a semiconductor and a conductor

In their neutral form conjugated polymers are semiconducting, however upon oxidation or reduction interband transitions form between the VB and CB, lowering the effective band gap and resulting in the formation of charge carriers along the polymer backbone. Semiconductors can be made highly conducting materials depending on the type of dopant used which creates either holes (p-type) or electrons (n-type) [12].

Polyacetylene (PA) is the basic material to be considered in order to understand band theory of conducting polymers due to its structural simplicity. PA is a simple chain of sp^2 hybridized carbon atoms with alternating single and double bonds leading to two degenerate neutral resonance structures. That means the ground states are thermodynamically equivalent (Fig. 1.3). Also extensive delocalization causes all the bond lengths to be equal. Upon oxidation radical cations form nonassociated positive charges called solitons.

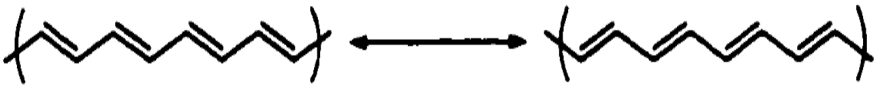


Figure 1.3 The degenerate ground state resonance structure for PA

Figure 1.4 shows the formation of a band structure as conjugation increases in a molecule. Repeating units' π orbitals can overlap throughout the chain [13]. As the number of repeating unit increases, the electronic levels no longer have discrete energies instead; they display contunium of the states and formation of band structures. The energy difference between the HOMO and the LUMO gives the band gap. Conduction for a polymer occurs via the movement of an electron from the highest occupied state to the next lowest unoccupied state [14].

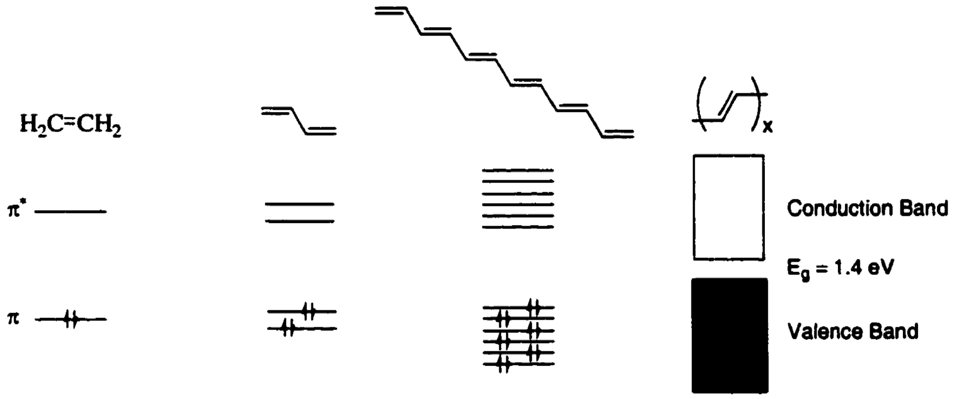


Figure 1.4 Generation of bands in polyacetylene

More complicated conducting polymers such as poly(p-phenylene) and polythiophene with aromatic repeating units have different scenario in terms of band theory. Their ground states are non-degenerate and they do not have equal ground state resonance forms. Poly(p-phenylene) exhibits both bezenoid and quinoid configurations (Fig. 1.5) [15].

Figure 1.5 Benzenoid and quinoid configurations for poly(p- phenylene)

Oxidation of these systems raises the energy level from which the electron is removed to the band gap region. Unlike the solitons for PA case, radical cations known as polarons are the main charge carriers during the initial oxidation. Further oxidation causes removal of unpaired electron of the polaron or combination of two polarons to form dications known as bipolarons (Fig. 1.6).

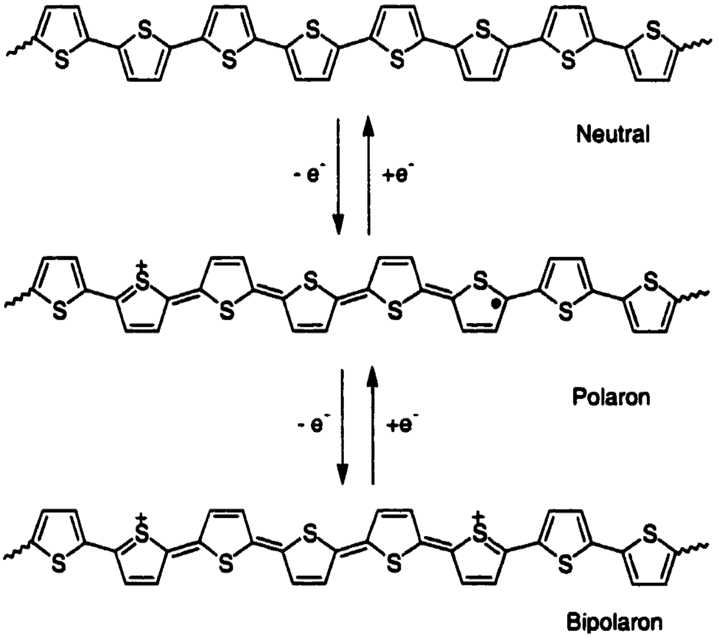


Figure 1.6 The charged states of poly(thiophene) upon oxidation

Via doping these charge carriers are formed and at high levels of doping they interact with each other to form a band which can eventually merge to create true metallic conductivity as was the case in PA (Fig 1.7) [16].

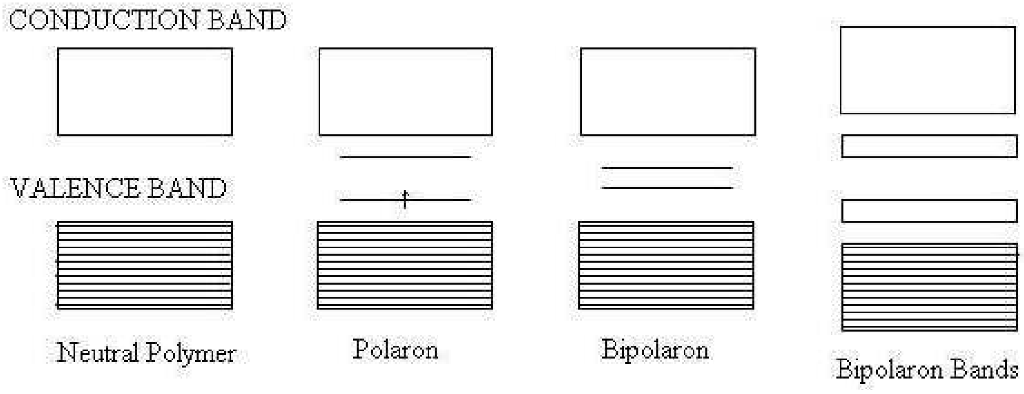


Figure 1.7 Charge carries and energy bands in the mid gap

1.3 Doping Process

As described, doping is necessary for a conjugated polymer to have conductivity. That is injection (ejection) of charge to (from) the polymer chain and should be reversible. This process can be accomplished by chemical, photochemical, interfacial or electrochemical means [17]. All types of doping methods consist of reversible oxidation and reduction reactions in order to proceed doping – dedoping. Complete doping to the highest concentrations yields reasonably high quality materials. However, attempts to obtain intermediate doping levels often result in inhomogeneous doping. Electrochemical doping eliminates such problems.

Electrochemical doping is performed by applying appropriate potentials to the polymer in a suitable medium. Figure 1.8 shows schematic illustration of the band diagrams for the p-doping (a) and n-doping (b) for a conducting polymer [18]. If the Fermi level of the electrode that is in contact with the conducting polymer film is lowered below the valence band of the polymer, a flow of electrons from the polymer to electrode will occur. This is termed as p-doping and it involves the extraction of the delocalized electrons from the p-orbital of the polymer. Likewise, if the Fermi level is raised above the conduction band of conducting polymer, then electrons flow in to the film. This is termed as n-doping and it involves the injection of the electrons into delocalized p-orbital of the polymer.

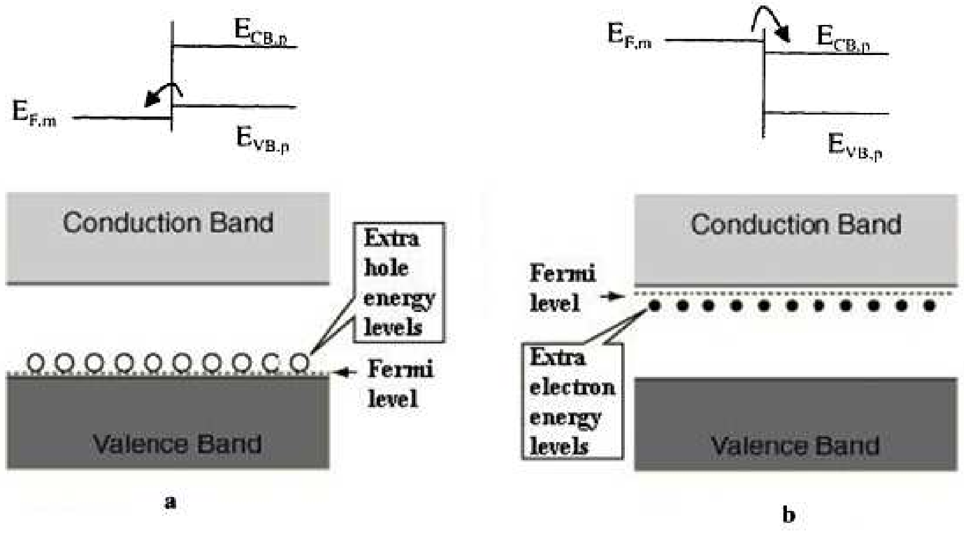


Figure 1.8 Schematic representation of doping for a conducting polymer; a) p-doping and b) n-doping

Upon oxidation p-doping removes electrons from the polymer chain producing positive charges on the polymer backbone. These charges can move in the polymer when placed in an electric field, acting as charge carriers. On the other hand, upon reduction n-doping donates electrons to the polymer, forming negative charges on the polymer chain. These electrons can move in the same direction in an electric field functioning as current carriers.

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 [19]. Negatively charged polymer chain can easily be oxidized due to the highly oxidizing agents in air. Thus, there are limited amount of n-dopable conducting polymers in literature when compared to the p-dopable ones [19-22].

1.4 Chromism

Chromism for a material is defined as a reversible change in materials color, absorbance or reflection resulting from an external effect. The effect which causes chromism can be temperature change (thermochromism), electromagnetic radiation (photochromism), change in pH (halochromism), mechanical (piezochromism) and electrochemical (electrochromism) [23].

Electrochromism, the most commercially utilized type which might have various potential applications, including displays, rear-view mirrors, smart windows, active optical filters and computer data storage is discussed in detail in the following section.

1.5 Electrochromism

Electrochromism is reversible and visible change in color or more conveniently in optical properties upon applied potential which leads to oxidation and reduction. Switching between the states results in the generation of different electronic absorption bands in visible region. The color changes between a transparent state and a colored state, or between the two colored states. The electrochromic materials may exhibit several colors termed as multichromic and the process is called as multicolor electrochromism [24]. The important characteristics of electrochromic materials are the switching times, the contrast ratios between different states, coloration efficiency meaning injected ejected charge per unit area, electrochromic memory and long term stability. For an electrochromic material, the electrochromic memory is the ability to remember color in the absence of current and the long term stability is the ability to retain electrochromic properties over a large number of switching cycles.

1.6 Types of Electrochromic Materials

Electrochromic materials have been known since 1968 [25]. Starting from the first discovery in inorganic materials, this phenomenon has been investigated by many scientists. A typical and most widely studied example of metal oxides is the tungsten trioxide (WO_3) system.

All tungsten sites in WO_3 structure have the oxidation state W_{VI} and it is a transparent thin film. When electrochemical reduction was applied, W_V sites are generated to give blue coloration to the film. Although, there is still controversy about the detailed coloration mechanism, it is generally accepted that the injection and extraction of electrons and metal cations (Li^+, H^+, etc.) play an important role [26]. The thin film of WO_3 can be reversibly turned to its transparent form by electrochemical oxidation. The generalized equation for the electrochromic process of WO_3 can be written as follows:

$$\underset{\text{(transparent)}}{WO_3} + xM^+ + xe^- \rightarrow \underset{\text{(blue)}}{M_xWO_3}$$

Many other transition metal oxides have been studied for their electrochromic properties. Oxides of V, Mo, Nb, and Ti are investigated for their cathodically and Ni, Co, and Ir are investigated for their anodically coloring behaviors [27]. Although there are commercialized WO_3 based applications, such systems generally suffer from slow switching times and non-extendable color variations.

Another types of electrochromic materials are viologens which are basically produced by diquaternization of 4,4'-bipyridyl, 1,1'-disubstituted-4,4'-bipyridilium salts [28]. Viologens are known to have three redox states (Fig 1.9) and among those the dication is the most stable and colorless one. Reductive electron transfer to viologen dication forms radical cations which are intensely colored. Choice of nitrogen substituents determines the colors of the different states.

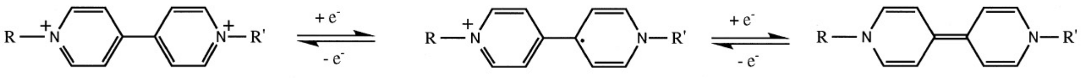


Figure 1.9 The three common viologen redox states, dication, radical cation, neutral species from left to right respectively

In order to be useful in commercial application an electrochromic material should satisfy all electrochromic performance parameters such as high contrast ratio, high coloration efficiency, long electrochromic memory and high term stability. Among many of electrochromic materials organic electrochromes, especially those based on conjugated polymers offer faster switching times and are much more easily modified to provide fine tuning in color with suitable band gap modification.

1.7 Electrochromism in Conducting Polymers

Interesting electrical and optical properties of conducting polymers are mainly due to the presence of a delocalized electronic structure in the UV- vis region related to the π-π^* transition as well as the stabilization of various charge carriers created upon doping. It is important to mention once more that all conjugated polymers are insulating in neutral state and become conducting in the doped state. Doping process changes their optical and mechanical properties and attract significant interest in the field of electrochromism, since they offer additional advantages such as low processing cost, enhanced mechanical properties, good UV stability, high coloration efficiency, fast switching ability and fine-tuning of the band gap through the modification of polymer’s chemical structure [29-37].

Of the many interesting conducting polymers that have been developed over the past 30 years, those based on polyanilines, polypyrroles, polythiophenes, polyphenylenes, and poly(p-phenylene vinylene)s (Fig 1.1) have attracted the most attention. Among these the polyaniline family is distinguished since it can be formed in large amounts and processable forms at relatively low cost. Unfortunately due to the possible presence of benzidine moieties (Fig 1.10) in the polymer backbone they might yield toxic, carcinogenic products upon degradation. Although polypyrrole and polythiophene as well as poly(p-phenylene vinylene) are more environmentally friendly systems, they have the disadvantage of being insoluble and infusible. In order to overcome these problems, numerous substituted derivatives of these polymers have been developed that carry alkyl, alkoxy, and other substituents along their backbones [38]. By controlling main-chain architecture and pendant groups [39-40] a broad variety of properties were made available from the parent systems. Although these side-chains provide a level of control of both the physical and electronic properties, often the ultimate accessible electronic properties were degraded relative to the parent [41]. In order to obtain a conducting polymer which satisfies the requirements of electrochromic devices structural architecture should be applied properly.

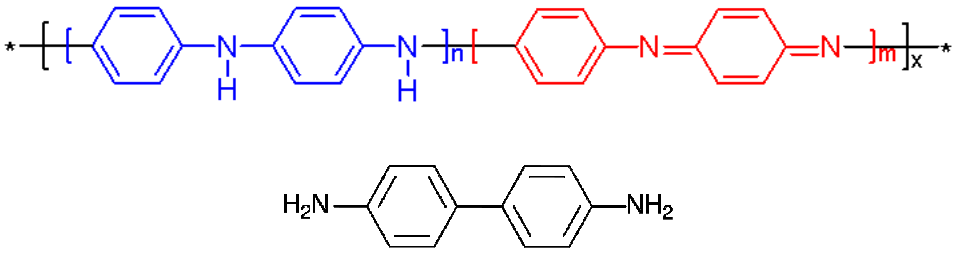


Figure 1.10 Chemical structures of polyaniline and benzidine

Electrochromism can be exploited in a series of optical devices with potential use in various applications, such as in display, storage, automotive industry (as rear-view mirrors and visors), and in architecture (as smart windows to control luminosity and save energy thought the control of sunlight transmission) [42].

1.8 Conducting Polymers Based on Thiophene and EDOT (ethylene dioxythiophene) Derivatives

1.8.1 Polythiophenes

Polythiophenes (PTh) are an important representative class of conjugated polymers due to their structural versatility and good environmental stability. PTh and its derivatives were well established in the field of conducting polymers and much research had been devoted to them. They can be used as electrical conductors, nonlinear optical devices, polymer LEDs, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices, and transistors [43].

PTh can be synthesized chemically by several methods. One of the first chemical preparations of PThs was the synthesis of polythiophene by a metal-catalyzed polycondensation polymerization of 2,5-dibromothiophene. Yamamoto's synthesis treats 2,5-dibromothiophene with Mg in tetrahydrofuran (THF) in the presence of nickel(bipyridine) dichloride. The Mg reacts with bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene, which is self-coupled with the Ni (II) catalyst to form a thiophene dimer carrying a MgBr at one end and a Br at the other. The PTh synthesized by this method leads to 78 % insoluble polymer that does not melt. The soluble fraction is low molecular weight oligomers [44]. Polymerization of 2,5-dihalothiophene can be accomplished by reacting the generated bromo-Grignard reagent of thiophene with a Ni (II) catalyst such as Ni(dppp)Cl_2 (dppp = 1,3-diphenylphosphinopropane). Systematic studies of the polymerization of 2,5-dihalothiophene have subsequently been performed primarily by Yamamoto's group [45] (Fig 1.11).

Figure 1.11 Yamamato method for chemical polymerization of thiophene

Wudl and co-workers stated that very good samples of PTh can be prepared by the polymerization of highly purified 2,5-diiodothiophene . First 2,5-diiodothiophene was reacted with Mg in ether at reflux. The formed iodomagnesioiodothiophene was isolated as a residue and redissolved in hot anisole, where upon Ni(dppp)Cl_2 was added and the mixture was heated at 100 ^oC for 5 h to induce polymerization [46].

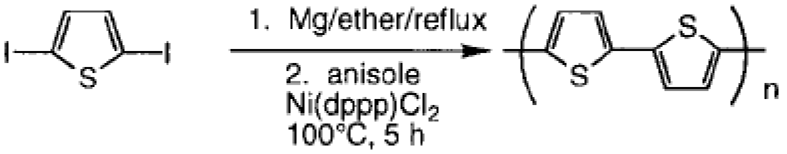


Figure 1.12 Wudl method for chemical polymerization of thiophene

Work on the polycondensation polymerization of 2,5- dihalothiophenes by Yamamoto has shown that essentially a quantitative yield of PTh can be obtained from 2,5-dibromothiophene, Ni(cod)$_2$ (cod = cyclooctadiene), and triphenylphosphine (PPh_3) at 60-80 ^oC in dimethylformamide (DMF) [45].

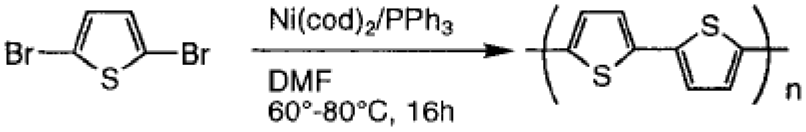


Figure 1.13 Polycondensation polymerization of 2,5- dibromoothiophene

Although the above methods have been generally used to prepare high quality PTh other methods were reported. Sugimoto described the synthesis of PTh by treating thiophene with $FeCl_3$ (Fig. 1.14). The treatment of thiophene with butyl lithium provides 2,5-dilithiothiophene that can be polymerized by $CuCl_2$. The acid-induced polymerization of thiophene was reported as early as 1883 producing tetrahydrothiophene units. A novel polymerization of thiophene vapor can produce encapsulated PTh in zeolites [47].

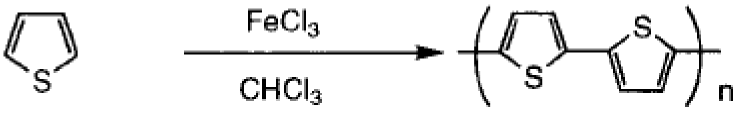


Figure 1.14 Sugimoto method for chemical polymerization of thiophene

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

In electropolymerization a coupling occurs between two electrolytically initiated radicals. The radical cation reacts with another radical cation to yield a neutral dimer by the loss of two protons. The oxidized dimer radical cation again attacks to form a trimer and the propagation proceeds to form polymer. Electropolymerization proceeds then through successive electrochemical (E) and chemical (C) steps, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface [48].

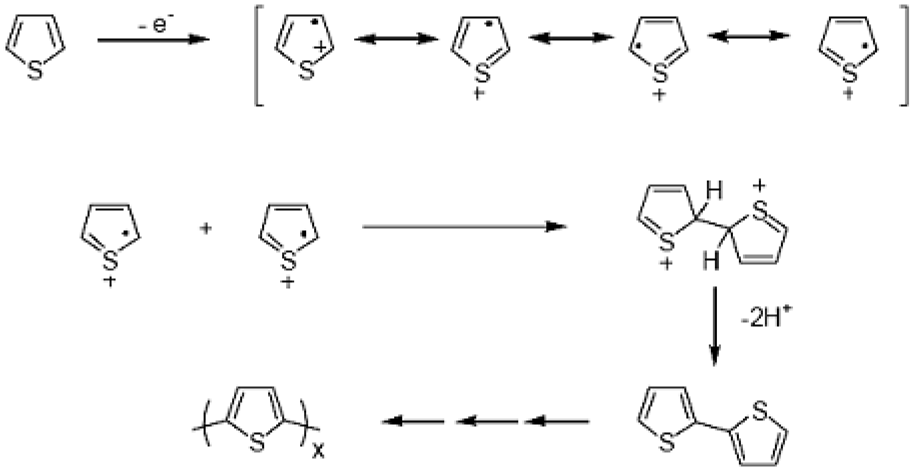


Figure 1.15 Electropolymerization mechanism of thiophene

High conductivity, relatively low band gap and the ease of introduction of side groups onto the β-positions of the polymer backbone make PTh an ideal polymer for electronic and optoelectronic applications. Due to its electron rich character of thiophene ring, PThs can be easily and reversibly oxidized by chemical or electrochemical means to form p doped highly conducting materials. The first electronic transition of undoped PTh (which strongly depends on the structure) lies between 300-500 nm. Upon doping, it undergoes a dramatic shift which tails from visible to IR region [49]. PTh displays color transition from red to blue upon doping.

1.8.2 Polythiophene Paradox

Although PThs can be synthesized by both electrochemical and chemical methods, electrochemical methods are of utmost importance for fundamental studies regarding synthesis and properties of the corresponding polymers [50]. This technique is rather simple, has high accuracy, precision and offers the possibility to control film thickness. It provides rapid analysis and the possibility to explore the in-situ growing process of the polymer and further analysis by electrochemical and spectroscopic techniques. Hence, it is generally preferred for preceding studies. In case of electrochemical polymerization of thiophene there is a phenomenon named as polythiophene paradox. That is; at potentials required to oxidize the thiophene monomer the polymer itself becomes overoxidized. Using constant current or constant potential polymerization, the product obtained is a mixture of polythiophene and overoxidized polythiophene [51].

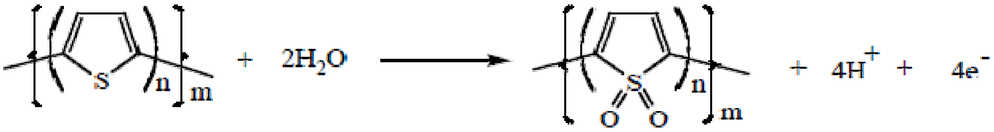


Figure 1.16 Chemical structures of polythiophene and over oxidized polythiophene

Several approaches has been explored to overcome this problem; one of which is the polymerization of thiophene from its oligomers such as 2,2′-bithiophene or 2,2′-5,2′′-terthiophene (Fig 1.17). Although thiophene oligomers can be electrochemically polymerized at lower potentials than the parent monomer, it was found that the resulting polymers exhibit lower average conjugation lengths and poor mechanical properties [52]. Xue et al. reported the low potential electrochemical synthesis of polythiophene in freshly distilled borontrifluoride diethyletherate (BFEE) [53]. It was found out that the resultant polymer has higher effective mean conjugation length with remarkable mechanical strength exceeding the aluminum sheets.

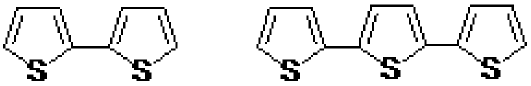


Figure 1.17 Chemical structures of 2,2′-bithiophene and 2,2′-5,2′′-terthiophene

However, studies have shown that the most effective approach is the synthesis of β-substituted thiophenes with electron donating groups having the ability to reduce the oxidation potential of the monomer and polymer. One of the simplest and intensely studied examples is 3-methylthiophene which has oxidation potential 0.2 V lower than the unsubstituted thiophene [54]. Studies concluded that introduction of a methyl group at the β position of the thiophene ring leads to a significant increase in the polymer conjugation length. p-type conductivity is enhanced due to the statistical decrease in a number of α-β′ couplings. Also the oxidation potential is decreased due to the inductive effect of the methyl group [55-56]. Hence, attachment of pendant groups to the thiophene ring is shown to be straightforward approach to reduce the band gap of a conducting polymer.

1.8.3 PEDOT

During the second half of the 1980s, scientists at the Bayer AG research laboratories in Germany developed a new polythiophene derivative, poly(3,4-ethylenedioxythiophene). This polymer, often abbreviated as PEDOT, was initially developed to give a soluble conducting polymer that lacked the presence of undesired α,β- and β, β -couplings within the polymer backbone. However, PEDOT was initially found to be an insoluble polymer [57]. Synthesis of PEDOT both chemically and electrochemically is very similar to that of PTh.

When PEDOT is oxidized, there is a change in its electronic structure, which is observable by an optical color change from dark blue to highly transmissive sky blue. Due to these optical properties and its high conductivity, PEDOT is currently being used in several applications; as an antistatic material in photographic film and plastic and transparent electrode material for inorganic electroluminescent lamps [58].

1.9 Low Band Gap Polymers

Minimizing the band gap is an important goal for maximizing the conductivity of CPs. Polymers with band gaps lower than 1.8 eV are considered to be relatively low band gap materials. Band gap determines the conductivity and color of the neutral polymer. Moreover, the band edges determine ease of doping and the stability in the doped states compared to the neutral forms. Low band gap polymers are relatively recent topic of research interest and these types of polymers have many interesting applications. Regardless of how the band energies line up, the low band gap often causes these polymers to be transparent in the doped state (p- or n-type). This makes them useful in a variety of devices such as electrodes and smart windows where the transparency can be exploited. As to the high gap polymers, the color of low gap polymers is dictated by the magnitude of the band gap. Since the difference between the edge of the VB and CB is smaller in low gap materials, the CB is generally more accessible to n-type doping even for low gap polymers with relatively large VBs. These classes of materials are significantly important since they are offering the transparency of low gap systems with the ability to be both n-type and p-type doped for the same polymer.

From the molecular architectural point of view there are five basic approaches to reduce band gap; controlling bond-length alternation (Peierls distortion), creating highly planar systems, inducing order by interchain effects, resonance effects along the polymer backbone, and using donor-acceptor molecules (Fig 1.18).

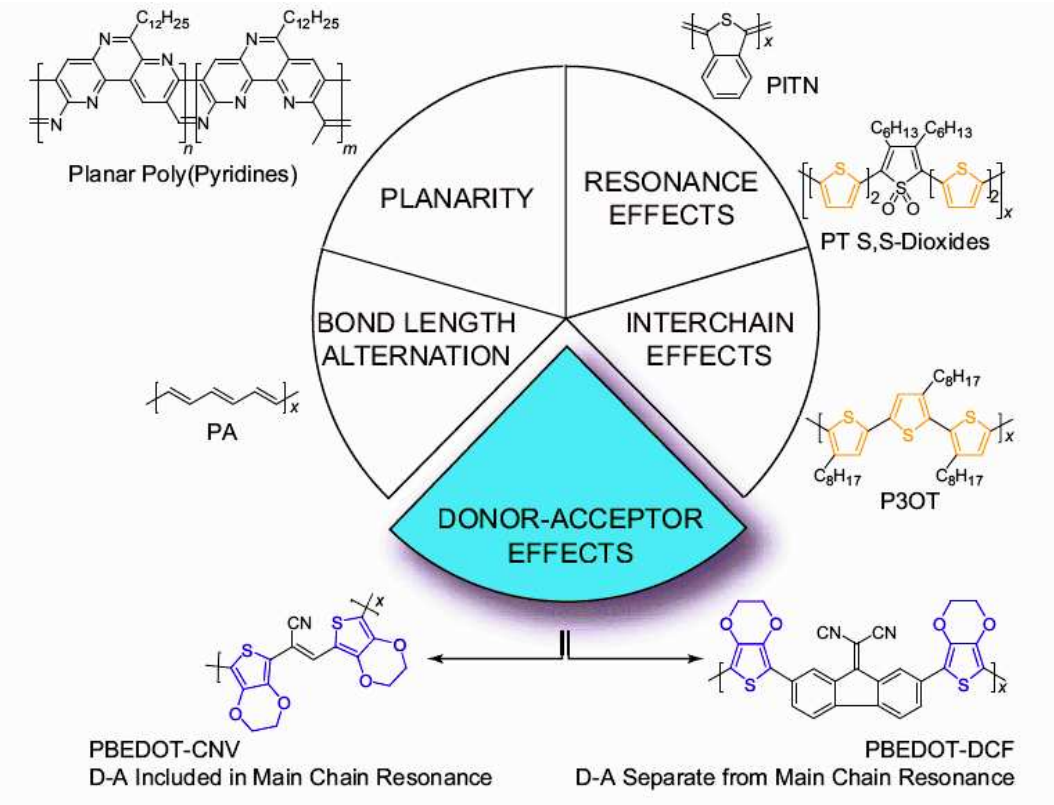


Figure 1.18 Overview of methods for the modification of band gap

Research over the last decade aimed almost exclusively to manipulate band gap via synthesizing polymers having alternating donor and acceptor moieties. The donor-acceptor route has by far the most utilized in terms of diversity in synthetic possibility and additionally avoiding solubility problems.

In order to obtain desired properties in a donor acceptor type polymer; donor and acceptor units should match properly. Cyano- groups are among the most extensively studied electron withdrawing substituents. By applying the Knoevenagel condensation a vast amount of bis(heterocycle)cyanovinylene monomers utilizing pyrrole, furan, thiophene, EDOT and EDOP as donor units were prepared. These polymers were cathodically coloring and have color variations between opaque blue in the neutral state to a transmissive light in oxidized state. A comprehensive study of Thomas et al. established that for a fixed acceptor, cyanovinylene, increasing the electron density around the acceptor reduces the resulting polymer band gap. As seen in Figure 1.19, studies have shown that the HOMO and LUMO energies of the DA polymer strongly resemble to those of the donor polymer and the acceptor polymer respectively. By increasing the electron donor strength, the bandgap is lowered from 1.6 eV for PBTh-CNV, 1.4 eV for PEDOT-CNV-Th, 1.2 eV for PTh-CNV-EDOT, and 1.1 eV for PBEDOT-CNV, PTh-CNV-EDOP, and PEDOT-CNV-EDOP [59-60].

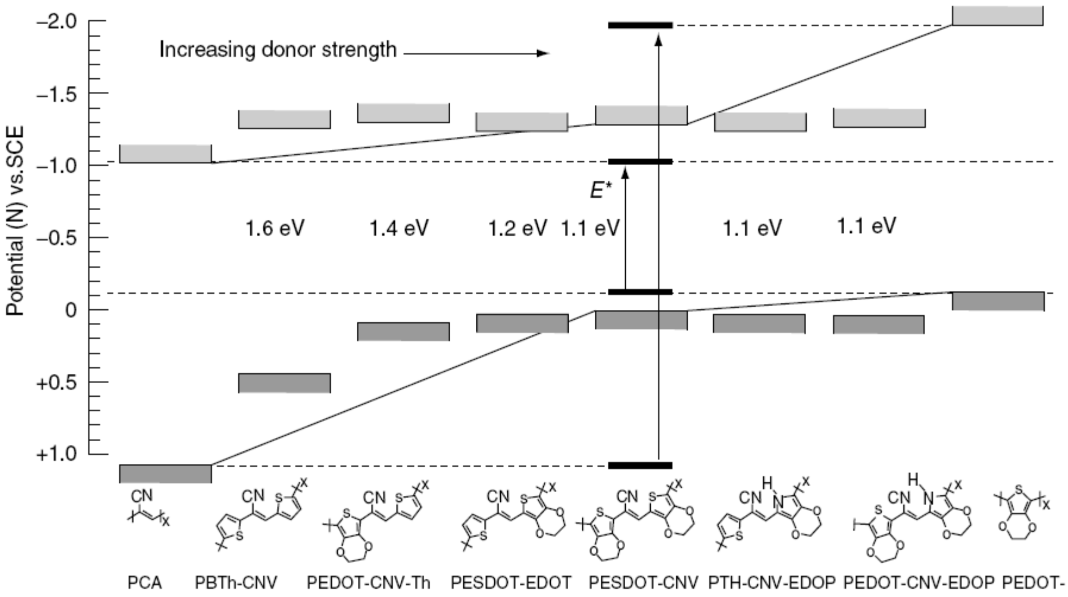


Figure 1.19 Approximate levels of the valence and conduction bands in a series of poly(bis(heterocycle)-cyanovinylene)s.

To date numerous BEDOT-arylenes have been synthesized and studied in order to obtain most suitable donor acceptor couple. Their bandgaps are ranging from 1.3 eV to 2.4 eV. The switching potentials and spectral variations of these polymers make them interesting candidates for electrochromic applications (Fig 1.20) [61-72].

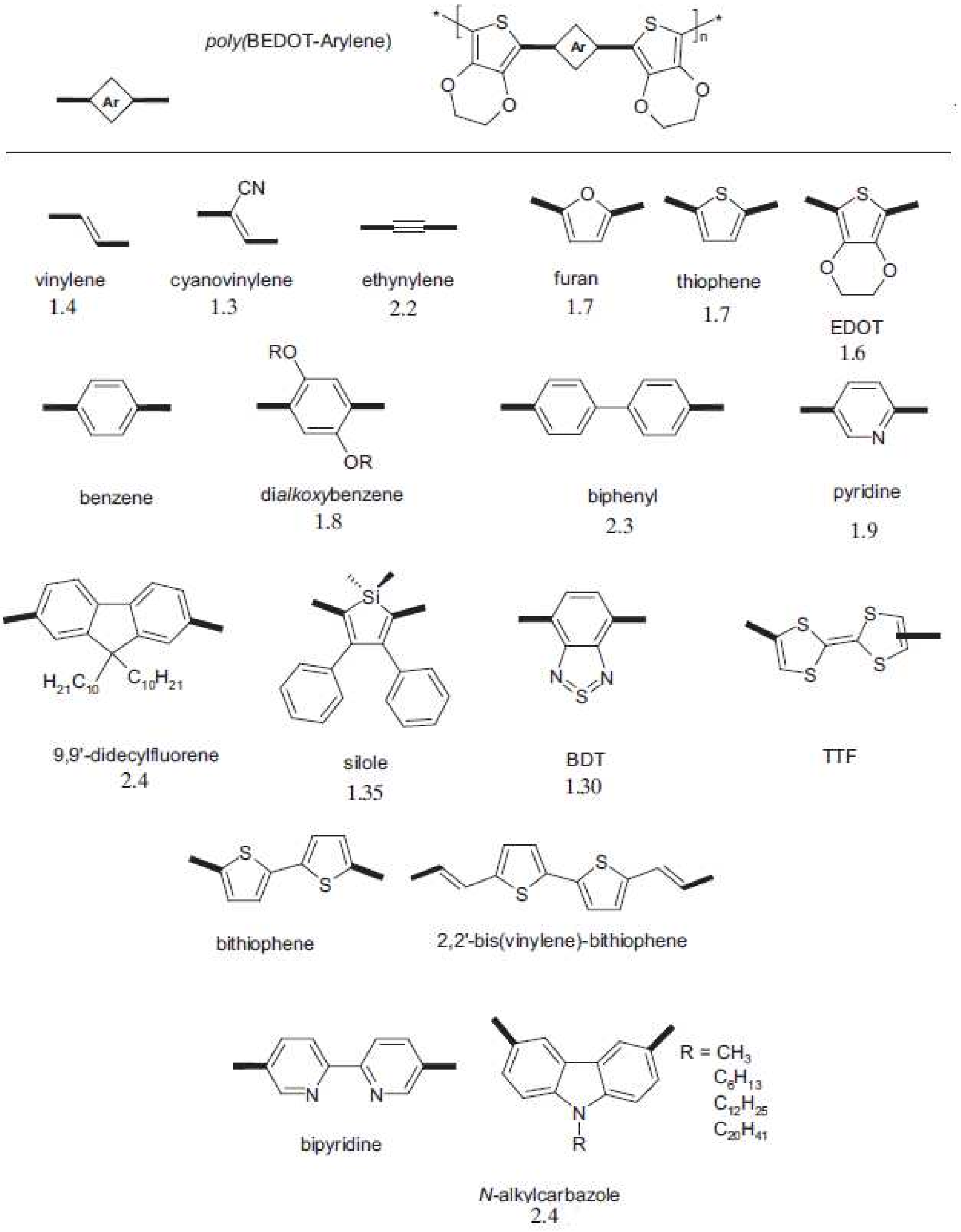


Figure 1.20 Chemical structures for several BEDOT- arylenes and their band gaps in eV.

1.10 Historical Overview of Electrochromism

Over the decades many of organic conducting polymers had been synthesized and extensively studied. Up to date a huge number of different polymers were synthesized in order to obtain fine color tuning, fast switching between extreme states, high optical contrast ratios and high coloration efficiency to use them in electrochromic device applications.

Aniline is the starting point where organic polymers, namely plastics, started to be used as the active layer in electrochromic devices and took place of their inorganic counterparts. Anodic polymerization of colorless aniline in solution yields polyaniline. Leucoemeraldine is an insulator since all rings are in benzenoid form and separated by -NH- or $-NH_2^+-$ groups, thus preventing conjugation between rings. Emeraldine as either base or salt has a ratio of three benzenoid rings to one quinoidal ring. This form of polyaniline is electrically conductive. Pernigraniline has equal proportions of quinoidal and benzenoid moieties and shows metallic conductivity. Electrodes bearing such polyaniline films are polyelectrochromic and exhibit the following reversible color changes as the potential is varied between -0.2 V to +1.0 V transparent leucoemeraldine yellow-green, emeraldine dark blue-black. Pernigraniline has an intense blue colour but appears black at very positive potentials if the film is thick (Fig 1.21) [73].

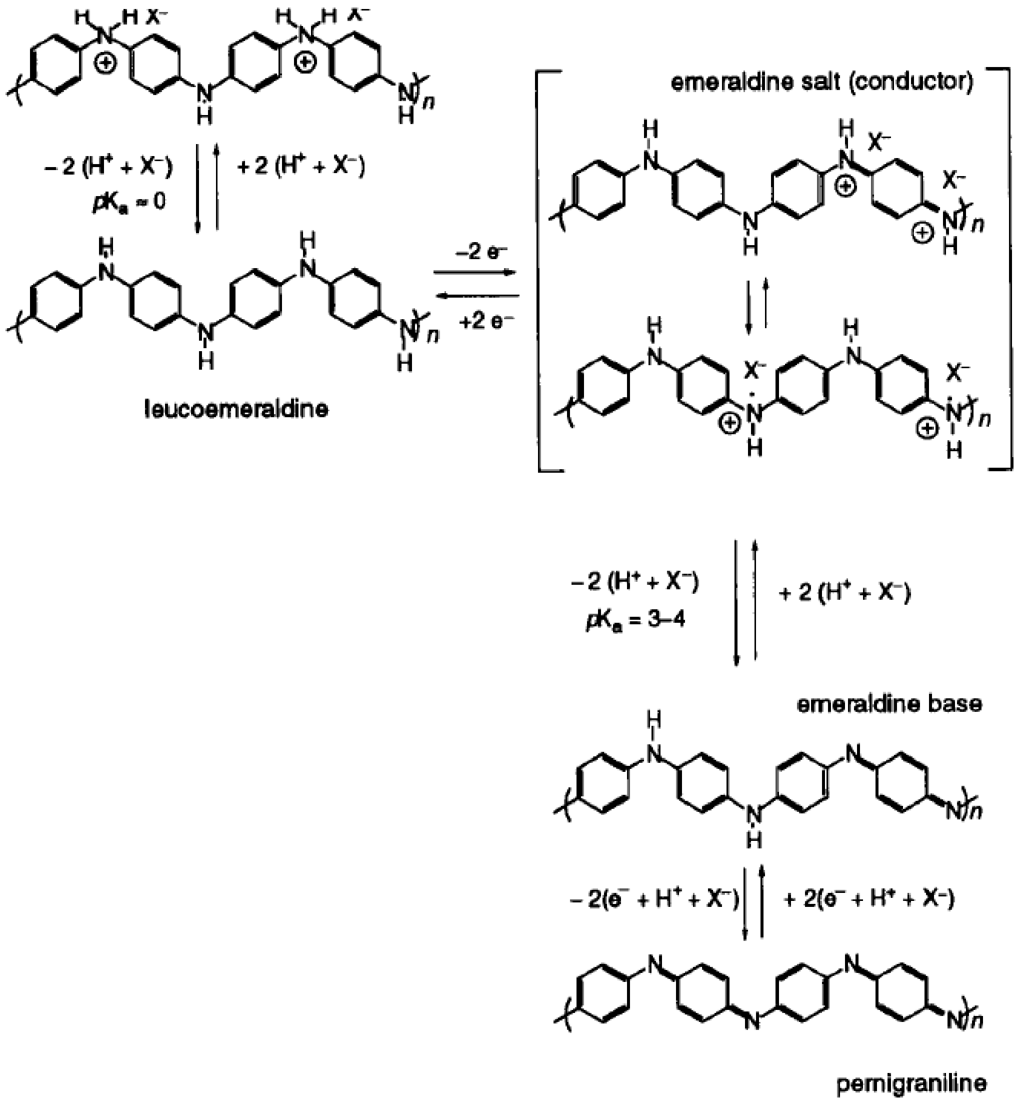
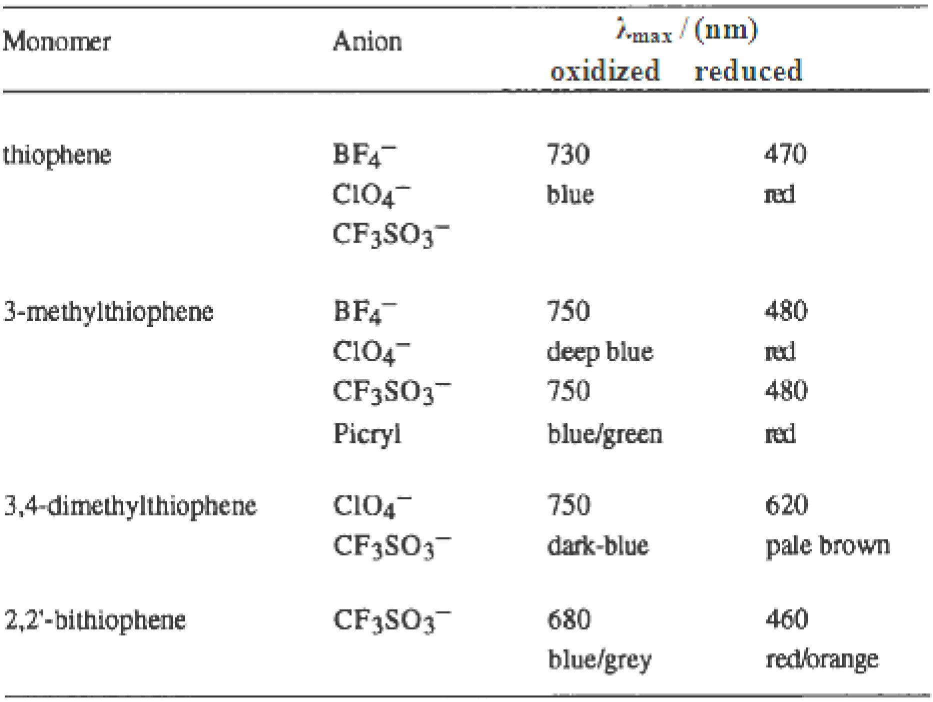


Figure 1.21 Oxidation reduction mechanism for polyaniline

The first reports of the electrochemical preparation of polypyrrole thin-films were reported by Dim et al. in 1979 [74-75]. The nature of the polymer product obtained by electro-oxidizing pyrrole depends greatly on the conditions used during electropolymerization. Removal of all dopant anions from polypyrrole yields a pale yellow film. However, complete de-doping is only achieved if films are extremely thin. The usual 'undoped' polypyrrole is yellow/green while doped (oxidized) polypyrrole is blue/violet.

Polythiophene derivatives were also taking great interest in order to increase color variety among organic electrochromes. The electrochromic properties of polythiophene and of the polymers of some of substituted thiophenes are produced in Fig. 1.22 [76].



Monomer	Anion	λ_{max} / (nm)	
		oxidized	reduced
thiophene	BF_4^-	730	470
	ClO_4^-	blue	red
	$CF_3SO_3^-$		
3-methylthiophene	BF_4^-	750	480
	ClO_4^-	deep blue	red
	$CF_3SO_3^-$	750	480
	Picryl	blue/green	red
3,4-dimethylthiophene	ClO_4^-	750	620
	$CF_3SO_3^-$	dark-blue	pale brown
2,2'-bithiophene	$CF_3SO_3^-$	680	460
		blue/grey	red/orange

Figure 1.22 Table of electrochromic properties of polythiophenes

Mark et al. have shown that the wavelength maxima of undoped poly(o1igothiophene) films decrease as the length of the oligothiophene monomer increases. The oxidation potentials do not vary much with oligothiophene (Fig 1.23) [77].

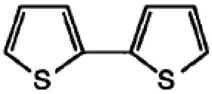
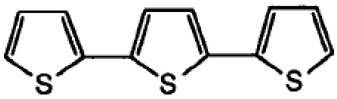
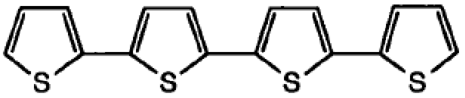
Monomer^a	λ/nm^b	E_{ox}/V
	519	0.95
	484	1.00
	356	1.04
	340	0.93

Figure 1.23 Table of absorption maxima and oxidation potentials for poly(o1igothiophene)s

Kathirgamanathan and Shepherd [78] have shown that poly(phenanthro[9, l0] thiophene) is electrochromic. This polymer is yellow in the potential range between -0.8 and 0 V, and red in the range 0 to 0.8 V.

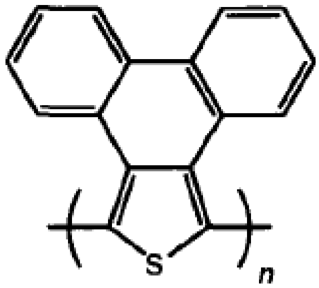


Figure 1.24 Chemical structure of poly(phenanthro[9, l0] thiophene)

In order to improve the properties required in electrochromism, conducting polymers were desired to be soluble and processable, fast switching with high optical contrasts and variable in colors. Toppare et al. showed that pyrrole and thiophene can be coupled appropriately in order to obtain these properties in several electrochromic polymers (SNS series) (Fig 1.25). Low oxidation potentials of monomers lead to easy electrochemical polymerization, and polymers exhibited band gaps between 1.94 and 2.2 eV with relatively low switching times 1.3 – 2 s [79-93].

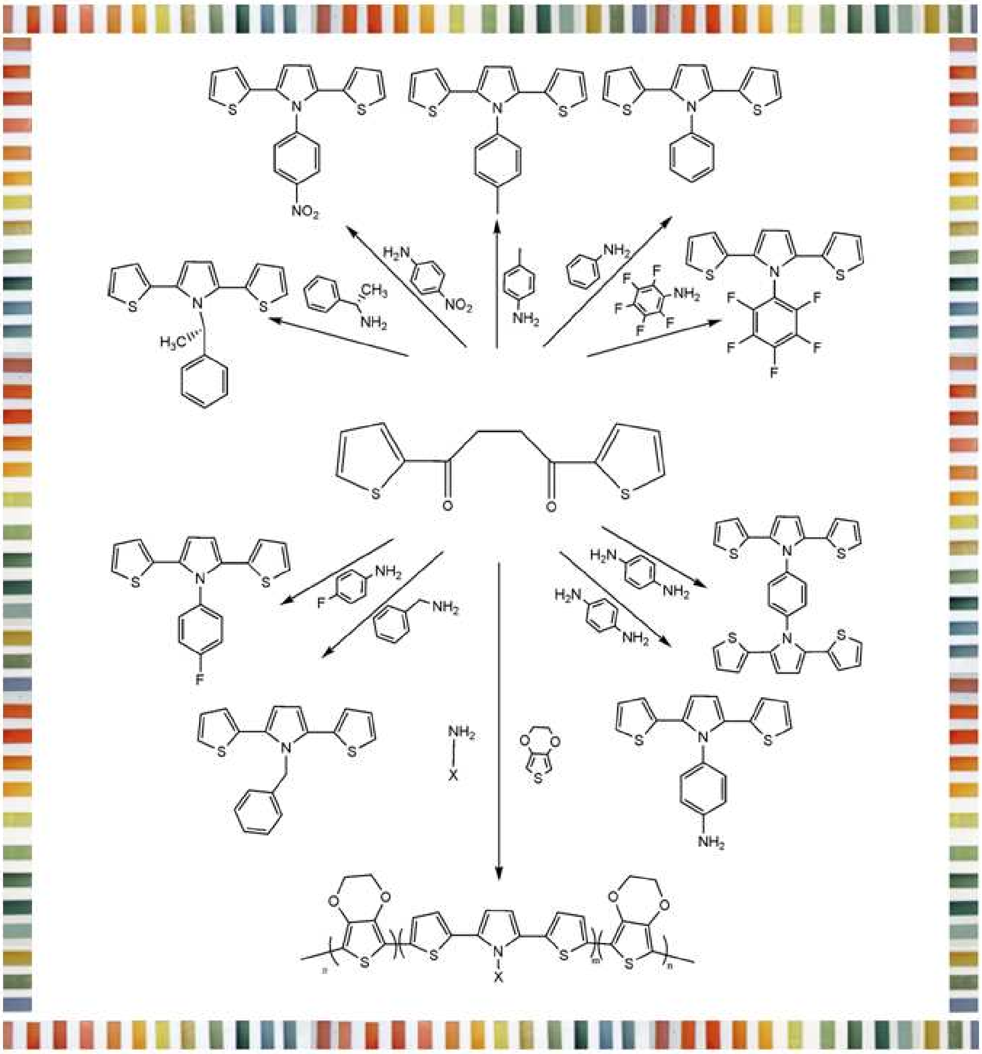


Figure 1.25 Chemical structures for the members of SNS series

Most of the conjugated polymers are colored in their neutral state because the energy difference between conduction band and the valence band lies within the visible region. Upon oxidation, π-π* transition decreases, and polaronic, bipolaronic bands emerge to produce a second color. While most electroactive polymers have the ability to exhibit two colors, only a few show multiple color states. Although poly(aniline) is the most attractive example of multicolor polymers with three distinct colored states it has low stability. After 300 cycles it loses almost all of its electrochromic properties [94-95].

To achive the goal of having full color space with minimum different polymer chains will lower the cost and increase the effectiveness of conducting polymers in electrochromic field. For this purpose, multicolor polymers and copolymers which have the ability to switch between different states for more than 5000 times were synthesized with several substituents. Electrochemical polymerization of a series of bisheterocycle-*N*-substituted carbazoles reveals transmissive canary yellow when fully reduced, transmissive lime green upon partial oxidation, and dark blue upon full oxidation (Fig 1.26) [96-97].

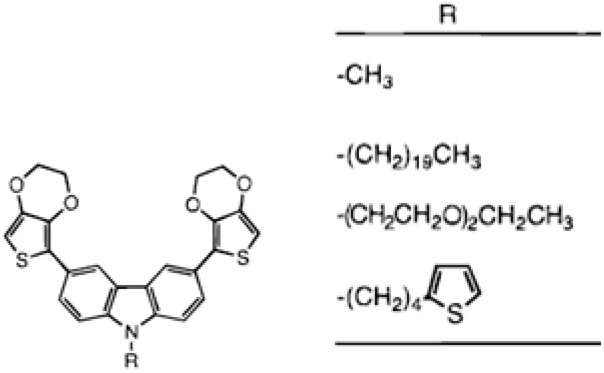


Figure 1.26 Example monomers of multicolor polymers

Substitutional modification to reach multicolor electrochromes was examined by different electron-donating alkyl chains. On pyrrole ring they caused a decrease in the oxidation potential of the monomers, thus facilitating electropolymerization, and also they distorted the coplanarity of the monomers and the resulting polymers. Poly(3-ethyl-2-(2-thienyl)-1*H*-pyrrole), poly(2), and poly(3-*n*-propyl-2-(2-thienyl)-1*H*-pyrrole), presented multicolor electrochromism (both cathodic and anodic) exhibiting several colors: blue-grayish (+0.8 V), light blue (+0.2 V), light brown (0 V), brown (-0.1 V), dark orange (-0.2 V) and light orange (-0.8 V) (Fig 1.27) [98].

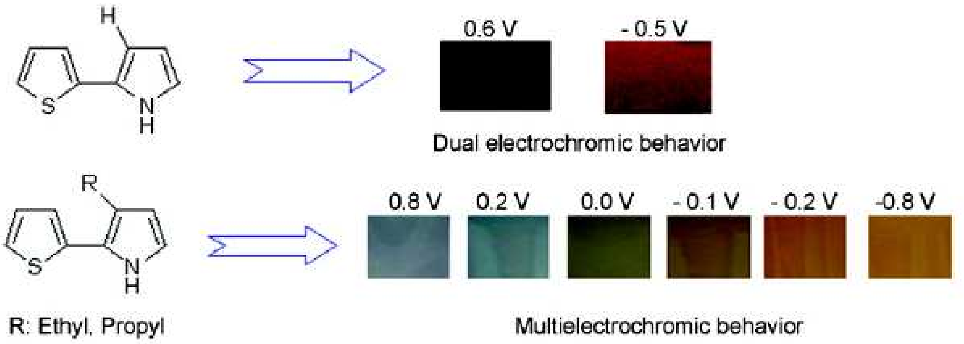
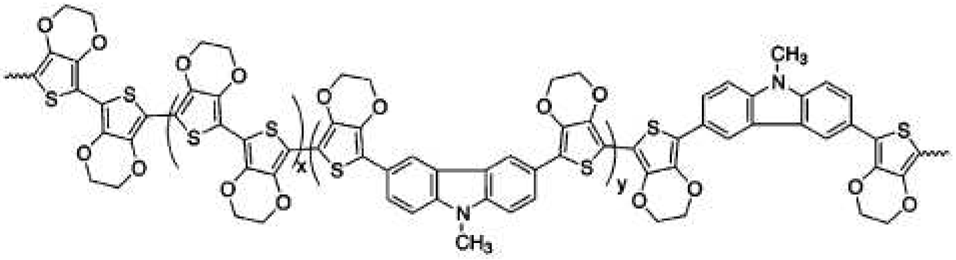
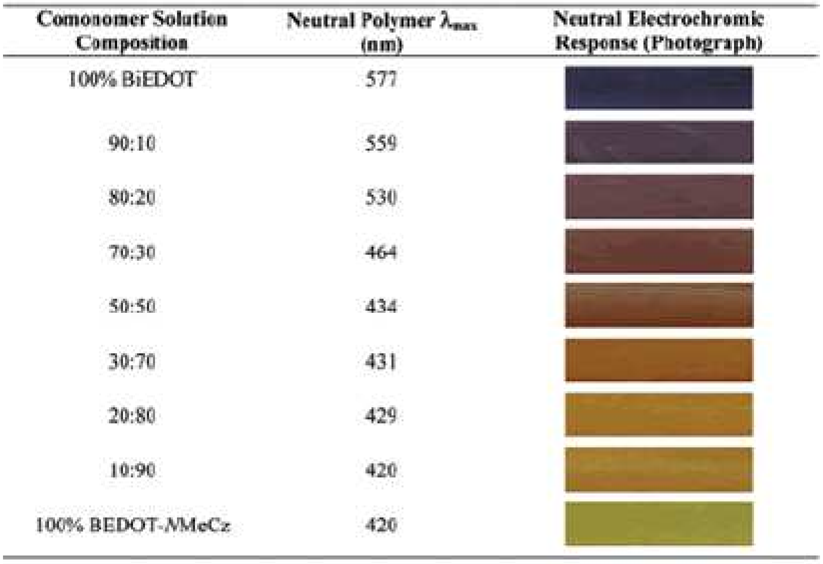


Figure 1.27 Structural modification in order to achive multicolor electrochromics

Multicolor electrochromes synthesized via electrochemical copolymerization can be formed as compositionally different copolymers by changing feed ratio of the monomers. Electrochemical copolymers of BiEDOT and 3,6-bis- (2-(3,4-ethylenedioxy)thienyl)-*N*-methylcarbazole (BEDOT-*N*MeCz) from nine comonomer solutions of varying concentration can be given as an example. The neutral copolymers possess colors ranging from blue (587 nm), to red (464 nm), to orange (429 nm), and finally to yellow (420 nm). Oxidized states of these polymers do not depend on initial comonomer concentration (Fig 1.28) [99].





Comonomer Solution Composition	Neutral Polymer λ_{max} (nm)	Neutral Electrochromic Response (Photograph)
100% BiEDOT	577	🟦
90:10	559	🟪
80:20	530	🟫
70:30	464	🟫
50:50	434	🟫
30:70	431	🟧
20:80	429	🟧
10:90	420	🟧
100% BEDOT-*N*MeCz	420	🟨

Figure 1.28 Chemical structures and effects of comonomer feed ratio on neutral state color of copolymer

On the other hand, stepwise switching of the polymer film with small increments of the applied potential, different shades of the same color can be achieved. Stepwise oxidation can change polymers oxidation state, resulting in different intensities of absorption at the same wavelength. For PEDOT, since this change is in the visible region, the polymer produces different tones of the same color which can be detectable by human eye (Fig 1.29). Stepwise oxidation of PEDOT film between its fully neutral (-0.9 V, dark blue color) and fully oxidized

(+1.0 V, sky blue color) states produces several different tones of the blue color [100].

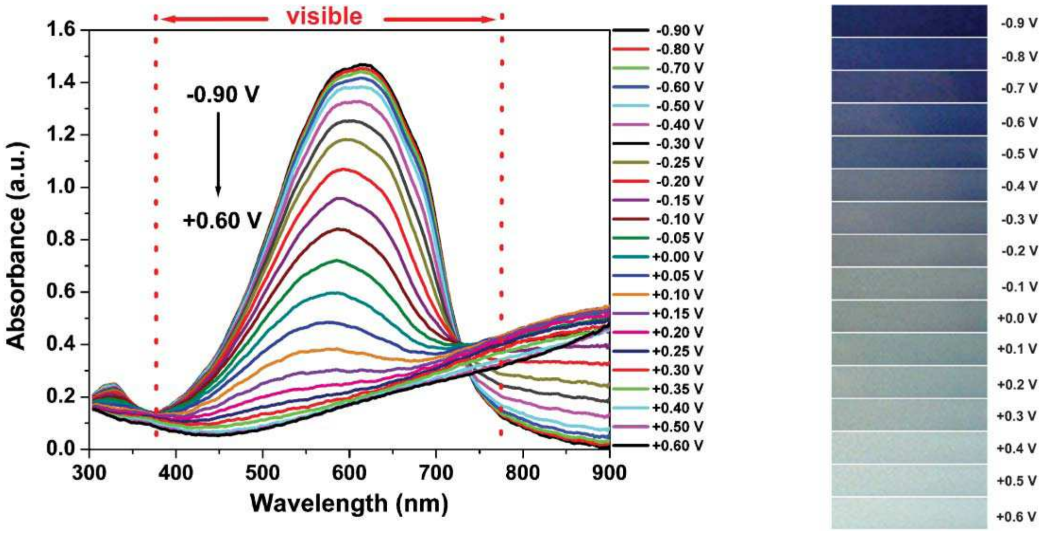


Figure 1.29 Absorbance change and different tones of the blue colors obtained by stepwise oxidation of PEDOT

Using the information gained from the previous works could lead to different colors and their tones for the polymers produced from the same monomers. If a copolymer prepared by changing feed ratios of the comonomers can change the color in the neutral state, applied potential during electrochemical copolymerization may also yield a similar result since it affects the monomer composition in the chain. For the copolymers of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine and EDOT varying the applied potential (with the same comonomer concentrations) resulted in eight different copolymers having maximum absorptions between 431 to 538 nm . In addition, by changing the working potential a total of 64 different colors were achieved (Fig. 1.30) [101].

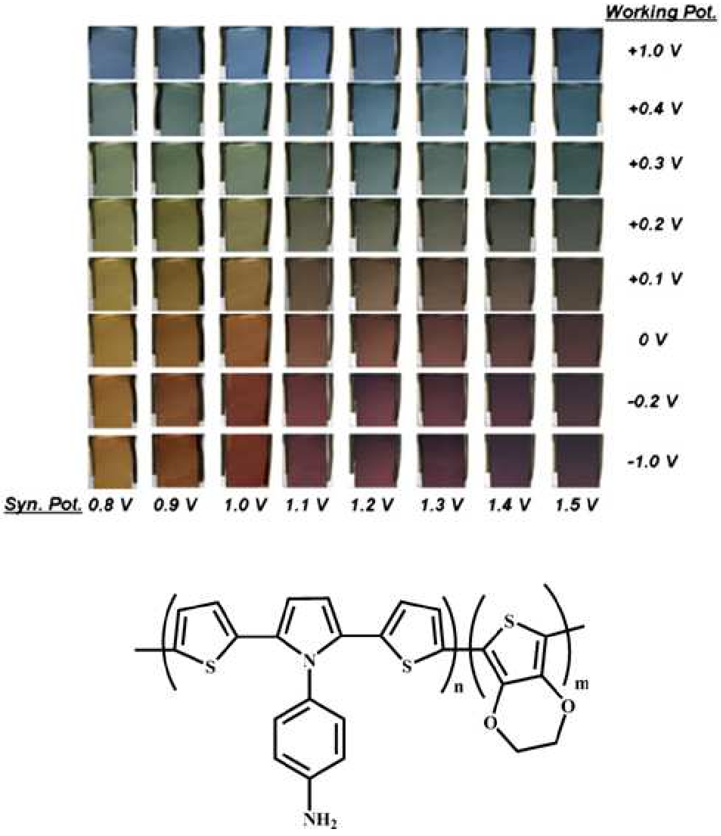


Figure 1.30 Colors for the **c**opolymer of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine and EDOT synthesized by varying the applied potential

Introducing different colors and different tones were not enough to satisfy scientists' curiosity. Conducting polymers are great candidates to be used as active layers in many devices such as organic light emitting diodes (OLEDs) and organic solar cells. If they could carry both positive and negative charges on the polymer chain, the efficiency of those devices would be increased [102]. Additionally, n doping can lead to color variation since it will change not only the charge carrier characteristics but also the oxitadion level of the polymer. Mobility of the positive charge is not a problem since almost all polymers have the tendency to be p-doped whereas n dopable polymers are limited for a handful of materials.

Due to the high sensitivity and reactivity of the anion charge carriers with oxygen and water, n-type doped systems are not stable under ambient conditions. This makes few examples of n dopable materials difficult to characterize during n doping. For p doping, formation of charge carriers can be detected in situ by combining a potentiostat with spectrometer which is a very useful technique to reveal true doping. However, characterization of n doping needs inert atmosphere and non-oxidizing working environment.

An important way to produce n dopable molecules is lowering the conduction band level for accessible oxidation and reduction. Nitrogen (may be more than one) containing heterocycles has the ability to lower the reduction potentials due to the lower molecular orbital energy of nitrogen compare to carbon (Fig 1.31) [103-104].

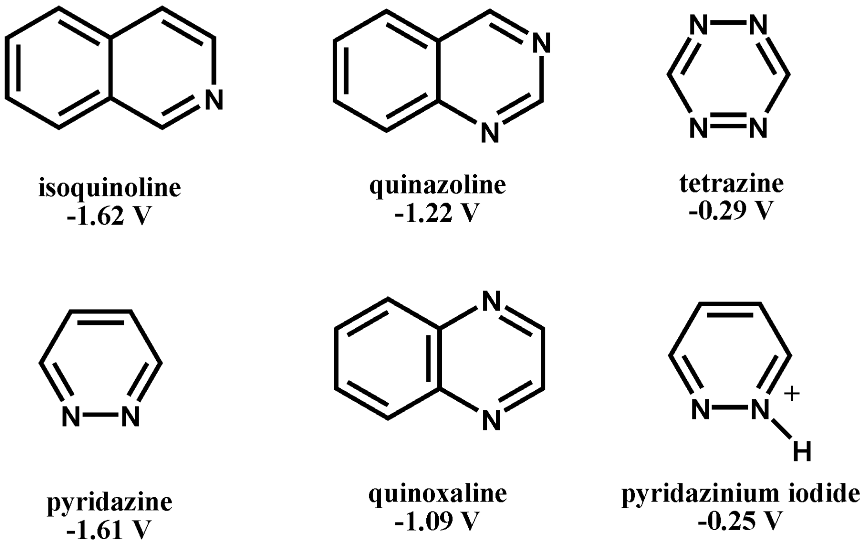


Figure 1.31 Reduction potentials of common nitrogen containing heterocyclics

However, by the help of donor acceptor theory electron rich groups could be coupled with these nitrogen containing heterocycles to yield relatively stable n doped polymers which allows to detect at least a couple of spectral changes upon reduction. Synthesis and electrochemical polymerization of 8,11-bis(4-hexylthiophen-2-yl)acenaphtho[1,2-b]quinoxaline (HTAQ) revealed a polymer that is susceptible to both p- and n-doping. The polymer has fast switching time and high optical contrast. Highly fused nitrogen containing acceptor group was utilized in the polymer backbone which was resulted in a polymer that has a significant potential for n-type doping (Fig 1.32) [105].

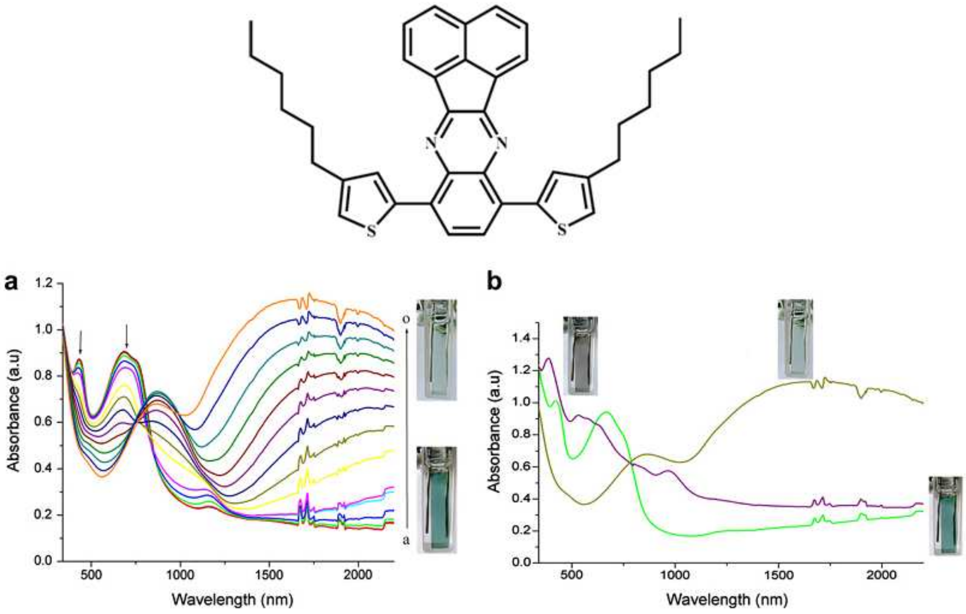


Figure 1.32 (a) p-Doping: spectroelectrochemistry of polymer film at applied potentials (V); (a) _0.3, (b) _0.2, (c) _0.1, (d) 0.0, (e) 0.1, (f) 0.2 (g) 0.3, (h) 0.4, (i) 0.5, (j) 0.6, (k) 0.7 (l) 0.8, (m) 0.9 and (n) 1.0. (b) n-doping: spectroelectrochemistry at -1.5 V, -0.3 V and +1.0 V

The three primary colors, red, blue, and green are required for commercial electrochromic application. When three legs of color space are completed, all other colors can be obtained according to color mixing theory [106]. This theory states that if two color stimuli are mixed, the resulting color stimulus will be between those two colors and tones of the new colors can be controlled by varying the amounts of the two. Although many red and blue colored polymers in their neutral form have been reported, no green colored conducting polymer was reported until breakthrough work of Sönmez et al. [107].

In order to have a green color, there should exist at least two simultaneous absorption bands in the red and blue regions of the visible spectrum. Additionally both absorption bands must be controlled simultaneously with the same applied potential.

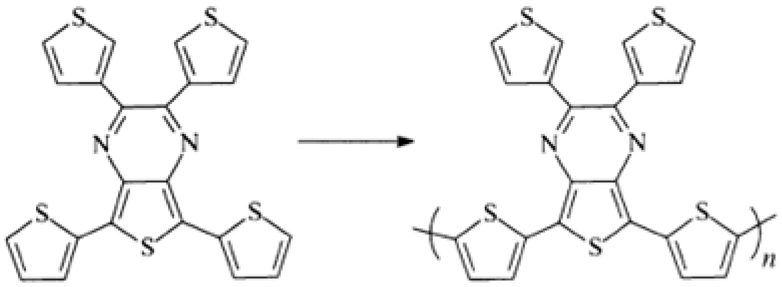


Figure 1.33 Structure of the first green electrochromic polymer

To be employed in displays, polymers should switch between one of the three primary colors and their transmissive states. Although poly (2,3-di(thien- 3-yl)-5,7-di(thien-2-yl)thieno[3,4-b]pyrazine) was the only option for green polymeric material, it has a brown colored oxidized state which limits its applications. Recently, Toppare et. al. showed that poly(4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo [1,2,5] thiadiazole) is the first truly green electrochromic polymer which has a highly transmissive sky blue oxidized state. The polymer has a band gap of 1.2 eV and it reveals two well separated absorption maxima at 428 nm and 755 nm [108].

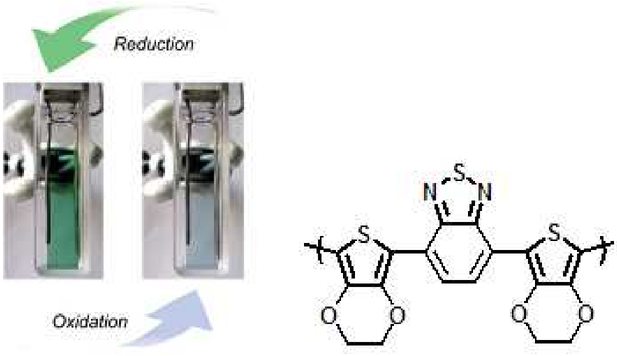


Figure 1.34 Structure of the first green to transmissive electrochromic polymer

Processable (soluble in common organic solvents), n dopable and green to highly transparent electrochromes were synthesized by Toppare et. al. [109-111] and later by Reynolds et al. [112].

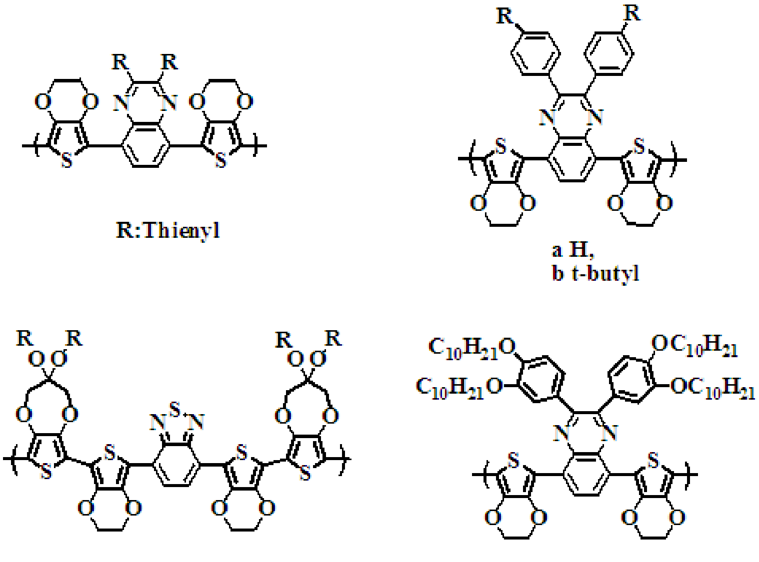


Figure 1.35 Structures of some green to transmissive electrochromic materials

While investigating the use of the donor–acceptor approach in designing novel polymers exhibiting two absorption bands in the visible, Reynolds et al. discovered that low- and high-energy transitions can be controlled by varying the repeat unit in order to obtain black to transmissive electrochrome [113]. Black to transmissive electrochromic materials are also very difficult to achieve, because the polymer should absorb all visible light. Thanks to donor acceptor theory these molecules were also integrated in the electrochromic field.

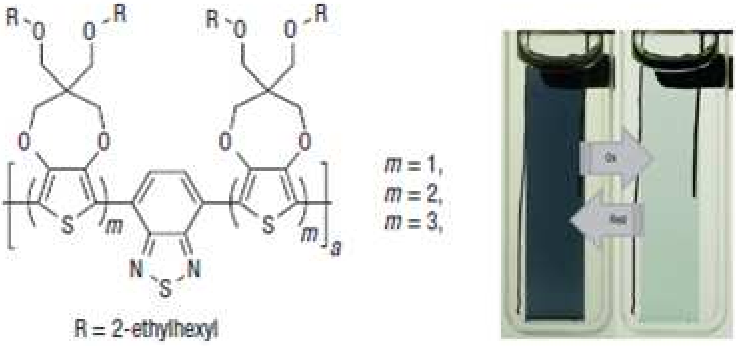


Figure 1.36 Structure of the black to transmissive electrochromic polymer

After all these investigations and improvements in the field of electrochromism new polymers should be designed to combine more than one property in order to achieve the most effective device. The importance of the studies examined in this thesis address the point where electrochromisim is taken one step further.

1.11 Aim Of This Work

Two new donor acceptor type monomers 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole (BEBT) and 2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (TBT) were synthesized and characterized. Their electrochromic properties and the potentials were shown by electrochemical and spectroscopic techniques. Aim of the studies for this thesis was enhancement in electrochromic properties of the blue and the red components of RGB (red, green, blue) color system. In order to achieve this goal, firstly the blue component EDOT and a new acceptor unit 2-dodecylbenzotriazole decided to be coupled. Additionally, for improvement studies of the red component polythiophene, 2-dodecylbenzotriazole coupled with thiophene and gave a unique polymer, PTBT. The surprising results explained in detail in the following chapters showed that aim was achieved successfully.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

Iron(III) chloride, (Aldrich), NaOH (Merck), tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich), $LiClO_4$ (Aldrich), NaClO4 (Aldrich), propylene carbonate (PC) (Aldrich) and poly(methylmethacrylate) (PMMA) (Aldrich) were used as received. Thiophene (Aldrich) was distilled before use. Dichloromethane (DCM) (Merck), nitromethane (Aldrich), methanol (Merck), tribtyl tin chloride (Aldrich), N-butyl lithium (Aldrich) and 3,4-ethylenedioxythiophene (EDOT) (Aldrich) were used without further purification. Anhydrous acetonitrile (ACN) and tetrahydrofuran (THF) purchased from Across were used as received.

2.2. Equipment

The cyclic voltammograms were recorded using VoltaLab PST050 and Solartron 1285 potentiostats. Measurements were performed at room temperature. A VoltaLab PST050 and a Solartron 1285 Potentiostats were used to provide a constant potential in the electrochemical polymerization. These devices can maintain the voltage difference between the working and reference electrodes at a constant desired value during the electrolysis and compensate for the voltage drop in the electrolysis solution. Electrolyses were performed in a one-compartment cell which was open to air atmosphere unless otherwise mentioned. The working electrode was ITO, counter electrode was platinum (Pt) and the reference electrode was silver (Ag) wire. A Varian Cary 5000 UV-Vis spectrophotometer was used to perform the spectroelectrochemical studies of polymer. Colorimetry measurements were done via a Conica Minolta CS-100 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra of the monomers and the catalytically produced polymer were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) with $CDCl_3$ as the solvent and chemical shifts (δ) were given in ppm relative to tetramethylsilane as the internal standard. Fluorescence measurements were conducted using a Varian Eclipse spectrofluorometer. Column chromatography of products was performed using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Reactions were monitored by thin layer chromatography with fluorescent coated aluminum sheets. Solvents used for spectroscopy experiments were spectrophotometric grade.

2.3. Procedure

2.3.1. Synthesis

2.3.1.1. Synthesis of 2-Dodecylbenzotriazole

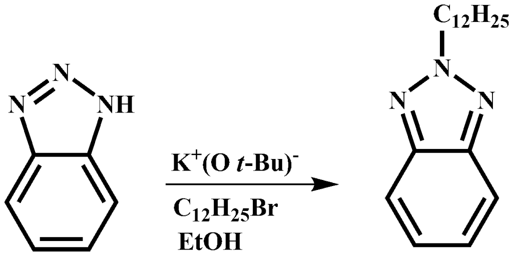


Figure 2.1 Synthetic route for 2-dodecylbenzotriazole

Synthesis of 2-dodecylbenzotriazole was performed according to methodology described in the literature for a similar compound [114]. 1,2,3-Benzotriazole (5.0 g, 42 mmol), potassium tert-butoxide (5.0 g, 44 mmol), and bromododecane (12.2 g, 49 mmol) were dissolved in methanol (50 mL). The mixture was refluxed for 12 h and monitored by TLC. After removal of the solvent by evaporation, the residue was dissolved in $CHCl_3$ and extracted with water. The organic extract was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography (3:2 chloroform:hexane; *R*f, 0.29) to obtain 2-dodecylbenzotriazole as a colorless oil (3.7 g, 31%).

2.3.1.2. Synthesis of 4,7-Dibromo-2-dodecylbenzotriazole

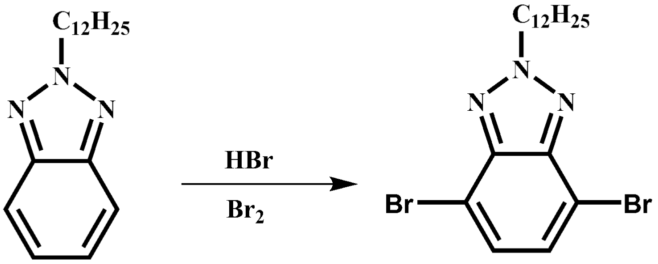


Figure 2.2 Synthetic route for 4,7-dibromo-2-dodecylbenzotriazole

Synthesis of 4,7-dibromo-2-dodecylbenzotriazole was performed according to a method described for a similar compound [114]. 2-Dodecylbenzotriazole (3.7 g, 13.1mmol) and an aqueous HBr solution (5.8 M, 15 mL) were added to a flask, and the mixture was stirred for 1 h at 100 °C. Bromine (5.9 g, 36 mmol) was added and the mixture was stirred for 12 h at 135 °C. After the mixture was cooled to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. With column chromatography (1:1 chloroform:hexane; *R*f, 0.33), 4,7- dibromo-2-dodecylbenzotriazole was obtained as light yellow oil (4.3 g, 75%).

2.3.1.3. Synthesis of tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane

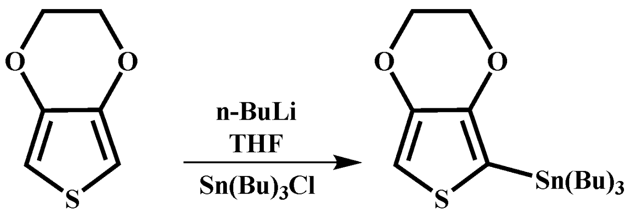


Figure 2.3 Synthetic route for tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane

Stannylation of EDOT was performed according to a method described in the literature [115]. EDOT (4 g, 28.1 mmol) was dissolved in THF (80 mL), and the solution was cooled to -78°C. n-Butyllithium (17.6 mL, 28.1 mmol) was added drop-wise, and the mixture was kept under stirring at -78°C during 1 h. Then, tributyltin chloride (9.2 g, 28.1 mmol) was added at -78°C via a syringe and the mixture was allowed to warm to room temperature with stirring for 24 h. At the end of the reaction, water (100 mL) was added to the mixture. The phases were separated and organic layer was extracted from the aqueous layer with CH_2Cl_2. All the organic layers were then washed with water, subsequently dried over $MgSO_4$ and concentrated to give product as a brown viscous liquid.

2.3.1.4. Synthesis of Tributyl(thiophen-2-yl) stannane

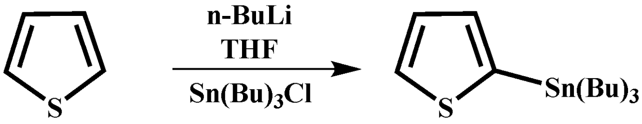


Figure 2.4 Synthetic route for tributyl(thiophen-2-yl) stannane

Synthesis of tributyl(thiophen-2-yl) stannane was carried out by following a literature procedure for a similar compound [116]. Thiophene (4.0 g, 47.1 mmol) was dissolved in THF, slowly lithiated with n-BuLi (29.5 mL, 47.1 mmol) and stirred for 30 min at -30°C. Then tributyl tinchloride (15.4 g, 47.1 mmol) was added dropwise at this temperature. The solution is stirred over night at room temperature and the solvent was evaporated to give crude compound as a brown oily residue.

2.3.1.5. Synthesis of 4,7-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] Triazole (BEBT)

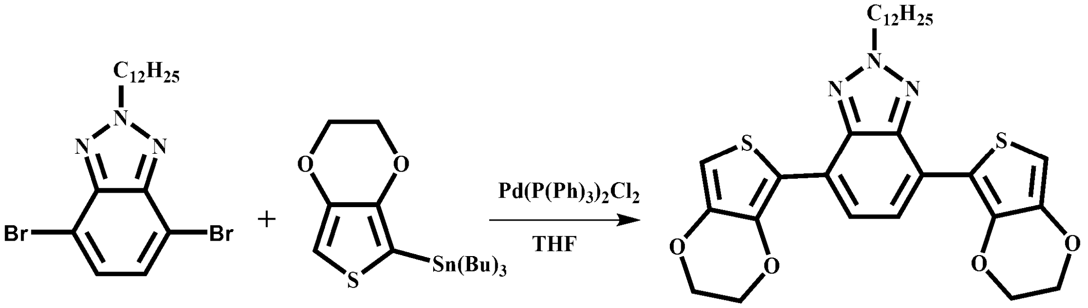


Figure 2.5 Synthetic route for BEBT

4,7-Dibromo-2-dodecylbenzotriazole (100 mg, 0.224mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane were dissolved in anhydrous THF (100 mL). The solution was purged with argon for 30 min and dichlorobis(triphenylphosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature under argon atmosphere. The mixture was refluxed for 24 h. Solvent was evaporated under a vacuum and the crude product was purified by column chromatography (2:1 chloroform:hexane; *R*f, 0.45) on silica gel to obtain 80 mg (63%) BEBT.

2.3.1.6. Synthesis of 2-Dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (TBT)

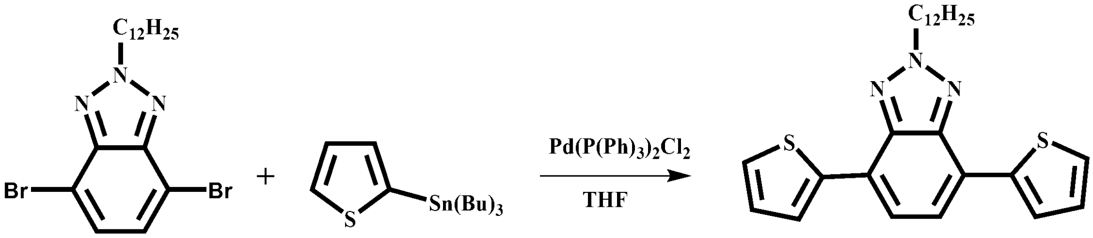


Figure 2.6 Synthetic route for TBT

4,7-Dibromo-2-dodecylbenzotriazole (100 mg, 0.224mmol), and tributyl(thiophen-2-yl) stannane were dissolved in anhydrous THF (100 ml) and dichlorobis(triphenylphosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature. The mixture was refluxed for 12 hours under argon atmosphere. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel to obtain 75 mg (74%) TBT.

2.4. Synthesis of Conducting Polymers

2.4.1. Electrochemical Polymerization

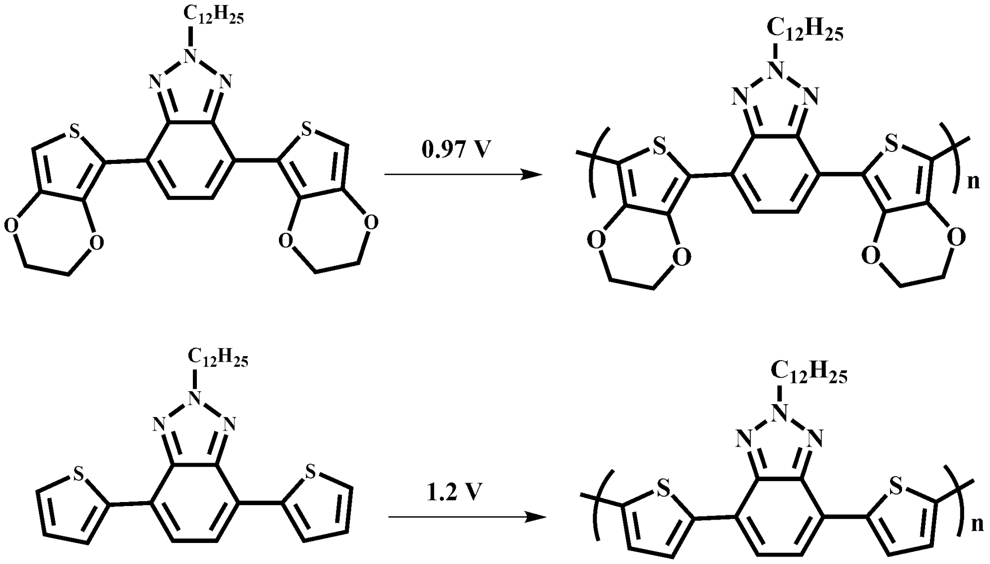


Figure 2.7 Electrochemical polymerization of BEBT and TBT

The in-situ potentiodynamic electropolymerization of both BEBT and TBT (1×10^{-2} M) were carried out by applying potentials between -0.5 V and +1.1 V at a scan rate of 100 mV/s in 0.1 M $TBAPF_6$ / DCM : ACN (5 / 95, v/v) solvent-electrolyte mixture. ITO coated glass slides were used as the working electrode; Pt was used as counter electrode, with Ag wire reference electrode. The free standing films formed were washed with ACN to remove unreacted monomer and excess electrolyte after electrolysis.

2.4.2. Chemical Polymerization of TBT (PII)

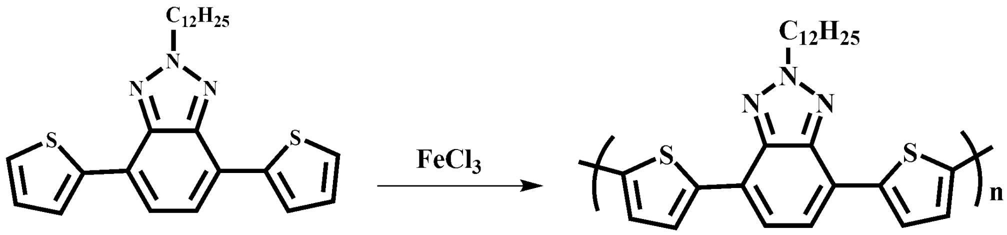


Figure 2.8 Chemical polymerization of TBT

100 mg TBT were dissolved in 10 mL of $CHCl_3$ under argon atmosphere. $FeCl_3$ (142 mg) was suspended in 10 mL of nitromethane and slowly added to the monomer solution. Yellow solution slowly turned to deep green and finally deep blue. Mixture was stirred for 4 h and then added into 200 mL methanol. The precipitate was dissolved in $CHCl_3$ and extracted with water several times. Organic phase was dried with magnesium sulfate and evaporated. Residue was dissolved in 50 mL THF and 50 mL hydrazine monohydrate was added. In order to de-dope the polymer completely, mixture was stirred for 12 h and during this period solution turned to dark red. THF was evaporated under reduced pressure. Chloroform was added to the residue and the organic phase was extracted several times with water. Combined organic phases were evaporated and the residue was stirred in acetone to remove unreacted monomers. The polymer was filtered and dried under vacuum to give PII as dark-red solid.

2.5. Characterization of Conducting Polymers

2.5.1. Cyclic Voltammetry (CV)

Cyclic voltammetry is a convenient way of analyzing the electroactivity of monomers and obtaining the oxidation-reduction peak potentials of the polymers.

CV scans linearly the potential of a stationary working electrode using a triangular waveform (Figure 2.9). During the potential sweep, the current resulting from the applied potential is measured by a potentiostat. Expected response of a reversible redox couple during a single potential cycle is given in Figure 2.10.

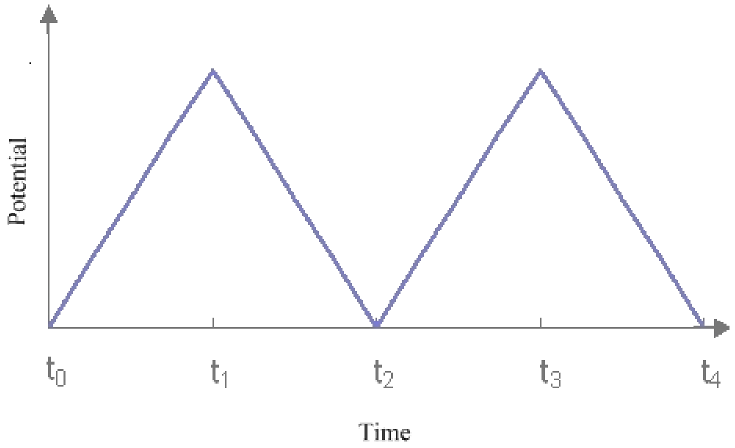


Figure 2.9 Cyclic voltammetry waveform

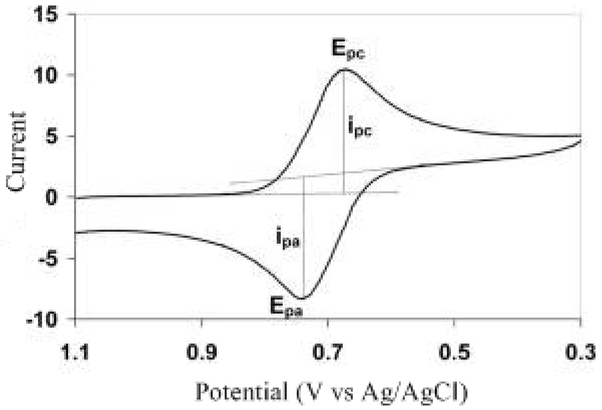


Figure 2.10 A cyclic voltammogram for a reversible redox process

The characteristic peaks in the CV are formed due to the diffusion layer near the electrode surface. The resulting current peak reflects the continuous change of concentration gradient with time. Hence, the increase in the current corresponds to the achievement of diffusion control, while current drop (beyond the peak) is independent of the applied potential.

The peak height, i_p, is directly proportional to the concentration, C, as described by the Randles-Sevcik equation:

$$i_p = 0.4463\, n\, F\, A\, C\, (n\, F\, v\, D / R\, T)^{1/2}$$

In this equation, n is the number of electrons appearing in half-reaction for the redox couple, v is the rate at which the potential is swept (V / sec), F is Faraday’s constant (96485 C / mol), A is the electrode area (cm^2), R is the universal gas constant (8.314 J / mol K), T is the absolute temperature (K), and D is the analyte’s diffusion coefficient (cm^2/sec). Note that if the temperature is assumed to be 25°C (298.15 K), the Randles-Sevcik equation can be written in a more concise form,

$$i_p = (2.687 \times 10^5)\, n^{3/2}\, v^{1/2}\, D^{1/2}\, A\, C$$

The Randles-Sevcik equation predicts that the peak current should be proportional to the square root of the sweep rate. For these processes, it was assumed that the reactants and products are soluble in solution and the surface processes (adsorption of reactants and products) can be neglected.

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

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

where Γ is the total amount of reactant initially present at the electrode surface. According to this equation the current peak depends linearly on scan rate. Thus, investigation of peak current intensity with respect to scan rate will indicate the nature of electrochemical process as being diffusion controlled or whether the polymer is well adhered to the electrode surface or not.

2.5.2. Spectroelectrochemistry

Spectroelectrochemistry is a powerful tool to probe unique species that are generated in-situ during redox reactions at electrode surfaces, by the combination of electrochemical and spectroscopic techniques that can be operated at the same time. During redox switching of conjugated polymers, changes in electronic transitions occur which lead to changes in absorbance. These changes make conjugated polymers useful in electrochromic applications such as smart windows, mirrors, etc. UV-Vis spectroscopy is used to monitor these electronic transitions. Spectra are recorded while the polymer is oxidized by increasing the potential stepwise. Spectroelectrochemistry experiments reveal some important properties of conjugated polymers such as band gap (E_g), λ_{max}, and the intergap states that appear upon doping like evolution of polaron and bipolaron bands. Similar studies were accomplished for electrochromic devices in order to investigate the spectral variations.

In order to probe electronic transitions upon doping-dedoping processes, spectral changes were investigated by UVvis- NIR spectrophotometer in a monomer free, 0.1 M $TBAPF_6$, ACN solution. Applied potentials were increased from -0.5 to 1.1 V for PBEBT and from 0.4 V to 1.2 V for PTBT where these polymers were coated on ITO glass slides potentiodynamically.

2.5.3 Switching Studies

Electrochromic switching studies are performed to monitor the percent transmittance changes as a function of time and to determine the switching time of the polymer at its λ_{max} by stepping potential repeatedly between the neutral and oxidized states. A square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry was used to investigate switching times and contrast in the polymer.

In order to study switching properties of polymers, PBEBT and PTBT were deposited on ITO-coated glass slides as thin films via potentiodynamic electrolysis in a 0.1 M $TBAPF_6$ and 1×10^{-2} M monomer solution in acetonitrile(ACN) and CH_2Cl_2 (95/5, v/v) at a scan rate of 100 mV/s. Square-wave potential utilized to polymer coated ITO slides in a monomer free $TBAPF_6$/ACN electrolyte solvent couple, between fully reduced states of polymers to fully oxidized states with a residence time of 5 seconds.

2.5.4 Colorimetry

Colorimetry analysis was performed to determine three attributes used to describe the color: hue, saturation and brightness. Hue represents the wavelength of maximum contrast (dominant wavelength) and is commonly referred to color. Saturation represents the purity (intensity) of the 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.

A commonly used scale that numerically defines colors was established in 1931 by The Commission Internationale de l’Eclairge (CIE system) with L*a*b, CIE color spaces (Figure 2.4). Color measurements were performed via Coloreye XTH Spectrophotometer.

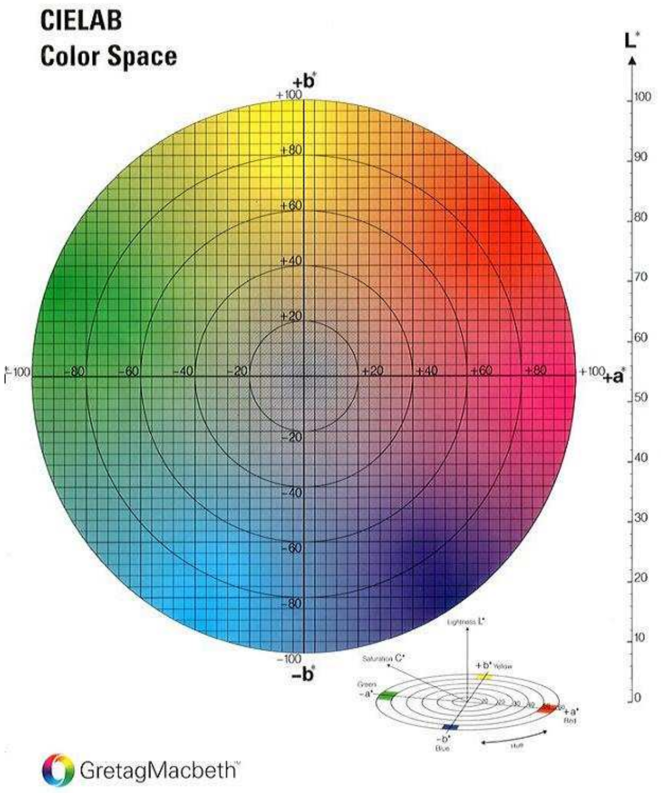


Figure 2.11 CIELAB color space

CHAPTER 3

RESULTS AND DISCUSION

3.1. Characterization

3.1.1 2-Dodecylbenzotriazole

^{1}H (400 MHz, $CDCl_3$, δ): 7.76 (m, 2H), 7.26 (m, 2H), 4.62 (t, J) 7.1 Hz 2H), 2.12 (m, 2H), 1.25-1.15 (m, 18H), 0.78 (t, J) 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.3, 126.1, 117.9, 56.6, 31.8, 30.0, 29.5, 29.4, 29.4, 29.3, 29.3, 29.0, 26.5, 22.6, 14.0.

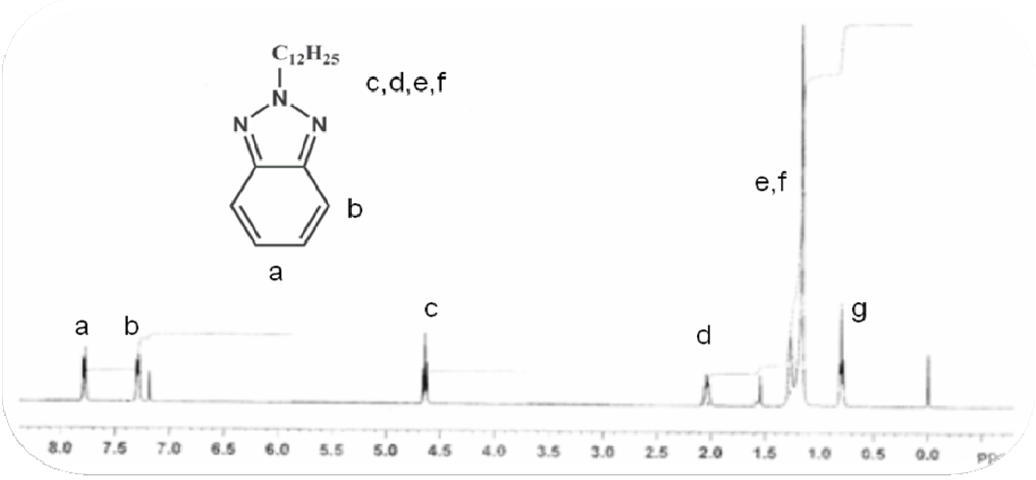


Figure 3.1 ^{1}H-NMR spectrum of 2-dodecylbenzotriazole

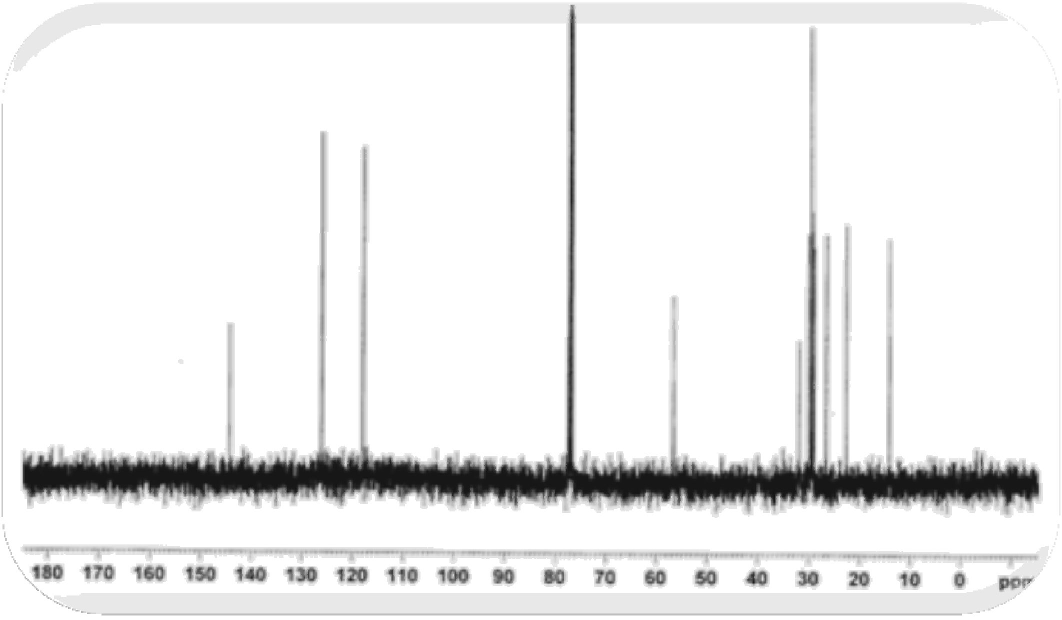


Figure 3.2 ^{13}C NMR spectrum of 2-dodecylbenzotriazole

3.1.2. 4,7-Dibromo-2-dodecylbenzotriazole

^{1}H (400 MHz, CDCl3, δ): 7.36 (s, 2H), 4.60 (t, *J*) 7.0 Hz, 2H), 2.10 (m, 2H), 1.38-1.12 (m, 18H), 0.80 (t, *J*) 6.9 Hz, 3H). ^{13}CNMR (100 MHz, CDCl3, δ): 143.7, 129.4, 109.9, 57.4, 31.8, 30.1, 29.5, 29.5, 29.4, 29.4, 29.3, 28.9, 26.4, 22.6, 14.0.

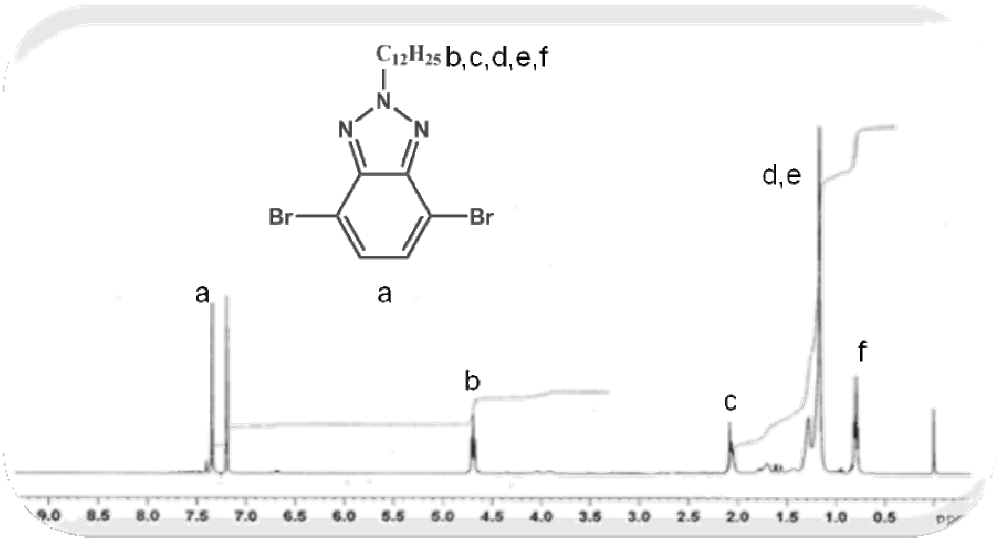


Figure 3.3 ^{1}H-NMR spectrum of 4,7-dibromo-2-dodecylbenzotriazole

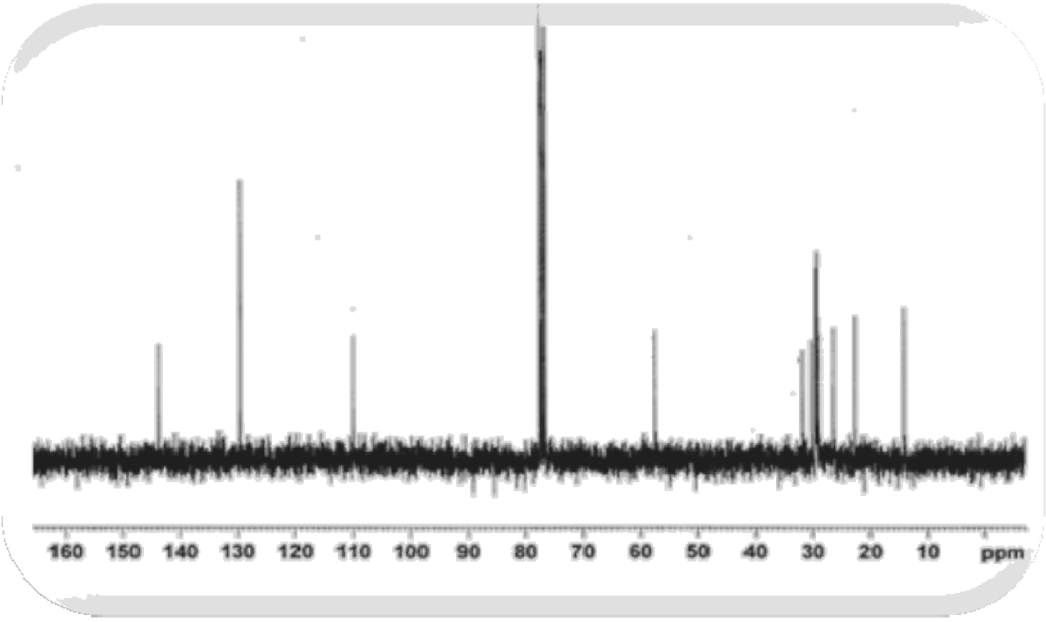


Figure 3.4 ^{13}C NMR spectrum of 4, 7-dibromo-2-dodecylbenzotriazole

3.1.3. 4,7-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] Triazole (BEBT)

^{1}H (400 MHz, CDCl3, *δ*): 8.00 (s, 2H), 6.40 (s, 2H), 4.60 (t, *J*) 7.0 Hz, 3H), 4.40(m, 4H), 4.22(m, 4H), 2.10 (m, 2H), 1.38-1.12 (m, 18H), 0.80 (t, *J*) 6.9 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6, *δ*): 141.6, 140.7, 139.8, 122.8, 120.6, 112.3, 101.2, 64.9, 64.0, 56.1, 31.2, 29.1, 28.9, 28.8, 28.8, 28.7, 28.6, 28.2, 25.8, 22.0, 13.9. MS (*m*/*z*): 567 [M+].

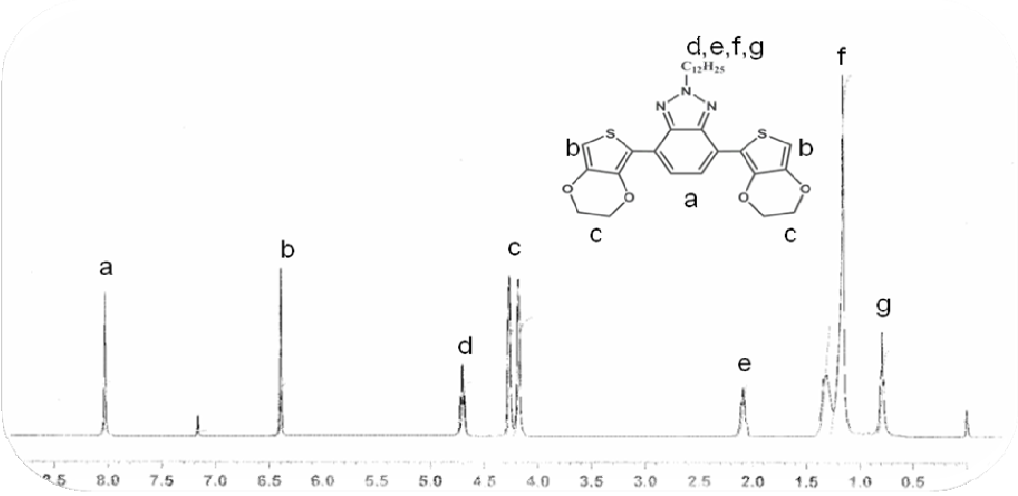


Figure 3.5 ^{1}H-NMR spectrum of BEBT

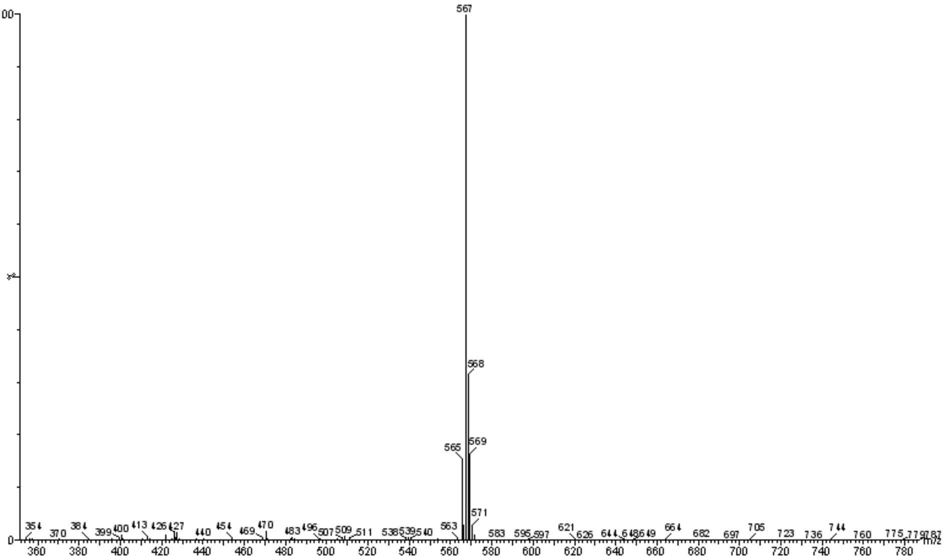


Figure 3.6 Mass spectrum of BEBT

3.1.4. 2-Dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (TBT)

^{1}H NMR (400MHz, $CDCl_3$, δ): 8.01 (d, *J*=5.6 Hz, 2H), 7.52 (s, 2H), 7.28 (d, *J*=6.0 Hz, 2H), 7.09 (t, J_A=8.8 Hz, J_B = 4.8, 2H), 4.60 (t, *J*=7.0 Hz, 2H), 2.10 (m, 2H), 1.38-1.15 (m, 18H), 0.80 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 142.4, 140.2, 128.4, 127.3, 125.8, 123.9, 123.0, 57.1, 32.2, 30.3, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 26.9, 22.9, 14.4.

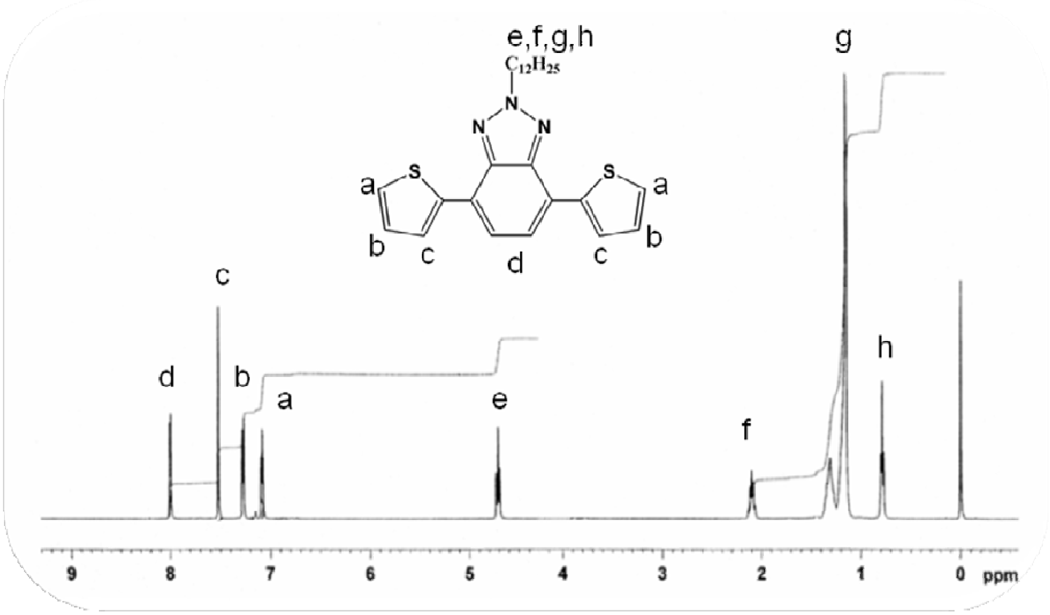


Figure 3.7 ^{1}H-NMR spectrum of TBT

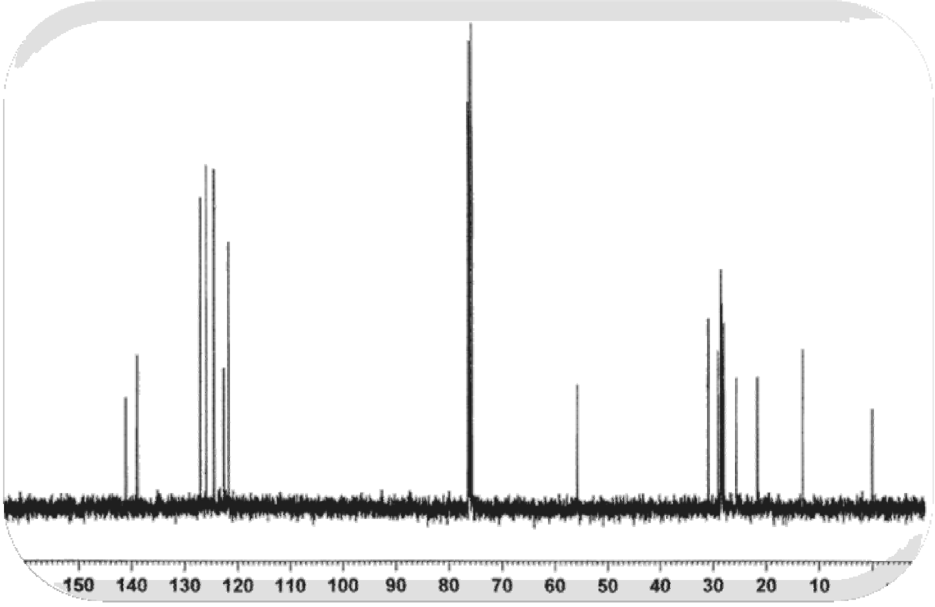


Figure 3.8 ^{13}C -NMR spectrum of TBT

3.2. Electrochemical and Electrochromic Properties of Benzotriazole Containing Polymers

3.2.1 Electrochemical and Electrochromic Properties of PBEBT

3.2.1.1. Electrochemistry of BEBT

Multiple scan voltammetry was performed in a 0.1 M TBAPF6 and 1 × 10^{-2} M BEBT solution applying potentials between -0.5 V and +1.1 V at a scan rate of 100 mV/s (Fig. 3.9). The solvent was chosen as the mixture of acetonitrile (ACN) and CH_2Cl_2 (95/ 5, v/v) due to the poor solubility of the monomer in ACN. Since the monomer bears an alkyl chain in the structure, the oligomers are soluble in pure CH_2Cl_2. Hence, a mixture of these two solvents was used as the solvent. The monomer oxidation potential was observed at 0.97 V, which is quite lower than the oxidation potential of EDOT. After the first cycle, an oxidation peak at 0.23 V and its reverse cathodic peak at -0.04 V appeared.

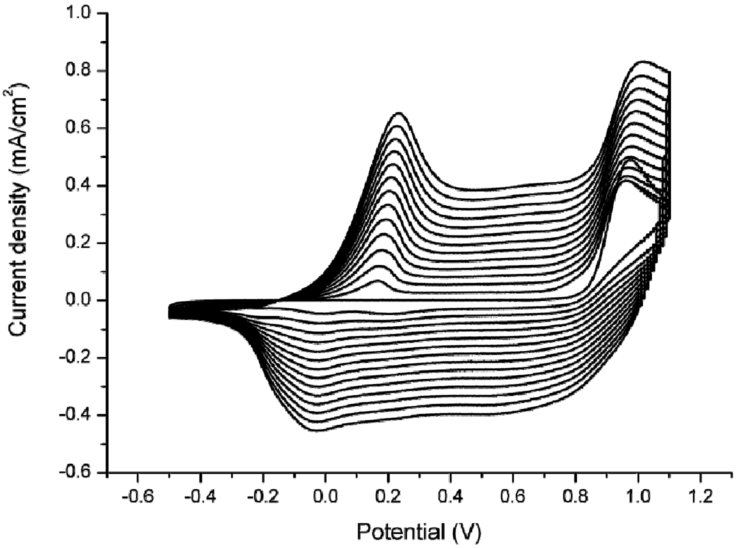


Figure 3.9 Repeated potential scan electropolymerization of BEBT at 100 mV / s in 0.1 M $TBAPF_6/CH_2Cl_2$/ACN on an ITO electrode

As seen in the figure (Fig 3.9) current density is increasing with repeated cycling. That shows that surface area of ITO is increasing due to the deposition of conducting polymer film on ITO surface. This result is an obvious proof that both the monomer and the polymer were electroactive and formation of a conducting polymer was taking place.

The polymer also revealed n doping properties where a reversible redox couple with an E_{ox} of -1.62 and E_{red} of -1.71 V, versus the same reference electrode, was observed for the n type doping and dedoping processes respectively (Figure 3.10). The anodic and cathodic peaks of PBEBT were proportional with the scan rate, indicating that the films were well-adhered and charge transfer process was not dominated by diffusion.

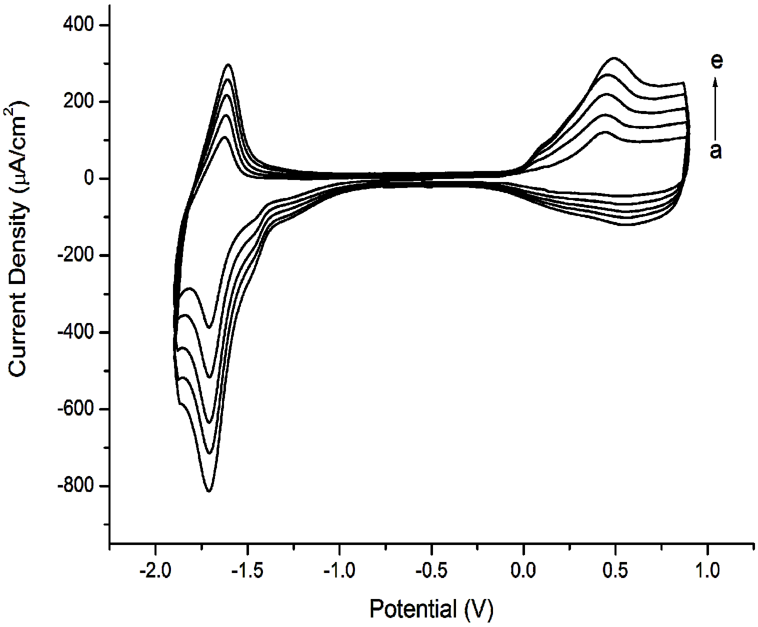


Figure 3.10 Scan rate dependence of a PBEBT film in TBAPF6/ACN: (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 mV s^{-1}

3.2.1.2 Optoelectrochemistry and electrochromic switching of PBEBT

To probe the optical changes upon doping, spectral changes were investigated by UV-vis-NIR spectrophotometer in a monomer free, 0.1 M TBAPF$_6$, ACN solution while increasing the applied potential from -0.5 to 1.1 V. Although PBEBT is a donor-acceptor type polymer and this type of materials usually show two distinct absorption maxima, [117] PBEBT revealed only one due to the dominant donor characteristic of the EDOT moiety (Fig. 3.11). The peak at 618 nm which corresponds to the π-π* transition of the neutral polymer is analogous to EDOT itself hence; the polymer is deep blue in the neutral state. The band gap of the polymer is 1.6 eV, which was calculated from the onset of the π-π* transition. As a result of charge carrier formation upon oxidation, the absorption in the visible region depletes and new absorption bands evolve at 900 nm and 1600 nm representing the formation of polaronic and bipolaronic bands [118]. PBEBT film is saturated blue (*Y*, 195, *x*, 0.209; *y*, 0.216) in its neutral state, and the color changes to highly transparent light blue (*Y*, 688; *x*, 0.288; *y*, 0.330) in the oxidized state. Although conducting polymers have great tendency to exhibit both p- and n-doping ability only a few of them show this notable property. The n-type polymers can be used in fabrication of many different types of polymer based electronic devices such as bipolar and pnp type field effect transistors. True n-type doping process can be proved by a reversible redox couple at negative potentials and more importantly, a drastic change in the NIR region upon reduction. As seen from Figure 4, PBEBT reveals a drastic change of 30 % in optical contrast upon reduction which is a critical proof that PBEBT is a true n-type dopable polymer [119]. The polymer had a pale bluish-gray (*Y*, 615, *x*, 0.298; *y*, 0.314) in the reduced state.

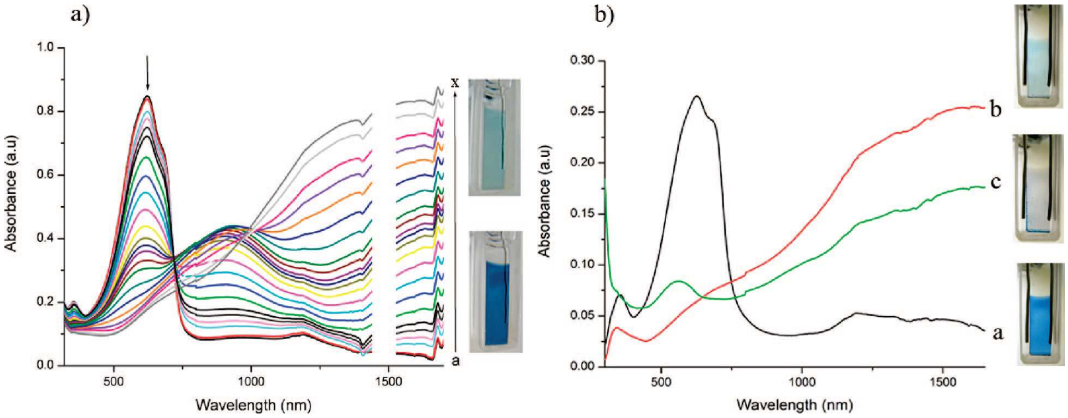
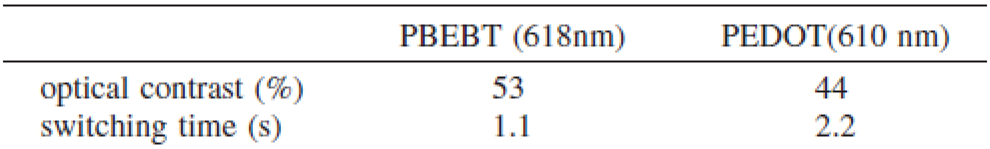


Figure 3.11 Spectroelectrochemistry of PBEBT film on an ITO coated glass slide in monomer-free, 0.1 M $TBAPF_6$/ACN electrolyte-solvent couple at applied potentials (V). *(a)* p-doping; (a) -0.5, (b) -0.4, (c) -0.3, (d) - 0.2, (e) -0.1, (f) 0.0, (g) 0.1, (h) 0.15, (i) 0.2, (j) 0.25, (k) 0.3, (l) 0.35, (m) 0.4, (n) 0.45, (o) 0.5, (p) 0.55, (q) 0.6, (r) 0.65, (s) 0.7, (t) 0.75, (u) 0.8, (v) 0.9, (w) 1.0, and (x) 1.1. *(b)* n-doping: (a) - 0.5, (b) 1.1, and (c) -1.71 V

3.2.1.3 Kinetic Properties of PBEBT

PBEBT revealed exceptional optical contrasts of 53 % at 618 nm and 71 % at 1600 nm (Fig. 3.12). PEDOT has 44 % optical contrast at around 600 nm. These optical contrast data for PBEBT are surprisingly better than the ones observed for PEDOT. Additionally, the PBEBT showed remarkable switching time of 1.1 s at 100 % optical contrast where PEDOT needs at least 2.2 s to achieve full switching (Table 3.1). This argument is valid even for a PBEBT film with an optical contrast greater than that of PEDOT.

Table 3.1 Optical contrast and switching time comparison between PBEBT and PEDOT



	PBEBT (618nm)	PEDOT(610 nm)
optical contrast (%)	53	44
switching time (s)	1.1	2.2

The coloration efficiency which provides information about the contrast ratio acquired for a certain amount of charge introduced in the material was calculated as 211 cm^2/C (at 95 % of full switch at 600 nm). It is the ratio between the change in optical density at a specific dominant wavelength and the injected/ejected charge per unit area of the electrode. As regards to the coloration efficiency PBEBT is remarkably higher than the coloration efficiency of PEDOT (183 cm^2/C).

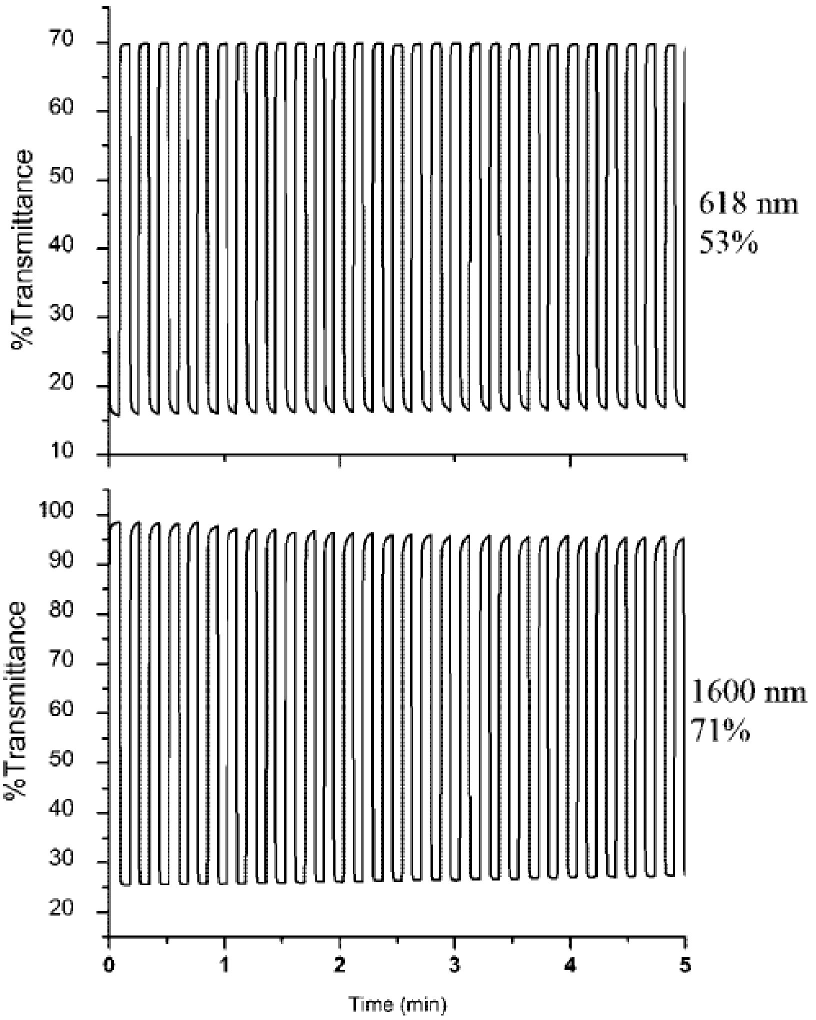
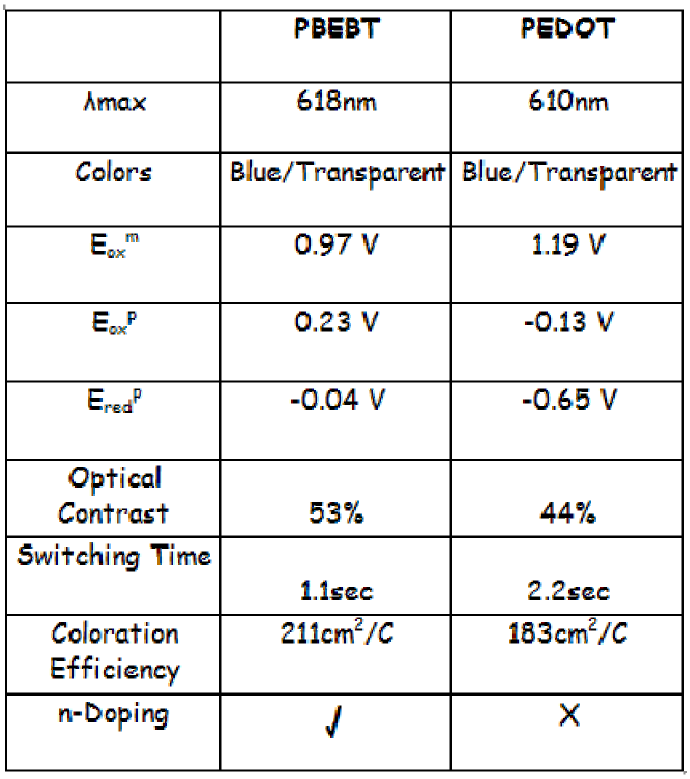


Figure 3.12 Electrochromic switching and percent transmittance change monitored at 618 and 1600 nm for PBEBT in 0.1 M TBAPF$_6$/ACN

Upon long term oxidation and reduction, conducting polymer films may lose their charge carrying and color change abilities partially. There are two distinct reasons for this losts; namely extrinsic and intrinsic effects. Extrinsically, external environmental agent such as oxygen, water, peroxides can attact to the charged sites of the polymer. If a conducting polymer is extrinsic unstable then it must be protected by a stable coating. Many conducting polymers, however, degrade over time even in dry, oxygen free environment. This is due to the intrinsic instability of conjugated polymer chain. The reason behind this kind of degradation is the possibility of an irreversible chemical reaction between charged sites of polymer and either the dopant counter ion or the p-system of an adjacent neutral chain. This produces an sp^3 hybridized carbon breaking the conjugation. In order to obtain industrially applicable conducting polymers for low cost optoelectronics, the long-term switching stability becomes a vital requirement for many electrochromic device applications, especially smart windows [120]. To determine the stability of the polymer, a film was deposited on a Pt wire using cyclic voltammetry (CV) from a solution of 0.01 M monomer in 0.1 M $TBAPF_6$/ CH_2Cl_2 electrolyte. The polymer films were cycled between their fully neutral and oxidized states in lithium perchlorate/ propylene carbonate (PC) electrolyte/solvent couple. Once electrochemical equilibration was reached (after 600 cycles), PBEBT revealed outstanding redox stabilities upon cycling, where less than 6 % decrease in total charge was observed even after 4000 cycles, indicating the robustness of PBEBT upon successive switchings.

Table 3.2 PBEBT vs. PEDOT : comparison of electrochemical and electrochromic properties



	PBEBT	PEDOT
λmax	618nm	610nm
Colors	Blue/Transparent	Blue/Transparent
E_{ox}^{m}	0.97 V	1.19 V
E_{ox}^{p}	0.23 V	-0.13 V
E_{red}^{p}	-0.04 V	-0.65 V
Optical Contrast	53%	44%
Switching Time	1.1sec	2.2sec
Coloration Efficiency	211cm^2/C	183cm^2/C
n-Doping	✓	X

3.2.2 Electrochemical and Electrochromic Properties of PTBT

3.2.2.1. Electrochemistry of TBT

The homopolymer of 2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d] [1,2,3] triazole (TBT) was synthesized both electrochemically (PI) and chemically (PII). PI was successfully produced by oxidative electropolymerization from an acetonitrile (ACN) solution containing 10^{-2} M TBT and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) on ITO coated glass slides. The monomer oxidation occurs at 1.2 V vs. Ag wire pseudo reference electrode (0.35 V vs. SCE). A reversible redox couple evolved at potentials 1.0 V and 0.6 V as the electroactive PI deposits on ITO surface (Fig. 3.13).

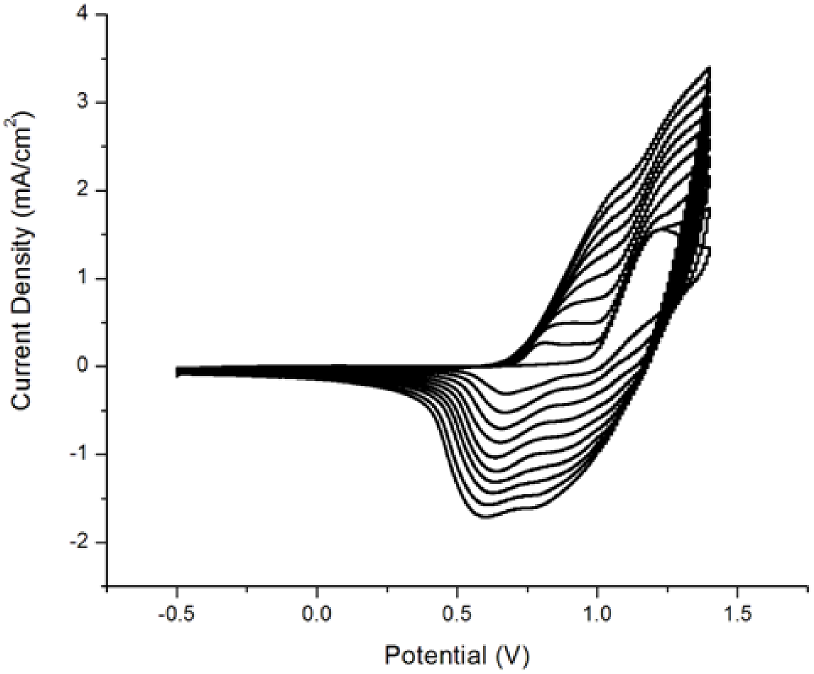


Figure 3.13 Repeated potential-scan electropolymerization of TBT in 0.1 M ACN/TBAPF$_6$ solvent-electrolyte system at a scan rate of 100 mVs^{-1} on ITO electrode

Chemically produced polymer, PII was spray coated onto ITO coated glass slides and its electrochemical behavior was determined in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in ACN. It revealed the same electrochemical properties as PI, as given by the single scan cyclic voltammetry (Fig. 3.14).

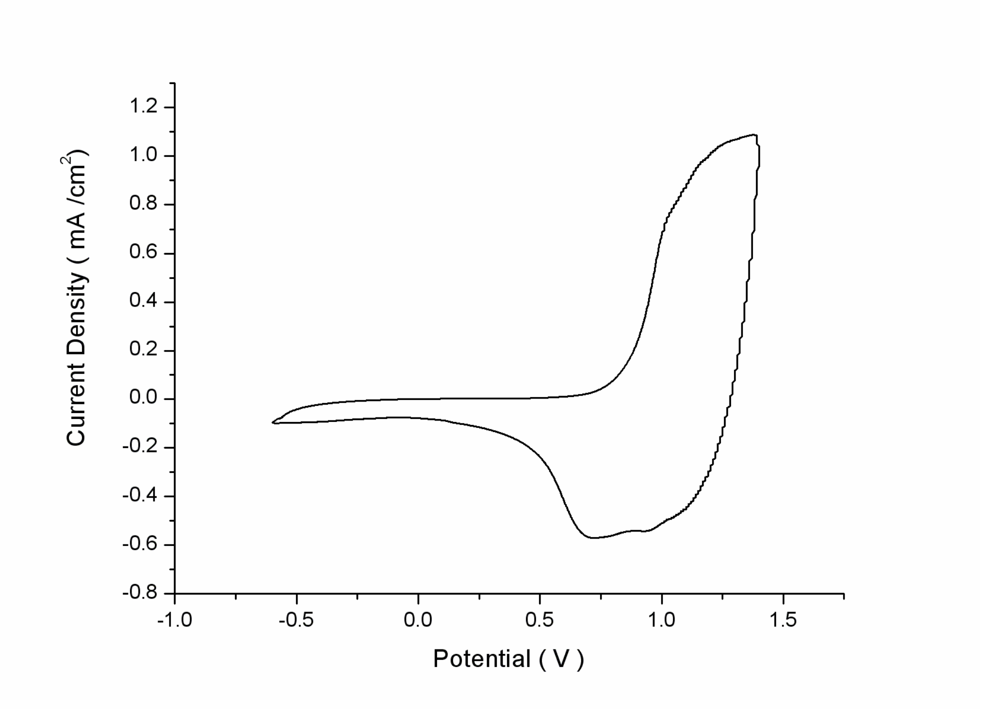


Figure 3.14 Single scan cyclic voltammetry of PII on an ITO electrode at 100 mV s^{-1} in 0.1M $TBAPF_6$/ACN

The unique n-doping property for conjugated polymer systems was clearly observed by cyclic voltammetry (CV) for PI with a reversible redox couple at -1.4 V (ox.) and -1.6 V (red.) versus Ag wire reference electrode. As seen from Fig. 3.15 the scan rate dependence of PI was investigated by CV and a true linear relation was observed between the peak current and the scan rate, which indicates the presence of a well adhered electroactive film with a non-diffusion limited redox process. Additionally even at high scan rates, oxidation and reduction processes were still reversible.

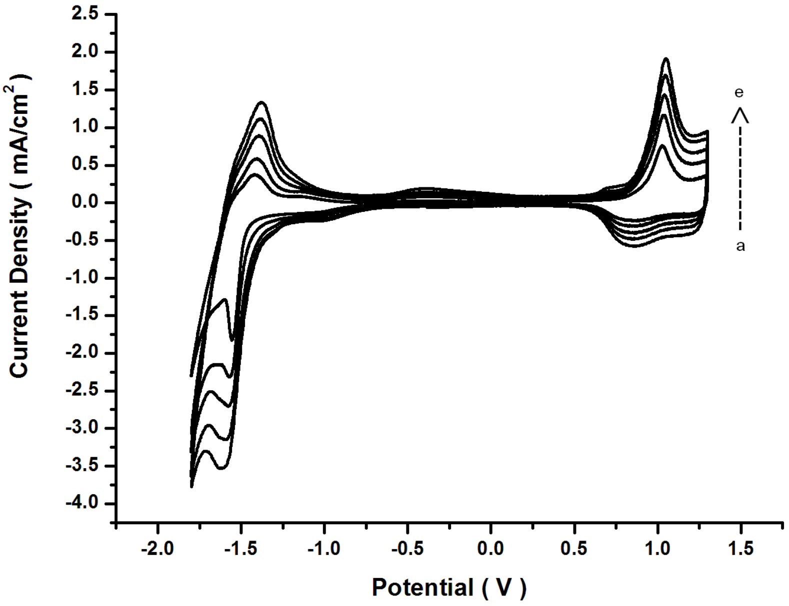


Figure 3.15 Scan rate dependence of PI film in ACN/$TBAPF_6$ at: (a) 100, (b)150, (c) 200, (d) 250 and (e) 300 mVs^{-1}

Scan rate dependence of PII was investigated by the same way. Linear relation between the peak current and the scan rate indicates electroactive spray coated PII film revealed reversible oxidation and reduction processes even at high scan rates and redox process was not limited by diffusion (Fig. 3.16).

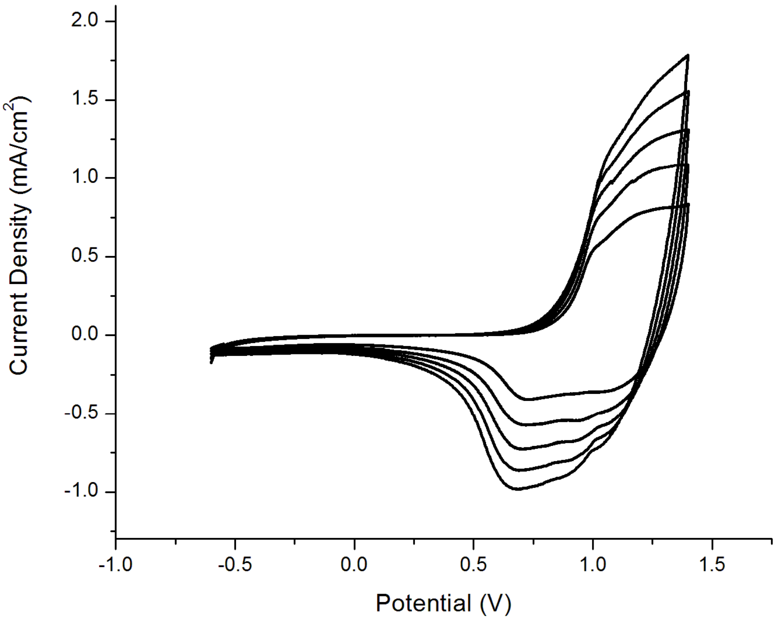


Figure 3.16 Scan rate dependence of PII film on ITO, in TBAPF$_6$/ACN at : (a)100, (b)150, (c)200, (d)250 and (e) 300 mV s^{-1}

3.2.2.2 Optoelectrochemistry and electrochromic switching of PTBT

The optoelectrochemistry of the polymer revealed an absorption maximum at 503 nm corresponding to the π- π^* transition of the polymer and the band gap of the polymer was calculated to be 1.65 eV from this transition (Fig. 3.17).

The polymer is deep red in its neutral state. Upon oxidation the absorption at 503 nm depletes and a new absorption band forms at 700 nm due to the formation of polaron band. Since the polaron band of the polymer is still in the visible region, polymer reveals several distinct colors. Upon oxidation, the deep red color of the polymer turns into brown. Further oxidation results in black which is a rare and significant property for an electrochromic polymer. Having black color in any state makes the polymer a significant candidate for smart window applications. A green color was observed as the doping proceeds. Generation of a green color in a polymeric system is remarkable since one should have two simultaneous absorptions at around 400 and 700 nm. As the potential was further increased, the polymer turns into a deep blue color. One remarkable point is that incremental increases in potential turn out to be enough to have all above mentioned colors. The corresponding Lab values for all colors can be found in Table 3.3.

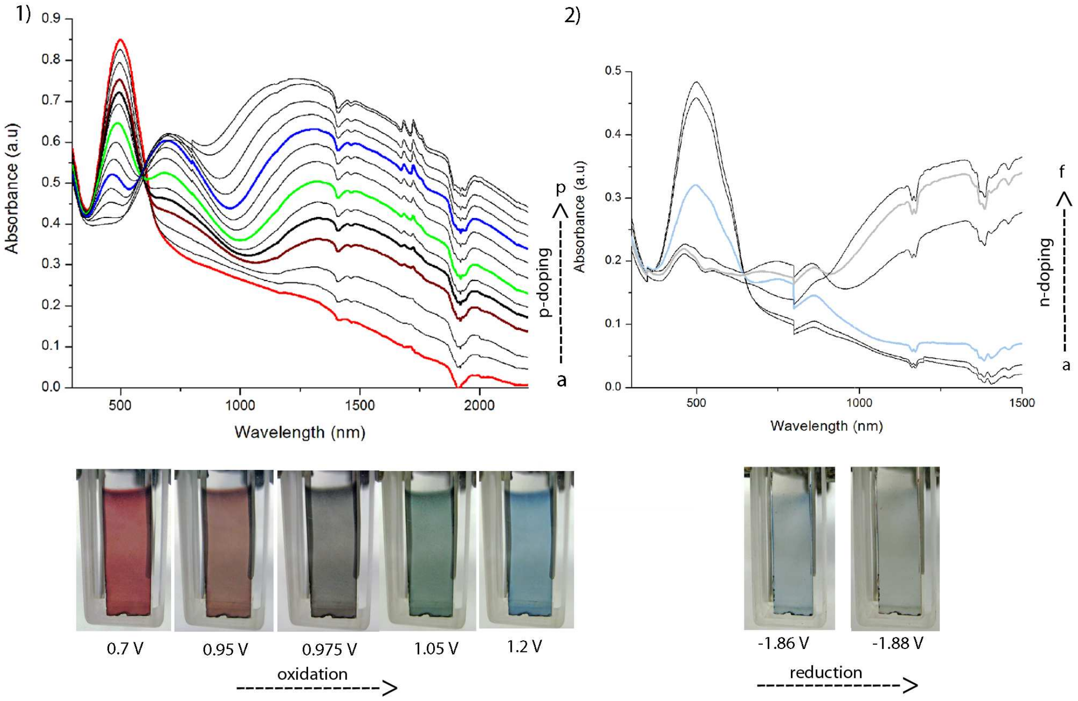


Figure 3.17 Electronic absorption spectra and the colors of PI film on ITO coated glass slide in a monomer free 0.1M TBAPF$_6$ /ACN electrolyte at applied potentials (V). (1) p-doping; (a) 0.700, (b) 0.800, (c) 0.850, (d) 0.900, (e) 0.925, (f) 0.950, (g) 0.975, (h) 1.00, (i) 1.05, (j) 1.10, (k) 1.15, (l) 1.20, (m) 1.25, (n) 1.30, (o) 1.35 and (p) 1.40 V. (2) n-doping; (a) -1.84, (b) -1.85, (c) -1.86, (d) -1.87, (e) -1.88, (f)-1.89 V

The unique property of PI should be clearly addressed at this point. The polymer reveals all three primary additive colors red, green and blue. This points out that with proper engineering, PI can be realized as a single component electrochromic display device.

Table 3.3 Lab values for the distinct colors of PTBT in different states

Colors	**L**	**a**	**b**
Red (p)	43.98	58.99	16.53
Brown (p)	55.59	17.26	16.67
Black (p)	67.32	0.148	1.72
Green (p)	67.67	-20.02	2.43
Blue (p)	64.71	-6.1	-38.72
Blue (n)	77.48	-7.64	-21.21
Transmissive (n)	86.67	2.78	-16.94

The reduction of a polymer does not necessarily mean an n-doping process is taking place. To identify a true n type doping, one should observe considerable structural and optical differences after the introduction of charge carries to the conjugated system. Hence, to clearly demonstrate the presence of n-type doping process, both the electrochemistry of the reduced state and the spectral changes upon reduction should be investigated. A similar study that can easily be performed for p-doping process, in theory, should also be repeated for n-doping process. However, this unique property for conducting polymers was observed in only handful of studies in literature. In these studies, the optoelectrochemistry of the polymer film in n-doping can only been observed in inert atmosphere conditions; only few data were acquired under ambient conditions [22]. During the investigation of PI it was striking to notice that six data were collected in the optoelectrochemistry studies, clearly showing that a true n-doping process occurs and it also reveals that the polymer shows a tremendous stability in its n-doped state. When the polymer is reduced (n-doped), it reveals a light blue color and upon further successive reduction, the polymer film becomes almost transparent, a highly desired property for these materials in electrochromic device applications. Properties observed for the absorption spectrum in polymer’s neutral state are much like that of polyhexylthiophene [121-122], one of the most promising materials for polymeric solar cell applications [123]. This makes PTBT a great candidate for solar cell applications.

As previously reported by Sonmez et. al., polymeric electrochromes can be used in memory device applications due to their small power requirements for optical changes and abilities to have different tones of colors in different oxidation states [124]. Color variation is the major parameter that can enhance the capacity of such devices. According to the color mixing theory, it is possible to obtain all colors by three primary additive colors, red, green and blue [125]. Up to date, this was possible via using different polymers which have a transmissive state to obtain these colors [126-127]. Now, both PI and PII make it possible to obtain all colors required for commercial electrochromic applications of conjugated polymers via using the same polymer in its different oxidation states, with the advantage of working in a very small potential range. This makes them outstanding candidates for data storage applications.

Solubility is a very sought property among conducting polymers since it enables processability. A conducting polymer soluble in common organic solvents can be spray or spin coated or drop casted on a surface. Application areas of conducting polymers are widened by soluble polymers since solubility provides coating on any surface where it is not possible to deposit electrolytically.

Polymerization yielded PTBT as a soluble conducting polymer which makes it industrially applicable since all the optoelectrochemical properties were also observed in spray coated PII just like those of electrochemically deposited PI (Fig. 3.18).

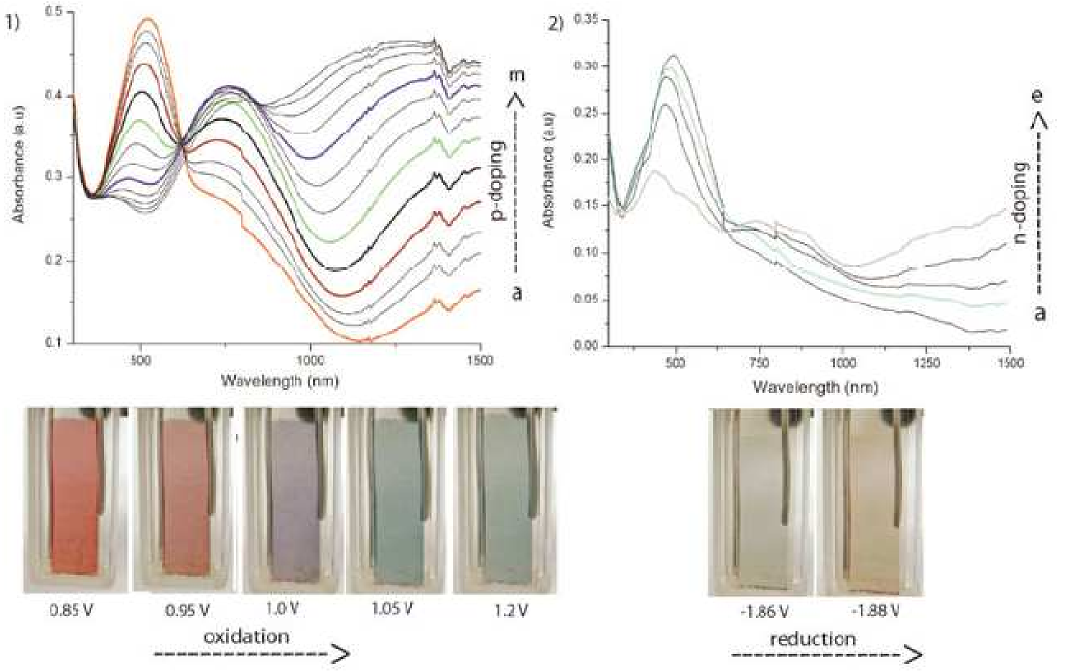


Figure 3.18 Electronic absorption spectra of PII film on ITO coated glass slide in monomer free, 0.1M TBAPF$_6$ /ACN electrolyte-solvent couple at applied potentials (V). 1) p-doping (a) 0.850, (b) 0.875, (c) 0.900, (d) 0.950, (e) 1.00, (f) 1.05, (g) 1.10, (h) 1.15, (i) 1.20, (j) 1.25, (k) 1.30, (l) 1.35 and (m) 1.40V. 2) n-doping (a) -1.84, (b) -1.85, (c) -1.86, (d) -1.87, (e) -1.88

3.2.2.3 Kinetic Properties of PTBT

Kinetic studies were performed to investigate the optical contrast and switching time of the polymer both in the visible and NIR regions (Fig. 3.19). The polymer film coated on ITO glass showed a 37 % optical contrast at 503 nm when switched between its reduced and oxidized states. The optical contrast value is significantly higher than the optical contrast of polythiophene. The switching time of the polymer was calculated as 2 s. This time period is the duration for switching among five different colors hence, not refers to switching between two colors which is the usual way of reporting switching times. That is to say, the reported time (2 s) cannot be considered as a long one since it stands for the time required for five color transitions. Thus, it is reasonable to claim that the switching time between any two colors is about 0.5 s on the average. The optical contrast of the polymer in NIR region was found to be 74 % with a switching time of 0.6 s which makes this polymer also a powerful candidate for NIR electrochromic applications. The NIR applicable materials are of particular interest since they are used for optical data transmission and the NIR dyes [128-129].

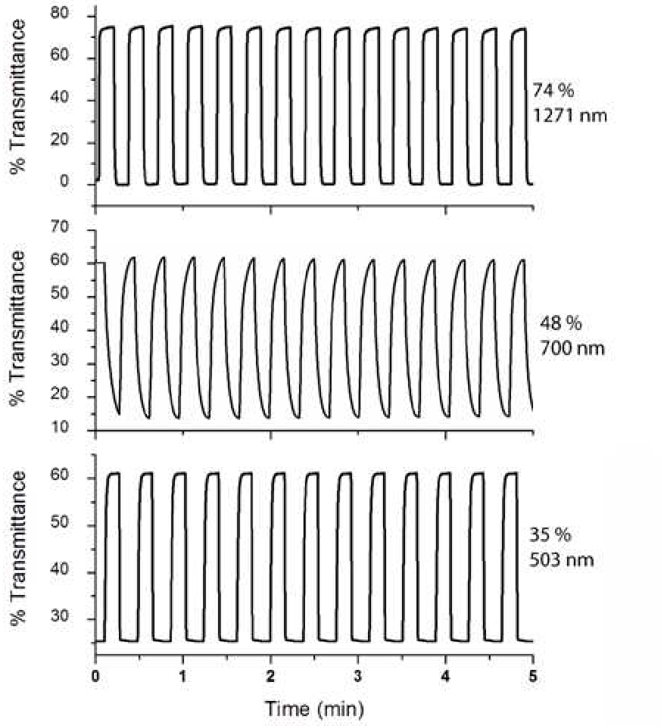


Figure 3.19 Electrochromic switching: Optical absorbance change monitored at 503, 700 and 1271 nm for PI in 0.1 M $TBAPF_6$/ACN while switching between its fully reduced and oxidized states

Chemically produced polymer film, PII was also studied for its kinetic properties. It showed a 42 % optical contrast at 525 nm when switched between its reduced and oxidized states. PII has 30 % optical contrast at 750 nm and 59 % at 1250 nm. The optical contrasts and the switching time behaviors of PII showed that chemically produced polymer can be used instead of PI since solubility allows mass production and processability. Also, PII has proven to be comparable to PI in terms of switching between extreme states (Fig. 3.20).

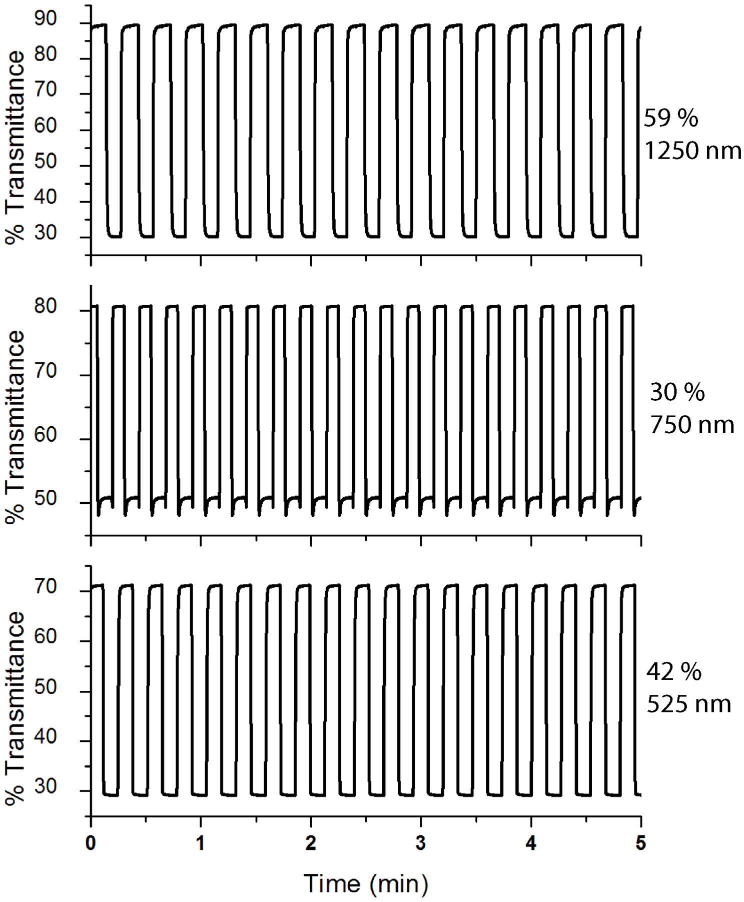


Figure 3.20 Electrochromic switching: Optical absorbance change monitored at 525, 750 and 1250 nm for PII in 0.1 M TBAPF$_6$/ACN while switching between its fully reduced and oxidized states

In order to study the stability of the polymer film, it was deposited on an ITO glass slide where the polymer was subjected to potential cycling between its neutral and oxidized states in 0.1 M TBAPF$_6$/ACN solvent–electrolyte couple. After 1000 cycles no considerable change in the optical density was observed. Since the injected and ejected charge per unit area is defined as the coloration efficiency, PI revealed high stability without any charge loss or any loss in coloration efficiency after repeated cycles. (Fig. 3.21)

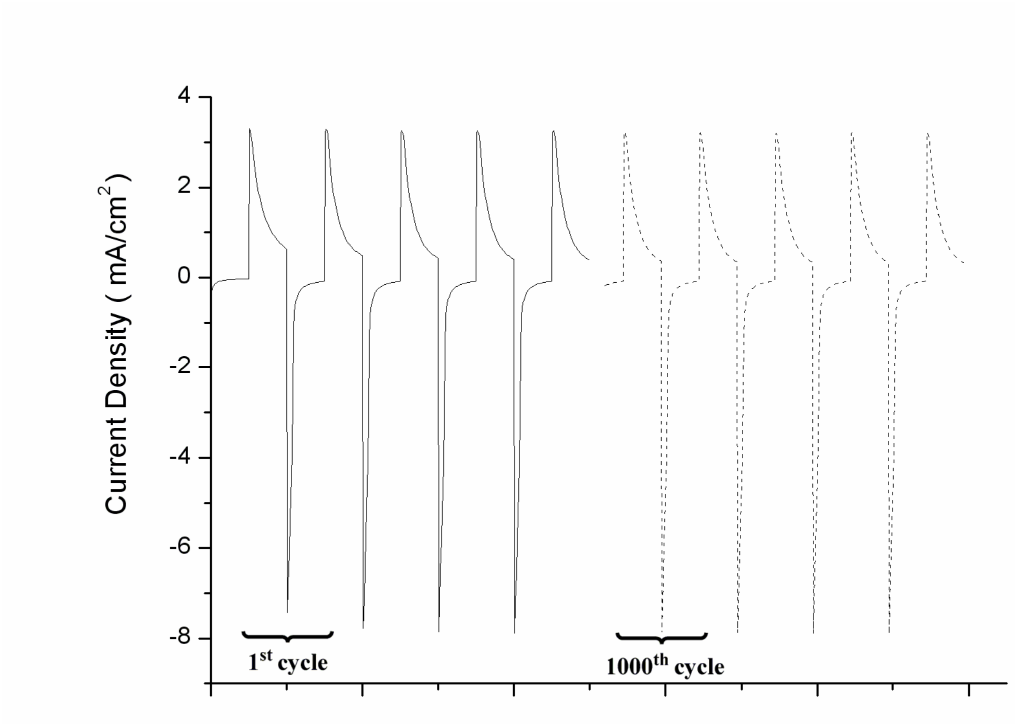


Figure 3.21 Chronoamperometry experiment for PI on ITO glass in 0.1 M TBAPF$_6$/ACN while switching between reduced and oxidized states. The first four cycles and the ones after the 1000th cycle were presented. Each interval on the x axis stands for 5 s

3.2.2.4 Optical Properties of PTBT

PTBT is a soluble polymer whether produced chemically or electrochemically. This property makes PTBT a great candidate as the active layer in solar cells and OLEDs. In order to obtain fluorescence spectra TBT, PI and PII were dissolved in chloroform and their spectra are depicted in Fig. 3.22. The solutions of TBT, PI and PII in chloroform were excited at 380 nm, 447 nm, and 496 nm at around their absorption maxima and maximum emission wavelengths of 454 nm, 542 nm and 569 nm were obtained respectively. Due to the extension of repeating unit in polymer chain, which was estimated from molecular weight determination, quenching is increasing (Table 3.4). Qualitative comparison suggests that the red shifted emission intensities are decreasing with increasing repeating unit.

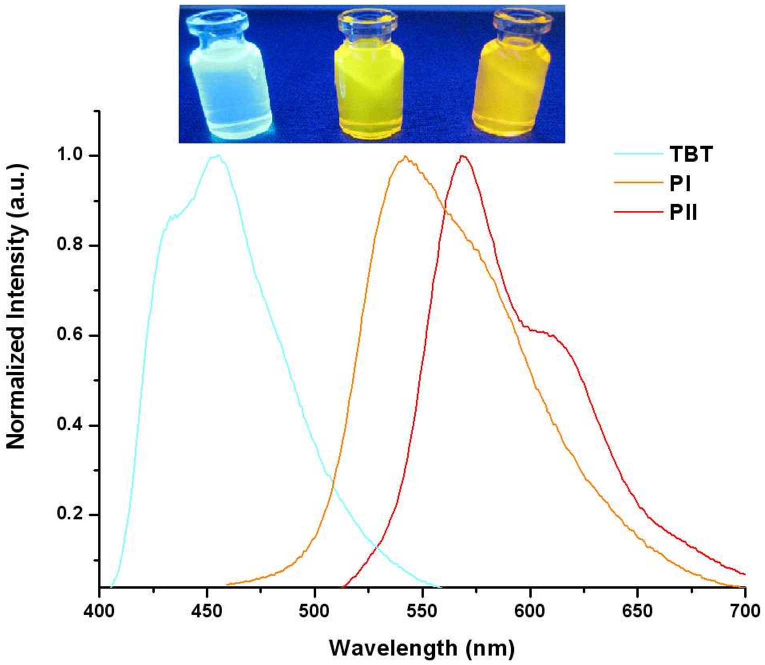


Figure 3.22 Emission spectra of TBT, PI and PII solutions in chloroform and emission photographs when solutions were exposed to a standard UV lamp (366 nm)

Difference in molecular weight between polymers leads to a longer absorption maximum wavelength for PII than that of PI. Thus, PI is orange-red in solution whereas PII is red (Fig. 3.23).

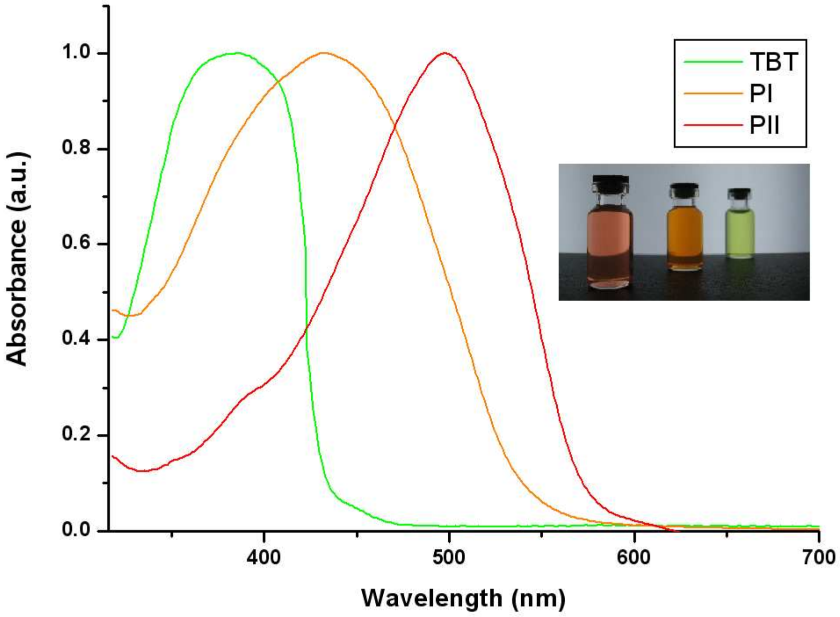


Figure 3.23 Solution optical absorbance spectra of TBT, PI, PII in $CHCl_3$

Table 3.4 GPC Molecular weight determination for PI and PII (in THF)

Polymer	*M_n (g/mol)*	*M_w (g/mol)*	*PDI*	*Avg. No. Rep. Un.*
PI	13000	23370	1.79	28
PII	43970	239640	5.45	97

CHAPTER 4

CONCLUSION

The D-A-D type monomers; BEBT and TBT were synthesized via alkylation, bromination, stannylation and the Stille coupling. Characterization of the materials were performed by NMR analysis. The polymers of the both monomers were synthesized by electrochemical methods and PTBT was also synthesized by means chemical methods. Cyclic voltammetry experiments, spectroelectrochemistry, kinetic studies and long-term switching experiments for the polymers were performed in order to investigate the electrochemical and electrochromic properties of the polymers.

PBEBT was shown that the presence of benzotriazole unit in the polymer backbone exceptionally enhanced the electrochromic properties of the “donor polymer”, namely, PEDOT. The optical contrast of the polymer was nearly 10 % higher than that of PEDOT, whereas the switching time was found to be the half of the value for PEDOT. The stability of polymer was at least as remarkable compared to the “donor polymer”. The ease of synthesis with relatively high yields makes this polymer the paramount choice in RGB based device applications as the blue leg component.

Studies for PTBT showed that both PI and PII combine reveal properties in a single material as a very promising multifunctional electrochromic polymer. The material reveals multicolor electrochromism with six distinct colors and high stability. The polymers have shown to be both p- and n-dopable. The spectroelectrochemistry of the n-doped state could be studied at ambient conditions, which signifies it as one of the most stable n-doped polymers in the literature. The polymers revealed very good optical contrast and switching times compared to the homopolymer of the donor unit (polythiophene). The polymers reveal black color upon oxidation, and are highly transparent in completely reduced state implying that they can be excellent candidates for highly efficient smart windows. PI also revealed 75 % optical contrast in the NIR region which makes it a significant candidate for NIR electrochromic device applications. PII has shown identical properties with PI which is important for large scale commercial applications. One of the most significant properties was to be able to observe all three primary colors in a single material. The saturation of the colors can be improved with small modifications in the polymer backbone and with intelligent engineering hence; a single component electrochromic display device can be realized. In addition, the polymer reveals highly efficient emission upon irradiation (LED applications). Strong absorption in the visible region makes this polymer a promising candidate for solar cell applications. PTBT will be a multipurpose material which will receive a great deal of the attention from industry.

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